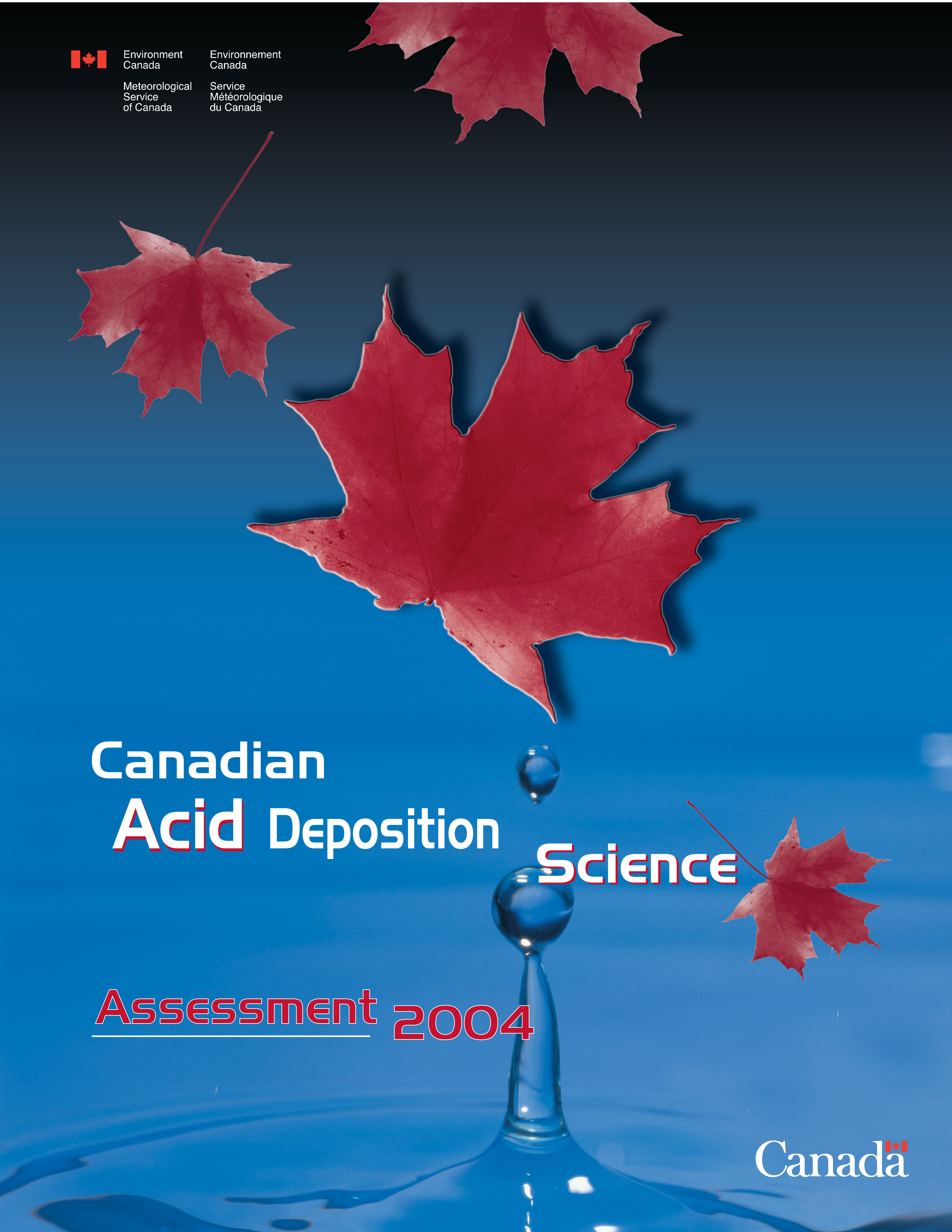

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TABLE OF CONTENTS

List of Figures

List of Tables

EXECUTIVE SUMMARY

While Canada has been very successful at reducing acid-causing emissions, acid deposition is still affecting the Canadian environment and the health of Canadians. Two methodologies, indicating best and worst cases, were used to estimate the impact of acid deposition on Canada. According to the two methodologies, approximately 21-75% of eastern Canada, corresponding to approximately 0.5-1.8 million km^2, continues to receive levels of acid deposition in excess of critical loads (i.e. the amount of acid deposition that a particular region can receive without being adversely affected). It is estimated that at least a further 75% reduction in sulphur dioxide (SO_2) emissions will be required from Canada and the U.S., beyond those agreed to in the Canada-U.S. Air Quality Agreement for 2010, in order to protect eastern Canadian ecosystems from damage by acid deposition. In eastern Canada, sulphur in deposition is still the predominant acidifying agent. However, it is possible that sustained high levels of nitrogen oxide (NO_x) emissions could result in the acidification of ecosystems in the future.

In western Canada (here defined as west of Ontario), there are large areas comprised of geology that is sensitive to acid deposition. These areas are located in northern and southeastern Manitoba, northern Saskatchewan, northeastern Alberta, Nunavut, the Northwest Territories and the coastal mountain ranges of British Columbia. At present, there is insufficient data on both the capacity of these ecosystems to safely assimilate acid deposition and levels of deposition. With a few exceptions, it is not possible to determine the extent to which acid deposition is affecting these potentially vulnerable ecosystems at this time.

In Canada and the U.S., major sources of acid-causing emissions are electric power generation, non-ferrous mining and smelting, upstream oil and gas operations and transportation. Major Canadian emissions sources that impact eastern Canada are located in Ontario and Quebec. Major emissions sources in the U.S., that impact eastern Canadian ecosystems, are located in the states of the Midwest, Great Lakes, Ohio River Valley and East Coast. Major emissions sources that impact western Canadian ecosystems are located in Alberta, southern Saskatchewan and northern Manitoba.

There are several factors that are decreasing, or have the potential to delay, the efficacy of emission reductions. The concentration of acid-neutralizing base cations in soils is being depleted as acid deposition continues. Consequently, the capacity of soils to neutralize acids is declining, thereby increasing the susceptibility of many regions to acid deposition. As acid deposition decreases, sulphur stored in forest soils is being released into lakes and rivers adding to the acid burden of these ecosystems. Under periods of drought followed by rain, wetlands which store sulphur from deposition, release it into lakes and streams resulting in episodic acidification events. In a few locations, excess nitrogen is leaving watersheds and acting as an additional acidifying agent to surface waters.

Despite factors that are decreasing the efficacy of emission reductions, improvements in the acidification status of many lakes are being observed, particularly those located near smelters which have dramatically reduced emissions. The pathway to recovery in many of these lakes is complex and slow and may result in permanently altered biological communities. The capacity for many of these lakes to support aquatic biota is improving however, and increases in waterbirds such as the Common Loon have been observed.

Acid deposition is linked to many other environmental issues. Acid deposition shares precursor emissions (SO_2 and NO_x) with ground-level ozone and particulate matter (a.k.a. smog). The pollutants that cause acid deposition contribute to climate change and climate change has the potential to affect the geographic extent and severity of acid deposition and its effects. Furthermore, acid deposition exacerbates the conversion of relatively non-toxic elemental mercury to highly toxic and bioaccumulative methylmercury. Hence, mitigating acid deposition benefits many other environmental, economic and human health issues.

Due to the wide-ranging impacts of acid deposition on humans and their environments, there are potentially many socio-economic benefits from acid deposition mitigation. For example, the emerging science linking acid deposition to reductions in the productivity of forests suggests that reducing acid deposition could have significant economic benefits to the forestry sector.

Clearly, the problem of acid deposition is not yet fully addressed. In eastern Canada, on-going efforts to reduce acid-causing emissions and better understand the complex and long-term impacts of this pollution will be essential for effectively managing the issue into the future. The presence of acid-sensitive geology and increasing emissions of SO_2 and NO_x suggests that new monitoring efforts should expand into the western provinces to ensure that acid deposition does not damage ecosystems in this region.

The 2004 Canadian Acid Deposition Science Assessment has been prepared by researchers from the federal and provincial governments and academia. This assessment builds upon the results presented in the 1997 Canadian Acid Rain Assessment and presents the latest research related to the following:

- progress towards reducing acid-causing emissions;
- response of the atmosphere to past, present, and future changes in emissions;
- new critical load estimates for aquatic and terrestrial ecosystems;
- effects on forests, soils, aquatic ecosystems, wildlife, and human health;
- recovery of aquatic ecosystems;
- linkages to other environmental issues;
- gaps in our understanding of the issue; and,
- on-going efforts to quantify the costs and benefits associated with reducing acid deposition.

The assessment consists of two documents, the Summary of Key Results and the Assessment. The Summary of Key Results synthesizes the major findings of the assessment in the context of ten questions and sub-questions put forth by the acid deposition policy and science communities. The Assessment presents a comprehensive review of acid deposition science in Canada.

CHAPTER 1

Introduction

H. Morrison

The 2004 Canadian Acid Deposition Science Assessment represents two firsts: It is the first major synthesis of acid deposition science in Canada since the launch of the Canada-wide Acid Rain Strategy for Post-2000; and, it is the first comprehensive examination of atmospheric and ecosystem responses to sulphur dioxide (SO_2) emission reductions achieved under Phase I of Title IV of the 1990 U.S. Clean Air Act Amendments.

The fifth acid deposition science assessment in Canada in the last 25 years, this report arrives at an interesting time in the lifecycle of this issue. Since completion of the last assessment[1], compelling new science has emerged linking chronic acidification of soils to forest decline and delays in aquatic ecosystem recovery. Large increases in emissions of SO_2 and nitrogen oxides (NO_x) from oil sands operations in northern Alberta are raising concerns that acid deposition could potentially impact the west. Despite widespread misconceptions that the issue is solved, new research indicates that the problem could linger for another 60 years or more in eastern Canada[2]. With public awareness and concern for the issue at low ebb, this is an opportune time to take stock and plan for the future.

What is acid deposition? Acid deposition is the end product of reactions between sulphur oxides (SO_x), nitrogen oxides (NO_x) and water in the atmosphere. Acid deposition reaches earth as precipitation (acid rain or fog) and as gases, acid aerosols and particles (dry deposition or sedimentation). The acidity (or pH) of acid deposition is influenced by atmospheric concentrations of sulphur- and nitrogen-derived acids and bases. Atmospheric levels of acids and bases are primarily determined by anthropogenic emissions of SO_x, NO_x, ammonia and base cations from sources such as base metal smelting, thermal electric power generation, upstream oil and gas and transportation. In eastern Canada, SO_2 emissions account for the majority of acidity in deposition.

Pollutants that cause acid deposition can travel hundreds and even thousands of kilometres from the source of emission. Due to long-range transport and the destructive nature of acids, acid deposition has a wide range of impacts on humans, their environments and economy over a broad geographic range. Acid deposition affects lakes, rivers, soils, forests, buildings, and human health. Acid deposition reduces the biodiversity of aquatic ecosystems and has the potential to alter the composition of species in terrestrial ecosystems.

Acid deposition shares precursor emissions (SO_x and NO_x) with ground-level ozone and particulate matter (a.k.a. smog). Nitrogen oxides can contribute to the formation of ozone in the presence of volatile organic compounds (e.g., solvents) and sunlight. Sulphur and nitrogen oxides can react with other chemicals to form particulate matter (PM). Both PM and ozone are known to adversely affect the health of individuals. Furthermore, smog and some smog precursors scatter or absorb light travelling through the atmosphere, which affects visibility and contributes to climate change.

Long-range transport, combined with the proximity of major sources of SO_x and NO_x emissions in the U.S. to Canada, means that solutions to Canada's acid deposition problem require emission reductions from both countries. In Canada, the Eastern Canadian Acid

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[1] Environment Canada, 1998. 1997 Canadian Acid Rain Assessment. Vols. 1-5. ISBN 0-662-2598-6

[2] Based on forecast modelling of ecosystem response to optimistic emission reduction scenarios from Clair et al. (2003) for Nova Scotia and New Brunswick and Aherne et al. (2003) for Ontario. Studies assume that factors that would slow ecosystem recovery such as forest management practices, forest fires and nitrate leaching are not occurring.

Rain Program (ECARP) represented the first coordinated effort of the federal government and the seven easternmost provinces to address this issue. This program, launched in 1985, achieved its goal of reducing SO_2 emissions to 50% of 1980 levels by 1994. In the U.S., amendments were made to the U.S. Clean Air Act in 1990, which specified deep cuts in SO_2 emissions by 1997 (Phase I), further cuts by 2010 (Phase II) and reductions in NO_x emissions. The Canada-U.S. Air Quality Agreement (AQA), signed in 1991, reaffirmed the commitments of both governments to reduce SO_2 and NO_x emissions and consult on, and develop, the means to address other transboundary air pollution issues.

When the ECARP was developed, it was hoped that SO_2 emission reductions by Canada and the U.S. would reduce the deposition of sulphates from precipitation (i.e., rain and snow) from levels as high as 40 kg per hectare per year to no more than 20 kg per hectare per year. The 20 kg per hectare per year "target load" , specified in 1983, was expected to protect aquatic environments that were moderately sensitive to acids. Although the 20 kg per hectare target is expected to be achieved by 2010, both the 1990 and 1997 Canadian Acid Rain Assessments concluded that many lakes and forests will continue to sustain damage from acid deposition. The 1990 assessment confirmed that a more meaningful measure of an ecosystem's capacity to receive acid deposition without sustaining damage is the "critical load." Critical loads are estimates of an environment's assimilative capacity, that is, the amount of acid deposition that a particular region can receive without being adversely affected.

The 1985 ECARP was a first step towards solving the acid deposition problem in Canada. In 1994, the federal, provincial and territorial governments began developing a long-term acid deposition management strategy for Canada that would mitigate the environmental and human health effects associated with acid deposition and acidifying emissions, respectively. Launched in 1998, the Canada-wide Acid Rain Strategy for Post-2000 (a.k.a. the *Strategy*) has a long-term goal "to meet the environmental threshold of critical loads for acid deposition across Canada." The *Strategy* is currently being implemented. It consists of the following five commitments:

- Pursuing further emission reduction commitments from the U.S.;
- Establishing new sulphur dioxide (SO_2) emission reduction targets in eastern Canada;
- Preventing pollution, and keeping "clean" areas clean;
- Ensuring the adequacy of acid rain science and monitoring programs; and,
- Reporting annually on SO_2 and NO_x emissions and forecasts, on compliance with international commitments, and on progress in implementing the strategy.

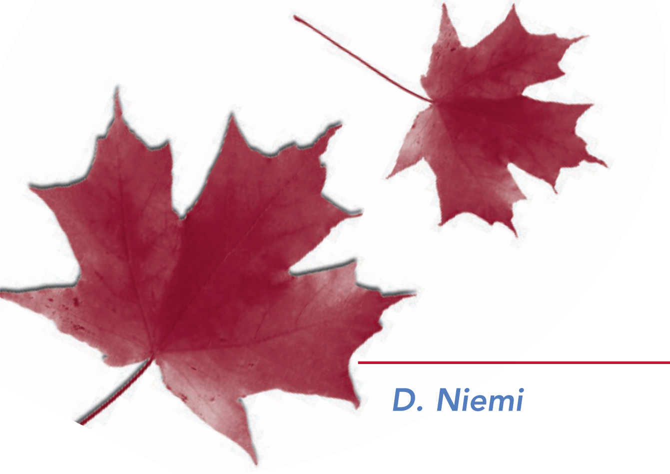
This assessment builds upon the results presented in the 1997 Canadian Acid Rain Assessment and presents our current scientific foundation for supporting the commitments of the *Strategy*. Preparation of this assessment began in 2001 with a series of workshops involving scientists and policy-makers from the federal and provincial governments and several universities. These workshops led to the development of a table of contents for the assessment as well as the following ten science questions that articulate the information needs of the science and policy communities:

1. Is acid deposition still affecting the Canadian environment and the health of Canadians? If so, where, how, and to what extent is it affecting these endpoints?
2. What are the current and forecasted trends in acid-causing emissions?
3. Where are the major industrial sources of acid-causing emissions that affect Canadian ecosystems?
4. Are further emissions reductions necessary in Canada and the U.S.? If so, by how much, and from where, do emissions need to be reduced?
5. Will NO_x reductions compensate for the need to reduce SO_2? Is nitrogen saturation a problem and how will changing NO_x emissions impact on Canadian ecosystems?
6. Are there other factors that might decrease the efficacy of emission reductions?
7. Are affected ecosystems recovering in response to past reductions in SO_2 emissions? If so, how is

recovery proceeding? If not, why, when, and under what conditions, can we expect recovery to acceptable environmental objectives? What role do NO_x emissions play?

8. What are some of the socio-economic benefits of acid deposition mitigation?
9. What are the linkages and implications of other environmental problems with acid deposition, in particular, ozone and particulate matter formation, climate change and mercury?
10. Where do we need to continue atmospheric and effects monitoring? Where should we focus future research efforts for acid deposition?

The goal of this assessment is to synthesize the current state of knowledge on acid deposition in Canada. This report and the Summary of Key Results are available on the Environment Canada website (**http://www.msc-smc.ec.gc.ca/saib/acid/acid_e.html**) and from the Science Assessment and Integration Branch, Meteorological Service of Canada, Environment Canada, 4905 Dufferin Street, Downsview, Ontario, M3H 5T4.



CHAPTER 2

Emissions of Pollutants Related to Acid Deposition in North America

D. Niemi

2.1 KEY MESSAGES

- Emissions of sulphur dioxide (SO_2) in Canada and the United States (U.S.) declined substantially between 1980 and 2000. These emissions are predicted to continue to decline between 2000 and 2020.
- Within Canada, emissions of SO_2 declined substantially in eastern Canada and to a lesser extent in western Canada between 1985 and 2000. Between 2000 and 2020, emissions of SO_2 are predicted to decline slightly in eastern Canada and increase in western Canada.
- Emissions of nitrogen oxides (NO_x) remained relatively constant in Canada and declined slightly in the U.S. between 1985 and 2000. Nitrogen oxides emissions are predicted to decline in both Canada and the U.S. between 2000 and 2020.
- Within Canada, emissions of NO_x declined substantially in eastern Canada and to a lesser extent in western Canada between 1985 and 2000. Between 2000 and 2020, emissions of NO_x are predicted to decline substantially in eastern Canada and increase in western Canada.

2.2 INTRODUCTION

Acid deposition is the end product of reactions between sulphur dioxide (SO_2), nitrogen oxides (NO_x) and water in the atmosphere. The acidity (or pH) of acid deposition is influenced by atmospheric concentrations of sulphur- and nitrogen-derived acids and bases. Atmospheric levels of acids and bases are primarily determined by anthropogenic emissions of SO_2, NO_x, ammonia and base cations. In eastern Canada, SO_2 emissions account for the majority of acidity in deposition.

Canada and the United States (U.S.) have been estimating emissions of pollutants responsible for or related to acid deposition since 1970. Currently, both countries compile comprehensive emission inventories for the following acid-causing or influencing pollutants:

- Nitrogen oxides,
- Sulphur oxides,
- Primary particulate matter[1] with an aerodynamic diameter less than or equal to 2.5 micrometers ($PM_{2.5}$); and,
- Ammonia (NH_3).

Environment Canada also compiled estimates of base cation emissions in 1995.

The Environment Canada Criteria Air Contaminants (CAC) inventory compiles information on the emissions of sulphur oxides (SO_x). Sulphur oxides emissions are primarily comprised of SO_2 plus a small amount of sulphur trioxide (SO_3). For consistency with the balance of this Assessment, SO_x emissions will be referred to as SO_2, recognizing that the loss of accuracy is acceptably small for narrative purposes.

Methods for estimating emissions are constantly evolving to reflect the latest statistics, emission measurements, and source characterization. Environment Canada (EC) and the U.S. Environmental Protection Agency (EPA) review and adjust their historical emission estimates regularly to reflect the most current methodologies and information. However, it is important to note that data on acid-causing emissions from years prior to 1985 are not directly comparable to more recent inventories.

---

[1] Major components of PM include sulphates, nitrates, ammonia and base cations.

2.3 EMISSIONS INVENTORIES

2.3.1 Canadian Criteria Air Contaminants Inventory

In Canada, data on emissions of pollutants responsible for acid deposition are compiled in the Criteria Air Contaminants (CAC) emissions inventory. The inventory is managed by Environment Canada with data from environmental agencies representing the provinces, territories, and specific regions of Canada. The inventory has been developed to track the progress of emission reduction initiatives, support scientific assessment of air pollution problems, inform the public, and fulfill reporting requirements of the various domestic and international protocols and agreements. The emissions sources in the inventory include: industrial facilities, non-industrial fuel combustion (which includes residential and electric power generation), transportation vehicles, incineration activities, and various other sources such as surface coating, road dust, and forest fires.

Historically, the CAC Inventory has been updated every five years. Currently, the Inventory has emission estimates and forecasts from 1970 to 2020 for NO_x, SO_2, particulate matter (PM_{10} and $PM_{2.5}$), and ammonia (NH_3). Since 2002, a number of industrial and commercial facilities have been required to report their Criteria Air Contaminants emissions to Environment Canada on an annual basis. With the collection of this information, Environment Canada has initiated a process to compile comprehensive emissions inventories for these pollutants annually.

The Canadian CAC Emissions Inventory is compiled with estimation techniques that are similar and comparable to the ones used in the U.S. for the National Emissions Inventory (NEI). In both countries, inventories include point sources, nonpoint (area) sources, and on-road and non-road mobile sources of emissions. Biogenic emissions are also estimated but not included in the emission summaries. Emissions inventories are developed using a variety of estimation techniques including, continuous emissions monitors (CEM), source testing, mass balance, emission factors, and models. Emission estimation models are generally used to quantify diffuse sources of emissions such as mobile sources and road dust.

Currently, the most comprehensive emissions inventory available in Canada for air quality modelling and data analysis is for the calendar year 2000. Emissions summaries are available on-line at the national, provincial, and territorial levels, and for major urban centres and communities, at the following locations: **http://www.ec.gc.ca/pdb/ape/cape_home_e.cfm**, and **http://gis.ec.gc.ca/npri/root/main/map.asp#skipNav**. A comprehensive emissions inventory for the calendar year 2002 is currently being compiled. A draft version of this emissions inventory will be available in the first quarter of 2005.

2.3.2 U.S. National Emissions Inventory

The U.S. EPA's Emission Factor and Inventory Group (EFIG) prepares a national database of air emissions information with input from numerous State and local air agencies, tribes, industry, and different U.S. programs and departments . As an example, SO_2 and NO_x emissions compiled annually by the EPA Clean Air Markets Division from electric power generation facilities and other sources subject to acid rain trading rules, are also included in the database. This database contains information on stationary and mobile sources that emit criteria air pollutants and their precursors, as well as hazardous air pollutants (HAPs). The database includes estimates of annual emissions of air pollutants in each area of the country by source. The National Emissions Inventory (NEI) includes emission estimates for all 50 States, the District of Columbia, Puerto Rico, and the Virgin Islands. Emission estimates for individual point or major sources (facilities), as well as county level estimates for area, mobile and other sources, are available currently for years 1990 and 1996 through 1999 for criteria pollutants, and for year 1999 for HAPs.

Data summaries of historical U.S. emissions from 1970 through 2002 can be found at: **http://www.epa.gov/ttn/chief/trends/index.html**.

2.3.3 Changes in methodologies

Since the inception of the CAC Emissions Inventory and the NEI, there have been several changes in the methodologies used to compile emissions information. The models used to estimate emissions of key air pollutants are constantly being updated. The Mobile 6 model is currently used in the two countries to estimate the emissions from on-road vehicles, and a new model has been developed and used in Canada to estimate the road dust emissions in the 1990, 1995 and 2000 emissions inventories. The U.S. EPA has also updated and improved the emission factors[2] for NO_X. These emissions factors are also used in Canada. Each successive NO_X emissions inventory has included an increasing number of facilities, thereby improving our knowledge of the various emission sources. In addition, emissions inventories are being improved continuously to reflect the latest statistics and measurements.

2.4 SOURCES OF AND TRENDS IN ACID-CAUSING EMISSIONS

2.4.1 Sources of SO_X, NO_X and NH_3 emissions

In Canada and the U.S., the primary source sectors of acid-causing gases in 2000/2001 were electrical power generation, non-ferrous mining and smelting, on-road vehicles, upstream oil and gas and agriculture (Table 2.1).

As described in Table 2.1, major emissions sectors in Canada and the U.S. are similar. Differences between Canada and the U.S. in the contribution of different source sectors to total emissions are due to differences in available natural resources and population demands between the two countries. For example, the largest source sector for SO_2 emissions in Canada is the non-ferrous mining and smelting sector followed by the electrical generation sector. In the U.S., the largest source sector for SO_2 emissions is the electrical power generation sector due to the large population and lower hydro electric generation capacity in this country.

2.4.2 Trends in emissions of SO_X, NO_X and NH_3

In Canada and the U.S., total SO_2 emissions have declined by approximately 50% and 40% respectively between 1980 and 2000 (Table 2.2). In eastern Canada, emissions of SO_2 have declined by 53% between 1985 and 2000 due to emission reductions in the electric power generation and non-ferrous mining and smelting sectors. In western Canada, emissions of SO_2 have declined by 6% over this period due to emission reductions in the non-ferrous mining and smelting sectors.

Table 2.1 Percentage contribution of major emitting sectors to total national emissions in Canada and the U.S. (2000/2001)[1]

Sector	SO_2		NO_X		NH_3	
	U.S.	Canada	U.S.	Canada	U.S.	Canada
Non-ferrous Mining & Smelting		32.5	-	-	-	-
Electrical Power Generation	69.8	27.2	22.9	11.4	-	-
Upstream Oil and Gas	0.4	14.8	0.3	13	-	-
On-road Vehicles	1.6	-	36.2	32.6	5.5	3.1
Off Road Vehicles	2.7	-	18	26.9	-	-
Industrial Fuel Combustion	13.8	-	11.5	-	-	-
Other Fuel Combustion	3.5	-	4.6	-	-	-
Agriculture (Animals)	-	-	-	-	87.3	55
Pesticides & Fertilizer	-	-	-	-	-	34.6
Chemical & Products	2.0	-	0.6	-	2	-

[1] U.S. and Canadian emissions percentages are not directly comparable since national emission totals are not comparable.

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[2] Emission factors are representative annual average values that relate the quantity of a pollutant emitted with an activity associated with the release of that pollutant (e.g. amount of pollutant emitted per unit of fuel consumed).

Table 2.2: Emissions of acid-causing gases from Canada and the U.S. (kilotonnes). Note: Eastern Canada includes all provinces east of Manitoba and western Canada includes all provinces west of Ontario and the territories.

		1970[1]	1975[1]	1980[1]	1985	1990	1995	1997	1999	2000	2010[2]	2020[2]
SO_2	**Canada**	7,210	5,790	4,643	3,802	3,259	2,629			2,379	2,244	2,156
	E.Can				2,624	2,040	1,342			1,238	1,093	973
	W.Can				1,180	1,214	1,234			1,115	1,265	1,284
	U.S.	28,380	25,944	23,568	21,188	20,980	16,927			14,833	10,669	9,158
NO_x	**Canada**	1,358	1,980	1,959	2,503	2,614	2,528			2,546	2,277	2,114
	E.Can				1,539	1,605	1,384			1,274	949	784
	W.Can				1,030	1,074	1,447			1,329	1,405	1,394
	U.S.	24,368	23,913	24,617	23,415	23,209	22,687			21,090	14,516	11,193
NH_3	**Canada**						551			584	702	872
	E.Can						203	204	207	209	247	284
	W.Can						347	361	369	374	455	588
	U.S.					3,929	4,235			4,532	4,547	4,754

[1] Canadian NO_X emissions for 1970 through 1980 are based on older methodologies and are not comparable to 1985 and beyond. SO_2 emissions are based on consistent methodology throughout the reporting period.

[2] U.S. emissions forecasts are based on REMSAD emissions summaries.

In Canada, emissions of NO_X have been relatively constant between 1985 and 2000. During this period, emissions of NO_X decreased by 17% in eastern Canada as a result of reductions in emissions from the transportation (heavy-duty diesel vehicles, light-duty gasoline vehicles) and non-ferrous mining and smelting sectors. In western Canada, NO_X emissions increased by 29% as a result of increases in emissions from the upstream oil and gas, electric power generation and transportation (i.e., light-duty gasoline vehicles) sectors.

Between 1985 and 2000, U.S. emissions of NO_X have declined slightly. Emissions of NO_X from the electric power generation sector increased from 1970 through to 1993 but declined after 1993 and are now at the same level as in 1970. Off-road vehicle emissions, other fuel combustion, and miscellaneous area sources of NO_X have also been increasing since 1970 but have begun to decline in the last few years.

In Canada, NH_3 emissions have increased by approximately 9% between 1995 and 2000. During this period, emissions have remained relatively constant in eastern Canada and have increased by 8% in western Canada. Western Canadian emissions of NH_3 have increased as a result of increases in commercial fertilizer and pesticide application and transportation (i.e. light duty gasoline trucks) emissions.

In the U.S., ammonia emissions increased by approximately 15% between 1990 and 2000.

2.4.3 Sources and emissions of base cations

Base cations are chemicals capable of neutralizing acids. These chemicals are also essential nutrients for plants (see Chapter 5). To assist in the development of a relationship between acid deposition and anthropogenic emissions of base cations, the base cation content of $PM_{2.5}$ emissions in the 1995 CEC inventory was determined (Table 2.3). Analysis of the base cation content of PM was performed at a national level and did not account for regional variations in the base cation content of PM sources.

Base cation emissions in Canada originate primarily from fugitive sources such as road dust, agriculture and construction activities. Of the basic cations included in this analysis, emissions of calcium (Ca^{2+}), potassium (K^+) and sodium (Na^+) predominated. These three basic cations are the most common in nature and are present in many fuels, especially coal.

Table 2.3 Estimated emissions of base cation in Canada in 1995 (tonnes).

Source	Chemical Symbol								
	Ba	Be	Ca	Ce	K	Mg	Na	Rb	Sr
Industrial Source	52	2	5,307	0	6,519	386	7,366	15	19
Non Industrial Fuel Combustion	41	0	465	0	6,626	4	24	2	29
Transportation	43	0	759	0	171	262	120	0	2
Incineration	1	0	35	0	53	2	130	0	0
Miscellaneous	4	0	257	0	279	6	740	1	0
Open Sources	527	0	15,446	0	11,086	1,209	1,139	24	109
Biogenics	0	0	423	0	4,576	0	1	0	0
TOTAL	**668**	**2**	**22,692**	**0**	**29,310**	**1869**	**9520**	**42**	**159**

Note: The information in this table was compiled using the 1995 CAC Inventory v2 and the U.S. EPA Speciate database v3.1. Regional variations in emissions were not included in these estimates.

2.5 GEOGRAPHICAL DISTRIBUTION OF ACID-CAUSING EMISSIONS

2.5.1 Geographical distribution of SO_2 emissions

In eastern Canada, SO_2 emissions are concentrated along the Windsor–Quebec City corridor with hotspots in south-central New Brunswick, east-central Nova Scotia and Newfoundland (Figure 2.1). The Windsor-Quebec City corridor is highly urbanized and has emissions sources that include thermal electric power generation and on-road transportation. The hotspots in south-central New Brunswick, east-central Nova Scotia and Newfoundland are sites of electrical power generation and other industrial emissions (e.g. mining and pulp and paper). In western Canada, high levels of SO_2 emissions are observed in Alberta and in defined hotspots in Manitoba and Saskatchewan. Emissions from Alberta are primarily from thermal electric power generation and oil sands operations. High emission areas in Saskatchewan are thermal electric power generation. In Manitoba, hotspots are the sites of non-ferrous mining and smelting industries.

2.5.2. Geographical distribution of NO_X emissions

The geographic distribution of NO_X emissions is very similar to the distribution of SO_2 emissions. This similarity is the consequence of common sources of SO_2 and NO_X. Eastern Canadian NO_X emissions are concentrated along the Windsor–Quebec City corridor, New Brunswick and Nova Scotia (Figure 2.2). In western Canada, high levels of NO_X emissions are observed in Alberta and at defined hotspots in Manitoba and Saskatchewan.

2.5.3 Geographical distribution of NH_3 emissions

Ammonia gas (NH_3) is emitted from both industrial and agricultural sources. Ammonia emissions are highest in south-central Alberta, southern Saskatchewan, southern Manitoba, and the Windsor-Quebec corridor (Figure 2.3). These regions are characterized by intensive farming and livestock operations.

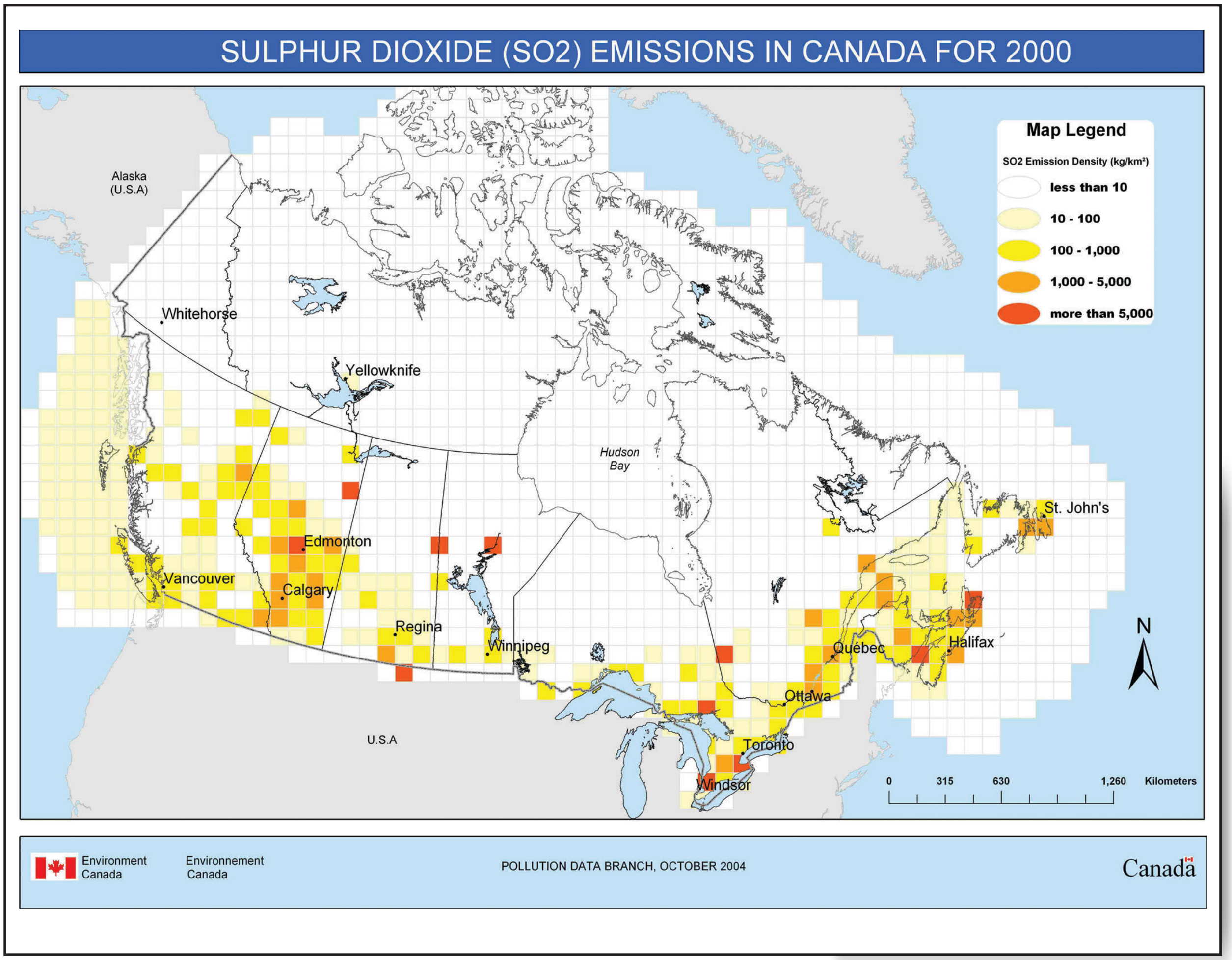

Figure 2.1: Distribution of total annual Canadian SO_2 emissions in 2000 (kg/km^2).

2.6 PROJECTIONS OF ACID-CAUSING EMISSIONS

Both Canada and the U.S. develop emission projections to assess the impact of current and future policies on pollutant emissions and air quality standards. The process of forecasting emissions for policy review involves two steps: 1) preparation of a base case projection; and 2) development of a control scenario.

The base case is a "business as usual" projection. This means that all current policies related to air quality are held constant over the projection period. The impacts of modified or additional control regulations that have not been officially implemented (at the time of forecast preparation) are not included. Hence, the base case represents a reference case against which the impacts of new emission reduction measures can be compared.

2.6.1 Description of Canadian emission projections

The Canadian CAC emission projections were developed using the 2000 CAC Emissions Inventory. These projections incorporate the emission reduction policies and measures described in the Canada-Wide Acid Rain Strategy for Post 2000 and the Ozone Annex of the Canada-U.S. Air Quality Agreement. These policies and measures include: Tier 1 and NLEV vehicles (National Low Emission Vehicles), Tier 2, and heavy duty vehicle NMHC (nonmethanehydrocarbon), NO_X, PM standards, and low sulphur on-road diesel and gasoline. Inputs

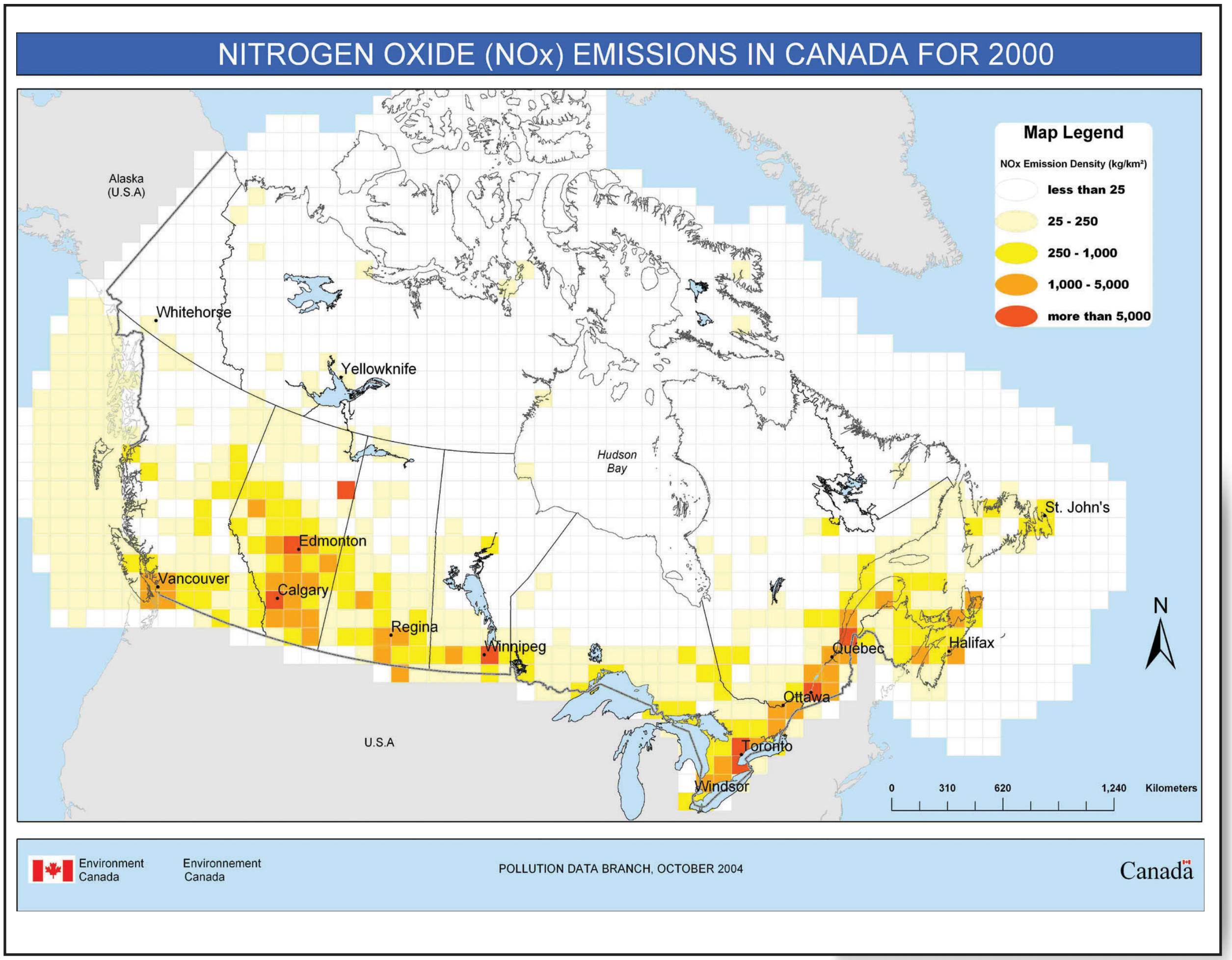

Figure 2.2: Distribution of total annual Canadian NO_x emissions in 2000 (kg NO_2/km^2).

from federal, provincial, and territorial governments and private industry have also been incorporated into the emission projections. These preliminary projections are currently being revised by the provincial and territorial authorities.

To project the CAC emissions into the future, annual growth factors were applied to the 2000 emissions for each industrial sector and category in each province or territory. The growth factors were calculated from surrogate data or indicators obtained from Natural Resources Canada (NRCan) and summarized in a report entitled *Canada's Emissions Outlook: An Update* (CEO99) (Analysis and Modelling Group, 1999). The national CAC projections are compiled using individual projections from the ten provinces and the three territories. The Canadian Energy Outlook was developed by NRCan and it incorporated the inputs received through various consultations with industries and different environmental organizations for the development of Canada's reference scenario to support the Climate Change National Implementation Strategy. The Canadian CAC emissions projections are based on similar assumptions to the ones developed for the Greenhouse Gases, which are provided in the CEO99. They provide a comprehensive and complete picture of the emissions for these pollutants in Canada.

The CAC emissions projections also include additional information such as:

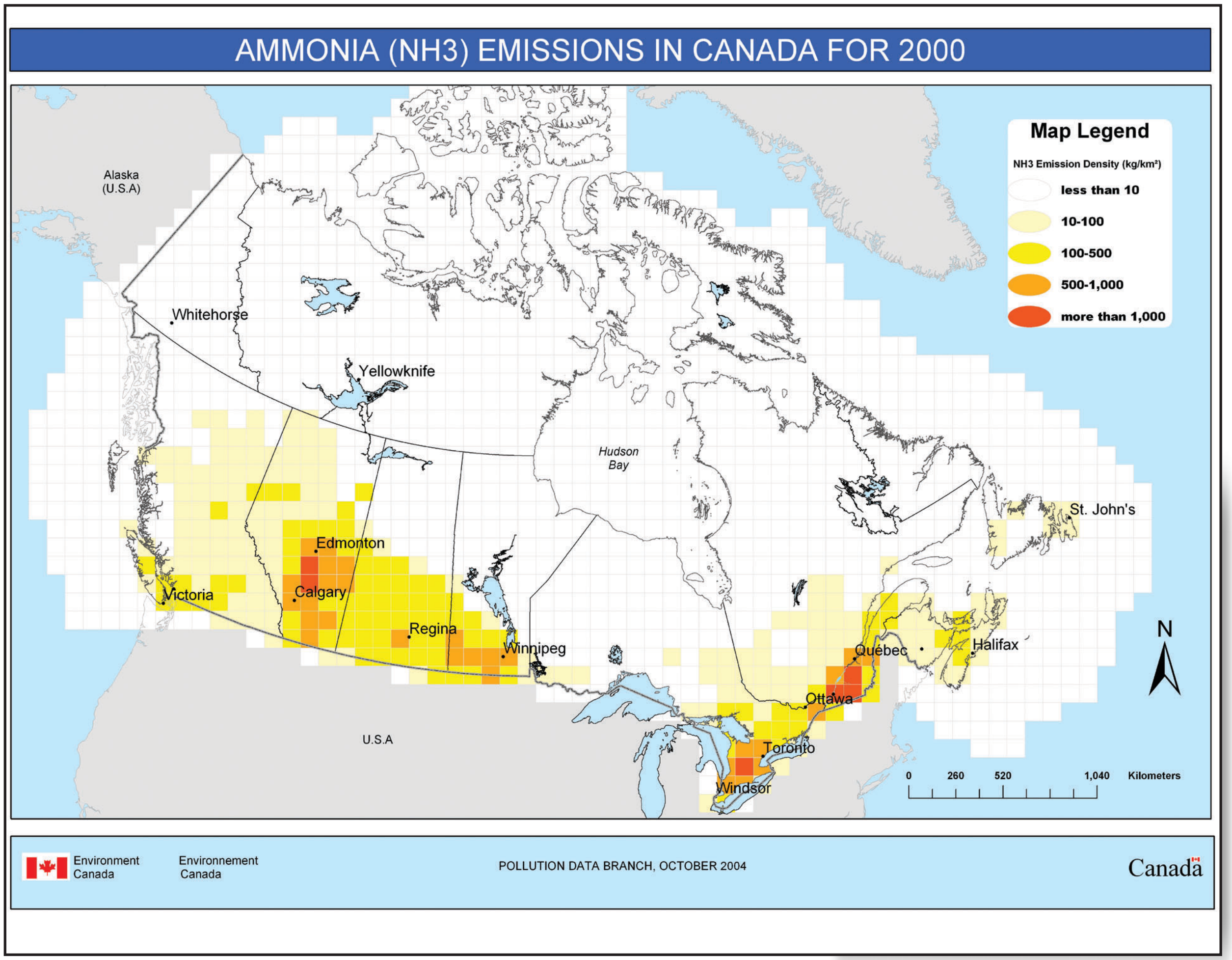

Figure 2.3: Distribution of total annual Canadian NH_3 emissions in 2000 (kg NH_3/km^2).

- On-road and non-road transportation emissions projections to the year 2020, developed using the Canadian version of the mobile emissions estimation model (MOBILE6.2C)
- Provincial information on projected changes in emissions obtained from the Quebec Ministry of the Environment, the Greater Vancouver Regional District (GVRD), the Ontario Ministry of Environment & Energy and Alberta Environment. Several other provinces and territories also provided emissions data for specific industrial sectors.

The CAC emissions forecasts also incorporate inputs received from stakeholders during the development of the previous forecast (based on the 1995 CAC Emissions Inventory). These inputs included:

- The Multi-pollutant Emission Reduction Analysis Foundation study for the Pulp and Paper Industry
- The impact of regulations under the Canadian Environmental Protection Act (CEPA) for volatile organic compounds (VOC) emissions from the Dry Cleaning industry, the Degreasing industry and the Surface Coatings industry by 2007.
- Emissions projections for the railways sector obtained from the Railways Association of Canada (RAC)

2.6.2 Description of the U.S. emission projections

Base case projections for the U.S. were calculated using methods and models designed to support EPA's rule for Low-Emission Non-road Diesel Engines and Fuel (40 CFR

Parts 9, 69 et al.) (US EPA, 2004). Included in the development of these estimates was an adjusted version of EPA's MOBILE5b model. This version accounted for changes anticipated at the time of this analysis to be included in the first release of MOBILE6, the March 2002 version of EPA's NON-ROAD model. It also accounted for stationary, point, and area sources; inventories (2020); and interpolations from projected inventories (2010) as designed to support the EPA proposed non-road rule in 2003. The emissions projection files were estimated, using the 1996 base year emissions inventory, by applying growth and control factors developed to simulate economic changes and control programs in place for each respective projection year. Emission projections include the specific Clean Air Act and Amendments emission reduction measures promulgated and proposed by EPA at the time of the non-road rule's publication in the Federal Register.

2.6.3 Projections of acid-causing emissions in Canada and the U.S.

In Canada, total emissions of SO_2 are projected to decline by approximately 4% between 2000 and 2020 (Table 2.2). In eastern Canada, emissions of SO_2 are predicted to decline by 21% between 2000 and 2020 while in western Canada emissions of SO_2 are predicted to increase by 15% over this period (Table 2.2). The reductions in eastern Canada are attributed to projected declines in emissions from the non-industrial fuel combustion sector, which includes residential and commercial fuel combustion and electric power generation emissions. Emissions reductions are also attributed to reductions from on-road and off-road transportation vehicles reflecting the impact of various emission reduction regulations. The predicted increase in emissions from western Canada is attributed to increases in emissions from the upstream oil and gas and electric power generation sectors.

In the U.S., total emissions of SO_2 are predicted to decline by approximately 28% and 38% from 2000 levels in 2010 and 2020, respectively (Table 2.2). The decline in SO_2 emissions is attributed primarily to reductions in emissions from the electric power generation sector.

In Canada, NO_x emissions are predicted to decline by approximately 10% and 17% from 2000 levels in 2010 and 2020, respectively (Table 2.2). Emissions of NO_x are predicted to decrease by 39% and increase by 5% between 2000 and 2020 in eastern and western Canada, respectively (Table 2.2). Reductions in emissions from eastern Canada are primarily due to predicted decreases in emissions from the on-road and off-road transportation sectors. The increase in emissions from western Canada is attributed to predicted increases in emissions from the upstream oil and gas and electric power generation sectors.

In the U.S., NO_x emissions are predicted to decline by approximately 31% and 47% from 2000 levels in 2010 and 2020, respectively (Table 2.2). These reductions are attributed to predicted decreases in emissions from on-road and off-road vehicles, electric power generation and small reductions from other sectors.

The reductions in SO_2 and NO_x emissions that have been and will be realized in Canada are primarily due to the institution of stringent vehicle emissions standards, reduced sulphur in fuels, changes in the primary base metal smelting sector and other smaller sectorial reductions. Some of the emissions reductions realized in western Canada have been off set by increases in other sectors such as the upstream oil and gas sector.

In 2020, NH_3 emissions are predicted to increase by approximately 49% and 5% from 2000 levels in Canada and the U.S. respectively (Table 2.2). Ammonia emissions are predicted to increase by 36% and 57% between 2000 and 2020 in eastern and western Canada, respectively (Table 2.2). These increases in emissions are attributed to increases in livestock and poultry production and commercial fertilizer and pesticide applications in both countries.

2.7 UNCERTAINTIES IN EMISSIONS INVENTORIES

The uncertainty of the emission estimates and of the emissions inventories are not quantified by Canada and the U.S. on a regular basis. The uncertainties of the emissions inventories may be small or large depending on the source, the pollutant, the time period, and the geographical area considered. The emissions inventories in Canada and the U.S. are compiled from provincial and state emissions inventories, which include emissions by facilities, emissions estimates for mobile vehicles, industrial, and non-industrial sources. These inventories are compiled using information on the materials consumed and produced, emission factors, emission measurements, estimation methodologies, and various statistics, which are often not adequately documented to assess the uncertainty.

The North American Regional Strategy for Tropospheric Ozone (NARSTO) organisation developed a qualitative rating of the uncertainties in emissions estimates from many sectors in Canada, the U.S. and Mexico. Information on the uncertainties associated with SO_2, NO_x, NH_3 and PM emissions in Canada and the U.S. are described in chapter four of their report entitled “Particulate Matter Science for Policy Makers: A NARSTO Assessment” (NARSTO, 2004).

2.8 Future directions

To date, the Canadian CAC Emissions Inventory has been compiled every five years. Environment Canada has initiated a process to compile comprehensive emission inventories for CAC pollutants on an annual basis through the National Pollutant Release Inventory (NPRI). Compilation of annual emissions inventories requires a high degree of involvement from the federal, provincial, and territorial governments. It is anticipated that annual inventories will be published within two years of the inventory year in the future. Environment Canada also intends to update the emission projections every 2 to 3 years.

Currently, emissions inventory research focuses on the development of improved statistics, methodologies, emission factors, and models to improve the emission estimates from industrial sources, on-road and non-road vehicles, agricultural activities, bakeries, construction, demolition, and residential wood combustion activities. It is expected that similar research will continue in the future and be expanded to include other sources and sectors, and the spatial and temporal variations of the emissions.

A large percentage of the emission rates currently used to estimate the emissions from industrial and non-industrial sources is based on measurements performed in the U.S. a number of years ago. There is a need to update these emission rates to reflect Canadian weather, characteristics of fuels, operations, industrial processes, and emission control equipment and practices. In the future, Environment Canada is planning to work in collaboration with industry and industrial associations to update these emission factors through source measurements.

Environment Canada has initiated a consultation process with industry and other interested parties to potentially expand the mandatory reporting requirements of the NPRI to include additional emissions information for different particulate matter species.

More accurate and timely emissions inventories will be developed in the future. This will help scientists gain a better understanding of the effects of emission sources on air quality. These improved emissions inventories will also provide a more robust foundation for policy makers to develop new emissions control strategies that will, in turn, improve air quality and the Canadian environment.

2.9 References

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NARSTO. 2004. Particulate Matter Science for Policy Makers. A North American Regional Strategy for Tropospheric Ozone Assessment. Cambridge University Press, Cambridge, UK. ISBN 0-521-84287-5. Also available at http://www.cgenv.com/Narsto/

US EPA . June 29, 2004. 40 CFR Parts 9, 69, et al., Control of Emissions of Air Pollution From Nonroad Diesel Engines and Fuel: Final Rule. Federal Register 69(124), 38957-39273. Also available at http://www.epa.gov/otaq/url-fr/fr29jn04.pdf

CHAPTER 3

Atmospheric Response to Past Emission Control Programs

R. Vet, J. Brook, C. Ro, M. Shaw, J. Narayan, L. Zhang, M. Moran, M. Lusis

3.1 KEY MESSAGES

- Wet, dry and total (wet + dry) deposition of sulphur and nitrogen species is highest in eastern Canada, particularly in southern Ontario and southern Quebec. A gradient exists from the highest deposition areas to lower deposition areas in the west, north and east parts of eastern Canada.
- New estimates of dry deposition at Canadian Air and Precipitation Monitoring Network (CAPMoN) monitoring sites indicate that dry deposition of sulphur and nitrogen species constitutes a larger proportion of total sulphur and nitrogen deposition than previously thought.
- The large-scale patterns of non-sea-salt-SO_4^{2-} wet deposition in eastern North America indicate that non-sea-salt-SO_4^{2-} deposition levels decreased markedly from the early 1990s to the late 1990s in response to SO_2 emission reductions in both eastern Canada and the eastern U.S.. In contrast, the patterns of NO_3^- wet deposition show minimal reductions in deposition since NO_x emissions changed little during that period.
- Source attribution studies indicate that at least half, and sometimes as much as two-thirds, of total (wet + dry) deposition of sulphur and nitrogen species, depending on location, in eastern Canada is attributable to sources in the eastern and Midwest U.S.. Eastern Canadian sources are also identified as major contributors to total deposition.

3.2 INTRODUCTION

Past Canadian and American acid rain assessments, as well as many journal publications over the last 20 years, have made the link between acid gas emissions and wet and dry acid deposition in Canada and the United States (U.S.). They have also shown that wet deposition of acidifying species in eastern Canada is due in part to Canadian emissions and in part to U.S. emissions that are transported and subsequently deposited in Canada. See, for example, the 1997 Canadian Acid Rain Assessment (Environment Canada, 1997) or Dennis et al. (1990).

The 1997 Canadian Acid Rain Assessment – Atmospheric Science Assessment Report Volume 2 (Environment Canada, 1997), which preceded this one, was primarily focused on two questions:

- What is the impact of the emission control programs in reducing sulphate deposition to date?
- What is the projected impact of the emission control programs in reducing sulphate deposition?

It was concluded in the 1997 Assessment that measurements from Canadian federal and provincial monitoring networks have shown a decrease in wet sulphate deposition over eastern Canada from the early 1980s to the early 1990s. This decrease is the result of concurrent reductions in sulphur dioxide emissions in eastern North America. Reductions in ambient air concentrations of sulphur dioxide and, to a lesser extent, particulate sulphate have also been observed; however, long data records are available from only six Canadian sites. While precipitation sulphate levels have been decreasing, precipitation acidity has not changed. This finding may be related to the fact that base cation levels in precipitation, which buffer acidity, have decreased significantly. In addition, the levels of nitrate in precipitation and air have not, in general, decreased systematically, a finding consistent with a lack of marked changes in eastern North American nitrogen oxide emissions.

Concerning the second question, state-of-the art mathematical modelling showed that the eastern Canadian wet sulphate deposition target load of 20 kg/ha/yr (i.e., the amount of acid deposition that was expected to protect aquatic environments that were moderately sensitive to acids) should be met for all areas of eastern Canada, with the possible exception of a small region in southwestern Ontario, following the implementation of the Canada–U.S. Air Quality Accord (CAAA). However, critical loads (i.e. the amount of acid deposition that a particular region can receive without being adversely affected) are generally lower than the target load. Model predictions showed that critical loads for sulphate will still be exceeded over large areas of eastern Canada, even after these control programs are fully implemented. A further reduction in sulphur dioxide emissions of 50% over and above those planned in the CAAA would still leave an area across central Ontario and Québec where the critical load of sulphate deposition would be exceeded.

The 1997 Assessment demonstrated that the acid deposition science program has been largely successful in quantifying reductions in wet sulphate deposition resulting from sulphur dioxide emission controls in North America during the 1980s and 1990s. However, a number of recommendations were made for filling some of the remaining scientific gaps:

- Conduct further research into the temporal trends of precipitation acidity – in particular, why acidity decreases have not paralleled decreases in sulphate concentrations.
- Better quantify nitrate deposition, especially the dry component, which could be a significant portion of the total.
- Better quantify deposition due to fog water in Eastern Canada.
- Maintain ongoing observations and analyses to describe temporal changes in the magnitude and spatial patterns of concentrations and total (wet plus dry plus droplet) deposition of the relevant species across Canada, with the same precision with which critical loads are known.

The Acid Deposition Monitoring and Research Program of Environment Canada has addressed the above recommendations, with the help of a funding enhancement from the Acid Rain Business Case, which became available in 2000. Due to the limited resources available, not all of the above recommendations could be addressed fully. A proper examination of temporal trends in acidity, for example, is linked to the need for major improvements in our emission inventories for base cations and ammonia, which will require resources well beyond those presently at our disposal. Similarly, only modest progress was possible in the subject of fog deposition. Finally, the erosion of acid rain monitoring activities since the 1990s, especially in Ontario, has introduced large uncertainties in some of the spatial analyses of the type reported in the 1997 Assessment.

Nevertheless, since the 1997 Assessment, significant progress has been made in quantifying dry deposition (particularly that of nitrogen compounds) over Canada, and new analytical methods have been developed for trend analysis and for linking source areas to receptors.

This chapter is based on an analysis of air, precipitation and fog chemistry data available up to 2003. The overall objectives of the chapter are the following: 1) Determine how atmospheric wet and dry deposition of acidic substances have been responding to the acid gas emission control programs which have been implemented to date in Canada and the U.S., with a focus on the major emission changes that occurred from the early 1990s to the early 2000s, and; 2) Determine the main contributing source areas to acid deposition in sensitive receptor areas in eastern Canada.

3.3 WET, DRY AND TOTAL DEPOSITION

3.3.1 Wet deposition

Federal and provincial monitoring networks have been measuring wet deposition on a regional scale in Canada since the late 1970s. The backbone of the federal/provincial networks has been Environment Canada's Canadian Air and Precipitation Monitoring Network (CAPMoN), which began operating in 1983 at which time it superseded the Canadian Network for Sampling Precipitation (CANSAP) and the Air and Precipitation Network (APN). In the U.S., wet deposition monitoring has been carried out since 1978 by the

National Atmospheric Deposition Program (NADP) as well as by state and industrial networks. The National Trends Network (NTN) and the Atmospheric Integrated Research Monitoring Network (AIRMoN) are subnetworks of NADP. In addition, NADP has collocated NTN stations at sites of the U.S. Clean Air Status and Trends Network (CASTNET). Unfortunately, in Canada, several provincial networks closed in the last decade leaving large gaps in the spatial coverage of wet deposition across the country. Provinces that have closed down their networks include British Columbia, Manitoba, Ontario and Newfoundland and Labrador. Networks that continue to operate in Canada at the time of writing include the federal Canadian Air and Precipitation Monitoring Network, the Precipitation Quality Monitoring Program in Alberta, le Réseau d'échantillonnage des précipitations du Québec, the Nova Scotia Precipitation Study Network and the New Brunswick Precipitation Monitoring Network. The status of precipitation monitoring in Canada and the U.S. as of June 2004 is shown in Figure 3.1 (excluding U.S. state networks).

Wet deposition measurements in the foregoing networks are made by chemically analyzing precipitation samples collected in wet-only deposition collectors. The wet deposition fluxes at the monitoring sites are calculated as the product of the measured ion concentration and precipitation depth (measured using collocated standard gauges). The CAPMoN and Nova Scotia networks collect samples on a daily basis while all other networks in Canada collect samples on a weekly basis except New Brunswick which combines daily samples into weekly-composite samples. In the U.S., the NTN network collects samples on a weekly basis while the AIRMoN network collects samples daily. The precipitation chemistry samples are sent to the respective network analytical laboratories for chemical analysis. Descriptions of the networks can be found at the following Web site: **http://www.msc.ec.gc.ca/natchem/precip/networks_e.html**.

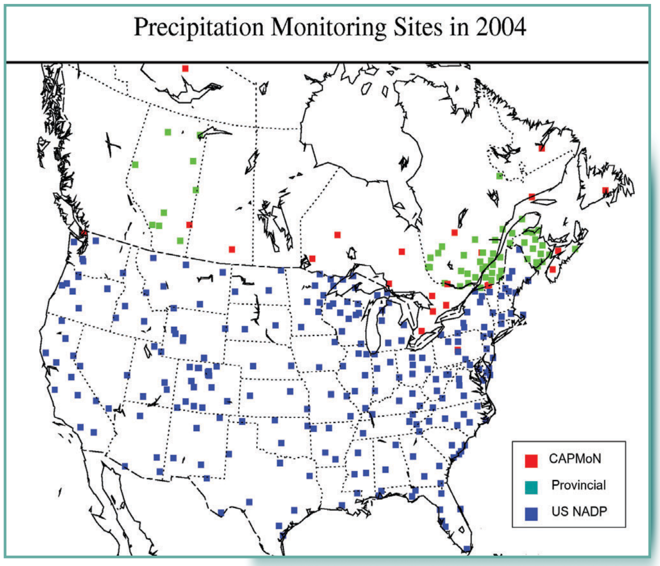
Precipitation Monitoring Sites in 2004

Figure 3.1: Federal, provincial and U.S. wet deposition monitoring sites operating as of mid-2004. CAPMoN refers to the Canadian Air and Precipitation Monitoring Network.

3.3.1.1 *A continental perspective of wet deposition*

Wet deposition data from all major U.S. and Canadian regional-scale monitoring networks are archived, quality assured and analyzed in the Canadian National Atmospheric Chemistry Database and Analysis Facility (NAtChem) which is operated by Environment Canada (**http://www.msc-smc.ec.gc.ca/natchem/**). The merged U.S. and Canadian data provide a basis for mapping and analyzing the spatial and temporal patterns of wet deposition over North America. To this end, regional-scale Canadian and U.S. wet deposition maps have been produced by the NAtChem facility for every year from 1980 to 2001. The deposition patterns are restricted geographically to the eastern half of the continent because of the paucity of data in western Canada. The eastern North American five-year mean patterns of wet sulphate (non-sea salt) and nitrate deposition and pH are shown in Figure 3.2 for the years 1996-2000. Five year average patterns were chosen to smooth out the year-to-year variability in the patterns. Non-sea-salt sulphate was estimated at all sites located within 100 km of salt water bodies using a sea-salt correction algorithm described in WMO (2005).

In Figures 3.2a/b, the wet deposition patterns of nssSO_4^{2-} (non-sea-salt sulphate) and NO_3^- over eastern North America appear as elongated bulls-eyes stretched along a southwest to northeast axis. Maximum nssSO_4^{2-} wet deposition (>25 kg/ha/yr) occurs in an area immediately south of Lake Erie in eastern Ohio and western Pennsylvania, very close to the high SO_2 emission area of the Ohio River Valley. The 20 to 25 kg/ha/yr area encompasses the entire Ohio River valley as well as a small section of southern Ontario. The acid-sensitive

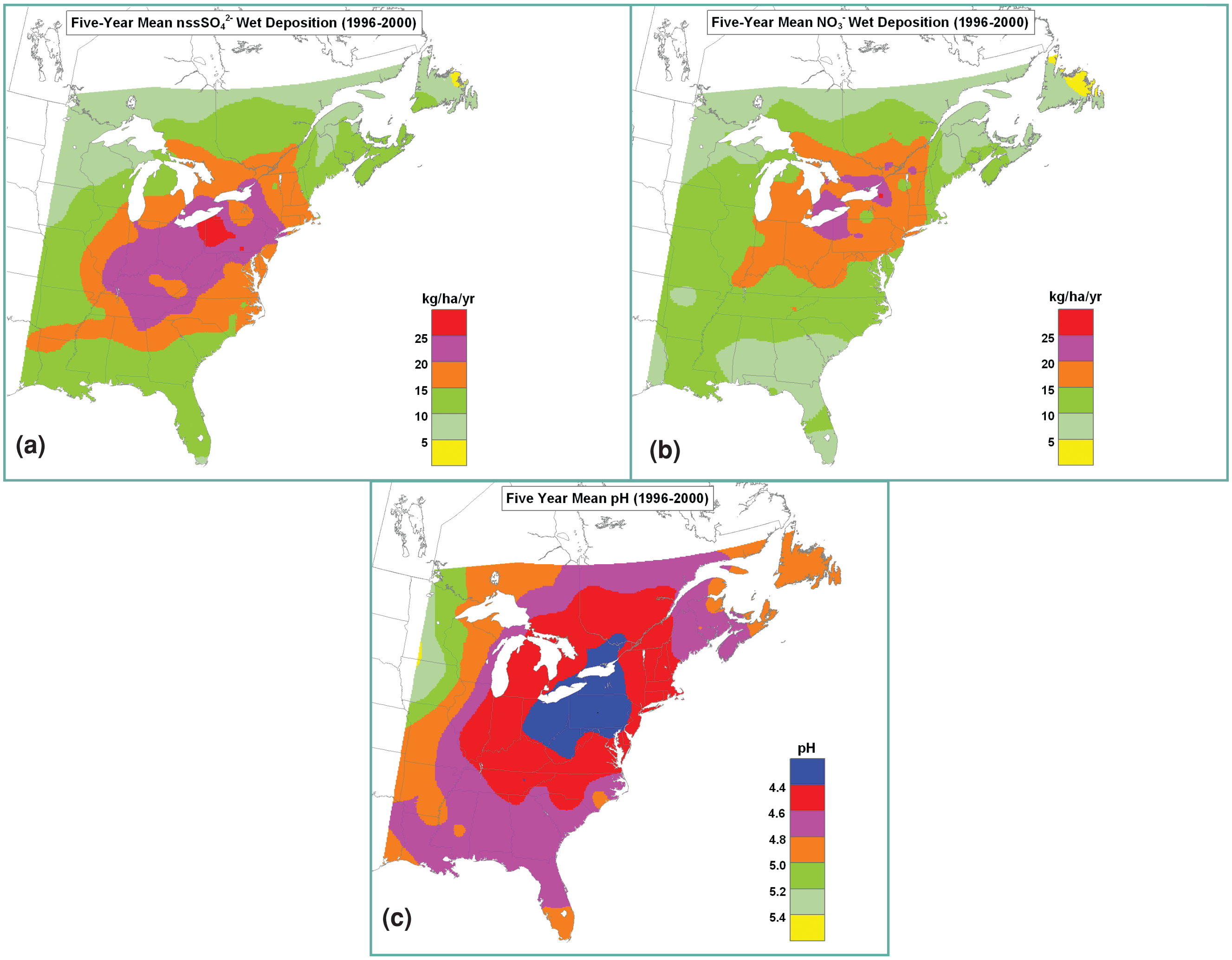

Figure 3.2: Five-year mean (1996-2000) patterns of (a) $nssSO_4^{2-}$ wet deposition, (b) NO_3^- wet deposition and (c) pH over eastern North America.

areas of the Canadian Shield in Ontario and Québec receive variable amounts of sulphate deposition, ranging from 20 kg/ha/yr in the south to less than 10 kg/ha/yr in the north. Figure 3.2b shows that NO_3^- wet deposition levels are also highest in eastern Ohio and western Pennsylvania. However, in contrast to sulphate, the area of maximum deposition encompasses a very large area of southern Ontario and part of northern New York. Interestingly, in Canada the 15 kg/ha/yr contours of both $nssSO_4^{2-}$ and NO_3^- deposition are roughly collocated.

The pH pattern shown in Figure 3.2c was determined from the 5-year precipitation-weighted mean concentrations of H^+ converted to pH. Minimum pH values of less than 4.4 occur in a large area of southern Ontario, part of southwestern Québec and in the states south of Lakes Erie and Ontario. Maximum pH values, ranging from 5.0 to 5.4, occur in the northwestern part of the map domain in both countries.

Consistent with past research (Environment Canada, 1997), the areas of highest $nssSO_4^{2-}$, NO_3^- and H^+ wet deposition in the U.S. generally occur near and downwind of the highest SO_2 and NO_X emission areas (i.e., the U.S. Midwest and Ohio River Valley). In Canada, highest deposition occurs along the Canada-U.S. border in southern Ontario and southern Québec. As discussed in previous Canadian and U.S. acid rain assessments (Environment Canada, 1997 and NAPAP, 1990), $nssSO_4^{2-}$, NO_3^- and H^+ wet deposition in Canada are strongly affected by both Canadian SO_2 and NO_x emissions and U.S. emissions that are transported into, and subsequently deposited in Canada. Readers can see the location of major SO_2 and NO_x sources in Canada and the U.S. from the 1990 emission inventory maps included in Appendix 3.1. Unfortunately, it was not possible to obtain post-1990 emission maps at the time of writing, so readers must keep in mind that emission levels have decreased since 1990 but the spatial distribution of sources has remained approximately the same. The balance of this chapter explores the relationship between Canadian and U.S. emissions and wet and dry deposition (as well as between concentrations in air and precipitation) in Canada. The 1990s and early 2000s, when SO_2 emissions declined substantially in both countries, provide a particularly interesting period for determining the spatial, temporal, and source-receptor relationships between emissions and atmospheric response.

The spatial patterns shown in Figure 3.2 were produced from data collected by the CAPMoN network in Canada, the NADP network in the U.S., and provincial networks in Ontario, Québec, New Brunswick, Nova Scotia and Newfoundland. The contours were produced by interpolating data from the various network measurement sites using an interpolation scheme known as Kriging (Isaaks and Srivastava, 1989). Difficulties were encountered when producing the contours in Ontario in 1999 and 2000 because the Ontario acid deposition monitoring network ceased operations in early 1999. To compensate for the missing 1999 and 2000 Ontario data, an assumption was made that the detailed spatial pattern of wet deposition in Ontario for 1999 and 2000 was the same as the 3-year-average spatial pattern in 1996-98. Using this assumption, the 1999 and 2000 Ontario patterns were interpolated from the limited number of federally-operated CAPMoN sites in Ontario as well as all available neighbouring provincial and state sites, and the interpolated annual deposition fields were corrected to match the 1996-98 spatial structure. The 5-year mean patterns in Ontario shown in Figure 3.2 were subsequently derived from a combination of the 1996-98 interpolated fields (produced from the provincial and federal sites in Ontario as well as all neighbouring provincial and state sites) and the 1999-2000 fields (produced from only the federal sites in Ontario and all neighbouring provincial and state sites) corrected to match the spatial structure of the earlier years.

To assess the potential impact of the two years of spatial corrections on the five-year average wet deposition patterns in Ontario (Figure 3.2), an uncertainty analysis was carried out by interpolating and comparing the 1996-1998 interpolated SO_4^{2-} wet deposition patterns created with and without the Ontario network data. The analysis showed that the omission of the Ontario network causes a 10-35% underprediction of wet deposition in the area east of Lake Huron and southern Lake Superior and a less than 10% overprediction in northern Ontario. Thus, the spatial correction for the missing Ontario data in 1999 and 2000 has the effect of increasing the magnitude of the wet deposition east of Lake Huron and southern Lake Superior and decreasing the magnitude in northern Ontario. The net result is a 5-year average wet deposition pattern that is more consistent with the years 1996 to 1998 than it would be without the corrections. **If the correction factors are totally wrong,** the result would be, at worst, a -10% to -15% error in the 5-year average wet deposition values in the area east of Lake Huron and southern Lake Superior and an error of less than +5% in northern Ontario. It is our feeling that the 5-year average patterns shown in Figure 3.2 are likely more accurate for having used the correction factors than not using them. However, this does not take away from the point that the closure of the Ontario network has increased the uncertainty of the annual wet deposition patterns in Ontario.

It is worth pointing out here that the 1996-2000 5-year average wet deposition patterns are used later in Section 3.4.3 to estimate the total wet deposition of SO_4^{2-} and NO_3^- in eastern Canada. As stated above, it is our feeling that using the correction factors in 1999 and 2000 serves to improve the accuracy of the wet deposition patterns and their resultant integrated deposition amounts. However, in the case that the correction factors are completely wrong, the uncertainty analysis described above indicates that total SO_4^{2-} wet deposition for eastern Canada would be in error by less than 5%. This is felt to be an acceptable level of error for the analyses described in Section 3.4.3.

3.3.1.2 A Canadian perspective of wet deposition

The Canadian Air and Precipitation Monitoring Network (CAPMoN) is the backbone of the wet deposition measurement program in Canada, having measured wet deposition nationally since the early 1980s. CAPMoN makes daily measurements of major ion concentrations in precipitation and air at rural and remote monitoring sites across Canada. The air concentration measurements are used to estimate dry deposition fluxes so that total deposition can also be determined. The greatest density of sites is located in eastern Canada where deposition fluxes and aquatic and forest sensitivities are highest. The locations of the CAPMoN precipitation and air chemistry monitoring sites as of June 2004 are shown in Figure 3.3 with the exception of the Esther (AB) and Sutton (QC) sites which were closed in 2002 but are included because their data are used extensively in later sections of this report. One site, Penn State, is located outside of Canada at State College, Pennsylvania, U.S.. This site is used to provide intercomparison data with the U.S. National Atmospheric Deposition Program/National Trends Network.

The spatial and temporal variability of wet deposition at CAPMoN sites is illustrated in Figures 3.4 and 3.5. Shown are the available annual sulphate and nitrate wet deposition values at selected CAPMoN sites during the period 1986 to 2002. Not all years are shown at all sites because several of the sites began operation part way through the 17 year period. To be included in the figures, all annual deposition values were required to meet the following annual data completeness criteria: (1) the precipitation chemistry sampler had to be operating for at least 90% of the year and (2) valid concentration data had to represent >70% of the precipitation that fell in the year. Figures 3.4 and 3.5 illustrate that sulphate and nitrate wet deposition is higher in eastern Canada than western Canada. In eastern Canada, the highest sulphate and nitrate wet deposition occurs in southern Ontario and southwestern Québec, with decreasing gradients toward the north and east (see also Figures 3.2a and 3.2b). Lowest deposition in eastern Canada occurs in northwestern Ontario (E.L.A.), northern Québec (Chapais), southern Newfoundland (Bay D'Espoir) and eastern Labrador (Goose Bay) – all located far from the major SO_2 and NO_x emission sources in Canada and the U.S..

In western Canada, wet deposition fluxes at three CAPMoN sites, i.e., Saturna (BC), Esther (AB) and Snare Rapids (NT), are generally lower than in the east. This is particularly true at Snare Rapids and Esther where

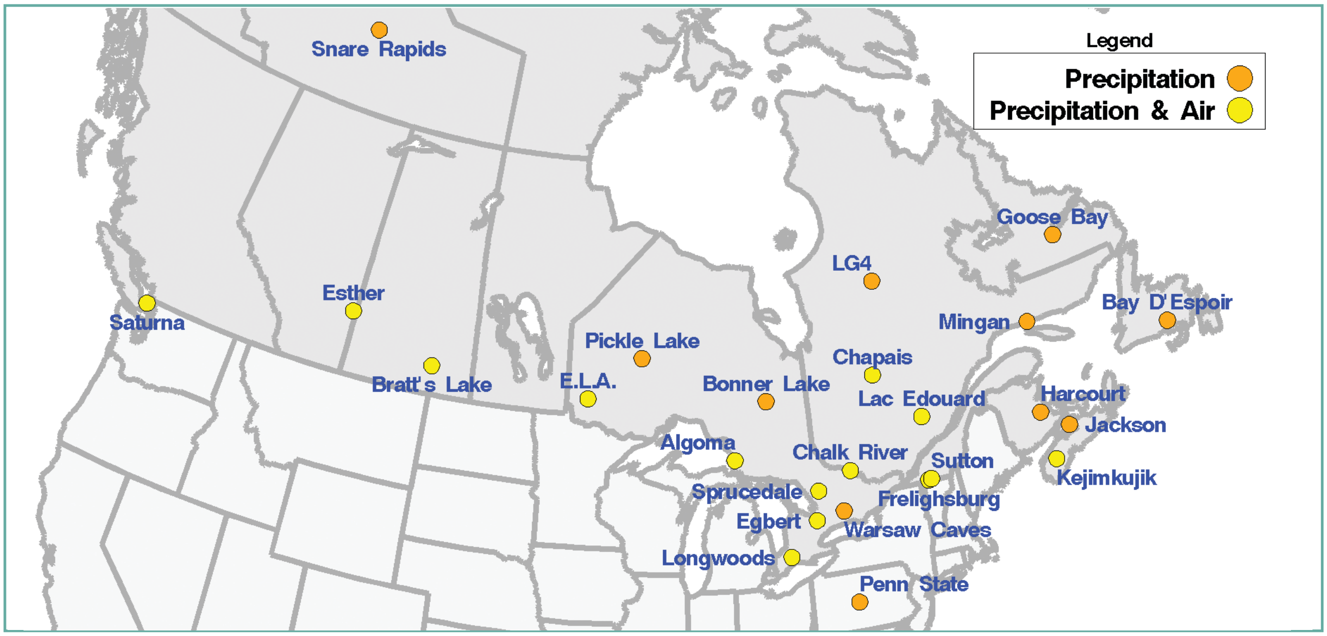

Figure 3.3: Location of CAPMoN precipitation chemistry/wet deposition and air chemistry/dry deposition monitoring sites in June 2004 (except for Esther and Sutton which closed in 2002).

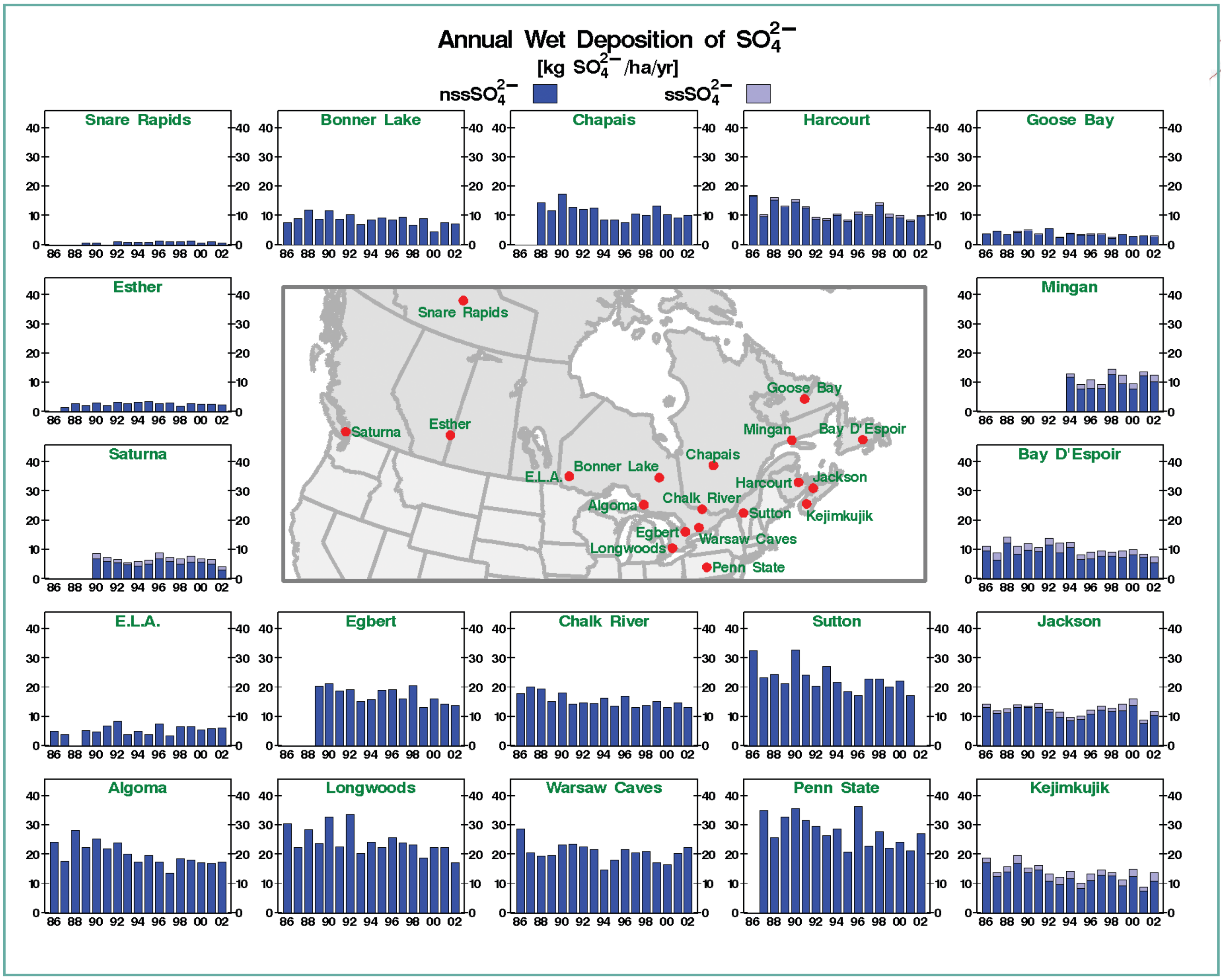

Figure 3.4: Annual wet deposition of non-sea-salt sulphate ($nssSO_4^{2-}$) and sea-salt sulphate ($ssSO_4^{2-}$) at CAPMoN sites across Canada from 1986 to 2002. The Bratts Lake CAPMoN site is not shown because its first full year of operation was 2002.

precipitation amounts are the lowest in the network. Note that sea-salt sulphate ($ssSO_4^{2-}$) and non-sea-salt sulphate ($nssSO_4^{2-}$) wet deposition fluxes are shown separately in the figures at all sites located within 100 km of the east and west coasts of Canada. At all other sites, the measured sulphate wet deposition fluxes are assumed to be $nssSO_4^{2-}$ only. Throughout this Chapter, $nssSO_4^{2-}$ is considered to be of anthropogenic origin caused by SO_2 emissions in Canada and the U.S.. The amount of measured sulphate contributed by sea salt at all of the coastal sites is relatively low compared to the anthropogenic $nssSO_4^{2-}$, i.e., less than 20% of the measured SO_4^{2-} by mass on annual basis.

As was the case with $nssSO_4^{2-}$ and NO_3^-, the wet deposition flux of all the major ions varies across Canada. This is shown in Figure 3.6. The coloured slices of the pie charts in the figure show the fractional abundance (in %) of $nssSO_4^{2-}$, NO_3^-, Cl^-, H^+, NH_4^+, Na^+, K^+, Ca^{2+} and Mg^{2+} (in equivalents) relative to the sum of the ions averaged over the three year period from 2000-2002. The area of each pie is directly proportional to the total ion equivalent wet deposition (i.e., the sum of all individual ion equivalents) at each site.

A number of observations can be made from the CAPMoN results shown in Figure 3.6:

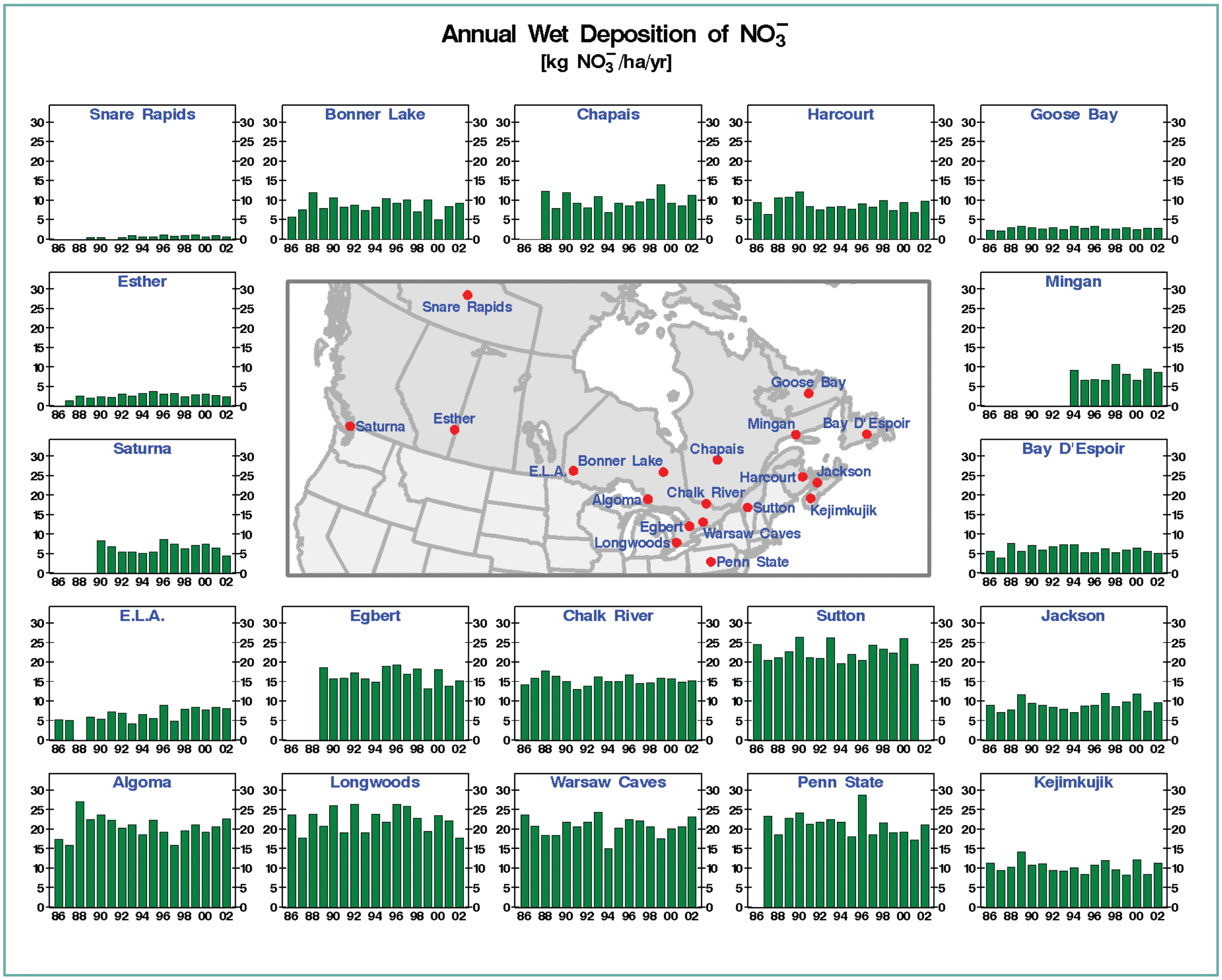

Figure 3.5: Annual wet deposition of nitrate at selected CAPMoN sites across Canada from 1986 to 2002. The Bratts Lake CAPMoN site is not shown because its first full year of operation was 2002.

- Total ion wet deposition is high at CAPMoN sites located within 100 km of the east and west coasts of Canada. Sea-salt Na^+ and Cl^- are the dominant ions wet deposited at these sites.
- Total ion deposition is also very high in southern Ontario and southern Québec (as well as at Penn State in the U.S.), due to the very high deposition of SO_4^{2-}, NO_3^-, and H^+. Southern Ontario and southern Québec are in the prevailing wind direction from the high SO_2 and NO_x emission areas of eastern Canada and the eastern U.S. (see discussion in Section 3.5).
- The areas of lowest total ion deposition are the Northwest Territories, Alberta, northern Ontario, northern Québec and Labrador. These areas are located far from major anthropogenic sources of SO_2 and NO_x.
- SO_4^{2-} and NO_3^- are the dominant anions and H^+ and NH_4^+ are the dominant cations at all non-coastal sites. These four ions constitute over three quarters of the total ion deposition at those sites.

3.3.2 Dry and total deposition

As will be seen in Chapters 5 to 8 of this Assessment, it is the total (i.e., wet plus dry) deposition which is of prime interest to ecosystem effects researchers. However, direct dry deposition measurements are difficult to make operationally because they require sophisticated instrumentation that does not lend itself easily to routine

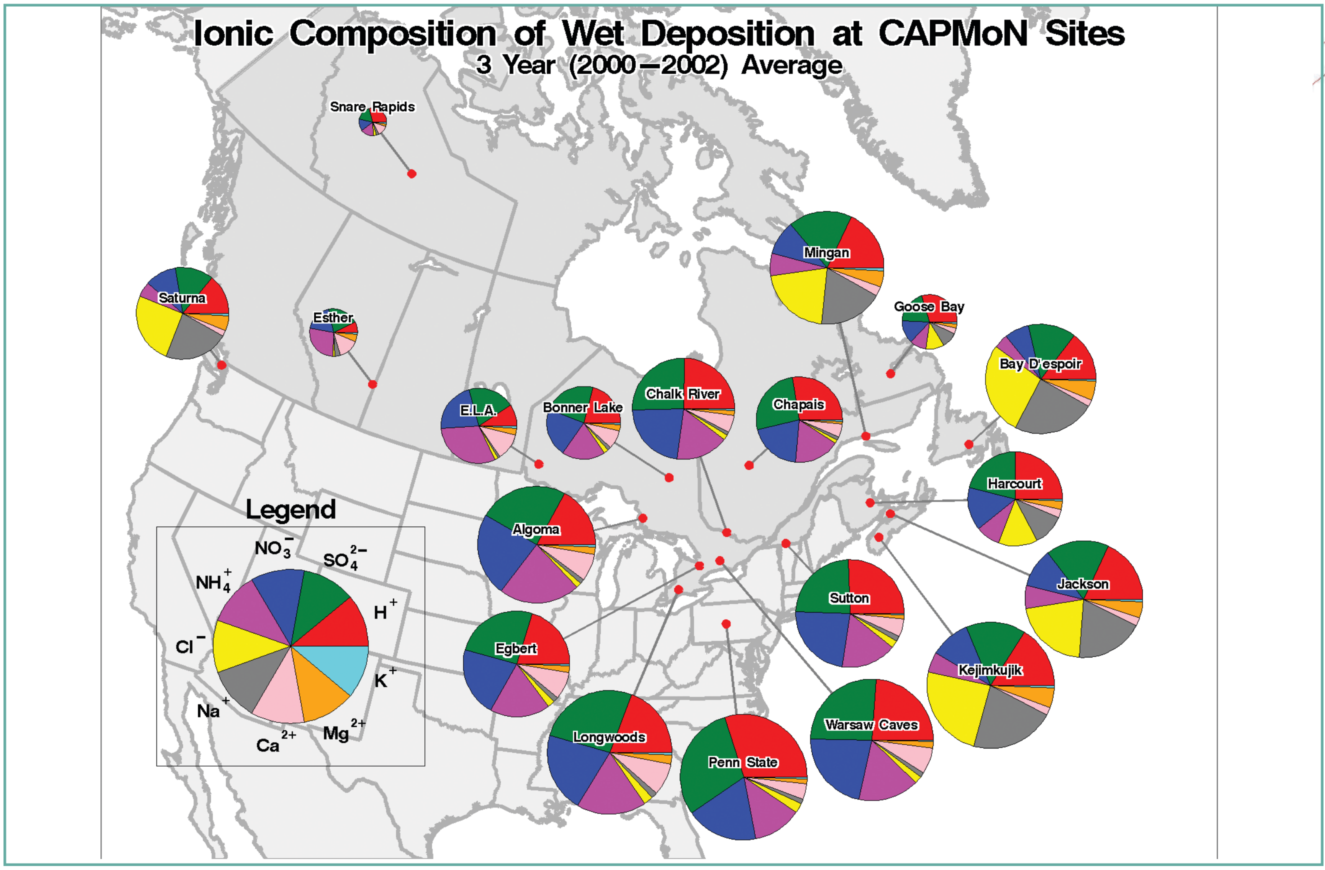

Figure 3.6: Ion composition of wet deposition at CAPMoN sites. Each coloured slice represents the percentage of the total ion wet deposition (in equivalents) contributed by that ion (see legend). The values were calculated as the 3-year average wet deposition fluxes of the individual ions for the period 2000-2002. The area of each circle is directly proportional to the total ion wet deposition (in equivalents) at that site.

monitoring at remote sites. To estimate dry deposition fluxes at CAPMoN sites, Environment Canada has adopted a combined measurement/modelling technique known as the inferential dry deposition method. In this method, dry deposition fluxes of gases and particles are calculated as the product of the ambient concentrations of those species (measured daily by the CAPMoN Network) and daily-average dry deposition velocities calculated using a modelling technique. Similar inferential approaches are used by the two national dry deposition monitoring networks in the U.S. (Baumgardner et al., 2002 and Meyers et al., 1998), namely, the Clean Air Status and Trends Network (CASTNET) operated by the Environmental Protection Agency and the Atmospheric Integrated Research Monitoring Network (AIRMoN) operated by the National Oceanic and Atmospheric Administration (NOAA).

In the past five years, Environment Canada has developed a new inferential dry deposition model for estimating dry deposition velocities at CAPMoN sites. The model, known as the RDM or the Regional Deposition Model (Brook et al., 1999; Zhang et al., 2001, 2003), incorporates the latest advancements in dry deposition science. It is driven by predicted meteorological fields from the Canadian weather forecast model (called the Global Environmental Multiscale Model — see Coté et al., 1997) and by specific land use, vegetation, and precipitation data at CAPMoN sites. RDM produces a set of dry deposition velocities calculated every 3 hours for gaseous SO_2, O_3, HNO_3 and particulate SO_4^{2-}, NO_3^-, Cl^-, Ca^{2+}, Mg^{2+}, K^+ and Na^+. The 3-hour deposition velocities are then averaged over 24-hour periods that correspond to the CAPMoN ambient air sampling intervals. RDM calculates the deposition velocities for these species using the so-called "resistance analogy" (Baumgardner et al., 2002 and Meyers et al., 1998) which takes into account the atmospheric, canopy and boundary layer resistances to gas and particle deposition. The sub-model for the gaseous species accounts for stomatal and non-stomatal uptake by vegetation using a "big-leaf" approach over short canopies and a "multi-layer" approach over tall canopies. The sub-model for particles accounts for the effects of Brownian diffusion, interception, impaction and particle rebound, all of which are functions of particle size and density.

The daily dry deposition fluxes of gaseous SO_2 and HNO_3 and particle-SO_4^{2-} and NO_3^- were calculated as the product of the RDM-generated 24-hour-average dry deposition velocities and the associated 24-hour average ambient concentrations measured at the sites by the CAPMoN filter pack system. Seasonal and annual dry deposition fluxes of Total S (i.e., SO_2 + p-SO_4^{2-}) and Total N (i.e., HNO_3 + p-NO_3^-) were calculated in kg S/ha/yr and kg N/ha/yr, respectively, by summing the daily fluxes of the gaseous and particle species. The flux estimates were made only for the period from December 1997 to December 2002 as this was the only period for which meteorological data from the Global Environmental Multi-Scale Model were available. Also, it should be noted that what is termed "Total N" in Sections 3.3.2.1 to 3.3.2.3 does not include a number of atmospheric nitrogen species (most notably, NH_3, NO, NO_2, peroxy acetyl nitrate or PAN) which contribute to dry deposition. The uncertainty introduced by this omission is discussed in Appendix 3.2.

Some comments are in order here about how the present estimation methods for dry deposition compare with those used in previous Assessments. The dry deposition velocities of SO_2 used to calculate the sulphur dry deposition fluxes at CAPMoN sites in this report are considerably higher than those used in the past (Sirois and Barrie, 1988). In contrast, the annual dry deposition velocities of HNO_3 and particle-NO_3^- are very close to the values used in the past. The new HNO_3 dry deposition velocities, however, include significant seasonal variability and the particle-NO_3^- velocities now account for both coarse and fine particle dry deposition. As a result, the historical dry deposition fluxes of SO_2, HNO_3 and p-NO_3^- are considered to be underestimated. Current estimates of dry deposition velocities and dry deposition fluxes, although limited to the 1998-2002 period, are considered the most accurate generated to date.

3.3.2.1 *Five-year average dry and total deposition*

The estimated five-year-average (1998-2002) dry deposition fluxes of sulphur and oxidized nitrogen at the eleven CAPMoN sites are shown in Figure 3.7. As context for the dry deposition fluxes, the figure also includes the 5-year average wet and total (i.e., wet + dry) deposition fluxes for the same period. Note that the sulphur deposition fluxes (both wet and dry) at Saturna and Kejimkujik include both sea salt sulphate and non-sea-salt sulphate while the other non-coastal sites include only non-sea-salt sulphate.

As already pointed out above, there are potential biases associated with the dry and total deposition fluxes of nitrogen (i.e., oxidized nitrogen). A discussion of the biases can be found in Appendix 3.2 and, based on the conclusions, readers should keep in mind the following uncertainties when considering the nitrogen dry and total deposition values shown below in Figures 3.7 to 3.14:

- In general, NO_2 dry deposition appears to be as important as HNO_3 + p-NO_3^- dry deposition in southwestern Ontario (close to the major NO_x emission areas of eastern North America) and less so at rural and remote sites away from southwestern Ontario.
- The annual dry deposition fluxes of nitrogen presented below are biased low by an estimated factor of 2 in southwestern Ontario and 1.4 in the rest of eastern Canada. No estimates are currently available for western Canada.
- The annual total deposition (i.e., wet + dry) fluxes of nitrogen are biased low by an estimated factor of 1.4 in southwestern Ontario and 1.1 in the rest of eastern Canada. No estimates are currently available for western Canada.

Several interesting observations about dry, wet and total deposition across Canada can be made from Figure 3.7. They are:

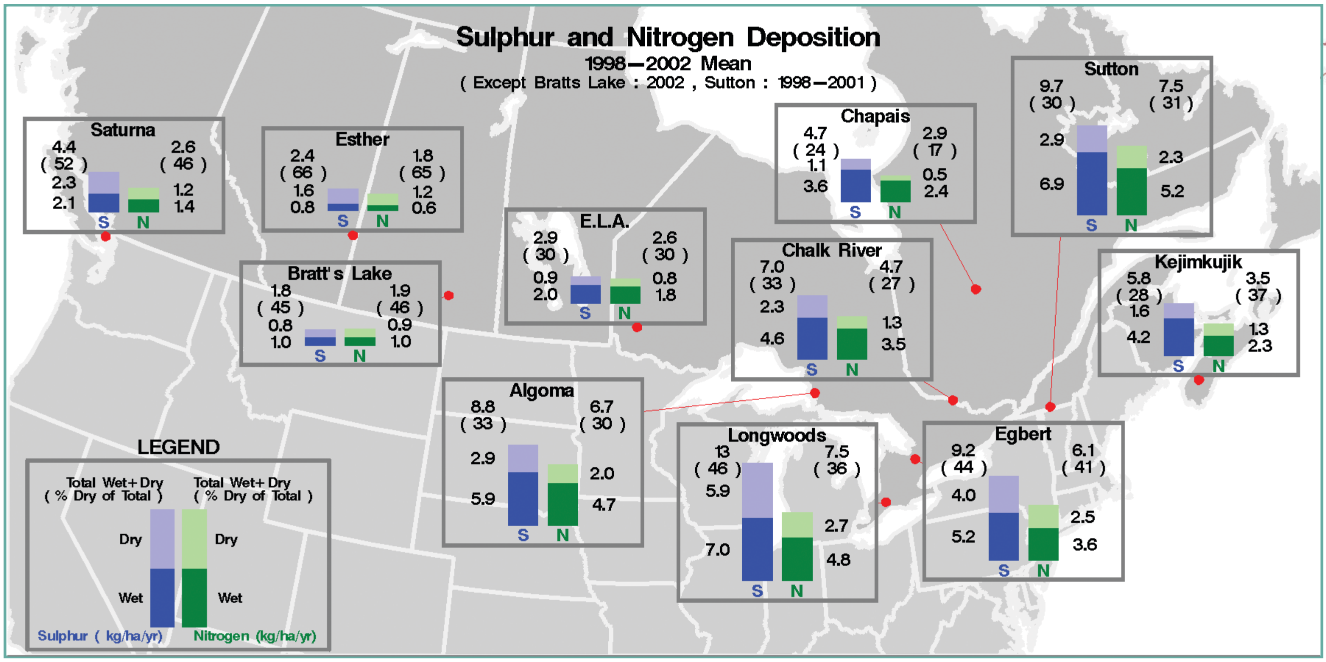

Figure 3.7: Five-year-average (1998-2002) dry, wet and total deposition fluxes of sulphur and oxidized nitrogen at CAPMoN dry deposition monitoring sites. The numbers in parentheses represent the five-year average ratios of dry-to-total deposition. Due to operating period limitations, the Bratt's Lake (SK) results represent only one year of measurements (2002) and the Sutton (QC) results represent four years of measurements. The oxidized nitrogen dry deposition values do not include NO, NO_2 or PAN dry deposition.

- The highest dry deposition fluxes of S and N occur in south/central Ontario (Longwoods, Egbert, Algoma, Chalk River) and southern Québec (Sutton). The lowest dry deposition fluxes occur in western Canada (Saturna Island, Esther, Bratt's Lake), northern Ontario (ELA) and northern Québec (Chapais). Moderate deposition values occur in Atlantic Canada (Kejimkujik). This pattern is similar to that for wet nssSO_4^{2-} and NO_3^- deposition.
- The highest 5-year average total (wet + dry) deposition fluxes of S and N occurred along the Windsor-Québec corridor. The lowest fluxes occurred in western Canada and northern Québec. The highest total deposition of S was 13.0 kg S/ha/yr at the Longwoods site in southwestern Ontario and the highest total deposition of N was 7.5 kg N/ha/yr at both the Longwoods (ON) and Sutton (QC) sites. The lowest values of total deposition occurred in the Prairies due to low amounts of precipitation at Esther (AB) and Bratt's Lake (SK).
- Wet deposition exceeds dry deposition at all CAPMoN sites except Saturna Island (BC) for S and Esther (AB) for both S and N. The exceptionally high dry deposition relative to wet deposition at Esther (AB) can be explained by the fact that this location receives extremely low amounts of precipitation that lead to very low fluxes of S and N wet deposition.
- Dry deposition is more important relative to wet deposition in western Canada than in eastern Canada. In eastern Canada, the relative contribution of dry deposition to total deposition is highest in southwestern Ontario. This is due largely to the very high concentrations of SO_2, HNO_3, p-SO_4^{2-} and p-NO_3^- resulting from the area's proximity to the major SO_2 and NO_x emission areas in southwestern Ontario and the U.S. Midwest. Northern Québec (and probably a large part of northern Ontario to the north of the CAPMoN sites) exhibits the lowest dry-to-total deposition ratio. The very low ambient concentrations of S and N gases and particles in this area are due to its remoteness from the major SO_2 and NO_x emission areas.
- As discussed in Appendix 3.2, the N dry deposition is underestimated because NO_2 and PAN dry deposition fluxes are not included. If NO_2 and PAN were included, the % of the total that is dry deposition could increase by an estimated +5% to

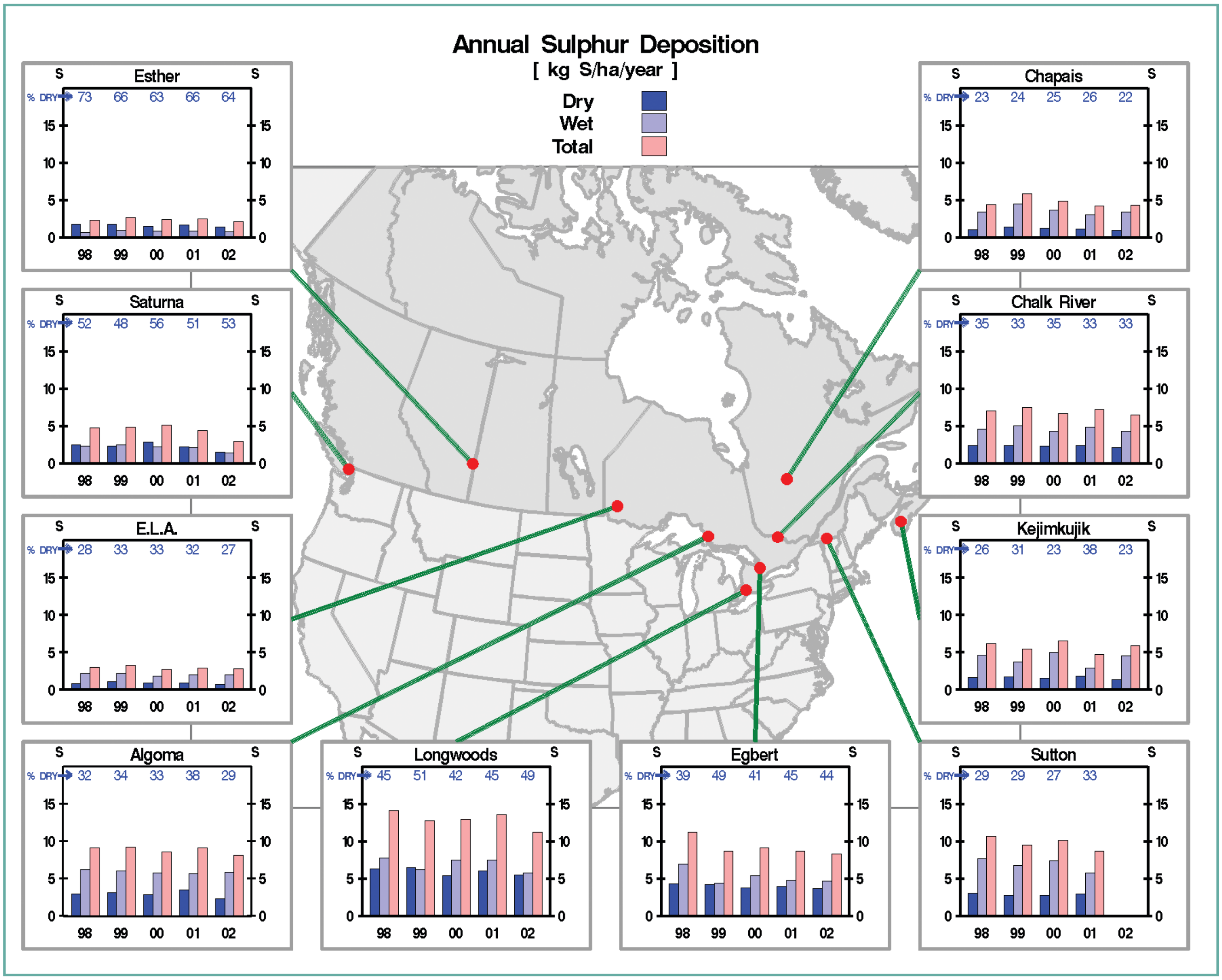

Figure 3.8: The annual dry, wet and total deposition fluxes of sulphur (in kg S/ha/yr) at CAPMoN dry deposition sites for the years 1998 to 2002. The numbers along the top axis of each graph represent the % Dry contribution of dry-to-total deposition for each year.

+10% in the rural/remote areas of eastern Canada and +15% to +20% in southwestern Ontario. For example, N % dry-to-total deposition (% Dry) could increase from 30% to 36% at Algoma and from 36% to 52% at Longwoods. Estimates are unavailable for western Canada.

3.3.2.2 *Annual dry and total deposition*

The previous section provides a multi-year average view of the contribution of dry deposition to total (wet + dry) deposition at CAPMoN sites. The present section discusses year to year changes in the dry, wet and total deposition fluxes at each site for the years 1998 to 2002.

Figures 3.8 and 3.9 show that the annual S and N fluxes of wet, dry and total deposition vary considerably at some sites (e.g., Longwoods, Egbert and Kejimkujik) and very little at other sites (e.g., Algoma, ELA). The annual contribution of dry-to-total deposition is presented along the top of each site plot as the % Dry ratio. The inter-annual variability of the dry and wet deposition fluxes and the dry-to-total deposition ratios is due to year-to-year variability in the SO_2 emissions and in the meteorological factors that determine ambient gas and particle concentrations and dry deposition velocities at the CAPMoN sites (e.g., temperature, sunshine, precipitation, wind direction, wind speed).

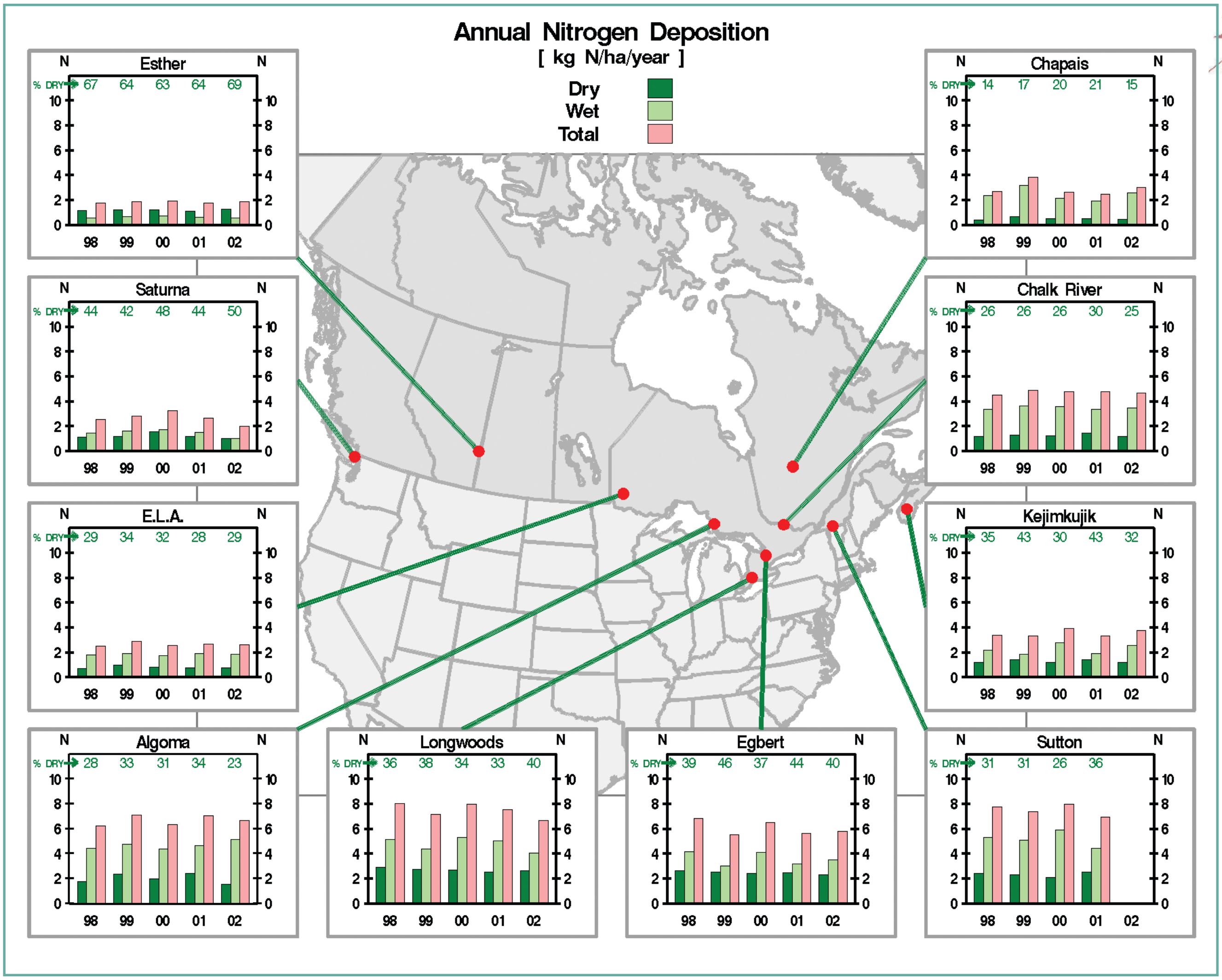

Figure 3.9: The annual dry, wet and total deposition fluxes of nitrogen (in kg N/ha/yr) at CAPMoN dry deposition sites for the years 1998 to 2002 (HNO_3 and p-NO_3 dry deposition only). The numbers along the top axis of each graph represent the % Dry contribution of dry-to-total deposition for each year.

3.3.2.3 *Seasonal dry and total deposition*

Seasonal wet, dry and total deposition fluxes of S and N are shown in Figures 3.10 and 3.11, respectively. So too are the seasonal % Dry ratios. The lower bars (representing the seasonal dry deposition contribution) and the upper bars (representing the seasonal wet deposition contribution) are additive, meaning that the top of the upper bar represents the sum of wet plus dry (i.e., total) deposition. Seasons are defined as Winter: December to February, Spring: March to May, Summer: June to August, and Fall: September to November and the graphs begin with the December 1997 – February 1998 winter season.

For S, the wet and dry deposition fluxes at most sites do not have consistent seasonal cycles in that the maximum and minimum fluxes do not occur systematically in the same season every year. Nonetheless, most sites in eastern Canada tend to have high wet deposition fluxes in the warm periods of the year and low wet deposition fluxes in the cold periods of the year. In contrast, the dry deposition fluxes at most sites in western Canada are slightly higher in the cold periods and lower in the warm periods. Saturna Island (BC) is an exception in that it shows good consistency from year to year with high levels of both wet and dry deposition occurring every fall and winter. The lack of strong, consistent seasonal cycles in

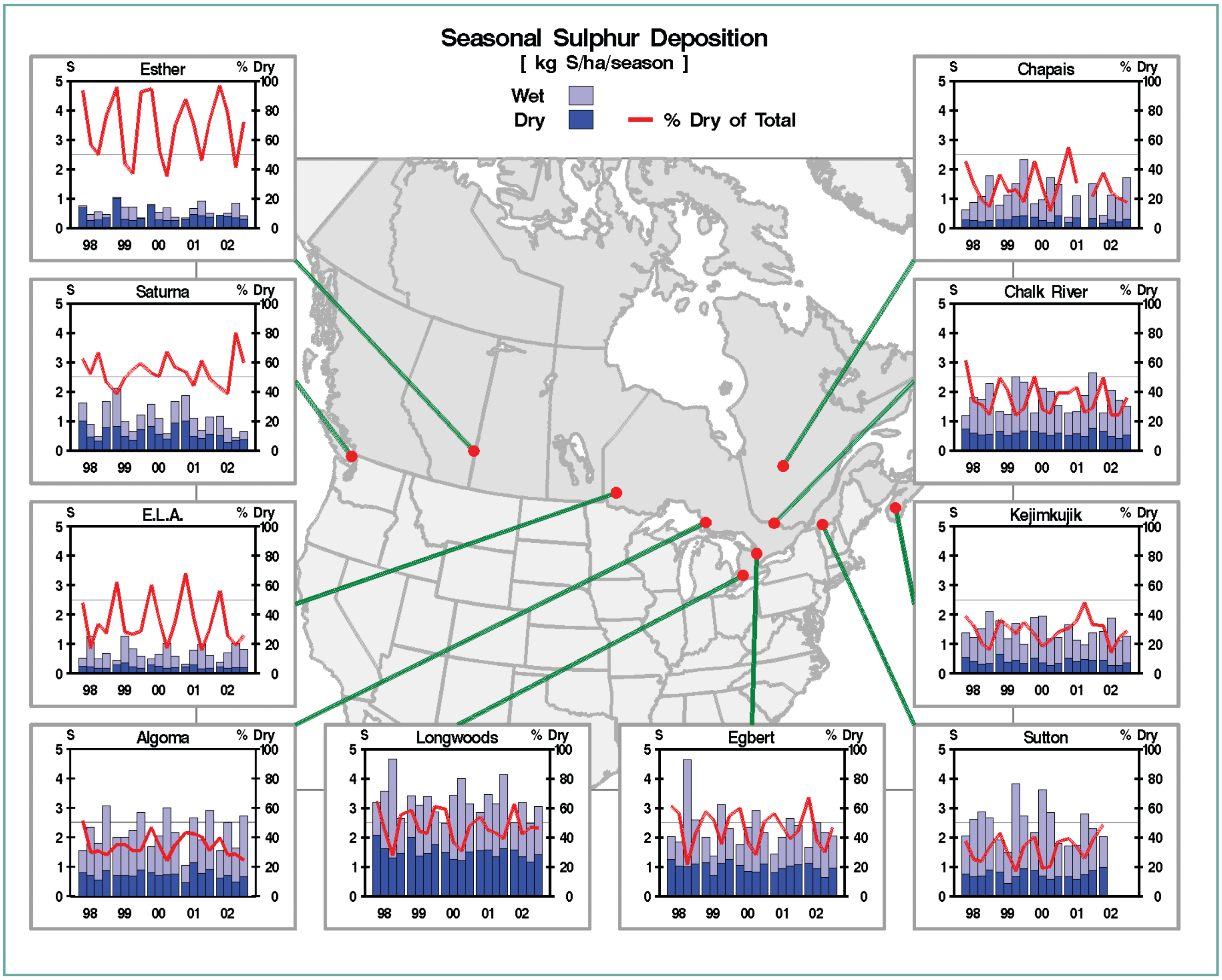

Figure 3.10: Seasonal values of dry, wet and total deposition of S (in kg S/ha/season) at CAPMoN sites for the years 1998 to 2002. The dry and wet deposition fluxes are additive so the tops of the upper bars represent total S deposition. The red line represents the % Dry contribution of dry-to-total deposition in each season. The horizontal line illustrates the level at which 50% of the total deposition is due to dry deposition. Seasons are shown in order of Winter, Spring, Summer and Fall and are defined as Winter: Dec/Jan/Feb; Spring: Mar/Apr/May; Summer: Jun/Jul/Aug and Fall: Sep/Oct/Nov.

the dry deposition fluxes at most sites is related to the complicated interplay of seasonally-varying SO_2 and p-SO_4^{2-} concentrations, dry deposition velocities and SO_2-to-SO_4^{2-} conversion rates.

As with S deposition, the wet, dry and total deposition fluxes of N vary markedly from season to season and year to year (Figure 3.11). Many of the eastern Canadian sites tend to have higher nitrogen wet and dry deposition fluxes in the summer but generally there is no year to year consistency in the seasons of maximum and minimum deposition. Only the two southwestern Ontario sites, Longwoods and Egbert, exhibit consistent seasonal cycles throughout the years, with highest dry deposition occurring in the summer and lowest in the winter. This appears to be driven predominantly by the very high concentrations and dry deposition velocities of HNO_3 in the summer. It is important to point out again that the dry deposition fluxes of N presented here are underestimated because they do not include the dry deposition fluxes of NO, NO_2, PAN and the reduced nitrogen species.

Although space limitations preclude a more detailed discussion, it should be pointed out that S dry deposition is primarily attributable to SO_2 and nitrogen

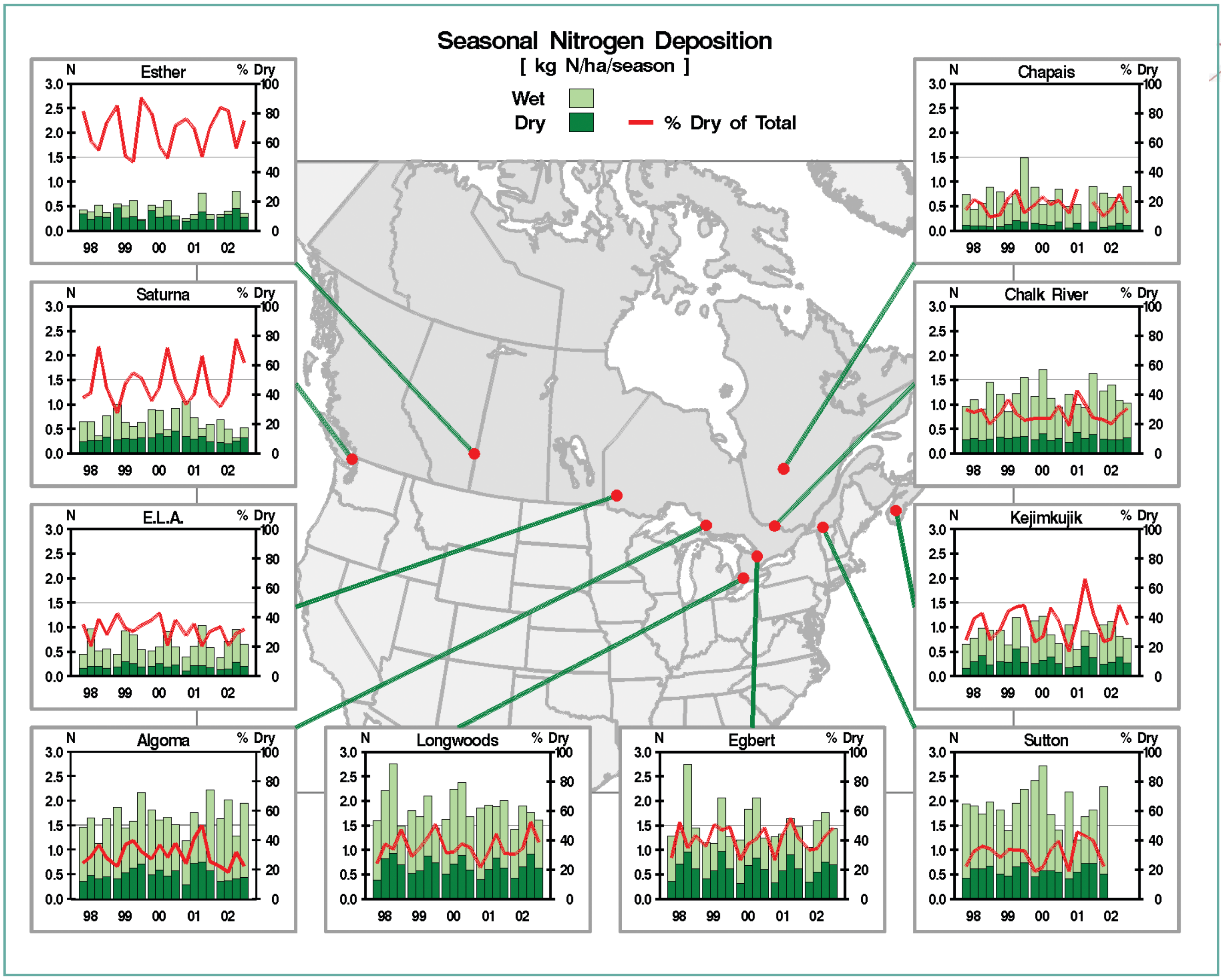

Figure 3.11: Seasonal values of dry, wet and total deposition of N (in kg N/ha/season) at CAPMoN sites for the years 1998 to 2002 (HNO_3 and p-NO_3^- dry deposition only). The dry and wet deposition fluxes are additive so the tops of the bars represent total N deposition. The red line represents the % Dry contribution of dry-to-total deposition during each season. The horizontal line illustrates the level at which 50% of the total deposition is due to dry deposition. Seasons are shown in order of Winter, Spring, Summer and Fall and are defined as Winter: Dec/Jan/Feb; Spring: Mar/Apr/May; Summer: Jun/Jul/Aug and Fall: Sep/Oct/Nov.

dry deposition is predominantly due to gaseous HNO_3. The greatest contribution of SO_2 to total S dry deposition occurs in the winter and the greatest contribution of HNO_3 to total N dry deposition occurs in the summer.

3.4 TEMPORAL CHANGES OF ACIDIFYING SPECIES IN AIR, PRECIPITATION AND WET DEPOSITION RELATED TO CHANGING EMISSIONS

Concentrations of acidifying species in air and precipitation change with time depending on changes in emissions, transport, dispersion, transformation and deposition. Several published studies have shown that reductions in SO_2 emissions in the U.S. in 1995 produced lower concentrations of SO_2 in air and SO_4^{2-} in precipitation at measurement sites across the U.S. (Holland et al., 2000, Lynch et al., 2000). We investigate in this section whether SO_2 and NO_x emission changes in eastern Canada and the eastern U.S. in the 1990s produced concomitant changes in the quality of air and precipitation in eastern Canada. The focus of this section is on the concentrations of major ions in precipitation and air because atmospheric concentrations respond more directly to changing emissions than do wet and dry

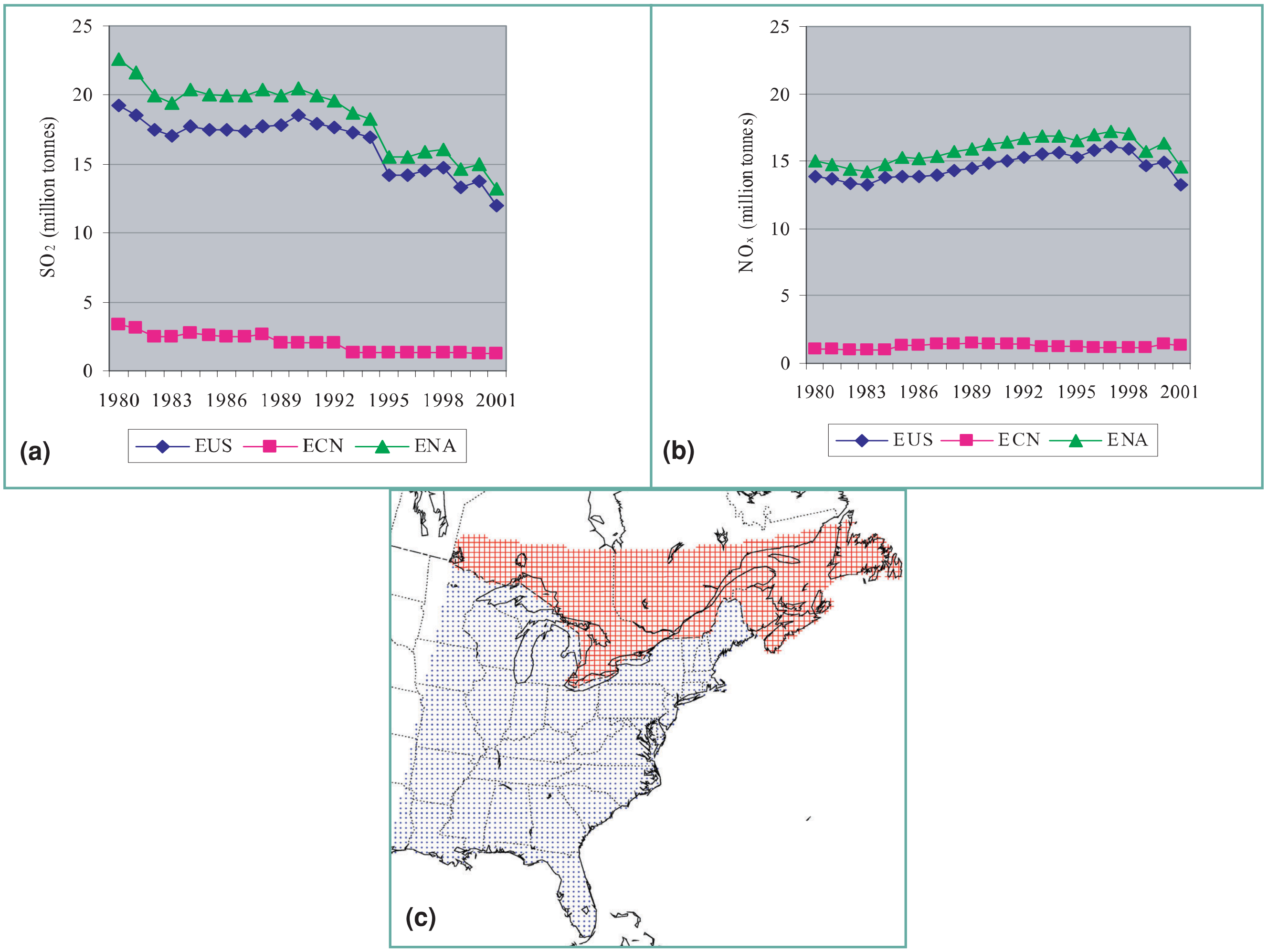

Figure 3.12: Integrated SO_2 (a) and NOx (b) emissions in MT/yr in eastern Canada (ECN), eastern U.S. (EUS) and eastern North America (ENA) from 1980 to 2001. Note the large reductions of SO_2 emissions in the eastern U.S. in 1995 and 1999 in response to Phase 1 and Phase 2 of the U.S. Clean Air Act Amendments. The area of integration is shown as a map insert (c).

deposition. This is because temporal changes in wet deposition fluxes are affected by both changing ion concentrations and changing precipitation amounts. Similarly, trends in dry deposition fluxes are affected by variations of both ambient air concentrations and dry deposition velocities. Thus, atmospheric trends due to emission changes are easier to detect using air and precipitation concentrations of sulphur and nitrogen species.

3.4.1 SO_2 and NO_X emission trends in eastern North America

As context for the trend analyses that follow, readers are referred to the 1990 SO_2 and NO_X emission maps shown in Appendix 3.1, with the caveat that emission levels have changed since 1990 but the distribution of sources has not changed. From this understanding of the emission distribution, it is useful to investigate the magnitude and distribution of changes in SO_2 and NO_X emissions in eastern Canada and the eastern U.S. between 1980 and 2001 (emission data post-2001 were not available at the time of writing for both countries). In the eastern U.S., SO_2 emissions (which comprise over 90% of the total SO_2 emissions in eastern North America) decreased dramatically in the years 1995 and 1999 in response to the Phase 1 and Phase 2 emission reductions mandated by Title IV of the U.S. Clean Air Act Amendments (CAAA). In eastern Canada, SO_2 emissions (which constitute less than 10% of the total eastern North American SO_2 emissions) also declined in the 1990s, although in a slow continuous fashion as opposed to the major step-function drops that occurred in the U.S. in 1995 and 1999.

Figure 3.12 shows the trend in total annual SO_2 emissions integrated over all states and provinces for the period 1980 to 2001. The Canadian emission data were obtained on a province-by-province and year-to-year basis from Environment Canada (1990) for the years 1980 to 1984 and from the Pollution Data Branch of Environment Canada for the years 1985 to 2001 (note that the 2000 and 2001 emission values are forecast values rather than emission inventory values). The U.S. emission data were obtained on a state-by-state and year-by-year basis from the U.S. Environmental Protection Agency. From the figure one can see that the total amount of SO_2 emitted in the eastern U.S. for the period 1995-98 (after the Phase 1 reductions) was 18.3% lower than the total emitted in the 5 year period (1990-94) leading up to the reductions. Similarly, in eastern Canada the 1995-98 average emissions were 24.2% lower than the 1990-94 emissions. After the Phase 2 reductions in 1999, eastern U.S. SO_2 emissions in the 3-year period 1999-2001 dropped another 8.1% below the 1995-98 average emissions and eastern Canadian emissions dropped 2.6% below the 1995-98 levels.

It is important to point out that, while total SO_2 emissions in the eastern U.S. dropped markedly in 1995 and again in 1999 and 2001, the rate at which emissions declined varied considerably from state to state. For example, SO_2 emissions in Pennsylvania dropped 7% from 1994 to 1995 and 10% from 1998 to 1999. In contrast, Ohio emissions dropped 34% from 1994 to 1995 and 27% from 1998 to 1999. Ohio, Illinois and several other states actually increased their emissions above the 1995 levels in 1996, 1997 and 1998 as a result of emission credit trading. The variable nature of the emissions in the individual states has important implications on concentration trends in air and precipitation at measurement sites since each site is influenced to a different degree by emissions and emission changes in the upwind states and provinces.

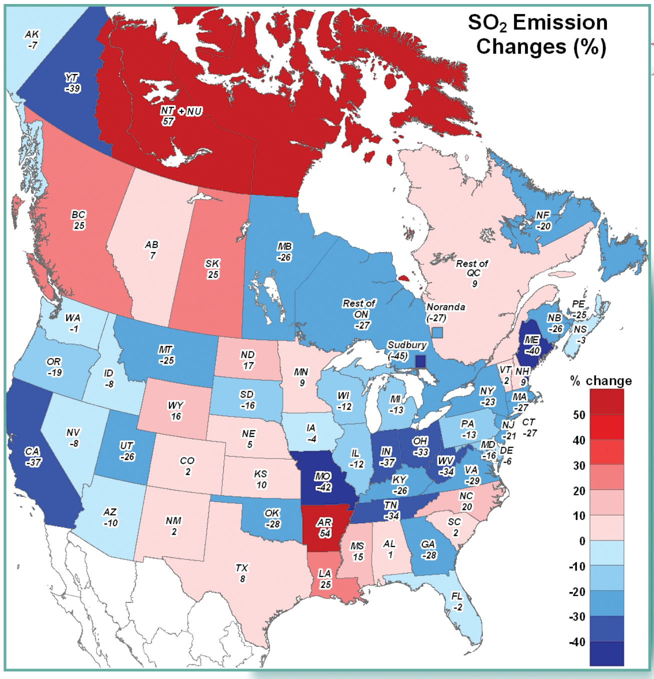

Figure 3.13: Provincial and state SO_2 emission changes (in %) from 1990-94 to 1996-2000. Calculated as the 5-year average emissions in 1996-2000 minus the 5-year average emissions in 1990-94 divided by the 5-year average emissions in 1990-94 and expressed as a percentage. Negative changes (in blue) indicate emission reductions from 1990-94 to 1996-2000 and positive changes (in red) indicate emission increases. The Sudbury (ON) and Noranda (PQ) smelters are shown separately from the rest of Ontario and the rest of Québec.

A more detailed perspective of SO_2 emission changes from the early to late 1990s is given in Figure 3.13 which shows the mean provincial and state SO_2 emission changes between the two 5-year periods 1990-94 (prior to the Phase 1 U.S. reductions) and 1996-2000 (including the Phase 1 and Phase 2 reductions). These two five-year periods were selected to match the periods used in the later discussion of sulphate wet deposition changes in the 1990s. Note that, in Figure 3.13, the emission changes in Ontario and Québec are shown in two parts – one for the major smelter emissions in Sudbury (ON) and Noranda-Rouyn (PQ) and one for the rest of Ontario and the rest of Québec. The smelter emissions were separated from the other emission sources in those provinces because they represent such a large portion of the total Ontario and Québec SO_2 emissions, i.e., 51% and 44% of the total Ontario and Québec emissions in the period 1990-94.

The changes in SO_2 five-year-average emissions from 1990-94 to 1996-2000 are quite different in the various provinces and states. In Canada, reductions of 20% to

45% occurred at the Sudbury and Noranda smelters and in the Provinces of Ontario, New Brunswick, Newfoundland and Labrador and Prince Edward Island. In the U.S., reductions of a similar magnitude occurred in the majority of states along and near the Ohio River Valley, i.e., Missouri, Indiana, Kentucky, Tennessee, Ohio, West Virginia, Virginia, New York and several northern states. Emission reductions in the eight states identified above are extremely important in the North American context as these states contributed one half of the total eastern U.S. emissions in 1990-94. Emissions in other jurisdictions including the province of Québec and the states of Minnesota, New Hampshire, Alabama, South Carolina and Vermont showed little change (+1% to +9%) while Arkansas, Louisiana, and North Carolina emissions actually increased from 20% to 54%. Average eastern Canadian SO_2 emissions dropped by 25% from 1990-94 to 1996-2000 and average eastern U.S. SO_2 emissions dropped by 20%. SO_2 emissions in western Canada (British Columbia, Alberta, Saskatchewan, Nunavut and Northwest Territories) increased between the two periods, as did the SO_2 emissions in most of the U.S. Midwest states. In contrast, emissions in the western U.S. states decreased .

Figure 3.14 provides a similar picture of NO_x emission changes from 1990-94 to 1996-2000 on a provincial and state basis (note that the NO_x emissions are expressed as NO_2). In terms of total emissions, the five-year average NO_x emissions in eastern Canada decreased by 12% between the two periods while the eastern U.S. NO_x emissions increased by 1%. The largest decreases in eastern Canada occurred in Newfoundland and Labrador (26%), Québec (14%), New Brunswick (12%) and Ontario (10%). In the eastern U.S., reductions of 1% to 28% occurred in the Ohio River Valley and the eastern seaboard while increases occurred in all other states. The largest percentage increases occurred in Minnesota (15%), Mississippi (28%) and Arkansas (31%). Note that the smelter emissions in Sudbury and Noranda-Rouyn are not shown separately in Figure 3.14 because NO_x emissions from the smelters are relatively low. Nitrogen oxide emissions in all of the western provinces and territories except British Columbia increased between the two periods. The same is true of all the U.S. Midwest and western states except California, North Dakota and Kansas.

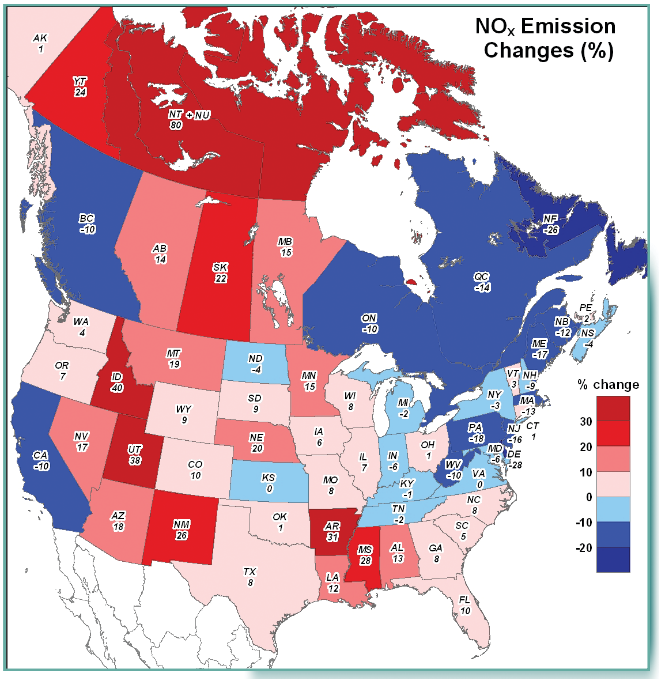

Figure 3.14: Provincial and state NO_x emission changes (in %) from 1990-94 to 1996-2000. Calculated as the 5-year average emissions in 1996-2000 minus the 5-year average emissions in 1990-94 divided by the average emissions in 1990-94. Negative changes (in blue) indicate emission reductions from 1990-94 to 1996-2000 and positive changes (in red) indicate emission increases.

The foregoing changes in the 5-year mean NO_x emissions provide no information on the year-to-year variability in NO_x emission reductions that began in 1999 as a result of Phase 2 of the Clean Air Act Amendments. This information can be found in the annual emission time series plots in Figure 3.16. NO_x emissions in the eastern U.S. increased by 3.2% from 1990-94 to 1995-98 and then decreased 9.5% (relative to the 1995-98 level) in 1999-2001 due to Phase 2 implementation. In contrast, total NO_x emissions in eastern Canada decreased 13.4% from 1990-94 to1995-1998 and then increased 9.2% in 1999-2000 (relative to the 1995-98 level).

3.4.2 Temporal trends of major ions in air and precipitation at selected measurement sites

This section explores whether SO_4^{2-} and NO_3^- concentrations in precipitation and SO_2, SO_4^{2-} , HNO_3 and NO_3^- concentrations in air show measurable changes in the 1990s in eastern Canada and eastern U.S. in response to

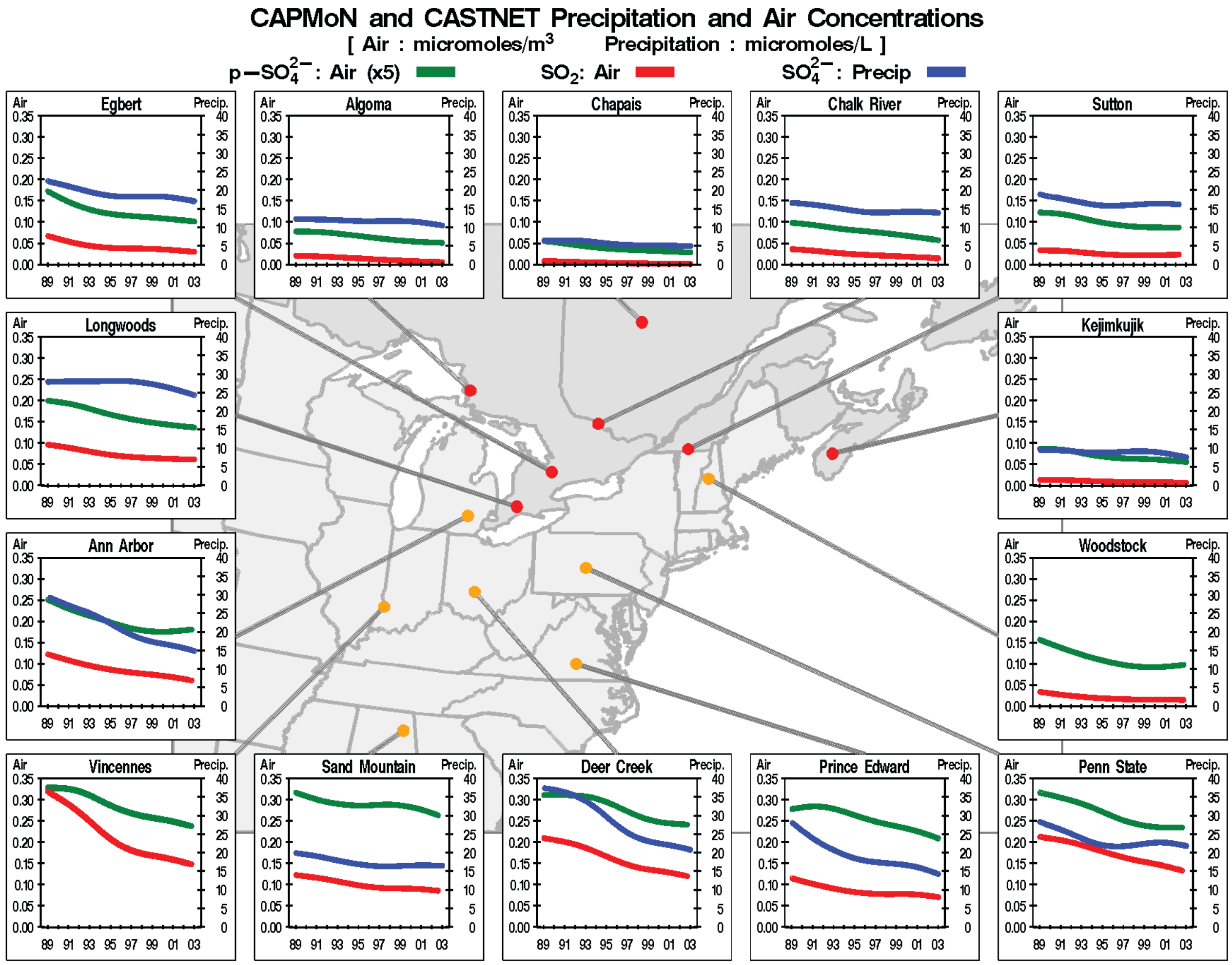

Figure 3.15: Time trends of SO$_2$ and SO$_4^{2-}$ concentrations in air and SO$_4^{2-}$ concentrations in precipitation at selected CAPMoN (in Canada) and CASTNET (in the U.S.) sites. The trends were generated using a Kernel smoothing technique. Sulphate concentrations in air are shown times a factor of 5 in order to match the scale of the other air species. Vincennes and Woodstock have no precipitation chemistry measurement data.

SO$_2$ and NO$_x$ emission changes that took place in that decade. The analyses are done both qualitatively and quantitatively.

3.4.2.1 *Qualitative analysis of trends at Canadian and U.S. measurement sites*

This analysis was done by visually inspecting the time trends of the aforementioned S and N species at selected rural/remote measurement sites of the CAPMoN network in Canada and the CASTNET network in the U.S. (**http://www.epa.gov/castnet/**). Figure 3.15 shows the time trends produced using a Kernel smoothing technique. Kernel smoothing is a sophisticated running-weighted-mean smoother (see Sirois, 1998 for details). In its application here, we used a 4 year bandwidth and a weighting scheme that reduces edge effect errors at the beginning and end of the series. However, like all time series techniques, the trend lines at the edges of the series are the most uncertain and should be interpreted with care. Both Canadian and the U.S. trends are shown in Figures 3.15 and 3.16 to emphasize the point that both countries share a single airshed which is influenced by both countries' emissions. Note that the precipitation trends of SO$_4^{2-}$ in Figure 3.15 represent nssSO$_4^{2-}$.

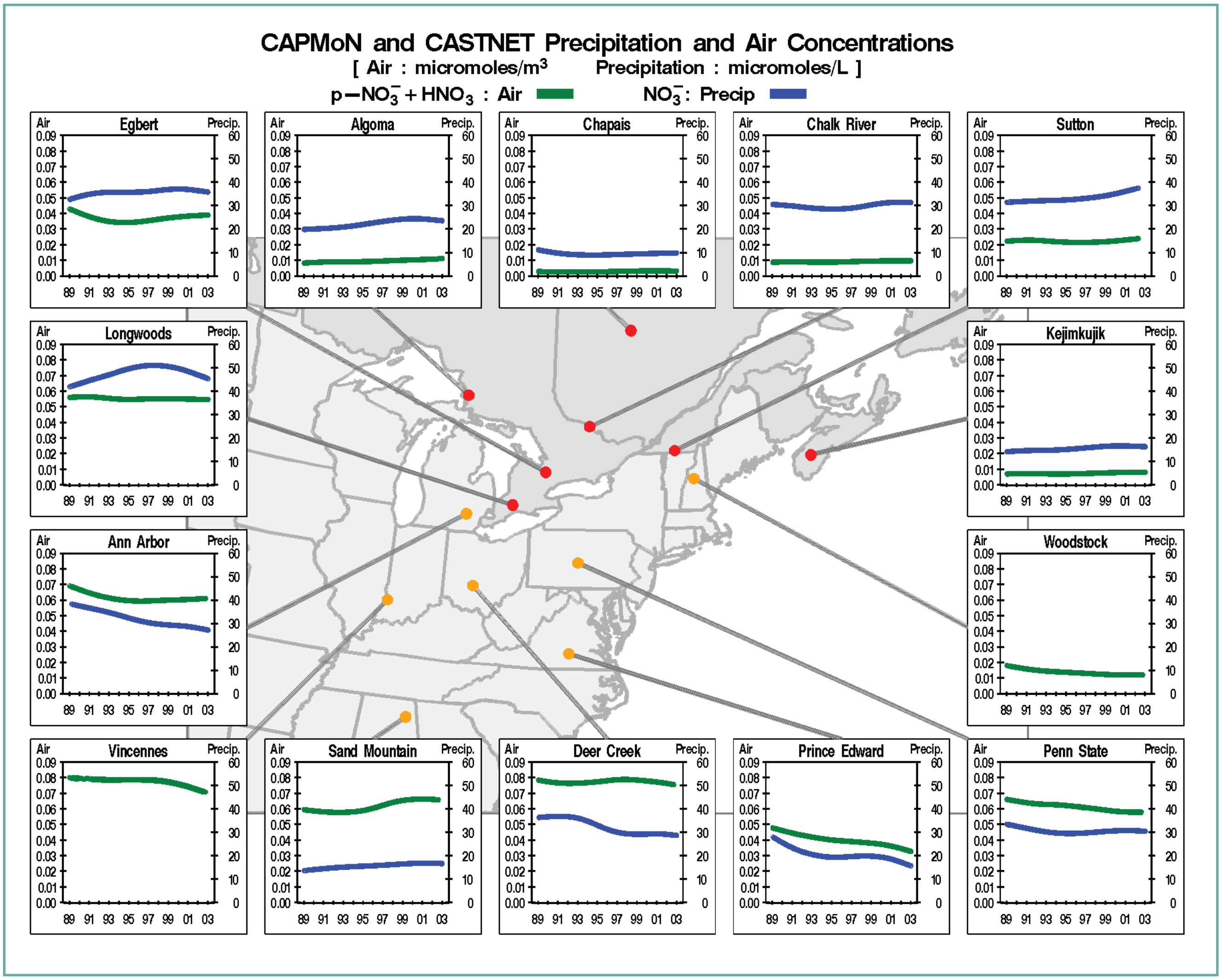

Figure 3.16: Time trends of Total-NO_3^- (i.e., HNO_3 + p-NO_3^-) concentrations in air and NO_3^- concentrations in precipitation at selected CAPMoN and CASTNET sites. The trends were generated using a Kernel smoothing technique. Vincennes and Woodstock have no precipitation chemistry measurement data.

The different shapes of the trend lines at the different sites reflect the fact that individual sites are affected by different SO_2 emission sources, all of which changed at different rates throughout the 1990s (see Figure 3.13). For example, the CASTNET measurement sites in Indiana, Ohio and Pennsylvania, which are located in the highest emission area of the U.S., show higher concentrations and markedly larger declines from the early to late 1990s than do sites located further away from the Ohio River Valley area. Ambient SO_2 and p-SO_4^{2-} concentrations and their associated rates of decline are generally much lower at Canadian sites than at U.S. sites. Exceptions to this occur at two CAPMoN sites in southwestern Ontario (Longwoods and Egbert) which are strongly affected by the high emissions in that area of Ontario as well as from the Ohio River Valley. The time trends in Figure 3.15 support the concept that SO_2 and p-SO_4^{2-} concentrations in air and nssSO_4^{2-} concentrations in precipitation in eastern Canada and the U.S. declined in response to the large emission reductions in the 1990s. This is consistent with Holland et al. (2000) and Lynch et al. (2000).

While the trend lines of SO_2 and p-SO_4^{2-} air concentrations tend to mimic each other, it is interesting to note that the trend lines for nssSO_4^{2-} concentrations in precipitation generally differ from those for air concentrations. In fact, at several sites in both countries, SO_4^{2-} concentrations in precipitation tended to decline in the early part of the

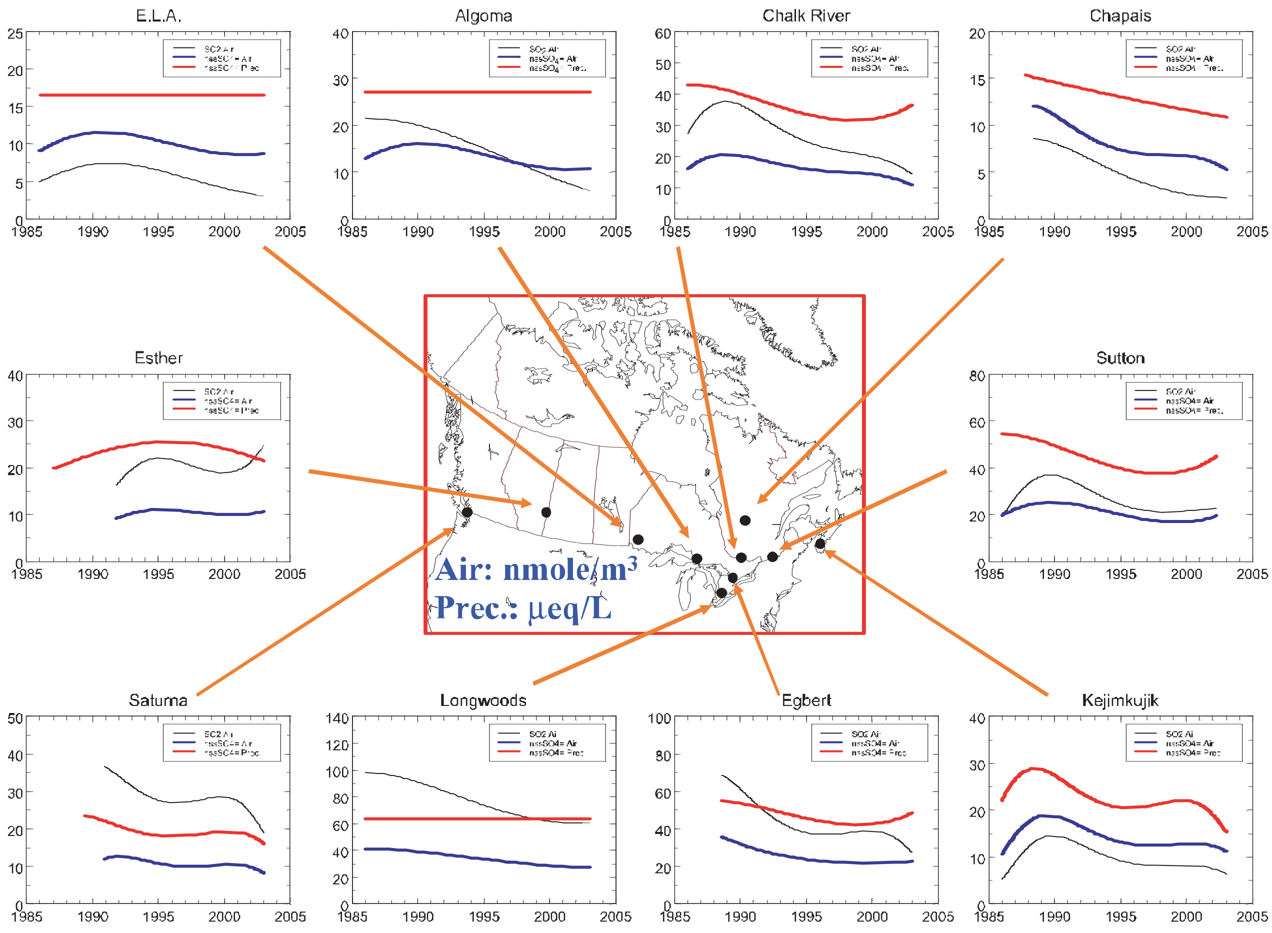

Figure 3.17: Long-term time trends of SO_2 and $nssSO_4^{2-}$ concentrations in air and $nssSO_4^{2-}$ in precipitation at CAPMoN sites. The trends were produced using a geometric least squares time series model published by Sirois (1993).

1990s and level off or even increase slightly at the end of the decade and early 2000s. The reasons for this are unclear but are likely related to the complex interplay of ambient concentrations with in-cloud chemical conversion, precipitation formation and precipitation scavenging.

In contrast to the SO_2 and p-SO_4^{2-} trend lines, the trends of Total-NO_3^- in air (i.e., HNO_3+p-NO_3^-) and NO_3^- in precipitation exhibit little or no consistency within and between sites (Figure 3.16). The fact that no systematic trends appear is consistent with the fact that NO_x emissions changed little in the 1990s.

3.4.2.2 *Quantitative analysis of trends at Canadian measurement sites*

Figure 3.15 qualitatively indicates that S concentrations in air and precipitation generally declined in the 1990s across most of eastern North America. To assess whether the declines were statistically significant, a quantitative statistical analysis was performed to estimate the magnitude and significance of the declines at CAPMoN sites (Canada only). The results, presented as the percent difference in major ion concentrations between the 5-year periods 1990-94 and 1998-2002, are shown in Table 3.1. The percent differences shown in the table were calculated as the differences between the 1990-94 and 1998-2002 average trend values shown in Figures 3.17 and

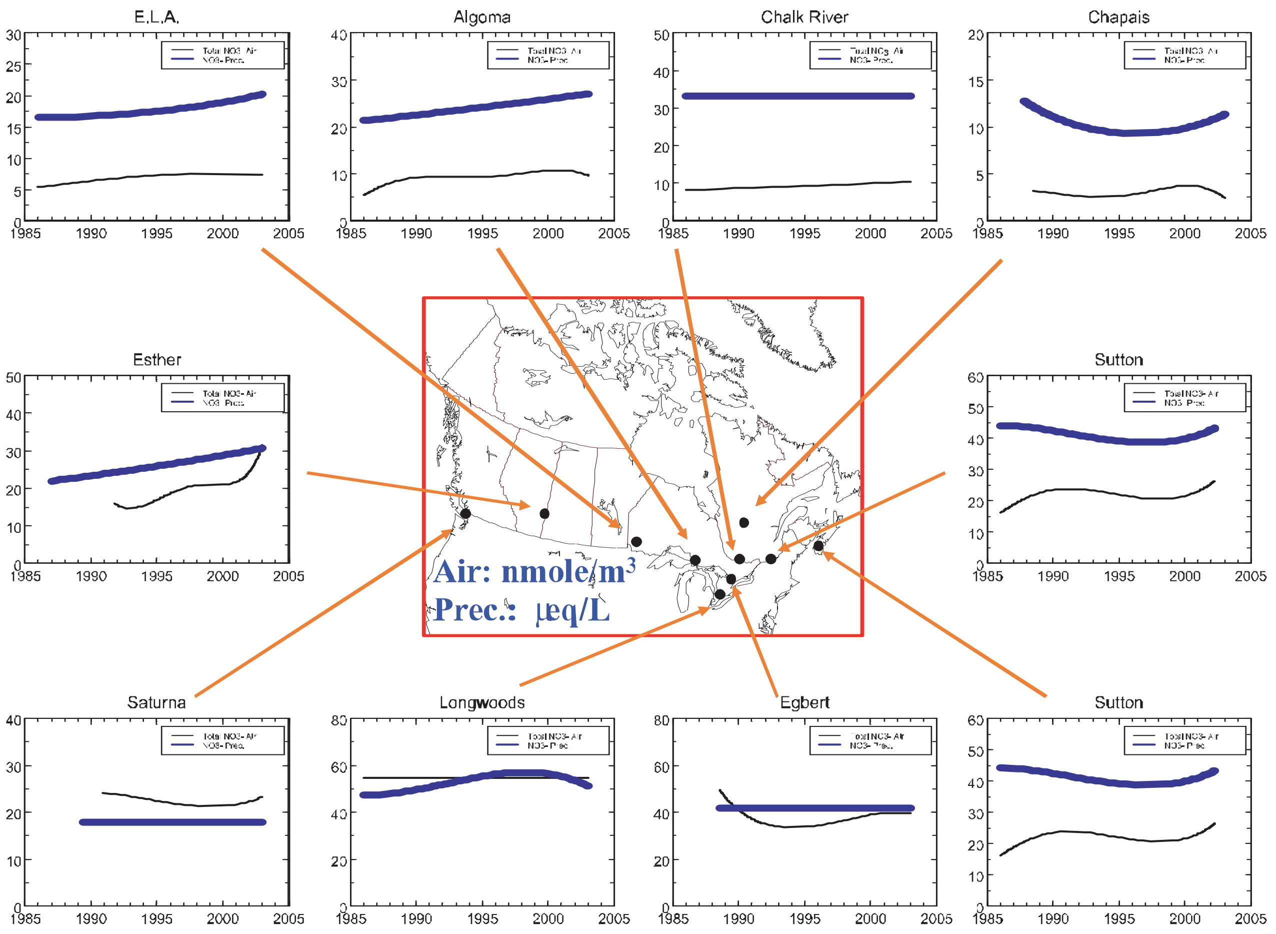

Figure 3.18: Long-term time trends of Total-NO$_3^-$ concentrations in air (i.e., HNO$_3$ + p- NO$_3^-$) and NO$_3^-$ concentrations in precipitation at CAPMoN sites. The trends were produced using a geometric least squares time series model published by Sirois (1993).

3.18 divided by the 1990-94 average value times 100. Note, however, the exceptions to the 5-year averaging periods at Sutton, Saturna and Esther as indicated in the footnotes of Table 3.1. The trend lines were calculated by a geometric least squares time series model published in Sirois (1993).

It is important to point out that this geometric least squares time series model includes a term that accounts for autocorrelation and, in the case of the precipitation trends, a term that accounts for the inverse relationship between ion concentration and precipitation amount. This means that the average trends (Figures 3.17 and 3.18) used to calculate the differences shown in Table 3.1 inherently account for periods of high and low precipitation because such periods can induce artificial trends in the concentration time series. In contrast, the Kernel smoothing technique used to generate the trends in Figures 3.15 and 3.16, does not account for autocorrelation or for the inverse relationship between precipitation amount and ion concentration. Readers should note that the percent difference values shown in Table 3.1 are statistically significant since the trend lines from which they were derived were significantly different at the 95% confidence level.

Table 3.1. Percentage differences in the 5-year-average trends of SO_2 and $nssSO_4^{2-}$ in air and $nssSO_4^{2-}$ in precipitation from 1990-1994 to 1998-2002 based on the geometric least squares time series model trends shown in Figures 3.17 and 3.18. The differences represent the 1998-2002 average concentration minus the 1990-94 average concentration divided by the 1990-94 average concentration. A non-zero value signifies the presence of a statistically significant difference; a zero value signifies no statistically significant difference.

Site	% Difference Between 1990-94 and 1998-2002 Average Trend Lines				
	Ambient Air			Precipitation	
	SO_2	$nssSO_4^{2-}$	Total-NO_3^-	$nssSO_4^{2-}$	NO_3^-
Eastern Canada					
E.L.A.	-45.2	-22.2	9.3	0	12.4
Algoma	-51.7	-28.7	12.7	0	11.9
Longwoods	-25.2	-22.0	0	0	5.4
Egbert	-22.9	-19.2	10.5	-11.8	0
Chalk River	-37.6	-24.3	11.7	-10.1	0
Sutton	-29.5[1]	-24.5[1]	-4.2[1]	-10.0[1]	-0.8[1]
Kejimkujik	-34.0	-21.0	12.9	-11.4	0
Western Canada					
Saturna	-16.4[2]	-16.3[2]	-7.0[2]	-8.3	0
Esther	0.43	-2.5[3]	47.4[3]	-3.9	18.1

[1] Sutton: 4-year average from 1998-2001 was used instead of a 5-year average since the site closed in 2002

[2] Saturna: 4-year average from1991-1994 was used instead of a 5-year average since 1991 was the first full year of air measurements

[3] Esther: 3-year average from 1992-1994 was used since 1992 was the first full year of air measurements.

It is useful at this point to mention a few words about the potential impact of edge effects on the percent difference values shown in Table 3.1. Here, the term *edge effects* refers to the impact of missing data at the two ends of the time series. While most smoothing techniques (e.g., the Kernel smoothing technique used to produce Figures 3.15 and 3.16) attempt to reduce edge effects mathematically, the least squares model used in this analysis is less sensitive to edge effects. This is because the trend lines are produced from a least squares best fit of available data and thereby do not rely on a weighting scheme using data that are not available from outside the time period. In spite of this, the trend line at the beginning and end of the time series is the most uncertain of the analysis. Fortunately, the average values from 1990-1994 are not subject to edge effects at the sites shown in Table 3.1 (except at Saturna and Esther for SO_2, SO_4^{2-} and Total-NO_3^- in air) because the time series began before 1990. The exceptional sites are prone to higher uncertainties due to the edge effects and the reduced number of years included in the averaging period. Likewise, edge effects at the end of the time series (i.e., at the end of 2002) increase the uncertainty of the results and must be borne in mind when interpreting the values in Table 3.1. Fortunately, the 5-year averaging reduces edge effect errors because only one year in five is highly vulnerable to these errors. It is therefore very unlikely that the results of this analysis (as discussed in the following two sections) will change dramatically after future data are added.

3.4.2.2.1 Sulphur

The concentration differences between the two periods tabulated in Table 3.1 confirm statistically that SO_2 concentrations declined between 1990-94 and 1998-2002 at all CAPMoN air concentration monitoring sites in eastern Canada. In the table, the non-zero delta values signify that the trends used to calculate the values were statistically significant while the zero values indicate that the trends were not statistically significant (based on the geometric time trend model). Declines of the order of 20%-30% occurred at CAPMoN sites located in the high concentration areas of southern Ontario/Québec (Longwoods, Egbert and Sutton), 40%-60% in the low concentration areas of northern Ontario/Québec (ELA, Algoma, Chalk River, Chapais), and 34% at the Kejimkujik site in Nova Scotia.

In western Canada, the site at Esther, Alberta showed essentially little change in SO_2 concentrations between the two periods (0.4%). Interestingly, total SO_2 emissions in Alberta also showed no net change between the two periods. In contrast, the site at Saturna Island, British Columbia showed a 16% drop in SO_2 concentrations in spite of the fact that total SO_2 emissions in British Columbia increased by approximately 25% from 1990-94 to 1998-2001. This suggests that the changes in total British Columbia SO_2 emissions do not represent the emission changes at the sources that directly influence the Saturna site (i.e., sources located predominantly in the Greater Vancouver Regional District and the state of Washington).

Air concentrations of p-SO_4^{2-} also declined from 1990-94 to 1998-2002 at most sites in eastern Canada although the magnitude of the p-SO_4^{2-} decline was generally less than that of SO_2. At those sites with data dating back as far as 1986, the SO_2 and p-SO_4^{2-} trend lines mimic each other very closely (see Figure 3.17). In fact, both SO_2 and p-SO_4^{2-} concentrations peak at roughly the same time, i.e., 1988-1992, and then decline slowly afterward. The coincidence of the SO_2 and p-SO_4^{2-} peaks and the subsequent downward trends provide a level of confidence that the SO_2 and nssSO_4^{2-} declines in the 1990s were both related to the decline in SO_2 emissions.

Esther (AB) showed a low magnitude (but statistically significant) decline in p-SO_4^{2-} concentrations between the two periods (-2.5%), which was also the case for SO_2 concentrations (-0.4%). At Saturna Island, nssSO_4^{2-} concentrations between the two periods decreased by 16%, exactly the same as SO_2.

Based on Table 3.1, it is clear that ambient SO_2 and p-SO_4^{2-} concentrations in eastern Canada dropped markedly between 1990-94 and 1998-2002. The p-SO_4^{2-} decline was 13% to 32% less than the SO_2 decline, depending on the site. Only at sites in southern Ontario and southern Québec (i.e., Longwoods, Egbert and Sutton) were the p-SO_4^{2-} declines roughly equal to those of SO_2 (i.e., within ± 5%). Reid et al. (2001) discuss the fact that p-SO_4^{2-} trends have been found in several previous studies to be less than SO_2 trends at sites in Canada and the U.S.. The authors present several possible reasons for this phenomenon – the most probable being, in this case, that p-SO_4^{2-} is a secondary pollutant with a longer residence time in the atmosphere than SO_2. This means that p-SO_4^{2-} and SO_2 concentrations at a given site, especially sites located far from major SO_2 sources, are likely associated with different source regions, each having its own change in emissions. This explanation is consistent with the fact that the Longwoods, Egbert and Sutton sites, all of which are located close to the largest SO_2 emission areas of eastern North America, have similar rates of SO_2 and p-SO_4^{2-} decline while the other sites, which have smaller declines in p-SO_4^{2-} than SO_2, are located farther from the major emission sources and are more likely affected by different source regions for SO_2 and p-SO_4^{2-}. Because different states had different emission trends in the 1990s (per discussion above), it seems reasonable that different source areas for SO_2 and p-SO_4^{2-} would contribute differently to SO_2 and p-SO_4^{2-} air concentration trends at different sites. This is confirmed later in Section 3.5 on source attribution.

As was the case with p-SO_4^{2-} in air, nssSO_4^{2-} concentrations in precipitation also showed net declines between 1990-94 and 1998-2002 in eastern Canada. However, these declines did not occur at all CAPMoN sites and they were generally smaller in magnitude than the declines of p-SO_4^{2-} in air. The trend lines in Figure 3.17 show that statistically significant downward trends occurred at Egbert, Chalk River, Chapais, Sutton and Kejimkujik, although Egbert, Chalk River and Sutton did show slight increases after 1999. The magnitude of the 1990-94 to 1998-2002 declines at Egbert, Chalk River, Chapais, Sutton and Kejimkujik ranged from 10% to 17% (see Table 3.1) or roughly 7% to 15% lower than the declines of p-SO_4^{2-} in air. Perplexingly, no statistically significant trends occurred at ELA, Algoma and Longwoods in contrast to the very substantial decreases of SO_2 and nssSO_4^{2-} in air at those sites.

The fact that nssSO_4^{2-} concentrations in precipitation declined to a lesser degree than SO_2 and p-SO_4^{2-} in air is undoubtedly related to the complexity of the atmospheric processes that lead to sulphate wet deposition – processes that involve a complex interplay of spatially- and temporally-varying emissions, transport, dispersion, oxidant formation, homogeneous chemical transformation, heterogeneous chemical transformation, cloud formation, in-cloud processing, precipitation scavenging and precipitation dynamics. We conclude from Table 3.1, therefore, that the greater the complexity of the atmospheric cycle for sulphur species, the less direct will be the effect of SO_2 emission reductions, i.e., SO_2 emission reductions will produce proportionately larger decreases of SO_2 concentrations in air than of p-SO_4^{2-} in air and nssSO_4^{2-} in precipitation. This means that as SO_2 emissions decline, sulphur dry deposition will decline faster than sulphur wet deposition as long as all the other factors remain constant (e.g., meteorology). This implies that SO_2 emission reductions must be larger to produce the same percentage change in nssSO_4^{2-} wet deposition as occurs for SO_2 and p-SO_4^{2-} dry deposition.

In western Canada, p-SO_4^{2-} concentrations in precipitation at Esther changed very little (< 4%) between 1990-94 and 1998-2002 although the trend line indicates that concentrations peaked in the 1995-96 time period (Figure 3.17). This lack of change is consistent with SO_2 and p-SO_4^{2-} in air. At Saturna Island, nssSO_4^{2-} concentrations in precipitation declined by 8% between the two periods, half the rate of decline of SO_2 and p-nssSO_4^{2-} concentrations in air. The trend lines in Figure 3.17 suggest that SO_2 and p-SO_4^{2-} concentrations had a slight downturn beginning in 2000.

3.4.2.2.2 Nitrogen

For Total-nitrate concentrations in air (i.e., HNO_3 + p-NO_3^-), most eastern Canadian sites showed a 9%-13% increase from 1990-94 to 1998-2002 (i.e., ELA, Algoma, Egbert, Chalk River and Kejimkujik) as seen in Table 3.1 and Figure 3.18. Exceptions to this were Chapais in northern Québec which had a 31% increase, Longwoods in southwestern Ontario which had no significant trend, and Sutton in southern Québec that showed a 4% decrease. The cause of the large percentage increase at Chapais is unknown but could be due to the fact that the concentrations at the site are so low that a slight increase produces a very large percentage change. The lack of a concentration trend at Longwoods and a minor decrease at Sutton (-4.2%) is likely related to minimal changes in NO_x emissions at the sources having the greatest influence on those sites.

For nitrate in precipitation at the CAPMoN sites in eastern Canada, all sites except ELA and Algoma showed either no significant trend or very minor changes (-1% to +5%) between the two periods. Such minimal changes are consistent with the fact that eastern North American emissions changed little between the two periods and that changes in precipitation-scavenged NO_3^- appear to be less sensitive to emission changes than are air concentrations (as was the case with precipitation sulphate). The large increases at ELA and Algoma may be explained by the fact that NO_x emissions actually increased from 1990-94 to 1996-2000 in the western states that strongly influence those sites, viz., Minnesota, Wisconsin, Idaho, Missouri and Illinois. Confirmation of the influence of these states is provided in Section 3.5.

In western Canada, the changes in Total-NO_3^- concentrations in air were very different at the Esther (AB) and Saturna Island (BC) sites. At Esther, Total-nitrate concentrations increased by 47% between the two periods. This is likely due to emission increases in the source regions of greatest influence on the site and is, in general, consistent with the 22% increase in total Alberta NO_x emissions between 1990-94 and 1998-2001 (note that 2002 data are not included in this calculation because emissions data were not available for that year at the time of writing). Nitrate concentrations in precipitation at Esther also increased markedly (18%) between the two periods. At Saturna Island, the nitrate concentrations decreased slightly (7%) between 1990-94 and 1998-2002. The corresponding change in total BC emissions between the two periods was a decline of 6%. Nitrate concentrations in precipitation showed no significant increase or decrease between the two periods – also consistent with the fact that ion concentrations in precipitation do not appear to respond to emission changes as directly as do concentrations in air.

In summary, Sections 3.4.2.2.1 and 3.4.2.2.2 indicate that SO_2 and p-SO_4^{2-} concentrations in air and nssSO_4^{2-} concentrations in precipitation decreased at most sites in eastern Canada from 1990-94 to 1998-2002. Although no causality has been proven, it is assumed that these decreases are directly related to the general reduction of SO_2 emissions in eastern North America. In contrast, nssSO_4^{2-} concentrations in precipitation appeared not to decrease as rapidly as SO_2 and p-SO_4^{2-} concentrations in air. This means that SO_2 emission reductions produce a larger response in S dry deposition than S wet deposition. Total-nitrate concentrations in air and precipitation at sites in eastern Canada changed little between the two periods – consistent with the minor change in eastern North American NO_x emissions between the two periods.

3.4.3 Temporal changes to large-scale patterns of wet deposition related to changing emissions

This section investigates the relationship between large-scale patterns of $nssSO_4^{2-}$ and NO_3^- wet deposition and SO_2 and NO_x emissions in eastern North America. It is based on the assumption that, if such a relationship exists, changing emissions in the 1990s should be reflected in changes to the large-scale wet deposition patterns.

3.4.3.1 Wet Deposition pattern changes related to changing emissions

Changes to the wet deposition patterns of $nssSO_4^{2-}$ and NO_3^- are assessed in the following sections.

3.4.3.1.1 Sulphur

The case was made in Section 3.4.2 that concentrations of $nssSO_4^{2-}$ in air and precipitation at individual measurement sites in eastern Canada declined throughout the 1990s and early 2000s in direct response to SO_2 emission reductions. It is reasonable then to ask whether the large-scale spatial patterns of $nssSO_4^{2-}$ wet deposition across eastern North America reflect these same changes. The following analysis indicates that, indeed, large-scale spatial patterns of $nssSO_4^{2-}$ wet deposition did change. This is illustrated in Figure 3.19 which shows the 5-year-mean $nssSO_4^{2-}$ wet deposition patterns for the periods 1990-1994 (prior to the large emission reductions seen in Figure 3.11) and 1996-2000 (the period that includes the Phase 1 and Phase 2 U.S. emission reductions of SO_2). Note that the 1996-2000 period was chosen for this analysis (as opposed to the 1998-2002 period used in the previous analysis in Section 3.4.1), because there was insufficient provincial data collected after 2000 to produce reliable large-scale patterns.

Comparing the 1990-1994 and 1996-2000 five-year average wet deposition patterns leads to the conclusion that $nssSO_4^{2-}$ wet deposition declined over a large area of eastern North America. Of particular note were the following changes:

- The 30-35 kg SO_4^{2-}/ha/yr area that appeared in 1990-1994 across eastern Ohio and western Pennsylvania disappeared completely in 1996-2000;
- The 25-30 kg SO_4^{2-}/ha/yr deposition area that occurred in 1990-1994 disappeared completely by

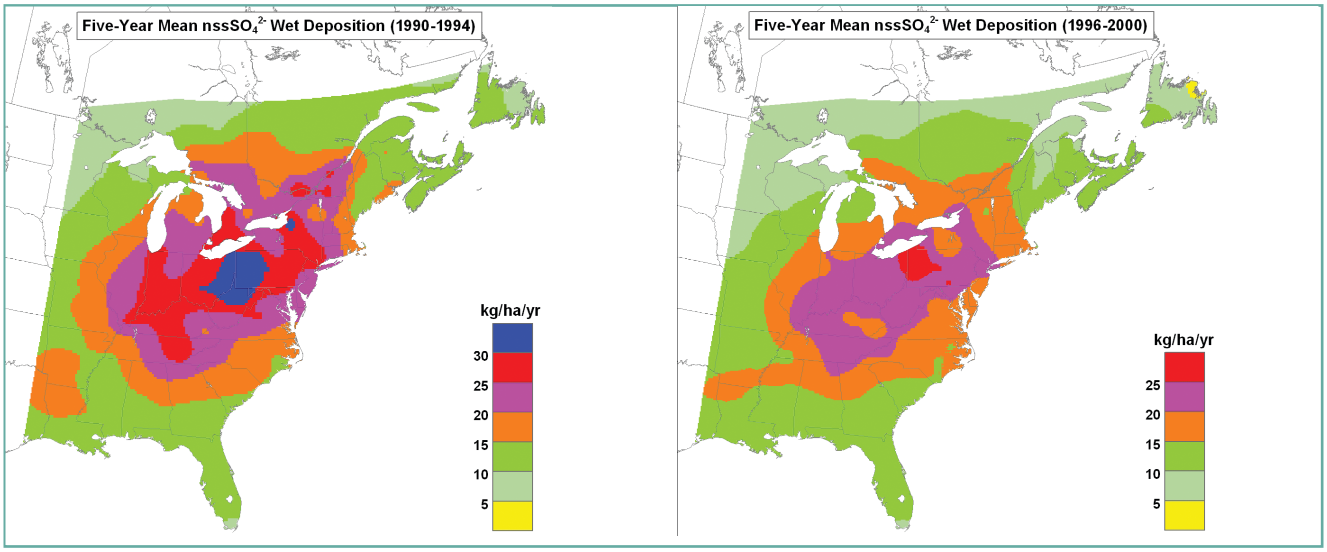

Figure 3.19: Changes to the spatial patterns of $nssSO_4^{2-}$ wet deposition (in kg/ha/yr) in eastern North America from the early to late 1990s. The map on the left (a) shows the 5-year-mean wet deposition pattern for the period 1990-1994 and the map on the right (b) shows the 5-year-mean pattern for the period 1996-2000.

1996-2000 in south-eastern Canada and declined markedly in the eastern part of the U.S., remaining only in a small area of eastern Ohio and western Pennsylvania;

- The areas enclosed by the 20-25 and 15-20 kg SO_4^{2-}/ha/yr isopleths declined in both eastern Canada and the eastern U.S.. In eastern Canada, both areas declined relatively steadily from the early 1980s to the late 1990s. In fact, the 20-25 kg SO_4^{2-}/ha/yr area approached near zero levels after 1998 (see Figure 3.20 for a graphical indication of the year to year changes in the areas). In quantitative terms, the area receiving equal or greater than 15 kg SO_4^{2-}/ha/yr declined 39% from 1990-1994 to 1996-2000 and the area receiving equal or greater than 20 kg SO_4^{2-}/ha/yr declined 76%. These changes clearly indicate that significant reductions occurred in the large-scale deposition patterns of $nssSO_4^{2-}$ in eastern Canada and, in turn, point to the success of the Canadian and U.S. SO_2 emission reduction programs throughout that period. It remains to be seen whether these substantial reductions were indeed sufficient to induce ecosystem recovery in acid-sensitive areas. This topic is discussed in terms of critical load exceedances for forest and aquatic ecosystems in Chapter 8.

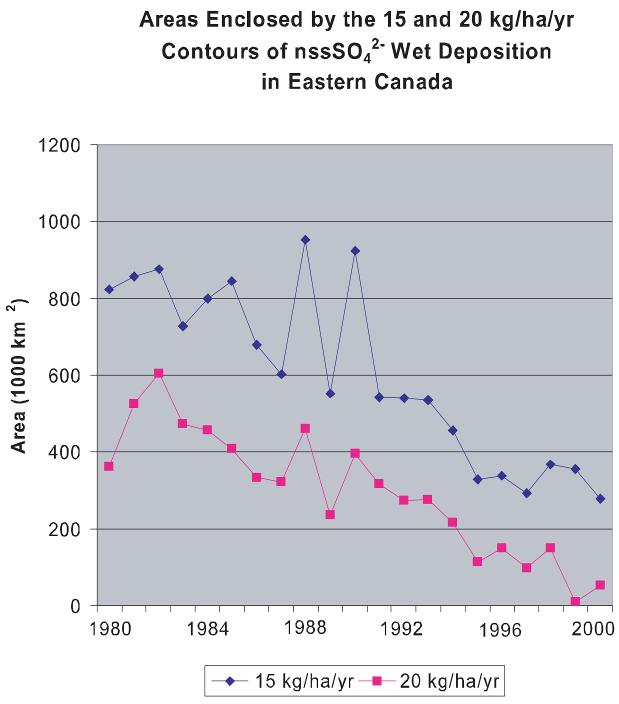

Figure 3.20: Areas of eastern Canada enclosed by the 15 kg/ha/yr and 20 kg/ha/yr contours of $nssSO_4^{2-}$ for the years 1980 to 2000. Note that the years 1988 and 1990 had high levels of precipitation that explain the very high values in those years.

The changes in the five-year $nssSO_4^{2-}$ wet deposition patterns from 1990-1994 to 1996-2000 are illustrated quantitatively in Figures 3.21a and d. Figure 3.21a shows the pattern of absolute differences calculated for each interpolated grid square by subtracting the 1990-1994 interpolated deposition from the 1996-2000 interpolated deposition. Negative differences appear in blue and represent decreasing sulphate wet deposition from the early to late 1990s while positive differences appear in red and represent increasing $nssSO_4^{2-}$ wet deposition. Figure 3.21d shows the pattern of percentage differences between the two periods, calculated as the absolute difference at each grid point divided by the 1990-1994 wet deposition value at the grid point. Differences of ±2 kg/ha/yr or ±10% are roughly within the expected measurement and interpolation uncertainty. Note that Figures 3.21b and e represent the absolute and percentage differences of the 5-year-average precipitation-weighted means of the daily $nssSO_4^{2-}$ concentrations and Figures 3.21c and f show the absolute and percentage differences in the 5-year mean precipitation depths. The combined set of diagrams provides an overall perspective on the relationship between deposition, concentration and precipitation depth.

Figure 3.21a shows that $nssSO_4^{2-}$ wet deposition decreased substantially over most of eastern North America between the two periods. The largest declines ranged from 4 to 10 kg/ha/yr, occurring in three bands oriented from the southwest to northeast (similar to the prevailing wind direction). The first band extends from Illinois through Lake Michigan to Lake Huron, central Ontario and western Québec; the second band extends from Kentucky to Ohio, Pennsylvania and New York; and the third band sits over the St. Lawrence River Valley in eastern Ontario and southern Québec.

Selected pockets of eastern Canada and eastern U.S. showed small increases in $nssSO_4^{2-}$ wet deposition, always

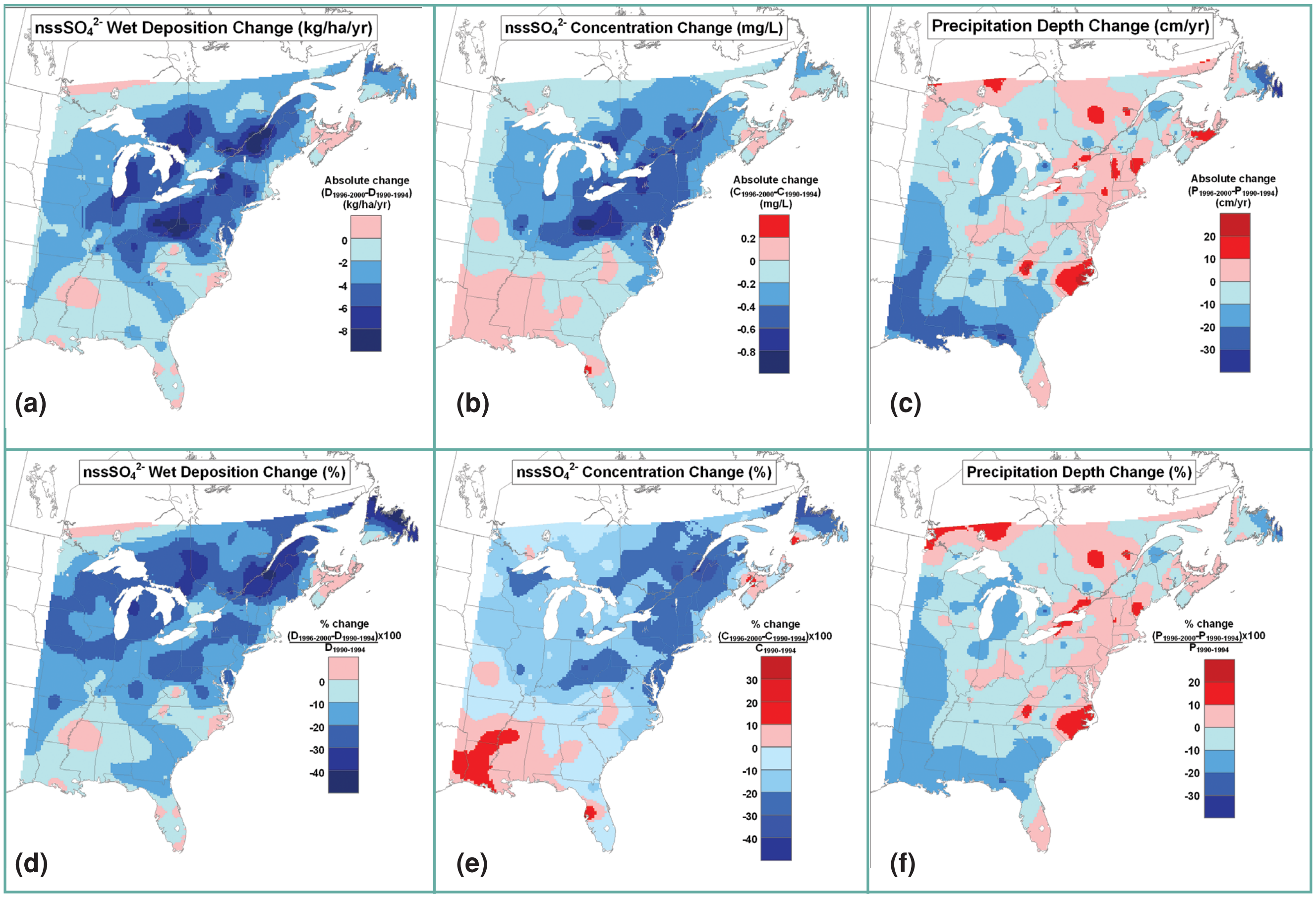

Figure 3.21: Absolute changes (top row) and percentage changes (bottom row) in 5-year-average wet nssSO_4^{2-} deposition (a,d), precipitation-weighted mean nssSO_4^{2-} concentrations (b,e) and precipitation depth (c,f) from 1990-1994 to 1996-2000. Blue colours represent decreases from 1990-1994 to 1996-2000 and red colours indicate increases from 1990-1994 to 1996-2000. Percentage change is calculated as 100 times the 1996-2000 minus 1990-1994 difference divided by the 1990-1994 value.

less than or equal to 2 mg/l or 10%. These areas were in northwestern Ontario, southwestern Newfoundland and central Nova Scotia, and parts of several southeastern states in the U.S.. Since wet deposition is the product of concentration and precipitation amount, the increases in deposition occurred because of increases in the precipitation-weighted mean concentration, the precipitation depth or both the concentration and depth in those specific areas. For example, the areas that show increased deposition in central Nova Scotia and eastern North Carolina experienced higher precipitation-weighted mean concentrations and precipitation depths in the 1996-2000 period, thereby producing increases in wet deposition. This can be seen in Figures 3.21 b and e, and c and f, which show the patterns of 1996-2000 minus 1990-1994 absolute and percentage differences in precipitation-weighted-mean concentrations and precipitation depth, respectively. Other areas with increasing wet deposition occurred because the percentage increase in concentration was slightly higher than the percentage decrease in precipitation depth (e.g., Northern Mississippi) and vice versa (e.g., northwestern Ontario). In a similar manner, the areas that exhibited decreased nssSO_4^{2-} wet deposition between the two periods did so because one or both of the precipitation-weighted mean-concentration field and the precipitation depth field decreased in the correct proportions.

Figures 3.21c and f show that the average precipitation amount did not change much between 1990-1994 and 1996-2000, i.e., with only a few exceptions, the changes in precipitation depth were less than ±10 cm or ±10%. This means that the decreases in the nssSO_4^{2-} wet deposition patterns seen in Figures 3.21a and d were induced mainly

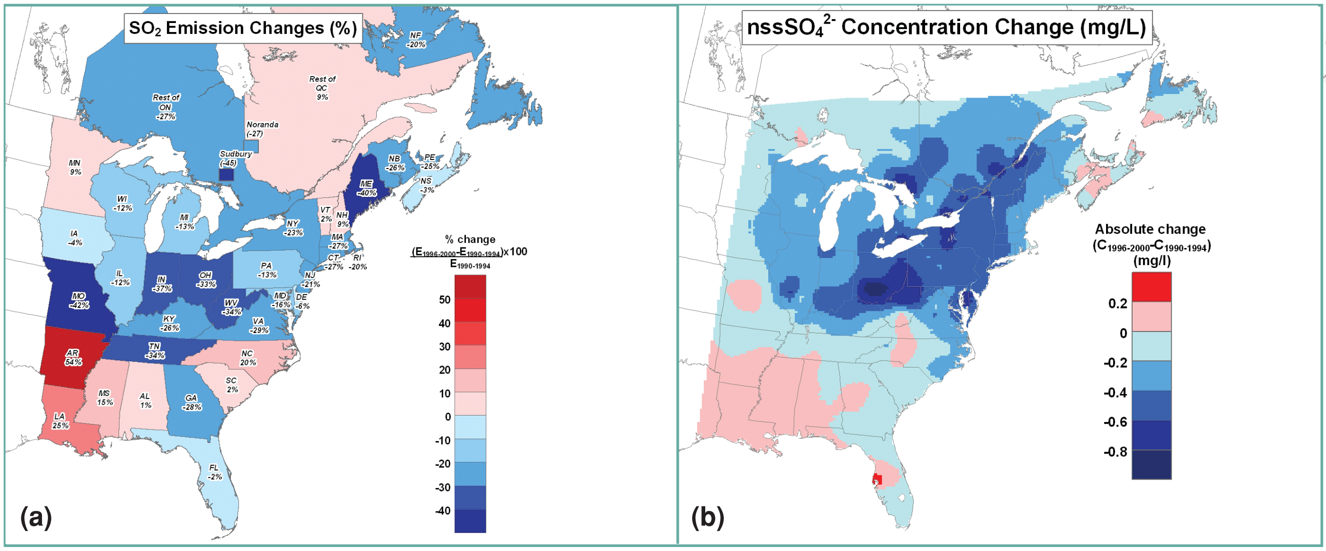

Figure 3.22: (a) Changes in SO_2 emissions (in %) and (b) changes in $nssSO_4^{2-}$ precipitation-weighted mean concentrations (in mg/l) from 1990-1994 to 1996-2000. Note that Sudbury and Noranda non-ferrous smelter emissions are plotted separately from the emissions in the rest of Ontario and the rest of Québec (left).

by decreasing precipitation-weighted mean concentrations. This being the case, there should be a relatively strong relationship between the pattern of SO_2 emission changes and the pattern of precipitation-weighted mean concentration changes. This is indeed the case, as seen in Figure 3.22 which shows the changing emissions and concentration patterns side-by-side.

It is clear from Figure 3.22 that there is close spatial correspondence between the SO_2 emission changes and the $nssSO_4^{2-}$ precipitation-weighted mean concentration changes from 1990-1994 to 1996-2000. The largest reductions in both emissions and concentrations occur in the areas around Sudbury, Noranda, the Ohio River Valley and the U.S. eastern seaboard where concentrations dropped by as much as 0.4 to 0.8 mg/l. The states in the southwest of the domain are interesting in that they show increasing emissions and precipitation-weighted mean concentrations and further enhance the general spatial correspondence between emission changes and concentration changes. The St. Lawrence River Valley in southern Québec is an exception since the $nssSO_4^{2-}$ concentrations in that area declined but the SO_2 emissions in the non-smelter area of Québec did not. This area is strongly affected by the long range transport and subsequent wet deposition of SO_2 emissions from southern Ontario, the Rouyn-Noranda smelter area, the Ohio River Valley and the U.S. eastern seaboard (see Section 3.5). This suggests that the large reductions seen in the precipitation-weighted-mean concentrations of southern Québec are likely due to emission reductions in those more distant upwind areas.

In summary, the spatial pattern analysis strongly suggests that SO_2 emission reductions in eastern Canada/eastern U.S. have produced declines in $nssSO_4^{2-}$ wet deposition and precipitation-weighted mean concentrations over large areas of eastern North America. Subsequent sections explore this relationship in a more quantitative fashion.

3.4.3.1.2 Nitrogen

In contrast to $nssSO_4^{2-}$, the wet deposition patterns of NO_3^- show only minor changes between the two periods (Figure 3.23). This is consistent with the minor changes to NO_x emissions throughout the 1990s (see Figure 3.12b).

The changes in the five-year NO_3^- wet deposition patterns from 1990-1994 to 1996-2000 are illustrated quantitatively in Figures 3.24a and d – as was done for SO_4^{2-} in Figures 3.21 a and d. Differences of ±2 kg/ha/yr or ±10% are roughly within the expected measurement and interpolation uncertainty. Note that Figures 3.24b and e represent the absolute and percentage differences of the

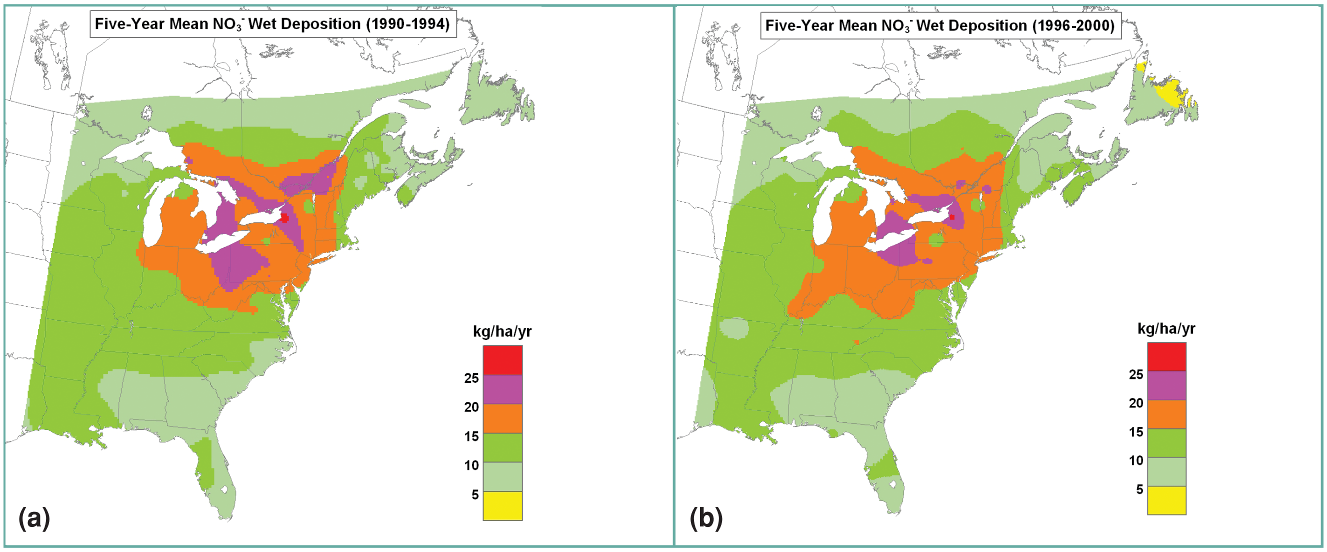

Figure 3.23: Spatial patterns of NO_3^- wet deposition over eastern North America in the early and late 1990s. The map on the left (a) shows the 5-year-mean wet deposition pattern for the period 1990-1994 and the map on the right (b) shows the 5-year-mean pattern for the period 1996-2000. No major changes between the two sets of patterns are apparent.

5-year precipitation-weighted mean NO_3^- concentrations and Figures 3.24c and f show the absolute and percentage differences in the 5-year mean precipitation depths. The combined set of diagrams provides an overall perspective on the relationship between deposition, concentration and precipitation depth.

In contrast to $nssSO_4^{2-}$, the NO_3^- wet deposition changes shown in Figure 3.24a and d are relatively small. In eastern Canada, the areas of increasing wet deposition (pink) are generally due to increasing precipitation depth while the areas of decreasing wet deposition are generally due to both decreasing precipitation depth and decreasing NO_3^- concentrations, e.g., along the St. Lawrence River in southern Québec. The exception to this is the increasing wet deposition area in southern New Brunswick and southern Nova Scotia which was affected by both increasing NO_3^- concentrations and increasing precipitation depth. In the U.S., a large area of increasing NO_3^- wet deposition occurs in the middle of the U.S. domain and is driven mainly by increasing precipitation-weighted mean concentrations as well as pockets of increasing precipitation depth. The areas of decreasing NO_3^- wet deposition in the eastern U.S. are due mostly to decreasing precipitation-weighted mean concentrations.

As was the case for $nssSO_4^{2-}$, NO_x emission changes should appear as changes in the precipitation-weighted-mean concentrations of NO_3^- (since wet deposition changes are complicated by changes to both the concentration and precipitation depth fields). Figure 3.25 shows that, even though emission changes between the 1990-1994 and 1996-2000 periods were relatively small, the general pattern of NO_3^- precipitation-weighted mean concentration changes corresponds very well to the pattern of emission changes. Note that the emission changes shown in Figure 3.25 for the provinces of Ontario and Québec are somewhat misleading to the eye because most of the NO_x sources (and therefore most of the NO_x emission changes) are located in the southern portions of the provinces where the concentration decreases also occurred.

In summary, the large-scale spatial patterns of NO_3^- precipitation-weighted-mean concentrations and wet deposition exhibited little change from 1990-1994 to 1996-2000 in direct response to the minimal changes in average NO_x emissions between the two periods. Nevertheless, there is a good spatial correspondence between the areas of increasing and decreasing NO_x emission changes and the areas of increasing and decreasing NO_3^- precipitation-weighted mean concentration changes.

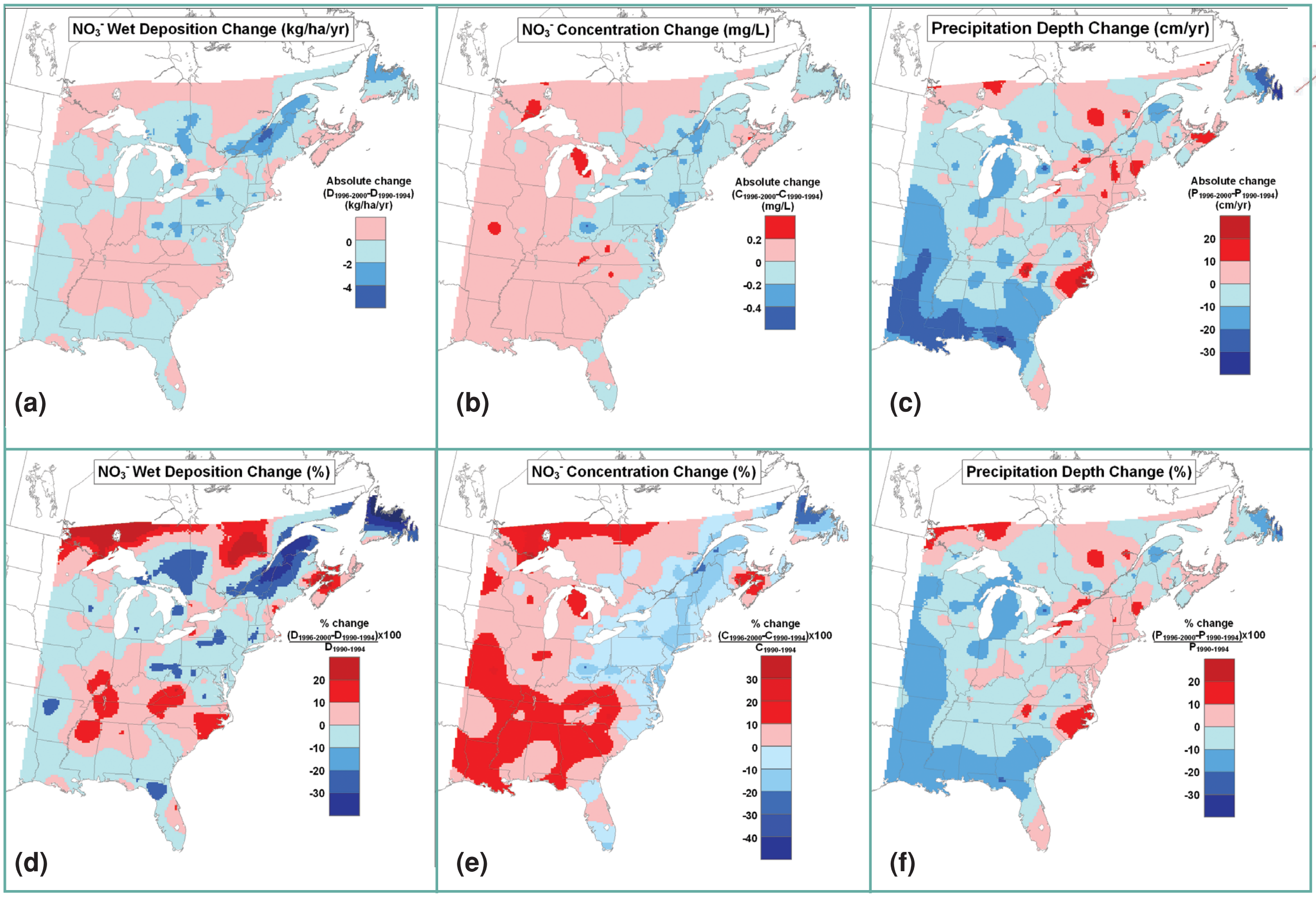

Figure 3.24: Absolute changes (top row) and percentage changes (bottom row) in 5-year-average wet NO_3^- deposition (a,d), precipitation-weighted-mean NO_3^- concentration (b,e) and precipitation depth (c,f) from 1990-1994 and 1996-2000. Blue colours represent decreases from 1990-1994 to 1996-2000 and red colours indicate increases. Percentage change is calculated as 100 times the 1996-2000 minus 1990-1994 difference divided by the 1990-1994 value.

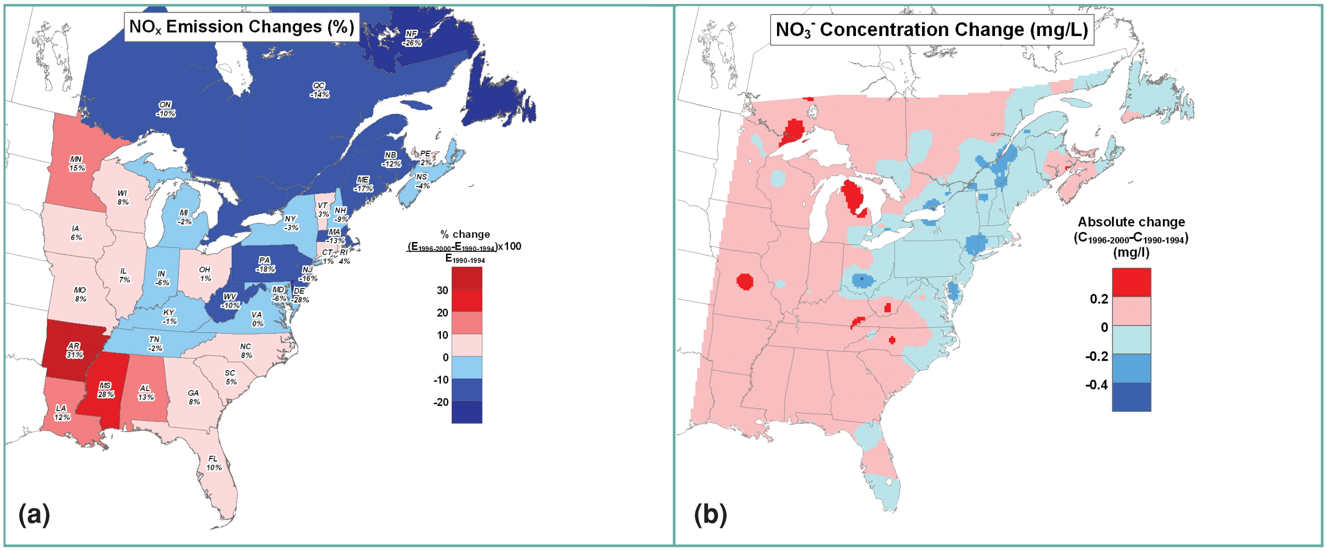

Figure 3.25: (a) Changes to NO_x emissions (in %) and (b) changes to NO_3^- precipitation-weighted mean concentrations (in mg/l) from 1990-1994 to 1996-2000. Note the correspondence between the areas of increasing and decreasing emissions and concentrations.

3.4.3.2 *The relationship between integrated emissions and integrated wet deposition in eastern North America*

In this section, the wet deposition patterns in Figures 3.19 and 3.23 are used to investigate the quantitative relationship between emission reductions and wet deposition changes on a continental scale. This analysis assumes that, over a large geographical area (e.g., eastern Canada and the eastern U.S.) and a long period of time (e.g., five years), the integrated wet deposition will be directly proportional to the integrated emissions over the same area. Thus, when emissions are reduced, it is assumed that the integrated wet deposition will be reduced proportionately. The objective of the analysis is to compare the 5-year average emissions and wet deposition amounts integrated over eastern North America for the two emission periods 1990-1994 and 1996-2000.

3.4.3.2.1 Sulphur

The relationship between the integrated SO_2 emissions and integrated wet $nssSO_4^{2-}$ deposition for the periods 1990-1994 and 1996-2000 are shown (as S) in Figure 3.26. Note that the integrated emission numbers were developed independently from the wet deposition numbers – the former coming from Canadian and U.S. emission inventories and the latter from the interpolated measurement data fields (Figures 3.19 and 3.23).

1990-1994. In the 1990-1994 period, Canadian and U.S. sources had 5-year-average emissions of 0.87 MT/yr and 8.83 MT/yr, respectively. This means that eastern Canada and eastern U.S., respectively, emitted 9% and 91% of the total eastern North American S emissions. During the same period, an estimated 0.79 MT of S was wet deposited in eastern Canada and 1.95 MT in the eastern U.S.. Overall then, eastern Canada produced just under 10% of eastern North American S emissions but received a disproportionately high 29% of eastern North American wet-deposited S. It is worth pointing out that the area of eastern Canada that received the 0.79 MT of $nssSO_4^{2-}$ wet deposition (1.693x108 ha) equaled approximately one half the area in the eastern U.S. that received 1.95 MT of wet deposition (3.213x108 ha). This means that the 5-year-average wet deposition per hectare in eastern Canada was 4.7 kg S/ha/yr compared to 6.1 kg S/ha/yr in the U.S.. Thus, even though eastern Canada emitted only 9% of eastern North American emissions, the average amount of sulphur wet deposited per hectare in eastern Canada was a disproportionately high 77% of the average sulphur wet deposited per hectare in the eastern U.S..

It is worth noting that the average depth of precipitation in the two countries was approximately equal during the two time periods, i.e., 107.41 cm/yr in eastern Canada versus 116.18 cm/yr in the eastern U.S.. Thus, the difference in deposition fluxes between the two countries

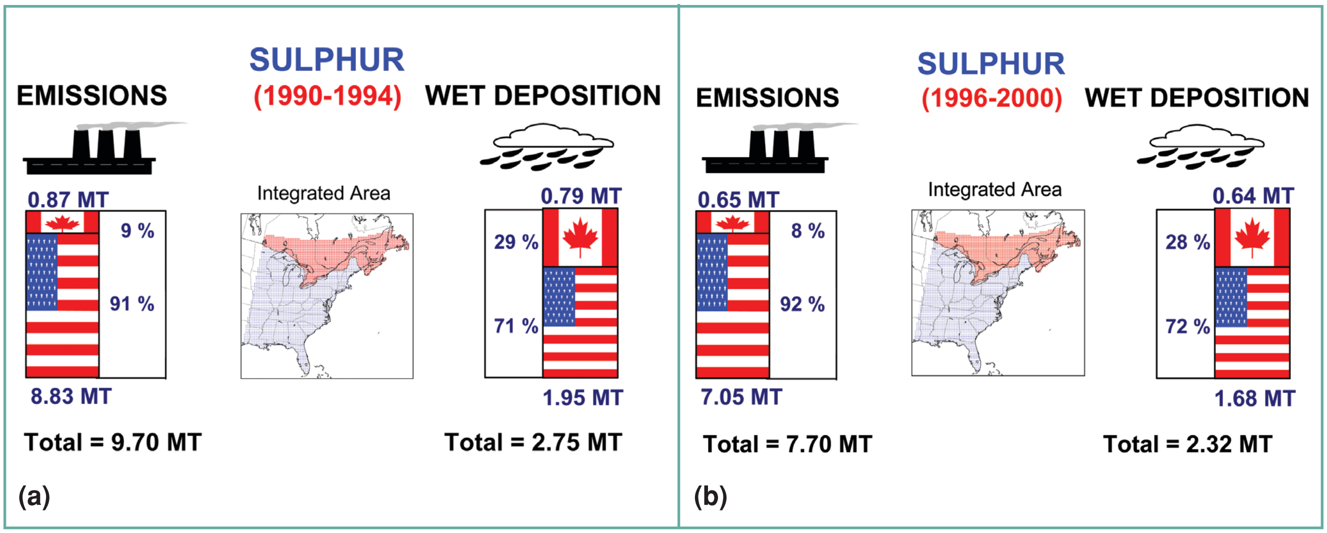

Figure 3.26: Integrated SO_2 emissions and integrated $nssSO_4^{2-}$ wet deposition over eastern Canada and the eastern U.S. for the 5-year period 1990-1994 (a) and 1996-2000 (b) expressed as megatonnes of sulphur per year. The area of integration is shown in the map inserts.

is not attributable to major differences in precipitation amounts between the two countries.

In light of the fact that the southern portions of eastern Canada are predominantly downwind of the major U.S. SO_2 emission areas (see Section 3.5), the most reasonable explanation for the disproportionately high deposition in eastern Canada is the long range transport and subsequent wet deposition of SO_2 from U.S. sources into Canada. This is discussed in detail in Section 3.4.3.3.

1996-2000. From 1990-1994 to 1996-2000, the 5-year average annual S emissions decreased by 0.22 MT/yr in eastern Canada and 1.78 MT/yr in the eastern U.S.. Nevertheless, the proportion of total North American emissions due to Canadian and U.S. sources stayed approximately the same in both periods at 8-9% and 91-92%. The integrated wet deposition of S in eastern Canada dropped by 0.15 MT/yr from 0.79 to 0.64 MT/yr between 1990-1994 and 1996-2000, while the integrated wet deposition in the eastern U.S. dropped by 0.27 MT/yr (from 1.95 to 1.68 MT/yr). As was the case with the integrated emissions, the fraction of eastern North American wet deposition that impacted Canada and the U.S. was essentially constant in the two periods, i.e., 28%-29% in eastern Canada and 71%-72% in the eastern U.S.. The above numbers indicate that eastern Canada experienced a much larger proportional decrease in S wet deposition per unit decrease in emissions than did the eastern U.S.. Specifically, eastern Canada experienced a rate of wet deposition decline equal to 0.68 MT per 1 MT emission reduction while the eastern U.S. experienced a smaller decline of 0.15 MT per 1 MT emission reduction. The fact that eastern Canada reduced its wet deposition so much faster than the eastern U.S. per unit emission reduction strongly supports the idea that some portion of U.S. SO_2 emissions is transported and subsequently wet deposited in eastern Canada.

To extend this analysis further, it was assumed that, a very large area (say as large as eastern North America) and over a long time period (say, many years), a linear relationship should exist between the integrated eastern North American emissions and integrated North American wet deposition flux. This proved to be the case, as is shown in Figure 3.27 where the annual integrated wet deposition fluxes are plotted against the annual integrated sulphur emissions for all 22 years from 1980 to 2001. The linear relationship between integrated emissions and integrated wet deposition is statistically significant (r=0.93; n=22) and, although no causality is proven, statistically supports the concept that Canadian and U.S. emission reductions from the early 1980s to the early 2000s have resulted in a major linear decline in integrated wet deposition in eastern North America. There is some scatter in the data in Figure 3.27 suggesting that integrated wet deposition varies strongly from year to year for a given level of emissions. This is to be expected in light of the strong inter-annual variability of meteorological factors that drive the atmospheric processes which ultimately lead to wet deposition (i.e., advection, turbulence, solar radiation, precipitation). This again supports the approach taken in most of this report that 5-year averaging periods are important for smoothing the inter-annual variability of meteorology and deposition.

For quantitative support of the foregoing discussion, statistical significance testing was carried out on the annual integrated SO_2 emissions and $nssSO_4^{2-}$ wet deposition fluxes to establish whether the changes after

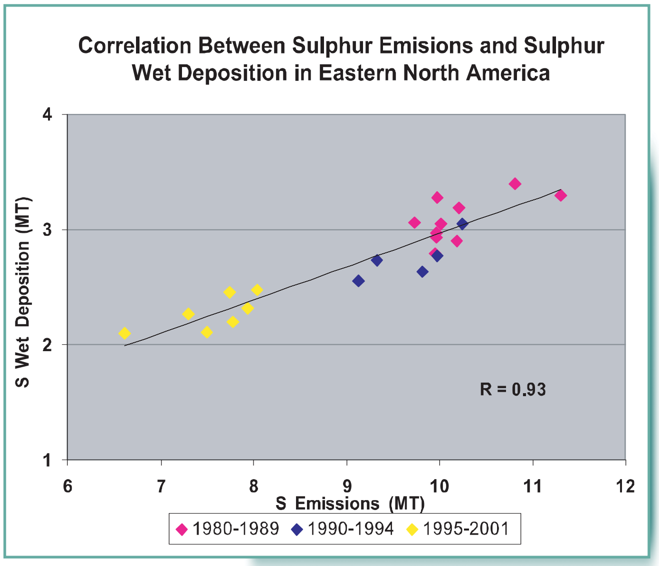

Figure 3.27: Linear correlation between S emissions (MT) and S wet deposition (MT) integrated over eastern North America for the years 1980-2001. Different coloured symbols identify the different periods: 1980-1989 (blue), 1990-1994 (pink) and 1995-2001 (yellow). R is the correlation coefficient.

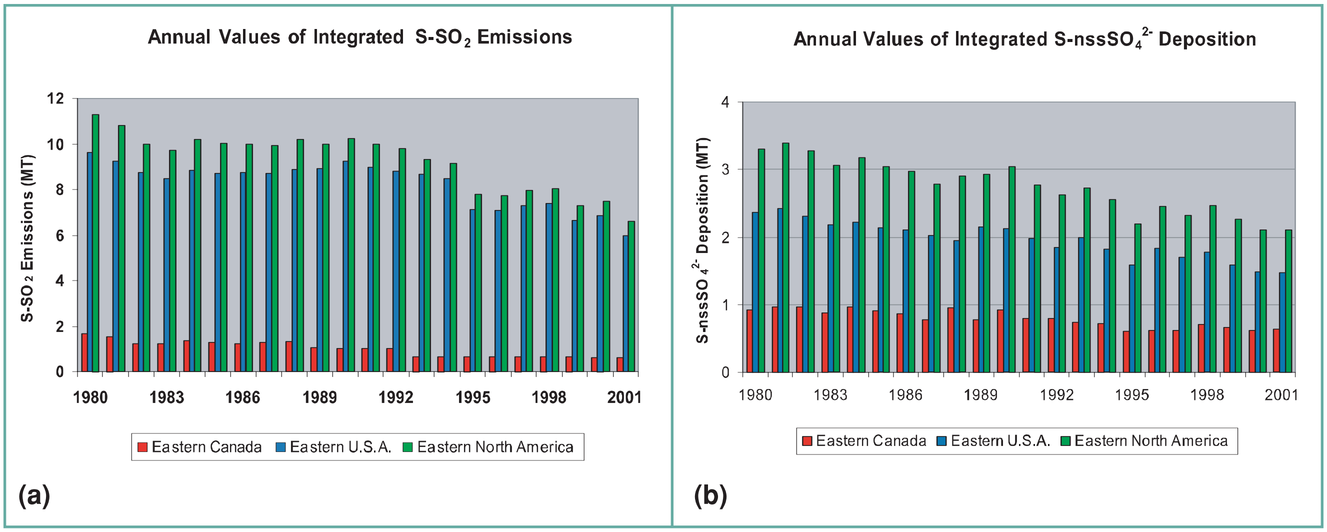

Figure 3.28: Annual values of integrated SO$_2$ emissions (a) and non-sea-salt SO$_4^{2-}$ wet deposition (b) in eastern Canada, eastern U.S. and eastern North America. The values were used to test for significant differences between the two periods 1984-1994 and 1995-2001.

1995 were indeed significantly different than those before 1995. Jonckheere's non-parametric test was used to compare the periods 1984-1994 versus 1995-2001 at a family-wise 90% confidence level (Jonckheere, 1954). Note that the periods chosen for this test were different from those used in the analyses discussed above in order to maximize the differences and the power of the testing. The results confirmed the presence of a statistically significant reduction in SO$_2$ emissions and nssSO$_4^{2-}$ wet deposition in each of the eastern U.S., eastern Canada, and eastern North America from 1984-1994 to 1995-2001. The large drop in 1995 can be seen visually in Figure 3.28 which represents the time series of annual integrated SO$_2$ emission and nssSO$_4^{2-}$ wet deposition values used in the testing.

We conclude that SO$_2$ emission reductions in the eastern U.S. and eastern Canada after 1995 resulted in a statistically significant decline of nssSO$_4^{2-}$ wet deposition over eastern Canada and the eastern U.S..

Unfortunately, the same analysis could not be carried out for total (i.e., wet and dry) deposition since the number of stations with dry deposition values is too small. It is to be hoped that future analyses will include dry and/or total deposition, since this might shed further light on the differing rates of decline for the different sulphur species, as discussed in Reid et al. (2001).

3.4.3.2.2 *Nitrogen*

The story for nitrogen is very different from that of sulphur. This is because, unlike SO$_2$, eastern North American NO$_X$ emissions increased throughout most of the 1980s and 1990s without showing any substantial decrease until 1999 (see Figure 3.12b). As a result, the integrated wet deposition of NO$_3^-$ over eastern North America did not show the strong decreases seen for sulphate.

Figure 3.29 shows that eastern Canadian NO$_X$ emissions constituted only 8% of the eastern North American total in 1990-94 and 7% in 1996-2000. In the same two periods, eastern Canada received a disproportionately high 32% of eastern North American NO$_3^-$ wet deposition. As with sulphur, it is assumed that the disproportionately high deposition in eastern Canada is due to the transboundary transport and wet deposition of eastern U.S. NO$_X$ emissions in eastern Canada.

Comparing Figures 3.29 a and b, it is interesting to note that the five-year-average N-NO$_X$ emissions in eastern Canada declined slightly (by 0.05 MT/yr) from 1990-1994 to 1996-2000 while the emissions in the eastern U.S. increased slightly (by 0.06 MT/yr). In spite of these changes, the amount of N that was wet deposited as NO$_3^-$ in eastern Canada and the eastern U.S. remained constant (0.43 MT/yr and 0.92 MT/yr, respectively). This

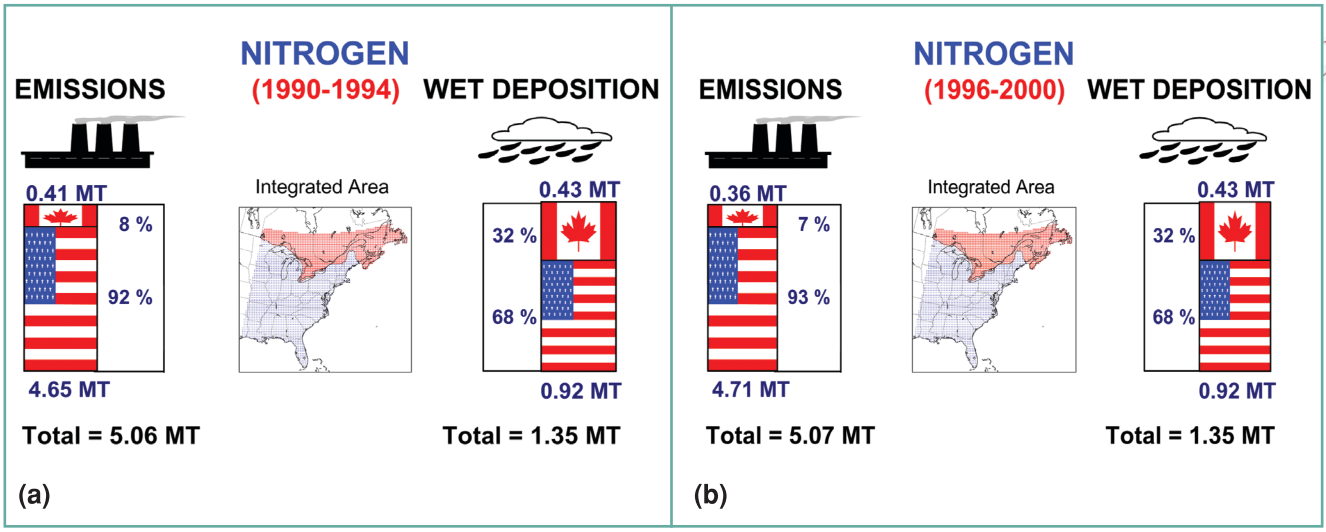

Figure 3.29: Integrated N-NO_x emissions and N-NO_3^- wet deposition over eastern Canada and the eastern U.S. averaged over the 5-year periods 1990-1994 (a); and 1996-2000 (b). The area of integration is shown in the map insert.

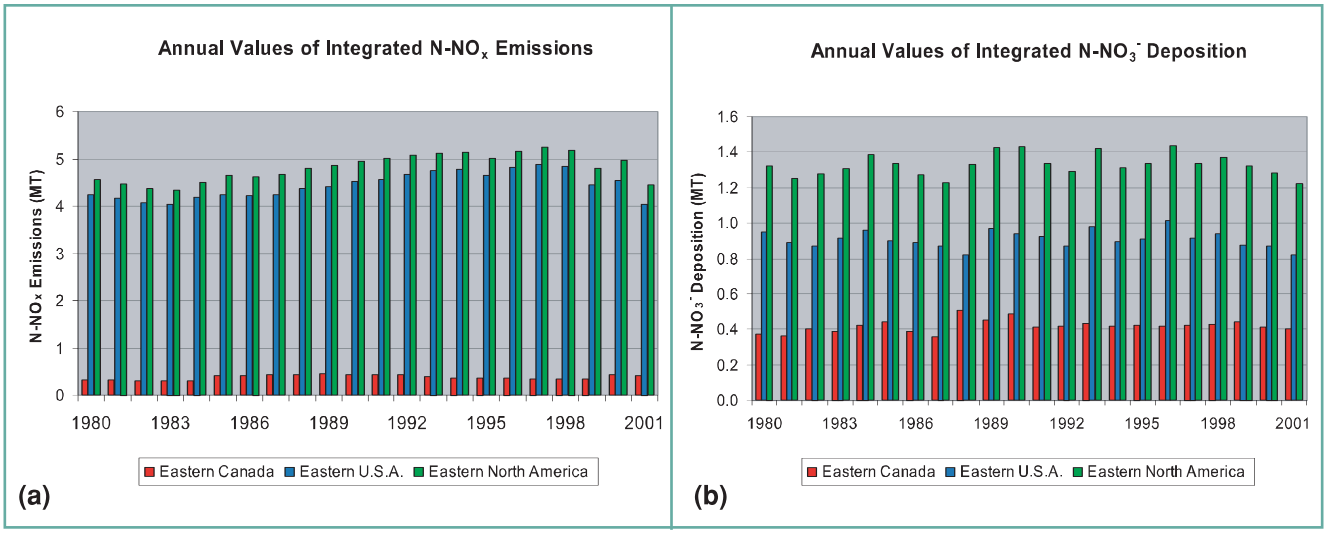

Figure 3.30: Annual values of integrated NO_x emissions (a) and NO_3^- wet deposition (b) in eastern Canada, eastern U.S. and eastern North America expressed as megatonnes of nitrogen per year. The values were used to test for significant differences between the two periods 1984-1994 and 1995-2001.

constancy, of course, is consistent with the fact that the large-scale NO_3^- wet deposition and concentration patterns shown in Figure 3.24 of Section 3.4.3.1 exhibited minimal change between the two periods. It is also consistent with the results of the Jonckheere statistical testing (Jonckheere, 1954) that detected no significant monotonic or step-function changes between the two periods. The annual integrated emissions and wet deposition data used for the testing is shown in Figure 3.30.

The five-year-average analysis discussed above says nothing about the relationship between NO_x emissions and NO_3^- wet deposition on an annual basis. However, Figure 3.31 shows that, indeed, a weak but statistically significant (at the 95% confidence level) linear relationship does exist between integrated emissions and integrated wet deposition from 1980 through 2001 (R=0.49; n=22). It is reasonable to expect that further NO_x emission reductions in the 2000s will result in a strengthening of this relationship.

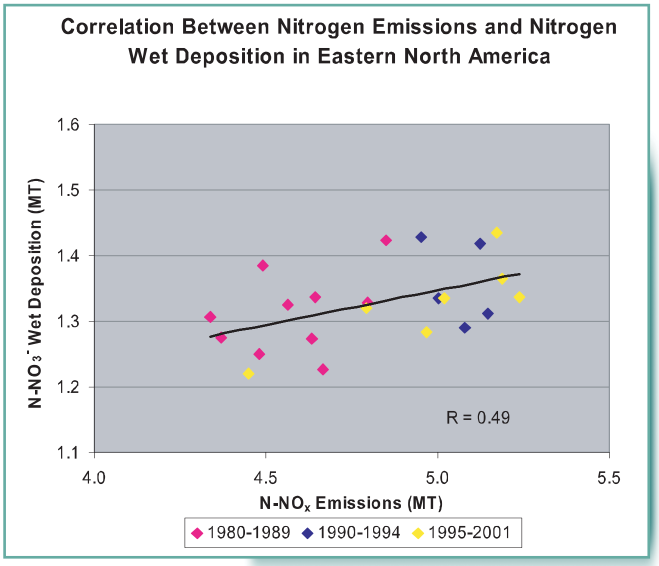

Figure 3.31: Linear correlation between annual N emissions and N wet deposition integrated over eastern North America for the years 1980-2001. Different coloured symbols identify the different periods: 1980-1989 (blue), 1990-1994 (pink) and 1995-2001 (yellow). R is the correlation coefficient.

In summary, averaged over five years, eastern Canadian and eastern U.S. N-NO$_X$ emissions changed little between 1990-1994 and 1996-2000 – as did the 5-year-average North American integrated N-NO$_3^-$ wet deposition values. In spite of this, eastern Canada received a disproportionately large amount of North American NO$_3^-$ wet deposition given its low percentage of North American NO$_X$ emissions. A weak statistical correlation is beginning to emerge between integrated nitrogen emissions and wet deposition.

3.4.3.3 *The influence of Canadian and U.S. emissions on wet deposition in eastern Canada and the eastern U.S.*

The five-year-average integrated emission and deposition values for sulphur and nitrogen, shown in Figures 3.26 and 3.29, indicate that a major imbalance exists between emissions and wet deposition in eastern Canada (see Section 3.4.3.2). The primary cause of this imbalance is hypothesized to be the long range transport into and subsequent wet deposition of U.S. emissions in eastern Canada. To investigate whether this is indeed the case, the emission and wet deposition values in Figures 3.26 and 3.29 were used to estimate, through a set of mass balance equations, the amount of S and N transported across the U.S.-Canada border and wet deposited in Canada, and vice versa. The methods and results are described below for S and N.

3.4.3.3.1 *Sulphur*

Estimates were made of the percentage of wet sulphur deposition in eastern Canada attributable to eastern U.S. SO$_2$ emissions and the percentage of sulphur wet deposition in eastern U.S. attributable to eastern Canadian SO$_2$ emissions. This was done using a set of mass balance equations produced from the integrated emission and wet deposition values in Figure 3.26 plus the following assumptions:

- Wet sulphur deposition in eastern Canada is produced by: (1) eastern Canadian emissions that are wet deposited in eastern Canada and (2) eastern U.S. emissions that are transported into and subsequently wet deposited in eastern Canada;
- Averaged over a 5-year period, the percentage of total eastern Canadian SO$_2$ emissions wet deposited in eastern Canada remains roughly constant, regardless of the five year period chosen and the changing SO$_2$ emissions in the period;
- Eastern Canadian SO$_2$ emissions that are not wet deposited in eastern Canada are either dry deposited in eastern Canada or transported out of the country (including off the continent and into the eastern U.S.); likewise, eastern U.S. emissions that enter eastern Canada and are not wet deposited are either dry deposited in, or transported out of, Canada;
- The five-year average wet deposition of anthropogenic and natural sulphur that is advected into the integration area is small compared to the wet deposition flux of anthropogenic sulphur emissions within the integration area; thus, the inflow term is not included in the mass balance equations. A sensitivity test on the validity of this assumption is discussed at the end of this section.

The mass balance equations state that the total amount of wet sulphur deposition in eastern Canada must be equal to the total eastern Canadian sulphur emissions multiplied by the fraction of emissions that is wet deposited in eastern Canada plus the total eastern U.S.

sulphur emissions multiplied by the fraction of emissions that is wet deposited in eastern Canada. The equations are:

For the 1990-1994 period... $WD_1 = 0.87A + 8.83B_1$ (Eq. 1)

For the 1996-2000 period... $WD_2 = 0.65A + 7.05B_2$ (Eq. 2)

where WD_1 = 0.79 MT sulphur/year = the integrated sulphur wet deposition in eastern Canada in 1990-1994

WD_2 = 0.64 MT sulphur/year = the integrated sulphur wet deposition in eastern Canada in 1996-2000.

0.87 and 0.65 = the 5-year average emissions of SO_2 (as S) in eastern Canada (in MT sulphur/yr) in the 1990-1994 and 1996-2000 periods, respectively

A = the fraction of eastern Canadian SO_2 emissions that is wet deposited in eastern Canada during both the 1990-1994 and 1996-2000 periods; note that A is assumed to be constant

8.83 and 7.05 = the 5-year average emissions of SO_2 (as S) in the eastern U.S. (in MT sulphur/yr) in the 1990-1994 and 1996-2000 periods, respectively

B_1 = the fraction of eastern U.S. S-SO_2 emissions wet deposited in eastern Canada in 1990-1994

B_2 = the fraction of eastern U.S. S-SO_2 emissions wet deposited in eastern Canada in 1996-2000

Equations 1 and 2 cannot be solved simultaneously but can be used to bracket a reasonable range of values for B_1 and B_2 by first assuming a reasonable range for A (the fraction of eastern Canadian emissions that is wet deposited in eastern Canada). Unfortunately, values of A are not available in the scientific literature so we chose to make the calculations for a range of A that has a high probability of encompassing the true value. On this basis, we chose values of A equal to 0.20 and 0.50, which means that between 20% and 50% of eastern Canadian emissions are wet deposited in eastern Canada. Justification for this range comes from the fact that there are only three fates for the eastern Canadian sulphur emissions during their atmospheric lifetime in eastern Canada, i.e., they will either be wet deposited, dry deposited or exported out of the country. It was felt that it would be highly unlikely for more than 50% and less than 20% of the emissions to be wet deposited because 1) this appears to be supported by the scientific literature as discussed in the evaluation of the mass balance results at the end of this section (see Table 3.3); and 2) the total eastern North American wet deposition for the two periods represent 28% and 30% of the total emissions (see for example Figure 3.26).

Equations 1 and 2 and the assumed values of A = 0.20 and 0.50 were used to calculate the associated values of B_1 and B_2 for the 1990-1994 and 1996-2000 periods, respectively. Equations 3 and 4, derived from Equations 1 and 2, were then used to estimate the associated values of F_1 and F_2 which represent the fraction of eastern Canadian wet sulphur deposition attributable to eastern U.S. sulphur emissions during the 1990-1994 and 1996-2000 periods, respectively, i.e.,

For the 1990-1994 period... $F_1 = 1 - 1.10A$ Eq. 3
For the 1996-2000 period... $F_2 = 1 - 1.02A$ Eq. 4.

The calculated values of B and F are summarized in Table 3.2 for the two periods. Interestingly, the values are consistent between the two periods – a fact that provides some confidence in the method. The major results of the calculations are as follows:

Table 3.2. Mass balance estimates of sulphur in eastern Canada.

Assumed Value of A	% of eastern U.S. emissions that is wet deposited in eastern Canada		% of eastern Canadian wet deposition that is attributable to eastern U.S. emissions	
	1990-1994	**1996-2000**	**1990-1994**	**1996-2000**
	B_1	B_2	F_1	F_2
0.20	7.0%	7.2%	78%	80%
0.50	4.0%	4.5%	45%	49%

- For the assumed values of A = 0.20 and 0.50, the estimated percentages of total eastern U.S. emissions that were wet deposited in eastern Canada were 7.0% and 4.0%, respectively, in 1990-1994 and 7.2% and 4.5%, respectively, in 1996-2000;
- For the same assumed values of A = 0.20 to 0.50, the estimated percentages of total eastern Canadian wet deposition attributed to emissions from the eastern U.S. were 78% and 45%, respectively, in 1990-1994 and 80% and 49% in 1996-2000.

These estimates suggest that only a very small fraction of eastern U.S. emissions (i.e., 4.0% to 7.2%) is wet deposited in eastern Canada, but that this small fraction is responsible for a very large proportion of the total wet sulphur deposition in eastern Canada (i.e., 45% to 80%). In turn, this suggests that further emission reductions in the eastern U.S. will be extremely important for further reducing sulphur wet deposition in eastern Canada.

A similar mass balance approach was used to estimate the percentage of the integrated wet sulphur deposition in the eastern U.S. that was attributable to eastern Canadian SO_2 emissions (equations not shown). The set of U.S. mass balance equations turned out to be extremely sensitive to A which represents the fraction of eastern U.S. emissions that is wet deposited in the eastern U.S.. The sensitivity was so great that the U.S. mass balance equations could only be solved if the values of A were less than 0.221 in 1990-1994 and less than 0.238 in 1996-2000. Above those values, the percentage contribution of eastern Canadian emissions to wet deposition in the eastern U.S. turned negative, i.e., unrealistic. When the values of A are assumed to range from 0.20 to the aforementioned maximum values, the estimated contributions of Canadian emissions to total wet deposition in the eastern U.S. range from 9% to 0%, respectively, in 1990-94 and 16% to 0% , respectively, in 1996-2000. Because U.S. SO_2 emissions are extremely high compared to Canadian emissions, the U.S. mass balance values of F, i.e., the contribution of Canadian SO_2 emissions to wet deposition in the eastern U.S., are considerably more sensitive to A than are the F values in the Canadian mass balance equations. For example, the coefficients in the Canadian mass balance equations (i.e., in Equations 3 and 4) are 1.10 and 1.02 compared to the corresponding coefficients of 4.53 and 4.20 in the U.S. mass balance equations. Thus, the coefficients in the U.S. mass balance equations are over 4 times larger than the coefficients in the Canadian equations. The importance of this is that very small changes in the assumed values of A in the U.S. case produce very large changes in the resultant values of F compared to the Canadian case. This means that the mass balance estimates of the percentage of eastern Canadian wet deposition attributable to eastern U.S. emissions is considerably less sensitive to the assumed values of A than are the corresponding percentages of eastern U.S. wet deposition attributable to eastern Canadian emissions. This is reasonable given that U.S. emissions are roughly an order of magnitude greater than Canadian emissions and that eastern Canada is in the prevailing downwind direction from the highest emission area in the U.S.. On a small scale, however, the influence of near-border Canadian sources on border U.S. states will be considerably higher than predicted by the large-scale mass balance equations.

It is extremely difficult to assess the accuracy of the foregoing estimates since values for A are not available in the literature. We therefore chose a *weight-of-evidence* approach wherein the mass balance estimates are compared to other available research results. The comparison is summarized as follows:

- The U.S. 1990 National Acid Precipitation Assessment Program State of Science and Technology Assessment on Acidic Deposition (Figure 5F-35, Volume 5, Dennis et al., 1990) estimated the

Table 3.3. Published estimates of continental deposition and off-continent export of sulphur as percentages of total sulphur emissions for eastern North America (with the exception of the last entry which applies to all of North America).

Authors	Method	Dry Deposition (%)	Wet Deposition (%)	Fog Deposition (%)	Net Export (%)	Remarks
Galloway and Whepdale, 1980	Monitoring data	31	38	-	30	-
Galloway et al., 1984	Climatological wind and pollutant data	36	28	-	30	-
Fay et al., 1986	Analytical model (1980-1982)	30 (25)	30 (25)	-	40 (50)	Numbers in brackets apply to eastern Canada
Brost et al., 1988	3-D Eulerian transport model		-	-	59%	59% advected eastward off the continent
Wojcik and Chang, 1997	3-D Eulerian transport model	17	32	-	51	-
Shannon and Sisterson, 1992	Monitoring data (1985-1987)	29	30	4	37	Numbers apply to all of North America

percentage contribution of Canadian SO_2 emissions to sulphate wet deposition in eastern Canada and the eastern U.S. using the U.S. Regional Acid Deposition Model (RADM). Based on an aggregation of 30 modelled wet deposition events (chosen to produce a representative annual average), the eastern Canadian SO_2 emissions were estimated in 1990 to cause 25% of the wet sulphur deposition in eastern Canada – with the other 75% being attributed to eastern U.S. SO_2 emissions. The 25% figure is an area-weighted average calculated from Figure 5F-35 of Dennis et al. (1990) for the purpose of this assessment. Since the RADM model domain is slightly smaller than the mass balance domain in Atlantic Canada, we estimate that the 25% figure might be as high as 30% to 35% over the full mass balance domain. If so, this translates to 65-70% of the total wet sulphur deposition in eastern Canada being caused by U.S. SO_2 sources. Note that the 65-70% range falls reasonably within the 45-80% range of the mass balance calculations in Table 3.2;

➪ Past scientific publications on the topic of sulphur mass balances in eastern North America are consistent with the input values used in the mass balance equations from Figures 3.30 and 3.31. The publications, summarized in Table 3.3 above, provide estimates of the percentage of eastern North American sulphur emissions that were wet deposited, dry deposited and exported off the continent during different time periods, mostly in the 1980s. The four most relevant publications estimate that 28-38% of eastern North American sulphur emissions were wet deposited in eastern North America (median = 30%). This compares well to our mass balance values in Figure 3.26 which indicate that 28% of eastern North American emissions were wet deposited in eastern North America in 1990-94 and 30% in 1996-2000. For future reference, it is worth noting that the total amount of sulphur exported off of the eastern half of the North American continent was estimated in the references to be at least as large as, if not larger than, the total wet deposition on the continent.

➪ Source attribution analyses presented later in Section 3.5 using a completely independent analysis technique suggest that U.S. SO_2 emissions are responsible for >70% of sulphur wet deposition along the border areas of eastern Canada. This percentage contribution is consistent with the bracketed range of 45% to 80% derived from the

> mass balance calculations. It is also consistent with a trajectory-based analysis carried out using 1981-1990 data from the Acidic Precipitation in Ontario Study Network (Shaw et al., 1992) which estimated that >71% of the sulphate and nitrate wet deposited at a site in southwestern Ontario was attributable to U.S. emissions and >47% was attributable to U.S. emissions at a site in southeastern Ontario.

In light of these considerations, we consider that the mass balance estimates, while not definitive, are consistent with other research results.

It is important to point out that the mass balance estimates in Table 3.2 are integrated over all of eastern Canada and the eastern U.S.. We expect, however, that the contribution of U.S. emissions to wet sulphur deposition in Canada (and vice versa) will vary spatially, i.e., with the highest contribution occurring near the U.S.-Canada border and the lowest contribution occurring away from the border in high Canadian emission areas. This is confirmed by the RADM model results of Dennis et al. (1990) where the percentage contribution of U.S. emissions to Canadian wet deposition was estimated as approximately 95% in southwestern Ontario and 35% in the Sudbury area.

Finally, to investigate the uncertainties in these mass balance results, we assessed the sensitivity of the mass balance calculations to two potentially important factors: (1) the flow of anthropogenic and natural sulphur emissions into the integration area and (2) the size of the integration area chosen for the analysis. To assess the first factor, we assumed an inflow area corresponding to a band of states and provinces approximately 1000 km wide to the west of the integration area. We then compared the SO_2 emissions in the inflow area to the emissions in the integration area. In the U.S., the SO_2 emissions in the inflow area in 1990-1994 amounted to only 12% of the within-area SO_2 emissions (with almost half of the 12% being from Texas). Given that some of the inflow emissions are deposited before being advected into the integration area, it is unlikely that the inflow SO_2 emissions have a major impact on the mass balance results. In Canada, the inflow area emissions in 1990-1994 represented roughly 35% of the total emissions within the integration area. However, roughly 80% of these inflow emissions are attributable to two non-ferrous smelters located in northern Manitoba roughly 800 km from the northwest edge of the integration area. Studies of these smelters (not presented here) indicate that a large proportion of the emissions are deposited in the area outside the integration area. This suggests that the amount of sulphur flowing into the eastern Canadian integration area is relatively small in comparison to the emissions within the integration area. This appears to be substantiated by the five-year-mean nssSO_4^{2-} wet deposition patterns in Fig. 3.19a and 3.19b which show that wet deposition values along the western and northern borders of the integration area are the lowest in the entire domain. This would not be the case if the smelter emissions exerted a strong influence on the integration area close to the smelters.

A similar assessment was done to estimate the influence of natural sulphur emissions that may potentially flow into the integration area from areas to the north. This was done by estimating the natural emissions of dimethyl sulphide and hydrogen sulphide from the Canadian Arctic Archipelego, the northern Canadian Boreal Region (lakes and soils), and the Canadian tundra. All numbers were adapted from Sharma et al. (1999). The estimated total of the natural emissions that could flow into the area of integration came to approximately 53 kT S/yr or about 6% of the 1990-1994 eastern Canadian anthropogenic sulphur emissions within the integration area. Again, given that a large fraction of these emissions would be deposited during advection to the integration area, it is very unlikely that the natural sulphur emissions would have a major impact on the mass balance results.

To test the effects of the inflow emissions on the eastern Canadian mass balance results in a more quantitative way, we carried out a set of conservative sensitivity calculations using Eq. 1 and Eq. 3. We conservatively assumed that one half of the Manitoba smelter emissions could be transported into the integration area and one quarter of the natural sulphur emissions could be wet deposited within the integration area. These numbers, when substituted into Eq. 1 and Eq. 3 resulted in a change in the F_1 values in Table 3.2 from 78% to 74% and from 45% to 36% for A = 0.20 and 050, respectively. This indicates that the value of F_1 (i.e., the percentage of Canadian wet deposition attributed to eastern U.S.

emissions) associated with A = 0.50 is somewhat sensitive to the amount of sulphur entering the integration area from Manitoba and Saskatchewan while the value of F_1 associated with A = 0.20 is not.

To assess the uncertainty associated with the choice of the area of integration, a sensitivity analysis was carried out for the 1990-1994 period by expanding the area of integration northward (in Canada) from 51° north latitude to 55° and eastward (in the U.S.) to the Mississippi River, thereby increasing the integrated wet deposition in eastern Canada by 38% and decreasing the eastern U.S. emissions by 9%. The increase in eastern Canadian wet deposition resulted in a change in the values of F_1 in Table 3.2 from 78% to 84% and from 45% to 60% for A = 0.20 and 0.50, respectively. This means that the mass balance analysis is relatively insensitive to the choice of the integration area in eastern Canada. The 9% decrease in U.S. emissions caused by decreasing the area of integration in the U.S. did not change the values of F_1 in Table 3.2 since F_1 is independent of the U.S. emission term (see Eq. 3).

In conclusion, the mass balance results appear to be slightly sensitive to the flow of natural and anthropogenic sulphur emissions into the area of integration and to the size of the integration area; however, this sensitivity does not alter our earlier conclusion that 45% to 78% of eastern Canadian sulphur wet deposition is due to eastern U.S. SO_2 emissions. Nevertheless, the exercise provided a conservative uncertainty range of 36% to 84%.

3.4.3.3.2 Nitrogen

The same mass balance approach was applied to the integrated nitrogen emissions and wet deposition values in Figures 3.29a and b. Similar assumptions were made for nitrogen as for sulphur (see Section 3.4.3.3.1), including the assumption that the fraction of Canadian NO_x emissions wet deposited in eastern Canada likely falls between 20% and 50%. The results are very similar to those for sulphur, i.e., if 20% to 50% of eastern Canadian NO_x emissions are wet deposited in eastern Canada, then 83% to 52%, respectively, of the nitrogen wet deposition in eastern Canada is attributable to eastern U.S. NO_x emissions. The estimated values of the Canadian contribution to U.S. wet nitrate deposition were also similar to those of sulphur, again being extremely sensitive to the high U.S. emissions. There is no way to evaluate the reasonableness of these assumptions or the results.

In summary, the integrated emissions and wet deposition values shown in Figures 3.26 and 3.29 suggest that eastern U.S. emissions contribute between roughly 50% and 80% of the integrated wet sulphur and nitrogen deposition in eastern Canada. This being the case, future emission reductions in the eastern U.S. will play an important role in reducing wet sulphur and nitrogen deposition in eastern Canada.

3.4.4 Acidic pollutant deposition due to ground-based cloud

In Volume Two of the 1997 Canadian Acid Rain Assessment (Environment Canada, 1997), fog/cloud water deposition of acidifying compounds was discussed. Geographic areas in eastern Canada experiencing frequent ground-based clouds were estimated to receive much more deposition than is indicated by the routine wet and dry deposition estimates. This generally includes areas above ~500-800 m in elevation, indicating that, with respect to Canadian ecosystems, high elevation areas of southern Québec and New Brunswick, as well as northern New England (U.S.), are potentially at risk. For eastern Canada, the best quantitative information is from the fog chemistry measurements and deposition modelling conducted for Roundtop Mountain and Mont Tremblant utilizing Chemistry of High Elevation Fog (CHEF; Schemenauer et al., 1995) measurements. At these sites, annual average fog sulphate deposition was estimated to be 33.3 kg/ha/y and 79.4 kg/ha/yr, respectively, in the years 1988-89 and 1986-91. The Roundtop Mountain cloud water deposition of sulphate represents one and a half times the wet sulphate deposition (precipitation only) amount of 21.8 kg/ha/yr measured in the valley at the base of the mountain at the Sutton CAPMoN site. This ratio can be expected to be much higher at Mont Tremblant given its estimated higher cloud water deposition. Fog nitrate and total strong acidity deposition is also significant in these “hot spot” areas. However, their relative amounts compared to wet deposition are not as great, based upon the comparison at Roundtop Mountain. Enhanced precipitation amounts in high elevation areas, which were also discussed in the 1997 Assessment, further increases the deposition amount not accounted for in the lower elevation wet and dry deposition information currently available.

In mountainous areas of eastern Canada, no new measurements and cloud deposition estimates have been collected since the previous assessment. This is due to the difficulty and expense of obtaining this information, particularly in the wintertime. The most relevant new information is from the U.S. Environmental Protection Agency Mountain Acid Deposition Program (MADPro). Under this program, cloud liquid water and chemistry measurements were collected in the summers of 1994 to 1999 at three locations in the Appalachian Mountains. These are the only systematic measurements in eastern North America since the MCCP (the U.S. Mountain Cloud Chemistry Program) and CHEF studies, which ended in 1989 and 1991, respectively. Two of the MADPro sites were considerably south of the Canada-U.S. border (Whitetop in Virginia and Clingman's Dome in Tennessee). The other MADPro site was Whiteface Mountain in northeast New York State, at the same location as during MCCP. Geographically, Whiteface Mountain is close enough to the high elevation areas in southern Québec to provide cloud chemistry and deposition data of relevance to Canada. In addition, recent analyses of the MCCP and CHEF data (Urquizo et al., 2003) indicate that similar meteorological factors influence the cloud water sulphate concentrations in the northeast U.S. and southern Québec. The MADPro measurements are described in detail by Baumgardner et al. (2003). There are some differences between the conclusions which can be drawn from the MADPRro and the earlier high elevation fog measurements, which serve to highlight the fact that estimating cloud water deposition is uncertain. However, there is reasonable consensus that cloud water deposition contributes a large fraction of the total sulphur and nitrogen deposition in high elevation areas frequently embedded in cloud. This in turn means that wet and dry deposition measurements made at low elevation sites will not represent nearby high elevation areas very well. Furthermore, Baumgardner's analysis of trends in fog water chemistry at the MADPro sites suggests that the reduction in SO_2 emissions in the mid 1990s has led to a reduction in sulphate in cloud water, though admittedly a more detailed analysis of these data is needed.

In Canada, the little research on fog water chemistry that has been done since the 1997 Assessment, has focused on coastal fog. Many coastal areas in Atlantic Canada experience fog on a relatively frequent basis, particularly during the summer. For example, at the airport at Saint John, NB, there are typically about 375 hours of fog per year (Table 3.4) where this observation site is located inland a few kilometers. Information on the deposition inputs from fog and the possible forest effects was provided in the 1997 Assessment based on a limited number of measurements and modelling studies conducted in southeast Nova Scotia and New Brunswick.

Subsequent to the 1997 Assessment, new fog chemistry measurements were made by the Canadian Forest Service (Roger Cox and Xin-Biao Zhu) on Pt. Lepreau, NB, during the summers of 1996, 1998 and 1999. Fog measurements had also been obtained at this location in 1987-1989. These two sets of data "straddle" the time period of significant SO_2 emission reductions in eastern North America, presenting an opportunity to determine the sensitivity of the ionic concentrations in coastal fog relative to changes in upwind emissions.

Table 3.4 shows that during the summer periods of 1987-1989 and 1996-1999, fog samples were collected for 31 and 29 separate events, respectively. Within these periods the number of samples collected in each year varied slightly, particularly in the first period. In general, the largest number of events sampled were in the months of July and August. A graphical summary of the concentrations during the two periods is shown in Figure 3.32. Before the SO_2 emission reductions (i.e., 1987-1989), the arithmetic average sulphate concentration was 318 μeq/L and after the reductions it decreased to 208 μeq/L. As expected, given the negligible change in NO_x emissions indicated above, a concentration decrease was not observed for nitrate, while for acidity (H^+) the relative decrease was in between that of sulphate and nitrate. Only the change in sulphate concentration between the two periods was statistically significant at the $\alpha = 0.01$ level using the t-test.

The arithmetic average sulphate-to-nitrate ratio changed from 2.58 to 1.57 between the two periods. If we assume that the changes in nitrate concentrations between the

Table 3.4. Statistical summary of coastal fog measurements at Point Lepreau, NB. Volume is in mL. Since sample volumes were not captured in 1998 and 1999, only arithmetic average concentrations (in μeq/L) are reported. Deposition (dep.) is in kg/ha based on fog water flux intercepted by coniferous forest, which occupied 75.4% land mass of Pt. Lepreau Peninsula. The number of hours of fog at Saint John Airport in each year is shown in the last column. Since only a portion of the fog events in a year were captured at Pt. Lepreau the annual deposition estimates from these events were scaled-up using the Saint John fog hours to provide representative annual totals (i.e., rates of deposition of acidity, sulphate and nitrate (μeq/m^2/h) were calculated by multiplying the seasonal mean concentrations (μeq/L) of sulphate, nitrate, and acidity with the fog-water deposition rate (L/m^2/h) assuming the fog occurrence rate as detected at the airport.

Year	No. of fog samples	Vol (mL)	SO_4^{2-} (μeq/L)	NO_3^- (μeq/L)	H^+ (μeq/L)	S dep. (μeq/m^2/h)	N dep. (μeq/m^2/h)	H^+ dep. (μeq/m^2/h)	No. hrs of fog at St. John
1987	5	440	329	167	347	2.61	0.29	0.043	239
1988	11	2183	278	112	254	4.44	0.39	0.063	482
1989	15	2676	348	119	257	5.69	0.43	0.066	493
1987-89	31	5299	318	133	286	12.81	1.17	0.180	1214
1996	8	1659	179	89	197	2.46	0.27	0.042	414
1998	13	-	225	164	207	2.43	0.39	0.035	326
1999	8	-	219	143	242	2.20	0.32	0.038	304
1996-99	29	-	208	132	215	7.19	0.99	0.120	1044

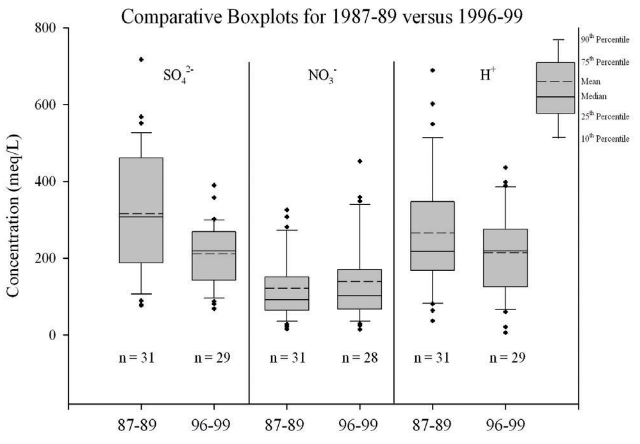

Figure 3.32: Comparative box plots of SO_4^{2-}, NO_3^- and H^+ concentrations in fog water at Pt Lepreau, NB for the two periods, 1987-1989 and 1996-1999. The number of samples included in each box plot is given by “n”.

two periods were due largely to changing meteorological conditions (since NO_x emissions changed only slightly) and if we assume that the meteorological variability affected sulphate concentrations in the same manner as nitrate concentrations, then there is a strong suggestion that sulphate in coastal fog water along the Bay of Fundy decreased in response to the SO_2 emissions reductions.

3.5 SOURCE ATTRIBUTION

The previous sections show that SO_2 emission reductions in eastern Canada and the eastern U.S. have led to reduced wet sulphur deposition in eastern North America. The question remains, however, as to whether measurement data at specific sites can be used to further our understanding of how much wet and dry deposition in eastern Canada is contributed by Canadian versus U.S. emissions? The integrated emissions and wet deposition numbers discussed in Section 3.4.3.2 suggest that U.S. emissions contribute a large proportion of eastern Canadian sulphur and nitrogen wet deposition. This section explores this question further by estimating the contributions of different source areas to wet, dry and total deposition in different regions of Canada (and in one region of the U.S.).

3.5.1 Method description

The data used for the source attribution analysis were collected by the Canadian Air and Precipitation Monitoring Network (CAPMoN) at sites shown in Figure 3.3. They consist of daily air and precipitation concentrations as well as derived estimates of daily wet deposition

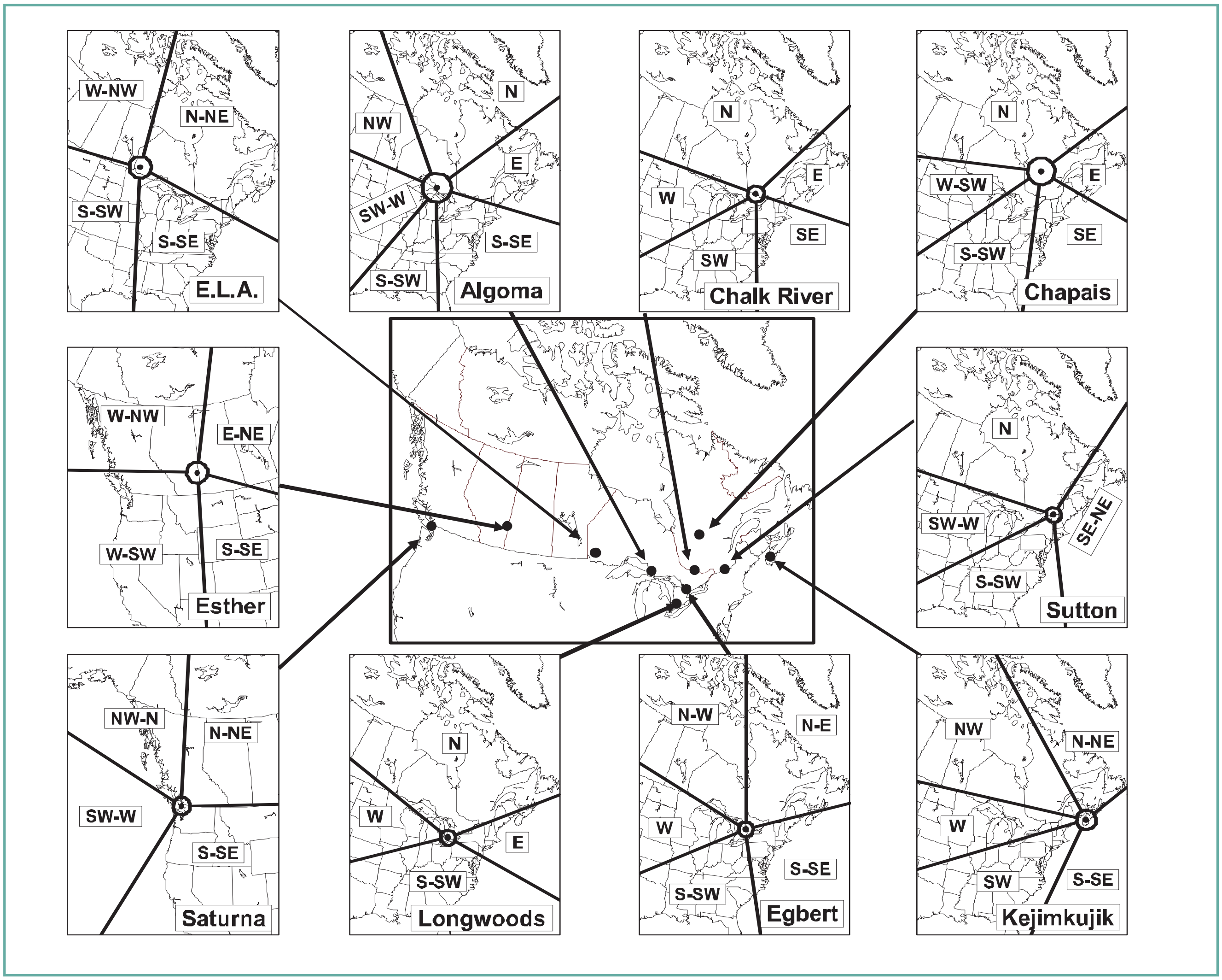

Figure 3.33: The angular sectors used for trajectory and data sorting at the ten CAPMoN sites.

of SO_4^{2-} and NO_3^-, daily dry deposition of SO_2, SO_4^{2-} and Total-NO_3^- (where Total-NO_3^- = HNO_3 + particle-NO_3^-) and daily total (wet + dry) deposition of sulphur and nitrogen (where the sulphur and nitrogen comprise all species above). The data cover the five-year period from 1998 to 2002, the time period for which dry deposition values are available in CAPMoN. Ten CAPMoN sites were used in the analyses – the only ten sites with five years of wet and dry deposition estimates from 1998-2002 (with one exception, Sutton, which had only four years).

The source attribution analysis entailed merging the daily CAPMoN measurement data with their associated 3-day back trajectories. The back trajectories were calculated in three dimensions by the Hemispheric Trajectory Model (HTM) (Voldner et al., 1981; Walmsley and Mailhot, 1982) using the analyzed meteorological fields of the Canadian Meteorological Centre. The precipitation chemistry and wet deposition data were analyzed in combination with 3-day back trajectories that began at the 850 mb level and varied horizontally and vertically in time based on the analyzed wind fields. The 850 mb level (approximately 1100 m) was selected as the starting level because it was considered an average pressure height representing regional-scale precipitation scavenging. The air chemistry and dry deposition data were analyzed in combination with trajectories that began at the 925 mb level (approximately 400 m) which was considered most

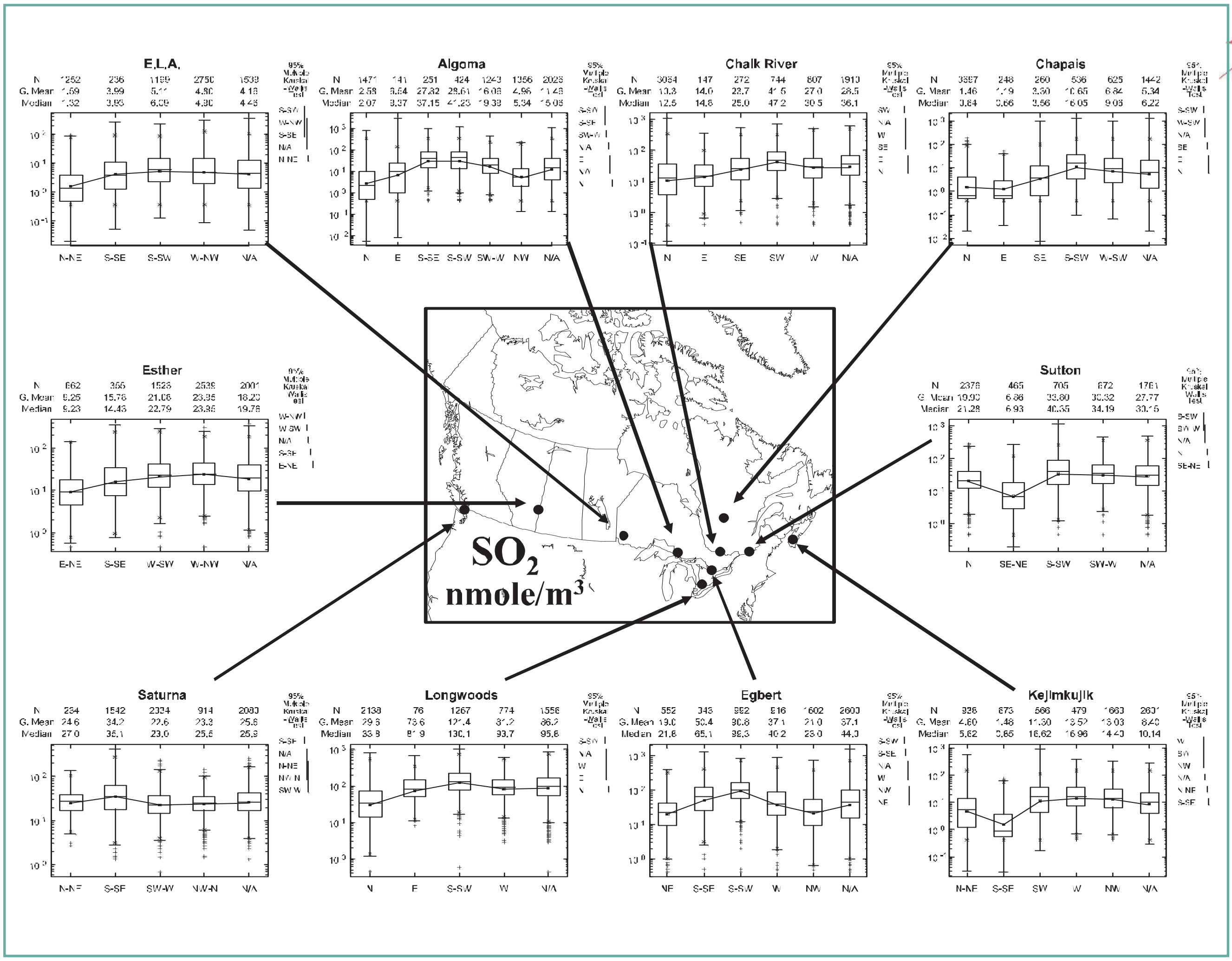

Figure 3.34: Sulphur dioxide concentrations in air (nmole/m^3): Box plots and related statistics for each angular sector for the years 1998-2002. The values printed above the box plots represent the number of trajectories (N) for the sector, the geometric mean of the concentration values for the sector and the median concentration for the sector. The Kruskal-Wallis significance test results are shown to the right of each box plot diagram, ordered from the highest to lowest medians with "not significant" differences shown by overlapping vertical bars. The box plots show the mean and median values (where the lines linking the box plots join the median values), the 25th percentile, 75th percentile, the median ± 1.5 times the interquartile range (end of bars) and the values falling outside of the latter values (shown by the + symbol).

representative of regional-scale flow in the mixed layer. Three-day back trajectories were selected as a reasonable compromise between 2-day and 4-day trajectories because they typically covered a distance of 1000-1300 km, thereby ensuring that they crossed most of the major source areas in eastern North America. Four trajectories were calculated daily at 0000, 0600, 1200 and 1800 hours UTC, and each trajectory was archived with its associated daily values of air and precipitation chemistry and wet and dry deposition, i.e., each of the four trajectories within any given daily CAPMoN measurement period was assigned that day's concentration and deposition values.

The source attribution analysis was carried out as follows:

1. **Trajectory and Data Sorting into Angular Sectors.** At each measurement site, 4 to 6 angular sectors were chosen to separate out the major SO_2 and NO_x emission areas that could influence wet and dry deposition at the site (see Figure 3.33). This was done using an a priori knowledge of the North American SO_2 and NO_x emission inventories. Every trajectory (4 per day throughout the 1998-2002 period) was then assigned to the sector in which it spent at least 70% of its 3-day history. The 70%

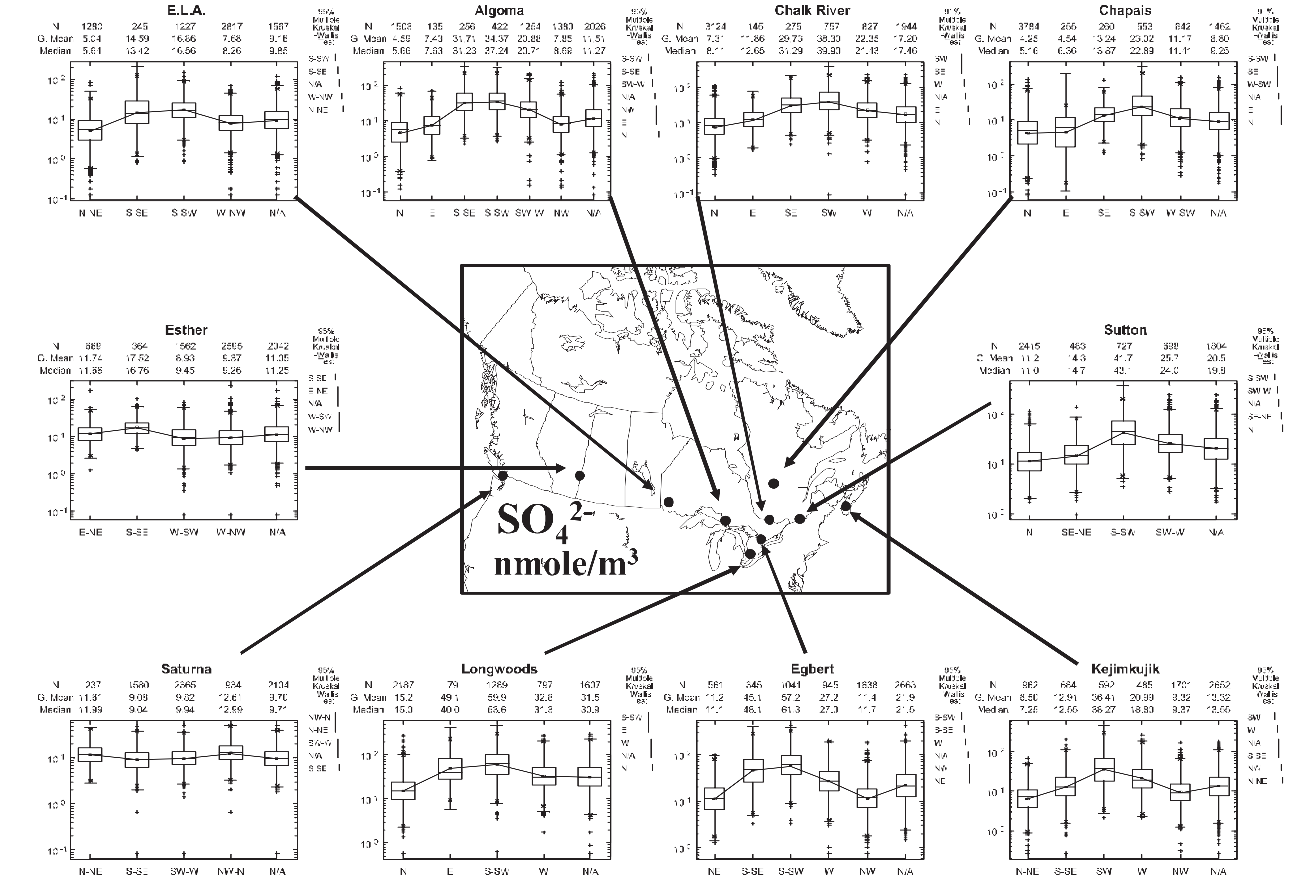

Figure 3.35: Sulphate concentrations in air (nmole/m^3): Box plots and related statistics for each angular sector as described in Figure 3.34.

requirement was chosen based on a sensitivity analysis using several different values. It did not include the portion of the trajectories within a circular no-counting zone of 100-200 km radius chosen arbitrarily around each site. This no-counting zone prevented confounding results due to the trajectories crossing between sectors as the sector areas narrowed near the site. All trajectories that were highly curved and did not spend 70% of their transit time in one sector were assigned to a separate category called the "Not Attributable" or "N/A" category. Each daily concentration and deposition value was then binned in the same sector to which its associated trajectories had been binned. The result was a set of sectored concentration and deposition values for each site. These data subsets were analyzed statistically in steps 2 and 3.

2. **Box Plots and Kruskal-Wallis Significance Testing.** The sectored subsets of concentration data at each site were used to produce box plots representing the distributional statistics of the sectors. The sectored data were then ranked from highest to lowest and the sector medians were tested for statistically significant differences using Kruskal-Wallis simultaneous significance tests at a family-wise 95% confidence level (Miller, 1981). Tests were done independently for each site. The box plots for all of the sites are shown in Figures 3.34 to 3.36 for SO_2, SO_4^{2-} and Total-NO_3^- (i.e., HNO_3 + NO_3^-)

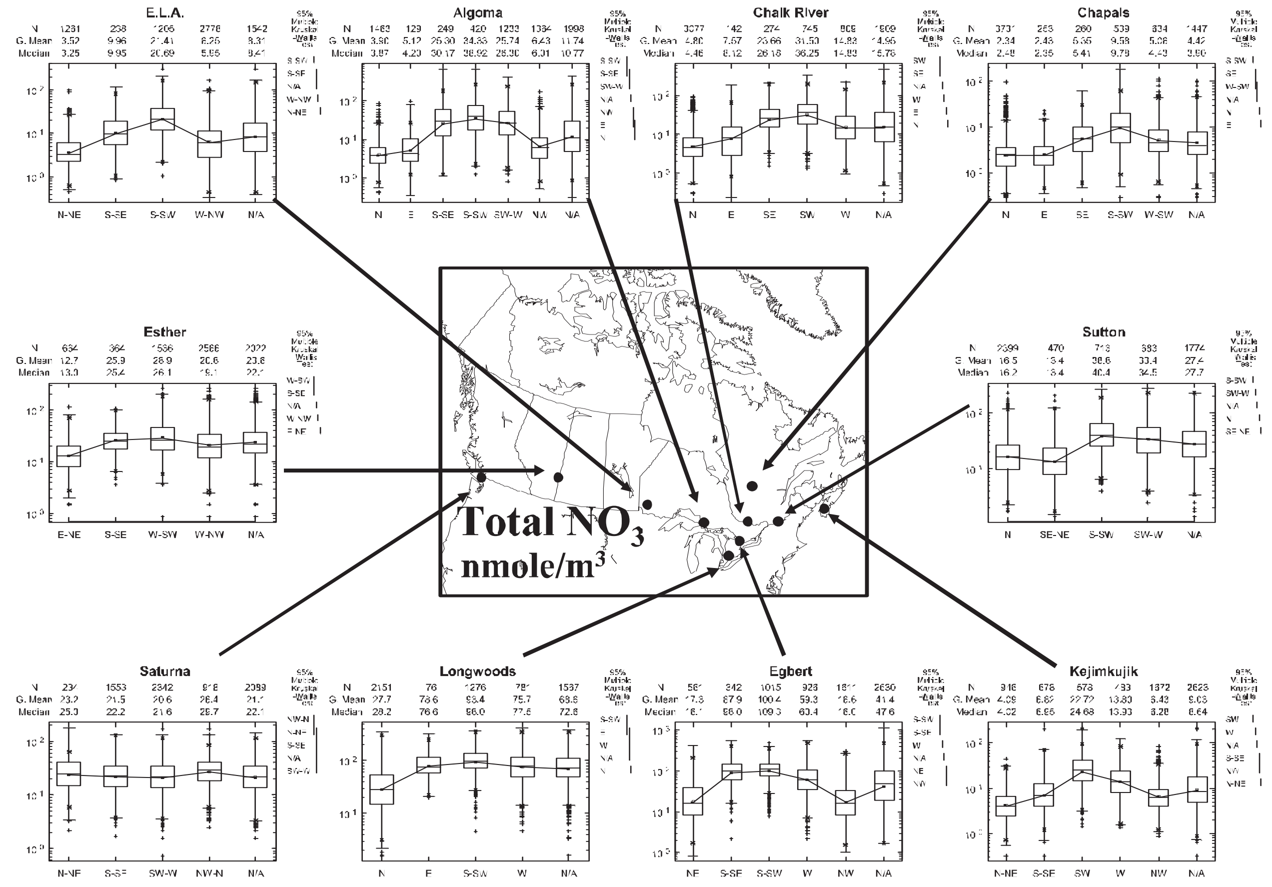

Figure 3.36: Total-NO$_3^-$ concentrations in air (nmole/m^3): Box plots and related statistics for each angular sector as described in Figure 3.34.

concentrations in air, and in Figures 3.37 and 3.38 for SO$_4^{2-}$ and NO$_3^-$ concentrations in precipitation (note that the concentration scales are logarithmic in these diagrams). The relative rankings of the sectors and the Kruskal-Wallis significance test results are plotted to the right of the box plots. The relative rankings are shown in descending order (highest at top, lowest at bottom). The Kruskal-Wallis results are presented with vertical bars joining sectors that are *not significantly different* from each other. Sectors that are not joined by the same bar are deemed to be *significantly different* from each other.

3. **Source Contribution Analysis.** The Source Contribution Analysis was used at each CAPMoN site to estimate the percentage contribution of each sector to total (wet + dry) deposition of the different sulphur and nitrogen species for the period 1998 to 2002. This was done by calculating the sum of the wet and dry deposition values for each of the individual species in each sector and dividing these sector sums by the overall all-sector sum of deposition (per species). This resulted in a percentage value that represents the fractional contribution of the sector to wet and dry deposition of each species at the site. The calculations were done for SO$_2$, SO$_4^{2-}$ and Total-NO$_3^-$ dry deposition and SO$_4^{2-}$ and NO$_3^-$ wet deposition. The percent contribution values appear in tabular form in the

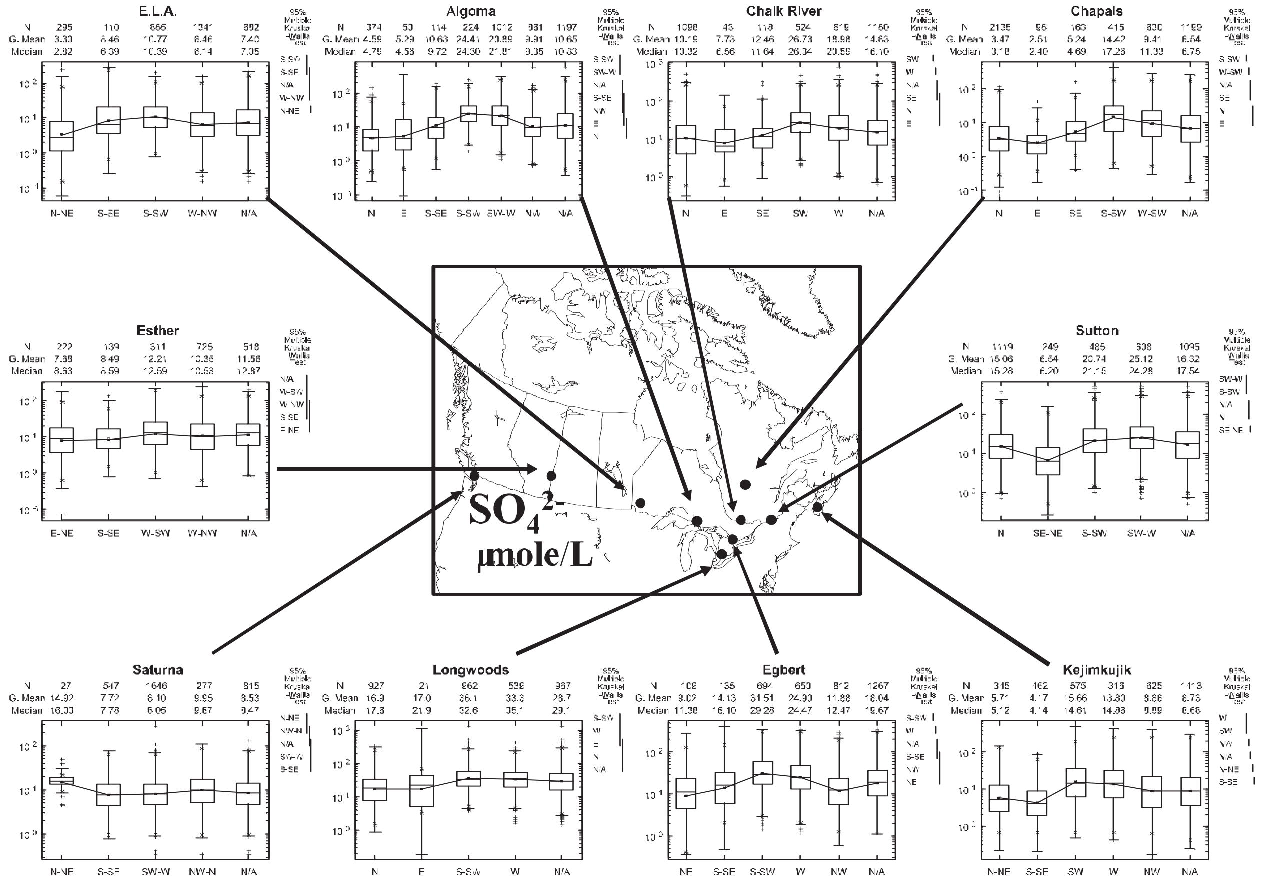

Figure 3.37: Sulphate concentrations in precipitation (µmole/L): Box plots and related statistics for each angular sector as described in Figure 3.34.

Results section that follows. The same technique was also applied to the sector-by-sector precipitation depth values at each site to determine the percent contribution of the individual sectors to total precipitation at each site. This turned out to be a useful statistic for understanding the sector-based contributions to wet deposition at the individual sites. Missing data was a minor issue in the analysis since the nine sites had a level of data completeness from 95 - 100% for SO$_4^{2-}$ and NO$_3^-$ in precipitation (with 5 sites over 99%) and from 93 - 97% for the various species in air.

A second and very important part of this analysis involved allocating the Not Attributable (N/A) deposition values for each species to the other sectors, i.e., assigning the deposition values associated with all highly curved trajectories into the other sectors. This was necessary in order to calculate the contributions of all sulphur and nitrogen species to total deposition. The method chosen was to allocate the Not Attributable fraction of each type of deposition to all of the other sectors in proportion to the sectors' percentage contribution values. For example, if 4 sectors contributed 5, 15, 20 and 40% of the deposition at a site and the Not Attributable category contributed the remaining 20%,

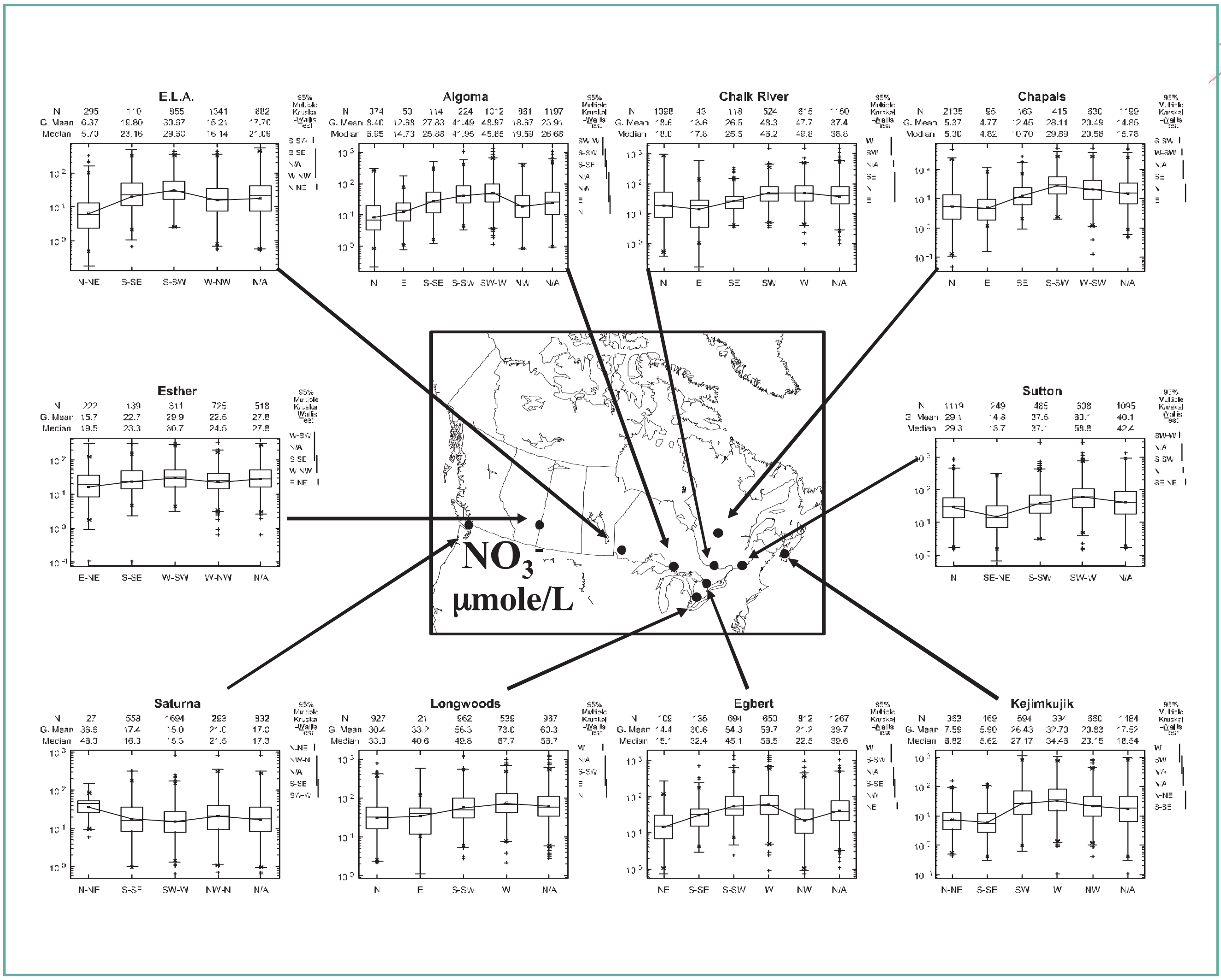

Figure 3.38: Nitrate concentrations in precipitation (µmole/L): Box plots and related statistics for each angular sector as described in Figure 3.34.

then that 20% was assigned to the four sectors in proportion to their 5, 15, 20 and 40% overall contributions. Readers should note that this is the same technique used by political pollsters, who assume that the undecided respondents to their poll will ultimately vote in the same proportion as the decided respondents.

The final part of the Source Contribution Analysis involved combining the species and estimating the percentage contributions of the individual sectors to the total sulphur deposition and total nitrogen deposition at each site. Here, total deposition means the sum of wet and dry deposition of all species. **Note that the nitrogen dry deposition results discussed hereafter refer strictly to the oxidized nitrogen species HNO_3 and particle-NO_3^- and do not include the dry deposition of NO_2 or the reduced nitrogen species NH_3 and particle-NH_4^+. Also note that the discussion of wet and dry deposition is given in terms of the various sulphur and nitrogen oxides while the discussion of total (wet + dry) deposition, by necessity, refers to total sulphur and total nitrogen summed over all the oxides.** The source contribution calculations were made from the five-year average wet and dry deposition values of the individual sulphur and nitrogen species (in kg S/ha/yr and kg N/ha/yr) presented in Section 3.3. At each site, the wet and dry deposition values were multiplied by the individual sector percentage contributions calculated previously and converted to sulphur or nitrogen units, as appropriate, to determine the amount of wet and dry

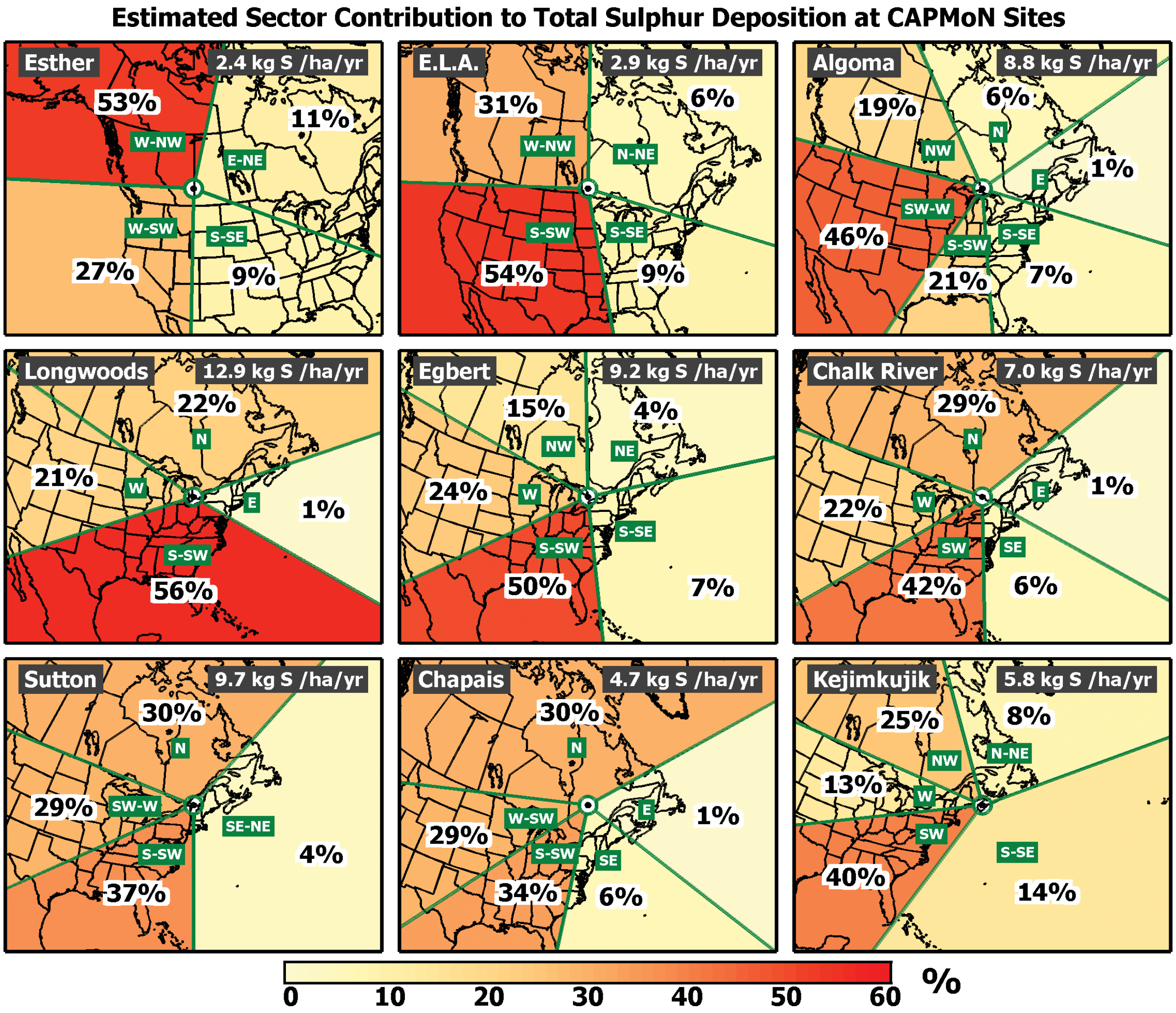

Figure 3.39: Percentage contribution of each sector to total (wet + dry) sulphur deposition at each CAPMoN site. The inset values in the top right corner of the diagrams indicate the total sulphur deposited at the sites.

deposition of each species (in kg S/ha/yr and kg N/ha/yr) attributable to each sector. Note that this procedure accounts implicitly for the contribution of the Not Attributable fraction. These amounts were then divided by the total deposition from all sectors to obtain the percentage contribution of each sector to the total deposition at that site. These values are tabulated in Tables 3.5 to 3.13 and shown graphically in Figures 3.39 and 3.40 for sulphur and nitrogen total deposition, respectively.

The interpretation of the sector percentage contribution to total deposition in Figures 3.39 and 3.40 can be somewhat misleading in cases where some sectors are decidedly larger or smaller than surrounding sectors. This is because a visual interpretation of the diagram may not allow for the fact that very large areas can contribute a great deal more deposition than small areas, and vice versa, simply by virtue of their larger or smaller areas. To assist in the interpretation of such cases, we have introduced the concept of normalizing each sector with the angular extent of the sector. The new metric then becomes the *percentage contribution per angular degree* for each sector. With this metric, a very small sector that contributes only a small fraction of the total deposition can be put on an even footing with larger sectors. The

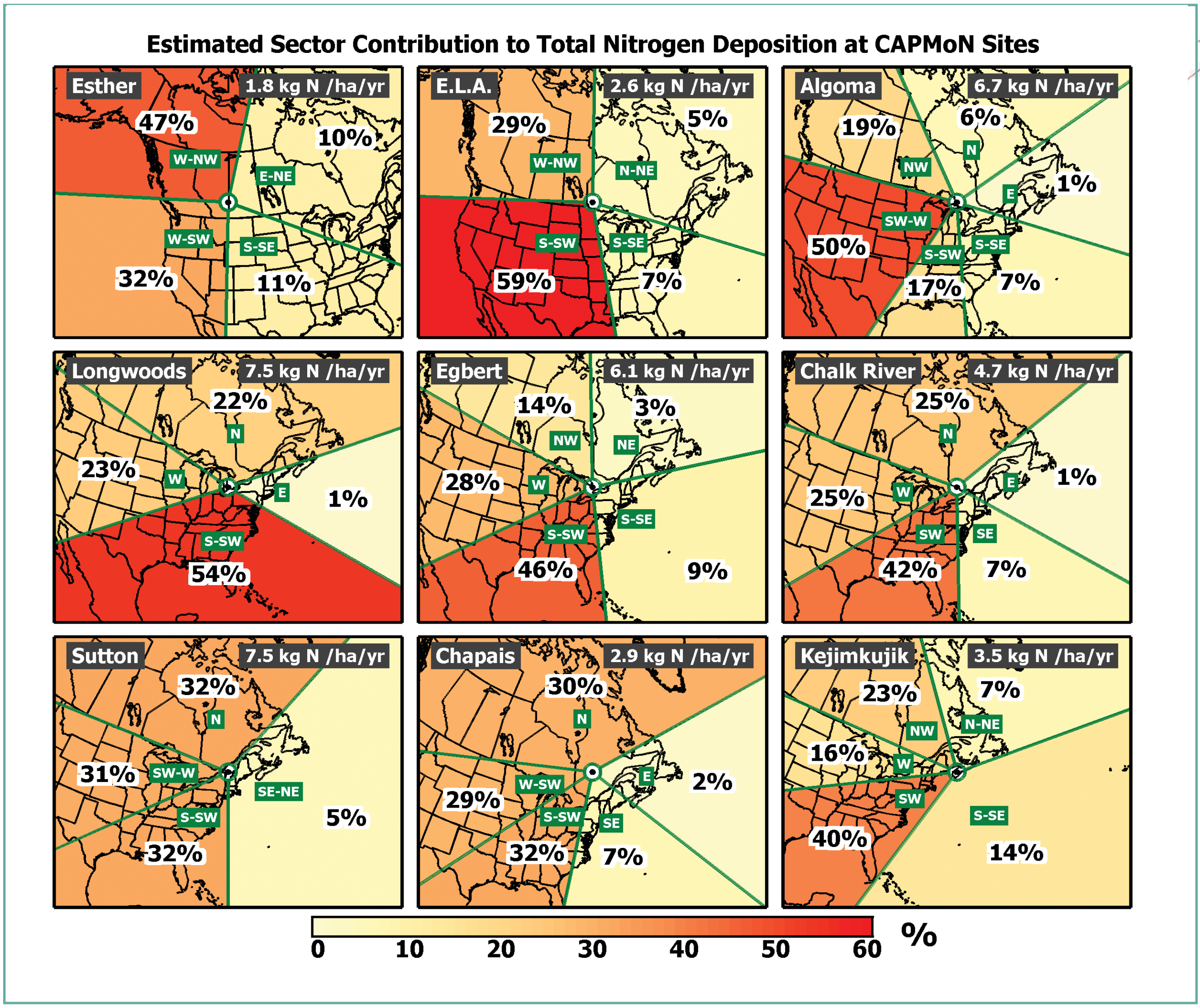

Figure 3.40: Percentage contribution of each sector to total (wet + dry) nitrogen deposition at each CAPMoN site. The inset values in the top right corner of the diagrams indicate the total nitrogen deposited at the sites.

plots of the percentage contributions per angular degree are given in Appendix 3.3 and are discussed in the text whenever deemed important to the interpretation.

The Source Contribution Analysis, combined with the box plot and Kruskal-Wallis significance testing, provides an excellent tool for understanding which emission areas make the largest and smallest contributions to sulphur and nitrogen deposition (and air quality) at CAPMoN sites. The results are interpreted and described from west to east across Canada in the following section. Also described are the results at a site in the U.S. (Penn State University) where the CAPMoN network operates a wet deposition sampler. To aid in the interpretation of the Source Contribution Analysis results, readers are referred to North American maps of 1990 SO_2 and NO_x emissions shown in Appendix 1. As mentioned earlier, emission levels have changed since 1990 but the spatial distribution of the sources has remained approximately constant.

3.5.2 Source attribution results

The Source Contribution Analysis results, in combination with the distributional statistics and Kruskal-Wallis test results, provide a synthesized view of source attribution relevant to the ten CAPMoN sites under consideration here.

West Coast

One CAPMoN site is located on the west coast of Canada on Saturna Island in the Strait of Georgia. The site, named Saturna, sits approximately 52 km south of the city of Vancouver, 43 km northeast of the City of Victoria and 143 km northwest of Seattle, Washington. Emission sources of SO_2 and NO_x are present on both sides of the U.S.-Canada border.

Figures 3.33 to 3.38 show the sectors and the box plot results for Saturna. Unfortunately, the results are extremely uncertain (for reasons presented below) and we have little confidence in their accuracy. As a consequence, we have chosen not to discuss the Source Contribution Analysis results any further in this section but have nonetheless included them for the purpose of completeness. We have also not shown the Saturna total deposition results in Figures 3.39 and 3.40 for this reason.

There are two reasons for the lack of confidence in the analysis results. The first is that all air mass trajectories in and around the Strait of Georgia, on which the analyses are based, are highly uncertain due to the complexity of the meteorology, the terrain, the atmospheric stability and the water/land/sea interaction in the area as well as the inadequate spatial and temporal resolution of the analyzed meteorological fields used to generate the trajectories (inadequate due to the foregoing complexities and to the lack of weather data off the Pacific coast). We therefore considered the trajectories generated for the area to be insufficiently accurate for the sectored box plot and Source Contribution Analysis. A detailed discussion of the problems and uncertainties associated with trajectories in the Saturna area is given in Snyder and Strawbridge (2004).

The second reason is related to the complexity of air pollution transport and dispersion along the southwest coast of British Columbia (which is in turn directly related to the first reason). Emissions from the Georgia Strait/Juan de Fuca Strait/Puget Sound area and emissions brought into the area by regional scale air masses are subject to very complicated transport and dispersion regimes due to the complex macro-, meso- and micro-scale flows and turbulence in the area. This complexity includes inflow and outflow winds from the Lower Fraser Valley, diurnally varying upslope and downslope winds in the mountain/valley areas, and the Wake Induced Stagnation Effect (WISE) described by Brook et al. (2004). WISE is responsible for widespread stagnation episodes in the Gulf Islands (of which Saturna is one) due to the convergence of flows from the Pacific Ocean, the Strait of Juan de Fuca and the Georgia Strait combined with a pronounced wake effect induced by Vancouver Island and the Gulf and San Juan Islands. These combined effects make air quality analysis and prediction very uncertain in that area and only detailed modelling work validated for the area is suitable for use.

In summary then, the major uncertainties associated with the trajectories and the complicated pollutant dynamics in the Georgia Strait, Juan de Fuca Strait and Puget Sound area have led us to believe that the sectored box plot and Source Contribution Analyses at Saturna are not reasonable. When representative trajectories are produced for the area at some time in the future, the results of these analyses will be published.

Southeastern Alberta

The Esther CAPMoN site, located in southeast Alberta, is the only CAPMoN site on the Canadian prairies with sufficient data to investigate source attribution. Esther is located 14 km from the Alberta-Saskatchewan border and 296 km north of the U.S.-Canada border. The site is semi-arid and surrounded by rangeland and tilled farmland. Only 4 years of wet and dry deposition data (1998-2001) are available at this site since it closed in 2002. Esther has the lowest multiple-year average deposition of all sites in the CAPMoN network, with total sulphur and nitrogen deposition levels of 2.40 kg S/ha/yr and 1.82 kg N/ha/yr. Dry deposition is estimated to account for 66% of the total sulphur deposition and 65% of the total nitrogen deposition at Esther -- due mainly to the small amount of wet deposition and precipitation that falls at the site each year.

Four angular sectors were selected for the Source Contribution Analysis and box plot presentations (Figure 3.33). The four sectors include western Canadian SO_2 and NO_x emission sources and two of the sectors, i.e., W-SW

Table 3.5. Esther (AB): Five-year average Source Contribution Analysis results for 1998-2002. The columns indicate the individual sector contributions (in %) to wet, dry and total (wet + dry) deposition at the site. The numbers in parentheses are the 5-year-average wet, dry and total deposition values for the individual species. The shaded cells identify the maximum percentage contribution for each type of deposition.

Deposition	Species	Fractional Contribution by Sector (%) Esther (AB)			
		W-NW	W-SW	S-SE	E-NE
Dry	SO_2 (1.44 kg S/ha/yr)	57	30	6	7
	SO_4^{2-} (0.16 kg S/ha/yr)	47	28	11	14
	Total-NO_3^- (1.19 kg N/ha/yr)	48	38	7	7
Wet	SO_4^{2-} (0.80 kg S/ha/yr)	47	21	15	17
	NO_3^- (0.63 kg N/ha/yr)	45	22	18	15
	Precipitation Amount (287 mm/yr)	45	18	16	21
Total (Wet + Dry)	Sulphur (2.40 kg S/ha/yr)	53	27	11	9
	Nitrogen (1.82 kg N/ha/yr)	47	32	10	11

and S-SE, also include U.S. emission sources in the west coast and Midwest states, respectively. The flow arriving at Esther is dominated by the W-NW sector followed, in decreasing order, by the W-SW, E-NE and S-SE sectors (based on the number of trajectory values, N, printed above the box plots in Figures 3.34 to 3.38).

The Source Contribution Analysis results for the years 1998-2001 are shown in Table 3.5. They indicate that the W-NW sector makes the largest contribution to the deposition (both wet and dry) of the sulphur and nitrogen species – ranging from 45-57% of the wet and dry deposition of the different species. This result is not surprising for the following reasons: (1) SO_2 and NO_x emissions are very high in the W-NW sector (from sources both in Alberta and northern British Columbia), (2) the number of trajectories from the W-NW sector far exceeds the number from the other sectors (i.e., almost twice the number of trajectories from the second highest sector and almost four times the number from the third highest sector), and (3) 45% of the precipitation that falls at Esther comes from the W-NW sector. It therefore appears that Alberta and northern British Columbia SO_2 and NO_x emission sources in the W-NW sector are the dominant sources affecting wet and dry deposition at Esther. The sector with the second highest contribution to wet and dry deposition at Esther is the W-SW sector - responsible for an estimated 21-22% of the wet deposition and 28-38% of the dry deposition of the various sulphur and nitrogen species. This sector includes emission sources in southern Alberta, southern British Columbia and the western U.S..

The two remaining sectors, S-SE and E-NE, account for very little sulphur and nitrogen wet and dry deposition at Esther, i.e., only 15-18% of the wet deposition and 6-14% of the dry deposition. This is due in part to the relatively infrequent flow through these sectors compared to the W-NW and W-SW sectors.

With regard to total deposition (i.e., the sum of wet plus dry deposition of all sulphur and all nitrogen species), the W-NW sector contributes an estimated 53% of the total sulphur deposition and 47% of the total nitrogen deposition (Table 3.5 and Figures 3.39 and 3.40). The second highest sector, W-SW, contributes 27% of the total sulphur deposition and 32% of the total nitrogen deposition. The other two sectors, S-SE and E-NE, contribute approximately 10% each. Given the geographical distribution of western Canadian and western U.S. SO_2 and NO_x sources, it is clear that most of the sulphur and nitrogen deposition at Esther is attributable to emissions in Alberta and, to some degree, British Columbia.

The box plot and Kruskal-Wallis significance test results (Figures 3.34 to 3.38) indicate that the highest SO_2 concentrations in air are associated with the W-NW sector, followed in decreasing order by the W-SW, E-SE and E-NE sectors. This is consistent with the distribution of SO_2 emissions in western Canada and explains why SO_2 dry deposition associated with the W-NW sector is the highest of all sectors, i.e., since ambient SO_2 concentrations and the frequency of flow are highest in that sector.

The situation for SO_4^{2-} in both air and precipitation is different to that of SO_2. Specifically, the S-SE sector, the sector with the fewest trajectories, has the highest SO_4^{2-} concentrations, followed in decreasing order by the second lowest trajectory sector (E-NE) and the two most frequent sectors (W-SW and W-NW) which are not significantly different. The very high concentrations of SO_4^{2-} in air associated with the S-SE sector may be explained as follows:

1. longer transport times from the SO_2 sources in that sector (i.e., from southern Saskatchewan and the north-central U.S. states) to Esther, thereby allowing for more oxidation of SO_2 to SO_4^{2-} during transport compared to S-SW and W-NW sectors where the emission sources are closer;
2. higher oxidant levels associated with the southerly flow in that sector (leading to increased production of SO_4^{2-});
3. higher emissions of NH_3 in that sector (thereby leading to higher levels of $(NH_4)_2SO_4$ production);
4. the less the precipitation, the less the amount of wet removal.

Interestingly, in contrast to SO_4^{2-} in air, the SO_4^{2-} concentrations in precipitation associated with the W-SW, W-NW and S-SE sectors are not significantly different from each other and the concentrations from the E-NE sector are the lowest of the four sectors, presumably because it contains fewer sources. The W-NW sector, with concentrations of SO_4^{2-} in precipitation that are not significantly different from the other sectors, contributes the highest fraction of SO_4^{2-} wet deposition because it produces the most precipitation of the four sectors (i.e., 45%).

The box plots of Total-NO_3^- in air and NO_3^- in precipitation indicate that the highest concentrations occur with flow from the W-SW and S-SE sectors. For both species, the W-SW concentrations are not significantly different from the S-SE concentrations. The W-NW sector and the E-NE sectors have the lowest concentrations (significantly different from the other two and each other), with the median of the E-NE sector being considerably lower than the three other sectors. Seasonal data plots (not shown here) indicate that Total-NO_3^- concentrations are much higher in the cold months (i.e., October-March) than in the warm months (April-September) in all four sectors. Supplementary information also indicates that the high Total-NO_3^- concentrations in the cold periods are mainly due to particle-NO_3^- while the high warm season concentrations (albeit considerably lower than the cold season concentrations) are mainly due to gaseous HNO_3. This result is consistent with known temperature effects on gas-particle partitioning of nitrogen species (i.e., p-NO_3^- formation is favoured under colder temperatures). This, in turn, suggests that the reason why the W-SW and S-SE sectors have the highest Total-NO_3^- concentrations is because they generally have higher levels of ambient ammonia and lower levels of SO_2 (relative to NO_x) in the winter (thereby making them optimal for particle-NO_3^- production) and higher levels of oxidants in the summer (thereby producing higher levels of HNO_3).

Nitrate concentrations in precipitation, as with Total-NO_3^- concentrations in air, are higher from the two southern sectors compared to the two northern sectors. Despite this, the W-NW sector has the highest wet deposition of NO_3^- which is due to the larger amount of precipitation associated with that sector.

Northwestern Ontario

One site, the Experimental Lakes Area (ELA), is located in the Boreal Forest region of northwestern Ontario, approximately 100 km east of the Ontario-Manitoba

Table 3.6. ELA - Experimental Lakes Area (ON): Five-year average Source Contribution Analysis results for 1998-2002 as described in Table 3.5.

Deposition	Species	Fractional Contribution by Sector (%) ELA (ON)			
		W-NW	S-SW	S-SE	N-NE
Dry	SO_2 (0.36 kg S/ha/yr)	61	24	5	10
	SO_4^{2-} (0.54 kg S/ha/yr)	40	38	8	14
	Total-NO_3^- (0.80 kg N/ha/yr)	39	48	5	8
Wet	SO_4^{2-} (2.03 kg S/ha/yr)	23	63	10	4
	NO_3^- (1.84 kg N/ha/yr)	25	64	8	3
	Precipitation Amount (776 mm/yr)	29	57	8	6
Total (Wet + Dry)	Sulphur (2.93 kg S/ha/yr)	31	54	9	6
	Nitrogen (2.64 kg N/ha/yr)	29	59	7	5

border and 90 km north of the Canada-U.S. border. The site is very remote and receives very low concentrations and deposition levels of sulphur and nitrogen oxides compared to the other CAPMoN sites in eastern Canada. For example, the five-year average (1998-2002) total sulphur deposition value at ELA is 2.93 kg S/ha/yr and the total nitrogen deposition value is 2.64 kg N/ha/yr. Dry deposition is estimated to account for 30% of the total sulphur and nitrate deposition at this site.

Four trajectory sectors (Figure 3.33) were selected for the Source Contribution Analysis (Table 3.6) and the Box plot/Kruskal-Wallis significance testing (Figures 3.34-3.38). Based on all measurement days, i.e., all days with air concentration data, the sector with the greatest number of trajectories is the W-NW sector followed in descending order by the S-SW and N-NE sectors (which have similar numbers of trajectories), and the S-SE sector (very few trajectories). For the subset of precipitation-only days, the order of the sectors is the same but the number of trajectories from the N-NE sector is considerably lower relative to the S-SW sector than it was for all days. This means that precipitation seldom occurs during flow from the N-NE sector.

Dry deposition of SO_2 is strongly dominated by the W-NW sector (61%), in spite of the fact that SO_2 concentrations from the W-NW, S-SW and S-SE sectors are not significantly different (see Figure 3.34). This contradiction can be explained simply by the fact that dry deposition occurs more frequently from the W-NW sector than from any of the other two sectors. In contrast, SO_4^{2-} dry deposition is contributed roughly equally by the W-NW and S-SW sectors (40% and 38%, respectively) due to the fact that the ambient SO_4^{2-} concentrations are significantly lower in the W-NW sector than in the S-SW sector while the number of dry deposition days (as indicated by the number, N, of trajectories in the box plot diagrams) is higher in the W-NW sector and lower in the S-SW sector. The net result is roughly equal dry deposition.

Dry deposition of Total-NO_3^- is dominated by the S-SW sector compared to the W-NW sector (48% versus 39%, respectively) due to the extremely high concentrations associated with the S-SW sector compared to the W-NW sector – high enough to compensate for the lower flow frequency from the S-SW sector. This suggests that emission sources in the SW-W and W-NW sectors are the major contributors to dry deposition of sulphur and nitrogen compounds at ELA. It is worth noting, however, that SO_4^{2-} and Total-NO_3^- concentrations in air associated with the S-SE sector are the second highest of all sectors, but they occur so infrequently that they have only a minor impact on dry deposition.

The wet deposition results differ from dry deposition results in that the S-SW sector accounts for almost two-thirds (63-64%) of the SO_4^{2-} and NO_3^- wet deposition at ELA. This high contribution is due to the fact that 57% of the precipitation at ELA comes from the S-SW sector and the SO_4^{2-} and NO_3^- concentrations in precipitation are the highest of all sectors. In contrast, the W-NW sector accounts for roughly one quarter of the wet deposition and 29% of the precipitation while the other two sectors account for only 11-14% of the wet deposition. As was the case with SO_4^{2-} and NO_3^- concentrations in air, the concentrations in precipitation were second highest from the S-SE sector. However, this sector does not have high wet deposition values because the frequency of flow and amount of precipitation is very low.

With regard to total (wet + dry) deposition (Figures 3.39 and 3.40), the S-SW is the highest contributing sector – accounting for 54% of the sulphur deposition and 59% of the nitrogen deposition. The W-NW sector is the second highest, contributing 31% of the sulphur and 29% of the nitrogen deposition. The other two sectors contribute less than 10% of the total deposition each. It appears then that SO_2 and NO_x emissions in the U.S. Midwest and West have the strongest influence on deposition and air and precipitation quality at ELA. This is due in large part to the U.S. emission sources being located upwind along the prevailing flow direction during most of the major precipitation episodes. Western Canadian emission sources also play an important, albeit secondary, role.

West-Central Ontario

The Algoma site is located at the Turkey Lakes Watershed study area in a remote area of West-Central Ontario, approximately 55 km northwest of Sault Ste. Marie (ON) and 12 km from the eastern shore of Lake Superior. The site is situated in a rugged mountainous area of the Pre-Cambrian Shield and is influenced by lake-effect precipitation from Lake Superior. For the period covered by the analysis below (1998-2002) only one Canadian SO_2 and NO_x emission source existed in the Algoma area, namely, a steel mill in Sault Ste Marie (approx. 55 km south of the site) with emissions of approx. 6 Ktonnes/yr in 2002. Prior to 1998, a sinter plant in Wawa (approx. 110 km north of the site) was the only other major source in the area. Emissions from the sinter plant were roughly 60 Ktonnes/yr in 1997, the last full year of operation (it closed in mid-1998).

The Algoma site receives high levels of wet deposition relative to the rest of eastern Canada. This is somewhat surprising considering its remote location and distance from major Canadian emission sources. The estimated five-year-average (1998-2002) total deposition values of sulphur and nitrogen at Algoma were 8.81 kg S/ha/yr and 6.67 kg N/ha/yr, respectively. Dry deposition is estimated to account for approximately 33% of the total sulphur deposition and 30% of the total nitrate deposition at the site.

Six angular sectors were selected for the Source Contribution Analysis at the Algoma site (Figure 3.33). Given the site's close proximity to the Canada-U.S. border and the paucity of Canadian emission sources in the area, these sectors provided an opportunity to assess the potential contribution of Canadian and U.S. emission sources on wet and dry deposition at the site. Three sectors, the NW, N and E sectors, comprise the *Canadian* sector (note that Maine is included in the E sector), while two sectors, the SW-W and S-SW sectors, make up the *U.S.* sector (note that the city of Sault Ste. Marie, Ontario is included in the SW-W sector), and the S-SE sector constitutes a *Combined Canada+U.S.* sector. The latter sector encompasses southern Ontario and the states south and east of Lake Ontario.

The Source Contribution Analysis results for dry, wet and total (wet + dry) deposition are shown in Table 3.7. They show that 56% of the SO_2, 60% of the SO_4^{2-} and 58% of the Total-NO_3^- dry deposition are associated with the *U.S.* sector (S-SW + SW-W). Interestingly, the SW-W sector, encompassing the *U.S.* Midwest and Great Plains, accounts for the largest fraction of the dry deposition, more so than the S-SW sector which encompasses the western portion of the Ohio River Valley and south. This is caused by: (1) the angular size (i.e., area) of the SW-W sector being considerably larger than the S-SW sector and (2) the number of days with flow from the SW-W sector

Table 3.7. Algoma: Five-year average Source Contribution Analysis results for 1998-2002 as described in Table 3.5.

Deposition	Species	Fractional Contribution by Sector (%) Algoma (ON)					
		NW	N	E	S-SE	S-SW	SW-W
Dry	SO_2 (1.70 kg S/ha/yr)	14	13	3	14	22	34
	SO_4^{2-} (1.23 kg S/ha/yr)	15	11	2	12	21	39
	Total-NO_3^- (2.00 kg N/ha/yr)	15	12	2	13	22	36
Wet	SO_4^{2-} (5.88 kg S/ha/yr)	21	3	1	4	20	51
	NO_3^- (4.67 kg N/ha/yr)	21	3	1	4	16	55
	Precipitation Amount (1172 mm/yr)	23	7	2	5	15	48
Total (Wet + Dry)	Sulphur (8.81 kg S/ha/yr)	19	6	1	7	21	46
	Nitrogen (6.67 kg N/ha/yr)	19	6	1	7	17	50

being roughly three times the number of days with flow from the S-SW sector, (i.e., more days of dry deposition from the SW-W sector). A very small portion of the dry deposition, 13%, is associated with the *Combined Canada+U.S.* S-SE sector which includes southern Ontario and the eastern U.S. states. This is not surprising given the low frequency of trajectories associated with that sector. However, the very high concentrations associated with air from that sector suggests that emissions in that sector are having a strong influence on high air concentration events at Algoma. Finally, the *Canadian* NW, N and E sectors contribute approximately 30% of the sulphur and nitrogen dry deposition at the site. Thus, it appears that U.S. SO_2 and NO_x emissions are responsible for >60% of the dry deposition at Algoma.

For wet deposition, approximately 70% of the SO_4^{2-} and NO_3^- wet deposition at the Algoma site is associated with the *U.S.* SW-W + S-SW sectors, which again encompass all of the U.S. states west of Lake Huron. Given that these two sectors account for roughly 60% of the total precipitation that falls at Algoma, it is not surprising that the combination of high precipitation and major emission sources in these sectors accounts for such a large fraction of the SO_4^{2-} and NO_3^- wet deposition. As was the case with dry deposition, the SW-W sector contributes the largest proportion of SO_4^{2-} and NO_3^- wet deposition at 51% and 55%, respectively – again, not surprising given that the same sector accounts for 48% of the total precipitation at Algoma. By comparison, the 3 *Canadian* sectors (NW, N and E) account for an estimated 25% of the wet deposition, with the dominant sector of the three being the NW. This seems reasonable since the NW sector has more frequent flow during precipitation than the other two sectors, it accounts for about one quarter of the precipitation at Algoma, and it encompasses most of western Canada's SO_2 and NO_x emission sources. The combined southern Ontario/eastern *U.S.* sector (S-SE) appears to contribute very little to the overall wet deposition, undoubtedly due to the fact that minimal precipitation (5%) and few trajectories are associated with that sector.

In terms of total (wet + dry) deposition, Table 3.7 and Figures 3.39 and 3.40 indicate that the SW-W sector is the dominant contributor, accounting for 46% of the total sulphur deposition and 50% of the total nitrate deposition at Algoma. The combined *U.S.* SW-W + S-SW sectors account for 67% of the total sulphur and nitrogen deposition while the combined *Canadian* NW+N+E sectors account for 26% and 27%, respectively. The *Combined Canada+U.S.* S-SE sector accounts for only 7% of the sulphur and nitrogen deposition. The dominance of the SW-W sector over the S-SW and NW sectors is due in part to the larger areas of the SW-W sector. By looking at the percentage contribution per angular degree (Figures A3.5 and A3.6 in Appendix 3.3), one can see that the SW-W sector is still dominant with a contribution of 0.65% per degree, but less so compared to the contribution of 0.55% per degree from the S-SW sector and 0.37% per degree from the NW sector. This suggests that emissions in the SW-W and S-SW sectors make roughly the same contribution to total deposition per angular degree, followed to a lesser degree by the NW sector. The N, E and S-SE sectors have very little impact per angular degree (0.02 to 0.10% per degree).

The Kruskal-Wallis tests on the sectored concentration data (Figures 3.4 to 3.38) indicate that the highest ambient concentrations of SO_2 and SO_4^{2-} are associated with the S-SW and S-SE sectors, followed by the high deposition SW-W sector (statistically significant). This suggests that the SO_2 emission sources in Sault Ste. Marie, Sudbury, southern Ontario, Michigan, Illinois and the Ohio River Valley in general lead to the relatively high concentrations at Algoma. The reason why the S-SW and S-SE sectors contribute a lower proportion of dry deposition compared to the SW-W sector, in spite of their higher ambient concentrations, is because flow from those sectors is considerably less frequent (based on the number of trajectories), as are their dry deposition velocities. The lower dry deposition velocities are due to fewer precipitation events coming from those sectors – the result of which is fewer occurrences of high surface wetness and therefore fewer cases of high dry deposition velocities.

The lowest concentrations of SO_2 and SO_4^{2-} (significantly so) are associated with the N sector followed by the E and NW sectors which are not significantly different from each other. The median concentration associated with the lowest sector is roughly 20 times lower than the median of the highest sector for SO_2 and 7 times lower for SO_4^{2-}. This makes sense given the paucity of SO_2 sources in the N sector. The concentrations of SO_4^{2-} in precipitation are highest in the S-SW sector (as was the case with air concentrations) but they are not significantly different from the concentrations in the SW-W sector. The exceedingly high frequency of flow in the SW-W sector compared to the E and NW sectors, coupled with its high concentrations and large contribution of precipitation (48%), accounts for its dominant contribution to SO_4^{2-} wet deposition at Algoma.

For Total-NO_3^- concentrations in air and NO_3^- concentrations in precipitation, the highest concentrations are associated with the SW-W sector followed by the S-SE and SW-W sectors. The lowest concentrations of Total-NO_3^- in air and NO_3^- in precipitation, as is the case with the sulphur species, are associated with the N sector (10 times lower than the highest sector for Total-NO_3^- and 6 times for NO_3^- in precipitation). Again, the fact that the lowest SO_2, SO_4^{2-} and Total-NO_3^- concentrations in air and SO_4^{2-} and NO_3^- concentrations in precipitation are associated with the N sector is not surprising given the lack of major SO_2 and NO_x sources in that remote area of northern Canada.

In summary, the *U.S.* SW-W and S-SW sectors account for an estimated two thirds of the deposition of sulphur and nitrogen at Algoma. These sectors also account for high concentrations of SO_2, SO_4^{2-} and NO_3^- in air and SO_4^{2-} and NO_3^- concentrations in precipitation. This points to the fact that U.S. emission sources in the upper Midwest and western Ohio River Valley have a dominant influence on sulphur and nitrogen deposition and air and precipitation quality at Algoma.

Southwestern Ontario

Two CAPMoN sites, Longwoods and Egbert, are located in southwestern Ontario. Longwoods is situated approximately 25 km west of the city of London, 30 km north of Lake Erie, 45 km southeast of Lake Huron, 75 km east of Sarnia and 135 km northeast of Detroit/Windsor. Longwoods has the highest sulphur deposition (12.89 kg S/ha/yr) and the second highest nitrogen deposition (7.47 kg N/ha/yr) of CAPMoN sites in Canada. Egbert is located approximately 180 km northeast of Longwoods, 65 km north-northwest of the northern boundary of the Toronto metropolitan area and 45 km south of Georgian Bay. Both sites are surrounded by agricultural activity and both are impacted by lake-effect precipitation from Lake Huron and Georgian Bay, respectively.

The pre-set angular sectors are not precisely the same for Longwoods and Egbert (Figure 3.33) since the N sector at

Table 3.8. Longwoods (ON): Five-year average Source Contribution Analysis results for 1998-2002 as described in Table 3.5.

Deposition	Species	Fractional Contribution by Sector (%) Longwoods (ON)			
		N	E	S-SW	W
Dry	SO_2 (5.47 kg S/ha/yr)	28	2	49	21
	SO_4^{2-} (0.47 kg S/ha/yr)	24	3	56	17
	Total-NO_3^- (2.69 kg N/ha/yr)	28	2	46	24
Wet	SO_4^{2-} (6.95 kg S/ha/yr)	17	1	62	20
	NO_3^- (4.78 kg N/ha/yr)	18	1	58	23
	Precipitation Amount (882 mm/yr)	19	1	62	18
Total (Wet + Dry)	Sulphur (12.89 kg S/ha/yr)	22	1	56	21
	Nitrogen (7.47 kg N/ha/yr)	22	1	54	23

Longwoods incorporates both the NW and NE sectors at Egbert and the border between the S-SW and E sectors at Longwoods is somewhat farther to the northeast than the same border at Egbert. The Source Contribution results are shown in Tables 3.8 and 3.10 as well as Figures 3.34 to 3.38.

By merging several sectors at Longwoods and Egbert, it is possible to compare roughly equivalent sectors at the two sites. For example, the combined S-SW + E sector at Longwoods is roughly equivalent to the combined S-SW + S-SE sector at Egbert, with the exception that the Egbert sector includes more of southwestern Ontario roughly from London in the west to Toronto in the east than does the same Longwoods sector. As well, the combined NW and NE sectors at Egbert are roughly equivalent to the N sector at Longwoods. The result is, in fact, a remarkable similarity in the % contribution values associated with the combined equivalent sectors at Longwoods and Egbert (see text below). Since the measurements and analyses were made independently at the two sites, this gives some assurance that the results are reasonably representative of southwestern Ontario and that both sites share the same general airshed characteristics and source regions.

The largest contribution to SO_2, SO_4^{2-} and Total-NO_3^- dry deposition and SO_4^{2-} and NO_3^- wet deposition comes from the S-SW sector at Longwoods (46-62%) and the S-SW sector at Egbert (41-52%). This sector also accounts for 54-56% of the total sulphur and nitrogen deposition at Longwoods and 46-50% at Egbert. At Egbert, only 10-13% of the SO_2, SO_4^{2-}, and Total-NO_3^- dry deposition and 6% of the SO_4^{2-}, and NO_3^- wet deposition is associated with the S-SE sector – due mainly to the low frequency of easterly and southeasterly flows at that site. By assuming that the same is true at Longwoods (confirmed by an independent and slightly different Source Contribution Analysis at Longwoods), most of the dry and wet deposition associated with the S-SW sector at Longwoods will, in fact, come from roughly the same area encompassed by the S-SW sector at Egbert (excluding the area of southwestern Ontario between Longwoods and Egbert). Thus, the sector that accounts for the highest percentage contribution of dry, wet and total deposition at both Longwoods and Egbert is the sector that includes southwestern Ontario, the Ohio River Valley and the southeastern U.S. It is worth noting that the high percentage of wet deposition associated with this S-SW sector is reasonable since it accounts for 45% of the precipitation at Egbert and 62% at Longwoods (note that

Table 3.9. Egbert (ON): Five-year average Source Contribution Analysis results for 1998-2002 as described in Table 3.5.

Deposition	Species	Fractional Contribution by Sector (%) Egbert (ON)				
		NE	S-SE	S-SW	W	NW
Dry	SO_2 (3.43 kg S/ha/yr)	6	10	43	20	21
	SO_4^{2-} (0.55 kg S/ha/yr)	5	13	47	20	15
	Total-NO_3^- (2.48 kg N/ha/yr)	6	13	41	25	15
Wet	SO_4^{2-} (5.21 kg S/ha/yr)	2	6	54	26	12
	NO_3^- (3.58 kg N/ha/yr)	2	6	49	29	14
	Precipitation Amount (819 mm/yr)	4	8	45	25	18
Total (Wet + Dry)	Sulphur (9.19 kg S/ha/yr)	4	7	50	24	15
	Nitrogen (6.06 kg N/ha/yr)	3	9	46	28	14

the Longwood's S-SW sector is roughly equivalent to the S-SW plus S-SE sectors at Egbert).

The second highest sector that contributes to wet, dry and total deposition at both sites is the W sector. This sector is roughly equivalent at both sites although the Egbert sector encompasses slightly more of southwestern Ontario then does Longwoods. The W sector contributes 21-23% of the total sulphur and total nitrate deposition at Longwoods and 24-28% at Egbert; it also is the sector that accounts for the second highest amount of precipitation at Egbert (25%) and Longwoods (18%). It is interesting to note that this sector's contribution to total nitrogen deposition is somewhat higher than to total sulphur deposition. This is consistent with the modelling results of Chapter 4 (Moran, 2005) and the wet deposition measurement results in Figure 3.2 which show that nitrate deposition has a more northerly centre-of-mass than does sulphate, i.e., a stronger influence of the west on nitrate than on sulphate.

A careful inspection of Tables 3.8 and 3.9 as well as Figures 3.34 to 3.38 suggests that the sectors at Longwoods and Egbert can be merged to create an effective *Canadian* sector (i.e., the N sector at Longwoods and the NW+NE sectors at Egbert) and an effective *Southwestern Ontario+U.S.* sector (i.e., the S-SW + E sectors at Longwoods and the S-SW + S-SE sectors at Egbert). At Longwoods, the *Southwestern Ontario+U.S.* sector encompasses the small section of southwestern Ontario from Longwoods to the U.S. border and, at Egbert, the same sector includes almost all of southwestern Ontario. The Source Contribution results for these two sectors indicate that approximately 72-86%, of the wet and dry deposition of sulphur and nitrogen species at Longwoods and Egbert is associated with the *Southwestern Ontario+U.S.* sector and 14%-28% with the *Canadian* sector. In terms of total sulphur and nitrogen deposition, the *Southwestern Ontario+U.S.* sector contributes roughly 78% at Longwoods and 81-83% at Egbert. This result is not surprising for two reasons: (1) the *Southwestern Ontario+U.S.* sector is responsible for approximately 80% of the precipitation that falls at the two sites and (2) this sector encompasses, and is located very close to, the high SO_2 and NO_x emissions of southwestern Ontario and the U.S. upper Midwest and Ohio River Valley in the U.S..

Unfortunately, the foregoing sector analysis does not allow us to separate out the relative contributions of southwestern Ontario emissions from those of the U.S. Midwest and Ohio River Valley. However, it is expected that a very high proportion of the sulphur and nitrogen deposition from the *Southwestern Ontario+U.S.* sector is due to the U.S. sources based on the fact that the total Canadian SO_2 emissions in southwestern Ontario within a 110 km radius of Longwoods represents only about 5% of the total SO_2 emissions in the northern tier of Great Lake states (i.e., those states that would be most influential on Longwoods including Minnesota, Wisconsin, Michigan, Ohio, Pennsylvania and New York) and 2% of the emissions in both the first and second tiers of states (comprising the previous states plus Iowa, Indiana, Kentucky, West Virginia and Virginia). The *Southwestern Ontario+U.S.* sector at Egbert accounts for a slightly higher percentage contribution of wet and dry deposition compared to the same sector at Longwoods. This is consistent with the fact that this sector includes more of southwestern Ontario emissions than does the same sector at Longwoods and points to a possible higher influence of southwestern Ontario emissions at Egbert.

The other statistical analyses provide further evidence that the south-southwest sectors have a dominant influence on Longwoods and Egbert air and precipitation quality. The sectored box plots and Kruskal-Wallis significance tests in air (Figures 3.34 to 3.38) clearly show the dominance of the S-SW sector over to the other sectors for SO_2, SO_4^{2-} and Total-NO_3^- concentrations in air as well as SO_4^{2-} concentrations in precipitation. Nitrate concentrations in precipitation however, are dominated by the W sector at both sites, a situation consistent with the centre of mass of nitrate wet deposition being located farther north than the centre of mass of sulphate wet deposition, as previously discussed. At Longwoods, the median values of the SO_2, SO_4^{2-} and Total-NO_3^- concentrations in air associated with the S-SW sector are 1.3 to 1.6 times higher than the next highest sector and 3 to 4 times higher than the lowest concentration sector (i.e., the N sector for all species). Similarly, at Egbert, the median concentrations associated with the S-SW sector are 1.1 to 1.5 times higher than the second highest sector and roughly 4 to 7 times higher than the lowest concentration northern sectors (NW and NE). The Kruskal-Wallis test indicates that the E and S-SE sectors, respectively, at Longwoods and Egbert have very high concentrations of SO_4^{2-} and Total-NO_3^-, second to the S-SW sector but the frequency of flow from those directions is the lowest of all sectors. This is followed by the W sector which has much more frequent flow than the easterly and southeasterly sectors. Thus, trajectories travelling over the high emission areas of southwestern Ontario and the U.S. Midwest and Ohio River Valley areas are responsible for the highest concentrations of acidifying species in air at both Egbert and Longwoods (as well as the highest fluxes as mentioned above). Concentrations of all species in air and precipitation are lowest in the *Canadian* sectors from northwest through northeast.

Since SO_4^{2-} and NO_3^- concentrations in precipitation are highest and second highest, respectively, from the SW sector and roughly half or more of the precipitation at Egbert and Longwoods comes from that sector, it is not surprising that 49-62% of SO_4^{2-} and NO_3^- wet deposition at the two sites is associated with the S-SW sector. The dominance of the S-SW sector for SO_4^{2-} and SO_2 dry deposition is also reasonable given the high frequency of flow and highest ambient concentrations associated with the S-SW sector.

Eastern Ontario

The Chalk River site is located in a remote area of eastern Ontario on the Canadian Shield, roughly 210 km north of the Canada-U.S. border, 300 km northeast of Toronto and 300 km northwest of Montreal. The site sits in a transition zone between the high-concentration Lower Great Lakes area and the low-concentration Northern Ontario/Northern Québec area. Ambient sulphur and nitrogen oxide concentrations and wet and dry deposition levels at the site are moderate for eastern Canada (see Figures 3.34 to 3.40). Dry deposition is estimated to contribute 33% of the total (wet + dry) sulphur deposition and 27% of the total nitrogen deposition at Chalk River.

Five pre-determined sectors were chosen for the Source Contribution and box plot analyses (Figure 3.33). Using the number of trajectories associated with each sector, it appears that the dominant transport sector for air arriving at Chalk River is the N sector, followed by the W and SW sectors. Flow from the SE and E sectors is very infrequent (see Figures 3.34 to 3.38)

The Source Contribution Analysis results for dry and wet deposition are shown in Table 3.10. They indicate that the largest proportion of SO_2 dry deposition comes from the N sector which accounts for almost one half (45%) the SO_2 dry deposition at Chalk River. This result seems to be

Table 3.10. Chalk River: Five-year average Source Contribution Analysis results for 1998-2002 as described in Table 3.5.

Deposition	Species	Fractional Contribution by Sector (%) Chalk River (ON)				
		N	E	SE	SW	W
Dry	SO_2 (1.61 kg S/ha/yr)	45	2	6	27	20
	SO_4^{2-} (0.73 kg S/ha/yr)	29	2	10	36	23
	Total-NO_3^- (1.26 kg N/ha/yr)	29	2	11	36	22
Wet	SO_4^{2-} (4.65 kg S/ha/yr)	23	1	5	48	23
	NO_3^- (3.47 kg N/ha/yr)	24	1	6	44	25
	Precipitation Amount (860 mm/yr)	26	2	8	38	26
Total (Wet + Dry)	Sulphur (6.99 kg S/ha/yr)	29	1	6	42	22
	Nitrogen (4.73 kg N/ha/yr)	25	1	7	42	26

quite reasonable in light of the fact that a major SO_2 emission source is located to the north-northwest of the Chalk River site (at Rouyn-Noranda, QC) and another is located close to the N sector's western border (at Sudbury, ON), and more dry deposition days occur in the N sector than in any other sector.

In contrast to SO_2, the SW sector accounts for the largest contribution of SO_4^{2-} and Total-NO_3^- dry deposition at Chalk River (i.e., 36% in both cases) as well as the largest contribution of SO_4^{2-} and NO_3^- wet deposition (48% and 44%, respectively). The dominance of the SW sector for SO_4^{2-} and Total-NO_3^- dry deposition is consistent with the results further west at the Longwoods and Egbert sites in southwestern Ontario, and with the fact that the highest air and precipitation concentrations of SO_4^{2-} and NO_3^- at all three sites are associated with the same SW sector. This implies that the higher-concentration air at Chalk River coming from the SW sector has typically travelled over the high SO_2 and NO_x emission areas of Ontario, the Ohio River Valley and the U.S. Midwest, during which time it was exposed to high oxidant levels which, in turn, lead to the conversion of SO_2 to SO_4^{2-} and NO_2 to NO_3^- and HNO_3. This is not the case for air arriving from the N sector which generally has fewer emission sources, lower temperatures, lower oxidant levels and therefore lower amounts of SO_4^{2-} and Total-NO_3^-.

The SW sector also accounts for most of the SO_4^{2-} and NO_3^- wet deposition at Chalk River (48 and 44%, respectively). This is because this sector has the highest SO_4^{2-} and NO_3^- concentrations in precipitation and the highest amount of precipitation (38%). The W and N sectors each contribute roughly equal amounts (around 25%) of the wet deposition while the E and SE sectors contribute very little (6-7%) due largely to low precipitation amounts associated with these sectors.

It is worth pointing out here that NO_3^- concentrations in precipitation from the W and SW sectors are not significantly different. This suggests that the W sector has a larger influence on NO_3^- wet deposition than SO_4^{2-} wet deposition which makes sense given the more northerly centre-of-mass of the NO_3^- deposition pattern compared to the SO_4^{2-} deposition pattern (Figure 3.2).

Chalk River's distant location from the U.S. border (approximately 200 km) makes it is impossible to combine trajectory sectors in a way that produces a Canadian sector and an U.S. sector as was done for sites closer to the border. The closest that one can come to this approach is to create a *Canadian minus Southern Ontario* sector and a *U.S. plus southern Ontario* sector. The former includes the N and E sectors while the latter includes the W + SW+ SE sectors (note that Sudbury is excluded from

Table 3.11. Sutton (QC): Five-year average Source Contribution Analysis results for 1998-2002 as described in Table 3.5.

Deposition	Species	Fractional Contribution by Sector (%) Sutton (QC)			
		N	SW-W	S-SW	SE-NE
Dry	SO_2 (1.80 kg S/ha/yr)	46	22	28	4
	SO_4^{2-} (1.06 kg S/ha/yr)	32	23	37	8
	Total-NO_3^- (2.33 kg N/ha/yr)	41	24	28	7
Wet	SO_4^{2-} (6.87 kg S/ha/yr)	26	31	39	4
	NO_3^- (5.18 kg N/ha/yr)	28	34	33	5
	Precipitation Amount (1260 mm/yr)	26	27	35	12
Total (Wet + Dry)	Sulphur (9.73 kg S/ha/yr)	30	29	37	4
	Nitrogen (7.51 kg N/ha/yr)	32	31	32	5

the former while Maine is excluded from the latter). Based on this approach, the percentage contributions of the *Canadian minus Southern Ontario* sector to SO_2, SO_4^{2-} and Total-NO_3^- dry deposition are 47%, 31%, and 31%, respectively and 24% and 25%, respectively to SO_4^{2-} and NO_3^- wet deposition. This means that the *U.S. + Southern Ontario* sector is estimated to contribute between 69% and 76% of the wet and dry deposition of these species, with the exception of SO_2 dry deposition which is lower at 53%. Thus, as was the case for the Algoma, Longwoods and Egbert sites, the high SO_2 and NO_x emissions in southern Ontario (including Sudbury), the Ohio River Valley and the U.S. Midwest appear to have a dominant influence on sulphur and nitrogen deposition at Chalk River.

In terms of total deposition, the combined U.S. plus southern Ontario SO_2 and NO_x emissions account for 70% of the sulphur and 74% of the nitrogen total deposition at Chalk River.

Southern Québec

The Sutton, QC site is located in an agricultural and forested area of southern Québec approximately 7 km north of the Vermont border and 90 km southeast of Montreal. The site sits in an area of high deposition with a 4-year annual average total (wet + dry) deposition of sulphur equal to 9.73 kg S/ha/yr and of nitrogen equal to 7.51 kg N/ha/yr. Sutton's total deposition of nitrogen is the highest of all CAPMoN sites. As a 4-year average (1998-2001), dry deposition is estimated to contribute 30% of the total (wet + dry) sulphur deposition and 31% of the total nitrogen deposition. Note that the Sutton site closed in 2002 so the analysis covers only a 4-year period. Flow from the N sector is dominant at Sutton followed by the S-SW, SW-W and SE-E sectors.

The results of the Source Contribution Analysis for Sutton are shown in Table 3.11. The largest proportion of SO_2 and Total-NO_3^- dry deposition is contributed by the N sector – the prevailing flow sector that includes the city of Montreal and the other major SO_2 and NO_x emission sources in the Province of Québec. Sulphate dry deposition, on the other hand, is highest from the S-SW sector (37%) followed by the N sector (32%).

The wet deposition results in Table 3.11 indicate that most of the precipitation at Sutton originates in the S-SW sector (35%), followed by the SW-W (27%), N (26%) and SE-NE (12%) sectors. Sulphate wet deposition is ordered the same way while NO_3^- wet deposition is slightly different with the SW-W and S-SW sectors making equally the highest contributions at 34 and 33%, respectively. It is the combined effect of trajectory frequencies, concentration levels and precipitation amounts in each sector that produces this overall ranking of wet deposition contributions. The reason that the highest proportion of SO_4^{2-} wet deposition comes from the S-SW sector while the highest proportion of NO_3^- wet deposition comes from the SW-W sector is because the S-SW sector has significantly higher SO_4^{2-} concentrations in precipitation than the SW-W sector while the SW-W sector is tied with the S-SW sector for the highest NO_3^- concentrations in precipitation (see Figures 3.37 and 3.38). The contributions of the SE-NE sector to precipitation concentrations and wet deposition of SO_4^{2-} and NO_3^- is very low.

With respect to source attribution, SO_2 and NO_x sources in Québec (i.e., in the N sector) appear to have the largest impact on dry deposition and, to a lesser but still important extent, on wet deposition at Sutton. This is due in large part to the prevailing flow from the N sector at Sutton. Nevertheless the combined SW-W and S-SW sectors account for over 50% of the dry deposition and approximately 70% of the wet deposition of sulphur and nitrogen at Sutton. This suggests that SO_2 and NO_x emission sources in southern and central Ontario (including Sudbury) and the eastern half of the U.S. have more influence on sulphur and nitrogen deposition in southern Québec than do emissions in Québec and Atlantic Canada.

In terms of total (wet + dry) deposition, Table 3.11 and Figures 3.39 and 3.40 confirm that SO_2 and NO_x emission sources in Ontario, the U.S. Midwest and the Ohio River Valley contribute most of the total sulphur deposition (66%) and total nitrate deposition (63%) at Sutton. This is followed by the sources in Québec and to some degree northern Ontario which contribute 30% of the total sulphur deposition and 32% of the total nitrogen deposition. Sources in Atlantic Canada and the U.S. northeast appear to have little influence (4%) on total deposition at Sutton.

Northern Québec

One site, Chapais, is located in a remote area of northern Québec approximately 500 km north of Montreal and 350 km northeast of the only major SO_2 emission source in the area – a non-ferrous smelter at Rouyn-Noranda. Wet and dry deposition at Chapais is low compared to the rest of eastern Canada with total (wet + dry) sulphur deposition equalling 4.7 kg S/ha/yr and total nitrogen deposition equalling 2.9 kg N/ha/yr (1998-2002 average). Dry deposition accounts for an estimated 24% of the total deposition of sulphur and 17% of the total deposition of nitrogen.

The Source Contribution Analysis results for Chapais are shown in Table 3.12 and the associated air and precipitation concentration box plots and Kruskal-Wallis test results are shown in Figures 3.34 to 3.38. As was the case with Chalk River and Sutton farther south, a very high proportion of the dry deposition of sulphur and nitrogen at Chapais is contributed by the N sector (38-44%). The Kruskal-Wallis test results and the sectored box plots suggest that the dominant contribution of the N sector is due to the high frequency of flow from that sector (more than double the frequency of all other sectors combined) rather than to high ambient concentrations since the N sector has the lowest or second lowest concentrations of all sectors. The S-SW sector is the second highest contributor to dry deposition because it has the highest SO_2, SO_4^{2-} and Total-NO_3^- concentrations of all sectors (statistically significant) and a moderate frequency of flow. The very high concentrations associated with the S-SW sector is reasonable given that the largest SO_2 and NO_x emission sources in eastern Canada and the eastern U.S. are located in that sector. The SE sector, which has the second highest concentrations of SO_4^{2-} and Total-NO_3^- (but not SO_2), accounts for only 5-7% of the dry deposition due to the infrequent number of trajectories associated with the sector. The E sector has both low concentrations and low flow frequencies, the result being very low dry deposition (2-3%).

The situation for wet deposition is different to that of dry deposition. For wet deposition, the S-SW and W-SW sectors account for 35 and 32%, respectively, of the SO_4^{2-} wet deposition and 33 and 31% of the NO_3^- wet deposition, followed in close order by the N sector which contributes 27 and 28%. The dominance of the S-SW and W-SW sectors is due in part to their very high concentrations of SO_4^{2-} and NO_3^- in precipitation (i.e., the highest of all sectors), in part to the moderately high frequency of trajectories from those sectors (i.e., second and third highest behind the N sector), and in part to the

Table 3.12. Chapais (QC): Five-year average Source Contribution Analysis results for 1998-2002 as described in Table 3.5.

Deposition	Species	Fractional Contribution by Sector (%) Chapais (QC)				
		N	W-SW	S-SW	SE	E
Dry	SO_2 (0.52 kg S/ha/yr)	38	25	30	5	2
	SO_4^{2-} (0.61 kg S/ha/yr)	40	19	30	8	3
	Total-NO_3^- (0.50 kg N/ha/yr)	44	19	27	7	3
Wet	SO_4^{2-} (3.57 kg S/ha/yr)	27	32	35	5	1
	NO_3^- (2.42 kg N/ha/yr)	28	31	33	7	1
	Precipitation Amount (1134 mm/yr)	36	23	26	12	3
Total (Wet + Dry)	Sulphur (4.70 kg S/ha/yr)	30	29	34	6	1
	Nitrogen (2.92 kg N/ha/yr)	30	29	32	7	2

fact that roughly 25% of the precipitation comes from each of these sectors. Thus, the S-SW and W-SW sectors combine to account for 64-67% of the wet deposition of SO_4^{2-} and NO_3^- and 49% of the precipitation. It is clear that the emissions in western Québec (west of Chapais), all of Ontario and the U.S. Midwest and Ohio River Valley areas make a major contribution to SO_4^{2-} and NO_3^- wet deposition at Chapais. In contrast, the N sector, which accounts for 36% of the precipitation at Chapais, contributes just under 30% of the SO_4^{2-} and NO_3^- wet deposition at Chapais because of the very low concentrations associated with that sector. Very little precipitation is associated with the E and SE sectors (3% and 12%, respectively) which, in combination with the very low concentrations, results in small percentage contributions to the wet deposition of SO_4^{2-} and NO_3^- (1% and 5-7%, respectively).

In terms of total (wet + dry) deposition of sulphur and nitrogen (Figures 3.39 and 3.40), the N, W-SW and S-SW sectors each contribute roughly 30% while the E and SE sectors contribute very little (1-2% and 6-7%, respectively). The strong contribution of the N sector relative to the W-SW and S-SW sectors is due in large part to the extremely large area subtended by the sector.

Looking at the results in an area-normalized manner, the N sector's percentage contribution per degree is roughly 3.5 times lower than the W-SW and S-SW sectors (see Figures A3.5 and A3.6 in Appendix 3.3). This suggests that emissions in the N sector are less influential than emissions in the other two sectors. It is impossible, however, to establish which emission areas in the W-SW and S-SW sectors are most influential on acid deposition in northern Québec. One can only assume that, with increasing distance from the Canada-U.S. border, the relative impact of U.S. versus Canadian emission sources on Canadian receptor areas will decrease.

Atlantic Canada

One CAPMoN site, at Kejimkujik National Park, is located in Atlantic Canada in central-southwest Nova Scotia. The site is approximately 250 km south-southeast of St. John (NB), 125 km west-southwest of Halifax (NS) and 245 km east of Acadia National Forest (ME). Dry and wet deposition levels at Kejimkujik are moderate compared to the rest of eastern Canada, with the 1998-2002 five-year-average total (wet + dry) sulphur deposition being 5.75 kg S/ha/yr and the total nitrogen deposition being 3.54 kg N/ha/yr. Dry deposition is estimated to contribute 28% of the sulphur total deposition and 37% of nitrogen total

Table 3.13. Kejimkujik (NS): Five-year average Source Contribution Analysis results for 1998-2002 as described in Table 3.5.

Deposition	Species	Fractional Contribution by Sector (%) Kejimkujik (NS)				
		NW	W	SW	S-SE	N-NE
Dry	SO_2 (1.02 kg S/ha/yr)	48	16	18	4	15
	nssSO_4^{2-} (0.58 kg S/ha/yr)	23	17	35	15	10
	Total-NO_3^- (1.28 kg N/ha/yr)	27	17	33	13	10
Wet	nssSO_4^{2-} (4.15 kg S/ha/yr)	19	12	46	17	6
	NO_3^- (2.26 kg N/ha/yr)	21	15	44	15	5
	Precipitation Amount (1374 mm/yr)	15	10	34	35	6
Total (Wet + Dry)	nssSulphur (5.75 kg S/ha/yr)	25	13	40	14	8
	Nitrogen (3.54 kg N/ha/yr)	23	16	40	14	7

deposition at Kejimkujik. Readers are reminded that SO_4^{2-} concentration and deposition values at Kejimkujik have been corrected for sea-salt sulphate so that all values in this discussion relate to non-sea-salt SO_4^{2-} (i.e., nssSO_4^{2-}) only.

Five trajectory sectors were selected for the Source Contribution Analysis (Figure 3.33). The Source Contribution Analysis results are shown in Table 3.13 and the box plots and Kruskal-Wallis test results are shown in Figures 3.34 to 3.38. The Source Contribution Analysis identifies the SW sector as the dominant contributor to nssSO_4^{2-} and Total-NO_3^- dry deposition (35% and 33%, respectively) and to nssSO_4^{2-} and NO_3^- wet deposition (35% and 46%, respectively) while the NW sector is the dominant contributor to SO_2 dry deposition (48%). The dominance of the SW sector for nssSO_4^{2-} and NO_3^- wet deposition is due to three factors, namely: (1) relatively high nssSO_4^{2-} and NO_3^- concentrations in air and precipitation, (2) a very large number of trajectories during precipitation events and a moderate number during dry deposition events, and (3) a relatively large contribution to total precipitation (34%).

For SO_2 dry deposition, the NW sector dominates the other sectors since it has the highest number of trajectories during dry deposition events (almost double the number from the second highest sector) and the second highest ambient SO_2 concentrations. The same sector also accounts for the second highest contributions to nssSO_4^{2-} and Total-NO_3^- dry deposition due in large part to its high number of trajectories relative to the other sectors. The fact that the SO_2 concentrations from the NW sector are higher than nssSO_4^{2-} and Total-NO_3^- concentrations (on a relative basis compared to the other sectors) suggests that they are strongly influenced by more localized Atlantic Region SO_2 sources.

It is interesting to note that the Ocean S-SE sector, in spite of having significantly lower concentrations than all the other sectors, accounts for a relatively large fraction of the nssSO_4^{2-} and NO_3^- wet deposition (17% and 15%, respectively) at Kejimkujik. This is because the S-SE sector accounts for a very large fraction of the precipitation (35%) that falls at the site. A visual inspection of trajectories travelling through that sector suggests that nssSO_4^{2-} and NO_3^- wet deposition from this sector originates with outflow from the east coasts of Canada and the U.S. with subsequent recirculation back to Nova Scotia during major precipitation events. The high deposition trajectories also confirm that the highest deposition often occurs with flow passing through the NW sector over northern Ontario, Québec and New Brunswick and through the SW sector with flow over the eastern seaboard of the U.S.. Interestingly, the trajectories show that few high deposition events are associated with flow from southern Ontario and the U.S. states west of the Appalachian Mountains. This is likely due to the strong blocking of the Appalachians on both flow and precipitation. This result is illustrated partially in Table 3.13 by the low contribution of the W sector, although the W sector does not include all of the area west of the Appalachians.

With respect to total (wet + dry) sulphur and nitrogen deposition at Kejimkujik (Figures 3.39 and 3.40), the largest contribution is attributed to the SW sector (40%) which encompasses most of the eastern U.S. from the Ohio River Valley south to the Gulf of Mexico and east to the Atlantic seaboard. Combining this sector with the W sector so that the combination encompasses the entire area of the eastern U.S. plus southern and central Ontario and southwestern Québec produces a total deposition contribution of 53% for sulphur and 56% for nitrogen. This demonstrates, as was the case for the other sites in eastern Canada, the importance of SO_2 and NO_x emission sources in Ontario, southern Québec and the eastern U.S.. It is important to point out that the second highest contribution to total deposition (23-25%) is attributed to the NW sector which encompasses western New Brunswick, most of northern Québec and eastern Maine. The large contribution of this sector is mainly because it accounts for most of the flow during non-precipitation periods and a very large percentage of the flow during precipitation periods (see trajectory statistics in Figures 3.34 to 3.38). In summary then, it appears that SO_2 and NO_x sources in eastern Canada and the eastern U.S. account for 75% of the S and N deposition at Kejimkujik National Park. Unfortunately, it is not possible to quantify the contribution of individual source areas with the exception that the Canadian contribution to total sulphur and nitrogen deposition is likely <46% and the U.S. contribution is likely >40% based on identifying the SW sector as an effective U.S. sector. These figures do not include the contribution of Canadian and U.S. emissions to off-continent flow that re-circulates back and is deposited at Kejimkujik from the Atlantic Ocean sector.

It is worth mentioning here that Kejimkujik is the only site in the CAPMoN network that has a major impact of SO_2 and NO_x sources in Atlantic Canada. This is because the prevailing flow directions at the other sites are from the north, west and southerly directions which do not include Atlantic Canada. In contrast, flow arriving at Kejimkujik is dominated by the NW and N-NE sectors which travel directly over Atlantic Canada and much of Québec.

Central Pennsylvania (U.S.)

The source attribution results presented so far have focused solely on CAPMoN measurement sites in Canada. The discussion therefore provides no indication as to whether the results are consistent with source attribution in the northern U.S. in the vicinity of the Canada-U.S. border. In order to gain an understanding, albeit limited, of source attribution south of the border, the same analyses were carried out at the one CAPMoN site located in the U.S.. This site, referred to hereafter as Penn State, is located near, and operated by The Pennsylvania State University at State College, Pennsylvania. CAPMoN began measuring wet deposition at Penn State in 1986 as part of a U.S.-Canada intercomparison study to determine the comparability of Canadian and U.S. precipitation chemistry/wet deposition measurements (Sirois et al., 2000). The intercomparison continues to this day. CAPMoN precipitation chemistry/wet deposition measurements are made at Penn State but air concentration measurements are not. This means that, unlike the results shown for the Canadian sites, the Source Contribution Analysis shown here is for wet deposition/precipitation chemistry data only.

The Penn State site is located in central Pennsylvania approximately 6 km from the town of State College and 250 km southeast of the Canada-U.S. border where it passes through Lake Erie at its closest point just west of Buffalo, NY. The measurement site sits in the middle of a broad valley between two ridges of the Appalachian Mountains where the primary land use is agricultural. The site itself is surrounded by forest. The five-year average wet deposition of sulphur from 1998-2002 is the highest of all sites in the CAPMoN network at 8.2 kg S/ha/yr and nitrogen wet deposition is the fourth highest at 4.5 kg N/ha/yr.

Five sectors were selected for the Source Contribution and box plot/Kruskal-Wallis analyses at Penn State (Figure 3.41). The Source Contribution Analysis results

Table 3.14. Penn State (PA): Five-year average Source Contribution Analysis results for 1998-2002 as described in Table 3.5.

Deposition	Species	Fractional Contribution by Sector (%) Penn State				
		N	NW	SW-W	S	SE-E
Wet	SO_4^{2-} (8.2 kg S/ha/yr)	5	9	73	6	7
	NO_3^- (4.5 kg N/ha/yr)	6	9	70	6	9
	Precipitation Amount (998 mm/yr)	6	7	64	9	14

are shown in Table 3.14. They indicate that a very high proportion of the wet SO_4^{2-} and NO_3^- deposition at Penn State is contributed by the SW-W sector (73% and 70%, respectively). This is not surprising since this sector includes all of the major SO_2 and NO_x emission sources in the Ohio River Valley and the U.S. Midwest and, additionally, accounts for an estimated 64% of the precipitation falling at the site. By comparison, the other four sectors contribute relatively small amounts of wet deposition, of the order of 5 to 10% each.

The dominant influence of SW-S sector emissions on Penn State wet deposition compares favourably to the equivalent Source Contribution Analysis results at Longwoods and Egbert located in southwestern Ontario. These two sites, roughly 375 km to the northwest and 410 km north-northwest of Penn State, respectively, receive less sulphur wet deposition than Penn State but are also strongly affected by the emission sources in the Ohio River Valley and the U.S. Midwest plus emission sources in southwestern Ontario. For example, a comparison of the impact of roughly equivalent sectors at the Penn State, Longwoods and Egbert sites gives the following results:

- Approximately 82% of wet sulphur deposition at Longwoods is attributed to the combined W + S-SW sectors compared to 79% attributed to the roughly equivalent S-SW + S sectors at Penn State; for nitrogen, the numbers are 81% and 76%, respectively;
- Approximately 81% of the wet sulphur deposition at Egbert is attributed to the combined S-SW + W sectors compared to 79% from the roughly equivalent S + S-SW sectors at Penn State; for nitrogen, the numbers are 78% and 73%, respectively.

It is important to be cautious when comparing these results since comparable sectors at the three sites do not encompass exactly the same source areas. Nevertheless, the results collectively point to SO_2 and NO_x emission

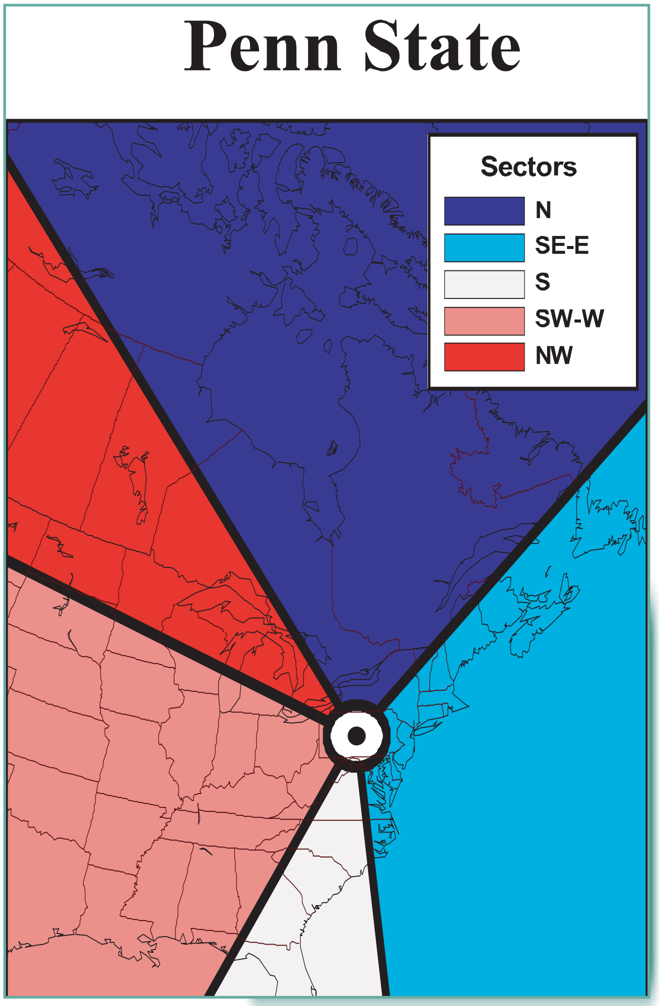

Figure 3.41: The five sectors used in the source attribution analysis at Penn State University.

sources in the areas of southwestern Ontario, the Ohio River Valley and the U.S. Midwest as the major contributors to sulphur and nitrogen wet deposition at the three sites. This is not an entirely surprising result given that these sectors also account for 70-80% of the precipitation at the three sites.

The box plot and Kruskal-Wallis test results (Figure 3.42) show that the SW-W sector has the highest SO_4^{2-} concentrations in precipitation (statistically significant) followed in descending order by the NW, N, S and SE-E sectors (where the N and S sector concentrations are not significantly different). Flow from the SW-W sector is also more frequent than in any other sector during precipitation as evidenced by its 1338 trajectories compared to 201 from the N, 184 from the SE-E, 97 from the S, 305 from the NW and 984 from the Not Attributable category. The median SO_4^{2-} concentration of the SW-W sector is 41.6 µmol/L which is not significantly different from the NW sector median of 44.2 µmol/L but is 3.1 times higher than the lowest sector median (SE-E). These numbers point to the very strong dominating influence of SO_2 sources in the Ohio River Valley, the U.S. Midwest and southern Ontario sources on precipitation chemistry at Penn State. Unfortunately, it is not possible to quantify the contributions of these areas separately. However, given that the SW-W has the highest SO_4^{2-} concentrations in precipitation as well as the most precipitation, it is not surprising that this sector accounts for the bulk of the sulphur wet deposited at the Penn State site. Thus, as is the case with southern Ontario, central Pennsylvania appears to suffer from having the largest SO_2 sources in North America aligned directly upwind along the prevailing flow direction during precipitation (see number of trajectories per sector in Figure 3.42).

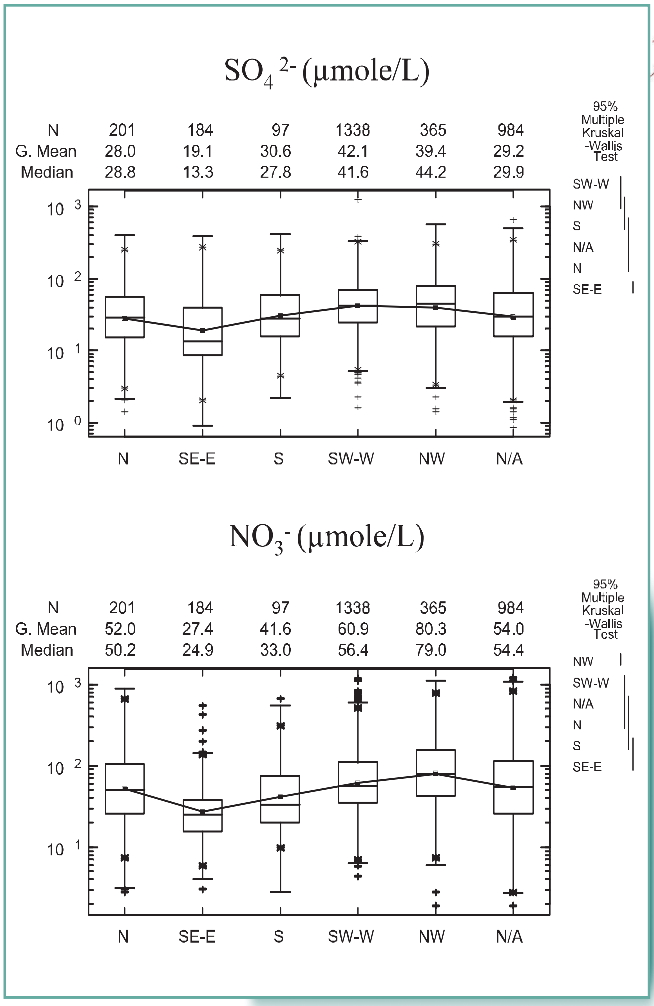

Figure 3.42: Penn State: Five-year box plot and Kruskal-Wallis significance test results for SO_4^{2-} and NO_3^- concentrations in precipitation for 1998-2002 (µmole/L).

The concentrations of NO_3^- in precipitation differ from SO_4^{2-} in precipitation in that the highest and second highest NO_3^- concentration sectors are the opposite to SO_4^{2-}, i.e., the NW and SW-W sectors have the highest and second highest NO_3^- concentrations while the SW-W and NW sectors, respectively, have the highest and second highest concentrations of SO_4^{2-} (all significantly different). This suggests that the dominant sources of NO_3^- in precipitation are generally located north of the dominant sources of SO_4^{2-} (i.e., more toward southern Ontario and the upper Midwest for NO_3^-). This result is consistent with three other sources of information: (1) the general spatial pattern of NO_3^- wet deposition in eastern North America as shown in Figure 3.2, (2) the spatial distribution of Total-NO_3^- concentrations in air published in Figure 6.13 and 6.14 of NARSTO (2004), and (3) the ADOM modelling results in Section 4.5.2.1.3 of Chapter 4 which predict a more northerly centre-of-mass for NO_3^- wet deposition than SO_4^{2-} wet deposition. In spite of the higher concentrations of NO_3^- in precipitation from the NW sector, the SW-W sector is still the dominant sector for NO_3^- wet deposition because it is the dominant contributor to precipitation at Penn State.

The Source Contribution Analysis results in Table 3.14 provide a unique opportunity to estimate or at least bracket the potential contribution of Canadian SO_2 and NO_x emissions to wet deposition at Penn State. This is done by assuming that the percentage contribution of the combined NW and N sectors is attributable only to Canadian emissions – ignoring the fact that a number of large U.S. emission sources are also located in these sectors in northern Pennsylvania and western New York. Using this assumption, it is estimated that the Canadian emissions could contribute as much as 14-15% of the sulphur and nitrogen that is wet deposited at Penn State. However, 14-15% is likely an overestimate because of the aforementioned influence of U.S. emissions in northern Pennsylvania and western New York.

While it is not possible to determine a more precise value than <14-15%, it is worth noting that this value is very close to the mass balance estimate of <16% calculated independently in Section 3.4.3.3. It is also consistent with the U.S. RADM model prediction of <5% published by Dennis et al. (1990) in the U.S. 1990 National Acid Precipitation Assessment Program State of Science and Technology Assessment on Acidic Deposition (acknowledging that emissions in the U.S. and Canada have changed markedly since those predictions were made). In light of the RADM model results, the estimated Source Contribution Analysis value of <14-15% may be quite high due to our starting assumption that this contribution is due to Canadian emissions alone. Nevertheless, the 14-15% serves as a conservative upper limit estimate of the possible contribution of Canadian emissions on deposition at Penn State.

In summary, SO_2 and NO_x sources in the SW-W sector, including sources in the Ohio River Valley and the eastern portion of the U.S. Midwest, contribute most of the SO_4^{2-} and NO_3^- wet deposition at Penn State (70-73%). The contribution of all U.S. sources is estimated at >85-86% and the possible contribution of Canadian sources is <14-15%.

3.5.3 Discussion and summary

The foregoing Source Contribution Analysis results clearly demonstrate that SO_2 and NO_x emission sources in eastern Canada and the eastern U.S. strongly affect acid deposition in eastern Canada. In itself, this is not a new scientific finding given that several previous Acid Deposition Science Assessments (e.g., Environment Canada, 1990, 1997; Dennis et al., 1990) have attributed wet deposition in eastern Canada to the long range transport of Canadian and U.S. emissions of SO_2 and NO_x. What is new and illuminating is our ability to produce quantitative estimates of the percentage contribution of the different emission areas to wet, dry and total deposition at specific measurement locations. This, coupled with new and better estimates of dry deposition, provides an opportunity to identify where emission reductions would be most effective in order to reduce exceedances of critical loads in eastern Canada. It also provides a measurement-based set of results that can be used to supplement the modelling work presented in Chapter 4 (Moran, 2005) in a weight-of-evidence analysis.

The source attribution results for total sulphur and total nitrogen deposition, presented in graphical form in Figures 3.39 and 3.40, are summarized as follows:

- In southeastern Alberta (Esther), sulphur and nitrogen deposition are predominantly influenced by emissions in Alberta and British Columbia and, to a lesser degree, emissions in the western U.S.
- In northwestern Ontario (ELA), emissions in the U.S. Midwest and West have the greatest influence on deposition (54-59%) followed by emissions in western Canada (29-31%).
- In west-central Ontario (Algoma), emissions in the U.S. Midwest and West have a dominant influence (67%) on sulphur and nitrogen deposition. Emission sources in western Canada are secondary (19%).
- In southwestern Ontario (Longwoods and Egbert), emission sources in southwestern Ontario and the eastern U.S. account for roughly three quarters of the deposition (74-77%). Given that emissions in the northern tier of U.S. states are roughly an order of magnitude larger than those in southwestern Ontario (and located very close to the Canada-U.S. border), it is very likely that emissions in the U.S. Ohio River Valley and Midwest are the dominant source of wet and dry deposition.
- In eastern Ontario (Chalk River) and southwest Québec (Sutton), total deposition is dominated (63-

67%) by emission sources in southern and central Ontario plus the Ohio River Valley and Midwest states of the U.S.. The smelter emissions at Sudbury and Rouyn-Noranda are included in these dominant source areas. Other sources in Québec and northern Ontario account for 25-32% of the deposition.

- In northern Québec (Chapais), 61-63% of the deposition is attributed to the major emission sources in northwestern Québec (mainly Rouyn-Noranda), all of Ontario south of James Bay, and the Ohio River Valley and Midwest. An inspection of high deposition trajectories suggests that Ontario and Québec emissions are much more influential in this northern area of Québec than in the more southerly areas of Ontario and Québec.
- In Nova Scotia (Kejimkujik), emissions from the east of the Appalachian Mountains in the U.S. appear to have a dominant influence on deposition (40%) followed by emissions in Ontario, Québec, New Brunswick and, to some extent the upper Midwest of the U.S. (38%). Emissions in the Ohio River Valley appear to have a considerably smaller impact than the emission areas already mentioned.
- In general, the influence of U.S. emissions decreases and the influence of Canadian sources increases with distance from the Canada-U.S. border.

The percentage contribution values quoted above contain a number of uncertainties that are difficult to quantify. These uncertainties include the following: uncertainties in defining the individual trajectory paths, uncertainties associated with assigning daily deposition values to all four trajectories in each sampling day, uncertainties in allocating the percent contributions from the Not Attributable category to the various sectors, uncertainties induced by multiple-sector trajectories that are erroneously assigned to the wrong emission sector and uncertainties in the daily wet and dry deposition values (particularly the dry deposition values since they are based on both measured and modelled results). Sensitivity analyses carried out during the Source Contribution Analysis suggest that the final results are not highly dependent on the choice of the trajectory starting height (i.e., 850 mb for wet deposition and 925 mb for dry deposition) or on the criterion chosen for assigning trajectories to the Not Attributable category (i.e., <70%). While it is possible to choose different methods for allocating the deposition values in the Not Attributable category to other sectors (e.g., using a clustering technique to objectively assign the trajectories to different clusters), several experiments with these techniques indicated that they would not change our overall conclusions. When time allows, future analyses will include a bootstrap or jackknife uncertainty analysis and a full comparison between the sector and clustering approaches to the Source Contribution Analysis.

In general, the Source Contribution Analysis results point to the very strong influence of eastern U.S. emissions on eastern Canadian deposition. For example, the four CAPMoN sites located near the Canada-U.S. border provide the best results for estimating the impact of Canadian versus U.S. emissions on deposition in eastern Canada since it is possible to eliminate most Canadian emissions from the U.S. sectors. The four near-border sites include ELA (ON), Algoma (ON), Longwoods (ON) and Sutton (QC). At ELA, U.S. emissions are estimated to contribute 54 - 63% of the *total* sulphur deposition and 59 - 66% of *total* nitrate deposition. Note that a range is given to account for the unknown contribution of southern Ontario sources. At Algoma and Longwoods, U.S. emissions are estimated to contribute >67% and >77%, respectively, of the total sulphur and nitrate deposition. The >77% value may be an overestimate since it includes the effect of Canadian emissions in the Windsor area of southwestern Ontario. Finally, at Sutton, U.S. emissions contribute an estimated 37-66% of the sulphur deposition and 32-63% of the nitrogen deposition. Here too, a range is given because it is not possible to account for the influence of southern Ontario emissions in the appropriate sectors. These, and the other source attribution results in this chapter, are corroborated in several ways, namely:

1. The Source Contribution Analysis results for wet deposition (Tables 3.5 to 3.14) compare very well to the independently-determined mass balance estimates of U.S. versus Canadian contributions to wet deposition (Section 3.4.3.3). The mass balance calculations suggest that U.S. emissions account for somewhere between 45% and 80% of eastern Canadian sulphate and nitrate wet deposition. By comparison, the Source Contribution Analysis results suggest that U.S. emissions contribute approximately

60 to 80% of the wet sulphate and nitrate deposition in the Canada-U.S. border region and <50 - 70% in the regions away from the border. The two sets of results are strikingly similar.

2. The Source Contribution Analysis results are consistent with the Dennis et al. (1990) modelling results based on runs of the U.S. RADM model with 1985 SO_2 emissions. For example, the RADM modelling results suggest that, for the modelled period, U.S. emissions contributed:
   - 70-75% of the SO_4^{2-} wet deposition at Algoma, compared to the current Source Contribution Analysis estimate of about 71%;
   - 90-95% of the wet deposition at Longwoods, compared to the Source Contribution Analysis estimate of roughly 80%;
   - 85-90% of the wet deposition at Egbert, compared to the Source Contribution Analysis estimate of less than 86%;
   - 80-85% of the wet deposition at Sutton, compared to the Source Contribution Analysis estimate of between 40% and 60%;
   - 70-75% of the wet deposition at Chalk River, compared to the Source Contribution Analysis estimate of considerably less than 76%;
   - 55-60% of the wet deposition at Chapais, compared to the Source Contribution Analysis estimate of considerably less than 72%;
   - 85-90% of the wet deposition at Kejimkujik compared to the Source Contribution Analysis estimate of considerably less than 75%;
   - >95% of the wet deposition at Penn State compared to the Source Contribution Analysis estimate of around 86%.

   In general then, the RADM model's estimated contributions are similar to or higher than the Source Contribution Analysis values. Since SO_2 emissions in eastern Canada and in the eastern U.S. have declined markedly from 1985 to 1998-2002, one must be cautious when comparing the two sets of results. Nevertheless, if the model were re-run today with 1998-2002 emissions and meteorology, it is unlikely that the general story would change, especially since emissions declined by roughly the same proportion in both countries. Thus, we feel that the Source Contribution Analysis complements the modelling evidence, thereby confirming that eastern U.S. emissions strongly affect wet SO_4^{2-} deposition in eastern Canada. The modelling results also corroborate the thought that Canadian emissions are increasingly important and U.S. emissions increasingly less important with distance from the Canada-U.S. border.

3. Unfortunately, the Source Contribution Analysis cannot identify which source areas within a given sector have the most influence on deposition in Canada. For this information, one must rely on the ADOM and ALSM modelling results presented in Chapter 4 (Moran, 2005) and elsewhere. The Chapter 4 modelling results suggest that the emission areas in the eastern U.S. that have the greatest influence on sulphur and nitrogen deposition in eastern Canada are located in the northern tier of states – within the U.S. Midwest, Great Lakes, Ohio River Valley, and east coast areas. Emissions in the southern tier of the U.S. states are, in fact, estimated to have very little influence on acid deposition in eastern Canada. The model results also suggest that certain emission areas in eastern Canada have the strongest influence on eastern Canadian deposition, namely:
   - for northwestern and west-central Ontario → western Canadian emissions,
   - for eastern Ontario → southern Ontario and Sudbury emissions,
   - for southern Québec → southern Ontario, Sudbury and Québec (north and south) emissions,
   - for northern Québec → Sudbury, Rouyn-Noranda, southern Ontario and southern Québec emissions,
   - for Nova Scotia → Ontario, Québec and Atlantic province emissions.

   These emission areas are similar to the general areas suggested by the Source Contribution Analysis.

The modelling work in Chapter 4 indicates that further emission reductions of the order of 75% or more are needed in both eastern Canada and the eastern U.S. in order to meet critical loads in eastern Canada. Moreover, it makes the point that a one tonne reduction of eastern Canadian emissions will be more effective at reducing wet deposition in eastern Canada than will a one tonne reduction of eastern U.S. emissions. This is because a higher fraction of one tonne of eastern Canadian emissions will be deposited in eastern Canada than of one tonne of eastern U.S. emissions. Thus, on a tonne-to-tonne basis, emission reductions in eastern Canada will be more effective than emission reductions in the eastern U.S.. Overall, however, because eastern U.S. emissions contribute such a large, if not dominant, fraction of eastern Canadian deposition (as identified by the Source Contribution Analysis), large emission reductions in both eastern Canada and the eastern U.S. are needed to meet critical loads. **Emission reductions targeted at specific high-contribution emission areas in both countries (as presented above) will be more effective at reducing acid deposition in eastern Canada than will a constant percentage reduction across all sources in eastern Canada and the eastern U.S..**

3.6 CONCLUSIONS

This chapter addresses the two objectives outlined in the Introduction, i.e., 1) establishing how atmospheric wet and dry deposition of acidic substances have been responding to the acid gas emission control programs implemented to date in Canada and the U.S., with a focus on the major emission changes that occurred from the early 1990s to the early 2000s, and; 2) assessing the main contributing source areas to acid deposition in sensitive receptor areas in eastern Canada. The major conclusions of the work are as follows:

- Wet, dry and total (wet + dry) deposition of sulphur and nitrogen species is highest in eastern Canada, particularly in southern Ontario and southern Quebec. A gradient exists from the highest deposition areas to lower deposition areas in the west, north and east parts of eastern Canada.
- New estimates of dry deposition at Canadian Air and Precipitation Monitoring Network (CAPMoN) monitoring sites indicate that dry deposition of sulphur and nitrogen species constitutes a larger proportion of total sulphur and nitrogen deposition than previously thought. Hence, the total deposition estimates of S and N in past publications are likely underestimated. In eastern Canada, the current work indicates that dry deposition contributes 24 to 46% of the total (wet + dry) sulphur deposition and 23 to 58% of the total (wet + dry) nitrogen deposition depending on the location (this includes the dry deposition of NO_2 and PAN based on the estimates in Appendix 3.2). The contribution of dry deposition to total deposition in eastern Canada is highest in the high deposition areas of southern Ontario and southern Quebec. Limited data in western Canada suggests that dry deposition constitutes a higher percentage of total (wet + dry) deposition than in eastern Canada.
- The large-scale patterns of non-sea-salt-SO_4^{2-} wet deposition in eastern North America indicate that non-sea-salt-SO_4^{2-} deposition levels decreased markedly from the early 1990s to the late 1990s in response to SO_2 emission reductions in both eastern Canada and the eastern U.S.. In contrast, the patterns of NO_3^- wet deposition show minimal reductions in deposition since NO_x emissions changed little between those periods.
- Mass balance estimates developed using wet deposition and emission totals for eastern Canada and the eastern U.S. suggest that eastern U.S. SO_2 emissions contribute between 45 and 80% of the non-sea-salt-SO_4^{2-} and NO_3^- wet deposition in eastern Canada. Better resolution within this range is not possible given the limitations of the analysis. Historical modelling results corroborate this range for non-sea-salt-SO_4^{2-} and, in fact, suggest that the range is likely between 65 and 70%.
- Source attribution studies indicate that at least half, and sometimes as much as two-thirds, of total (wet + dry) deposition of sulphur and nitrogen species, depending on location, in eastern Canada is attributable to sources in the eastern and Midwest U.S.. Eastern Canadian sources are also identified as major contributors to total deposition.
- The source attribution analysis suggests that emission reductions are needed in both eastern Canada and the eastern and Midwest U.S. in order to eliminate critical load exceedances in eastern Canada. Within eastern Canada, largest emission reductions are required in Ontario (southern Ontario for both SO_2 and NO_x and Sudbury for SO_2 alone) and Quebec (southern Quebec for both SO_2 and NO_x and Rouyn-Noranda for SO_2 alone). In the U.S., largest reductions are needed in the states of the

U.S. Midwest in order to reduce deposition in northwestern Ontario, in the states around the Great Lakes and the Ohio River Valley in order to reduce deposition in the remainder of Ontario and Quebec, and in the states of the Ohio River Valley and the East Coast in order to reduce deposition in Atlantic Canada.

- The modelling results described in Chapter 4 of this Assessment confirm that the emission areas identified above are reasonable and further suggest that targeted emission reductions would be more effective than an overall percentage reduction in all emission areas. Specifically, the most effective emission reductions in the U.S. should be targeted at the northern tier of the Midwest, Great Lakes, Ohio River Valley, and East Coast states. The combined measurement-based and modelling results provide further weight-of-evidence support for the source attribution results described herein.
- Insufficient deposition data are available in western Canada to make similar attributions in that area. However, a single measurement site on the prairies near the Alberta-Saskatchewan border produced source attribution results consistent with computer model results which indicate that western Canadian emissions are largely responsible for deposition in western Canada.

The research that produced the foregoing conclusions also led to the identification of a number of shortcomings in Canada's acid deposition research program. If these shortcomings are not addressed in the near future, it will be extremely difficult, if not impossible, to establish the efficacy of future emission reduction programs and to determine where and by how much critical loads are being exceeded in Canada. The major shortcomings are as follows:

- Nitrogen deposition measurements are not adequate. There is a pressing need to add NH_3 and NO_2 dry deposition measurements to the suite of measurements currently being made at the air monitoring sites in CAPMoN.
- The number of sites that measure dry deposition in Canada is insufficient. The 12 CAPMoN sites provide inadequate spatial coverage and leave large areas of eastern and western Canada unmonitored. More measurement sites are needed in both eastern and western Canada.
- The recent closure of wet deposition monitoring networks in Ontario and Newfoundland and Labrador severely limits Canada's ability to monitor acid deposition in eastern Canada. For example, wet deposition maps like those in Figure 3.2 can no longer be produced due to the paucity of data. Likewise, the lack of regional-scale acid deposition monitoring networks in British Columbia, Saskatchewan and Manitoba makes it impossible to produce maps of wet deposition in western Canada and to identify areas where critical loads are being exceeded. High quality wet deposition monitoring networks are needed in all of these provinces.

3.7 ACKNOWLEDGEMENTS

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appendix 3.1

SO_2 and NO_x emission maps (1990)

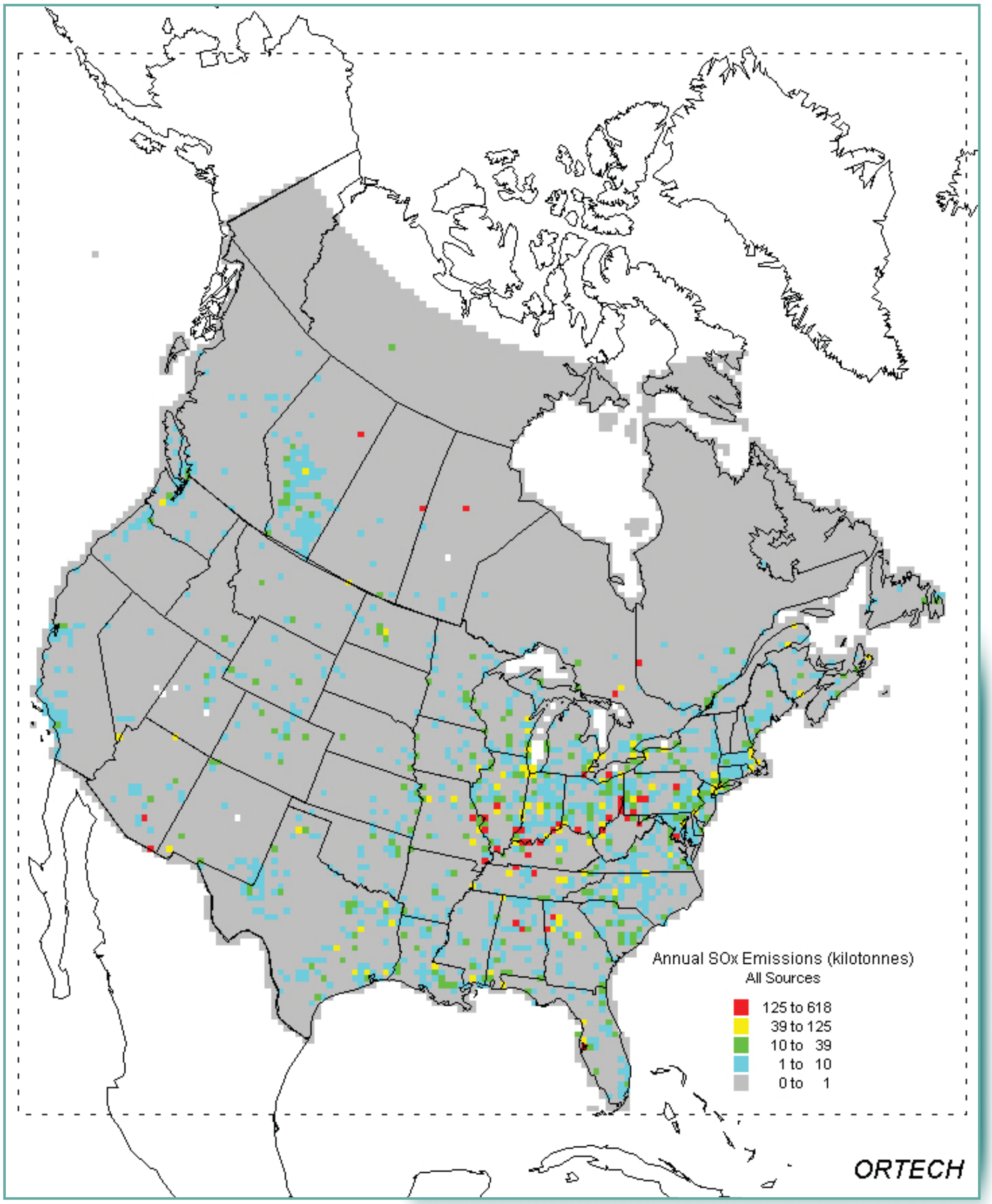

Figure A3.1: Distribution of 1990 total annual Canadian and U.S. SO_2 emissions in Ktonnes SO_2/grid cell/yr (Meteorological Service of Canada, 2001).

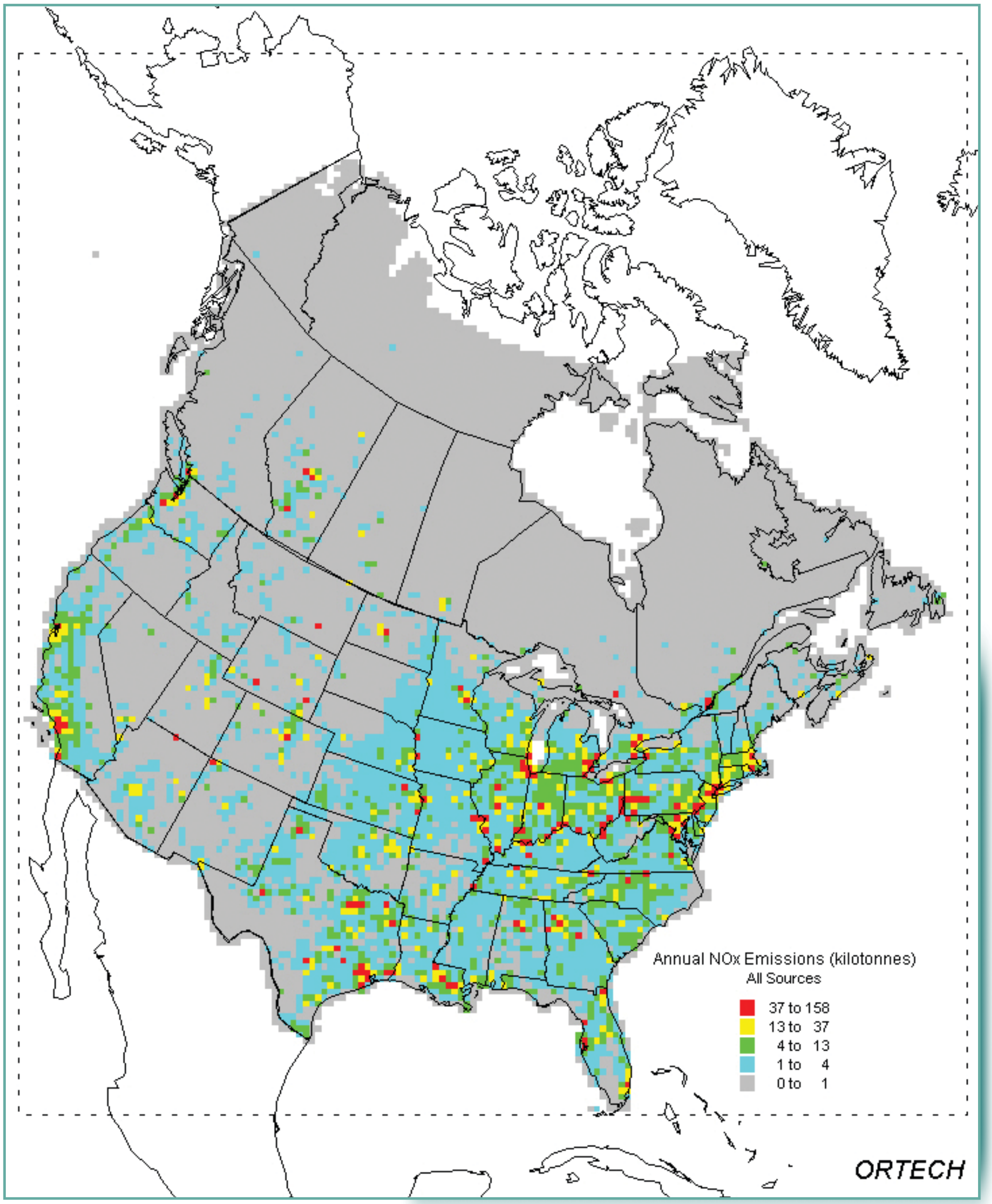

Figure A3.2: Distribution of 1990 total annual Canadian and U.S. NO_x emissions in Ktonnes NO_2/grid cell/yr (Meteorological Service of Canada, 2001).

appendix 3.2

Uncertainty of the estimated dry and total deposition fluxes of nitrogen

Since the inception of CAPMoN, the calculated dry deposition fluxes of nitrogen have been underestimated because several atmospheric nitrogen species (i.e., NH_3, NO, NO_2 and PAN) are not measured and not included in the flux calculations. Unfortunately, the magnitude of the underestimation, referred to hereafter as a *negative bias*, has to date been unknown. In order to estimate the negative bias and its spatial variability, the Meteorological Service of Canada undertook two major studies in the early part of the 2000s.

The first study, known as the Nitrogen Scoping Study, consisted of a number of intensive measurement campaigns during which the ambient concentrations of all major nitrogen compounds (including NH_3, NO, NO_2 and PAN) were measured at selected CAPMoN sites for 3 to 4 week periods. These measurements provided a basis for producing first estimates, albeit for short periods of time, of the negative biases induced by not measuring those species in CAPMoN. Analysis on the complete data set from this study is under way at the time of writing of this Assessment, so only partial results are reported here.

The second study, the Nitrogen Modelling Study, involved the use of an air quality forecast model, CHRONOS, to estimate the ambient concentrations of the missing nitrogen species at CAPMoN sites for the year May 2002 to April 2003 and the use of these concentrations to estimate the magnitude of the negative biases. Because some of the short term Nitrogen Scoping Study measurement periods overlapped with the model results, we were able to adjust the model-predicted concentrations to match the measured concentrations and thereby enhance the validity of the modelled fluxes. The negative biases estimated using the two approaches are discussed below.

A3.2.1 THE NITROGEN SCOPING STUDY: SHORT-TERM ESTIMATES OF UNCERTAINTY

The Nitrogen Scoping Study consisted of a set of field studies, each 3 to 4 weeks in duration, during which measurements were made of the ambient concentrations of the most prevalent atmospheric nitrogen compounds. These measurements provide a basis for estimating, albeit for short periods, the dry deposition fluxes of the various nitrogen compounds at different CAPMoN sites.

At the time of writing, the five-year Nitrogen Scoping Study comprised 17 field studies carried out at 8 different CAPMoN sites. Reported here are the results of the first three studies that took place at Frelighsburg (QC) in November 2002, Egbert (ON) in February/March 2002 and Frelighsburg (QC) in April/May 2002. The results of these studies provide a first indication of the relative importance of the different nitrogen species to total N dry deposition. Although NO was measured during these field studies, NO dry deposition fluxes are extremely low due to its small dry deposition velocity. Thus, dry deposition fluxes of NO are not considered any further in this discussion. For the three studies only, PAN was also not included because measurements were not made. However, its contribution to the total nitrogen dry deposition budget is expected to be relatively minor. PAN measurements were made in later studies and the contribution of PAN is estimated in the Nitrogen Modelling Study.

The dry deposition fluxes of the different nitrogen species were calculated as the product of measured air concentrations and estimated dry deposition velocities (Vd). The values of Vd were calculated using MSC's Regional Dry Deposition model (RDM) adapted for analysis of the short-term Scoping Study data. RDM is

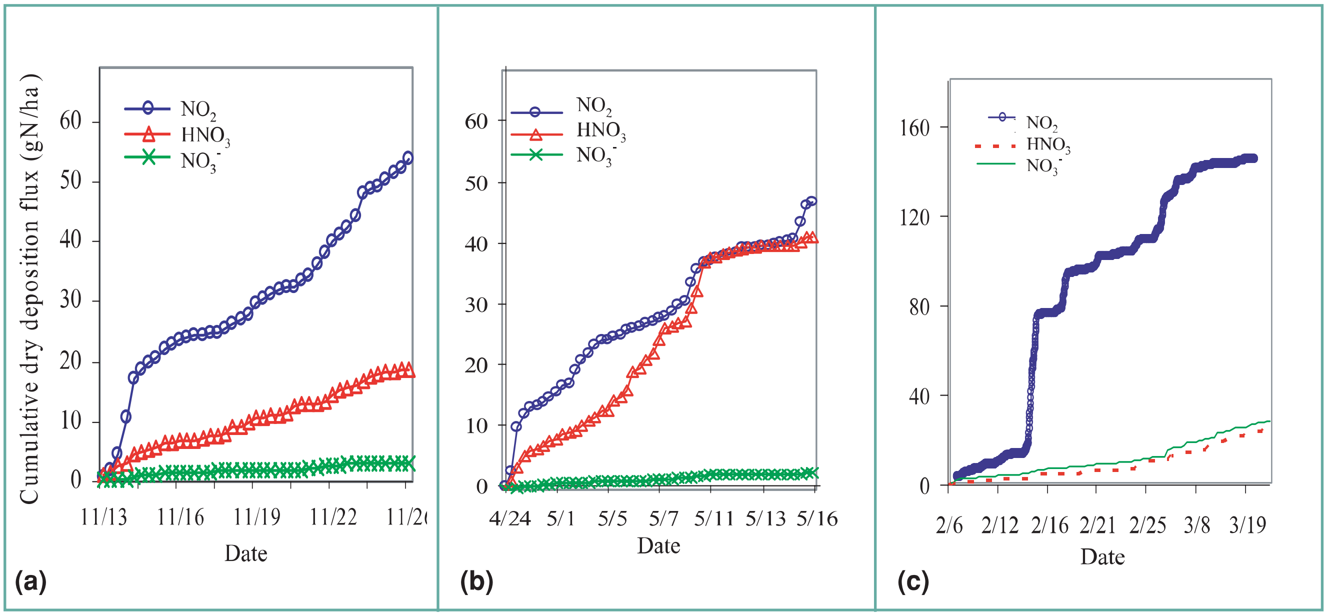

Figure A3.3: Cumulative dry deposition fluxes of NO_2, HNO_3 and p-NO_3^- during the first three scoping studies: (a) Freligshburg (QC) Nov.10-28, 2001 (b) Freligshburg (QC) Apr. 23-May 16, 2002 and (c) Egbert (ON) Feb. 6-Mar. 28, 2002.

described earlier and in Brook et al. (1999) and Zhang et al. (2001), with recent improvements described in Zhang et al. (2003). Meteorological inputs for the dry deposition model were obtained from a combination of on-site meteorological measurements, nearby meteorological station data, and/or archived GEM (Global Environmental Multiscale) forecast model output.

Figure A3.3 shows the estimated cumulative dry deposition fluxes of NO_2, HNO_3 and p-NO_3^- throughout the three field studies. NO_2 was found in all three studies to contribute more than 50% of the total nitrogen dry deposition. HNO_3, in spite of its much higher dry deposition velocities, contributed considerably less than 50% during the November Freligshburg study and the February/March Egbert study, and only slightly less during the April/May Freligshburg study. The low contribution of HNO_3 during the cold part of the year at Freligshburg and Egbert is not surprising given that HNO_3 concentrations are generally low under cold temperature conditions. It is worth noting that NO_2 concentrations and dry deposition fluxes tend to be very episodic, alternating through periods of high and low concentrations (and fluxes) at the CAPMoN sites. This is particularly so at Egbert which is located 65 km north-northwest of the northern boundary of the Toronto metropolitan area.

The estimated cumulative dry deposition fluxes for the first three studies are shown in Table A3.1. It is clear from the table that NO_2 was the single largest contributor to the total dry deposition flux of oxidized nitrogen in all three studies. For example, NO_2 dry deposition was responsible for 58% of the total oxidized nitrogen dry deposition flux during the first Freligshburg study (Nov. 10-28, 2001), 54% during the second Freligshburg study (Apr. 23-May 16, 2002) and 78% during the Egbert study (Feb. 7-Mar. 28, 2002). Since NO_2 concentrations are generally high at Freligshburg and Egbert because of their proximity to major metropolitan areas (Montreal and Toronto, respectively), the contribution of NO_2 at those sites is likely higher than at other rural/remote CAPMoN sites. For example, in a separate study at a remote CAPMoN site in Nova Scotia (Kejimkujik), we estimate that approximately 24% of the oxidized nitrogen dry deposition flux and only 8% of the total (wet + dry) nitrogen flux was due to NO_2. Given that the concentrations of NO_2 at Kejimkujik are very low relative to elsewhere in eastern Canada, these values likely represent a lower bound for CAPMoN sites.

Table A3.1. Cumulative dry deposition fluxes (in kg N/ha/study) and the fraction of total N dry deposition contributed by NO_2, HNO_3 and p-NO_3^- in the first three field studies.

Species	Frelighsburg , QC Nov. 10-28, 2001		Frelighsburg, QC Apr. 23-May 16, 2002		Egbert, ON Feb. 07-Mar. 28, 2002	
	Dry Deposition Flux (kg N/ha)	Fraction of Total Dry Deposition Flux (%)	Dry Deposition Flux (kg N/ha)	Fraction of Total Dry Deposition Flux (%)	Dry Deposition Flux (kg N/ha)	Fraction of Total Dry Deposition Flux (%)
NO_2	0.061[1]	58	0.052[3]	54	0.184[5]	78
HNO_3	0.038[2]	36	0.042[4]	43	0.025[6]	11
p-NO_3^-	0.006[2]	6	0.003[4]	3	0.027[6]	11
Total	0.105		0.097		0.236	

[1] 17.5 day total

[2] 17.9 day total

[3] 23.3 day total

[4] 22.6 day total

[5] 46.8 day total

[6] 44.3 day total

Based on results to date, we estimate that the unmeasured nitrogen species in CAPMoN represent half to three quarters of the total dry deposition fluxes at CAPMoN sites during the short study periods. This, in turn, makes a case that CAPMoN should begin making routine measurements of NO_2 at all CAPMoN sites. A similar conclusion was reached for the dry deposition fluxes of reduced nitrogen species since CAPMoN measures only p-NH_4^+ and not gaseous NH_3. In the three short-term Scoping Studies, we estimate that gaseous NH_3 dry deposition accounted for roughly 70%, 70% and 50% of the total reduced nitrogen dry deposition flux during the studies. This suggests that routine measurements of NH_3 should also be undertaken in the CAPMoN network.

A3.2.2 THE NITROGEN MODELLING STUDY: ANNUAL ESTIMATES OF UNCERTAINTY

The objective of the Nitrogen Modelling Study was to provide one-year estimates of dry and total deposition fluxes of NO_2, PAN, HNO_3 and p-NO_3^- at seven CAPMoN sites in eastern Canada. This was done by making model predictions of ambient NO_2 and PAN concentrations which were, in turn, combined with measured HNO_3 and NO_3^- concentrations and estimated dry deposition velocities. The modelled concentrations were predicted by the Meteorological Service of Canada's regional air quality forecast model known as CHRONOS (Pudykiewicz et al., 1997). Major conclusions drawn from one full year of model estimations (May 1, 2002 to April 30, 2003) are presented below.

The combined modelled/measured flux estimates indicate that the annual N dry deposition fluxes at seven CAPMoN sites ranged from a low of 1 kg/ha/yr to a high of 5 kg/ha/yr (Figure A3.4a). The results indicate that HNO_3 and NO_2 are the two dominant species that contribute to dry deposition. Using the NO_2 model predictions scaled upward to match the Scoping Study measurement data, we determined that, on an annual basis, HNO_3 contributes 36%-63% of the total Nitrogen dry deposition, NO_2 contributes 14%-46%, p-NO_3^- contributes 9%-20%, and PAN contributes 2%-15% (Figure A3.4b), depending on location. In general, NO_2 dry deposition appears to be as important as HNO_3 plus p-NO_3^- dry deposition in southwestern Ontario close to the major NO_x emission areas of eastern North America and less so at rural and remote sites away from southwestern Ontario.

The outcome of the modelling study allows us to evaluate the impact of not including NO_2 and PAN in the estimates of CAPMoN nitrogen dry deposition fluxes. If NO_2 and PAN fluxes were included in the nitrogen dry deposition estimates, then the original dry deposition fluxes without NO_2 and PAN would need to be multiplied by an enhancement factor which accounts for the unmeasured fluxes. The estimated enhancement factors for the period of the modelling study (May 1, 2002 to

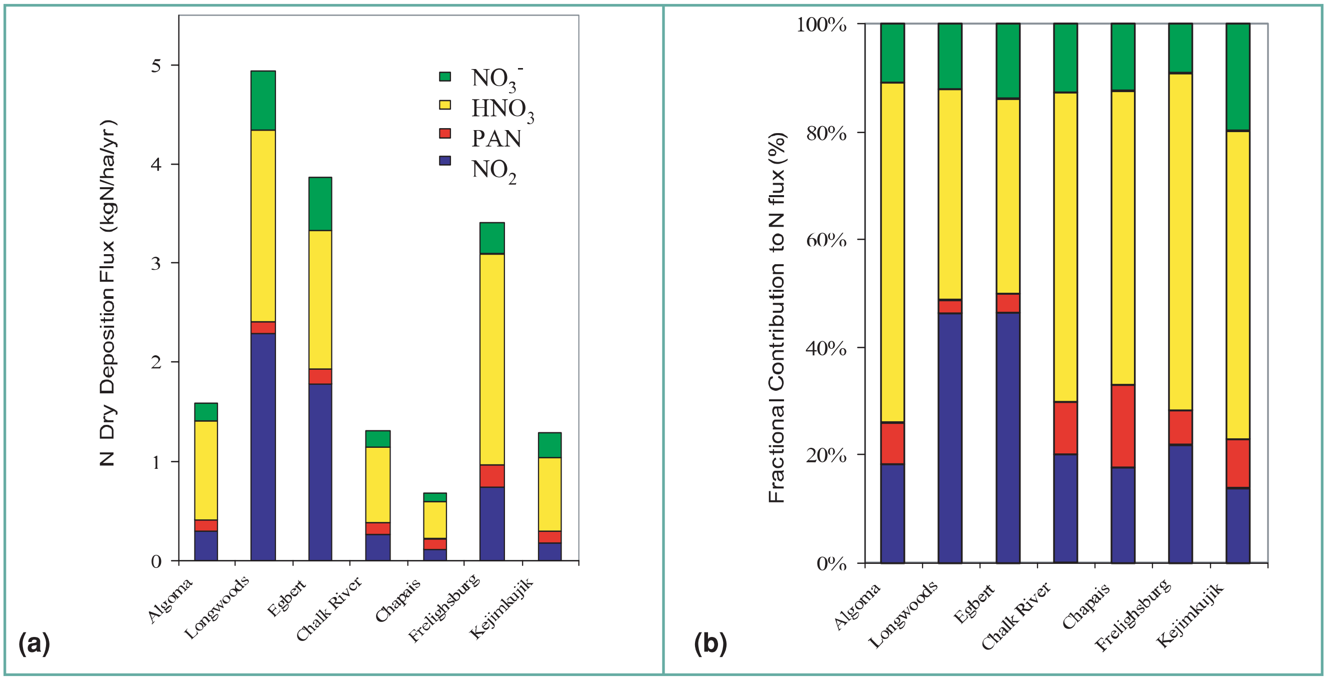

Figure A3.4: Annual dry deposition fluxes (a) and associated fractional contributions to N dry deposition (b) from NO_2, PAN, HNO_3 and NO_3^- using adjusted model NO_2 concentrations and measured HNO_3 and NO_3^- concentrations.

April 30, 2003) in eastern Canada are approximately 2.0 in southwestern Ontario (i.e., near the major NO_X emission areas) and 1.3 to 1.5 in the rest of eastern Canada.

A3.2.3 OVERALL ESTIMATES OF UNCERTAINTY

By combining the results of the Nitrogen Scoping and Nitrogen Modelling Studies, it was possible to estimate the overall uncertainty or negative bias in the CAPMoN dry and total deposition fluxes due to the lack of NO_2 and PAN measurements. The method involved a number of steps. First, we assumed that the Nitrogen Modelling Study dry deposition adjustment factors (which account for the additional dry deposition due to NO_2 and PAN) are representative of the period from 1998-2002. Second, we multiplied the nitrogen dry deposition fluxes for 1998-2002 by the *dry deposition adjustment factor* of 2.0 at sites in southwestern Ontario and 1.3-1.5 at sites elsewhere in eastern Canada. Third, we added the ‘adjusted dry deposition fluxes’ for 1998-2002 to the measured wet deposition fluxes for those years to determine the total (wet + dry) deposition of nitrogen. Fourth, we calculated the *total deposition adjustment factors* for including NO_2 and PAN versus not including NO_2 and PAN. Finally, we estimated the amount by which the % Dry ratio of dry-to-total deposition would need to be adjusted if NO_2 and PAN dry deposition were to be included.

Following this methodology, our best estimate of the multiplicative *enhancement factors for total (wet + dry) deposition* (which accounts for NO_2 and PAN dry deposition) is 1.4 for sites in southwestern Ontario and 1.1 for sites in the rest of eastern Canada. This means that the total deposition fluxes shown in Figure 3.7 that do not include NO_2 and PAN dry deposition are approximately 40% low in southwestern Ontario and 10% low in the rest of eastern Canada.

Similarly, if NO_2 and PAN dry deposition fluxes are included, the % Dry ratios shown in Figure 3.7 would increase by approximately +16% in southwestern Ontario and +7% elsewhere in the country (e.g., the Longwoods % Dry ratio would increase from 36% to 52% and the Algoma % Dry ratio would increase from 30% to 37%).

The foregoing discussion makes a strong case for adding measurements of ambient NO_2 and NH_3 to the CAPMoN network in order to provide better estimates of total nitrogen dry deposition fluxes at CAPMoN sites.

Area-normalized percentage contributions by sector

Figures A3.5 and A3.6 below show the area-normalized percentage contribution maps for the individual sectors at all CAPMoN sites in units of percentage contribution of total deposition per angular degree.

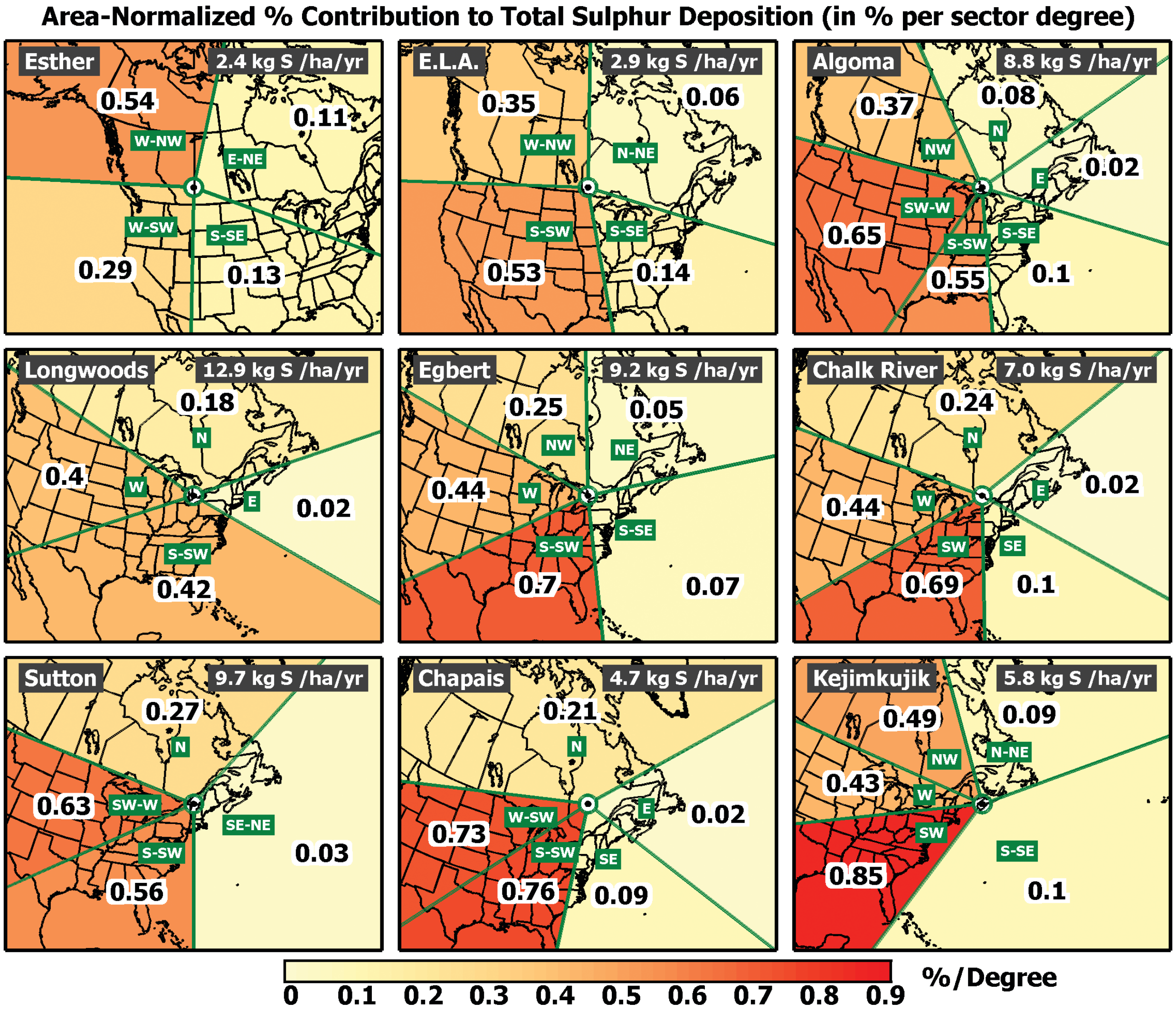

Figure A3.5: Percentage contribution per angular degree of each sector to total (wet + dry) sulphur deposition at the CAPMoN sites. The inset values in the top right hand corner of the diagrams indicate the total sulphur deposited at each site.

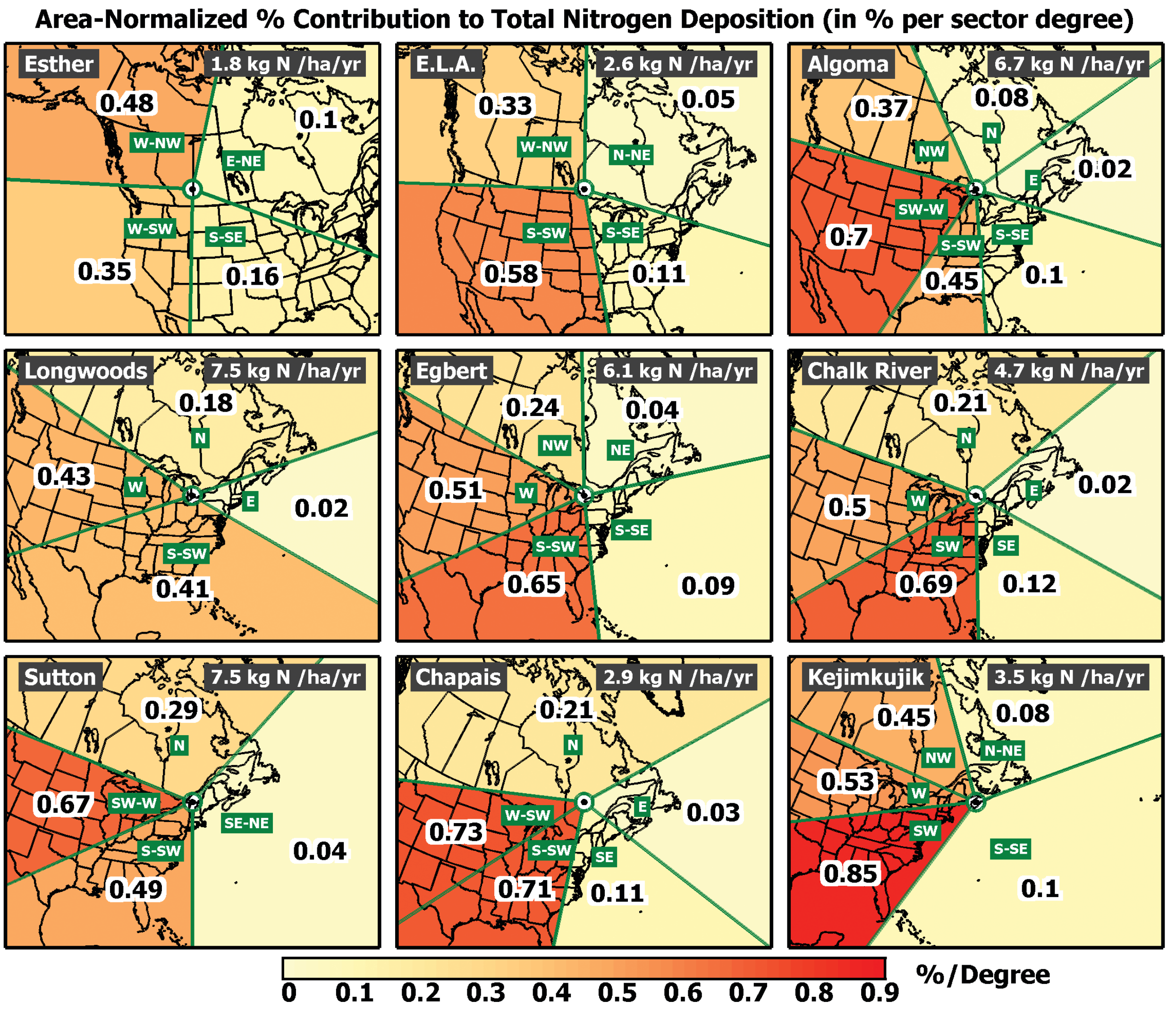

Figure A3.6: Percentage contribution per angular degree of each sector to total (wet + dry) nitrogen deposition at the CAPMoN sites. The inset values in the top right hand corner of the diagrams indicate the total nitrogen deposited at each site.

CHAPTER 4

Current and Proposed Emission Controls: How Will Acid Deposition Be Affected?

M.D. Moran

4.1 KEY MESSAGES

- Four different regional acid-deposition models (RELAD, ADOM, IAM, ALSM) have been used since the 1997 *Assessment* to investigate acid deposition in either western or eastern Canada, including the simulation of a number of new future-year SO_2 and NO_x emission control scenarios. The consideration of NO_x control programs represents an important step beyond the 1997 *Assessment*, in which only SO_2 emission control scenario results were reported.
- A number of annual simulations for western Canada, centred on the province of Alberta, have been performed with the RELAD Lagrangian acid deposition model for both sulphur and nitrogen species. The results of these simulations, when considered together with emission maps and acid deposition measurements, suggest that western Canadian SO_2 and NO_x emission sources are the primary contributors to acid deposition in western Canada.
- Results from five SO_2 emission control scenarios for eastern Canada simulated with ADOM, a comprehensive Eulerian acid deposition model, were reported in the 1997 *Assessment*. ADOM has since been run for 15 more future-year emissions scenarios, including three scenarios in which concurrent changes in NO_x emissions were considered. For the most realistic of the new SO_2 scenarios considered, ADOM predicted that 1997 sulphate critical loads for aquatic ecosystems would still be exceeded in central Ontario and Quebec. Only for the most stringent SO_2 emission control scenario which considers a further 75% reduction from projected 2010 SO_2 emissions, is the critical load "gap" closed.
- An analysis of other ADOM SO_2 emission scenarios suggests that further SO_2 emissions reductions in Ontario, Quebec, New Brunswick, and Nova Scotia from 1985 ECARP emission caps, as agreed to under the Canada-Wide Acid Rain Strategy for Post-2000, will reduce the extent of the land area in eastern Canada currently in exceedance of aquatic critical loads. It was also found that for the same overall emission reduction, the *geographic distribution* of the SO_2 emissions reductions in eastern Canada may affect the extent of critical load attainment.
- An analysis of pairs of similar ADOM SO_2 emission scenarios provided quantified contributions for a number of source regions to wet sulphate deposition in eastern Canada and suggests that both Canadian and U.S. SO_2 and NO_x emissions contribute to acid deposition in eastern Canada. On a tonne-vs-tonne basis, Canadian SO_2 emissions have a greater impact *within Canada* than do U.S. emissions, but at the same time U.S. SO_2 emissions have historically been 4 to 6 times larger than Canadian SO_2 emissions (see Chapter 2).
- SO_4^{2-} and NO_3^- deposition fields predicted by ADOM have been combined on a molar basis for several scenarios to yield effective acidity deposition fields that can be compared with the new multi-pollutant critical load field for eastern Canadian forest ecosystems (see Chapter 8).

4.2 INTRODUCTION

This chapter is an update to the material on regional acid deposition modelling presented in Volume 2 ("Atmospheric Science Assessment Report") of the 1997 *Canadian Acid Rain Assessment* (Environment Canada, 1998a). New modelling results obtained for different parts of Canada in the seven years since the 1997 *Assessment* have contributed to a deeper understanding of the impact of changes in emissions of acidifying gases on Canada and to the formulation of new emission control programs. These new results are summarized in this chapter.

To begin, what is the role of emissions-based atmospheric models in acid deposition science? A crucial link in understanding and managing acid deposition is the ability to connect *quantitatively* the magnitudes and geographic distributions of acidifying emissions to the resulting air-concentration patterns and wet-, dry-, and total-deposition patterns of acidifying species. As suggested in the 1990 *Canadian Acid Rain Assessment* (RMCC, 1990), regional acid deposition models provide our best means of estimating quantitative source-receptor relationships for acid deposition.

Regional acid deposition models are prognostic numerical models that, when given the emission rates of acidifying pollutants to the atmosphere and the prevailing meteorological conditions, predict the atmospheric concentrations and deposition of those pollutants and their products based on a combination of first-principle and empirical representations of the relevant physical and chemical processes in the atmosphere. Regional acid deposition models are members of the larger class of what are variously called long-range-transport models, regional air quality models, emission-based models, source-based models, source-oriented models, and source models. They are typically more complicated than regional photochemical models and less complicated than regional particulate matter air quality models (e.g., Seigneur and Moran, 2003).

Regional acid deposition models are particularly important tools because they are the only means to predict *future* air concentration and deposition patterns based on estimated future emission levels. Consequently, they can be used to address questions such as how effective might a proposed emission control program be? How large a further emission reduction would be required to reach a desired environmental objective such as a critical load? And how much does a particular source type or source region contribute to deposition at a particular location?

Any regional acid deposition model can be assigned to one of two categories based on the nature of the spatial reference frame used in the model. Those categories are *Lagrangian* (or trajectory) models and *Eulerian* (or grid) models (e.g., Pasquill and Smith, 1983). Lagrangian acid deposition models use a reference frame that follows the movements of individual air parcels from source to receptor. Chemical transformations and removal processes take place within the parcels, and the transport processes that are not resolved by the mean advective transport (e.g., vertical turbulent diffusion) may increase the size of parcels or (in some multi-layer models) move chemical species between parcels. Eulerian acid deposition models, by contrast, employ a reference frame that is fixed in space. Their simplest form is the box model, but most Eulerian models are three-dimensional grid-based models. Chemical and physical transformations are treated *in situ* within each grid cell and transport and diffusion processes move chemical species between grid cells.

Lagrangian models are usually simpler in their formulation and less demanding in their computational and input requirements than Eulerian models. However, they are also more limited because they generally do not treat some atmospheric physical processes realistically, including differential advection due to vertical wind shear, vertical transport, and chemical reactions with other air parcels. For policy and regulatory purposes where there is a need for realistic representations of all relevant processes, three-dimensional Eulerian grid models are preferred. However, Lagrangian acid deposition models can still be useful for screening assessments, where their lower computational requirements are an asset, and for studies where realistic treatments of chemical and aerosol processes are required but simpler representations of transport and diffusion processes are acceptable.

The rest of this chapter reviews progress since the 1997 *Assessment* in applying regional acid deposition models, both Lagrangian and Eulerian, in eastern and western Canada to understand acid deposition better and to evaluate the efficacy of current, proposed, and potential emission control measures. Both SO_2 and NO_x control programs are considered and summarized in terms of atmospheric impacts. Note that the consideration of NO_x control programs represents an important step beyond the 1997 *Assessment*, in which only SO_2 emission control scenarios were considered. A number of the scenarios considered in this chapter will also be discussed in Chapters 7 and 8 from the point of view of ecosystem impacts and benefits.

4.3 CONCLUSIONS OF THE 1997 ASSESSMENT

Given that this Assessment has been structured as an update to the 1997 *Assessment*, some of the major acid deposition modelling-related results presented in the 1997 *Assessment* are presented as follows:

1. A Lagrangian regional acid deposition model, the AES[1] Lagrangian Sulphur Model (ALSM), was used to estimate annual SO_4^{2-} wet deposition for base year 1985 and for three future year SO_2 emission control scenarios - 1994, 1997, and 2010 - that correspond to the phased implementation of SO_2 emission reductions required under existing Canadian and U.S. legislation (1985 Eastern Canada Acid Rain Control Program, 1990 U.S. Clean Air Act Amendments). The ALSM results suggested that by 2010 the sulphate wet deposition target load of 20 kg SO_4^{2-}/ha/yr would be met for all areas of eastern Canada with the possible exception of a small region in southeastern Quebec. On the other hand, if an aquatic-effects-based critical load is used instead of a target load as the criterion for environmental protection, then the ALSM predictions suggested that critical load values would be exceeded by as much as 10 kg/ha/yr over large areas of eastern Canada even after the current control programs are fully implemented.
2. The ALSM was used to derive an atmospheric sulphur budget for the province of Alberta, which in 1990 was the second largest emitter of SO_2 and NO_x to the atmosphere in Canada (after Ontario). The ALSM estimated that for the 1990 meteorological year, (a) dry deposition was responsible for roughly 75% of total sulphur deposition in Alberta (a much higher percentage than in eastern Canada) and (b) of the sulphur entering Alberta's airshed from Alberta sources (90%) and from British Columbia (10%), 26% was removed by dry and wet deposition, 3% was transported northward into the Northwest Territories, nearly 70% was transported eastward into Saskatchewan, and 4% was transported southward into the United States.
3. Two annual North American source-receptor matrices (SRMs) for SO_4^{2-} wet deposition for the years 1980 and 1985 were combined to produce a single SRM for use in the acid deposition Integrated Assessment Model (IAM). The IAM is a framework of models that includes an atmospheric source-receptor module and a number of component effects modules, including an aquatic-chemistry module and several waterfowl- and fish-effects modules. The IAM was used in some of the analyses reported in the Aquatic Effects volume of the 1997 *Assessment*.
4. Results from a preliminary version of a comprehensive Eulerian regional acid deposition model, the Acid Deposition and Oxidant Model (ADOM), were presented in the 1990 *Assessment*. More extensive and detailed performance evaluation results were presented in the 1997 *Assessment* for an improved version of ADOM. Based on case studies from the 1988-1990 Eulerian Model Evaluation Field Study (EMEFS), a comparison of model predictions to EMEFS measurements for various important chemical species suggested the following conclusions:
    - *Sulphur*: Total sulphur is well simulated by ADOM; wet-deposited SO_4^{2-} shows no bias but scatter is often large; ambient SO_2 and SO_4^{2-} aloft show considerable scatter.
    - *Nitrogen*: ADOM most often underpredicts high measured values of NO_3^- in air; NO_3^- in precipitation is reasonably well simulated, with large scatter; ambient NO_2 aloft is underpredicted, but total airborne nitrate is reasonable, with the exception of very high values, which are underpredicted.
    - *Oxidants*: The dynamic range of ozone concentrations predicted by the model is too small (i.e., highs are underpredicted and lows are overpredicted); H_2O_2 is underpredicted aloft during high oxidant periods.

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[1] Atmospheric Environment Service (AES) was the previous name (until 1999) of the Meteorological Service of Canada (MSC).

5. On the basis of the results of the EMEFS evaluations, an international external peer review committee concluded that (a) ADOM can be used to evaluate total sulphur and nitrate deposition on a regional scale averaged over a month or more but (b) ADOM, in its present form, is not recommended for use in developing emission control strategies for ozone (ERP, 1994).
6. A technique called episode aggregation was implemented for ADOM to allow this short-term episodic model to be used to estimate annual fields of various species for a "climatological" year rather than a particular meteorological year. This was done by simulating 33 three-day periods with ADOM and then using empirically-derived weighting factors to aggregate (i.e., combine) all of the 3-day concentration or deposition fields to estimate annual wet deposition totals and mean annual ambient concentrations.
7. Comparison of the ADOM aggregated annual deposition for 1989 emissions to the 5-year mean deposition (1986–1990) observed at 45 grid squares showed very little bias in the model's annual estimates of SO_4^{2-} wet deposition. The mean absolute percentage error was 23% ± 21% (i.e., a majority of the ADOM aggregated estimates were within 2–44% of the observed values). For NO_3^- wet deposition there was a bias towards underprediction by an average of –29%. A majority of the ADOM aggregated NO_3^- wet deposition estimates were within 10–60% of the observed mean 1986-1990 annual deposition.
8. After a decade of development and evaluation, ADOM was applied for the first time to address policy questions regarding acid deposition in eastern Canada. SO_2 emission reduction scenarios for 1994, 1997, and 2010 as well as a 1989 base case were simulated by ADOM.
9. The ALSM and ADOM models gave qualitatively similar answers for very similar future year emission scenarios for 1994, 1997, and 2010 despite considerable differences in the structure and formulation of these two models. The weight of evidence provided by considering both sets of model results increased confidence in each of the sets of model results.
10. Finally, a "post-2010" scenario was examined with ADOM that was based on an additional uniform 50% reduction in SO_2 emissions in North America over and above the existing legislated reductions expected by 2010. ADOM predicted that even for a reduction in SO_2 emissions of this magnitude, a band of residual sulphate deposition above critical load roughly 222,000 km^2 in area (about four times the size of Nova Scotia) would still be present across central Ontario and Quebec, although deposition in the Maritimes would be below the critical load values.

4.4 DESCRIPTION OF MODELS AND METHODOLOGY

A number of regional acid deposition models have been used in Canada over the years to investigate the acid deposition issue. This section provides an overview of five acid deposition models that have been applied or considered in Canada since the 1997 *Assessment*, with particular attention paid to the ADOM model, the only comprehensive Eulerian model of the group. The following sections describe results from the applications of these models, new developments related to these models, a new regional acid deposition model that is currently under development, suggestions for future work, and conclusions.

4.4.1 AES Lagrangian Sulphur Model (ALSM)

The ALSM is a long-range transport and transformation model for SO_2 and SO_4^{2-}. In the past it was also referred to as the AES-LRT model and the LRTAP model, and it has been used for the past 20 years in studies of sulphur acid deposition in eastern North America (e.g., Olson et al., 1982, 1983; Clark et al., 1989; Olson and Oikawa, 1989; RMCC, 1990). The ALSM is a one-and-a-half-layer model with linear sulphur chemistry and month- or season-dependent process parameterization coefficients (e.g., monthly dry deposition velocities, seasonal mixing heights). The horizontal grid associated with the model is 52 by 58 grid points in size with 127 km by 127 km spacing between grid points on a polar stereographic projection of the Northern Hemisphere. Wind and precipitation fields are obtained from Canadian Meteorological Centre archived analyses. Wet deposition is parameterized as the product of a scavenging ratio and six-hourly precipitation amounts. Four trajectories are considered per receptor site per day, and the integration time step is three hours.

The 1997 *Assessment* reported on results obtained with the ALSM model (a) for three future year SO_2 emission control scenarios over eastern North America for the years 1994, 1997, and 2010 based on the 1985 meteorological year and (b) for an investigation of concentrations, deposition, and transboundary flux of SO_2 emissions in Alberta for the 1990 meteorological year. As well, SO_4^{2-} wet deposition source-receptor matrices for 40 North American source regions (see Figure 4.27) and 15 receptors in northeastern North America (see Figure 4.28a) that had been calculated by the ALSM for the 1980 and 1985 meteorological years were used as the basis for the source-receptor module of the Integrated Assessment Model (see below). Since then, as discussed in the “New Developments” section (see Section 4.6.1), the ALSM is now being used to perform source attribution studies for sulphur species and to calculate larger (and contourable) sulphur source-receptor matrices.

4.4.2 AES Lagrangian Nitrogen Model (ALNM)

The ALNM is an extension of the ALSM that has been used to calculate a nitrogen budget for eastern Canada and nitrogen source-receptor matrices for 15 receptors in eastern North America (Olson et al., 1990, 1992). Six chemical species – three nitrogen species, one volatile organic compound (VOC) species, O_3, and OH – and six reactions have been added to the ALSM. The nitrogen species are (a) NO_2, (b) IN (inorganic nitrate; i.e., sum of HNO_3 and particulate nitrate), and (c) PAN (peroxyacetic nitric anhydride), and the VOC species is ALD (sum of all aldehyde precursors of PAN).

PAN formation is treated as reversible, allowing for the reformation of NO_2. As a result, the chemical mechanism is nonlinear, since the equilibrium between NO_2 and PAN will depend upon the *total* concentrations of these two compounds contributed by all source regions. Other notable aspects of the ALNM are (a) the consideration of only a single lumped hydrocarbon species, ALD (although aldehydes are the most important class of organic compounds for nitrogen chemistry), (b) the assumption that the peroxyacetyl radical PA is always in steady state, (c) the assumption that there is no coupling between sulphur and nitrogen species, (d) the treatment of O_3 and HO as prescribed fields (spatially-uniform O_3 and OH concentrations are prescribed using monthly averaged values with month-dependent diurnal profiles), and (e) the neglect of reduced nitrogen species (i.e., ammonia and ammonium) (Bouchet and Moran, 2002). As discussed in Section 4.6.2, efforts are now underway to calculate new nitrogen SRMs using a more advanced Lagrangian nitrogen model than the ALNM.

4.4.3 Integrated Assessment Model (IAM)

The Integrated Assessment Model (IAM) for acid deposition is a PC-based model designed to represent the entire acid deposition system from emissions through atmospheric transport, transformation, and removal to aquatic, forest, agricultural, visibility, wildlife, materials, and health effects. In essence it consists of a set of component models from individual disciplines linked within an overall integrating framework. At the present time, these component models include an atmospheric source-receptor module and a number of effects modules, including an aquatic-chemistry module and several waterfowl and fish effects modules (e.g., Lam et al., 1998). This approach allows the control costs and damage costs for various emission scenarios to be considered at the same time within the same framework.

The version of the IAM that was used in the 1997 *Assessment* (see Volume 3, “The Effects on Canada’s Lakes, Rivers and Wetlands”) was capable of assessing the ecological impact at selected receptor sites in eastern North America of SO_2 emission changes occurring across the continent (Jeffries et al., 1999, 2000). It could be run in either a scenario mode to predict the impact of SO_2 emission changes on SO_4^{2-} wet deposition or in an optimization mode to calculate the SO_2 emission changes required to achieve a desired change in SO_4^{2-} wet deposition levels.

The atmospheric source-receptor relationship used in the IAM is based on two annual sulphate wet deposition source-receptor matrices calculated using the ALSM model for two meteorological years, 1980 and 1985. In order to minimize the impact of interannual meteorological variability, these two source-receptor matrices were combined to produce a single optimized source-receptor matrix (Lam et al., 1998). The combined matrix minimizes prediction error at the individual receptor sites for three data sets: (a) 1980 emissions and the observed 1980–1983 mean annual SO_4^{2-} wet deposition field; (b) 1990–1993 emissions and the observed 1990–1993 SO_4^{2-} wet deposition field; and (c) the decadal changes in both emissions and SO_4^{2-} wet deposition fields.

The IAM can be used to perform quick evaluations of the impact of regional SO_2 emission changes on SO_4^{2-} wet deposition at a limited number of receptor sites. Selected SO_2 emission scenarios can then be examined more thoroughly with the more detailed regional acid deposition model such as the Acid Deposition and Oxidant Model (ADOM). A comparison of IAM predictions with ADOM predictions is presented in Section 4.5.2.2.1, and a set of four new SO_2/NO_x emission scenarios developed for use by the IAM for this *Assessment* are described in Section 4.5.2.2.2. New sulphur and nitrogen SRMs that are being developed for use in the IAM are then discussed in Sections 4.6.1 and 4.6.2.

4.4.4 Regional Lagrangian Acid Deposition Model (RELAD)

The REgional Lagrangian Acid Deposition model (RELAD) is a three-layer regional-scale Lagrangian model that simulates ground-level concentrations and wet and dry deposition of six sulphur and nitrogen species: SO_2; H_2SO_4; $(NH_4)_2SO_4$; NO_x (= NO_2 + NO); HNO_3; and NH_4NO_3. It is based upon a U.S. EPA Lagrangian sulphur deposition model named RELMAP (REgional Lagrangian Model of Air Pollution) to which a simplified treatment of nitrogen chemistry and removal from the MESOPUFF-II model (Eder et al., 1986; Scire et al., 1984) have been added.

A 1° by 1° latitude-longitude grid is typically used for RELAD applications in western Canada. The model top is set to a single seasonal mixing height throughout the domain. The gridded three-hourly meteorological fields required by RELAD are obtained from objective analyses of hourly surface station data (wind, precipitation, temperature, vertical stability, sky cover, humidity) and 12-hourly upper air station data (wind). Emissions from aggregated sources are treated as discrete puffs that are released every 12 hours and expand horizontally during transport. Point and area emission sources are treated differently; during the daylight hours both point and area sources are assumed to be well mixed throughout all three model layers, but at night area-source emissions are injected into the first model layer whereas point-source emissions are injected into the second model layer and decoupled from the surface. The transformation of SO_2 to SO_4^{2-} depends upon solar insolation, moisture content, and season. NH_3 and O_3 fields are not predicted and must instead be specified. The treatment of dry deposition depends on species, land use, vertical stability, and season. The treatment of wet deposition is based on washout ratios and depends upon precipitation rate and cloud type, where one cloud type is assumed for each season.

Additional details about RELAD may be found in Cheng et al. (1995) and McDonald et al. (1996). Applications of RELAD in western Canada since the 1997 *Assessment* are reviewed in Section 4.5.1.

4.4.5 Acid Deposition and Oxidant Model (ADOM)

4.4.5.1 *Model description*

ADOM is a comprehensive, three-dimensional, regional-scale, episodic Eulerian transport-chemistry model. ADOM is comprehensive in the sense that it has been designed to consider all of the important processes that govern the fate of acidifying pollutants and oxidants in the atmosphere. These include pollutant emission, atmospheric transport and diffusion, gas-phase chemistry, aqueous-phase chemistry, cloud mixing and scavenging, and dry and wet deposition.

The acid deposition version of ADOM has usually been run for a 33 by 33 uniform horizontal grid with 127-km grid spacing and 12 logarithmically-spaced vertical layers up to 10 km. The model domain covers eastern North America (e.g., Figure 4.4). Hourly emissions of 18 species are considered both from area sources and from roughly 3,000 individual point sources. Hourly gridded meteorological fields, including wind, temperature, vertical diffusivity, mixed-layer height, cloud cover, cloud type, and stratiform and cumuliform precipitation that have been obtained from a combination of observations and numerical weather prediction model forecasts are input for each hour of ADOM simulation (e.g., Venkatram et al., 1988; Scholtz et al., 1988).

The gas-phase chemistry mechanism, known as the ADOM-II mechanism, consists of 114 reactions amongst 47 species, including isoprene. The aqueous-phase chemistry mechanism consists of 25 reactions amongst 13 species. Two cloud modules are used, a cumuliform module to represent small-scale (i.e., subgrid-scale) convective clouds and precipitation, and a stratiform module to represent large-scale clouds and precipitation. Both cloud modules serve to act as aqueous-phase chemical reactors, scavenge pollutants within cloud, and mix pollutants vertically. Below-cloud scavenging of particles and soluble gases by precipitation is also represented. Dry deposition of a number of gaseous species and particulate sulphate, nitrate, and ammonium is parameterized using species-specific resistance formulas that account for variations in surface properties associated with changing land-use category and for diurnal and seasonal changes in these surface properties (e.g., Stockwell and Lurmann, 1989; Fung et al., 1991; Karamchandani and Venkatram, 1992; Padro et al., 1993).

4.4.5.2 *Episode aggregation*

To estimate annual concentration and deposition fields with ADOM, which is a detailed and computationally demanding short-term or episodic model, an episode-aggregation technique is used. Specifically, ADOM is run for 33 three-day events or “episodes” drawn from all seasons from the years 1988 and 1990. Aggregated annual estimates are then calculated for a given quantity by combining the 33 mean three-day fields predicted by ADOM for that quantity using pre-calculated episode-specific gridded weighting-factor fields.

Episode aggregation is a semi-empirical technique (i.e., partly dependent on data) because the gridded weighting-factor fields needed to combine ADOM episode predictions are pre-determined from historical meteorological fields and from air-chemistry and precipitation-chemistry measurements at stations (Brook et al., 1995a,b; Environment Canada, 1997a). In order to create the gridded weighting-factor fields from scattered station measurements, a horizontal interpolation technique called kriging was used (e.g., Finkelstein, 1984; Federov, 1989; Schaug et al., 1993). One limitation of this approach, however, is that kriging can only estimate values within the confines of the convex hull (the area that is defined by drawing connecting lines between every pair of stations and then deleting all interior lines) determined by the geographic distribution of measurement stations on the periphery of the measurement network. Hence, the spatial coverage of the ADOM-aggregated annual fields is constrained by the spatial coverage of the historical weighting-factor fields determined from kriged station measurements, even though the “raw” ADOM-predicted fields cover the entire ADOM domain (e.g., Figure 4.10). Note that because the spatial coverage of the precipitation-chemistry networks in eastern North America was and is more extensive than that of the air-chemistry networks, the convex hull for such air species as SO_2, SO_4^{2-}, NO_x, and t-NO3 is smaller than that for precipitation-chemistry species (e.g., Figures 4.8 vs. 4.10).

As discussed in Environment Canada (1997a), gridded weighting-factor fields based on measurement data were determined for five precipitation-chemistry species (wet deposition of SO_4^{2-}, NO_3^-, NH_4^+, H+; precipitation) but only one air-chemistry species (SO_4^{2-}). In order to estimate the annual concentrations of three other air-chemistry species (SO_2, NO_x, and t-NO_3), the same gridded weighting-factor fields used for aggregating SO_4^{2-} event air concentrations were also used for aggregating SO_2, NO_x, and t-NO_3 event air concentrations. Doing so introduces an additional approximation but was necessary given the lack of gridded weighting-factor fields specific to SO_2, NO_x, and t-NO_3.

4.4.5.3 *Performance evaluation*

ADOM performance has been evaluated against both precipitation-chemistry measurements and surface and upper-air air-chemistry concentration measurements for a number of species and time and space scales (e.g., Fung et al., 1992; Macdonald et al., 1993; Li et al., 1994; Hoff et al., 1995; Sirois et al., 1995; Banic et al., 1996; Moran, 1998). The overall model performance of ADOM, along with that of RADM, a comprehensive acid deposition model used by the U.S. EPA, has also been assessed by an international, external peer-review panel (ERP, 1994; U.S. EPA, 1995). The panel concluded that they would have confidence in the ability of ADOM and RADM to represent total sulphur and nitrogen loading of the atmosphere and deposition at seasonal and annual time scales and regional space scales.

4.4.5.4 *Wet deposition and ambient concentration calibration*

A final adjustment step is performed for two ADOM predicted annual fields in order to minimize the impact of statistical fluctuations in the episode-aggregation approach resulting from the relatively small number of episodes used (33) to represent the full range of meteorological conditions contributing to the long term transport and chemical climatology of eastern North America (Environment Canada, 1997a). The ADOM annual SO_4^{2-} wet deposition field estimated by episode aggregation for each future year scenario is multiplied by the ratio of the observed 1986-1990 mean annual SO_4^{2-} wet deposition field to the predicted annual SO_4^{2-} wet deposition field for the ADOM 1989 base-case simulation (scenario “BASE89”; see Section 4.5.2.1.1). The same adjustment step is performed for the annual NO_3^- wet deposition field using the corresponding observed 1986-1990 mean annual wet field. No calibration was performed for the annual ambient concentration fields (SO_2, SO_4^{2-}, NO_x, and t-NO_3), on the other hand, because of a lack of sufficient measurements for these species for the 1986-1990 period (cf. Section 4.4.5.2).

This adjustment procedure is equivalent to multiplying the observed field by the ratio of the future year to base case predicted fields, and it has the advantage of making use of available observations to augment model predictions. It also emphasizes ADOM’s prediction of relative changes as opposed to absolute changes for different scenarios. The same procedure was used with the ALSM predictions included in the 1997 *Assessment*. Other agencies have used this calibration procedure as well; for example, the U.S. EPA guidance documents for ozone and PM attainment modelling recommends this same approach, and refers to the ratios of model-predicted scenario to model-predicted base-case fields as relative-reduction-factor fields (e.g., U.S. EPA, 1999, 2001b).

4.4.5.5 *Critical load exceedance calculation*

The primary environmental measure that has been used to evaluate future year deposition fields predicted by ADOM for ecological sustainability is the sulphate-wet-deposition critical load field for eastern Canadian aquatic ecosystems that was developed during the 1990 *Assessment* (RMCC, 1990). This field is shown in Figure 4.1 plotted on a grid with 42.3 km by 42.3 km grid spacing (cf. Fig. 3.1 of Environment Canada (1997a)). (Note that an updated critical load field for Canadian aquatic ecosystems and a new critical load field for Canadian forest ecosystems are discussed in subsequent chapters of this Assessment, but these new critical load fields were not available in time to be employed in this chapter.)

To identify areas with SO_4^{2-} wet deposition critical load exceedances, that is, with wet deposition values greater than critical load, the predicted scenario annual SO_4^{2-} wet deposition field (in units of kg SO_4^{2-}/ha/yr) on the ADOM 127 km by 127 km grid was first horizontally interpolated to the higher-resolution, 42.3 km by 42.3 km critical load grid by bilinear interpolation. The critical load field was then subtracted from the scenario SO_4^{2-} wet deposition field for each scenario. Any positive values correspond to areas where the SO_4^{2-} wet deposition is predicted to remain higher than the critical load value for the same area.

Note that the impact of acid deposition actually depends on total deposition, that is, on the sum of both wet and dry deposition. As discussed in Chapter 3, dry deposition is a much more difficult quantity than wet deposition to measure. In developing the SO_4^{2-} deposition critical load field a decade ago, dry deposition was accounted for in a crude way by dividing the critical load SO_4^{2-} total deposition value by 1.15, based on the assumption that SO_4^{2-} dry deposition is equal to 15% of SO_4^{2-} wet deposition (e.g., Jeffries et al., 2000). Sulphate wet deposition was thus assumed to be a surrogate for SO_4^{2-} total deposition. Note, too, that a lake sacrifice level of 5% was assumed in calculating these aquatic-ecosystem-based critical load values; that is, the critical load value is the SO_4^{2-} total deposition that can be sustained or tolerated by 95% of area lakes rather than 100%.

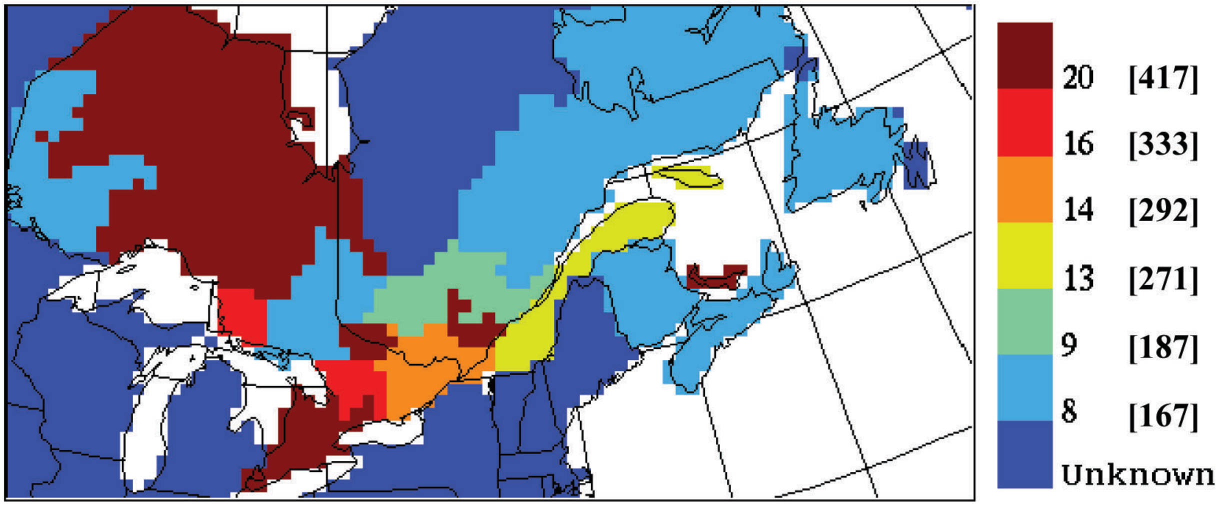


Figure 4.1: Plot of SO_4^{2-} wet-deposition critical load field for eastern Canada at 5% lake-sacrifice level in units of kg SO_4^{2-} /ha/yr [and eq/ha/yr] (based on Environment Canada [1997]).

4.4.5.6 *Recent developments*

ADOM has also been extended or modified by several groups for air quality applications other than acid deposition. Venkatram et al. (1994) introduced a simpler gas-phase chemistry mechanism into ADOM to produce a simplified photochemical model for use as an NO_x/VOC emission control strategy screening tool. Gong et al. (1999) linked ADOM to a high-resolution mesoscale meteorological model to study ozone formation and transport. Venkatram et al. (1997) used ADOM as the starting point for a regional visibility model. Mercury versions of ADOM have been developed independently by Pai and his co-workers (Pai et al., 1997, 1999) and by Petersen and his co-workers (Petersen et al., 1998, 2001). Other groups have implemented the code or algorithms for selected ADOM process parameterizations in other air quality models (e.g., Environment Canada, 1997b; Pudykiewicz et al., 1997; Moran et al., 1998; Kaminski et al., 2002).

4.5 APPLICATIONS OF REGIONAL ACID DEPOSITION MODELS

4.5.1 Western Canada

Acid deposition in western Canada has not received as much attention as in the more highly industrialized areas of eastern North America, but unlike other regions of the continent, emissions of acidifying gases have increased in Alberta over the past decade. In 1990, Alberta emitted 485 Kt of SO_2 and 542 Kt of NO_x and was the second-largest emitter of these pollutants in Canada (after Ontario). By 1999, these values had increased to 596 and 629 Kt, respectively, so that the province of Alberta is now the largest emitter of both SO_2 and NO_x in Canada (Environment Canada, 2004a). A cluster of major SO_2 sources is located in the Fort McMurray area in northeastern Alberta, but the central region of Alberta has numerous smaller SO_2 sources that together add up to produce a significant effect on pollutant levels downwind from that area (Chapter 2, Figure 2.1). The geographic distribution of Alberta NO_x emissions is roughly similar to that for SO_2 emissions, with the largest emissions located in the Calgary-Edmonton corridor (e.g., Chapter 2, Figure 2.2; Foster et al., 2001; Environment Canada, 2004a).

As noted in Section 4.4.1, the ALSM has been used to derive an atmospheric sulphur budget for the province of Alberta (McDonald et al., 1996). The ALSM estimated for the 1985 meteorological year that (a) dry deposition was responsible for roughly 75% of total sulphur deposition in Alberta (a considerably higher percentage than in eastern Canada), and (b) of the sulphur entering Alberta's airshed from Alberta sources (90%) and from British Columbia (10%), 26% was removed by dry and wet deposition, 3% was transported northward into the Northwest Territories, nearly 70% was transported eastward into Saskatchewan, and 4% was transported southward into the United States. McDonald et al. (1996) also presented an atmospheric sulphur budget for Alberta from western Canadian sources as determined by a second Lagrangian acid deposition model, the RELAD model (see Section 4.4.4). The two budgets predicted by different acid deposition models for different meteorological years were quite similar. RELAD estimated for the 1990 meteorological year that (a) dry deposition was responsible for roughly 50% of total sulphur deposition in Alberta (considerably less than predicted by the ALSM), and (b) of the sulphur entering Alberta's airshed from Alberta sources (89%) and from British Columbia (11%), 18% was removed by dry and wet deposition, 5% was transported northward into the Northwest Territories, nearly 70% was transported eastward into Saskatchewan, and 5% was transported southward into the United States.

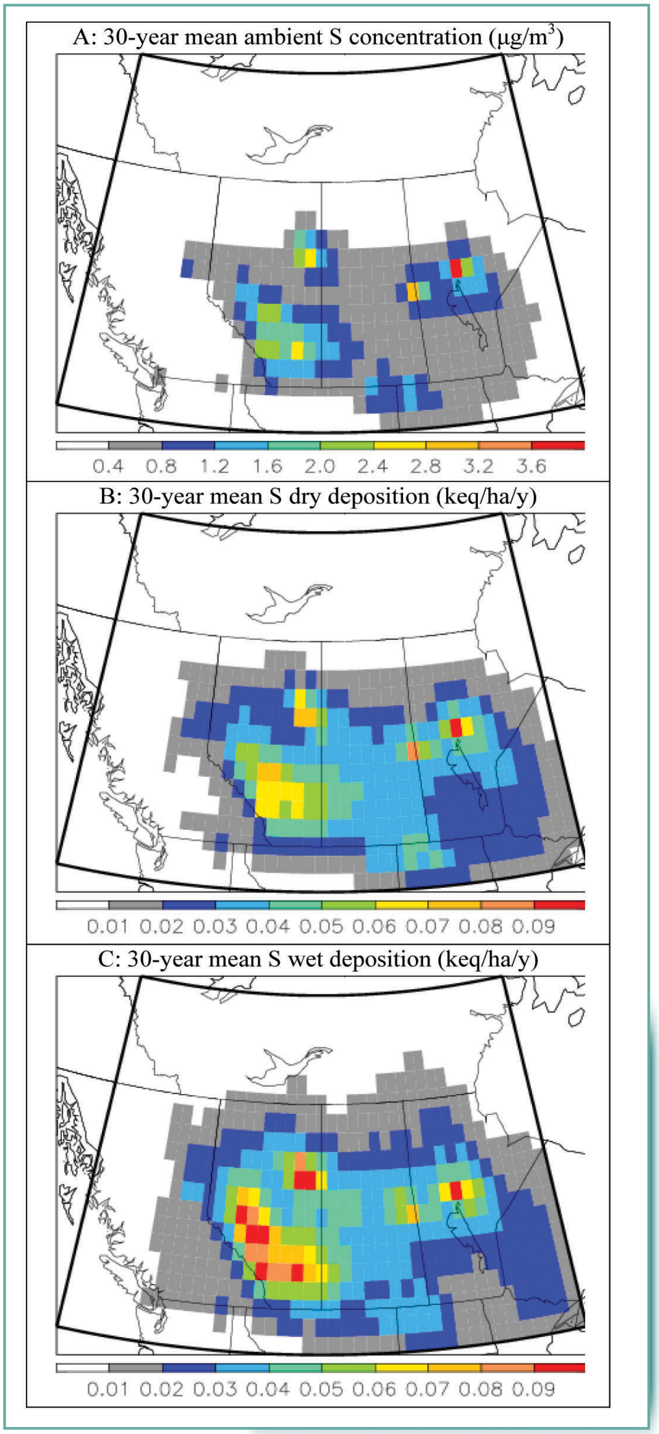
A subsequent paper by Cheng and Angle (1996) addressed the impact of year-to-year variations in meteorology on modelled sulphur and nitrogen budgets for Alberta. Their metric for interannual variability was the coefficient of variation (COV), defined as the standard deviation divided by the mean. Based on 10 years of RELAD results for the period 1981-90, interannual variability for the annual concentrations of the primary species SO_2 and NO_x was 3 to 21% and 4 to 23%, respectively, and at least double those values for the secondary species (H_2SO_4, $(NH_4)_2SO_4$, HNO_3, NH_4NO_3). The corresponding interannual variability for SO_2 and NO_x annual dry deposition was larger than for annual concentrations, 6 to 32% and 8 to 30%, respectively, while for SO_2 and NO_x annual wet deposition the values are larger again, 13 to 67% and 9 to 50%, respectively. Interannual variability of dry and wet deposition of the four secondary species again tended to be larger than for their precursors.

The 10-year-mean atmospheric sulphur budget calculated by RELAD for the 1981-90 period was similar to the one-year sulphur budget calculated by RELAD for the 1990 meteorological year: (a) dry deposition was responsible for just over 50% of total sulphur deposition in Alberta; and (b) of the sulphur entering Alberta's airshed from Alberta sources (90%) and from British Columbia sources (10%), 9% (11% COV) was removed by dry deposition and 9% (18% COV) by wet deposition, 6% (17% COV) was transported northward into the Northwest Territories, 65% (6% COV) was transported eastward into Saskatchewan, and 8% (28% COV) was transported southward into the United States.

Interestingly, in spite of considerable differences between nitrogen and sulphur chemistry and removal, the 10-year mean atmospheric nitrogen budget calculated with RELAD for Alberta was very similar to the sulphur budget: (a) dry deposition was responsible for just over 45% of nitrogen total deposition in Alberta; and (b) of the nitrogen entering Alberta's airshed from Alberta sources (82%) and from British Columbia sources (18%), 8% (13% COV) was removed by dry deposition and 10% (16% COV) by wet deposition, 8% (19% COV) was transported northward into the Northwest Territories, 65% (9% COV) was transported eastward into Saskatchewan, and 4% (33% COV) was transported southward into the United States.

RELAD is now being used as part of Alberta's acid deposition management framework, which was developed by Alberta's Clean Air Strategic Alliance, a multi-stakeholder advisory group, and which is overseen by Alberta Environment under the Province of Alberta's 1995 *Environmental Protection and Enhancement Act* (e.g., Foster et al., 2001). Under this framework, receptor sensitivity is addressed by consideration of (a) critical loads, (b) target loads, and (c) monitoring loads. *Critical load* maps based on soil sensitivity to acid input and on lake sensitivity to acid input have been produced on a 1° by 1° latitude-longitude grid for the entire province. Based on precipitation chemistry measurements and on RELAD modelling results, no part of Alberta is thought to be in exceedance of critical load values at present. For purposes of acid deposition management, *target loads* have been established at 90% of the critical loads to provide an additional level of protection given uncertainties associated with measurements and with RELAD and other acid deposition models (note the difference with eastern Canada, where target loads were set in the 1980s at levels above critical loads as an interim target since actual acid deposition in eastern Canada at the time was greater than both). New development and emissions are to be managed to ensure that all parts of Alberta remain below these target loads. Another layer of protection is provided by the establishment of *monitoring loads*, which have been set to 70% of the critical loads. If RELAD or another acid deposition model predicts that current or future levels of deposition may exceed the monitoring load, then monitoring and research activities are triggered in the areas in exceedance of the monitoring load. RELAD has identified one such grid cell on the Alberta-Saskatchewan border for 1990 Canadian emissions, and measurement studies have been initiated in this area. Results are expected to be reported in the 2004 province-wide acid deposition assessment that is currently underway (Foster et al., 2001).

One of the modelling activities in the 2004 Alberta-wide acid deposition assessment is the determination of the most representative meteorological year for annual modelling calculations in the 2004 assessment and future acid deposition-management applications. Annual average concentrations and annual depositions of sulphur and nitrogen species were calculated using RELAD for the 1971-2000 period using 30 years of meteorological data and 1995 emissions. Figures 4.2 and 4.3 show the 30-year mean annual concentrations and deposition of S and N predicted by RELAD. The three highest predicted S concentrations in Figure 4.2a are associated with the Fort McMurray area of Alberta and the large non-ferrous smelters at Flin Flon, Manitoba and Thompson, Manitoba, whereas the two highest N concentrations in Figure 4.3a correspond to the grid cells containing the cities of Calgary and Edmonton. Based on the 30 one-year RELAD runs for the 1971-2000 period, 1980 was found to be the year that produces results in Alberta and Saskatchewan most similar statistically to the 30-year mean fields shown in Figures 4.2 and 4.3. Lastly, one other acid deposition model, CALPUFF, has been applied in environmental assessments in the Fort McMurray/Oil Sands Region of Alberta (e.g., RWDI West Inc., 2003).


A: 30-year mean ambient S concentration (μg/m^3)

B: 30-year mean S dry deposition (keq/ha/y)

C: 30-year mean S wet deposition (keq/ha/y)

Figure 4.2: 1971-2000 mean annual fields due to 1995 Canadian emissions only predicted by RELAD for (a) sulphur surface air concentration (as μg S/m^3), (b) sulphur dry deposition (keq/ha/y), and (c) sulphur wet deposition (keq/ha/y). The RELAD domain is indicated by the dark black outline. Each grid cell is 1° of latitude by 1° of longitude in size. Note that multiplication of the colour scale for panels (b) and (c) by 48 will convert units of kiloequivalents to units of kg SO_4, yielding an alternate set of contour intervals (0.0, 0.48, 0.96, 1.44, 1.92, 2.40, 2.88, 3.36, 3.84, 4.32).

4.5.2 Eastern Canada

4.5.2.1 New ADOM *emission control scenarios and pseudo-scenarios*

The results from five SO_2 emission control scenarios simulated by the comprehensive Eulerian acid deposition model ADOM were reported in the 1997 *Assessment*. In the last seven years, another 15 SO_2 emission control scenarios and three NO_x emission control scenarios have been run with ADOM in support of various policy development initiatives. All of these scenarios are listed

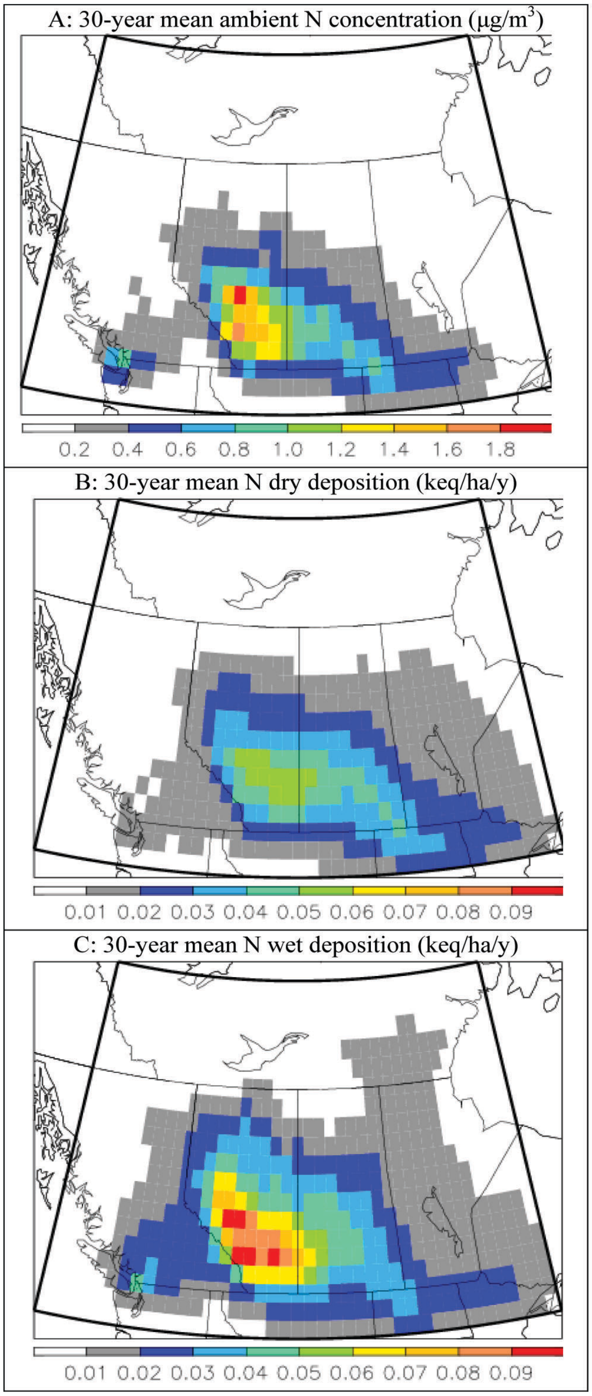


Figure 4.3: Same as Figure 4.2 except for (a) nitrogen surface air concentration (as μg N/m^3), (b) nitrogen dry deposition (keq/ha/y), and (c) nitrogen wet deposition (keq/ha/y). Note that multiplication of the colour scale for panels (b) and (c) by 62 will convert units of kiloequivalents to units of kg NO_3^-, yielding an alternate set of contour intervals (0.0, 0.62, 1.24, 1.86, 2.48, 3.10, 3.72, 4.34, 4.96, 5.58).

in Tables 4.1 (SO_2 scenarios) and 4.2 (NO_x scenarios) in rough chronological order.

Following the 1997 *Assessment*, four more SO_2 emission control scenarios ("25FCAP", "T5CUS2", "5CONLY", "75FCAP") and a first NO_x emission control scenario ("NOXSCEN") were run in support of the development of a new Canada-wide Acid Rain Strategy for Post-2000 to update the 1985 Eastern Canada Acid Rain Control Program (see AETG, 1997; Federal/Provincial/Territorial Ministers of Environment and Energy, 1998). Second, another eight SO_2 emission control scenarios ("PST2010A" to "PST2010F" to "PST2010b") were run to support the implementation of the new Canada-wide Acid Rain Strategy for Post-2000 by four eastern provinces (ARM Consultants, 2000, 2002b; Environment Canada, 2002a). Third, an ADOM SO_2 emission control scenario ("HLFO") was run to examine the impact in eastern Canada of proposed reductions in the sulphur content of the light fuel oils and heavy fuel oils currently used in Canada (ARM Consultants, 2002a; Environment Canada, 2003c). And fourth, two combined SO_2/NO_x emission control scenarios ("NOX2B", "NOX3P") were recently run with ADOM, the first to examine the co-benefits for acid deposition of legislated and potential SO_2 and NO_x emission controls arising from the management of other air pollution issues and the second to examine the benefits of additional acid deposition-related controls (WxPrime Corp., 2004).

In the SO_2 and NO_x scenario descriptions that follow, some of the ADOM scenarios listed in Tables 4.1 and 4.2 will be referred to as "rollback" scenarios whereas others will be referred to as "realistic" scenarios. These terms are used to distinguish between simpler scenarios, in which emissions from all sources in a particular geographic region or even the entire modelling domain are reduced by the same relative amount (e.g., de Nevers and Morris, 1975), and more complicated scenarios, in which emission reductions are targetted by source type (e.g., coal-fired power plants, heavy-duty diesel trucks) and by jurisdiction. Rollback scenarios are commonly used to explore the impact of emission reductions in general terms and can be thought of as emission-sensitivity simulations. That is, they explore how the atmosphere might react to a hypothetical change in emissions but they provide no information as to how such changes

Table 4.1. Total SO_2 emissions within ADOM domain for 1989 base case and nineteen future-year emission control scenarios. The six key control scenarios are highlighted in yellow.

Scenario Name	Nominal Year	SO_2 Emissions (Ktonnes/yr)			Fraction of BASE89	Implementation Strategy	Comments
		Canada	U.S.	Total			
BASE89	1989	2,688	17,511	20,199	1.00	Current	Base case, effectively 1988-90 average
CCONLY	1994	1,939	17,862	19,801	0.98	Sectoral	Cdn controls (CC) + overcompliance, new U.S. sources
CCUSA1	1997	1,939	14,865	16,804	0.83	Sectoral	1990 U.S. CAAA Title IV Phase 1 cuts, Canada same as 1994
CCUSA2	2010	1,939	12,446	14,385	0.71	Sectoral	1990 U.S. CAAA Title IV Phase 2 cuts, Canada same as 1994
5CONLY	2030	1,320	12,446	13,766	0.68	Regional Rollback	50% Cdn SOMA red'ns from 1985 ECARP caps, U.S. same as 2010
25FCAP	2030	1,738	9,335	11,072	0.55	Uniform Rollback	25% Cdn red'ns from 1985 ECARP caps, 25% U.S. from 2010
T5CUS2	2030	1,277	8,794	10,071	0.50	Regional Rollback	Same as "5CCUS2" except Saskatchewan, Manitoba, Newfoundland, and US SE, SW and W left at 2010 levels
5CCUS2	2030	969	6,223	7,192	0.36	Uniform Rollback	50% cut from "CCUSA2" 2010 scenario
75FCAP	2030	579	3,112	3,691	0.18	Uniform Rollback	75% Cdn red'ns from caps, 75% US from 2010
PST2010A	2030	1,636	5,578	7,214	0.36	Regional Rollback	50% ON, 45% QU, 25% NB + NS from caps, 55% US from 2010
PST2010B	2030	1,636	4,967	6,603	0.33	Regional Rollback	50% ON, 45% QU, 25% NB + NS from caps, 60% US from 2010
PST2010C	2030	1,610	6,204	7,814	0.39	Sectoral/ Reg. Rollbk	50% ON but major sources targetted, 50% QU but Noranda Inc. Rouyn-Noranda targetted, 25% NB + NS from caps, 50% US from 2010
PST2010D	2030	1,601	8,116	9,717	0.48	Sectoral/ Reg. Rollbk	Same as "PST2010C" except 30% NB and NBPC redistribution, 25% NS but NSPC redistribution, and 60% red'n in 20 NE US states but rest at 2010 levels
PST2010E	2030	1,601	4,984	6,585	0.33	Sectoral/ Reg. Rollbk	Same as PST2010D except all U.S states reduced by 60% from 2010
PST2010F	2030	1,520	6,204	7,724	0.38	Sectoral/ Reg. Rollbk	Same as "PST2010C" except Ontario reductions are smaller in Sudbury area and larger in southern Ontario and both NB and NS reductions are 50% and redistributed; 50% U.S. reduction from 2010
PST2010a	2030	1,690	5,578	7,268	0.36	Regional Rollback	50% ON, 34% QU, 25% NB + NS from caps, 55% US from 2010
PST2010b	2030	1,690	4,967	6,657	0.33	Regional Rollback	50% ON, 34% QU, 25% NB + NS from caps, 60% US from 2010
HLFO	2010	1,759	12,446	14,205	0.70	Sectoral	Reductions in Canadian heavy- and light-fuel-oil sulphur content
NOX2B	2020	1,427	12,426	13,400	0.66	Sectoral	Includes all Cdn & U.S. control programs legislated as of 2003
NOX3P	2020	1,219	8,252	9,067	0.45	Sectoral	"NOX2B" + Cdn post-2000 Acid Rain + U.S. Clear Skies program

Table 4.2. Total NO_x emissions within ADOM domain for 2010 base case and three future-year emission control scenarios.

Scenario Name	Nominal Year	NO_x Emissions (Ktonnes/yr)			Fraction of CCUSA2	Strategy	Comments
		Canada	U.S.	Total			
CCUSA2	2010	1,109	13,252	14,361	1.00	Current	Base case, effectively 1988-90 average
NOXSCEN	2030	866	10,464	11,330	0.79	Sectoral/ Reg. Rollbk	45% reduction in S Ontario and 30% reduction in Montreal region from all sources; 60% reduction from U.S. major point sources and 30% reduction from U.S. mobile sources in 20 northeastern states
NOX2B	2020	1,035	9,788	10,823	0.75	Sectoral	Includes all Cdn & U.S. control programs legislated as of 2003
NOX3P	2020	983	7,908	8,891	0.62	Sectoral	"NOX2B" + Cdn post-2000 Acid Rain + U.S. Clear Skies program

might be achieved in practice. Realistic scenarios, on the other hand, are often confirmatory in nature. That is, they test whether proposed and often detailed emission control measures will achieve their objectives, and they inherently provide more information on how the emission reductions might be achieved in practice.

4.5.2.1.1 Descriptions of selected SO_2 emission control scenarios

Results from 16 of the 20 SO_2 scenarios listed in Table 4.1 will either be discussed or referenced in this chapter. Descriptions of these 16 scenarios follow, beginning with six key scenarios: "BASE89"; "CCUSA2"; "75FCAP"; "PST2010F"; "NOX2B"; and "NOX3P". Briefly, these six key scenarios can be characterized as follows:

- Scenario "BASE89" is representative of the 1988-90 period before implementation of the "first generation" of Canadian and U.S. acid rain control programs that were passed into law from 1985 to 1990. This scenario thus provides a baseline for assessing the impact of Canadian and U.S. SO_2 emission control programs, both implemented and proposed. Results for this scenario were reported in the 1997 *Assessment*.
- Scenario "CCUSA2" describes the SO_2 emissions expected to occur in 2010 after full implementation of the "first generation" of Canadian and U.S. acid rain control programs. This scenario thus provides a useful point of comparison for assessing newer "second-generation" SO_2 emission control programs. Results for this scenario were reported in the 1997 *Assessment*.
- Scenario "75FCAP" is a simple uniform rollback scenario that has the lowest SO_2 emissions of any of the SO_2 emission control scenarios considered with ADOM. After an upward adjustment of Canadian SO_2 emissions to legislated caps, both Canadian and U.S. emissions from the "CCUSA2" 2010 scenario are assumed to be reduced by a further 75%. Together the "CCUSA2" scenario and this scenario effectively "bracket" all of the other ADOM future year SO_2 scenarios run since the 1997 *Assessment*.
- Scenario "PST2010F" extends the "CCUSA2" scenario to consider the additional SO_2 emission reductions that were announced by the provinces of Ontario, Quebec, New Brunswick, and Nova Scotia in response to the Canada-wide Acid Rain Strategy for Post-2000 plus an assumed further 50% reduction or rollback in U.S. SO_2 emissions (relative to the "CCUSA2" scenario).
- Scenario "NOX2B" is a realistic update to scenario "CCUSA2" to include changes in SO_2 (and NO_x) emissions arising from projected population and economic growth and from legislated control programs such as on-road and off-road mobile source controls that have been designed to manage air issues other than acid deposition. The nominal projection year for this scenario is 2020.
- Scenario "NOX3P" combines scenario "NOX2B" with the second generation of both Canadian and U.S. acid rain control programs. This realistic scenario deserves particular attention because it represents the best estimate, as of 2004, of the SO_2 (and NO_x) emissions that will occur in 2020 in the absence of other new control programs over the next 15 years.

The other 10 ADOM SO_2 emission control scenarios described in this section have been included because of insights that can be gained about the contribution of different source regions or source types by contrasting them with one of the key scenarios or amongst themselves (see Table 4.5).

S1. Scenario "BASE89"

The name of this realistic scenario is an abbreviation of "Base year 1989". The emission inventories used to build the emission files for this base scenario were the 1985 Canadian and 1985 U.S. national emission inventories (see Saeger et al., 1989). However, in order to represent actual emissions during the 33 ADOM aggregation events (see Section 4.4.5.2) as realistically as possible, the seasonal emission records from the 1985 NAPAP modellers's emission inventory were supplemented by actual hourly emission data collected for four pollutant species (SO_2, SO_4^{2-}, NO, and NO_2) for 19 major SO_2 sources in Canada and 114 major SO_2 sources in the United States during the 1988–1990 period (e.g., Dennis et al., 1990; Kaplan et al., 1995) These sources were responsible for approximately 75% of Canadian and 64% of U.S. SO_2 emissions in 1985. See Environment Canada (1997a) for more details about this scenario.

S2. Scenario "CCUSA2"

Scenario "CCUSA2" (abbreviation of "Canadian controls and U.S.A. 1990 CAAA Title IV Phase 2 controls") is a future year SO_2 emission control scenario that was designed to quantify the impact of (a) the 1985 Eastern Canada Acid Rain Program (ECARP), which was initiated in 1985 and subsequently formalized by a series of bilateral federal provincial agreements (e.g., Environment Canada, 1994), and (b) the acid deposition provisions (i.e., Title IV, Phases 1 and 2) of the 1990 U.S. Clean Air Act Amendments (CAAA) (e.g., U.S. EPA, 1990). The nominal projection year for this scenario is 2010, since that is the year in which the U.S. CAAA SO_2 control program will be fully implemented (the 1985 ECARP SO_2 reductions having been fully implemented by 1994: e.g., Environment Canada, 1994).

Scenario "CCUSA2" starts from the "BASE89" scenario. It is a very realistic scenario in that SO_2 emission reductions were modelled at the smokestack level for seven smelters and 11 power plants in Canada (see Table 4.3) and for 110 power plants in the U.S. The U.S. power plant emissions are based on SO_2 emission allowances for 2010 from version 3.11 of the U.S. EPA's National Allowance Data Base; no SO_2 emissions trades are considered. SO_2 emissions from minor point sources, area sources, and on-road and off-road mobile sources, on the other hand, are assumed to remain unchanged from the levels contained in the 1985 NAPAP modellers' emission inventory. See Environment Canada (1997a) for more details about this scenario.

Following from these assumptions, total Canadian SO_2 emissions in the ADOM domain are reduced by 28% from 1989 levels and total U.S. SO_2 emissions in the ADOM domain are reduced by 29% for this scenario (see Table 4.1). The spatial distribution of SO_2 emissions for this scenario on the ADOM grid is shown in Figure 4.5a. Note, though, that as discussed in Environment Canada (1997a) and AETG (1997), the Canadian emissions considered in this scenario were lower than the ECARP cap for the eastern provinces by 395 Ktonnes/yr due to actual or announced overcompliance by some major Canadian SO_2 sources. This can be seen from the eastern Canadian SO_2 emissions total for this scenario (including part of Saskatchewan) of 1,939 Ktonnes/yr reported in Table 4.1 vs. the ECARP cap (excluding Saskatchewan) of 2,300 Ktonnes/yr (e.g., Environment Canada, 1997a). Also, NO_x emissions for this scenario are different from those for the "BASE89" scenario because the supplemental hourly NO_x emissions data for 133 major sources that were used in the "BASE89" scenario were not considered in this scenario.

S3. Scenario "75FCAP"

The scenario name "75FCAP" is an abbreviation of "75%-From-Cap". This very simple rollback scenario is closely based on the "CCUSA2" scenario: after first adjusting the values of some major eastern Canadian SO_2 sources upwards by 395 Ktonnes to match the targets specified under the 1985 ECARP (see Table 3.5 of Environment Canada (1997a)), all Canadian and U.S. SO_2 emissions in the ADOM domain from all source types are simply reduced by 75% (i.e., multiplied by a factor of 0.25). This combination of emission changes results in a net reduction in SO_2 emissions from 1989 levels on the ADOM domain of 82% (Table 4.1). NO_x emissions for this scenario, on the other hand, are unchanged from those in the “CCUSA2” scenario. See AETG (1997) for more details about this scenario (under the name “Scenario 3”).

S4. Scenario “PST2010F”

The name “PST2010F” is an abbreviation of “Post-2010 Scenario F”. This semi-realistic scenario considers further SO_2 emission reductions beyond the “CCUSA2” scenario. In Canada, the additional SO_2 reductions are due to implementation of the Canada-wide Acid Rain Strategy for Post-2000, which requires further reductions in SO_2 emissions from four eastern Canadian provinces: Ontario; Quebec; New Brunswick; and Nova Scotia (Federal/ Provincial/Territorial Ministers of Environment and Energy, 1998). All four provinces have committed to further 50% reductions in SO_2 emissions relative to their 1985 ECARP caps of 885, 500, 175, and 189 Ktonnes/yr, respectively (Environment Canada, 2002a).

Major SO_2 point sources will likely be targetted for much of these additional reductions. In this scenario, total Ontario SO_2 emissions are reduced by 50% but the reductions are proportionately greater for a handful of major point sources. SO_2 emissions from the INCO and Falconbridge smelters in Sudbury are reduced by 50%, SO_2 emissions from the Algoma Iron Ore foundry in Wawa are reduced by 100% (in fact this facility was shut down in 1998), and SO_2 emissions from the three largest Ontario Power Generation (OPG) power plants (Nanticoke Generating Station, Lambton GS, Lakeview GS) are reduced by 35%, 69%, and 100%, respectively (see Table 4.3). SO_2 emissions from all other Ontario sources are reduced by 36%. Quebec SO_2 emissions are reduced by 50%, with the bulk of the reductions (92%) imposed on the Noranda Horne smelter at Rouyn, Quebec. Both New Brunswick and Nova Scotia SO_2 emissions are reduced by 50%, with the largest reductions being made at the Trenton and Lingan Generating Stations in Nova Scotia and at the Dalhousie and Grand Lake Generating Stations in New Brunswick. The other two Canadian provinces that were party to the 1985 ECARP, Manitoba and Newfoundland, are assumed to remain at their 1994 caps (550 and 45 Ktonnes/yr, respectively), and Saskatchewan is assumed to remain at 1985 levels. Finally, emissions from all U.S. SO_2 sources are assumed to be reduced across the board by 50% from the estimated 2010 levels considered in scenario “CCUSA2”.

The net result of these various SO_2 control measures is a reduction in SO_2 emissions on the ADOM domain of 46% relative to the “CCUSA2” scenario and 62% relative to the 1989 base scenario (see Table 4.1). NO_x emissions for this scenario, on the other hand, are unchanged from those in the “CCUSA2” scenario. See ARM Consultants (2002b) for more details about this scenario.

S5. Scenario “NOX2B”

The scenario name “NOX2B” is an abbreviation of “NO_x Scenario 2 Base”. This scenario and scenario “NOX3P” are the most realistic of the 20 ADOM SO_2 scenarios run to date. The starting points for this scenario are the 1995 Canadian national Criteria Air Contaminants (CAC) emissions inventory and the 1996 U.S. national CAC emissions inventory. Next, emission “forecasts” were made using annual growth factors for each SO_2 and NO_x emission source sector for each jurisdiction (Canadian provinces and U.S. states or counties) to construct estimated Canadian and U.S. national future year inventories for the projection year 2020. The growth factors are themselves based on forecasts of a number of socioeconomic indicators and other surrogates or activity factors such as human population, vehicle population, economic output by industrial sector, fuel consumption, and vehicle kilometers travelled.

Lastly, the impacts of various legislated emission-reduction measures were accounted for. For Canada these measures include the 1985 ECARP and new controls on *on-road mobile sources* (Tier 1, NLEV, and Tier II light-duty vehicle emission standards; heavy-duty vehicle NO_x, VOC, and PM emission standards; and low-sulphur fuel for on-road gasoline and diesel vehicles). The enabling act of Parliament for the regulations on on-road mobile sources is the Canadian Environmental Protection Act, 1999 (see Environment Canada, 1999, 2002b, 2003a; and Government of Canada, 2001, 2003). Note that new Canadian regulations for *off-road mobile diesel sources* (e.g., Environment Canada, 2003b) were not considered. For the U.S., reductions were associated with *on-road mobile sources* (Tier 1, NLEV, and Tier II light-duty vehicle emission standards; heavy-duty vehicle NO_x, VOC, and PM emission standards; and low-sulphur fuel for on-road gasoline and diesel vehicles), *off-road mobile diesel sources* (i.e., the “Nonroad Rule”), and *stationary sources* (SO_2 and NO_x emission reductions mandated under Title IV of the

1990 CAAA; 1998 NO_x SIP call reductions [i.e., summertime NO_x caps in 19 eastern states and Washington, D.C.]; and some state-specific emission caps)(see U.S. EPA, 1990, 1998a,b, 2000a,b, 2001a, 2003a,b).

SO_2 emissions for this 2020 scenario on the ADOM domain are only modestly smaller (by 7%) than those for the 2010 "CCUSA2" scenario: i.e., 13,400 vs. 14,385 Ktonnes SO_2/yr (Table 4.1). NO_x emissions for this scenario, on the other hand, are considerably smaller (by 25%; see Table 4.2). Note, however, that these differences in overall SO_2 and NO_x emissions between the "CCUSA2" and "NOX2B" scenarios arise from three sources: (a) differences in the base-year emission inventories considered; (b) differences in the growth projections applied between the inventory base year and the nominal year of the scenario; and (c) differences in assumptions about the control technologies applied and the effectiveness and rates of penetration of these technologies.

In terms of differences in the magnitude of emissions for the two base-year emission inventories considered, SO_2 emissions on the ADOM domain for the 1995/1996 base inventories (i.e., "NOX2B" scenario) were 22% smaller than those for the 1985 emission inventories (i.e., "CCUSA2" scenario) – 15,760 vs. 20,199 Ktonnes SO_2/yr– whereas NO_x emissions on the ADOM domain were 23% *larger* – 17,641 vs. 14,361 Ktonnes NO_2/yr. The difference in SO_2 emissions between the two sets of inventories is not very surprising since the significantly lower SO_2 emissions in the 1995 Canadian and 1996 U.S. emission inventories reflect implementation between 1985 and 1995/96 of SO_2 emission control measures required under the terms of the 1985 ECARP and 1990 U.S. CAAA. Note from Table 4.1 that the total SO_2 emissions value on the ADOM domain for the 1997 "CCUSA1" emission scenario, which accounted for these two legislated programs, was 16,804 Ktonnes/yr, about 6% larger than the 1995/96 value of 15,760 Ktonnes/yr. The 7% difference in SO_2 emissions between the "NOX2B" and "CCUSA2" scenarios is thus due mainly to the difference between the sets of base-year inventories. The combination of increases in SO_2 emissions from some sources due to future population and economic growth and reductions due to various new pieces of legislation affecting SO_2 emissions that have been enacted in Canada and the U.S. since 1990, on the other hand, appear to cancel out.

The large difference in NO_x emissions between the two sets of inventories, on the other hand, was not expected. It appears, on the basis of the NO_x emissions reported in the 1995 Canadian and 1996 U.S. emission inventories, that Canadian and U.S. NO_x emissions were significantly underestimated in the 1985 NAPAP emissions inventory. As a consequence, the NO_x emission reductions reflected in the "NOX2B scenario" due to controls in both Canada and the U.S. on NO_x emissions from motor vehicles and to controls in the U.S. on NO_x emissions from large boilers are actually even larger than comparison to the "CCUSA2" scenario suggests (Table 4.2). Relative to 1995/96 levels, the NO_x emissions considered in scenario "NOX2B" are in fact reduced by 39% vs. the 25% reduction relative to the "CCUSA2" scenario. More details about this scenario are given in the reports by the Canada-United States Air Quality Committee (2004) and WxPrime Corp. (2004).

S6. Scenario "NOX3P"

The name "NOX3P" is an abbreviation of "NO_x Scenario 3 Projected". This scenario is identical to the "NOX2B" scenario except for the inclusion of one additional reduction initiative in Canada and one piece of proposed U.S. legislation: (a) the Canada-wide Acid Rain Strategy for Post-2000; and (b) the 2003 U.S. Clear Skies Initiative. The Canada-wide Acid Rain Strategy for Post-2000 is also modelled in scenario "PST2010F" (S4 scenario). The goal of the proposed 2003 U.S. Clear Skies Initiative is to increase the reductions in SO_2 and NO_x emissions from the U.S. electric power generation sector that were already required under Title IV of the 1990 U.S. CAAA. The same SO_2 "cap and trade" approach administered by the U.S. EPA's Acid Rain Program is to be continued under the Clear Skies Initiative, but the Title IV 2010 cap on the electric power sector of 8.95 Mtons (8.12 Mtonnes) of SO_2 emissions nationally is to be reduced further to 4.5 Mtons/yr (4.08 Mtonnes/yr) in 2010 and to 3 Mtons/yr (2.72 Mtonnes/yr) in 2018. For NO_x emissions from the electric power sector, a "cap and trade" approach would be introduced: NO_x emissions from this sector were 5.1 Mtons/yr (4.63 Mtonnes/yr) in 2000 but are to be capped at 1.7 Mtons/yr (1.54 Mtonnes/yr) in 2018 (see Section A of http://www.epa.gov/clearskies/technical.html).

Given these two additional control programs, SO_2 emissions on the ADOM domain are reduced by 37% relative to the "CCUSA2" scenario (9,067 vs. 14,385 Ktonnes SO_2/yr) and by 55% relative to the 1989 base scenario (see Table 4.1). They are still higher, however, than those for the "PST2010F" scenario (7,724 Ktonnes/yr), but for just the Canadian portion of the ADOM domain, SO_2 emissions are smaller for both the "NOX2B" and "NOX3P" scenarios as compared to the "PST2010F" scenario. The NO_x emissions for this scenario are 32% smaller than those for the "CCUSA2" scenario and 50% smaller than 1995/96 NO_x emissions on the ADOM domain. Note that provincial and state SO_2 and NO_x emission totals for this scenario are provided in Table 7.4 (Chapter 7), and SO_2 emissions assumed for major Canadian point sources are listed in Table 4.3. See the reports by the Canada-United States Air Quality Committee (2004) and WxPrime Corp. (2004) for more details about this scenario.

S7. Scenario "5CCUS2"

The scenario name "5CCUS2" is an abbreviation of "50% Reduction from Scenario CCUSA2". That is, this scenario is simply a 50% rollback of scenario "CCUSA2" SO_2 emissions in both Canada and the United States. This scenario was considered in the 1997 *Assessment*; see Environment Canada (1997a) for more details. It was also discussed in the AETG (1997) report under the name "Scenario 2(a)".

S8. Scenario "5CONLY"

The name "5CONLY" is an abbreviation of "50% Reduction for Canada Only". This simple scenario is very similar to the "CCUSA2" scenario; the only difference is that Canadian SO_2 emissions in the eastern-Canada Sulphur Oxide Management Area (or SOMA) are rolled back by 50% from the provincial caps mandated under the 1985 ECARP. The SOMA for southeastern Canada was instituted under the terms of the 1994 UN Economic Commission for Europe Second Sulphur Protocol (or *The 1994 Oslo Protocol on Further Reductions of Sulphur Emissions*) so as to target emission reductions geographically in order to achieve maximum environmental benefit. Such an approach is valuable for a large, sparsely populated country like Canada. The SOMA for southeastern Canada is described in Environment Canada (1998b, 2004b) and its location is shown (approximately) on the ADOM domain in Figure 4.4a. Relative to scenario "CCUSA2", SO_2 emissions in this scenario are reduced by 32% in the Canadian portion of the ADOM domain (recall the 395 Ktonnes/yr overcompliance considered in scenario "CCUSA2") but only by 4% for the entire domain. On the other hand, as discussed in Section 4.5.2.1.4, because of the close similarity of the SO_2 emission fields for this scenario and scenario "CCUSA2", comparing ADOM results for this scenario relative to those for scenario "CCUSA2" shows the impact of emissions in the Canadian SOMA. The spatial distribution of SO_2 emission reductions for this scenario is shown on the ADOM grid in Figure 4.6a. Note that there are no reductions in Manitoba or Newfoundland as these provinces lie outside of the SOMA. See AETG (1997) for more information about this scenario, where it is referred to as "Scenario 2(b)". (Note that this earlier report mentions a 50% reduction in SO_2 emissions for "eastern Canada" for this scenario but does not mention that these reductions were confined to the SOMA.) Also, as discussed in Section 4.5.2.1.2.N2, this SO_2 control scenario was run simultaneously with the "NOXSCEN" NOx/VOC emission control scenario (in the sense that emissions of all three pollutants were modified in a single scenario).

S9. Scenario "T5CUS2"

The scenario name "T5CUS2" is an abbreviation of "Targetted 50% Reduction from Scenario CCUSA2". This scenario is very similar to scenario "5CCUS2" except that the 50% rollbacks in SO_2 emissions from the "CCUSA2" scenario are restricted to the provinces of Ontario, Quebec, New Brunswick, Nova Scotia, and Prince Edward Island (P.E.I), and to the 20 northeastern U.S. states shown in Figure 4.4b. SO_2 emissions from the provinces of Saskatchewan, Manitoba, and Newfoundland and Labrador and from the southern and midwestern U.S. states remain at the same levels as in the "CCUSA2" scenario. The goal of this scenario was to see how much impact emission reductions from more distant sources would have on sensitive areas in southern Ontario, southern Quebec, New Brunswick, and Nova Scotia (see Section 4.5.2.1.4). Relative to scenario "CCUSA2", Canadian SO_2 emissions in the ADOM domain for this scenario are reduced by 34% and U.S. emissions in the ADOM domain are reduced by 29% (cf. Table 4.1). The spatial distribution of SO_2 emission reductions for this scenario is shown on the ADOM grid in Figure 4.6b. It is clear from this figure that no reductions have been made in the U.S. southeastern or midwestern states.

S10. Scenario "PST2010A"

The name "PST2010A" is an abbreviation of "Post-2010 Scenario A". It is similar in design to scenario "PST2010F" described above (S4 scenario). In scenario "PST2010A" the province of Ontario is assumed to reduce annual SO_2 emissions by a further 50% from the 1985 ECARP cap (885 to 443 Ktonnes SO_2/yr), the province of Quebec by a further 45% (500 to 275 Ktonnes/yr), and New Brunswick and Nova Scotia/PEI each by a further 25% (175 to 131 and 194 to 146 Ktonnes/yr, respectively). The United States is assumed to reduce its annual SO_2 emissions by a further 55% from 2010 levels (12,446 to 5,578 Ktonnes/yr). All of these reductions are assumed to be linear rollbacks. The geographic distribution of the reductions relative to scenario "CCUSA2" is shown in Figure 4.6c. Unlike the two previous scenarios, SO_2 emission reductions are specified over most of eastern and central North America. The SO_2 emissions assumed for major Canadian point sources are listed in Table 4.3. See ARM Consultants (2000) for more details about this scenario.

S11. Scenario "PST2010a"

This scenario is very similar to scenario "PST2010A". The only difference is that SO_2 emissions from Quebec sources are reduced by 34% as compared to 45% in scenario "PST2010A". As a result, Canadian SO_2 emissions on the ADOM domain for this scenario are only 3% higher than for the "PST2010A" scenario and domain-total SO_2 emissions are only 1% higher. However, as described in Section 4.5.2.1.4, comparing ADOM results for this scenario relative to those for scenario "CCUSA2" shows the impact of Quebec SO_2 emissions on the rest of eastern North America (see Figure 4.18). More details about this scenario are given in ARM Consultants (2000).

S12. Scenario "PST2010B"

This scenario is very similar to the "PST2010A" scenario. The only difference is that U.S. SO_2 emissions are reduced to 40% of 2010 levels, that is, a 60% reduction, as compared to the 55% reduction considered in scenario "PST2010A". Thus, as discussed in Section 4.5.2.1.4, comparing ADOM results for this scenario shows the impact of a uniform reduction in U.S. SO_2 emissions on the ADOM domain (see Figure 4.19). More details about this scenario are given in ARM Consultants (2000).

S13. Scenario "PST2010C"

The name "PST2010C" is an abbreviation of "Post-2010 Scenario C" This scenario is more complicated than scenario "PST2010A" and more like scenario "PST2010F" (S4 scenario). Instead of simple rollbacks, the SO_2 emission reductions in Ontario and Quebec are assumed to be targetted by source sector and/or facility and hence are non-uniform geographically. In Ontario, total provincial SO_2 emission reductions are again 50% from the 1985 ECARP cap, but several major point sources are assigned separate reductions: the INCO and Falconbridge facilities in Sudbury are reduced by 75% from current caps (from 365 to 91 Ktonnes SO_2/yr); the OPG Lambton, Nanticoke, and Lakeview coal-fired generating stations are each reduced by 50% from current caps (from 175 to 88 Ktonnes/yr), and the Algoma Iron Ore foundry in Wawa is reduced from a cap of 125 Ktonnes/yr to zero. To balance the reduction in these six sources from a total of 665 Ktonnes/yr to 179 Ktonnes/yr, all other Ontario SO_2 sources are increased uniformly by 20% from 220 to 264 Ktonnes/yr, for an overall emissions total for the province of 443 Ktonnes/yr, the same as scenario "PST2010A". In Quebec, the Noranda Horne smelter in Rouyn is reduced from a cap of 272 Ktonnes/yr to 43 Ktonnes/yr, a 100 Ktonne/yr reduction from 1997 levels and a 229 Ktonne/yr (84.2%) reduction from the 1985 ECARP cap, while all other sources in the province are reduced uniformly by 9.2% (from 228 to 207 Ktonnes/yr), for an overall percent reduction of 50% (or 250 Ktonnes/yr) from the 1985 ECARP cap. All other Canadian SO_2 emissions are treated as in scenario "PST2010A". Finally, U.S. emissions are reduced by 50% from 2010 levels, the same as in scenario "PST2010F" but less than scenarios "PST2010A" and "PST2010B". The SO_2 emissions assumed for major Canadian point sources are listed in Table 4.3. See ARM Consultants (2000) for more details about this scenario.

S14. Scenario "PST2010D"

Scenario "PST2010D" builds on scenario "PST2010C". The reductions in Ontario and Quebec are the same as in scenario "PST2010C", that is, targetted by source sector and non-uniform geographically, but some source-specific reductions are also applied in New Brunswick and Nova

Scotia. In New Brunswick, an overall reduction of 30% from the 1985 ECARP cap is made (175 to 122 Ktonnes SO_2/yr) as compared to the 25% reduction applied in the "PST2010A", "PST2010B", and "PST2010C" scenarios (175 to 131 Ktonnes/yr), for an additional reduction of 9 Ktonnes/yr. In addition, the emissions levels before reductions assumed for four New Brunswick Power thermal generating stations are changed; in effect decreasing power-plant emissions in the north of the province and increasing them in the south (see Table 4.3). In Nova Scotia the same overall reduction of 25% applied in the "PST2010A", "PST2010B", and "PST2010C"scenarios is again assumed, but the emissions levels assumed for four Nova Scotia Power Inc. thermal generating stations are also changed, again decreasing power-plant emissions in the north of the province and increasing them in the south (see Table 4.3). The reason for these source-specific changes in both New Brunswick and Nova Scotia is to reflect the current relative distribution of power-plant SO_2 emissions in these two provinces. The relative SO_2 emissions distribution for these facilities used in scenarios "PST2010A", "PST2010B", and "PST2010C" was based on emissions levels contained in the 1985 National Acid Precipitation Assessment Program (NAPAP) modeler's emissions inventory (Saeger et al., 1989).

In the United States, geographically-targetted emission reductions are also implemented. SO_2 emissions from

Table 4.3. SO_2 emission values (Ktonnes SO_2/yr) assumed for major Canadian point sources in 11 ADOM future-year emission control scenarios.

ADOM Record	Source	CCUSA2	5CONLY	PST2010A, PST2010B	PST2010C	PST2010D, PST2010E	PST2010F	HLFO	NOX2B	NOX3P
3419	Trenton GS, NS	21.2	21.2	32.1	32.1	18.8	15.0	21.2	6.0	4.2
3420	Tuft's Cove GS, NS	0.0	0.0	0.0	0.0	15.0	0.0	0	0.0	0.0
3421	Tuft's Cove GS, NS	0.0	0.0	0.0	0.0	3.8	0.0	0	0.0	0.0
3422	Pt. Tupper GS, NS	3.2	7.0	10.6	10.6	15.0	10.0	3.2	0.9	0.6
3423	Lingan GS, NS	75.2	42.0	63.6	63.6	56.3	47.0	75.2	21.1	14.7
3424	Grand Lake GS, NB	28.1	17.3	27.0	27.0	20.0	12.4	28.1	11.3	11.3
3425	Courtenay Bay GS, NB	3.9	1.9	3.0	3.0	6.0	3.7	0	1.6	1.6
3426	Dalhousie GS, NB	11.5	10.9	17.0	17.0	5.6	1.5	0.6	4.6	4.6
3427	Dalhousie GS, NB	38.7	19.3	30.2	30.2	1.4	2.8	0.6	15.5	15.5
3428	Coleson Cove GS, NB	23.0	14.0	21.9	21.9	50.0	30.9	0	9.2	9.2
3429	Noranda Gaspé, Murdochville, QU	44.9	32.7	32.8	49.2	49.2	49.2	44.9	44.9	41.6
3430	Noranda Horne, Rouyn, QU	105.2	120.2	120.9	38.0	38.0	38.0	105.2	105.2	97.4
3431	Noranda Horne, Rouyn, QU	14.5	15.9	16.0	5.0	5.0	5.0	14.5	14.5	13.4
3432	INCO, Copper Cliff, ON	0.1	0.0	0.0	0.0	0.0	0.0	0.1	0.1	0.0
3433	INCO, Copper Cliff, ON	264.4	132.2	125.4	66.1	66.1	132.2	264.4	246.1	170.7
3434	Falconbridge, Sudbury, ON	74.8	49.9	47.3	24.9	24.9	49.9	74.8	69.7	48.3
3435	Algoma Iron Ore, Wawa, ON	0.5	0.3	0.2	0.0	0.0	0.0	0.5	0.5	0.3
3436	Algoma Iron Ore, Wawa, ON	59.4	62.3	59.1	0.0	0.0	0.0	59.4	55.3	38.3
3437	Lakeview GS, Toronto, ON	15.8	11.3	10.8	11.3	11.3	0.0	15.8	14.7	10.2
3438	Lakeview GS, Toronto, ON	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
3439	Lambton GS, Sarnia, ON	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
3440	Lambton GS, Sarnia, ON	42.7	31.3	29.7	31.3	31.3	19.4	42.7	39.8	27.6
3441	Nanticoke GS, Nanticoke, ON	61.1	44.9	42.6	44.9	44.9	57.7	61.1	56.9	39.5
3442	Nanticoke GS, Nanticoke, ON	0.1	0.0	0.0	0.0	0.0	0.1	0.1	0.1	0.1
3443	INCO, Thompson, MB	219.5	219.5	268.3	268.3	268.3	268.3	219.5	218.6	218.6
3444	Hudson Bay M & S, Flin Flon, MB	219.5	219.5	268.3	268.3	268.3	268.3	219.5	218.6	218.6
	Total Emissions	**1327.4**	**1073.8**	**1227.2**	**1013.1**	**999.3**	**1011.4**	**1251.6**	**1155.0**	**986.5**

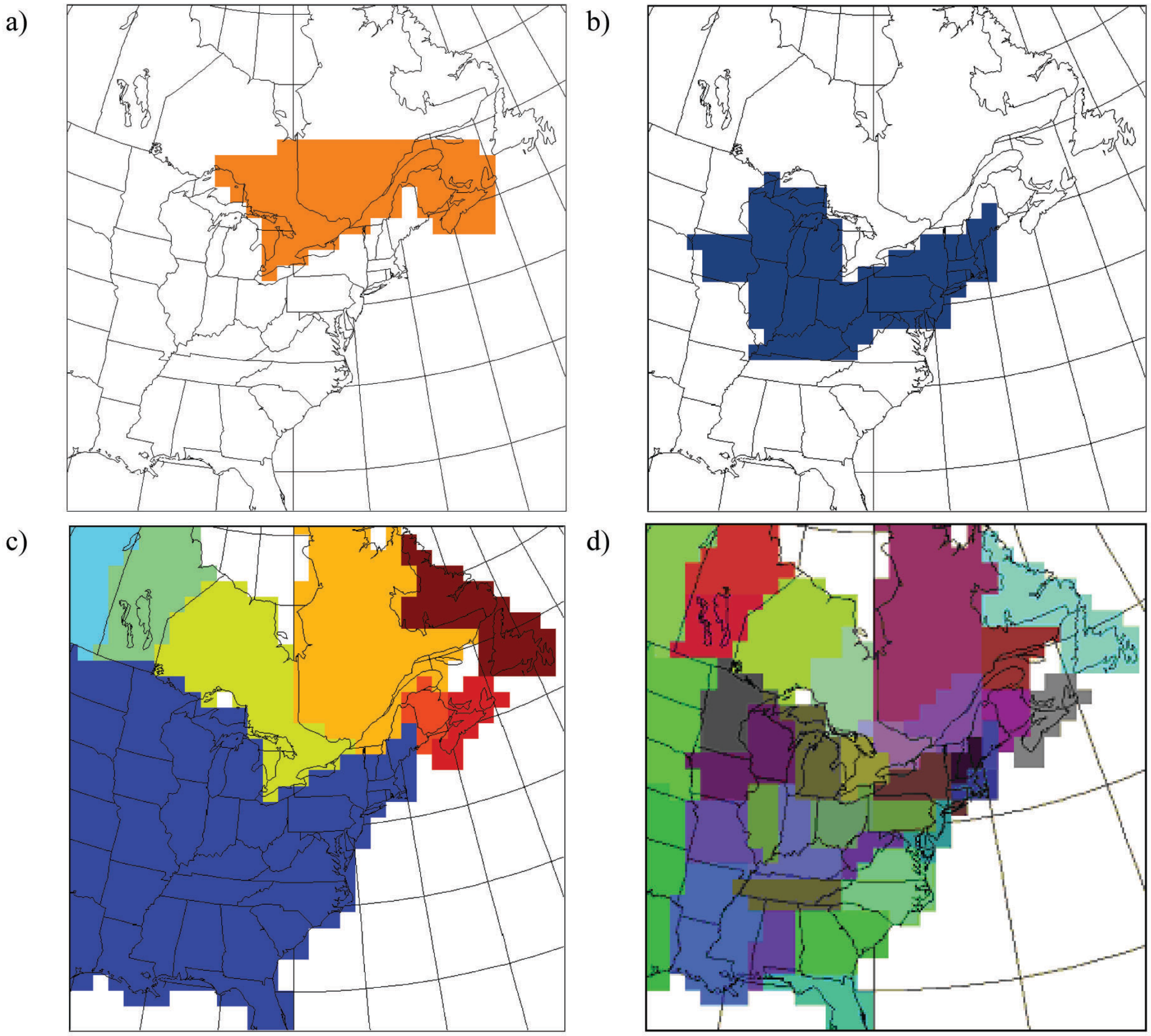


Figure 4.4: Jurisdictional masks used for scaling base-case emissions in implementing some ADOM emission-control scenarios: (a) Canadian SOMA region [scenario "5CONLY"]; (b) 20 northeastern U.S. states [scenarios "T5CUS2", "PST2010D"]; (c) eastern Canadian provinces [scenarios "PST2010A" to "PST2010F", "HLFO"]; and (d) eastern Canadian provinces and U.S. state and multi-state source regions [scenarios "NOX2B", "NOX3P"].

the 20 northeastern U.S. states (plus the District of Columbia) shown in Figure 4.4b are reduced by 60%, but emissions in the other U.S. states located in the ADOM domain are left at their 2010 levels. Interestingly, even though the size of the percentage emission reduction is larger in this scenario than in scenario "PST2010C" (60% vs. 50%), because it is restricted in this scenario to just the northeastern region, total U.S. emissions in the ADOM domain are about 1,900 Ktonnes/yr larger in this scenario than in scenario "PST2010C" (see Table 4.1). Note too that this same set of northeastern U.S. states was considered in another geographically-targetted ADOM emissions scenario, "T5CUS2" (S9 scenario). See ARM Consultants (2000) for more details about this scenario.

S15. Scenario "PST2010E"

The name "PST2010E" is an abbreviation of "Post-2010 Scenario E". This scenario is the same as scenario "PST2010D", except that U.S. emissions are reduced uniformly by 60% for all states (as was done in scenario "PST2010B") rather than just for the 20 northeastern

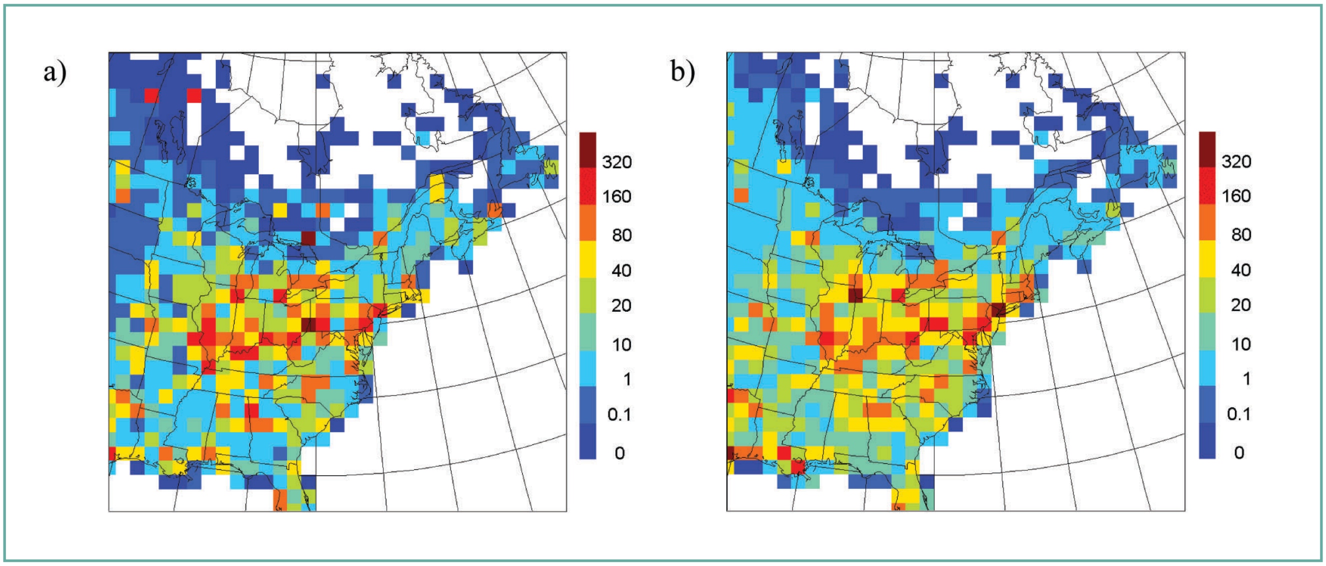


Figure 4.5: Gridded annual emissions (kilotonnes/year) of (a) SO_2 and (b) NO_x (as NO_2) for ADOM scenario "CCUSA2".

states. As a result, the reduction in U.S. SO_2 emissions in this scenario relative to scenario "PST2010D" is about 3,100 Ktonnes/yr, a value about 50% larger than the 1985 ECARP SO_2 emissions cap for all of eastern Canada and over twice the Post-2000 Canada-wide Acid Rain Strategy cap of 1475 Ktonnes/yr for eastern Canada. As discussed in Section 4.5.2.1.4, by comparing ADOM results for this scenario vs. those for scenario "PST2010D", it is then possible to estimate the influence on eastern Canada of SO_2 emissions from only the southern and midwestern U.S. states (see Figure 4.20). More details about this scenario are given in ARM Consultants (2000).

S16. Scenario "HLFO"

The scenario name "HLFO" is an abbreviation of "Heavy/Light Fuel Oil". This scenario was designed to investigate the impact of introducing stricter European sulphur-content limits on heavy fuel oils (HFOs) and light fuel oils consumed in Canada. Based on Canadian fuel-oil statistics supplied by Statistics Canada, it was estimated that combustion of reduced-sulphur-content fuel oils would reduce SO_2 emissions in the Maritimes, Quebec, Ontario, and the Prairie provinces by 111, 28, 34, and 0 Ktonnes/yr, respectively. In the Maritimes, New Brunswick accounts for 56% of the reduction, Nova Scotia for 20%, Prince Edward Island for 2%, and Newfoundland and Labrador for 22%. Part of the reason for the large impact of this control measure in the Maritimes is that four major SO_2 point sources in the Maritimes – three power plants in New Brunswick and one power plant in Nova Scotia – use HFO as a fuel, unlike Quebec and Ontario, where no major SO_2 point sources use HFO.

The "HLFO" scenario was implemented starting from the emission files for the "CCUSA2" scenario, by reducing SO_2 emissions from the four Maritime point sources that burn HFO (see Table 4.3) and then scaling back SO_2 area sources in Ontario, Quebec, and the four Maritime provinces to account for the rest. The provincial mask used to scale the area sources is shown in Figure 4.4c. The geographic distribution of the reductions is shown in Figure 4.6d. The overall reduction in Canadian SO_2 emissions on the ADOM domain relative to the "CCUSA2" scenario is 9%, while U.S. SO_2 emissions are unchanged. The predicted atmospheric impact of these sector-specific SO_2 emission reductions is discussed in Section 4.5.2.1.4 (see Figure 4.17). Additional details about this scenario are given in ARM Consultants (2002a) and Environment Canada (2003c).

4.5.2.1.2 Descriptions of NO_X emission control scenarios

Emissions of NO and NO_2, two other major acidifying gases that together are commonly referred to as "NO_X", have not changed by much at all in eastern North America over the past two decades. This means that as SO_2 emissions are reduced in future years, the acid

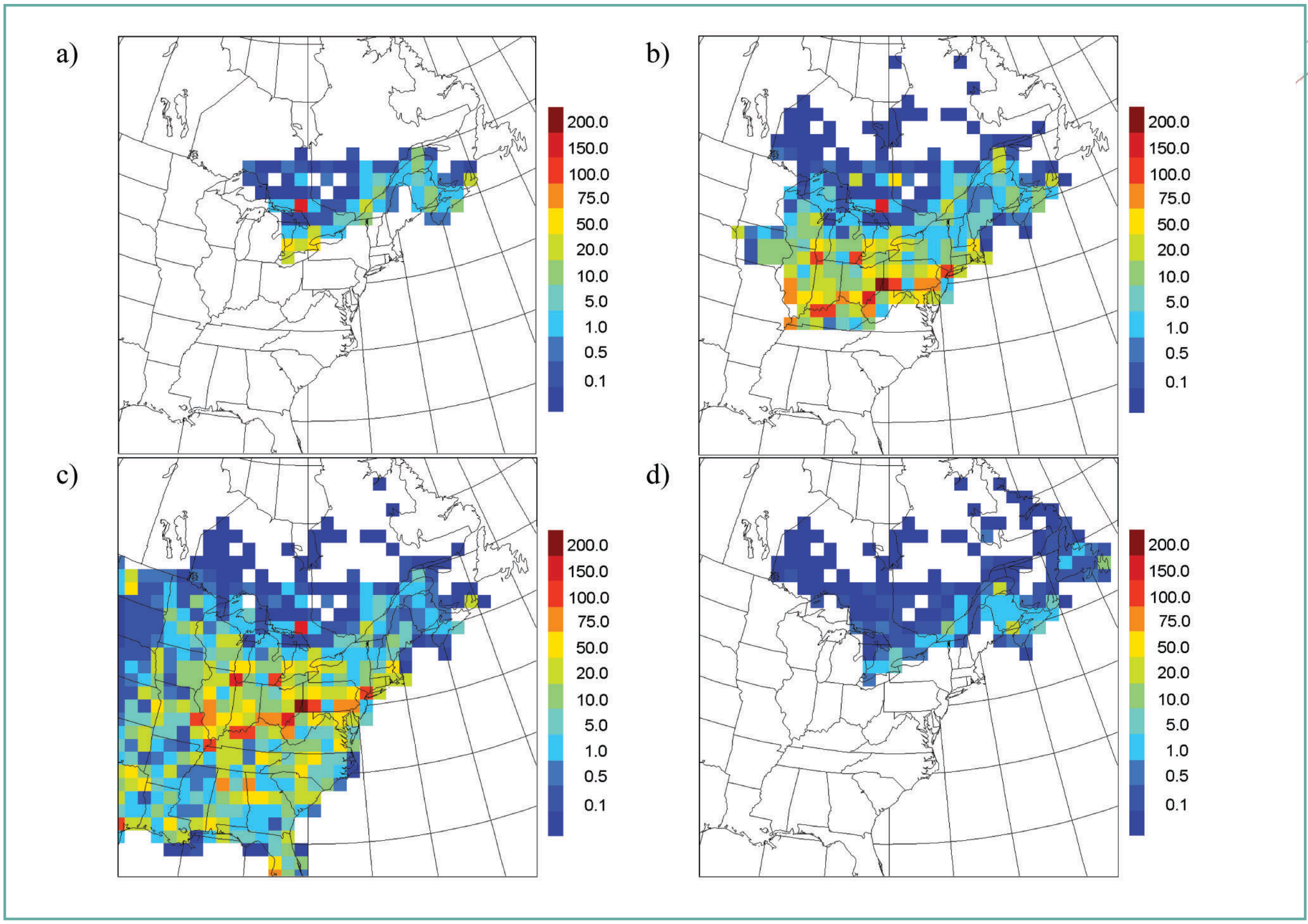


Figure 4.6: Gridded SO_2 emissions changes (kilotonnes SO_2/year) for some other ADOM scenarios vs. scenario "CCUSA2": (a) 5CONLY; (b) T5CUS2; (c) PST2010A; (d) HLFO.

deposition impacts of NO_x emissions will become relatively more important. It is thus important to consider the acid deposition impact of reductions in NO_x emissions as well as SO_2 emissions. As listed in Table 4.2, four NO_x emission-control scenarios have been considered to date with ADOM. These four scenarios have the following characteristics.

N1. Scenario "CCUSA2"

This scenario is a "pure" SO_2 control scenario as described in the previous section, but it served as the starting point for the three ADOM NO_x emission control scenarios. NO_x emissions in this scenario are based on the 1985 Canadian and U.S. national CAC emission inventories (see Saeger et al., 1989). The spatial distribution of NO_x emissions for this scenario on the ADOM grid is shown in Figure 4.5b.

N2. Scenario "NOXSCEN"

The scenario name "NOXSCEN" is an abbreviation of "NO_x Emission Scenario", reflecting the fact that this scenario was the first NO_x emission control scenario to be run with ADOM. This relatively complicated, geographically-targetted rollback scenario was implemented by applying some NO_x emission reductions to the "CCUSA2" scenario. In Canada, NO_x emissions from all sources are reduced by 45% in the Ontario portion of the Windsor-Quebec City corridor and by 30% in the greater Montreal region. In the U.S., point-source NO_x emissions are assumed to be reduced by 60% and mobile-source NO_x emissions are assumed to be reduced by 30% in the 20 northeastern U.S. states shown in Figure 4.4b. Overall, NO_x emissions in the ADOM domain are reduced by 21% from the "CCUSA2" scenario to 11,330 Ktonnes NO_2/yr (Table 4.2). The spatial distribution of NO_x emission reductions for this scenario is shown on the ADOM grid in Figure 4.7a. Note that SO_2 emission reductions were also considered for this scenario, which appears in Table 4.1 as scenario "5CONLY" (see Section 4.5.2.1.1.S8). More details about this scenario can be found in AETG (1997) under the name "Scenario 4".

N3. Scenario "NOX2B"

Most aspects of this realistic 2020 bi-pollutant emission control scenario were described in the previous section (see S5 scenario). Relative to the 2010 "CCUSA2" scenario, NO_x emissions for this scenario on the ADOM domain are reduced by 25% (10,823 vs. 14,361 Ktonnes NO_2/yr) in combination with the SO_2 emission reduction of 7%. Relative to the 1995/96 base inventories, NO_x emissions for this scenario are reduced by 39% (10,823 vs. 17,641 Ktonnes NO_2/yr). A large fraction of the reductions in NO_x emissions are due to control measures targetting on-road and off-road mobile sources. The spatial distribution of NO_x emission reductions for this scenario is shown on the ADOM grid in Figure 4.7b. See the Canada-United States Air Quality Committee (2004) and WxPrime Corp. (2004) reports for more details about this scenario.

N4. Scenario "NOX3P"

Most aspects of this realistic 2020 bi-pollutant emission control scenario were described in the previous section (see S6 scenario). Relative to the 2010 "CCUSA2" scenario, NO_x emissions for this scenario on the ADOM domain are reduced by 38% (8,891 vs. 14,361 Ktonnes NO_2/yr) in combination with the SO_2 emission reduction of 37%. Relative to the 1995/96 base inventories, NO_x emissions for this scenario are reduced by 50% (8,891 vs. 17,641 Ktonnes NO_2/yr). The additional NO_x emission reductions in this scenario relative to the "NOX2B" scenario are due primarily to reductions in NO_x

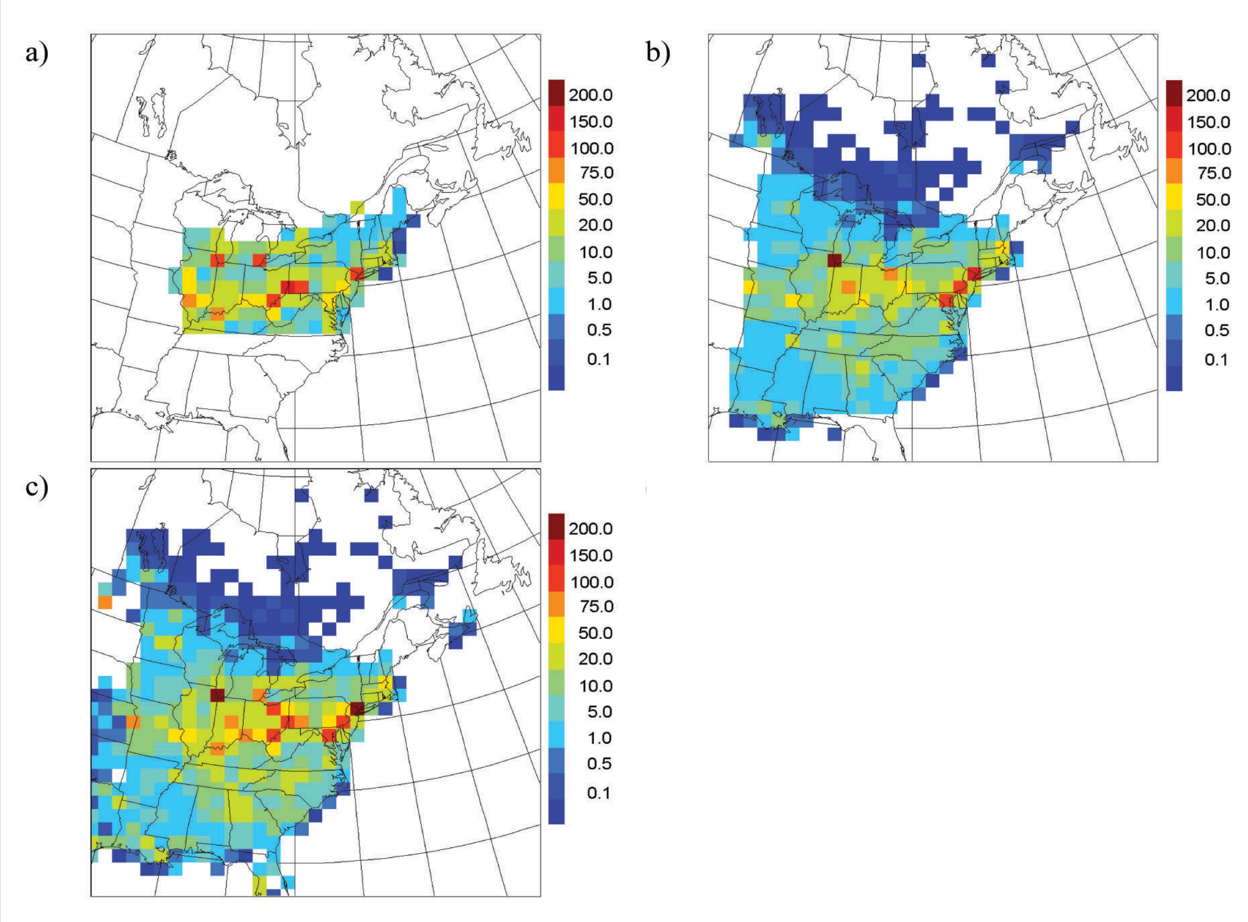


Figure 4.7: Gridded NO_x emissions changes (kilotonnes NO_2/year) for three other ADOM scenarios vs. scenario "CCUSA2": (a) NOXSCEN; (b) NOX2B; and (c) NOX3P.

emissions from U.S. power plants required under the 2003 U.S. EPA Clear Skies Initiative proposal. The spatial distribution of NO_x emission reductions for this scenario is shown on the ADOM grid in Figure 4.7c. See the Canada-United States Air Quality Committee (2004) and WxPrime Corp. (2004) reports for more details about this scenario.

4.5.2.1.3 Results of key ADOM simulations

A total of 17 different ADOM emission control scenarios were described in the two previous subsections. In order to keep the presentation, analysis, and interpretation of ADOM model results to a manageable size, only selected results from the six key SO_2 scenarios described in Section 4.5.2.1.1 and from one additional NO_x emission control scenario will be presented and compared in this section. A number of additional analyses for these and other ADOM scenarios related to source-region contributions and "pseudo-scenarios" follow in the next section.

The seven scenarios considered in this section span the entire SO_2 and NO_x emission range of the scenarios considered with ADOM, so that while other scenarios differ in detail, these scenarios represent the range of atmospheric changes predicted to occur in response to the full range of modelled emission changes. Results will be presented for three sulphur-species concentration and deposition fields, three oxidized-nitrogen-species concentration and deposition fields, and one combined field.

Sulphur Species Results for Key Scenarios

Annual SO_2 air concentration

Plots of predicted annual near-surface SO_2 air concentration patterns are shown for the six key SO_2 emission control scenarios in Figure 4.8. As SO_2 is a primary (i.e., directly emitted) pollutant, its concentration is highest near major sources. For example, in Figure 4.8a, areas of elevated SO_2 ambient air concentrations can be seen in the vicinity of isolated major SO_2 sources at Flin Flon and Thompson, Manitoba, Wawa and Sudbury, Ontario, and Rouyn, Quebec, as well as the Ohio Valley in the U.S. and major urban centres such as Chicago, Detroit, Cleveland, Pittsburgh, Toronto, and Montreal. These same sources and source regions are evident in the gridded SO_2 emissions field shown in Figure 4.5a for the "CCUSA2" scenario. Note that as discussed in Section 4.4.5.2, predicted annual SO_2 (and SO_4^{2-}) air concentrations are not available for northeastern New Brunswick and the Gaspé, Prince Edward Island, Cape Breton, Newfoundland and Labrador, and eastern and northern Quebec due to a lack of available measurement data needed by the episode aggregation technique.

The scenarios in Figure 4.8 have been ordered by domain-total SO_2 emissions in descending order (cf. Table 4.1). As a consequence, maximum annual SO_2 ambient concentrations decrease from a value of 15.7 $\mu g/m^3$ in Figure 4.8a, the "BASE89" scenario with SO_2 emissions before implementation of the first generation of SO_2 emission reductions, to a value of 10.9 $\mu g/m^3$ in Figure 4.8d, the realistic "NOX3P" 2020 scenario, to a value of 1.6 $\mu g/m^3$ in Figure 4.8f, the hypothetical "75FCAP" scenario. At the domain level, annual SO_2 emissions for the "75FCAP" scenario are roughly a factor of six smaller than those considered for the "BASE89" scenario.

Annual SO_4^{2-} air concentration

Since SO_4^{2-} is mainly a secondary pollutant resulting from chemical transformations of SO_2 in the atmosphere during transport and mixing, the plots of predicted annual near-surface SO_4^{2-} air concentration fields shown in Figure 4.9 are smoother than the SO_2 plots shown in Figure 4.8. The overall structure of the SO_4^{2-} air concentration fields reflects a regional-scale "averaging" of SO_2 emissions by dispersion and chemical transformation, so that the largest SO_4^{2-} air concentrations are predicted to occur in the Ohio Valley region of the United States, where there is a cluster of major SO_2 sources (see Figure 4.5a). Maximum annual SO_4^{2-} ambient concentrations are predicted to decline from 5.4 $\mu g/m^3$ for the "BASE89" scenario (Figure 4.9a) to 2.9 $\mu g/m^3$ for the "NOX3P" scenario (Figure 4.9d) to 1.5 $\mu g/m^3$ for the "75FCAP" scenario (Figure 4.9f). These predicted decreases in ambient SO_4^{2-} air concentrations will also result in a decrease in ambient $PM_{2.5}$ concentrations, since SO_4^{2-} is known to be an important constituent of $PM_{2.5}$ in eastern North America (e.g., Brook et al., 1997; Vet et al., 2001; NARSTO, 2004).

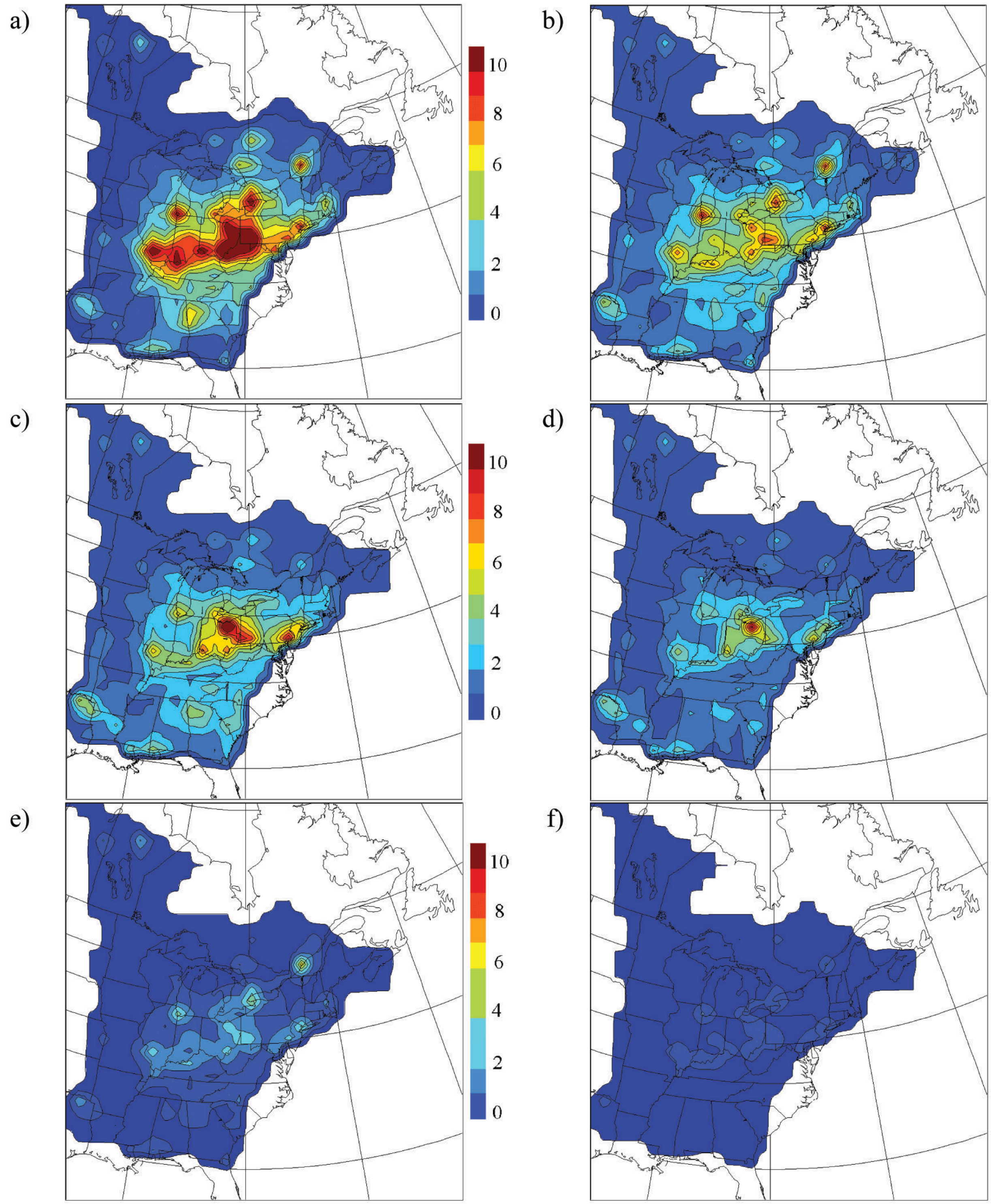


Figure 4.8: Plots of ambient annual near-surface SO_2 air-concentration patterns in units of μg SO_2/m^3 for ADOM scenarios (a) BASE89, (b) CCUSA2, (c) NOX2B, (d) NOX3P, (e) PST2010F, and (f) 75FCAP.

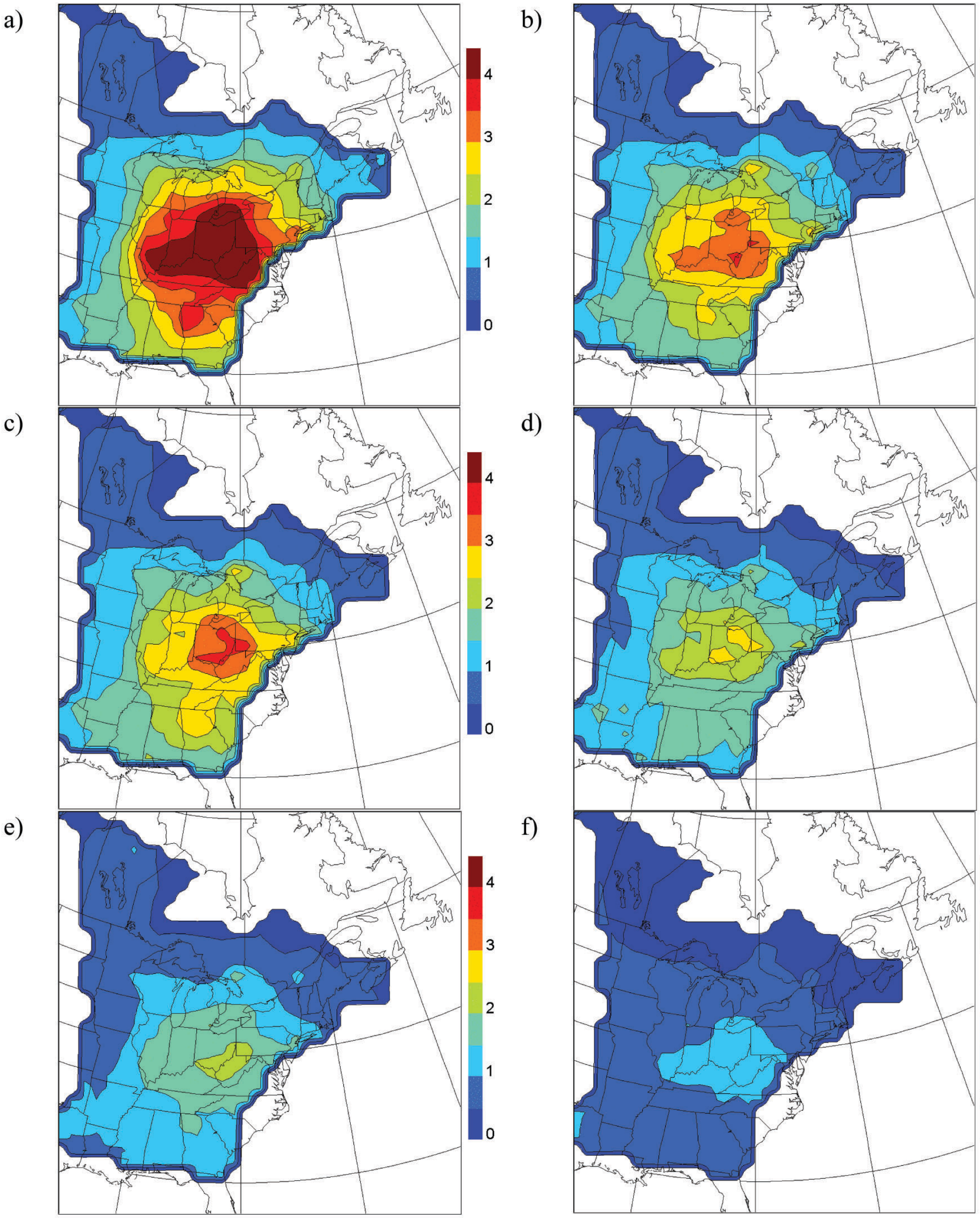


Figure 4.9: Plots of ambient annual near-surface SO_4^{2-} air-concentration patterns in units of $\mu g\ SO_4^{2-}/m^3$ for ADOM scenarios (a) BASE89, (b) CCUSA2, (c) NOX2B, (d) NOX3P, (e) PST2010F, and (f) 75FCAP.

Annual SO_4^{2-} wet deposition

Figure 4.10 shows plots of calibrated annual SO_4^{2-} wet deposition patterns for the six key SO_2 scenarios. Again, the scenarios have been ordered by domain-total SO_2 emissions in descending order, and the SO_4^{2-} wet deposition fields respond accordingly. For example, the 20 kg/ha/yr isopleth, which corresponds to the target load for eastern Canada that was set in the 1980s, encloses much of southern Ontario and southern Quebec for the "BASE89" scenario (Figure 4.10a) but has vanished for the SO_2 emission reductions associated with the "NOX3P" scenario scenario (Figure 4.10d), which is based on the most likely set of SO_2 and NO_x emissions for 2020. The 10 kg/ha/yr isopleth can also be seen to retreat westward across the Maritimes for this set of six scenarios. And maximum annual SO_4^{2-} wet deposition is reduced from 38 kg SO_4^{2-}/ha/yr in the "BASE89" scenario (Figure 4.10a) to 19 kg/ha/yr in the "NOX3P" scenario (Figure 4.10d) to 11 kg/ha/yr in the "75FCAP" scenario (Figure 4.10f).

As expected, the overall patterns in this figure are similar to the corresponding SO_4^{2-} air concentration patterns in Figure 4.9. The agreement, however, is less good in the southwestern quadrant, but in considering Figure 4.9, it should be borne in mind that the ADOM predictions of annual SO_4^{2-} air concentrations obtained through episode aggregation were found to be biased low for the southern U.S. but were unbiased for eastern Canada (Environment Canada, 1997a, p. 2-171).

SO_4^{2-} deposition critical load exceedance

Figure 4.11 is based upon Figure 4.10. It shows the SO_4^{2-} wet deposition critical load exceedance fields or critical load "gaps" calculated for eastern Canada for the six key ADOM SO_2 scenarios. The SO_4^{2-} wet deposition critical load field for eastern Canada was developed during the 1990 *Assessment* (RMCC, 1990), but comparable critical load values are not available for the U.S. Those regions of eastern Canada predicted to be in exceedance for each emissions scenario have SO_4^{2-} total depositions greater than can be neutralized by natural weathering processes. Negative critical load exceedance values indicate atmospheric deposition levels lower than the local critical load value, that is, sustainable acid deposition levels.

For the "BASE89" scenario (Figure 4.11a), much of eastern Canada can be seen to be significantly in exceedance of the SO_4^{2-} wet deposition critical loads. The increasingly large reductions in SO_2 emissions in the other five key scenarios are reflected in this figure either by reductions in the size of the *area* of the critical load gaps (i.e., SO_4^{2-} wet deposition is reduced to levels below the critical load value) or by reductions in the size of the critical load gaps themselves. For example, for the "NOX3P" scenario, SO_4^{2-} wet deposition levels in both the Maritimes and in southwestern Ontario are predicted to fall below critical load values, although a band of critical load exceedances is predicted to remain across central Ontario and central Quebec.

As discussed in Environment Canada (1997a), the size of the area of eastern Canada in exceedance of critical load is one possible metric for comparing different scenarios quantitatively. Values of this quantity are summarized in Table 4.4 for all 20 ADOM SO_2 emissions scenarios that have been run to date. The table entries corresponding to the six key ADOM SO_2 emission control scenarios are highlighted. Consistent with Figure 4.11, the size of the area in exceedance of critical load decreases monotonically across these six scenarios. The impact of the first generation of SO_2 emission controls can be seen in the decrease in exceedance area from a value of 1.14×10^6 km^2 for scenario "BASE89" to a value of 0.79×10^6 km^2 for scenario "CCUSA2". For the "NOX3P" scenario, Nova Scotia and Newfoundland and Labrador are predicted to have achieved critical load and New Brunswick has only a very small area above critical load; the exceedance area for this scenario has decreased to 0.33×10^6 km^2. Table 4.4 is also useful for quantifying the differences between very similar scenarios. For example, scenarios "PST2010a" and PST2010A" differ only by 54 Ktonnes/yr of SO_2 emissions from Quebec, but Table 4.4 shows a corresponding difference of 10,000 km^2 in exceedance area.

It should be noted, however, that these predictions of improvements in critical load exceedances may be too optimistic for two reasons. First, as discussed in the 1990 *Assessment* and 1997 *Assessment*, the critical load field used for eastern Canada is defined in terms of SO_4^{2-} *total* deposition, that is, the sum of SO_4^{2-} wet and dry deposition. However, due to a lack of SO_4^{2-} dry deposition measurement data at the time, SO_4^{2-} dry deposition was assumed to contribute to total deposition at levels equal

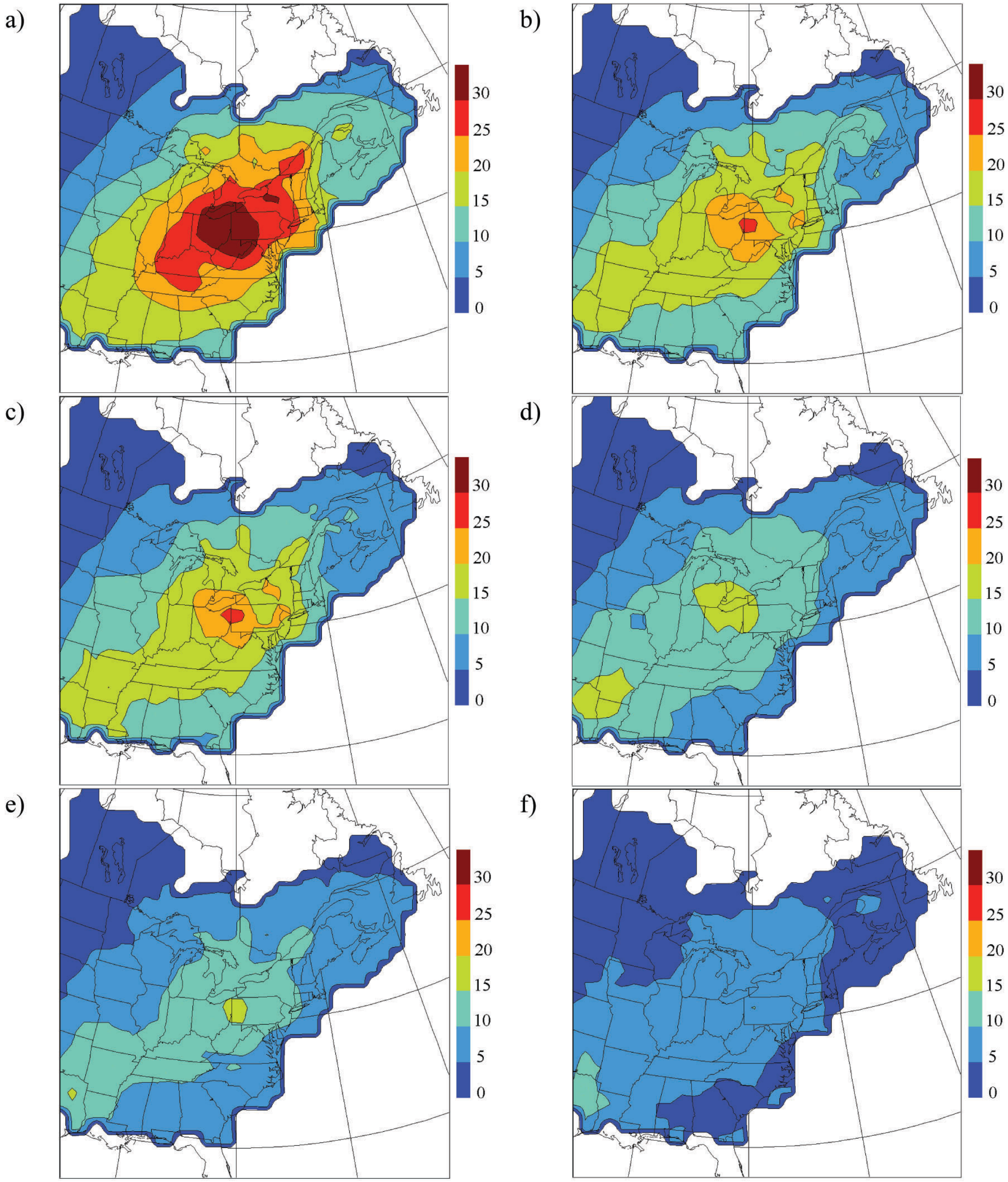


Figure 4.10: Plots of calibrated annual SO_4^{2-} wet deposition patterns in units of kg SO_4^{2-}/ha/yr for ADOM scenarios (a) BASE89, (b) CCUSA2, (c) NOX2B, (d) NOX3P, (e) PST2010F, and (f) 75FCAP.

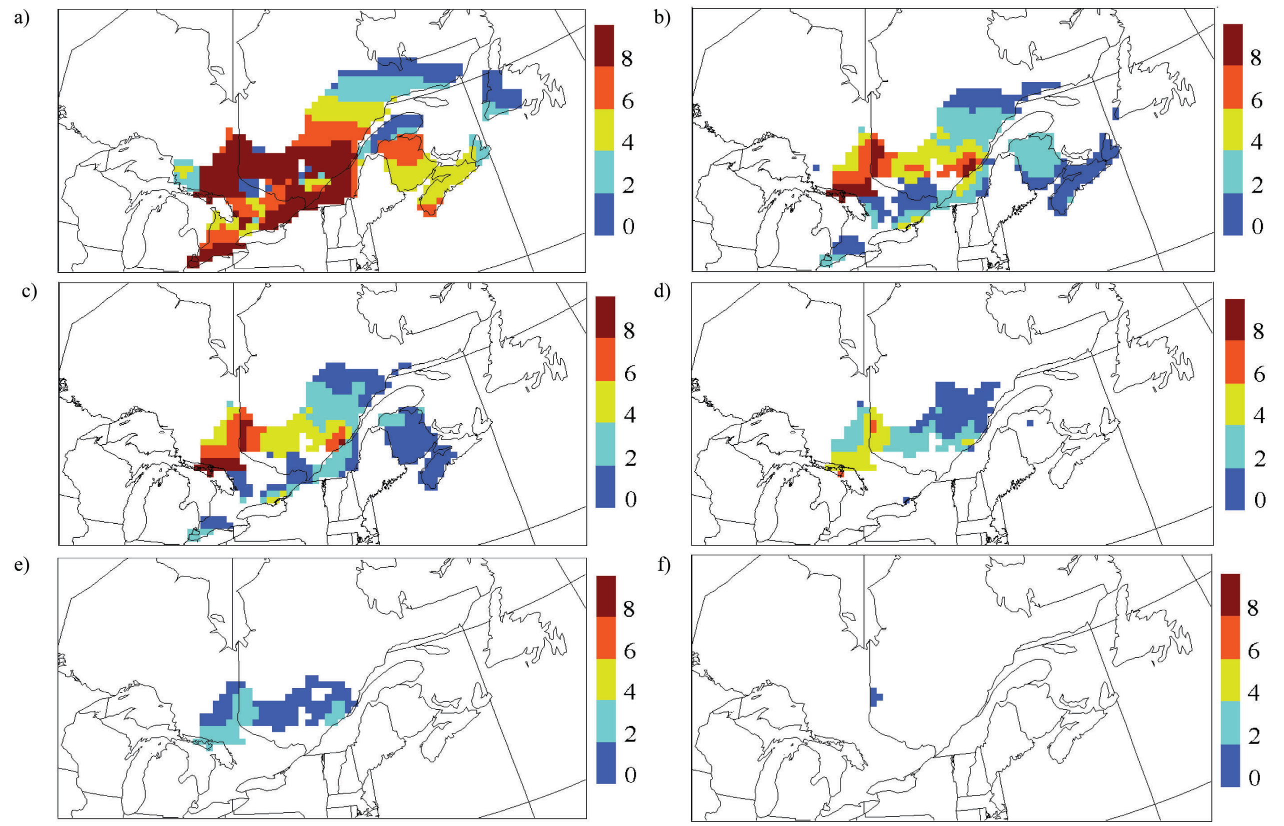


Figure 4.11: Plots of annual SO_4^{2-} deposition critical load exceedance fields (units of kg SO_4^{2-}/ha/yr) for ADOM scenarios (a) BASE89, (b) CCUSA2, (c) NOX2B, (d) NOX3P, (e) PST2010F, and (f) 75FCAP.

to 15% of SO_4^{2-} wet deposition everywhere in eastern Canada except in the vicinity of Sudbury, Ontario, where a contribution of 25% was assumed. But as discussed in Chapter 3 (Section 3.3.2.2) of this *Assessment*, recent measurements suggest that the contribution of SO_4^{2-} dry deposition to SO_4^{2-} total deposition in eastern Canada is considerably higher and ranges from 30% to 90% of SO_4^{2-} wet deposition. As a result, when the critical load SO_4^{2-} total deposition is expressed in terms of SO_4^{2-} wet deposition, the SO_4^{2-} wet deposition levels are *lower* (i.e., more sensitive) than those calculated assuming a SO_4^{2-} dry deposition contribution of only 15%. Second, the critical load field used in the 1997 *Assessment* only considered the impact of acid deposition on aquatic ecosystems. As discussed in Chapter 5 (Effects on Forests and Watershed Soils) of this Assessment, critical loads have now been calculated for forest ecosystems in eastern Canada in terms of the sum of sulphate and nitrate deposition. Accordingly, it is now necessary to account for nitrate deposition as well in assessing critical load attainment for forest ecosystems.

Oxidized Nitrogen Species Results for Key Scenarios

Although the only ADOM predictions considered in the 1997 *Assessment* were of sulphur species, ADOM can also predict the transformation and removal of nitrogen species. In fact, as will be discussed in the next section, changes in NO_x emissions can also affect SO_2 and SO_4^{2-} air concentrations and deposition. Since forest ecosystems are impacted by nitrate deposition as well as by sulphate deposition, four NO_x emission reduction scenarios have been simulated with ADOM (*cf.* Section 4.5.2.1.2). The ADOM predictions of the nitrogen species fields for these four scenarios can then be presented in the same manner as the sulphur species fields were for the SO_2 emission control scenarios.

Table 4.4. Area of SO_4 wet deposition critical load exceedance areas in eastern Canada by province for 20 ADOM SO_2 emission control scenarios. The six key control scenarios are highlighted in yellow.

Scenario Name	Nominal Year	Area (x 1,000 km^2)					
		Ontario	Quebec	New Brunswick	Nova Scotia	Nfld & Labrador	All Eastern Canada
BASE	1989	288	598	97	82	72	1136
CCONLY	1994	281	539	97	82	45	1043
CCUSA1	1997	267	447	100	82	14	911
CCUSA2	2010	204	406	95	82	4	791
5CONLY	2030	166	358	95	70	0	689
25FCAP	2030	107	313	89	16	0	526
T5CUS2	2030	95	174	0	0	0	268
5CCUS2	2030	93	129	0	0	0	222
75FCAP	2030	5	2	0	0	0	7
PST2010A	2030	95	147	0	0	0	242
PST2010B	2030	93	120	0	0	0	213
PST2010C	2030	93	138	9	0	0	240
PST2010D	2030	93	163	16	0	0	272
PST2010E	2030	79	59	0	0	0	138
PST2010F	2030	93	154	0	0	0	247
PST2010a	2030	95	157	0	0	0	252
PST2010b	2030	95	141	0	0	0	236
HLFO	2030	204	399	95	82	0	780
NOX2B	2020	175	374	95	39	0	684
NOX3P	2020	97	227	2	0	0	326

Annual NO_x air concentration

Figure 4.12 shows plots of predicted ambient annual near-surface NO_x air-concentration patterns for these four NO_x emission control scenarios. Note that NO_x consists of both NO and NO_2; to obtain this figure, NO_x fields have been calculated by expressing the ADOM NO fields in NO_2 mass units and then adding them to the ADOM NO_2 fields. Like Figure 4.8, Figure 4.12 displays considerable "structure" since NO_x, like SO_2, is a primary pollutant. One difference, though, is that NO_x emissions from urban centres are relatively more important than SO_2 emissions from urban centres, since the transportation sector is a very important NO_x source. This sector is associated with population centres, whereas coal-fired power plants and non-ferrous smelters, which are the dominant SO_2 source sectors, are often located away from cities. For example, compare the greater importance of the Ohio River Valley in Figure 4.8b vs. Figure 4.12a for the "CCUSA2" scenario. Identifiable urban centres in Figure 4.12a include Minneapolis-St. Paul, Chicago, Detroit, Cleveland, Toronto, Montreal, Kansas City, St. Louis, Cincinnati, the Washington-Boston corridor, Dallas-Fort Worth, and Atlanta.

The scenarios in Figure 4.12 have been arranged by domain-total NO_x emissions in descending order (cf. Table 4.2). Domain-total NO_x emissions are reduced by 32% from the "CCUSA2" scenario to the "NOX3P" scenario. The maximum predicted annual NO_x ambient concentration decreases from a value of 21.3 $\mu g/m^3$ in Figure 4.12a, the "CCUSA2" scenario, to a value of 12.8 $\mu g/m^3$ in Figure 4.12d, the "NOX3P" scenario.

Annual t-NO_3 air concentration

Unlike sulphate, which strongly favours the particle phase, nitrate can co-exist in the atmosphere in both the gas phase (nitric acid or HNO_3) and the particle phase (p-NO_3). ADOM predicts total inorganic nitrate (t-NO_3), the

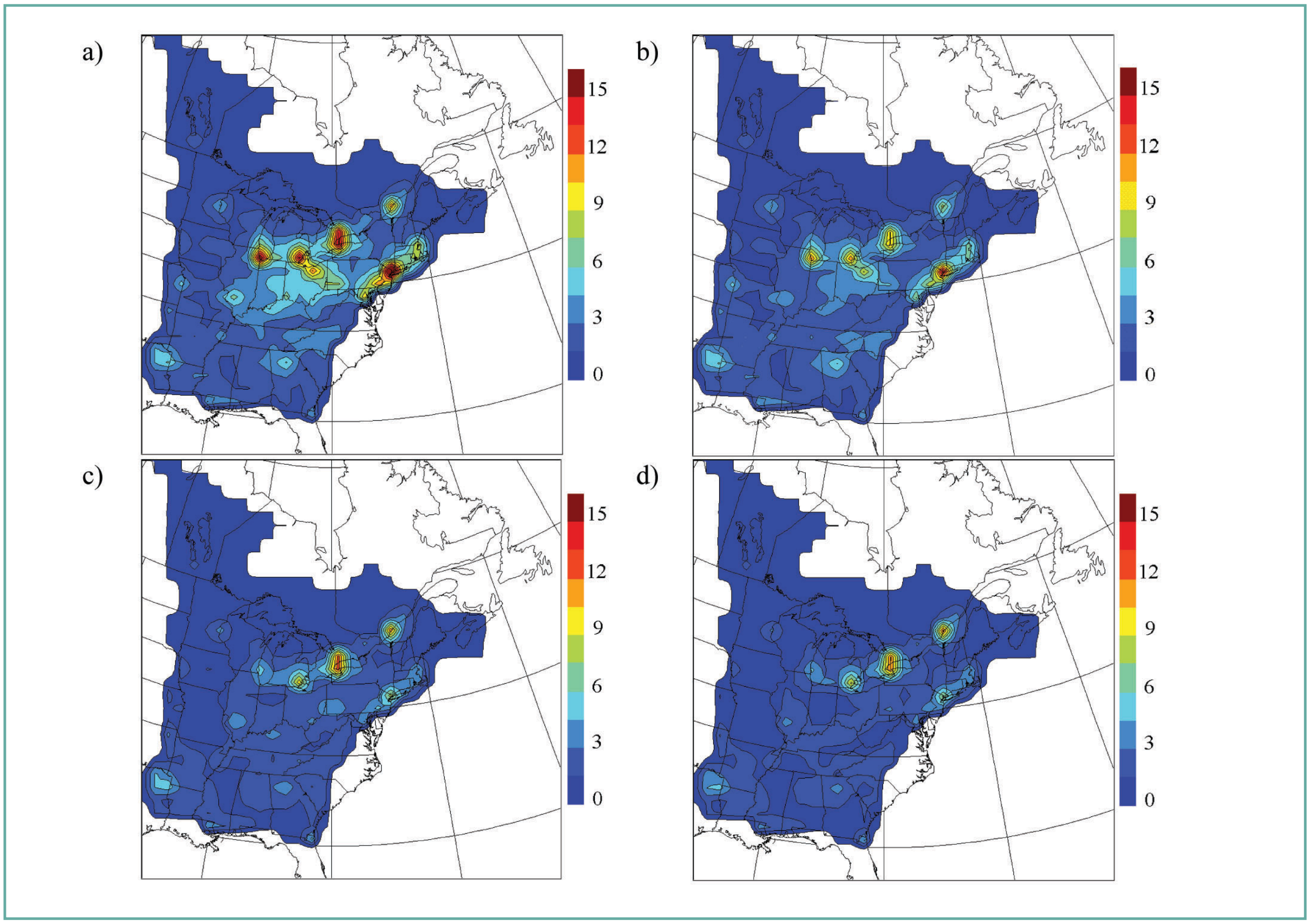


Figure 4.12: Plots of ambient annual near-surface NO_X air-concentration patterns in units of $\mu g\ NO_2/m^3$ for ADOM scenarios (a) CCUSA2, (b) NOXSCEN, (c) NOX2B, and (d) NOX3P.

sum of these two phases. Figure 4.13 shows plots of ambient annual near-surface t-NO_3 air concentrations for the four ADOM NO_x emission control scenarios. Since t-NO_3, like SO_4^{2-}, is a secondary pollutant, this figure is smoother than Figure 4.12 (*cf*. Figures 4.8 and 4.9). The maximum predicted t-NO_3 air concentrations range from 3.7 $\mu g/m^3$ for scenario "CCUSA2" (Figure 4.13a) to 3.1 $\mu g/m^3$ for scenario "NOX3P" (Figure 4.13d).

Annual t-NO_3 wet deposition

Figure 4.14 shows plots of calibrated annual t-NO_3 wet deposition patterns for the four NO_x scenarios. Again, the scenarios have been arranged by domain-total NO_x emissions in descending order, and the t-NO_3 wet deposition fields respond as expected to the emissions reductions. For example, the 10 kg NO_3^-/ha/yr isopleth encloses much of eastern North America for the "CCUSA2" scenario (Figure 4.14a) but has shrunk in size for the "NOX3P" scenario so that it only covers southern Ontario and the Montreal area (Figure 4.14d). Maximum predicted NO_3^- wet deposition values range from over 20 kg NO_3^-/ha/yr for scenario "CCUSA2" (Figure 4.14a) to 15 kg/ha/yr for scenario "NOX3P" (Figure 4.14d). Note again that the "NOX3P" scenario deserves particular attention since it is based on the most likely set of SO_2 and NO_x emissions for 2020.

As expected, the overall patterns in Figure 4.14 are similar to the corresponding t-NO_3 air concentration patterns presented in Figure 4.13. Also, like the NO_x air concentrations vs. the SO_2 air concentrations (Figure 4.12 vs. Figure 4.8) and the t-NO_3 air concentrations vs. the

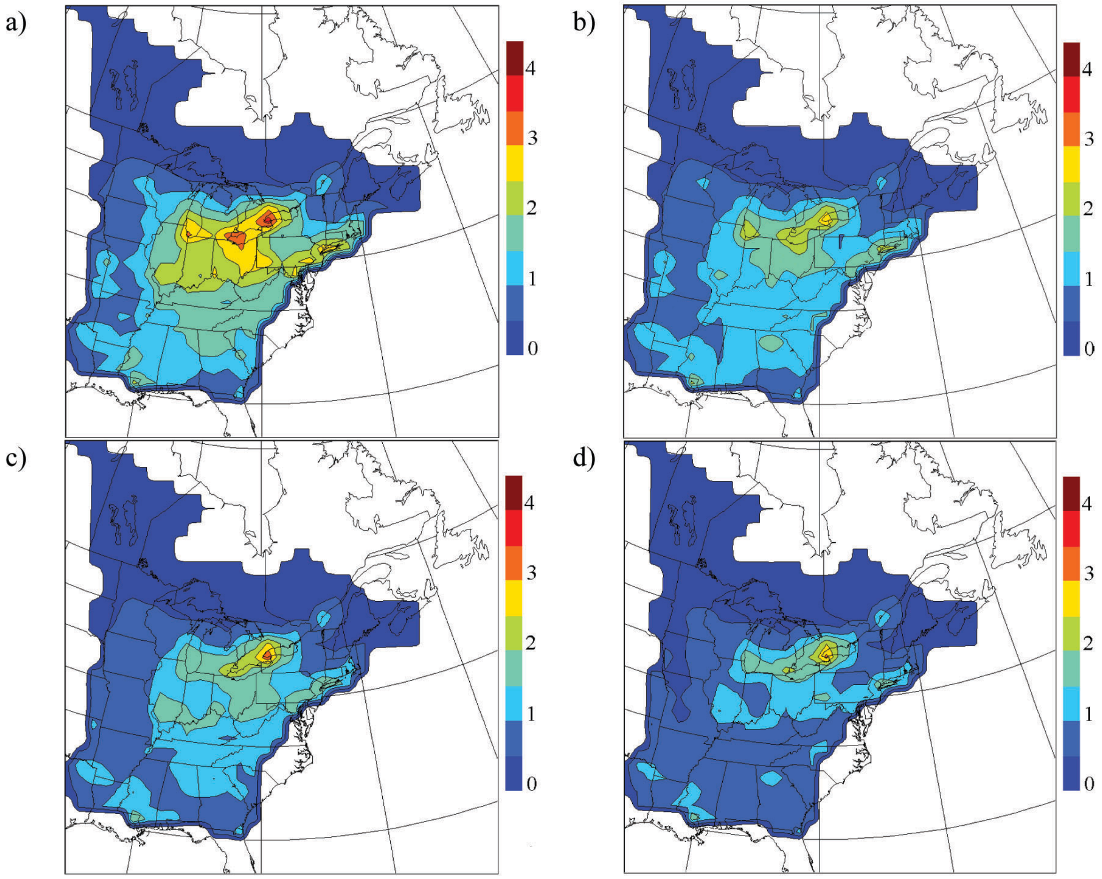


Figure 4.13: Plots of ambient annual near-surface t-NO_3 air-concentration patterns in units of µg NO_3^- /m^3 for ADOM scenarios (a) CCUSA2, (b) NOXSCEN, (c) NOX2B, and (d) NOX3P.

SO_4^{2-} air concentrations (Figure 4.13 vs. Figure 4.9), the NO_3^- wet deposition maxima tend to be located to the north of the SO_4^{2-} wet deposition maxima, that is, over southern Ontario vs. the Ohio-Pennsylvania state line south of Lake Erie. This is consistent with the "centre of gravity" for NO_x emissions being situated further north than that for SO_2 emissions (see Figure 4.5).

Annual Effective Acidity Wet Deposition For Key Scenarios

Finally, the annual SO_4^{2-} and NO_3^- wet deposition fields predicted by ADOM can be combined to produce an annual effective acidity wet deposition field in units of equivalents H^+/ha/yr, where the effective acidity is defined to be the sum of SO_4^{2-} and NO_3^- wet deposition in H^+ equivalent units. Figure 4.15 shows plots of this field for four scenarios: "BASE89", "CCUSA2", "NOX2B", and "NOX3P". Multiplicative factors of 20.83 (=1000/(96/2)) and 16.13 (=1000/62) were used to convert the SO_4^{2-} and NO_3^- wet deposition fields from units of kilograms of SO_4^{2-} and kilograms of NO_3^- to units of equivalents. The combinations of SO_2 and NO_x emission reductions for the three future year scenarios yield quite distinctive effective acidity patterns for each scenario. For scenario 'NOX3P' vs. scenario 'CCUSA2', effective acidity is predicted to decrease by at least 30% over much of eastern North America (WxPrime Corp., 2004). The maximum annual value for scenario "NOX3P" is 550 eq/ha/yr over Detroit. Compare this to the minimum sulphate-plus-nitrate critical load of ≤500 eq/ha/yr for forest ecosystems that is presented in Chapter 8.

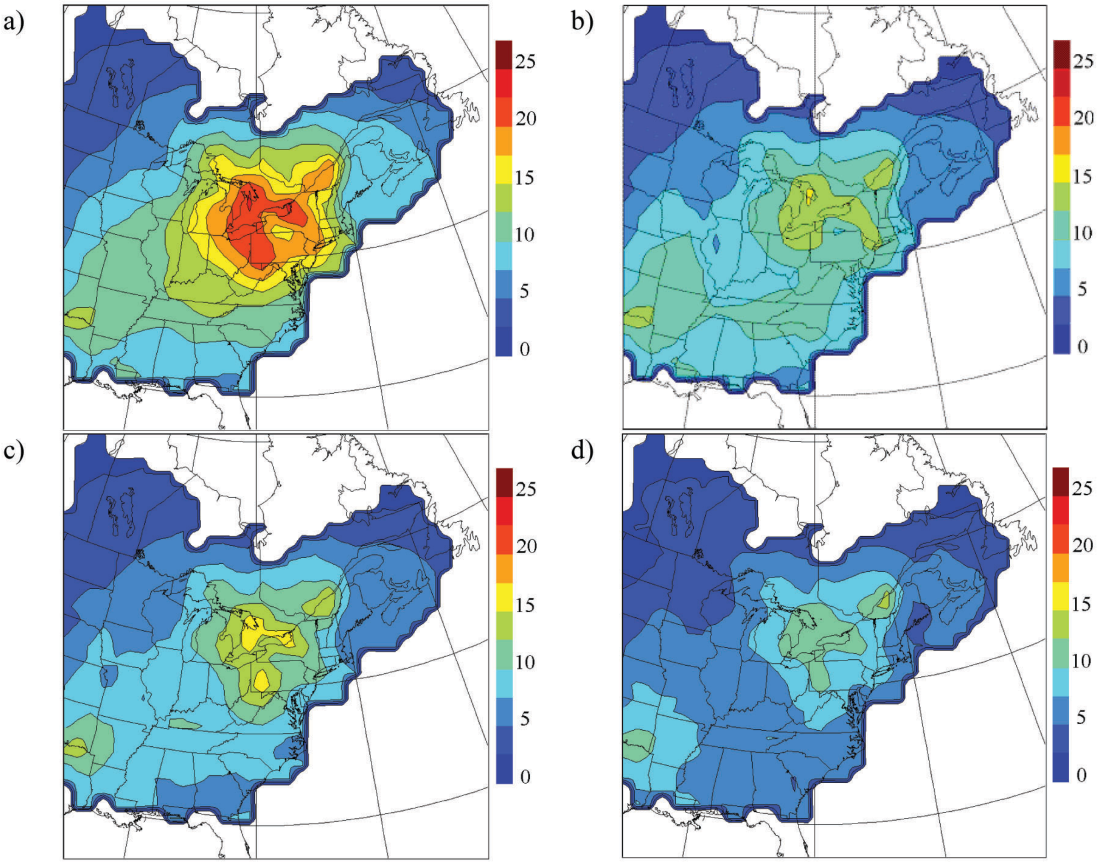


Figure 4.14: Plots of calibrated annual t-NO_3 wet deposition patterns in units of kg NO_3^- /ha/yr for ADOM scenarios (a) CCUSA2, (b) NOXSCEN, (c) NOX2B, and (d) NOX3P.

4.5.2.1.4 Additional analyses of ADOM simulations

Influence of Different Source Regions

The availability of a "library" of 20 ADOM SO_2 emission control scenarios (see Table 4.1) makes it possible to infer source-receptor relationships for some source regions by contrasting selected pairs of scenarios. Table 4.5 lists six pairs of scenarios that differ only in the SO_2 emissions from a particular source region or sector. The difference between a predicted quantity such as annual SO_4^{2-} air concentration for each pair of scenarios is then due to the difference in SO_2 emissions from that one source region alone and can be examined to see the contribution or influence of that one region. Three of the scenario pairs in Table 4.5 are connected to Canadian sources only, two are connected to U.S. sources only, and one is connected to source regions in both countries. The common metric that will be considered in this section for all scenario pairs is annual SO_4^{2-} wet deposition due to its relevance for critical load assessment.

It is important to note that this approach assumes implicitly that, at least on an annual basis, atmospheric sulphur chemistry is linear. That is, a percentage reduction in sulphur emissions leads to equal percentage reductions in sulphur concentrations and deposition. (If the percentage reduction in SO_2 emissions is not uniform geographically, however, then the resulting percentage reductions in sulphur concentrations and deposition will also not be uniform geographically, even for linear sulphur chemistry). A number of studies have found that the assumption of linear sulphur chemistry is a reasonable approximation in eastern North America on a seasonal or annual time scale (e.g., Misra et al., 1989; Dennis et al., 1990). Given the property of linearity,

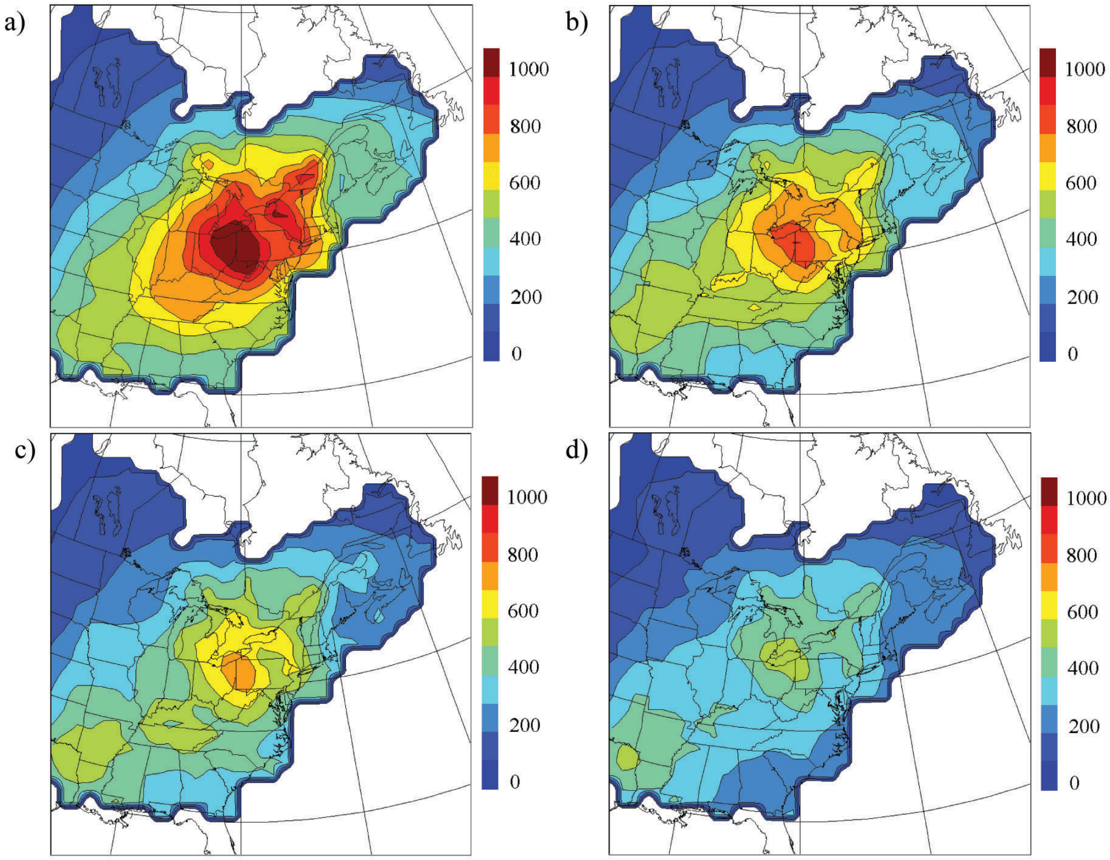


Figure 4.15: Plots of annual effective acidity deposition patterns in units of eq/ha/yr for ADOM scenarios (a) BASE89, (b) CCUSA2, (c) NOX2B, and (d) NOX3P.

Table 4.5. Summary of selected pairs of ADOM SO_2 emission control scenarios useful for source contribution investigation and their key differences.

No.	Scenario Pair	Difference	Targetted Source Region
1	CCUSA2 – 5CONLY	In "5CONLY" scenario, Canadian SOMA sources are rolled back 50% from "CCUSA2" scenario but U.S. sources are left unchanged.	All Canadian SOMA sources
2	CCUSA2 – HLFO	In "HLFO" scenario, emissions from HFO/LFO combustion in Maritimes, Quebec, and Ontario.	Canadian HFO/LFO sector (in ADOM domain)
3	PST2010a – PST2010A	Quebec emissions were reduced by 34% in"PST2010a" scenario but by 45% in "PST2010A" scenario.	Quebec
4	PST2010A – PST2010B	U.S. sources are reduced by 55% in "PST2010A" scenario but by 60% in "PST2010B" scenario.	All U.S. sources (in ADOM domain)
5	PST2010D – PST2010E	In "PST2010D" scenario, only 20 northeastern U.S. states have 60% rollback but in "PST2010E" scenario *all* U.S. emissions are reduced by 60%.	U.S. southeastern and midwestern states
6	T5CUS2 – 5CCUS2	In "T5CUS2" scenario, only sources in Canadian SOMA and 20 northeastern U.S. states have 50% rollback from "CCUSA2" scenario. In "5CCUS2" scenario, *all* sources have 50% rollback.	SK, MB, NF and U.S. southeastern and midwestern states

scenarios can then be treated as additive. One consequence for the case of a different percentage change in SO_2 emissions is that the output difference field can be scaled by the same factor as the SO_2 emission difference field to yield the result that would have been obtained if the SO_2 emission difference field had had the scaled value instead (without the need to re-run the acid deposition model). As will be discussed below, such scaling permits the "normalization" of scenario-pair difference fields and enables comparison of the contribution of different source regions for the same relative change in emissions. It also permits the construction of "pseudo-scenarios" without the need to run ADOM.

It should also be noted that linear sulphur chemistry may be a less good assumption if NO_x and/or VOC emissions are also changed at the same time as SO_2 emissions are changed. The reason is that changes in NO_x and/or VOC emissions can change the oxidative capacity of the atmosphere, which in turn controls the rate of conversion of SO_2 to SO_4^{2-} (e.g., Stockwell et al., 1988; Stein and Lamb, 2002). For the 20 ADOM SO_2 emission control scenarios listed in Table 4.1, though, VOC emissions were held constant in all of the scenarios except one ("5CONLY"), and only three scenarios ("5CONLY"/"NOXSCEN", "NOX2B", and "NOX3P") considered a simultaneous change in SO_2 and NO_x emissions.

Within-Canada-Only SO_2 Emission Reductions

Uniform Reductions - Eastern Canada

The first scenario pair listed in Table 4.5 differs only in the level of SO_2 emissions in eastern Canada. As described in Section 4.5.2.1.1.S8, SO_2 emissions for scenario "5CONLY" were reduced only in the eastern-Canadian SOMA (see Figures 4.4a and 4.6a) relative to the "CCUSA2" scenario. The reduction was 50% from the 1985 ECARP provincial caps, which corresponds to a reduction of 619 Ktonnes/yr, or 32% of the SO_2 emissions in the Canadian portion of the ADOM domain relative to the "CCUSA2" scenario. The reduction for the entire domain, however, is only 4%.

As a consequence of the reduction in SO_2 emissions, levels of all sulphur-related fields should be lower for the "5CONLY" scenario vs. the "CCUSA2" scenario. Figure 4.16 shows actual and percent differences in the annual SO_4^{2-} wet deposition field for the "CCUSA2" scenario minus the "5CONLY" scenario. Note that the convention has been adopted here to subtract the scenario with the smaller overall SO_2 emissions from the scenario with the larger overall SO_2 emissions. The resulting difference fields thus tend to be dominated by positive differences, where positive differences indicate a *decrease* in the output field as a consequence of the decrease in SO_2 emissions. "Hot" colours in contoured plots of the difference fields will

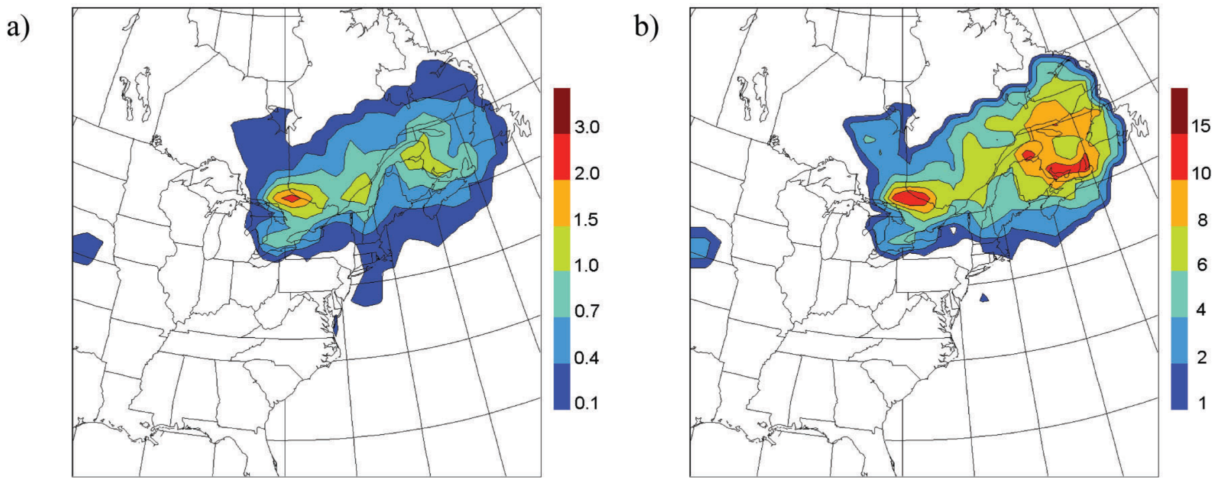


Figure 4.16: Plots of (a) actual difference and (b) percent difference in predicted annual SO_4^{2-} wet deposition (units of kg SO_4^{2-}/ha/yr) between ADOM SO_2 emission control scenarios "CCUSA2" and "5CONLY". Panel (b) was calculated as (CCUSA2 - 5CONLY) / CCUSA2. The corresponding difference in Canadian SO_2 annual emissions between the two scenarios is 619 Ktonnes/yr, or 32% from "CCUSA2" scenario levels.

indicate larger positive differences (decreases), whereas "cool" colours indicate smaller positive differences or even negative differences (increases).

The largest decreases in annual SO_4^{2-} wet deposition shown in Figure 4.16 are found in Ontario and Quebec, the provinces with the largest SO_2 emissions in eastern Canada (Figure 4.5a). Decreases in eastern Canada are in the 0-3 kg SO_4^{2-}/ha/yr range, and percent decreases are in the 0-25% range, with the largest percent differences occurring along the Sudbury, Ont.–Rouyn, Quebec corridor. Some decreases also occur in the northeastern U.S. as a result of the reduction in Canadian emissions, but the largest percent decrease in the U.S. is only 5%. Similar results were predicted for a similar scenario simulated by the U.S. EPA Eulerian acid deposition model, RADM (see Dennis et al., 1990, p. 25).

Single Source Sector – Combustion of Heavy and Light Fuel Oils

The second scenario pair listed in Table 4.5 permits the impact of a reduction in SO_2 emissions from a Canadian emission source *sector* to be quantified. Scenario "HLFO" (see Section 4.5.2.1.1.S16) differs from scenario "CCUSA2" only in a reduction in SO_2 emissions from Canadian sources combusting heavy fuel oil and light fuel oil. As shown in Figure 4.6d, although this change results in only a small reduction in SO_2 emissions in the provinces of Ontario and Quebec, the largest users of heavy and light fuel oils in Canada are the Atlantic provinces and hence the largest reductions in SO_2 emissions occur in these eastern provinces. In 1999, fuel-oil combustion contributed 327 Ktonnes of SO_2 emissions Canada-wide, but in scenario "HLFO" these emissions are reduced by 180 Ktonnes/yr, which corresponds to a 9% reduction in SO_2 emissions from the Canadian portion of the ADOM domain relative to scenario "CCUSA2" (and to a 1% reduction overall).

Figure 4.17 shows actual and percent differences in the annual SO_4^{2-} wet deposition field for the "CCUSA2" scenario minus the "HLFO" scenario. Decreases in eastern Canada are in the 0.0-0.75 kg SO_4^{2-}/ha/yr range, and percent decreases are in the 0-8% range, with the largest actual decreases and percent decreases concentrated in the Atlantic provinces. Ontario and Quebec, on the other hand, are predicted to receive relatively minor benefits from emission reductions from the fuel-oil combustion sector.

Single Province – Province of Quebec

The third scenario pair listed in Table 4.5 allows the impact of an 11% rollback of SO_2 emissions from the province of Quebec on annual SO_4^{2-} wet deposition in eastern North America to be quantified. Scenarios "PST2010A" (Section 4.5.2.1.1.S10) and "PST2010a" (Section 4.5.2.1.1.S11) have nearly identical further

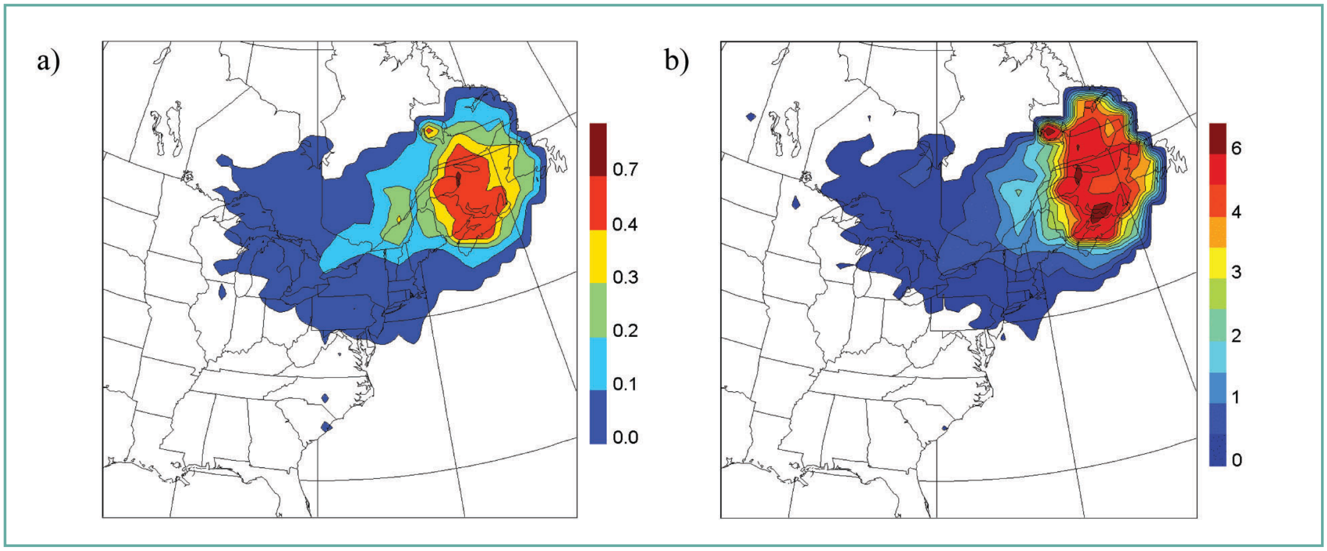


Figure 4.17: Plots of (a) actual difference and (b) percent difference in predicted annual SO_4^{2-} wet deposition (units of kg SO_4^{2-}/ha/yr) between ADOM SO_2 emission control scenarios "CCUSA2" and "HLFO". The corresponding difference in Canadian SO_2 annual emissions between the two scenarios is 180 Ktonnes/yr, or 9% for eastern Canada from "CCUSA2" scenario levels.

reductions in SO_2 emissions relative to scenario "CCUSA2", with the exception that in scenario "PST2010A", Quebec SO_2 emissions are rolled back by 45%, whereas in scenario "PST2010a", they are only reduced by 34%. The actual difference in SO_2 emissions between scenarios "PST2010a" and "PST2010A" is 54 Ktonnes/yr, a small amount relative to the domain-total SO_2 emissions for scenario"PST2010A" of 7,214 Ktonnes/yr (see Table 4.1).

It is also useful, for purposes of comparison with other scenario-pair difference fields, to scale the annual SO_4^{2-} wet deposition difference field calculated for this Quebec scenario pair. Assuming linear sulphur chemistry, if we scale the annual SO_4^{2-} wet deposition difference field by a factor of 5/11, then this corresponds to scaling the difference in SO_2 emissions by the same factor. The result is that the scaled annual SO_4^{2-} wet deposition difference field is the one that would have been obtained if the input SO_2 emissions for Quebec for the "PST2010A" scenario had differed from those for the "PST2010a" scenario by only 5% instead of 11%. This corresponds to a reduction in Quebec SO_2 emissions of 25 Ktonnes/yr rather than 54 Ktonnes/yr. More details on this scaling procedure are provided below in the section on "pseudo-scenarios".

Figure 4.18 shows *scaled* actual and percent differences in the annual SO_4^{2-} wet deposition fields for the "PST2010a" scenario minus the "PST2010A" scenario. Decreases in eastern Canada are in the 0–0.14 kg SO_4^{2-}/ha/yr range, and percent decreases are in the range of 0–1.4%. Actual decreases are largest in the vicinity of major Quebec source regions, including the Noranda Horne smelter at Rouyn, Quebec (located south of James Bay and close to the Ontario border) and the Montreal metropolitan area. The largest percent differences occur in the vicinity of Rouyn and along the St. Lawrence River. Note that this comparison illustrates the important point that emission reductions have the greatest impact close to the source, i.e., locally, so that an emitting jurisdiction itself tends to derive the largest benefits from its own emission reductions.

Within-U.S.-Only SO_2 Emission Reductions

As is clear from Table 4.1, a wide range of U.S. SO_2 emissions have also been considered in various ADOM scenarios. Table 4.5 identifies two pairs of ADOM SO_2 emission control scenarios that differ only in the level of U.S. SO_2 emissions assumed. Examination of these scenario pairs allows the impact of U.S. SO_2 emissions on Canada to be estimated.

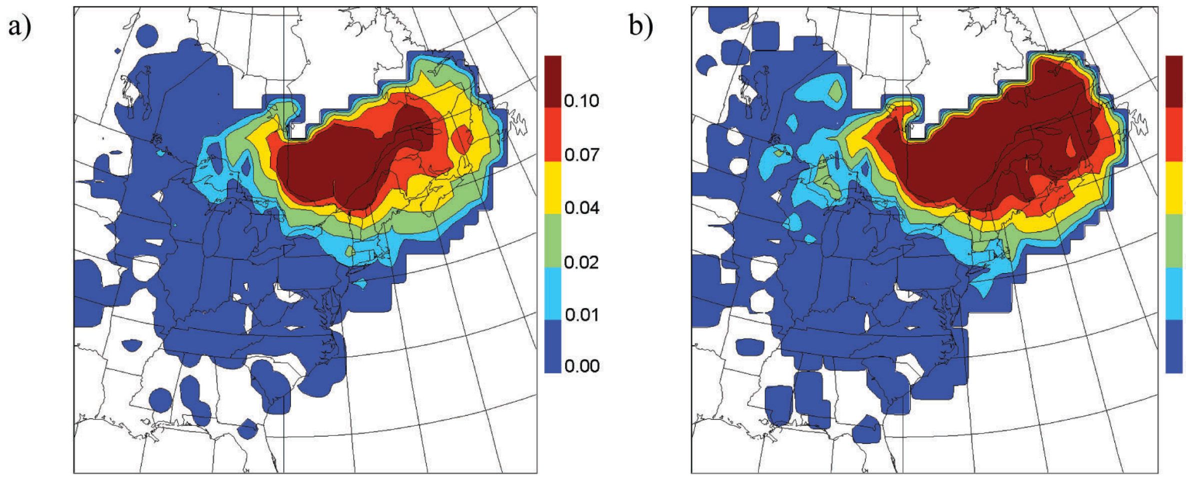


Figure 4.18: Plots of scaled (a) actual difference and (b) percent difference in predicted annual SO_4^{2-} wet deposition (units of kg SO_4^{2-}/ha/yr) between ADOM SO_2 emission control scenarios "PST2010a" and "PST2010A". The two panels were calculated as (5/11)*(PST2010a - PST2010A) and (5/11)*(PST2010a - PST2010A) / PST2010a, respectively. The corresponding difference in Canadian SO_2 annual emissions between the two scenarios is 25 Ktonnes/yr, or 5% of Quebec emissions and 1.5% of eastern Canadian emissions from "PST2010A" scenario levels.

Uniform Reductions – Midwestern and Eastern United States
Scenarios “PST2010A” (Section 4.5.2.1.1.S10) and “PST2010B” (Section 4.5.2.1.1.S12) are nearly identical, with the exception that in scenario “PST2010A”, U.S. SO_2 emissions are rolled back by 55% relative to the “CCUSA2” scenario, whereas in scenario “PST2010B”, they are rolled back by 60%. The differences between ADOM-predicted fields for these two scenarios thus show the impact of a further 5% uniform reduction in U.S. SO_2 emissions from expected levels in year 2010. The actual difference in SO_2 emissions between these two scenarios is 611 Ktonnes/yr, which is equivalent to 37% of the Canadian SO_2 emissions considered in both scenarios (and virtually identical to the change in Canadian SO_2 emissions for the “CCUSA2”–“5CONLY” scenario pair).

Figure 4.19 shows actual and percent differences in the annual SO_4^{2-} wet deposition fields for the “PST2010A” scenario minus the “PST2010B” scenario. According to Figure 4.19a, a 5% reduction in U.S. SO_2 emissions from 2010 levels will result in a reduction in annual SO_4^{2-} wet deposition from over 0.8 kg SO_4^{2-}/ha/yr in southwestern Ontario to 0.1–0.4 kg/ha/yr in the Atlantic provinces and central Quebec and Ontario. In percentage terms, Figure 4.19b suggests that an overall 5% reduction in U.S. SO_2 emissions will result in a 1–4% reduction in SO_4^{2-} wet deposition in eastern Canada (relative to the 2010 “CCUSA2” scenario).

It is also interesting to compare Figure 4.19 to Figure 4.18 and to Figure 4.16. Figure 4.19 shows the impact of a 5% reduction in U.S. SO_2 emissions, while Figure 4.18 shows the impact of a 5% reduction in SO_2 emissions from Quebec. In terms of the impact on Quebec, the 5% reduction in U.S. emissions reduced annual SO_4^{2-} wet deposition in Quebec by 1–5%, whereas the 5% reduction in Quebec emissions only reduced SO_4^{2-} wet deposition in Quebec by 0.2–1.4%, a factor of 4 or 5 less. However, the actual reduction in SO_2 emissions considered for the two jurisdictions was 611 and 25 Ktonnes/yr, respectively, a factor of about 25 less. This suggests that the impact on eastern Canada of SO_2 emission reductions in Canada vs. the U.S. is larger on a tonne-vs.-tonne basis, consistent with our expectation that pollutant impacts should be greatest near their source and then decrease with distance from the source. However, this effect is counterbalanced for this comparison by the greater magnitude of SO_2 emissions in the U.S. vs. Canada.

In the case of Figure 4.16 vs. Figure 4.19, the former shows the impact of a 619 Ktonne/yr reduction in SO_2 emissions from eastern Canada whereas Figure 4.19 shows the impact of a 611 Ktonne/yr reduction in SO_2 emissions across the U.S. portion of the ADOM domain. The largest actual and percent reductions in annual SO_4^{2-} wet deposition over eastern Canada are 3 kg SO_4^{2-}/ha/yr and 20% in Figure 4.16 vs. 0.8 kg/ha/yr and 4% in Figure

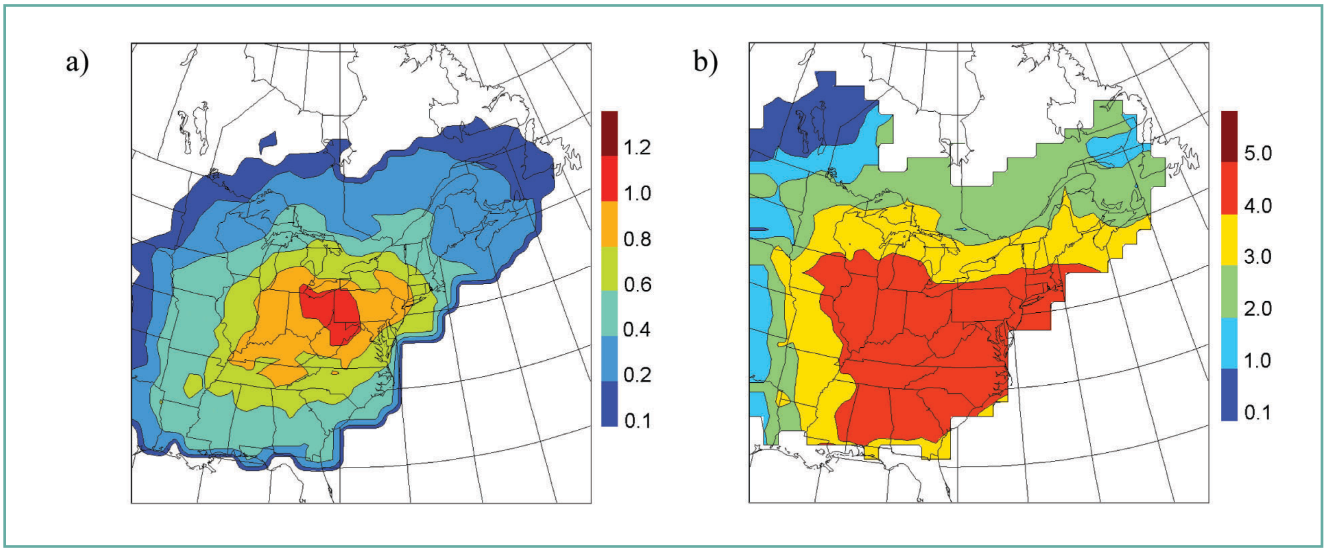


Figure 4.19: Plots of (a) actual difference and (b) percent difference in predicted annual SO_4^{2-} wet deposition (units of kg SO_4^{2-}/ha/yr) between ADOM SO_2 emission control scenarios “PST2010A” and “PST2010B”. Panel (b) was calculated as (PST2010A - PST2010B) / CCUSA2. The corresponding difference in U.S. SO_2 annual emissions between the two scenarios is 611 Ktonnes/yr, or 5% of U.S. emissions from “CCUSA2” scenario levels.

4.19, again supporting the conclusion that on a tonne-vs.-tonne basis, SO_2 emission reductions in eastern Canada have more of an impact on eastern Canada than do equal emission reductions in the U.S.

Targetted Reductions – Midwestern and Southern United States Only

Scenarios "PST2010D" (Section 4.5.2.1.1.S14) and "PST2010E" (Section 4.5.2.1.1.S15) are also nearly identical, with the exception that in scenario "PST2010D", U.S. SO_2 emissions were rolled back by 60% relative to the "CCUSA2" scenario only in the 20-state northeastern region shown in Figure 4.4b, whereas in scenario "PST2010E", they were rolled back by 60% in all U.S. states in the ADOM domain. The difference between these two scenarios is thus due to the contribution of U.S. SO_2 emission sources *outside of* the northeastern 20-state group shown in Figure 4.4b, i.e., southern and midwestern U.S. states. The actual difference in SO_2 emissions between these two scenarios is 3,132 Ktonnes/yr, a very large value that is equivalent to 32% of the domain-total SO_2 emissions for scenario "PST2010D" and very close to twice the Canadian SO_2 emissions considered in both scenarios.

The difference between the annual SO_4^{2-} wet deposition fields predicted by ADOM for these two scenarios is thus due to a 60% reduction in emissions for those U.S. states outside of the 20-state northeastern region. If the resulting actual and percent annual SO_4^{2-} wet deposition difference fields are then divided by 12, this will give an estimate of the impact of a 60% / 12 = 5% reduction in emissions from these southern and midwestern states, allowing the impact of a 5% emissions reduction in these states from scenario "CCUSA2" levels to be compared with the impact of a 5% emissions reduction in all U.S. states in the ADOM domain (Figure 4.19).

Figure 4.20 shows actual and percent differences in the annual SO_4^{2-} wet deposition field for the "PST2010D" scenario minus the "PST2010E" scenario after scaling by a factor of 1/12. In comparison to Figure 4.19, the actual and percent differences are considerably smaller and are shifted southward. Over eastern Canada, predicted reductions in annual SO_4^{2-} wet deposition from 0.1–0.2 kg SO_4^{2-}/ha/yr in southern Ontario to less than 0.1 kg/ha/yr in the Atlantic provinces and central Quebec and Ontario. In percentage terms, Figure 4.20b suggests that an overall 5% reduction in U.S. SO_2 emissions in the U.S. states farther away from eastern Canada will result in less than a 1% reduction in SO_4^{2-} wet deposition in eastern Canada vs. up to 4% for the all-state case (Figure 4.19).

The contribution that U.S. emissions make to SO_4^{2-} wet deposition in eastern Canada is also suggested by the differences in the critical load exceedance area for these

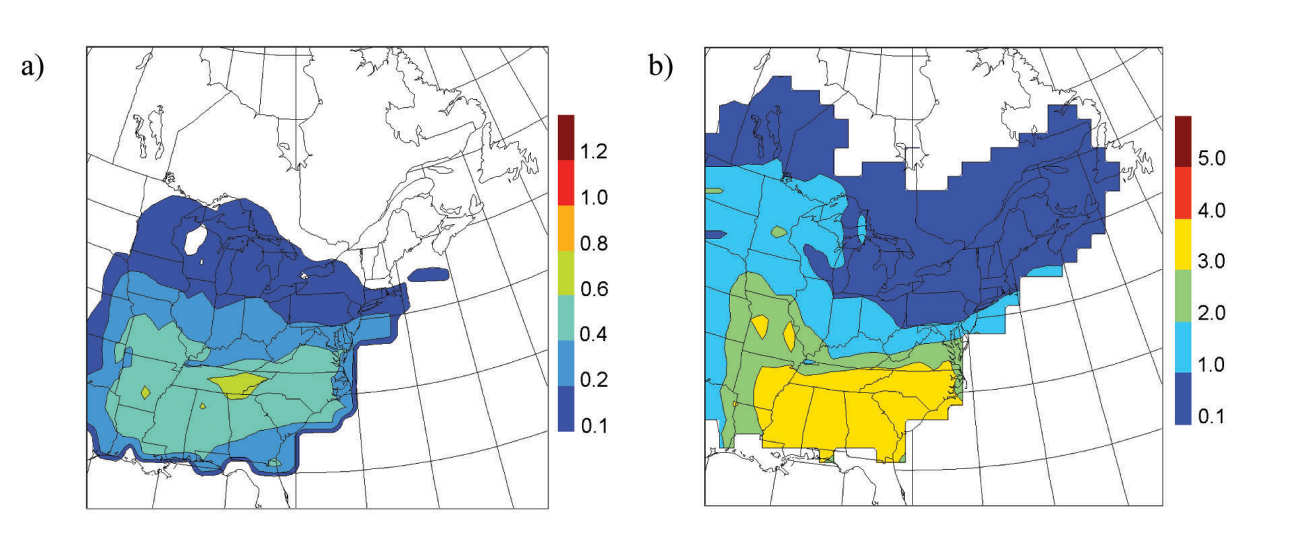


Figure 4.20: Plots of (a) actual difference and (b) percent difference in predicted annual SO_4^{2-} wet deposition (units of kg SO_4^{2-}/ha/yr) between ADOM SO_2 emission control scenarios "PST2010D" and "PST2010E". The two panels were calculated as (1/12)*(PST2010D - PST2010E) and (1/12)*(PST2010D - PST2010E) / CCUSA2, respectively. The corresponding difference in U.S. SO_2 annual emissions between the two scenarios is 261 Ktonnes/yr, or 2% of U.S. emissions from "CCUSA2" scenario levels.

scenario pairs. According to Table 4.4, the difference in the critical load exceedance area for eastern Canada between scenarios “PST2010D” and “PST2010E” is 134,000 km^2, reflecting the impact of the larger reductions in U.S. SO_2 emissions for the latter scenario. The corresponding difference for the scenario “PST2010A”–“PST2010B” pair is 29,000 km^2, but the difference in U.S. SO_2 emissions is also a factor of five smaller for this pair (see Table 4.5).

Targetted Reductions – Northeastern United States Only

Since Figures 4.19 and 4.20 consider the impact of a 5% reduction in U.S. SO_2 emissions for all states in the ADOM domain and for the non-northeastern states from scenario “CCUSA2” levels, respectively, it follows that by taking the difference of these two sets of difference fields, the influence of a 5% emissions reduction in only the 20-state northeastern region can also be determined. That is, the impact of reducing SO_2 emissions by 5% from all U.S. states in the ADOM domain (Figure 4.19) will be equal to the impact of reducing emissions by 5% in the 20 northeastern states (Figure 4.21) plus the impact of reducing emissions by 5% in the non-northeastern states (Figure 4.20). (This methodology is discussed further in the following section on “Pseudo-scenarios”.)

Interestingly, Figure 4.21 is very similar over Canada to Figure 4.19. According to Figure 4.21a, a 5% change in emissions from the northeastern region will result in a reduction in annual SO_4^{2-} wet deposition from 0.4–0.8 kg SO_4^{2-}/ha/yr in southern Ontario and from 0.1–0.4 kg/ha/yr in the Atlantic provinces and central Quebec and Ontario. In percentage terms, Figure 4.21b suggests that an overall 5% reduction in U.S. SO_2 emissions will result in a 1–4% reduction in SO_4^{2-} wet deposition in eastern Canada. In contrast, for a 5% change in emissions from the non-northeastern U.S. states in the ADOM domain, the corresponding impact on SO_4^{2-} wet deposition is less than 0.2 kg SO_4^{2-} ha/yr and less than 1% (Figure 4.20). Thus, the 20-state northeastern region has a larger influence on SO_4^{2-} wet deposition levels in southeastern Canada than do the other U.S. states in the ADOM domain for the same percentage emissions change.

Cross-Border SO_2 Emission Reductions

For the last scenario pair in Table 4.5, “T5CUS2” and “5CCUS2”, scenario “T5CUS2” is a combination of 50% emission reductions in two source regions that have already been discussed, the eastern Canadian SOMA region (cf. Figure 4.16) and the 20 northeastern U.S. state region (cf. Figure 4.21), while the “5CCUS2” scenario is essentially a 50% rollback of the “CCUSA2” scenario. The difference between these two scenarios should thus reveal the contribution of peripheral jurisdictions on the

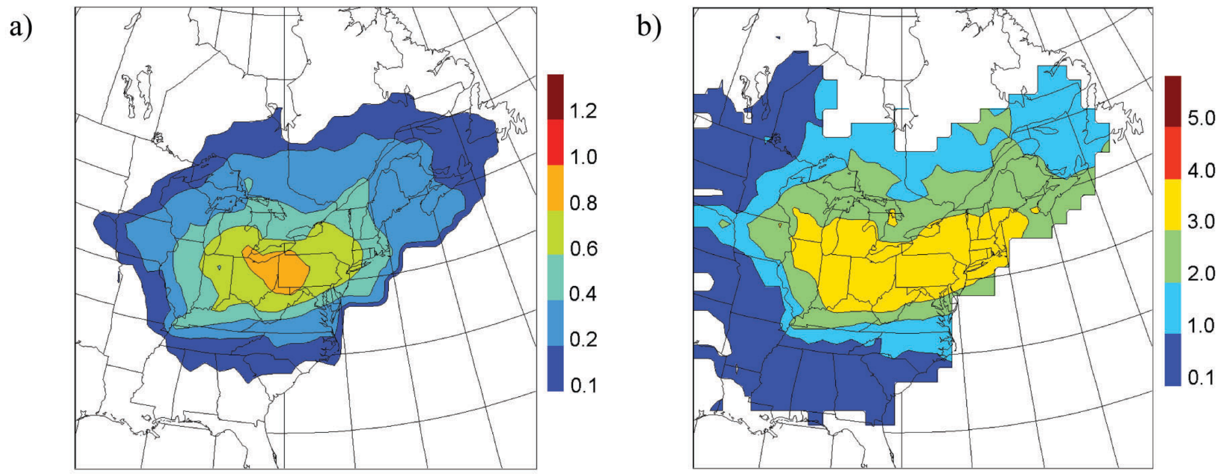


Figure 4.21: Plots of the impact of a 5% geographically-targetted decrease in U.S. SO_2 emissions from 2010 levels for the 20 northeastern states on predicted annual SO_4^{2-} wet deposition (units of kg SO_4^{2-}/ha/yr) in (a) actual and (b) percentage terms. The two panels were calculated as (PST2010A - PST2010B) - (1/12)*(PST2010D - PST2010E) and (PST2010A-PST2010B) / CCUSA2 - (1/12)*(PST2010D - PST2010E) / CCUSA2, respectively. The corresponding difference in U.S. SO_2 annual emissions between the two scenarios is 350 Ktonnes/yr, or 3% of U.S. emissions from “CCUSA2” scenario levels.

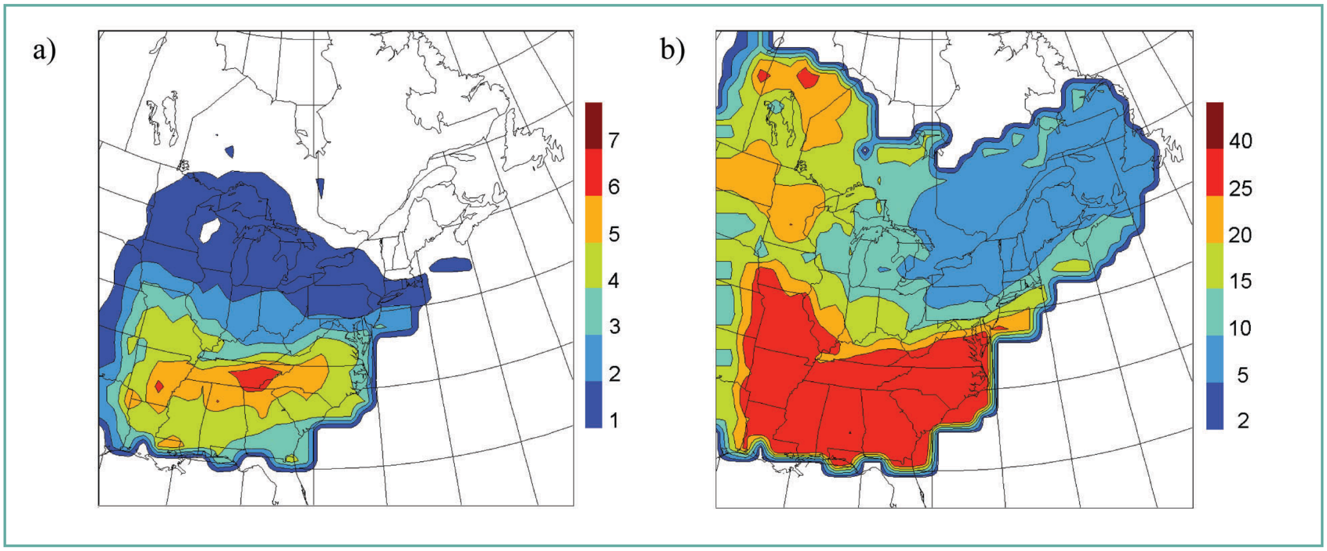


Figure 4.22: Plots of (a) actual difference and (b) percent difference in predicted annual SO_4^{2-} wet deposition (units of kg SO_4^{2-}/ha/yr) between ADOM SO_2 emission control scenarios "T5CUS2" and "5CCUS2". Panel (b) was calculated as (T5CUS2 - 5CCUS2) / CCUSA2. The corresponding difference in SO_2 annual emissions between the two scenarios is 2,879 Ktonnes/yr, or 20% for total emissions from "CCUSA2" scenario levels.

ADOM domain, that is, the westernmost and easternmost Canadian provinces of Saskatchewan, Manitoba, and Newfoundland and Labrador and the midwestern and southern U.S. states. Figure 4.20 showed the contribution of the midwestern and southern U.S. states for 5% of scenario "CCUSA2" emissions, so the difference between the "T5CUS2" and "5CCUS2" scenario annual SO_4^{2-} wet deposition fields for 50% of scenario "CCUSA2" emissions that is shown in Figure 4.22 should be qualitatively similar. This is in fact the case, and these peripheral source regions can be seen to have a relatively minor influence on SO_4^{2-} wet deposition in eastern Canada. A 50% reduction in SO_2 emissions in these peripheral jurisdictions results in a reduction in SO_4^{2-} wet deposition of less than 1 kg SO_4^{2-}/ha/yr outside of the Great Lakes region of Ontario and less than a 10% reduction in SO_4^{2-} wet deposition in southern and central Ontario, in Quebec, and in the Maritime provinces.

Pseudo-Scenarios

It is clear from Figures 4.19 to 4.21 how important the contribution of U.S. SO_2 emissions is to annual SO_4^{2-} wet deposition levels in Canada. The information in these three figures and the other figures related to Table 4.5 can also be used in conjunction with the assumption of linear sulphate chemistry to create "constructed scenarios" or "pseudo-scenarios". That is, for an annual SO_2 emission field "constructed" using the SO_2 emission field for an existing ADOM scenario and the SO_2 emission-difference field for a pair of scenarios from Table 4.5, the sulphur-species output fields that ADOM would predict for the "constructed" SO_2 emission field can be estimated using the output fields from the selected existing ADOM scenario and the output-difference fields associated with the same Table 4.5 pair of scenarios. This technique was in fact used already in preparing Figures 4.18 and 4.20, where SO_2 emission differences and ADOM output differences were "normalized" to allow comparison of these figures with Figure 4.19, and in preparing Figure 4.21, which is simply the difference between the annual SO_4^{2-} wet deposition fields from Figures 4.19 and 4.20. The big advantage of such "pseudo-scenarios" is that they make use of ADOM results that are already available without the need to re-run ADOM. Several other applications of this technique will be discussed in this section.

Influence of the Redistribution of Emissions Reductions within Provinces

As described in Table 4.1, scenarios "PST2010B" (Section 4.5.2.1.1.S12) and "PST2010C" (Section 4.5.2.1.1.S13) are quite similar, but there are three differences between them. First, in scenario “PST2010B” Quebec SO_2 emissions are reduced by 45%, but in scenario “PST2010C” they are reduced by 50%. Second, in scenario “PST2010B” U.S. SO_2 emissions are reduced by 60%, but in scenario “PST2010C” they are only reduced by 50%. And third, in scenario “PST2010B” Ontario and Quebec SO_2 emissions are rolled back uniformly, but in scenario “PST2010C” they are reduced by changing different sources by different amounts. Without the first two differences, however, it would be possible to compare the two scenarios directly to investigate how important the spatial distribution of emission reductions *within* provinces is.

In order to put scenarios “PST2010B” and “PST2010C” on a more common footing, we can make use of two of the source-region contribution results from the previous section. Figure 4.18 shows the impact of a uniform 5% reduction in Quebec SO_2 emissions on SO_4^{2-} wet deposition. If we combine this field with the “PST2010B” SO_4^{2-} wet deposition field, we will get an estimate of the SO_4^{2-} wet deposition that would have been predicted by ADOM if the “PST2010B” scenario had considered a 50% rollback of Quebec SO_2 emissions instead of a 45% rollback. That is, we have created a “pseudo-scenario” and estimated the ADOM result without running ADOM. Algebraically, this scenario has the form

Pseudo-scenario B =
PST2010B – (5/11)*(PST2010a – PST2010A)

Similarly, Figure 4.19 shows the impact of a 5% reduction in U.S. SO_2 emissions on SO_4^{2-} wet deposition. If we combine two times this field with the “PST2010C” SO_4^{2-} wet deposition field, we will get an estimate of the SO_4^{2-} wet deposition that would have been predicted by ADOM if the “PST2010C” scenario had considered a 60% rollback of U.S. SO_2 emissions instead of a 50% rollback. Algebraically, this scenario has the form

Pseudo-scenario C =
PST2010C – 2*(PST2010A – PST2010B)

Given these adjustments the only difference between these two new “pseudo-scenarios” will be the spatial distribution of the SO_2 emission reductions in Ontario and Quebec. If we then compare these two “pseudo-scenarios”, we can learn what impact the spatial distribution of SO_2 emission reductions within a particular jurisdiction can have.

Figure 4.23 shows the difference between the annual SO_4^{2-} wet deposition fields for pseudo-scenario B minus pseudo-scenario C. In pseudo-scenario C, emissions from major sources in Wawa and Sudbury, Ontario and Rouyn,

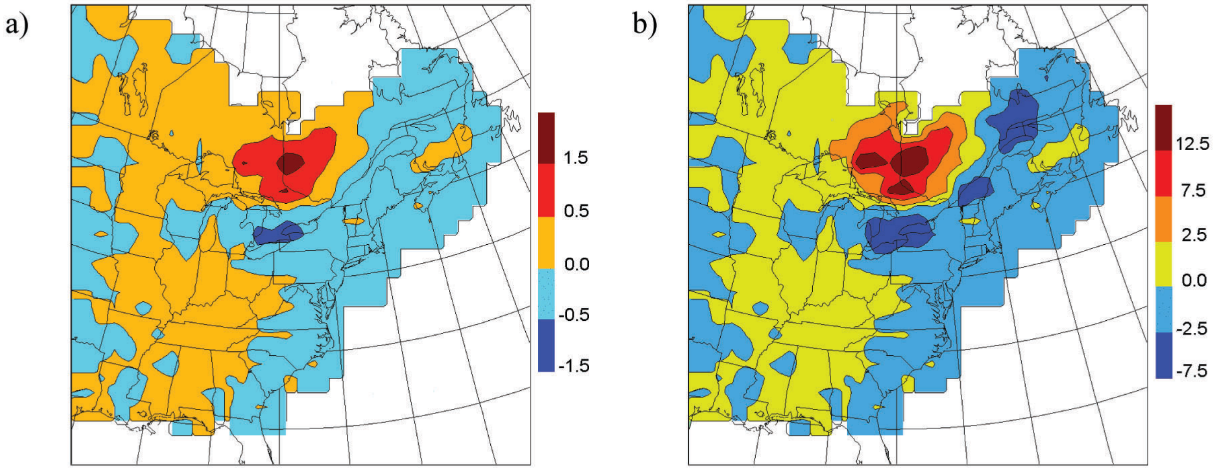


Figure 4.23: Plots of the impact of redistributing emission reductions in Ontario and Quebec from uniform reductions to source-specific reductions in (a) actual (units of kg SO_4^{2-}/ha/yr) and (b) percentage terms. Calculated as [Pseudo-scenario B - Pseudo-scenario C] and [Pseudo-scenario B - Pseudo-scenario C] / [Pseudo-scenario B], respectively.

Quebec are reduced by considerably more than they are in pseudo-scenario B (see Table 4.3), suggesting that SO_4^{2-} wet deposition should be smaller in these areas than in pseudo-scenario B. Thus, the difference between the two SO_4^{2-} wet deposition fields in these areas should be positive. In contrast, in southern Ontario, emissions from the three large OPG coal-fired stations in Sarnia, Nanticoke, and Toronto are reduced by the same amount in both pseudo-scenarios, while other sources in southern Ontario are reduced in pseudo-scenario B but *increased* in pseudo-scenario C. The net result in southern Ontario should thus be increased SO_4^{2-} wet deposition for pseudo-scenario C compared to pseudo-scenario B and hence negative values in the annual SO_4^{2-} wet deposition difference field. This is exactly the behaviour observed in Figure 4.23 for Ontario, with relative increases as large as 10% and relative decreases as large as 5%. Similar behaviour is observed in southern Quebec along the St. Lawrence River, where the emission reduction in pseudo-scenario C is only about 9% vs. 50% in pseudo-scenario B. Conversely, for the Noranda Horne smelter at Rouyn in northwestern Quebec close to the Ontario border, the reduction in pseudo-scenario C is 84% vs. 50% in pseudo-scenario B.

A similar comparison can be performed for scenarios "PST2010C" (Section 4.5.2.1.1.S13) and "PST2010E" (Section 4.5.2.1.1.S15) to examine the impact of a redistribution of emission reductions in New Brunswick and Nova Scotia. The former scenario assumes a 50% rollback of U.S. emissions whereas the latter scenario assumes a 60% rollback, so a similar adjustment to the previous example must first be made to align the U.S. reductions. Again, the largest impact of the reduction redistribution (not shown) is predicted to occur within these two provinces (ARM Consultants, 2000).

Sensitivity to a Range of U.S. Emission Reductions

Pseudo-scenarios are also useful in addressing the uncertainties associated with U.S. emissions reductions on critical load attainment in Canada. Many of the ADOM SO_2 emission control scenarios listed in Table 4.1 make fairly detailed assumptions about Canadian control measures but simply assume a certain uniform reduction in U.S. emissions. Given the major impact that U.S. SO_2 emissions have on sulphur concentrations and deposition in eastern Canada, it would be useful for a particular Canadian control scenario to consider a range of U.S. emissions in the absence of better information about possible future U.S. control measures. This could be accomplished by re-running ADOM many times, but a simpler alternative is to construct a set of pseudo-scenarios by using Figure 4.19a.

Figure 4.24 shows a comparison of the critical load exceedance field predicted by ADOM for scenario "PST2010E" (Section 4.5.2.1.1.S15), for which further U.S. SO_2 emissions reductions of 60% from 2010 levels were assumed, to pseudo-scenario estimates of the critical load exceedance fields that would result given the same Canadian emission reductions but smaller further U.S. SO_2 emission reductions of 50%, 40%, 20%, and 0%. These pseudo-scenarios were created by subtracting 2X, 4X, 8X, and 12X the difference field shown in Figure 4.19a from the annual SO_4^{2-} wet deposition pattern for scenario "PST2010E", and then subtracting the critical load field shown in Figure 4.1 from the annual SO_4^{2-} wet deposition field for each pseudo-scenario.

As the magnitudes of the assumed further U.S. SO_2 emission reductions are reduced, the Maritimes again go into non-attainment (Figure 4.24b) and the critical load exceedance "hot spots" in central Canada grow larger. For further U.S. emission reductions of only 20%, parts of southern Ontario, all of New Brunswick, and much of Nova Scotia are predicted to be in non-attainment (Figure 4.24d), and the situation is worse still if no additional U.S. cuts from 2010 levels are assumed (Figure 4.24e). These constructed scenarios thus suggest the extent to which the success of additional Canadian SO_2 emission controls will be influenced by the level of further U.S. actions. The same approach was used by ARM Consultants (2002) for the "PST2010F" scenario to examine the impact of rollbacks to U.S. SO_2 emissions of 20%, 40%, and 60% vs. the 50% rollback considered in that scenario (not shown).

Note that the fifth member of this set of pseudo-scenarios, the one with no further U.S. SO_2 emission reductions ("PST2010E&US0"), has been compared with the key ADOM 2010 ("CCUSA2") scenario (ARM Consultants, 2000). This comparison allows the impact of the Canadian SO_2 emission reductions in scenario

"PST2010E" to be considered in isolation, just as was shown for the "CCUSA2"–"5CONLY" scenario pair in Figure 4.16.

Test of Pseudo-Scenario Methodology

The results for the above pseudo-scenarios were obtained without running ADOM directly, thus avoiding the very considerable effort associated with applying ADOM to a new emission scenario. However, as noted above the pseudo-scenario methodology is predicated upon the linearity of atmospheric sulphur chemistry and can only be expected to provide an *estimate* of the fields that would be predicted by ADOM for the same input SO_2 emissions field. It would thus be worthwhile to test and evaluate the performance of this methodology.

The obvious test is to run ADOM for the same SO_2 emissions field as considered for a pseudo-scenario and then compare the results. It is possible to do this test for one of the ADOM scenarios listed in Table 4.1 by considering a pseudo-scenario constructed from three other ADOM scenarios from that table. Consider that the difference in SO_2 emissions between scenarios "PST2010a" and "PST2010b" is the same as between scenarios "PST2010A" and "PST2010B" – a 5% rollback in U.S. emissions. By taking the difference between the annual SO_4^{2-} wet deposition fields predicted by ADOM for scenarios "PST2010a" and "PST2010b", it is then possible to determine the impact of such a 5% uniform decrease in U.S. emissions on annual SO_4^{2-} wet deposition as was done in constructing Figure 4.19. This difference field can then be added to the "PST2010B" annual SO_4^{2-} wet deposition field to estimate the ADOM prediction if the rollback in U.S. SO_2 emissions had only been 55% rather than 60%. But ADOM scenario "PST2010A" considered a U.S. rollback of 55%, so if we calculate the difference between the ADOM-predicted SO_4^{2-} wet deposition field for scenario"PST2010A" and the constructed version of the same field based on ADOM results for scenarios "PST2010B", "PST2010a", and "PST2010b", we would expect to see only very small differences if the pseudo-scenario methodology is reasonably accurate.

This difference field is shown in Figure 4.25. The values of the grid-cell differences are, in fact, small and range from -0.02 to 0.025 kg SO_4^{2-}/ha/yr. Since the annual SO_4^{2-} wet

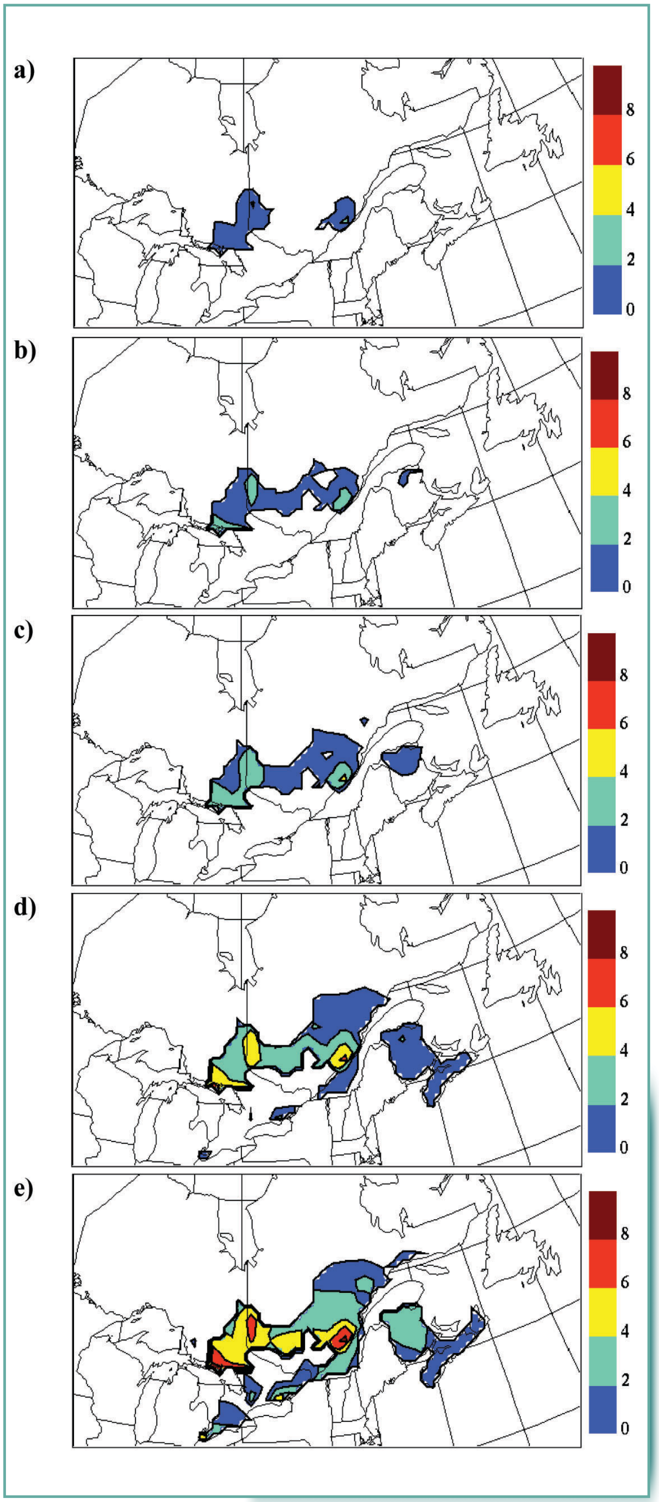


Figure 4.24: Plots of the SO_4^{2-} wet deposition critical load exceedance fields (units of kg SO_4^{2-}/ha/yr) for ADOM scenario "PST2010E" with different U.S. SO_2 emissions reductions from 2010 levels: (a) 60% reduction; (b) 50% reduction; (c) 40% reduction; (d) 20% reduction; and (e) 0% reduction.

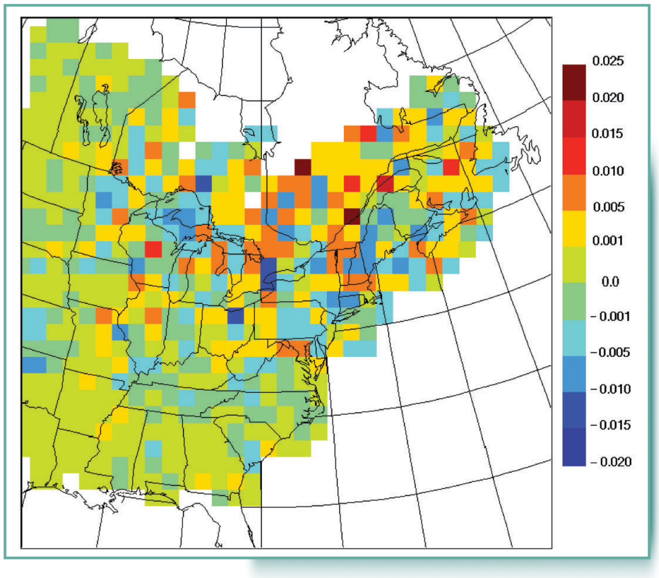


Figure 4.25: Difference between annual SO_4^{2-} wet deposition field for scenario "PST2010A" calculated by ADOM and a pseudo-scenario A calculated as PST2010B + (PST2010a - PST2010b) in units of kg SO_4^{2-}/ha/yr.

deposition field for scenario "PST2010A" has values in the 5 to 15 kg SO_4^{2-}/ha/yr range, and even the changes associated with a 5% change in Quebec emissions alone are in the 0.02 to 0.14 kg/ha/yr range (see Figure 4.18), uncertainties in the ±0.025 kg/ha/yr range associated with pseudo-scenario calculations are probably acceptable in many cases. However, the use of large weighting factors will likely magnify errors resulting from the use of this approach (e.g., the factor of 12 used to construct pseudo-scenario "PST2010E&US0" in Figure 4.24).

4.5.2.2 *New applications of the* IAM

This section describes two applications of the existing IAM model that was described in Section 4.4.3. The next section, Section 4.6, then describes several projects intended to improve the treatment of atmospheric source-receptor relationships in the IAM.

4.5.2.2.1 Comparison of IAM and ADOM results

As described in Section 4.4.3, the IAM uses a "reduced-form" representation of atmospheric source-receptor relationships for sulphur species in the form of a linear 40x15 transfer matrix based on source-receptor matrices for two meteorological years that were produced by the ALSM model. Since this approach is much simpler than the complex calculations performed by ADOM, it is also much easier and faster to use than ADOM and it allows access to the IAM's emission-reduction optimization capabilities and to the IAM's effects modules. The two models can thus be used in tandem, with the IAM applied first as a screening tool to identify promising control strategies out of a large set of possibilities and ADOM applied next to provide a more detailed and accurate evaluation of a small set of promising emission scenarios identified by the IAM.

A natural question to ask, though, is "How similar are the predictions of the two models"? ADOM predicts many more species than the IAM over a larger region and at levels above the ground as well as at ground level. In terms of common predictions, both models can predict annual SO_4^{2-} wet deposition at 13 receptor sites in eastern North America (two of the IAM's 15 receptor sites, Nitchequon, Quebec and Gander, Newfoundland, lie outside of the area treated by the episode aggregation technique used by ADOM for making estimates of annual deposition fields).

Figure 4.26 presents scatterplots of IAM vs. ADOM predictions at these 13 receptor sites for the six key ADOM scenarios discussed in Section 4.5.2.1.3. While there is some scatter present, the overall agreement for each scenario is good, and both models predict a similar reduction in peak annual wet deposition at the 13 receptor sites, from values of about 35 kg SO_4^{2-}/ha/yr for the "BASE89" scenario to values under 10 kg/ha/yr for the "75FCAP" scenario. This comparison thus supports the use of the IAM as a useful screening tool for ADOM.

4.5.2.2.2 Description of new IAM emission-control scenarios

The IAM was used in the 1997 *Assessment* to model aquatic- and wildlife-related effects of four future year SO_2 emission scenarios. Four new future year emission control scenarios have been prepared for this *Assessment* for use with the IAM. Emissions of both SO_2 and NO_x are considered. These new IAM emission-control scenarios are related to some of the ADOM emission-control scenarios described in Section 4.5.2.1, but further processing has been performed in order to aggregate the scenario emissions to the simpler source-region format required by the IAM. The reason is that, whereas the other acid deposition models described in this Chapter require gridded emissions, the IAM requires source-region-based emissions for 40 North American source regions (see Figure 4.27).

The new IAM scenarios correspond to nominal projection years 1995/96, 2010, 2020, and 2060. Since they are being used to consider cumulative acid deposition effects on both aquatic and terrestrial ecosystems, they have been developed to be used together to describe what amounts to a 65-year-long emission scenario. That is, they portray four "snapshots" of the projected change in North American SO_2 and NO_x emissions between 1995 and 2060. The guiding assumption in constructing these scenarios is that for each project year, the scenario should reflect the minimum level of emissions that can be expected given current emission controls and further controls that are likely to be implemented in the near term. As a historical scenario, the 1995/96 scenario considers actual emissions. For the 2010 and 2020 IAM SO_2/NO_x scenarios, all of the Canadian and U.S. emission control programs described in Section 4.5.2.1 are assumed to have been implemented. The 2020 IAM scenario is thus identical to the "NOX3P" ADOM scenario, which makes the same assumption. And for the 2060 scenario, which is beyond most current policy development "horizons", a further 25% rollback of both SO_2 and NO_x emissions from 2020 levels has been assumed.

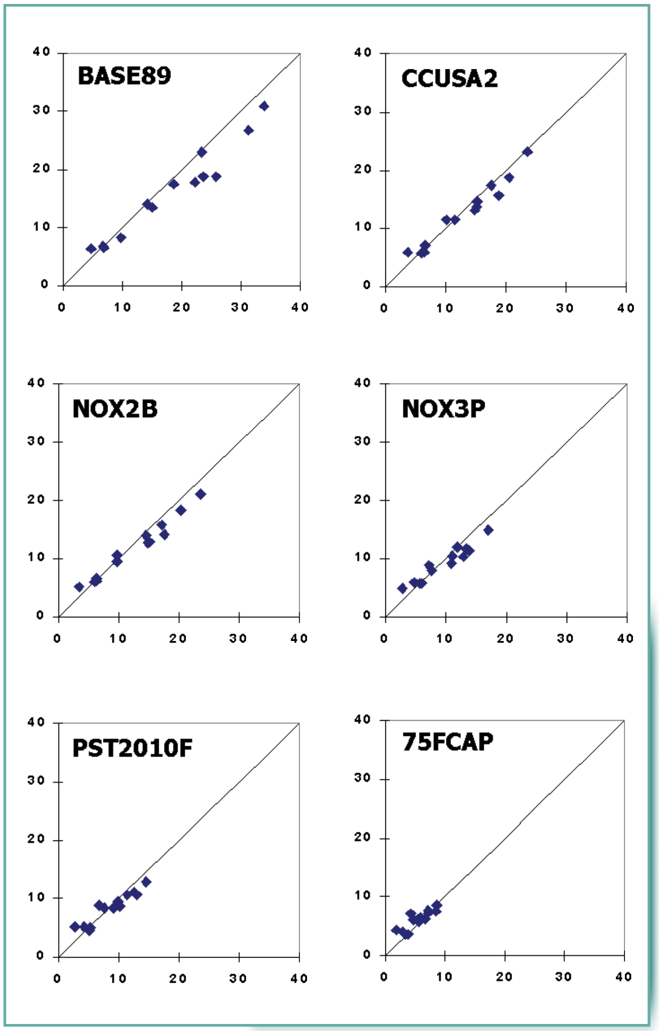


Figure 4.26: Scatterplots of annual SO$_4^{2-}$ wet deposition (units of kg SO$_4^{2-}$/ha/yr) predicted by the ADOM (x-axis) and IAM (y-axis) models for 13 receptor sites in eastern North America for ADOM scenarios (a) BASE89, (b) CCUSA2, (c) NOX2B, (d) NOX3P, (e) PST2010F, and (f) 75FCAP.

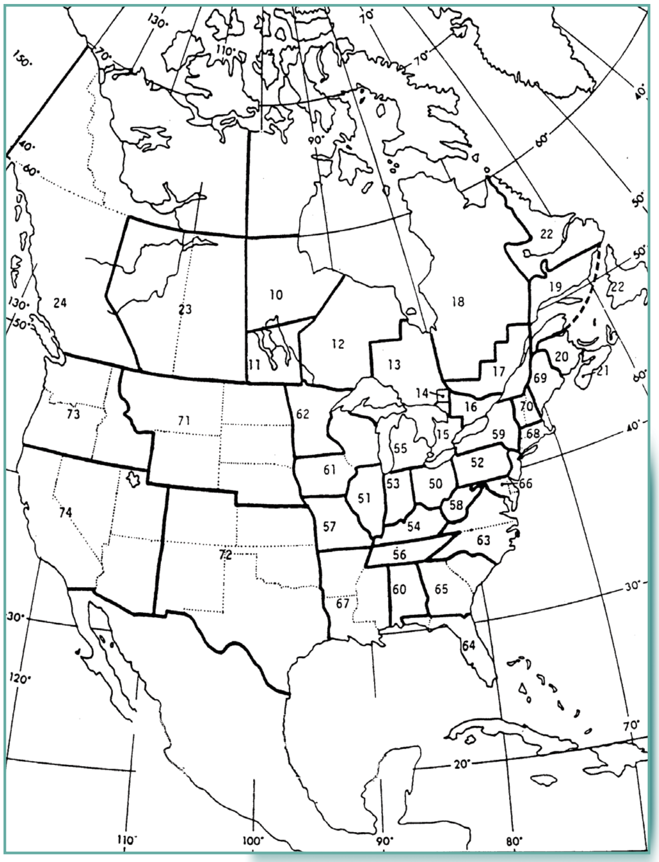


Figure 4.27: Location of 40 source regions considered by IAM. Fifteen of these source regions are located in Canada and 25 are located in the U.S.. Note that most of the source region boundaries follow existing provincial and state boundaries.

Table 4.6. Total Canadian and U.S. SO_2 emissions (Ktonnes SO_2/yr) and NO_x emissions (Ktonnes NO_2/yr) for four new IAM scenarios (highlighted in yellow) and four IAM emission-control scenarios from the *1997 Assessment*.

Nominal	Assessment	Canada		U.S.A.		Total	
Year	Year	SO_2	NO_x	SO_2	NO_x	SO_2	NO_x
1985	1997	3,650		20,900		24,550	
1990-93	1997	3,078		19,910		22,988	
1994	1997	2,788		19,910		22,698	
1995/96	2004	2,634	2,764	16,712	22,342	19,346	25,106
2010	1997	2,788		15,282		18,070	
2010	2004	2,236	2,406	10,646	14,486	12,882	16,892
2020	2004	2,091	2,316	9,138	11,165	11,229	13,481
2060	2004	1,568	1,737	6,854	8,374	8,422	10,111

Given these assumptions, as shown in Table 4.6 the new 2010, 2020, and 2060 IAM scenarios are more stringent than the four IAM emission-control scenarios considered in the 1997 *Assessment*. The resulting ecosystem impacts of these new scenarios should thus be correspondingly greater than the impacts considered in the previous *Assessment*. In terms of SO_2 emissions, however, note that even the 2060 IAM scenario assumes roughly twice the level of SO_2 emissions that were considered in the "75FCAP" ADOM scenario. The four new IAM scenarios are described in more detail in Section 7.6.2 and the scenario emissions by source region are summarized in Table 7.4 (Chapter 7).

4.6 NEW DEVELOPMENTS

4.6.1 New sulphur source contribution studies and SRMs

Two significant limitations of the current version of the IAM are related to the SO_4^{2-} wet deposition source-receptor matrix used to describe the atmospheric source-receptor relationship between SO_2 emissions to the atmosphere and the resulting annual SO_4^{2-} wet deposition field. This 40 x 15 "transfer" matrix summarizes the contributions of 40 source regions covering North America (see Figure 4.27) to 15 receptor sites in eastern North America, 12 in southeastern Canada and three in the northeastern U.S. (see Figure 4.28a). One limitation of considering only 15 receptors is that for many effects data sets such as lake-chemistry data sets, the measurement sites may be located hundreds of kilometers from the nearest atmospheric receptor site. The need for co-located atmospheric inputs then demands horizontal interpolation of some sort, which will in turn introduce additional uncertainty due to interpolation error. A second limitation is that 15 irregularly spaced data points are not really enough to permit the drawing of spatial contour fields such as those presented in the previous chapter. Both of these limitations would be addressed if new sulphur source-receptor matrices could be created for a larger set of receptor sites with both greater geographic coverage and higher spatial density (i.e., smaller between-site spacing). The availability of such a larger set of atmospheric receptor sites would both reduce interpolation error in estimating atmospheric inputs at effects measurement sites and justify the drawing of spatial contour fields.

The ALSM model described in Section 4.4.1 is being used to create new sulphur source-receptor matrices for an expanded set of 200 receptors distributed across most of Canada and the continental U.S.. The locations of these receptors are shown in Figure 4.28b. This new receptor set includes the original 15 IAM receptors but adds another 80 receptor sites in Canada and 105 receptor sites in the U.S.. Two considerations in the selection of receptor sites were to choose locations where air quality measurement stations are located and to minimize sampling errors in representing current observed fields. Of these 200 receptors, 151 are located at precipitation-chemistry or air-chemistry station sites, an advantage for model performance evaluation. The density of receptors is greatest in eastern North America, where the highest regional air concentrations and deposition of sulphur species are measured (e.g., Figure 3.2a).

The ALSM computational grid consists of 52 x 58 = 3,016 grid points with 127 km grid spacing. The ALSM has been run for all of the 1990 meteorological year using gridded SO_2 and SO_4^{2-} emissions for base year 1990 and treating all 3,016 grid points as receptor sites. Annual fields of SO_2, SO_4^{2-}, and total sulphur air concentrations and SO_2, SO_4^{2-}, and total-S dry, wet, and total deposition were calculated, where total sulphur is the sum of contributions from SO_2 and SO_4^{2-} in units of sulphur mass. Figures 4.29a and 4.30a show the 1990 annual SO_2 and SO_4^{2-} air concentration fields predicted by the ALSM for the full set of 3,016 grid points. If we then “sample” these two fields at the 200 receptor sites shown in Figure 4.28b with bilinear interpolation and plot contoured spatial fields based only on these 200 data points, we obtain close approximations of the two original fields using about 1/15th the number of data points. The contoured sampled fields are shown in Figures 4.29b and 4.30b. The sampled annual SO_2 air concentration field in Figure 4.29b is within ±3.0 μg/m^3 of the full grid field shown in Figure 4.29a; the relative differences associated with the largest actual differences of –2.5 and 3.0 μg/m^3 are –10% and 18%, respectively. The sampled annual SO_4^{2-} air concentration field in Figure 4.30b is within ±0.6 μg/m^3 of the full-grid field shown in Figure 4.30a; the relative differences associated with the largest actual differences of –0.33 and 0.56 μg/m^3 are –4% and 7%, respectively.

The use of the ADOM model to estimate the contribution of different source regions was discussed in Section 4.5.2.1.4. The ALSM can perform similar calculations. For example, Figure 4.31 shows ALSM predictions of annual total sulphur air concentration and annual total sulphur wet deposition for 1990 SO_2 and SO_4^{2-} emissions from all 40 source regions in Figure 4.27. To calculate SRMs, the ALSM is then run 40 more times, once for each source region, with emissions from all of the other source regions set to zero (e.g., Olson et al., 1983). The relative contribution of each source region can then also be calculated by taking the ratio of a field of interest from the run considering emissions from only one particular source region to the same field from the run that considered all 40 source regions. Figure 4.32 gives one

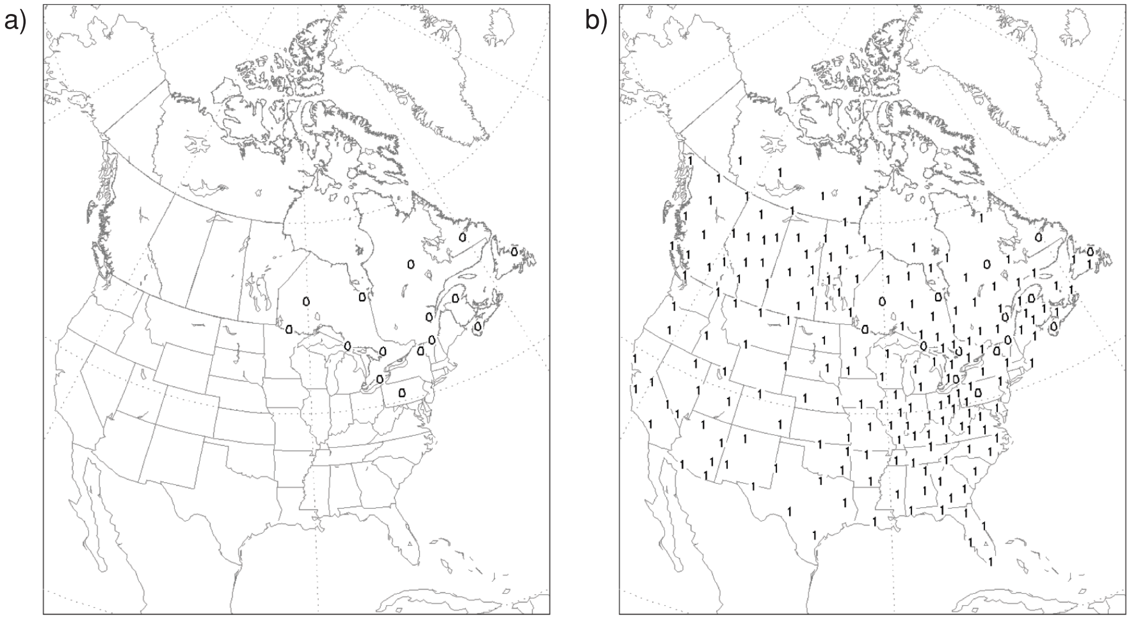


Figure 4.28: Location of (a) 15 receptors considered by earlier versions of IAM and (b) new expanded set of 200 receptors.

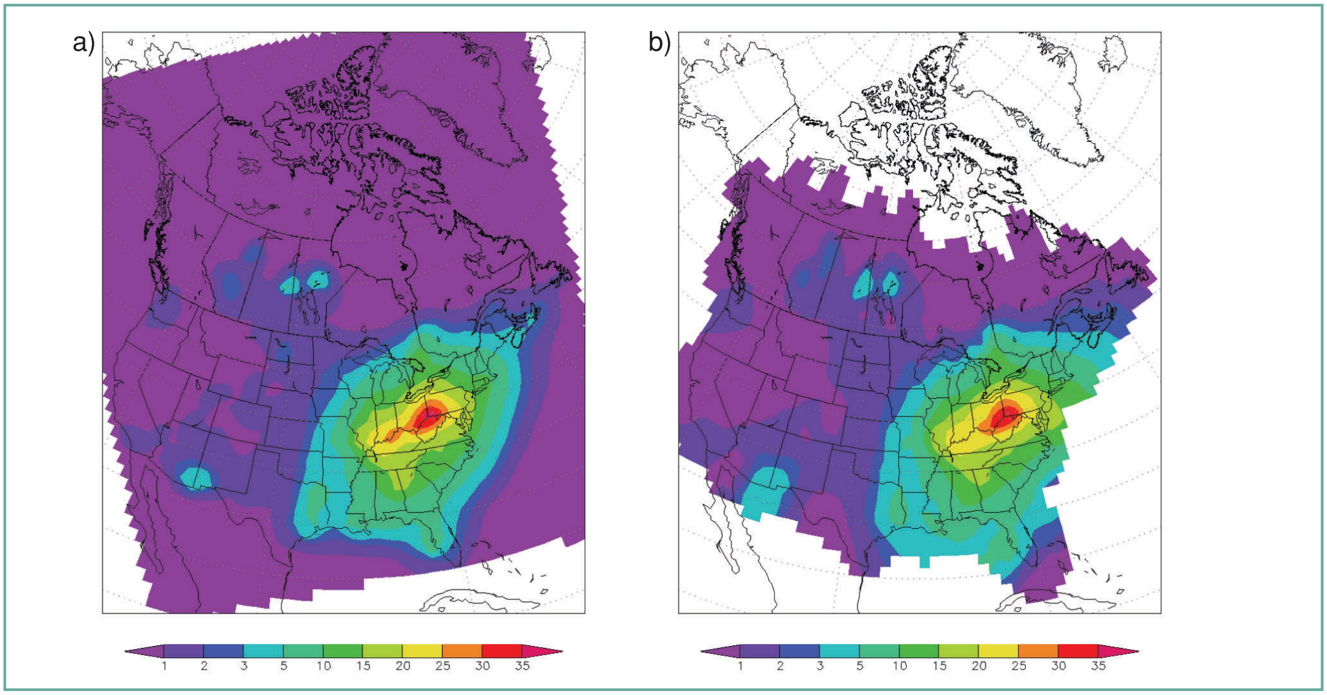


Figure 4.29: Annual 1990 SO_2 air concentration fields (a) predicted by the ALSM for the full set of grid points and (b) obtained by horizontal interpolation from 200 point values extracted from full field. Units are $\mu g\ SO_2/m^3$. Contouring was performed by the GrADS visualization package.

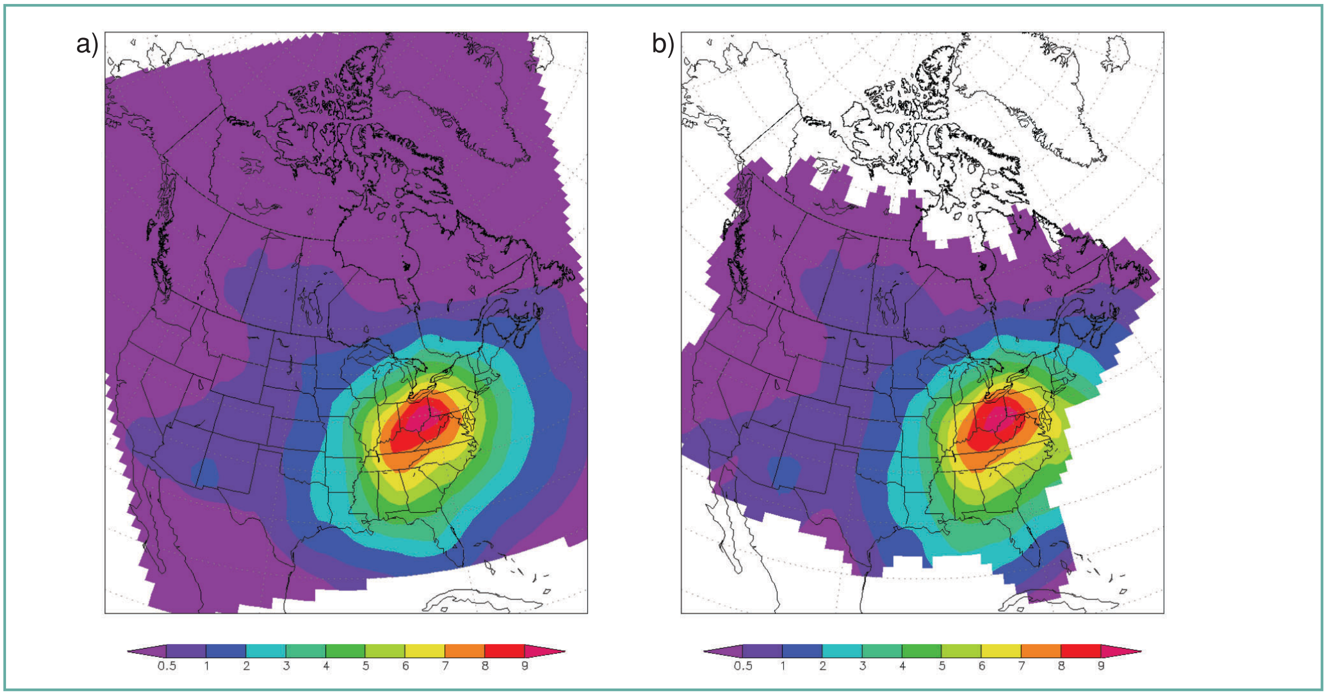


Figure 4.30: Same as Figure 4.29 but for annual 1990 SO_4^{2-} air concentration fields. Units are $\mu g\ SO_4^{2-}/m^3$.

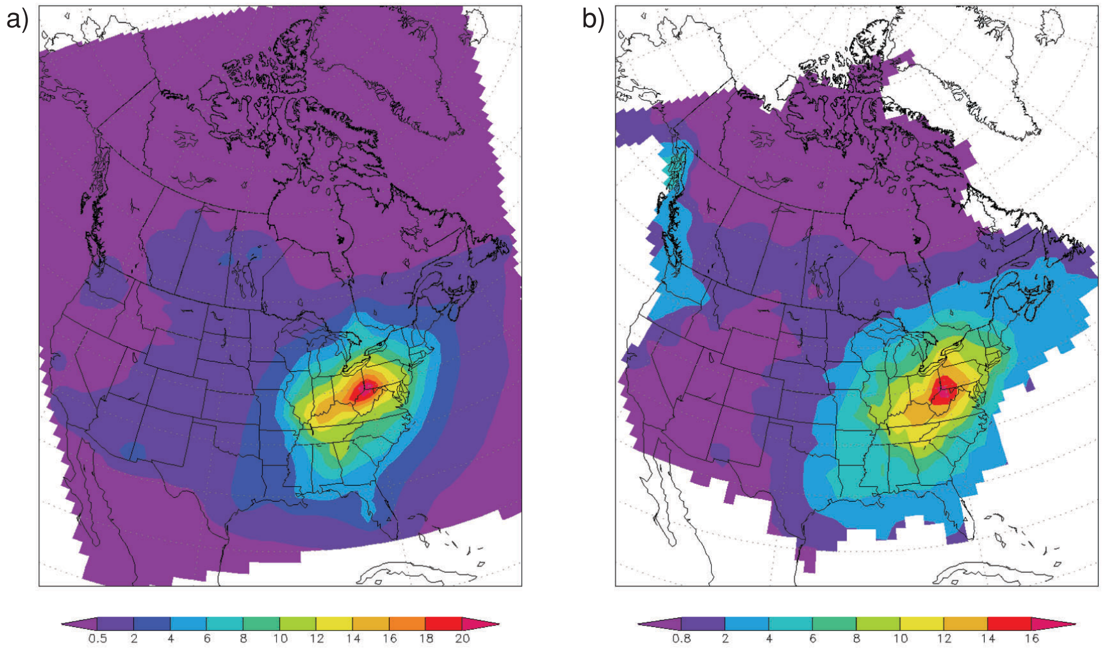


Figure 4.31: ALSM-predicted annual 1990 total sulphur (a) air concentration (μg S/m^3) and (b) wet deposition (kg S/ha/yr) for emissions from all 40 North American source regions.

example, showing the actual and percent contribution of the northern Manitoba source region, which is dominated by emissions from the large smelting facilities at Flin Flon and Thompson, to total sulphur air concentration and total sulphur wet deposition. The atmospheric "footprint" of the northern Manitoba SO_2 sources can be seen to reach into neighbouring provinces and states.

The U.S. EPA's RADM acid deposition model, which uses a grid with 80 km spacing, has also been used to estimate the percent contribution to total sulphur deposition of another set of 53 smaller source regions in the eastern U.S. for base year 1985 and future year 2010 (U.S. EPA, 1995). To the extent that source regions can be matched, there is reasonable qualitative agreement between the percent-contribution fields predicted by ALSM and RADM. For example, ALSM source region 70 (Vermont/New Hampshire) and RADM source region 46 are reasonable matches, and ALSM source region 50 (Ohio) can be compared to the sum of RADM source regions 14, 15, 16, 20, and 22. Figure 4.33 compares ALSM/IAM source region 58 (West Virginia) to RADM source region 20 (OH/WV/KY border). There is rough agreement between the 10% and 5% and 6% isopleths, and both figures display a tighter gradient to the west of the source region vs. the east and an elongation to the northeast.

4.6.2 New nitrogen source-receptor matrices

The acid deposition effects and policy communities would like to have annual source-receptor matrices (SRMs) for North America for both sulphur and nitrogen species. Such SRMs have been developed previously by the Meteorological Service of Canada (MSC) using the ALSM and ALNM models, but only for a limited number of receptor sites (15) and only for oxidized nitrogen in the case of the ALNM. Moreover, as discussed in Section 4.4.2, whereas atmospheric nitrogen chemistry is very complex, the ALNM considers only a very simple gas-phase chemical mechanism and only one VOC species, prescribes monthly mean oxidant concentration fields, and ignores reduced-nitrogen species and nitrate gas-particle partitioning. Thus, although the ALNM could be run to create oxidized nitrogen SRMs for a more recent meteorological and emissions year for a larger number of

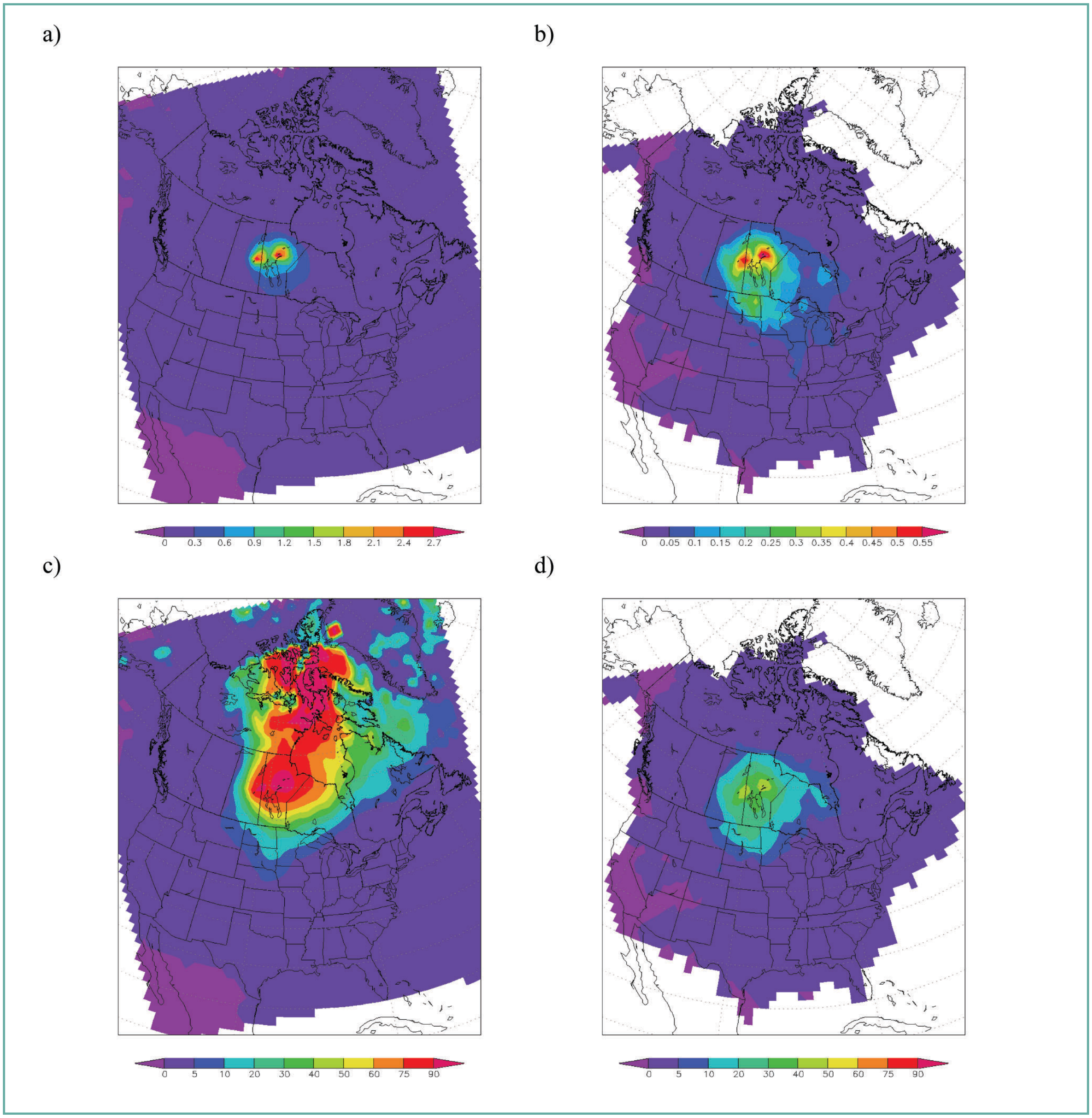


Figure 4.32: ALSM-predicted annual 1990 (a) total sulphur air concentration ($\mu g\ S/m^3$), (b) total sulphur wet deposition (kg S/ha/yr), (c) percent contribution to total sulphur air concentration, and (d) percent contribution to total sulphur wet deposition for emissions from ALSM/IAM source region 10 (northern Manitoba).

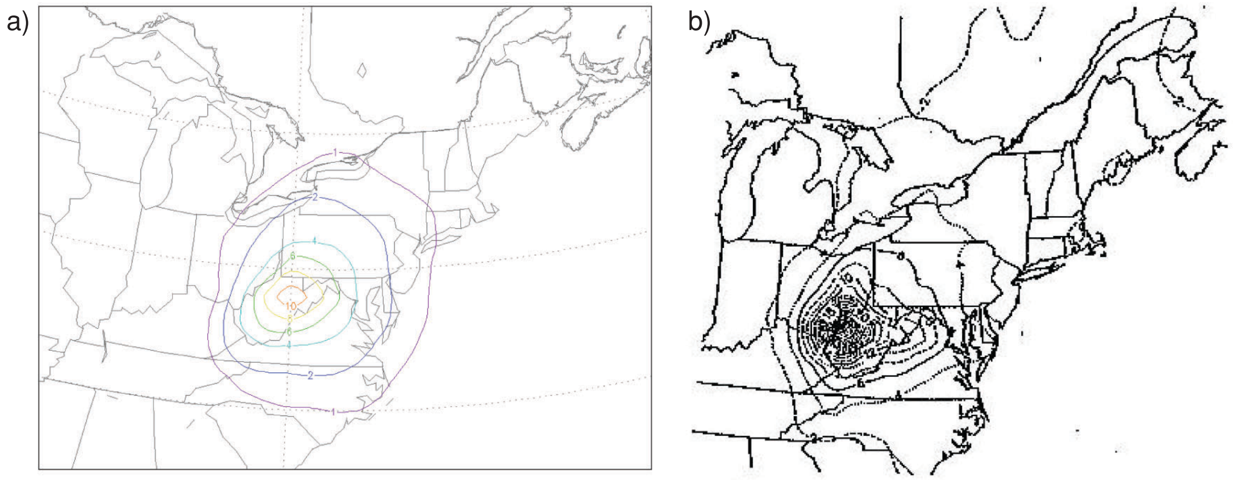


Figure 4.33: Percent contribution to total sulphur deposition predicted by (a) ALSM for 1990 emissions from ALSM/IAM source region 58 (West Virginia) and (b) RADM for 1985 emissions from RADM source region 20 (OH/WV/KY border). Panel (b) has been taken from U.S. EPA (1995).

receptor sites, it is not clear whether this model can provide a sufficiently accurate representation of atmospheric nitrogen chemistry.

Bouchet and Moran (2002) investigated other approaches to address this requirement, including European work to develop SRMs for nitrogen species and for ozone (e.g., Bartnicki, 1999, 2000; EMEP, 1998; Simpson, 1992; Simpson et al., 1997). Their recommendation was that the AES Lagrangian Oxidant Model (ALOM), a Lagrangian chemical transport model with a detailed gas-phase chemistry mechanism previously used for summer-time ozone modelling (Environment Canada, 1997b) should be (a) extended to include particle sulphate, nitrate, and ammonium and attendant process representations (aqueous-phase and heterogeneous chemistry; particle dry and wet deposition), (b) tested and evaluated, and (c) used to create SRMs for both sulphur and oxidized and reduced nitrogen species. Either 70 or 200 receptor sites will be used, depending upon model speed. It will also be possible to compare the new SRMs generated for sulphur species with those generated previously using the simpler ALSM.

Work is underway now to extend ALOM for nitrogen modelling. Note that, given the changes that are required to ALOM to introduce inorganic aerosol physics and chemistry process representations, an appropriate new name for the extended version of ALOM might be LIAM (“Lagrangian Inorganic Aerosol Model”).

4.6.3 Status of a new Eulerian Acid Deposition Model

AURAMS is a new, size-resolved, chemically-characterized, episodic Eulerian regional particulate matter (PM) modelling system that has been developed by MSC for air quality (AQ) research, management, and forecasting. The acronym AURAMS stands for **A U**nified **R**egional **A**ir quality **M**odelling **S**ystem. AURAMS consists of three main components: a regional emissions processing system; a nonhydrostatic meteorological model; and a regional PM air quality model. The term “Unified” is used because a comprehensive, size- and composition-resolved, regional PM model must consider emissions of both primary PM components and gaseous PM precursors, atmospheric transport and diffusion, aerosol processes such as nucleation, condensation, coagulation, and activation, gas-phase, aqueous-phase, and heterogeneous chemistry, and wet and dry removal of both particles and trace gases. Such a model is thus by default a multi-pollutant AQ model applicable to other AQ issues such as photochemical oxidants and acid deposition, since many of the atmospheric processes and

PM precursor species important for PM must also be considered for these other AQ issues. The ability to consider multiple air pollutants simultaneously will then enable AURAMS to be applied for integrated AQ planning and management.

AURAMS has been constructed following to the design described in Moran et al. (1998) using four major existing "building blocks":

(a) a regional emissions processing system, the Canadian Emissions Processing System, or CEPS (e.g., Scholtz et al., 1999; Makar et al., 2003a);

(b) a nonhydrostatic mesoscale meteorological model, initially MC2, the Mesoscale Compressible Community model (e.g., Benoit et al., 1997), and now GEM, the Global Environmental Multiscale meteorological model (Côté et al., 1998a,b);

(c) a gas-phase chemical transport model, the Canadian Hemispheric and Regional Oxidant and NO_x System, or CHRONOS (Pudykiewicz et al., 1997; Sirois et al., 1999); and

(d) an aerosol module employing a sectional size representation, the Canadian Aerosol Module or CAM (Gong et al., 2003).

To build the AURAMS regional PM chemical-transport model, CAM has been merged with a restructured version of CHRONOS and more PM chemical components (nitrate, ammonium, elemental carbon, organic carbon, crustal material) and process representations (aqueous-phase chemistry, heterogeneous chemistry, secondary organic aerosol formation, size- and composition-resolved primary PM emissions) have been added. Chemical transport in AURAMS is calculated using the semi-Lagrangian advection algorithm of Smolarkiewicz and Pudykiewicz (1991) followed by mass-consistency and mass-conservation adjustments. The gas-phase chemistry mechanism employed by CHRONOS is the ADOM-II mechanism (Stockwell and Lurmann, 1989) with 114 reactions and 47 species, 29 of which are advected and 16 of which are emitted. CAM includes size-dependent treatments of nucleation, condensation, coagulation, dry deposition, gravitational settling, and in-cloud and below-cloud particle scavenging. A sectional approach is used to represent aerosol size distribution; presently, 12 sections spanning the radial size range from 0.005 to 20.48 μm are used. Dry deposition of 13 gas-phase species and seven particle species is considered, including SO_2, H_2SO_4, NO_2, HNO_2, HNO_3, HNO_4, NH_3, PAN, and particle SO_4^{2-}, NO_3^-, and NH_4. Wet deposition of five gas-phase species and seven particle species is considered, including SO_2, H_2SO_4, HNO_3, and particle SO_4^{2-}, NO_3^-, NH_4, and crustal material.

For AURAMS to replace ADOM in Canada as the acid deposition model of choice, two more steps are required. First, performance evaluations of AURAMS to date have focused on comparisons with ambient air concentration measurements of a number of gas and particle species (e.g., Canada-United States Air Quality Committee, 2004). Additional evaluations of AURAMS performance focused on acid deposition are required, especially ones employing the available and relatively abundant North American precipitation chemistry data sets. The requirement would be to demonstrate that AURAMS can at least match ADOM in predictive skill for acid deposition. Second, AURAMS is a very demanding model computationally, and to date it has been used only for episodic simulations of at most one or two weeks. However, the focus of acid deposition models is typically seasonal and annual predictions. A methodology is required to be able to use AURAMS to carry out such long term simulations. Seigneur and Moran (2003) identified two approaches that have been used to address this problem: (a) model simplification; and (b) episode aggregation. Both of these approaches have disadvantages. A third possible approach is simply a "brute force" approach, bringing to bear sufficient computational resources. Whichever approach is chosen, a key requirement is to be able to carry out several scenario simulations in an "acceptable" amount of time.

Note that pioneering analyses of the magnitude of the contribution of subgrid-scale variability to point measurement grid-volume-average incommensurability were carried out with surface network data collected during the Eulerian Model Evaluation Field Study (EMEFS) (e.g., Seilkop et al., 1993). One very important finding was that even for air concentrations of secondary pollutants such as particulate sulphate and ozone, subgrid-scale variability is much larger than measurement errors for acid deposition models with grid spacing on the order of 50 km or greater. Time averaging does reduce subgrid-scale variability, but Dennis et al. (1990) found that even for monthly mean precipitation-weighted SO_4^{2-} and NO_3^- concentrations in precipitation, the variability for an 80-km grid cell is roughly 50%. These results need to be considered in assessing AURAMS model performance.

The next section identifies some aspects of acid deposition modelling where further work could improve the state of the science. Among the topics identified are some possible improvements to the AURAMS modelling system, including the evaluation of dry deposition predictions, implementation of pH prediction, emissions processing for implementation of new emission control scenarios, and higher spatial resolution.

4.7 SUGGESTIONS FOR FUTURE WORK

The previous section described ongoing work to improve existing acid deposition models and to develop new and better models. As well as continuing these efforts, there are also a number of other areas in acid deposition modelling for Canada where further work is needed.

Although current acid deposition models predict both dry and wet deposition, as discussed in Chapter 3, it has not been possible until very recently to make measurements of dry deposition on a routine basis at multiple sites. As a consequence, it has not been possible to evaluate model predictions of dry deposition directly, although evaluations of model predictions of air concentrations under non-precipitating conditions do provide a partial indirect evaluation of dry deposition given the importance of this process in determining ambient air concentrations. Efforts now need to be made to acquire appropriate sulphur and nitrogen dry deposition data sets to allow the evaluation of model predictions of dry deposition directly. Examination of nitrogen dry deposition should include the contributions of NO_2 and total NH_3 dry deposition as well as vapour-phase nitric acid and particulate nitrate. Having confidence in dry deposition predictions would then allow model predictions of *total* acid deposition to be supplied to various effects modellers, thus avoiding the assumptions that have had to be made until now to estimate the contribution of dry deposition to sulphur and nitrogen total deposition.

Both ammonia and nitric acid have markedly higher dry deposition velocities than particulate ammonium and particulate nitrate. In order to predict air concentrations of total ammonia (ammonia plus particulate ammonium) and total inorganic nitrate (nitric acid plus particulate nitrate), it is necessary to predict the partitioning of total ammonia and total nitrate between the gas and particle phases. This partitioning in turn depends in a complex manner on temperature and concentrations of total sulphate, total ammonia, total nitrate, and water vapour. Of the acid deposition models discussed in this chapter, only ADOM and AURAMS treat this phase partitioning process explicitly, and ADOM employs only a very simple phase-partitioning algorithm whereas AURAMS uses a state-of-the-science formulation (see Makar et al., 2003b). The proper representation of inorganic gas-particle partitioning is likely to become even more important when emission scenarios consider changes in emissions of multiple pollutants, including combinations of SO_2, NO_x, and NH_3. Such scenarios are in fact becoming increasingly common as part of the development of PM control strategies, for which acid deposition reduction constitutes an important co-benefit. Accordingly, the influence of inorganic gas-particle partitioning on emission-scenario results needs to be investigated.

For some effects modelling, the controlling atmospheric input is not a particular acidifying species such as sulphate or nitrate but rather total acidity. Unfortunately, prediction of pH is particularly difficult because it requires the concentrations or depositions of *all* acidifying species to be estimated correctly, including total ammonia and base cations. Base cations pose a particular problem since they are present in crustal material (i.e., fugitive dust) in varying proportions and since emissions of bulk crustal material are still not well characterized, especially for such natural sources as windblown dust and forest fires, which are intermittent and strongly dependent on both meteorological conditions and surface conditions. However, the increased focus on PM as an air quality issue has resulted in improvements in the availability of measurements of crustal material concentrations in the atmosphere and in estimates of emissions of crustal material. If additional information is available about the elemental composition of crustal material, ideally varying geographically, then a model such as AURAMS could be used to predict pH.

However, model skill in predicting pH will almost certainly be lower than for those individual acidifying species such as sulphate and nitrate, whose gaseous precursor emissions are known with greater certainty.

The key environmental metric that has been used to date by atmospheric chemistry modellers in Canada to asses the ecological sustainability of future year deposition fields for eastern Canadian aquatic ecosystems is a critical load field that is based on wet sulphate deposition. New critical load fields for Canadian aquatic and terrestrial ecosystems have been developed as part of the present Assessment. These new critical load fields need to be used to assess the ecological sustainability in eastern and western Canada of predicted future year acid deposition fields.

The preparation of the input emissions used by acid deposition and other AQ models is an ongoing area of need. For example, in order to evaluate model performance against air-chemistry and precipitation-chemistry measurements for a particular year, emission fields representative of that year first need to be prepared and provided as input for the model. Similarly, as emission control scenarios become more realistic and source-type- and jurisdiction-specific, the level of effort required to implement these scenarios in terms of preparation of the emission fields supplied to the acid deposition models becomes increasingly onerous. Furthermore, as emission scenarios are increasingly multi-pollutant in nature, the number of pollutant species that must be processed for each scenario increases. There is thus a need for access to sophisticated emissions processing systems that can be used to prepare detailed gridded emission fields relatively quickly for different inventory base years and different emission control scenarios.

To evaluate acid deposition model performance against newer sets of air-chemistry and precipitation-chemistry measurements as they become available, it is also necessary to create year-long files of meteorological fields for input to the acid deposition model. While Lagrangian acid deposition models typically only require gridded wind fields for one or more levels plus precipitation fields, the meteorological requirements for comprehensive Eulerian models are much greater. The use of ADOM has been handicapped by the lack of a dedicated meteorological model to prepare these fields. However, the meteorological data sets that were prepared for ADOM for a number of periods (e.g., portions of 1988 and 1990) did have the advantage that they included the assimilation of some meteorological measurements, in particular precipitation. AURAMS has a dedicated meteorological model (GEM), but at present it is not able to assimilate precipitation or other meteorological measurements. Efforts thus need to be made to improve the input meteorological fields used by acid deposition models.

All of the ADOM and ALSM results discussed in this chapter were calculated on a 127 km by 127 km grid. Similarly, RELAD uses a 1° latitude by 1° longitude grid, which corresponds roughly to a 111 km by 91 km grid. While secondary species such as sulphate and nitrate have relatively smooth fields and weak gradients, primary species such as SO_2, NO, and NO_2 have much stronger gradients, especially close to sources. Moreover, near-source removal by dry deposition for major sources and plume-environment interactions are very poorly resolved for such large grid spacings (e.g., Dennis et al., 1990; Gillani and Godowitch, 1999). There are thus likely to be benefits realized in model accuracy, at least in source regions where plume chemistry and dry deposition near sources are important processes, from the use of smaller grid spacing and improved spatial resolution.

4.8 CONCLUSIONS

This chapter has reviewed progress since the 1997 *Canadian Acid Rain Assessment* in applying regional acid deposition models in Canada to improve our understanding of acid deposition and to evaluate the efficacy of current, proposed, and potential emission control measures. Both SO_2 and NO_x control programs have been considered and summarized in terms of their atmospheric impacts. Here are some major accomplishments and conclusions from this review:

- Four acid deposition models (RELAD, ADOM, IAM, ALSM) have been used since the 1997 *Assessment* to investigate acid deposition in eastern or western Canada, including the simulation of a number of new future year SO_2 and NO_x emission control scenarios. The consideration of NO_x control programs represents an important step beyond the 1997 *Assessment*, in which only SO_2 emission control scenarios were considered.

- The RELAD Lagrangian acid deposition model has been used to perform a number of annual simulations for western Canada centred on the province of Alberta for both sulphur and nitrogen species. Ten year mean atmospheric sulphur and nitrogen budgets calculated from RELAD results for the 1981-1990 period based on western Canadian emissions were found to be quite similar, and the mass fractions of sulphur and nitrogen removed in Alberta by dry deposition (~9%) were estimated to be comparable to the mass fractions removed by wet deposition. Estimates have also been made of year-to-year variability in sulphur and nitrogen concentrations and dry and wet deposition; interannual variability generally increased in going from annual concentration to dry removal to wet removal and from primary species to secondary species. RELAD is now being applied by Alberta Environment as part of Alberta's acid deposition management framework under the Province of Alberta's 1995 *Environmental Protection and Enhancement Act*.
- For western Canada, RELAD and ALSM acid deposition model results, emission maps, and acid deposition measurements suggest that Canadian SO_2 and NO_x emission sources are the primary contributors to acid deposition in that region.
- The 1997 *Assessment* reported on the results of five SO_2 emission control scenarios simulated with ADOM, a comprehensive Eulerian acid deposition model. Since then ADOM has been run for 15 more future year emissions scenarios, including three scenarios in which concurrent changes in NO_x emissions were also considered. Some of these new scenarios were simple rollback scenarios but the majority were more realistic in nature. The results of these scenario runs have helped to guide Canadian policy development for acid deposition management, including *The Canada-wide Acid Rain Strategy for Post-2000* and proposed reduction of sulphur content in light and heavy fuel oils.
- ADOM results presented in the 1997 *Assessment* suggested that sulphate critical loads for aquatic ecosystems would still be exceeded in central Ontario and Quebec even for a further 50% reduction from projected 2010 SO_2 emissions from both Canadian and U.S. sources (scenario "5CCUS2"). A similar result was also found for the most realistic of the new ADOM SO_2 scenarios considered, the "NOX3P" scenario, although ADOM did predict that no part of eastern Canada would be subject to annual SO_4^{2-} wet deposition above the interim 20 kg/ha/yr target load for this scenario. Only for the most stringent SO_2 emission control scenario, a further 75% reduction from projected 2010 SO_2 emissions, is the critical load "gap" closed (scenario "75FCAP"). Unfortunately, the aquatic SO_4^{2-} critical load values from the 1990 Assessment are themselves not stringent enough due to an underestimation of the contribution of dry deposition in their original determination, so that even larger SO_2 emission reductions might be required to achieve true critical loads. However, these conclusions need to be re-examined in view of the recent development of an updated critical load field for Canadian aquatic ecosystems (see Chapter 8).
- An analysis of other ADOM SO_2 emission scenarios suggests that further SO_2 emissions reductions in Ontario, Quebec, New Brunswick, and Nova Scotia from 1985 ECARP emission caps will reduce the extent of the land area in eastern Canada currently in exceedance of aquatic critical loads.
- Forest ecosystems are impacted by nitrate deposition as well as sulphate deposition. Results from three new ADOM NO_x emission control scenarios quantify reductions in nitrate deposition associated with reductions in NO_x emissions. Qualitatively similar behaviour is evident in the differences between primary and secondary nitrogen species (i.e., NO_x vs. nitrate) and primary and secondary sulphur species (i.e., SO_2 vs. sulphate). One interesting difference in behaviour between the sulphate and nitrate fields is that ADOM predicts the location of the nitrate "centre of gravity" to be over southern Ontario, north of the sulphate "centre of gravity" over the eastern Ohio Valley. The reason for this northward displacement is likely due to differences in the geographic distributions of NO_x and SO_2 emissions.

- Predicted SO_4^{2-} and NO_3^- fields can be combined on a molar basis to yield effective acidity fields. Changes in effective acidity concentration and deposition fields provide useful metrics to compare the integrated impact of different SO_2/NO_x emission control scenarios. These predicted effective acidity deposition fields should also be compared with the new multi-pollutant critical load field for Canadian forest ecosystems (see Chapter 8).
- An analysis of different pairs of similar ADOM SO_2 emission scenarios has provided information about the contribution of various source regions to wet sulphate deposition in eastern Canada. ADOM results suggest that both Canadian and U.S. SO_2 and NO_x emissions contribute to acid deposition in eastern Canada. For example, U.S. SO_2 emission reductions beyond those currently legislated will further reduce critical load exceedances in eastern Canada, particularly in the Maritimes and particularly for reductions in the upper Ohio Valley and northeastern U.S. On the other hand, ADOM results suggest that on a tonne-vs-tonne basis, Canadian SO_2 emission reductions have a greater impact *within Canada* than do U.S. reductions of the same absolute amount. Also, for the same overall emission reduction, the *geographic distribution* of SO_2 emissions reductions in eastern Canada may affect the extent of critical load attainment
- Access to the ADOM "library" of 20 SO_2 scenarios combined with an assumption of linearity of the atmospheric sulphur system for an annual time scale permits ADOM "pseudo-scenarios" to be constructed, in which linear combinations of output from ADOM scenarios that have already been run can be used to estimate results for certain new rollback scenarios without the need to re-run ADOM. These pseudo-scenarios provide a useful new analysis and screening tool.
- The IAM is based on the ALSM, a simpler acid deposition model than ADOM, so that the IAM has been used as a screening tool to help select scenarios to be run with ADOM. However, ALSM and ADOM were shown in the 1997 *Assessment* to give similar results for similar annual SO_2 emission scenarios. Now IAM and ADOM predictions have also been compared to the limited extent possible (at 13 points) for a number of annual SO_2 emission scenarios and were found to give comparable results, supporting the usefulness of the IAM as a screening tool. The IAM also has some features such as an emission-reduction optimization capability that are not available in ADOM.
- Four new year-specific combined SO_2/NO_x emission control scenarios for the years 1995/96, 2010, 2020, and 2060 have been constructed for use with the IAM to provide one possible 65-year-long projected atmospheric deposition time series (see Chapter 7). Previous ADOM results suggest, however, that some areas of eastern Canada will still be in exceedance of aquatic sulphate critical loads even for the IAM 2060 SO_2 scenario.
- Acid deposition model development work has continued on a number of fronts. First, the set of receptors considered by the ALSM Lagrangian acid deposition model has been greatly expanded to permit (a) consideration of almost all of North America and (b) preparation of contour plots. New sulphur source-receptor matrices are being developed with the ALSM for this expanded set of receptors for a new meteorological year (1990). Preliminary estimates of the contributions of 40 individual North American source regions to overall sulphur concentration and deposition have already been made and sample results were shown. Second, a new Lagrangian inorganic aerosol model is being developed to permit a better estimation of nitrogen SRMs for both oxidized and reduced nitrogen species. These new nitrogen SRMs can then be incorporated into the IAM. And third, a new comprehensive Eulerian regional particulate matter model, AURAMS, has been developed. One expected application of AURAMS is as a replacement for ADOM for long term regional acid deposition modelling once it is possible to run AURAMS routinely for annual periods.
- Finally, for comprehensive Eulerian acid deposition models, additional improvements should be possible in modeling total deposition, pH of precipitation, and total ammonia and total nitrate phase partitioning, in emissions processing for new emission control scenarios, in provision of more accurate input meteorological fields, and in enhanced spatial resolution.

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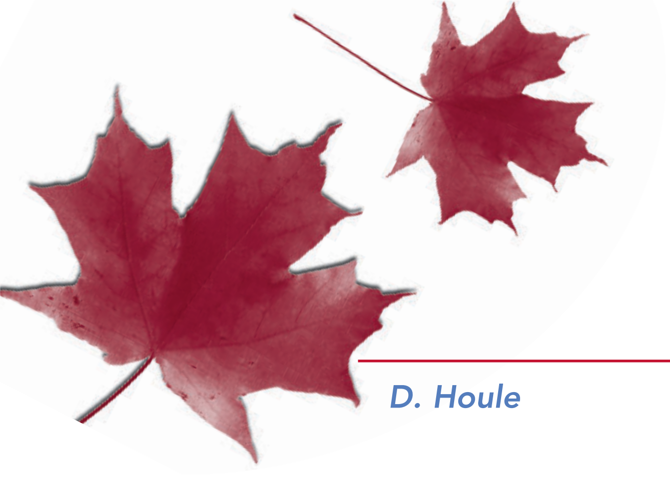

CHAPTER 5

Effects on Forests and Soils

D. Houle

5.1 KEY MESSAGES

- Net losses of base cations from forested catchments in eastern Canada are widespread, particularly for calcium (Ca^{2+}). Recent studies support the relationship between loss of base cations from acidified soils and reduced growth rates and health of trees.
- There is mounting evidence that the size of base cation reservoirs in watershed soils determines the extent to which acid deposition acidifies surface waters and the response of surface water pH to reductions in acid-causing emissions.
- In most eastern Canadian forested catchments, the release of sulphate into surface waters exceeds the amount of sulphate received via acid deposition. Likely sources of this “extra” sulphate are desorption of sulphate bound to soil and/or release of sulphate during the decomposition of organic matter. Both of these processes generate acids. Surface water critical load models, which are based solely on sulphate inputs from deposition, underestimate critical load exceedances in watersheds that exhibit substantial net sulphate exports.
- Nitrogen saturation does not appear to be a problem at most eastern Canadian sites; however, the long-term impact of chronic nitrogen inputs is uncertain and remains a major concern.

5.2 INTRODUCTION

In recent years, there have been an increasing number of scientific papers documenting a decline in soil quality and forest health resulting from exposure to acid deposition. Recognition of the relationship between acid deposition and soil quality first began to emerge when researchers at calibrated forested catchments across eastern Canada and the northeastern U.S. began to observe net losses of base cations from soils (Houle et al., 1997; Kirchner and Lydersen, 1995; Likens et al., 1996; Watmough and Dillon, 2003a). In many cases, the rate of base cation depletion was greater than the rate of replenishment via atmospheric deposition and soil weathering. Base cations such as calcium (Ca^{2+}), magnesium (Mg^{2+}) and potassium (K^{+}) are essential nutrients for the maintenance and growth of trees. In recognition of the relationship between base cation availability in soil and tree vitality, concerns have emerged about the long term viability of forests, particularly in base cation-poor regions in eastern Canada.

At the same time, our understanding of the complex relationship between soil properties, surface water quality and recovery of acidified ecosystems has been evolving. Surface areas of lakes and streams usually comprise less than 15% of a watershed catchment area. Consequently, surface water quality is largely determined by the quality of water leaving catchment soils rather than the quality of precipitation landing directly on the surface of a lake or stream.

Reactions between the chemical components of precipitation and soil determine the chemistry of water leaving catchment soil. A decline in base cation concentrations in soil lessens the capacity of soil to neutralize acids from precipitation thereby increasing the acidity of water entering lakes and streams. A decline in the capacity of soils to neutralize acids has the potential to negate some of the positive effects of reductions in precipitation acidity achieved by acid rain abatement efforts in Canada and the U.S. Since the capacity of aquatic ecosystems to support biota is linked to the acidity of surface waters, there is concern that loss of base cations from soils is hindering the recovery of species richness in aquatic ecosystems.

Another area of uncertainty with respect to acid deposition is the impact of nitrogen on soil chemistry, trees and surface water quality. Nitrogen oxide emissions in eastern North America are high and have remained relatively constant since 1985. Nitrogen is an essential nutrient for tree growth and is often limiting in eastern Canadian ecosystems. However, deposition of nitrogen, in excess of the capacity of terrestrial ecosystems to use it, could lead to an excess of inorganic nitrogen in soils which will contribute to the acidification of soils and surface waters and to further depletion of base cations (Fenn et al, 1998; Currie et al., 1999; Aber et al., 1998; Stoddard, 1994).

The objective of this chapter is to synthesize our current understanding of the effects of acid deposition on soil quality and forest health. This chapter is an update of volume 4 of the 1997 Canadian Acid Rain Assessment entitled "The Effects on Canada's Forests". The chapter includes reviews of published scientific papers and original studies produced since 1995. A discussion of scientific gaps and future research requirements concludes the chapter.

5.3 CONCLUSIONS OF THE 1997 ASSESSMENT

S. Couture, C. Gagnon and D. Houle

Four key findings related to acid deposition and forest health emerged from the 1997 Canadian Acid Rain Assessment (Volume 4: The Effects on Canada's Forests) (Environment Canada, 1997).

1. Forest decline was found to be related to acid deposition. In a study carried out in the Bay of Fundy, New Brunswick in Canada's east coast, prevalent browning of leaves, premature leaf fall, and twig and branch death of the white birch and mountain paper birch of the area were reported and related to recurring episodes of acidic fog (Cox et al., 1996). Polluted cloud and rainwater were also considered threats to forest health at mid to high altitudes where forests are already under severe natural stress. Red spruce decline at high elevations in the Appalachian Mountains had been strongly linked to increases in the aluminium/calcium ratio of wood tissues and to increases in respiration (McLaughlin et al., 1991).
2. The acid deposition target load of 20 kg wet sulphate/ha/yr was concluded to be too high to protect sensitive forest ecosystems.
3. Changes in tree physiology were observed in trees exposed to acid deposition. Various physiological effects were reported for foliar surfaces and leaching, plant reproduction, frost hardiness, as well as growth. A study on foliar surface carried out under laboratory conditions, simulating acid rain, demonstrated that the structure of the needle wax of red spruce and Sitka spruce is degraded from crystalline to an amorphous form at pH levels approximating ambient forest conditions (Krywault et al., 1996; Bytnerowicz et al., 1998). It was also demonstrated that acid rain increases foliar leaching, which results in reductions of foliar nutrient concentration and growth (Hogan, 1992). Effects on forest plant reproduction were also observed in white birch and mountain paper birch near the Bay of Fundy where they frequently intercept acidic (pH < 3.5) marine advection fogs. Reproductive systems of these wind-pollinated plants were reported to be inhibited below pH 5.6 (Hughes and Cox, 1994). Acid precipitation was found to affect a tree's protection against frost. A relationship was found between leaf sulphate content and frost hardiness. A 0.1% increase in foliar sulphur content caused a 2.7°C decrease in frost hardiness of red spruce (Sheppard, 1994). Reductions in the growth rate of root biomass were documented for white ash and jack pine following acid rain treatment at pH 3.0 (MacDonald et al., 1986; Chappelka and Chevone, 1986; Amthor, 1986).
4. Changes in soil chemistry were observed with increased acidity, with respect to soil biota, decomposition, and nitrogen turnover. Increased acidity was found to reduce microbial diversity, nitrification, ammonia volatilization, and microbial respiration (Mahendrappa, 1982, 1989, 1991), which eventually leads to a reduction in forest productivity. Soil acidification and depletion of base cations were investigated as effects on soil chemistry. In Ontario, the ambient levels of acid rain have accelerated the loss of base cations from soils that support a sugar maple forest (Foster et al., 1992). Also, from studies in Québec, foliar nutrient deficiencies in sugar maple have been linked to cation imbalances in soil (Ouimet and Camiré, 1995).

In the conclusions of the assessment, key research needs were also identified:

1. Focus critical load calculation on sensitive forest ecosystems and on the most sensitive tree species.
2. Place greater focus on impacts of wet and dry forms of nitrogen deposition.
3. Integrate cumulative impacts of UV-b, ground level ozone, heavy metals and acid precipitation.
4. Incorporate economic impacts of the effects of acid precipitation on the forest sector.
5. Better understand and assess the long term impacts of chronic nutrient depletion from forest soils for sensitive ecosystems.

5.4 EFFECTS OF ACID DEPOSITION ON SOILS AND FORESTS

S. Watmough and R. Ouimet

5.4.1 Base cation depletion and forest health

Net loss of base cations from the exchangeable pool in soils is leading to a decline in the base cation saturation and pH of soils. Because Ca^{2+} and Mg^{2+} are essential plant nutrients, low levels of these elements in soils may ultimately lead to a decline in forest health (Bernier and Brazeau, 1988), a decrease in tree growth (McLaughlin, 1998; Watmough, 2002; Duchesne et al., 2002), a decrease in the freeze tolerance of trees (Dehayes et al., 1999; Schaberg et al., 2002), and an increase in tree sensitivity to biotic stresses such as insect defoliation and disease (Horsley et al., 2000; Kolb and McCormick, 1993). Quantifying the relationship between acid deposition, base cation depletion and forest health is difficult. The role of site conditions in predisposing forest response (Bailey et al., 2004), climate (Payette et al., 1996), extreme soil freezing events (Robitaille et al., 1995), forest fires (Lamontagne et al., 2000), insect outbreaks (Webb et al., 1995; Eshleman et al., 1998; Duschesne et al., in preparation) and other factors confound the response of trees to acid deposition. The following sections describe our current understanding of the observed response of trees to base cation depletion caused by acid deposition.

5.4.1.1 Base cation depletion and forest growth and vitality

A number of studies in eastern North America have observed an association between soil acidification and a decline in the rate of tree growth (Bondietti et al., 1989, 1990; McLaughlin, 1998; Shortle and Smith, 1988; Shortle et al., 1995; Watmough, 2002; Duchesne et al., 2002). In several of these studies, it was observed that an increase in tree growth, as assessed by tree ring width, occurred during the middle part of the 20th century. This increase in tree growth was followed by a steady decline in growth in recent decades (Hornbeck and Smith, 1985; Shortle and Smith, 1988). The increased growth was attributed to an initial fertilization effect from base cations that had been mobilized as the soil acidified. This period of elevated tree growth was followed by a steady decline in growth rates concomitant with a loss of base cations from the exchangeable soil pool and an increase in bioavailable forms of aluminum (Al^{3+}) as soil acidification progressed (Bondietti et al., 1989).

The following studies support the hypothesis that prolonged acidification of soils results in an initial fertilization effect on trees, from the mobilization of base cations, followed by a decline in growth rate, as base cations are leached from the soil and Al^{3+} bioavailability increases. An increase in the base cation content of wood and foliage in response to soil acidification has been observed in short term studies in which forest soils were artificially acidified (Hutchinson et al., 1998; Watmough et al., 1999a). For example, red spruce had elevated levels of Ca^{2+} and Mg^{2+} in wood rings formed during the middle of the 20th century. Wood rings laid down after that period exhibited a steady decrease in Ca^{2+} and Mg^{2+} and an increase in wood Al^{3+} concomitant with a decline in tree growth (Bondietti et al., 1990). Watmough (2002) reported that 43% of the variation in growth of sugar maple in central Ontario could be explained by concentrations of Ca^{2+} and Al^{3+} in wood, with poor growth associated with low Ca^{2+} and high Al^{3+} concentrations. Mohamed et al. (1997) also reported that high Al^{3+} levels were found in the wood of declining sugar maple in Ontario. In an extensive survey of more than 14,000 trees in Ontario, McLaughlin (1998) reported an association between low base cation saturation and high Al^{3+} levels in soil and symptoms of decline in sugar maple and sugar maple mortality. McLaughlin (1998) further estimated that, after the mid 1960s, forest growth in Ontario had declined by between 0.66 and 0.96 m^3/ha/yr. This decline in forest growth was greatest on poorly buffered soils.

In Québec, forest scientists observed that atmospheric sulphur (S) and nitrogen (N) deposition, forest floor exchangeable acidity, and growth and health of sugar maple were interrelated (Duchesne et al., 2002). In this study (14 sites), the trend in basal area growth of sugar maple was negatively related to the rate of decline in the health of the stands, forest floor exchangeable acidity, and S and N deposition. The reduction in the rate of growth reached 17% in declining maple stands compared to healthy ones. The decline in growth of the stands started in the early 1960s, many years before the appearance of visual symptoms of decline. These results were corroborated by the re-examination of data from a previous study (16 sites) by Payette et al. (1996) where no relationship was found between acid deposition and maple growth based on tree ring width. Using the same tree core data set, but using tree basal area increment instead of tree ring width, the new study indicated that tree growth showed an inverse relationship with tree decline between 1955 and 1989, irrespective of tree age (Duchesne et al., 2003). Re-examination of these data suggested that the growth and health of these trees has been impaired since the mid-1950s.

The relationship between base cation depletion in soils and reduced tree health and growth is also supported by liming experiments. Studies performed in Quebec showed that a reduction in soil acidity through liming improved sugar maple growth and health. Furthermore, growth responses were linearly related to the rate of lime application (Moore et al., 2000) and soil exchangeable Ca^{2+}:acidity ratio (Houle et al., 2002).

In addition to its effects on tree growth, depletion of base cations in soils is also associated with a decline in tree health. At sites that are extremely sensitive to acid deposition in Canada, characterized by low levels of exchangeable base cations, nutrient levels in soil may be approaching limits that are detrimental to tree health. Deficiencies of Ca^{2+}, Mg^{2+} and K^+ measured in sugar maple foliage have been associated with forest decline and increased sensitivity to insects, fungi and climate perturbations throughout eastern North America (Bernier and Brazeau, 1988; Horsley et al., 2000; Kolb and McCormick, 1993; Ouimet and Camire, 1995). In some studies, symptoms of decline have been reversed and tree growth improved by the addition of base cation-rich fertilizers (Moore et al., 2000). Adams and Hutchinson (1992) found that symptoms of decline in sugar maple in Ontario were more pronounced as Ca^{2+} concentrations decreased and Al^{3+} levels increased in roots.

In the last five years, evidence of the impact of acid deposition on soil quality and tree vitality has accumulated. Studies profiled in this chapter demonstrate that acid deposition negatively affects tree growth and health and these effects progress over several decades.

5.4.1.2 *Base cation depletion and frost hardiness and tolerance to abiotic and biotic stress*

Low levels of base cations in foliage can pre-dispose trees to natural stresses including freezing, drought and insect defoliation. A number of studies have indicated that a decrease in foliar membrane associated calcium (mCa^{2+}) can decrease the tolerance of trees to freezing (Dehayes et al., 1999; Schaberg et al., 2002), particularly for trees growing at the edge of their range at high elevation sites. The decrease in mCa^{2+} may be caused by declining Ca^{2+} pools in soil, increased N fertilization and Ca^{2+} leaching from leaves caused by acid fog (Jiang and Jagels, 1999; Shaberg et al., 2000, 2002) and acidic deposition (Houle et al., 1999).

Low levels of base cations may also decrease the ability of trees to withstand defoliation by insects or drought. For example, Demchik and Sharpe (2000) reported that northern red oak (*Quercus rubra*) in southwestern Pennsylvania growing on sandy soils with low base cation saturation and low Ca^{2+}: Al^{3+} ratios were more susceptible to drought than nearby oak growing on more base cation-rich soils. Similarly, Horsley et al. (2000) reported that sugar maple decline in Pennsylvania resulted from an interaction between low Mg^{2+} (and Ca^{2+}) and stress caused by defoliation.

5.4.2 Acidification and soil microbes

Endomycorrhizal fungi and other microbes associated with roots play a vital role in nutrient uptake by trees. Ouimet et al. (1995) reported that soil chemistry regulates fine root colonization by endomycorrhizal fungi and directly impacts sugar maple nutrition and health. In this study, frequency of endomycorrhization was positively correlated with soil pH and soil exchangeable Mg^{2+}, and negatively correlated to the proportion of H^+ and Al^{3+} held on the soil exchange complex. In keeping with the role of endomycorrhizal fungi in nutrient uptake by trees, sugar maples in Québec, with visible symptoms of decline, had fewer fungi associated with their roots and were found to be under more severe nutrient stress than healthy sugar maples. In experimental studies, Thirukkumaran and Morrison (1996) reported that the application of sulphuric acid (H_2SO_4) alone, or in combination with nitric acid (HNO_3), caused a decrease in soil microbial respiration, biomass, and microbial biomass carbon. This decrease, however, was observed at pH levels approximately six times the mean ambient level received at high acid deposition watersheds such as the Turkey Lakes in southcentral Ontario.

5.4.3 Direct impact of acid deposition on foliar surfaces and reproduction

At coastal sites or high-elevation sites that receive frequent acid fog episodes, direct tree damage by acid rain may occur (Cox et al., 1996; Kouterick et al., 2001). Laboratory studies have indicated that the structure of needle wax of some tree species degrades from a crystalline to an amorphous form at pH levels observed in eastern Canada (Percy and Baker, 1991; Percy et al., 1990). Some studies have related forest decline to enhanced uptake of trace metals in foliage at low pH levels (Watmough et al., 1999b) and high concentrations of trace metals often found in acid fog at high elevation sites (often an order of magnitude higher than rainfall) (Lin et al., 1995; Gawel et al., 1996). One consequence of the altered wax chemistry is increased loss of water and increased retention of solutes that may enhance the uptake of damaging ions (Percy and Baker, 1991).

Other direct impacts of acid deposition on plants and trees include the following: Reproductive systems of wind-pollinated plants are vulnerable to acid deposition. Hughes and Cox (1994) reported that pollen germination and base physiological responses of white birch and mountain paper birch near the Bay of Fundy are inhibited below pH 5.6. Acid deposition can leach base cations from foliar surfaces (Sayre and Fahey, 1999). Photosynthesis in both yellow poplar and red spruce have been found to decrease after treatment with acid rain at pH 3.0 (Meng et al., 1994; Roberts, 1990). Generally, however, the negative effects of acid deposition on leaf properties (photosynthesis, growth, etc.) are only evident at levels rarely found in most Canadian environments (Dixon and Kuja, 1995; Hogan, 1998; Scott et al., 1989).

5.4.4 Forest growth and critical loads

Many areas in eastern Canada receive levels of acid deposition that exceed the buffering capacity of soils (i.e., exceed the critical load for acidity: See Chapter 8). Using the Acid Rain Early Warning System (ARNEWS) dataset, Moayeri (2001) showed that forest canopy transparency (a measure of lack of foliage) was related to the exceedance of the critical loads for soils. Sugar maple growth in Ontario has also been observed to be lower in areas where the critical load for soils is exceeded (Watmough, 2002). Analyses from the RESEF network in Québec show that, between the 1970s and the 1990s, hardwood and the coniferous stands located in areas where the critical load was exceeded had a growth rate 30% lower than forest sites located in areas with no exceedance (Ouimet et al., 2001). These observations, however, do not imply a causal relationship between acid deposition and forest growth. It must be kept in mind that richer soils, characterized by high exchangeable base cation content, will be less likely to show critical load exceedances than poor soils, and that an unknown proportion of the 30% difference in growth rates may be attributable to intrinsic site characteristics rather than acid deposition exclusively. Nevertheless, acid deposition exceeds critical loads over much of eastern Canada (Arp et al., 1996; Ouimet et al., 2001; Watmough and Dillon, 2003b) suggesting that a large portion of eastern Canadian forests are potentially vulnerable to the effects of acid deposition. Further information and discussion on critical loads is found in Chapter 8.

5.5 SOURCES, TRANSPORT AND FATE OF S IN CANADIAN WATERSHEDS

C. Eimers and D. Houle

In recent decades, major reductions in sulphur dioxide (SO_2) emissions in North America have resulted in decreases in the concentration of sulphate (SO_4^{2-}) in surface waters located within eastern Canada (Houle et al., 1997; Clair et al., 1995; Kemp, 1999) and the northeastern United States (Stoddard et al., 1999). For some lakes, reductions in SO_4^{2-} concentrations have led to decreases in acidity levels, but for other lakes, no improvements in the pH status of surface waters have been observed (Bouchard, 1997; Stoddard et al., 1999). This section addresses the current status of inputs and outputs (budgets) of S in eastern Canadian watersheds in the context of decreasing S deposition.

5.5.1 S budgets and S reservoirs for catchments in eastern Canada

Input-output budgets for conservative chemicals enable the inference of biogeochemical processes occurring within a catchment or lake. Since SO_4^{2-} levels in headwater lakes are largely a function of inputs of SO_4^{2-} from the terrestrial catchment, information on the balance between SO_4^{2-} inputs and outputs can give insights into the status of S in catchment soils and to the potential response of receiving waters to changes in SO_4^{2-} deposition.

5.5.1.1 Elements of the input-output budget calculation

Input-output budgets are represented most simply as:

input – output = net change

A more complete elemental budget would consist of:

[atmospheric deposition (wet, dry, fog) + weathering + groundwater transfer + amendments (e.g., fertilizer, liming)] – [stream flow + groundwater seepage + gaseous emissions + biomass removal (e.g., timber harvesting)] = net change

Long-term acidification monitoring programs in eastern Canada are located in watersheds that exhibit relatively simple hydrology and acid-sensitive geology. In most of these catchments, groundwater is not an important component of the water balance. Input of SO_4^{2-} via mineral weathering is assumed to be minor at most sites because the bedrock is relatively impervious and soils are thin (e.g., Houle and Carignan, 1995). Furthermore, emissions of reduced S gases from aerobic upland forested catchments that characterize the sites are generally negligible. Therefore, the S budget at these undisturbed (i.e. not harvested) forest sites can be simplified to:

atmospheric deposition – stream export = net change.

5.5.1.2 S budget results for eastern Canadian catchments

Average input-output budgets for SO_4^{2-} were calculated for 35 of the catchments in the long-term acidification monitoring programs (Figure 5.1) in Ontario, Québec, and Nova Scotia. Budgets were calculated by comparing SO_4^{2-} export via stream flow with input via bulk deposition over the period 1993-1996. In the majority of catchments (29/35), SO_4^{2-} export exceeded SO_4^{2-} input (Figure 5.2). The net export of SO_4^{2-} was substantial and represented 35-105% of SO_4^{2-} input at catchments in south-central Ontario, 3-69% at catchments within the Turkey Lakes watershed in central Ontario, 50-92% at Lake Clair and Lake Laflamme in Québec, and 31% at the Moose Pit Brook in Nova Scotia. In contrast, SO_4^{2-} was retained at catchments in the Experimental Lakes Area (NWIF, EIF, NEIF) in northwestern Ontario, at the wetland-dominated DE5 and DE6 sub-catchments of Dickie Lake in south-central Ontario, and at the Hermine catchment in Québec. Catchment data for Hermine, however, contradicted the soil data which indicated the net export of S (Courchesne et al., 2001).

Net export of SO_4^{2-} from these catchments (e.g. negative SO_4^{2-} budgets) could be due to either (a) an internal source of S, or (b) an underestimation of input of S through dry deposition. Recent measurements and models indicate that dry deposition is generally a relatively small (<25%) component of the total S input to catchments that are located remotely from point sources of S emissions (Baumgardner et al., 2002; Sirois et al., 2001). New data (See Chapter 3), however, suggest that previous dry S deposition estimates were probably low,

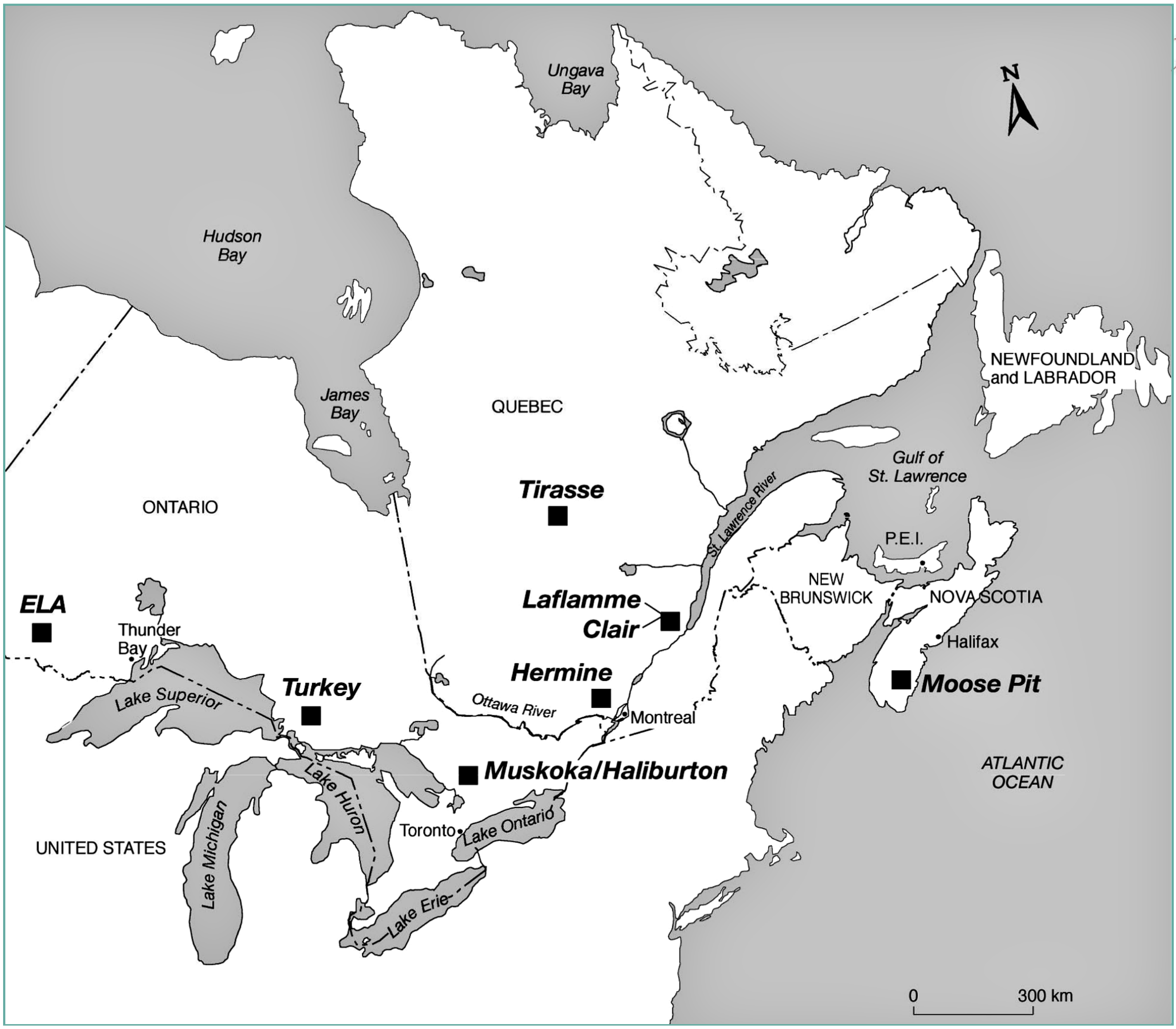

Figure 5.1: Location of the catchments for which results are included in this compilation.

and that dry deposition may constitute 35% of total deposition at many sites. Since the net export of S at the majority of catchments exceeds inputs by at least this much, dry deposition cannot be entirely responsible for net losses. In addition, Houle et al. (1995) have demonstrated that soluble organic S, which is not currently measured in surface waters (as opposed to SO_4^{2-}), may represent 10 to 20% of the total S exported from Québec lakes (n=1243) suggesting that the amount of S exported from catchments is underestimated in the same proportions.

5.5.1.3 *Potential internal sources of S export*

Net release of SO_4^{2-} from within catchments can occur via four processes:

- weathering of S-containing minerals
- oxidation of reduced S compounds
- desorption of inorganic SO_4^{2-}
- mineralization or organic-S compounds

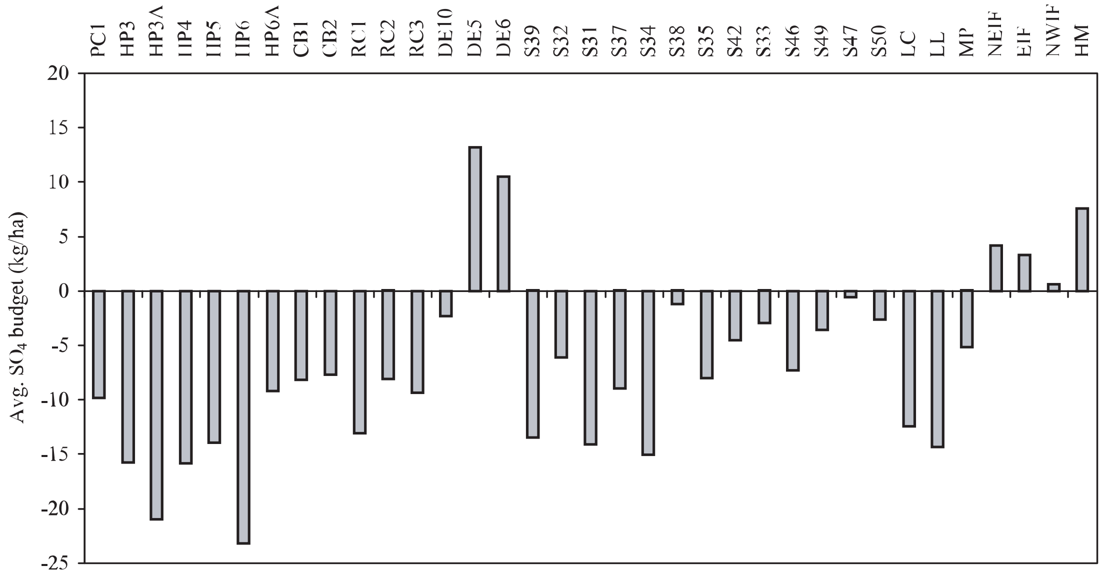

Figure 5.2: Average SO_4^{2-} input-output budgets (1993-1996) at 35 catchments in eastern Canada. Negative budgets indicate that stream export exceeds SO_4^{2-} input in bulk deposition. The data used in this compilation are from Watmough et al. (submitted).

5.5.1.3.1 Weathering

Watersheds described in this study are comprised of forests growing on soils that are derived from glacial till and igneous bedrock. Weathering inputs of S from these types of watersheds are generally minor; typically granite contains less than 100 mg S/kg (Mitchell et al., 1992). At Lac Laflamme, for example, weathering contributes ~ 1% to the S output (Houle and Carignan, 1995). On the other hand, in forest systems in which the soils are formed from sedimentary materials, the contribution of weathering to S budgets can be important (Mitchell et al., 1986). Substantial S-mineral deposits have not been reported at any of the Canadian long-term monitoring sites considered in this assessment (Jeffries and Snyder, 1983; Houle and Carignan, 1995); therefore, the contribution of weathering to S budgets in this study is considered to be negligible.

5.5.1.3.2 Oxidation of reduced S compounds

Wetlands contain soils that are frequently or continuously waterlogged and are typically anoxic at the bottom. Sulphate reduction during anaerobic decomposition results in the production of sulphides, which are stable storage products for S under oxygen-limited conditions. Total S concentrations in wetland soils are often an order of magnitude higher than in adjacent upland soils (Eimers et al., 2003). When the water level goes down during dry periods, oxygen penetrates into formerly anaerobic wetland soils resulting in S oxidation and release of SO_4^{2-}. Hence, climatic changes can cause temporal variability in SO_4^{2-} fluxes from wetland-dominated catchments, and blur the expected relationship between decreased SO_4^{2-} deposition and SO_4^{2-} concentrations in drainage waters (Dillon et al., 1997; Eimers and Dillon, 2002). A substantial net release of SO_4^{2-} following summer drought periods has been reported at wetland-dominated catchments located in the Turkey Lakes watershed, the Muskoka-Haliburton region, and at the Experimental Lakes Area (Bayley et al., 1986; LaZerte, 1993; Devito, 1995; Jeffries et al., 2002). Most of these sites, however, have a low wetland component and well-drained soils therefore the oxidation of reduced S compounds is not expected to be a widespread and important process that could explain the observed S losses over the three year period covered in this study.

5.5.1.3.3 Desorption

Sulphate that is adsorbed to the surface of soil minerals is in kinetic equilibrium with SO_4^{2-} in soil solution; therefore, a decrease in SO_4^{2-} inputs to soil through declining deposition is expected to cause the release (desorption) of SO_4^{2-} from soil surfaces (Chao et al., 1962; Reuss and Johnson, 1986). Hern (1990), for example, showed that nearly three times as much SO_4^{2-} was released from the soil at Plastic Lake in south-central Ontario (equilibrium pH of ~ 5) at an initial SO_4^{2-} concentration of 5 mg/l compared to 10 mg/l.

In Germany and the Czech Republic, input-output budgets shifted from positive (net retention) to negative (net export) in the early 1990s, coinciding with a sudden and drastic decline (>50%) in SO_4^{2-} deposition (Prechtel et al., 2001). In eastern Canada, SO_4^{2-} deposition generally began to decline in the early 1970s, but most monitoring programs began in the late 1970s (e.g., Dorset area study catchments) to early 1980s (e.g., Turkey Lakes watershed, Lake Laflamme watershed). The longest record of water quality monitoring is from the Experimental Lakes Area (ELA) with data extending back to 1971. Sulphate input-output budgets at ELA shifted from generally negative in the 1970s (average of -11% compared to bulk deposition inputs) to mainly positive in the 1980s (average of +5%), possibly indicating that a new equilibrium had been reached.

At ELA, pools of accumulated S in soils are small, which corresponds with a combination of extremely shallow soils and historically low deposition inputs. In theory, sites with relatively small S stores should have a more rapid positive response to decreases in deposition than sites with larger pools of accumulated S. For example, the Plastic Lake catchment in ELA has relatively thin soils (average 50 cm) and negligible till deposits, but extremely high adsorbed SO_4^{2-} concentrations which contribute to a pool in the soil of 290 kg S-SO_4/ha. Net export of S from upland soils at Plastic Lake is ~6 kg S-SO_4/ha/year, which indicates that, assuming SO_4^{2-} concentrations in deposition continue to decrease, net release could be sustained by desorption processes for up to several decades (Eimers et al., 2004).

In contrast, Houle and Carignan (1995) suggested that adsorbed S-SO_4 reservoirs in the soils of the Lake Laflamme watershed are rapidly reaching equilibrium (within 3-4 years) with respect to SO_4^{2-} concentrations in the soil solution (Table 5.1). It then follows that the adsorbed SO_4^{2-} reservoir cannot be solely responsible for long-term release. On the other hand, in this modelling exercise, the adsorbed pool was treated as discrete with

Table 5.1. Site locations and characteristics; average bulk SO_4^{2-} deposition and net budget for 1993-1997, unless otherwise noted.

Sites	Lat	Long	Area (ha)	P (mm)	Bulk SO_4^{2-} deposition (kg/ha)	[(export- input) /input]*100	References[2]
Muskoka-Haliburton (15 catchments)	45-48	78-79	10-190	990	21-25	-35 to -105%	Eimers and Dillon, 2002
Turkey Lakes (13 catchments)	47	84	4-67	1300	20	-3 to -69%	Beall et al., 2001
Experimental Lakes Area (ELA) - 3 catchments	49	93	12-170	690	5-8	+10 to +64%	Watmough et al., in review
Lake Laflamme	47	71	68	1300	13-21	-92%	Houle and Carignan, 1992
Lake Clair	46	71	226	1350	21-28	-50%	Houle et al., 1997
Lake Tirasse	49	73	56	810	9 (avg. 1997-00)	-36%	Watmough et al., in review
Hermine	45	74	5	1150	33 (avg. 1994-97)		Courchesne et al., 2001
Moose Pit Brook	44	65	42	1350	10-14[1]	-31%	Watmough et al., in review

[1] sea-salt corrected

[2] References for detailed descriptions of sampling methods and site characteristics

deposition as the sole input. Also, the predicted SO_4^{2-} concentration in the pool was systematically lower than the observed concentration. This gap between observed and predicted values was attributed to the mineralization of organic S. Although the amount of adsorbed SO_4^{2-} in the soil is generally small compared to the pool of organic S, desorption of SO_4^{2-} could be a long-term source of SO_4^{2-} to drainage waters, particularly if concentrations of adsorbed SO_4^{2-} are sustained through a continuous release of SO_4^{2-} from organic S compounds.

5.5.1.3.4 Mineralization

Mineralization (the transformation of organic S into inorganic SO_4^{2-}) and immobilization (the transformation of inorganic SO_4^{2-} into organic S) are microbial processes that occur concurrently within the soil. Mineralization may be a source of SO_4^{2-} to drainage waters if SO_4^{2-} release from organic S compounds exceeds the rate of SO_4^{2-} immobilization. A number of studies have suggested that mineralization is responsible for net SO_4^{2-} export from catchment soils (Houle et al., 2001; Novak et al., 2000; Driscoll et al., 1998; Löfgren et al., 2001). Factors that affect the biological cycling of S are of critical importance to S budgets because of the large size of the organic S pool in most forest soils (i.e., potential source of net SO_4^{2-} export) (Figure 5.3).

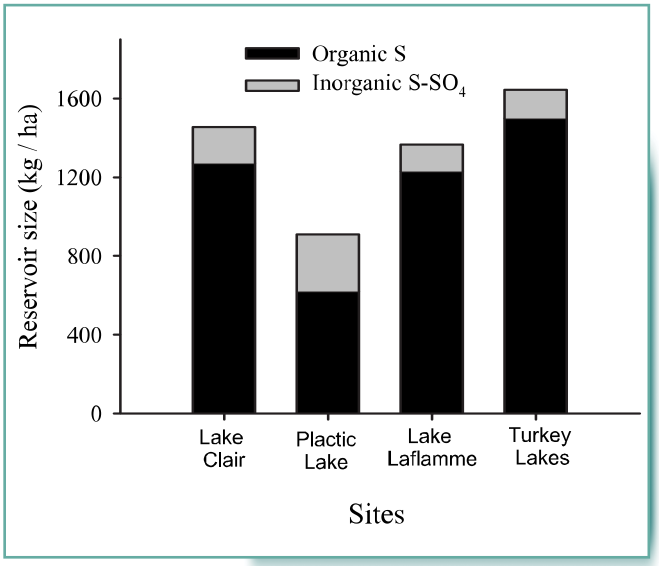

Figure 5.3: Size of S pool in soils of Plastic lake (data from Neary et al., 1987; Eimers, 2002; Eimers et al., 2004), Lake Clair (Houle, unpublished data), Lake Laflamme (Houle and Carignan, 1992) and Turkey lake (Mitchell et al., 1992) catchments.

Gélineau et al. (1989) observed that 32-61% of the S leaving the catchment at Lake Laflamme in Québec originated from organic S mineralization. It is unclear, however, why mineralization would currently exceed immobilization. If mineralization is the reason for net S export, it might be a response to changing S deposition or to variations in climate. If mineralization is a reaction to changing S deposition, this would imply that the sizes of organic S reservoirs are, to some extent, controlled by S deposition or S availability. Houle et al. (2001), however, reported that there was no relationship between S deposition and the size of organic S reservoirs along a gradient of S deposition levels for 21 forested sites. Novak et al. (2001) reported that the S concentration in litter was linearly related to S deposition in five Czech catchments; however, the number of monitored catchments was low and the size of organic reservoirs and the inclusion of S-rich mineral soils were not reported. In the laboratory and *in situ*, Houle et al. (2001, 2004a) used $^{35}SO_4^{2-}$ additions to show that S did not accumulate in soils on a short term basis despite a strong recycling of $^{35}SO_4^{2-}$.

Changes in climate could influence mineralization and SO_4^{2-} immobilization by affecting biological processing of S. Since mineralization and immobilization are microbe-mediated, both are sensitive to factors that influence biological activity including soil moisture and temperature. Some studies have suggested that changes in climate, particularly increases in temperature, have resulted in net S mineralization (Houle and Carignan, 1995; Driscoll et al., 1998). Foster (1989) reported a positive temperature effect on rates of S mineralization in organic surface soil (F-horizon) at the Turkey Lakes watershed. Fluctuations in moisture can also stimulate organic matter decomposition and increase rates of mineralization. For example, laboratory experiments using peat and forest floor material collected at the Plastic Lake catchment and at S32 in the Turkey Lakes watershed indicated a net release of SO_4^{2-} in response to drying and re-wetting of organic material (Eimers et al., 2003). Field monitoring studies have also reported increased SO_4^{2-} concentrations in leachate from surface organic soil (LFH horizon) following summer dry periods (LaZerte and Scott, 1996; Eimers et al., 2004). Similarly, Courchesne et al. (2001) observed higher SO_4^{2-} concentrations in soil water at the Hermine study watershed (north of Montreal), following dry summers.

5.5.1.4 *Implications of net S losses to soil and surface water acidity*

Since the release of SO_4^{2-} from soils is accompanied by cation (i.e., Ca^{2+}, Mg^{2+}, K^+, Na^+, H^+, Al) leaching, net export of SO_4^{2-} from catchments is a concern. Progressive leaching of base cations (Ca^{2+}, Mg^{2+}, K^+, Na^+) from soils causes soil acidification (replacement of base cations on soil exchange sites with H^+ and Al^{3+}) which can eventually lead to the drainage of acidified soil solutions into surface waters. When water leaving the catchment is acidified, it delays the recovery of acidified surface waters. The lack of improvement in acid neutralizing capacity (ANC) and pH that has been noted at a number of lakes in eastern North America and Europe has been attributed to the depletion of soil base cation pools. Continued net SO_4^{2-} export will further delay recovery (Stoddard et al., 1999; Kirchner and Lydersen, 1995; Watmough and Dillon, 2003). Furthermore, critical load models, which calculate the maximum deposition that a region can receive without showing negative effects, are based on SO_4^{2-} inputs in deposition rather than export in stream water, the latter being a truer indicator of effects on soil. Therefore, critical load models will underestimate the potential impact of SO_4^{2-} deposition in catchments that exhibit substantial net SO_4^{2-} losses.

5.6 N CYCLING IN FOREST SOILS AND THE POTENTIAL LINKS WITH THE N SATURATION PHENOMENON

While S emissions have been decreasing over the last 20 years in the northeastern U.S., N deposition levels have remained high (Erisman and deVries, 2000; Driscoll et al., 2001) and, by some accounts, are expected to increase by as much as 25% in the next 25 years (Galloway et al., 1995). Nitrogen deposition was identified as a risk to forest ecosystems almost 20 years ago (Nihlgard, 1985). While the majority of temperate forests are usually N limited, a growing number of forests are showing signs of N saturation (Johnson et al., 1991; Stoddard, 1994; Aber et al., 1995; Nodvin et al., 1995; Dise and Wright, 1995; DeWalle and Pionke, 1996; Williard et al., 1997).

Nitrogen saturation occurs when the capacity of terrestrial ecosystems to retain N is at its limit. Deposition of N, in excess of the capacity of terrestrial ecosystems to use it, can lead to an excess of inorganic N in soils that could contribute to the acidification of soils and surface waters and to further depletion of base cations (Fenn et al, 1998; Currie et al., 1999; Aber et al., 1998; Stoddard, 1994). Besides reducing soil fertility, leaching of nitrate (NO_3^-) can increase the rate of eutrophication of lakes and streams (Fenn et al, 1998; Erisman and deVries, 2000) and potentially affect the quality of drinking water. At present, however, the mechanisms controlling N retention and saturation in terrestrial ecosystems are poorly understood (Magill et al., 2000).

Section 5.6 is comprised of four contributions to our understanding of N retention and saturation in eastern Canadian ecosystems. The first contribution provides an overall picture of N budgets for eastern Canadian forested catchments. The remaining three contributions, describe more detailed experimental works that are intended to illustrate our current understanding of the processes governing N soil dynamics and the potential for N retention in eastern Canada. The experimental studies were performed at three forest types each dominated either by sugar maple, balsam fir, or black spruce. Together these tree species dominate the forests of eastern Canada.

5.6.1 N budgets for forested watersheds

S. Watmough

In many parts of eastern Canada, the potential is high for N deposition to exceed the capacity of terrestrial ecosystems to use N. Methods used to calculate the critical load for acidity of forests are based largely on the assumption that NO_3^- leaching will increase as N accumulates in soils (Arp et al., 1996; Ouimet et al., 2001; Watmough and Dillon, 2003). Nitrate leaching from soils is predicted to increase as forests approach N saturation (Aber et al., 1991). Nitrogen saturation of forested catchments may occur when chronic N deposition increases ammonium (NH_4^+) and NO_3^- levels, in excess of plant or microbial demand (Aber et al., 1991). Potential effects of N saturation, in addition to increased NO_3^- leaching and associated base cation losses from soils, include altered fluxes of trace gases, increased N levels in trees, nutrient imbalances as other nutrients become limiting, and greater tree sensitivity to freezing and pests (Aber et al., 1989; Bowden et al., 1991; Schaberg et al., 2002; Skeffington and Wilson, 1988). A synthesis of data from 126 forest sites in Europe demonstrated that, above a threshold of about 10 kg N/ha, N leaching increased as N deposition increased (Dise et al., 1998; Stoddard et al., 2001). In some areas of Europe that receive extremely high levels of N deposition (up to 70 kg N/ha/yr), shifts in the composition of herbaceous species, from plants adapted to low N levels to those that favour high N conditions, have been reported (Falkengren-Grerup, 1995; Kellner and Redbo-Torstensson, 1995).

Long-term exposure to high levels of N deposition may produce similar responses in eastern North American forests to those observed in European forests. Consequently, there is a concentrated effort to detect early signs of N saturation in North American forests. Both short-term manipulation experiments and long-term forest catchment monitoring studies have been conducted. Results from experimental studies have shown conflicting responses to N amendments. Short-term experimental studies have elicited many of the responses that are expected under conditions of N-saturation (Magill et al., 1997). In some cases, however, there were no substantial increases in N leaching despite the addition of large amounts of N (Christ et al., 1995). It is important to note that these short-term studies involved additions of N that far exceed levels of deposition that occur now and are expected to occur in the future.

Results from long-term monitoring sites in Canada have also failed to provide convincing evidence for N saturation. Presently, with the notable exception of the Turkey Lakes, the majority of forest catchments in eastern Canada retain between 83% and 100% of the N (NO_3^- + NH_4^+) that is input by deposition (Figure 5.4). Generally, NO_3^- accounts for 50-60% of total N deposition, whereas N export is dominated by NO_3^-. These mass balance studies do not take into account N inputs via dry deposition that may increase N input into soils by 30–70%, or N inputs through N-fixation. They also do not include estimates of denitrification, losses of organic N, or losses of N from trees that are removed during harvest. These mass balance results should therefore be treated as approximate values; nevertheless, they do indicate that forests in eastern Canada are accumulating between approximately 4 and 10 kg N/ha/yr.

There is uncertainty as to whether low-level N accumulation will result in N saturation and whether detection of early stages of N saturation in the field signals the onset of acidification and eutrophication problems. Traditionally, it has been assumed that an increase in NO_3^- levels in streams is an early indicator of N saturation (Aber et al., 1989); however, annual NO_3^- export from forest catchments in eastern North America can vary greatly between adjacent catchments.

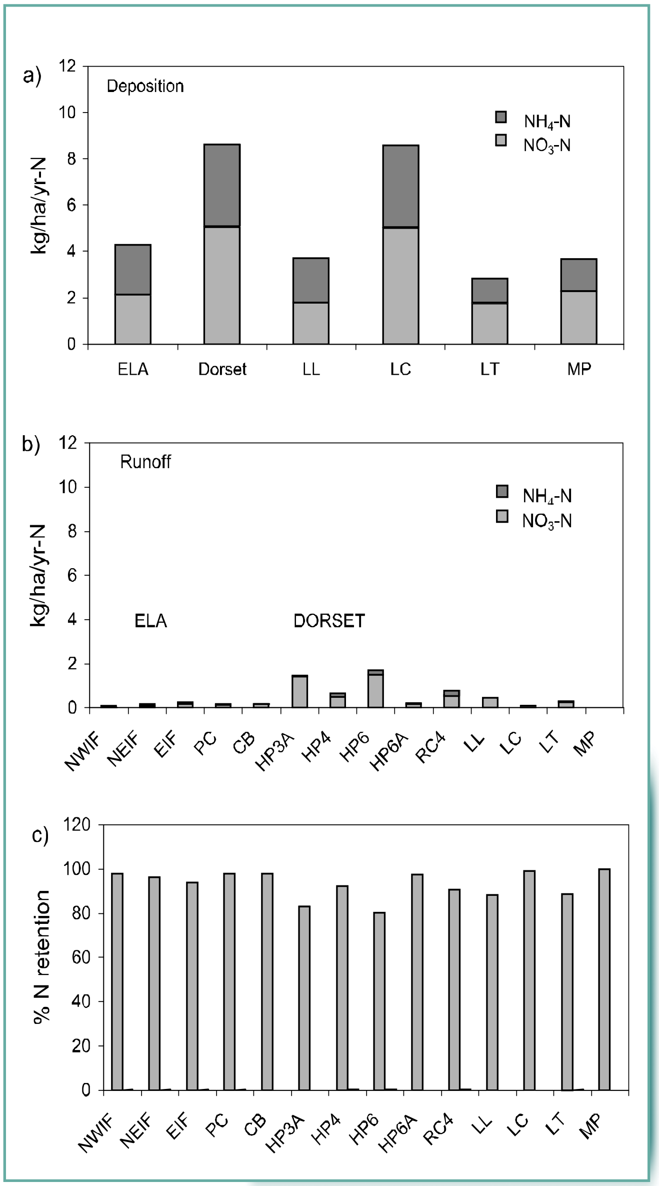

Figure 5.4: Nitrogen fluxes (NH_4^+, NO_3^-) in deposition (a), catchment output (b) and % net retention (c) for eastern Canadian sites. The data used in this compilation are from Watmough et al. (submitted).

Annual NO_3^- export appears to be influenced by both biotic (e.g., tree species composition) and abiotic (e.g., depth of till, slope) factors; the relative importance of these factors being variable between regions (Creed and Band, 1998; Devito et al., 1999; Dillon and Molot, 1990; Schiff et al., 2002; Watmough and Dillon, 2002). In some cases, NO_3^- export from adjacent forest catchments can vary by an order of magnitude (Schiff et al., 2002). Recent studies have observed that NO_3^- concentrations in streams in forested catchments can vary considerably between years, and inter-annual changes are related to a number of different climate variables. Mitchell et al. (1996), for example, suggested that an increase in NO_3^- export from four forested catchments in New England was related to an anomalous cold period in the winter of 1990. These researchers proposed that subsequent soil freezing may have resulted in root damage causing greater NO_3^- export. Murdoch et al. (1998) reported a positive relationship between NO_3^- concentrations in streams in a forested catchment in New York and mean annual air temperature, but also noted that high NO_3^- levels occurred in the winter of 1990.

Some studies have indicated that chronic N inputs have led to an increase in forest growth (Nellemann and Thomsen, 2001). While the fertilization effects may be beneficial initially, growth in excess of other plant nutrients such as Ca^{2+}, Mg^{2+}, K^+ or phosphorus may ultimately lead to nutrient imbalances in trees and to subsequent damage.

At present, the long-term impact of chronic N inputs is uncertain and remains a major concern. A concerted effort must be made to understand the transport and fate of N in ecosystems and potential consequences of continued N accumulation on Canadian forests. It is also important to improve our understanding of the relationship between N inputs to forests and carbon (C) sequestration as this has implications for climate change (Brydges, 1998).

5.6.2 N *mineralization rates in eastern Canadian forest sites*

R. Boutin, R. J. Foster, M. B. Lavigne and D. Paré

In 1996, as part the Productivity Program of the Forest Ecosystem Processes Network, the Canadian Forestry Service (CFS) initiated a project called ECOLEAP (Extended COncertation to Link Ecophysiology And forest Productivity). Under ECOLEAP, a study was initiated on *in situ* net N mineralization (the transformation of organic N into inorganic NO_3^-) at 11 eastern Canadian forest sites. The objective of the study was to determine functional relationships between specific biophysical factors related to site, climate, species composition, and ecosystem net primary productivity (NPP).

Incubation bags (10 reps./site) containing *in situ* mixed organic (FH) and mineral (0-20 cm layer) soil were periodically buried and removed at eight sites dominated by balsam fir (*Abies balsamea* L. Mill.) and three sites dominated by sugar maple (*Acer saccharum* Marsh.). The balsam fir sites were situated in areas that had different climatic conditions. These sites represented a climatic gradient in order to measure potential changes in soil respiration under conditions that might simulate a warming climate (Lavigne et al., 2003). Buried bag incubations were initiated in May/June of 1997 and monitored monthly for 4-5 months. In October/November, the bags were re-buried for the winter period (until May/June of 1998).

In order to measure inter-annual variation, incubations were carried out for two more years (until June 2000) at a subset of two sugar maple sites and two balsam fir sites. In June 2000, incubations were initiated at two other sites dominated by black spruce (*Picea mariana* Mill.) and maintained until October 2002. Nitrogen-$NH_4$and N-NO_3 concentrations and pools of total organic C and total N were measured for the two soil layers under study in order to calculate net N mineralization (NNM) in kg/ha/yr. Table 5.2 shows site locations and identification.

Results for the year 1997-1998 indicated that the total annual net N mineralization (ANM) rate in the FH layer, expressed per g of oven dry soil, varied from 2,250 µg/g in the relatively rich soil and uniform maple stand of St-Gilles (STG, 1 site), south of Québec city, to an average of 305 (72-700) µg/g in the balsam fir sites surveyed in north and south New Brunswick (NNB, 3 sites and SNB, 3 sites) (Table 5.3). Between these two extremes, ANM reached 1,881 (1725-2037) µg/g in the mixed hardwood stands of Duchesnay (DUC, 2 sites), north of Québec City, and 741 (695-786) µg/g in the balsam fir sites of

Table 5.2 Location and identification of observed sites in the net nitrogen mineralization study.

Balsam fir (*Abies balsamea*)		Sugar maple (*Acer saccharum*)		Black Spruce (*Picea mariana*)	
Location	**Site**	**Location**	**Site**	**Location**	**Site**
Montmorency Forest, QC75 km North of Québec City	FOM A FOM B FOM B+	Duchesnay, QC 40 km NW of Québec City	DUC A DUC B+	Lake Tirasse, QC 400 km NW of Québec City	TIR
Green River, northern NB 80 km NE of Edmundston	NNB A NNB B- NNB B+	Saint-Gilles, QC 30 km SW of Québec City	STG A	RESEF 203, QC 350 km NW of Québec City	RES
Acadia Forest, Fredericton, central NB	SNB A SNB B- SNB B+				

Table 5.3 Annual net nitrogen mineralization (µg N/g/yr), %N, C/N an pH for the organic layer (FH) and the top mineral layer (0-20 cm) of 13 eastern Canadian forest sites representing three dominant species. SM= sugar maple; BF= balsam fir; BS = black spruce.

Site	Dominant Species	Organic layer FH					Mineral layer 0-20 cm				
		ANM		%N	C/N	pH	ANM		%N	C/N	pH
		Mean	s.d.			($CaCl_2$)	Mean	s.d.			($CaCl_2$)
STG	SM	2250	621	1.51	20.4	4.71	56	9	0.14	13.5	4.25
DUCA	SM	1725	481	2.36	20.9	3.64	113	28	0.60	20.0	3.76
DUCB+	SM	2037	388	1.99	21.1	3.29	160	13	0.53	18.6	3.73
FOMA	BF	786	321	1.91	27.4	3.30	21	8	0.21	19.9	3.58
FOMB+	BF	695	238	2.03	21.0		38	12	0.26	23.3	3.73
NNBA	BF	220	357	1.41	30.7	2.95	63	45	0.41	20.4	3.34
NNBB-	BF	700	239	1.27	31.9	2.82	39	27	0.43	22.2	3.04
NNBB+	BF	72	422	1.38	32.9	2.93	32	22	0.37	20.2	3.09
SNBA	BF	141	151	0.98	37.2	3.05	27	42	0.16	26.0	3.17
SNBB-	BF	300	500	1.06	36.2	3.18	6	13	0.13	21.0	3.38
SNBB+	BF	395	196	1.07	34.0	3.05	2.4	20	0.18	24.2	3.27
RES	BS	174	78	0.91	53.3	2.68	4.3	4	0.10	35.3	3.50
TIR	BS	84.1	63	0.84	58.6	2.70	-0.4	2	0.06	33.5	3.75

Montmorency Forest (FM, 2 sites) in the Laurentian Shield. Mean ANM for the FH layer of the black spruce sites (TIR and RES; years 2000-2002) was also very low (84-174 µg/g). ANM was correlated positively with total N concentration (r=0.67) and pH (r=0.81), but correlated negatively (r=-0.70) with the C/N ratio (Table 5.3).

The highest mean ANM for the mineral layer was measured in the sugar maple stands (137 (113-160) µg/g and 56 µg/g in the DUC and STG sites respectively). In the balsam fir stands, ANM in the mineral layer was higher in the NNB sites (45(37-63) µg/g) than in the FM (30 (21-38) µg/g) and SNB sites (12 (2-27) µg/g). The lowest values for the mineral layer were for the black spruce site (4 µg/g for RES and near 0 (-0.4) µg/g for TIR). Similar to the FH layer, ANM in the mineral layer was correlated positively (r=0.82) with total N concentration and negatively (r=-0.53) with the C/N ratio, but the correlation with pH was weak (r=0.33).

After a period of one year, regardless of the layer type, the greatest amount of mineralization (measured as proportion of the initial total N) was measured at the sugar maple stands, followed by the balsam fir stands, and the black spruce stands; values for the latter were very low (Figure 5.5). In the sugar maple stands, 7 to 15% of the total N in the FH layer had been mineralized, corresponding to an average of 41(33-47) kg N/ha

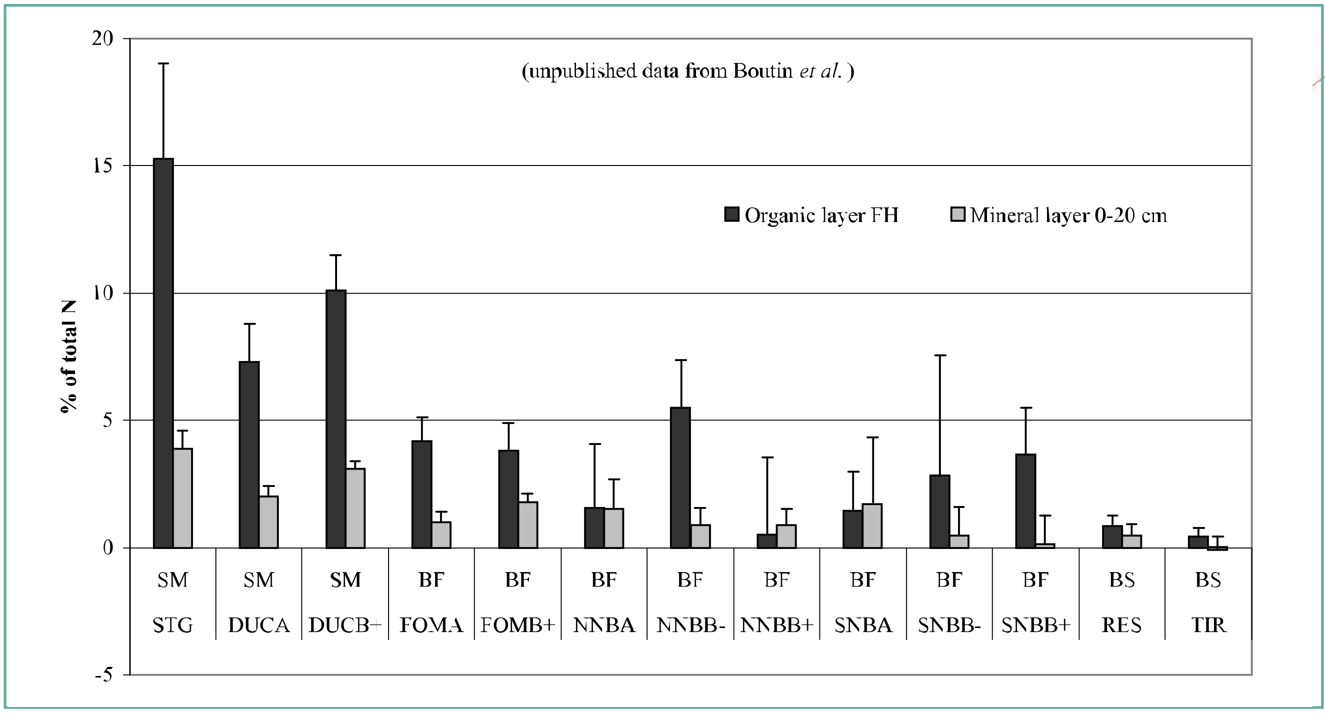

Figure 5.5: Annual net nitrogen mineralization (% of total N) in the organic layer (FH) and the top mineral layer (0-20 cm) of 13 eastern Canadian forest sites representing three dominant species. Error bars represent standard deviation. SM= sugar maple; BF= balsam fir; BS = black spruce.

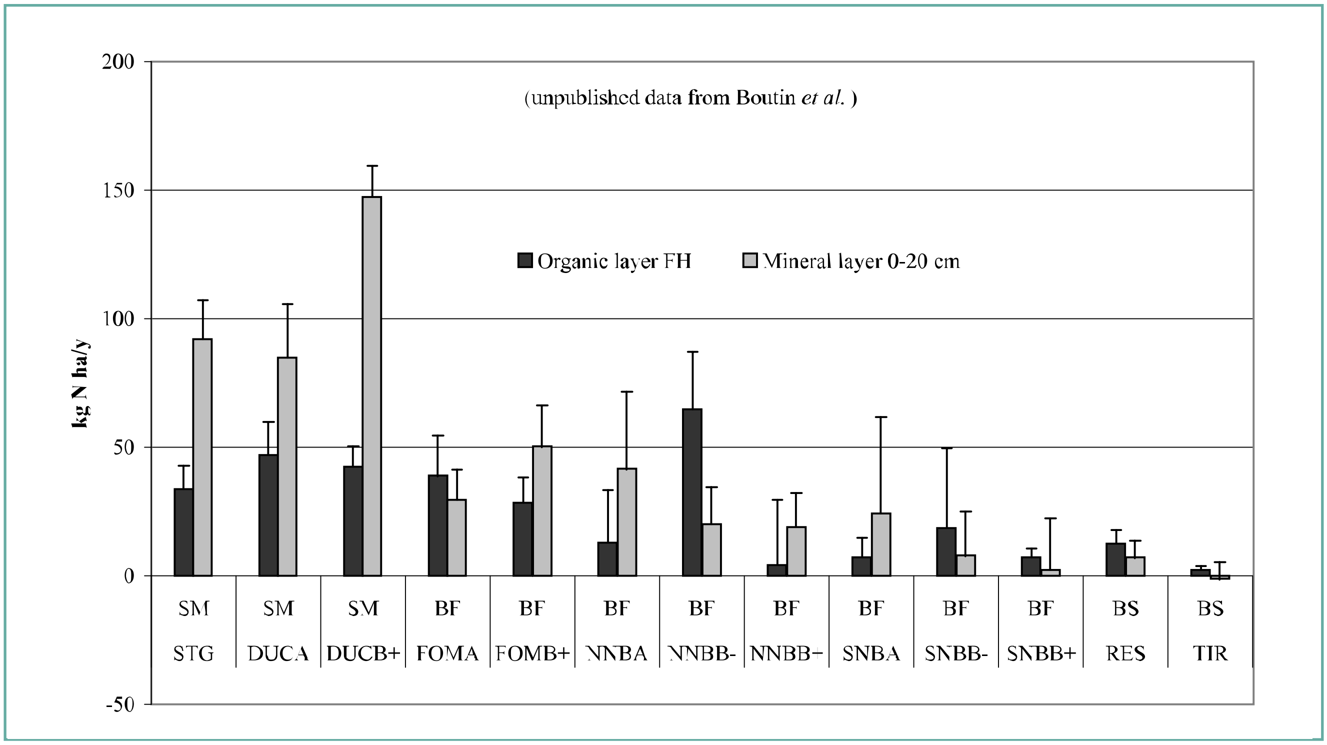

Figure 5.6: Annual net nitrogen mineralization (kg N/ha) in the organic layer (FH) and the top mineral layer (0-20 cm) of 13 eastern Canadian forest sites representing three dominant species. Error bars represent standard deviation. SM= sugar maple; BF= balsam fir; BS = black spruce.

(Figure 5.6). The FH layer of the balsam fir stands had mineralized 0.5 to 5.5% of the total N (average 25 (4-65) kg/ha) while the balsam fir stands had only mineralized 0.5 to 0.9% (average 7 (2-13) kg/ha). The proportion of N released in the top mineral layer was significantly less than in the FH layer (2-4%, 0.1-1.8% and –0.1-0.5% for sugar maple, balsam fir and black spruce stands respectively). Despite these lower values, on the basis of area, the amount of N mineralized in the mineral layer compared to the FH layer was 2.6 times more (108 kg/ha) in the sugar maple stands, and 10% more (27.5 kg/ha) in the balsam fir stands. Meanwhile, only 2.9 kg/ ha were mineralized in the mineral layer at the black spruce sites compared to 7.4 kg/ha in the FH layer.

Nitrification ratios (net nitrification/net mineralization) observed in the sugar maple stand were almost 110% at the STG site and equally high in the mineral and organic layers. At the DUC site, the nitrification ratio in the organic layer was between 25 and 40% (Figure 5.7). Net nitrification was strongly restricted in all balsam fir stands, particularly in the organic layers, with nitrification ratio values ranging from <1 to 8%. Net nitrification was also limited in most mineral layers of the NB sites (7-19%, not including one rich site (NR=88%) in SNB). Net nitrification was less restricted (58-99%) in the mineral layer at FOM. At the black spruce sites, a net immobilisation of NO_3^- occurred in the FH layer of RES (NR=-0.9%) while in TIR the nitrification ratio was 14%. Only 4% of the N mineralized in the mineral layer of RES was in NO_3^- form. No nitrification ratio was calculated for the mineral layer of TIR because of the occurrence of net N immobilization.

An analysis of the annual total net production of NO_3^- in the two layers (Figure 5.8) reveals that, in almost all sites, most NO_3^- production (75-98%) occurred in the mineral layer. Total NO_3^- production was greatest in the sugar maple stands (109-162 kg/ha/yr) followed by the balsam fir stands on the FOM sites (19-52 kg/ha/yr). Nitrate production was relatively low in the balsam fir sites of New Brunswick (1- 4 kg/ha/yr) but still significantly higher than in the black spruce stands (<1 kg/ha/yr). Net nitrification in the FH layer was strongly correlated to pH (r=0.94) while the correlation to pH in the mineral layer was weaker (r=0.68).

5.6.2.1 *Discussion*

Nitrogen mineralization, the endogenous production of NO_3^- from soil organic matter (SOM), requires two processes: ammonification (conversion of mineral N to NH_4^+) and nitrification (conversion of NH_4^+ to NO_3^-). The first process consumes 1 mol of H^+ per each mol of organic N transformed into NH_4^+ while the second produces 2 mol of H^+ per each mol of NH_4^+ oxidized into NO_3^-. Thus, each mol of NO_3^- produced from SOM in a given soil layer will add an acid charge of 1 mol of H^+ to that soil layer. If the roots of plants absorb the NO_3^-, neutralization will occur. It is thus very important that forest management practices avoid disturbing the soil and root structures of plants in such a way that optimum uptake of NO_3^- is disrupted, especially in sites where the potential for nitrification is high (Prescott et al., 2003). For example, if all NO_3^- ions measured at the sugar maple sites (in the incubation experiment) were leached from the rooting zone, the acidification charge produced in one year would be equivalent to 30-45 years of acid deposition at a mean pH of 4.6 and an annual mean precipitation of 1000 mm. A deep frost experiment conducted in 1990 at the Duchesnay experimental forest (in a site similar to the DUCA and DUCB+ sugar maple sites), in which strong root mortality was induced, showed very important NO_3^- production and leaching (Boutin and Robitaille, 1995). The very low N mineralization rates found on BS sites, suggests that plants may access N from organic sources. Selective removal and absorption of labile organic N by ectomycorrhizas fungi has been observed in the field (Read and Perez-Moreno, 2004). The activity of these organisms is strongly limited and also not measurable with the buried bag technique designed to monitor net change in mineral N. On the contrary, sugar maple roots are colonized by arbuscular mycorrhizas fungi which are known for their very limited capacity to absorb organic N (Aerts and Chapin, 2000).

The results of this study indicate a strong effect of forest type and soil organic matter quality on N cycling. The rates of N mineralization and nitrification are much faster in sugar maple sites, followed by balsam fir sites and finally by black spruce stands. This gradient also reflects changes in atmospheric deposition (Table 5.4) as sugar maple sites receive 9 kg N/ha/yr, compared to 6 kg N/ha/yr received in the Montmorency forest balsam fir site and

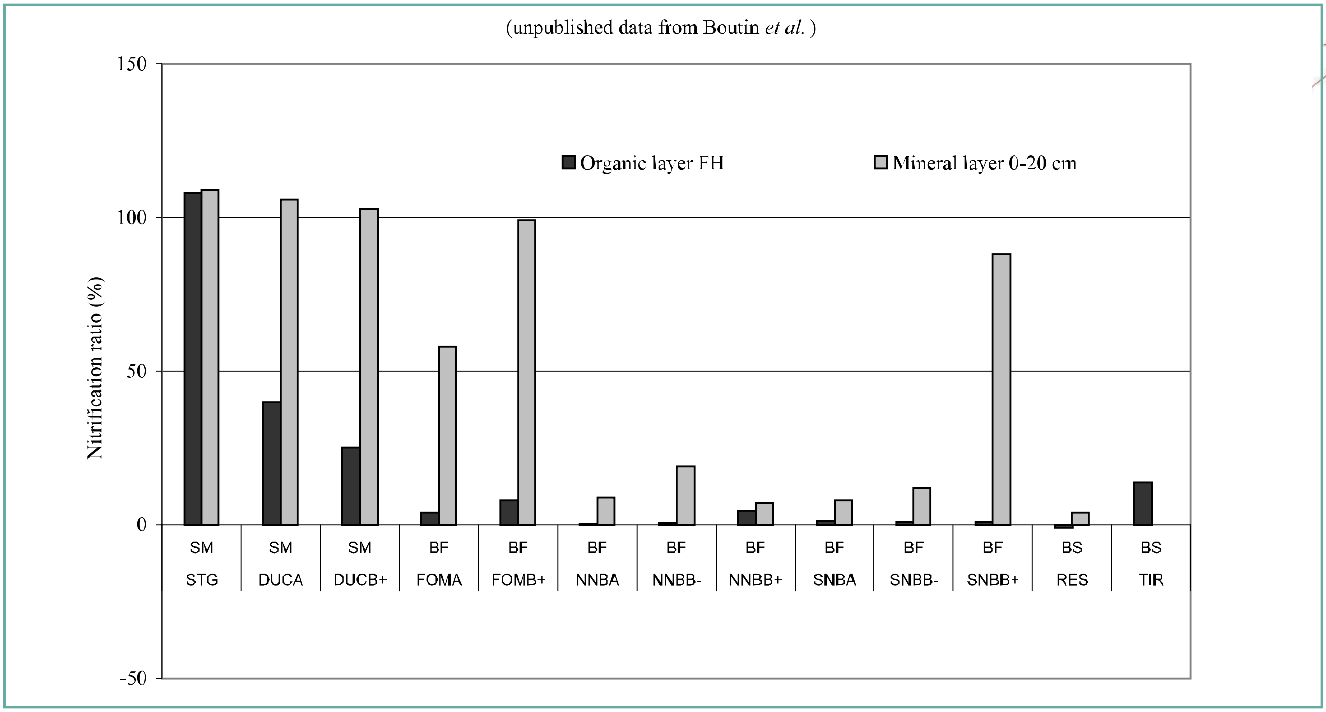

Figure 5.7: Nitrification ratio (net nitrification / net mineralization) in the organic layer (FH) and the top mineral layer (0-20 cm) of 13 eastern Canadian forest sites representing three dominant species. SM= sugar maple; BF= balsam fir; BS = black spruce.

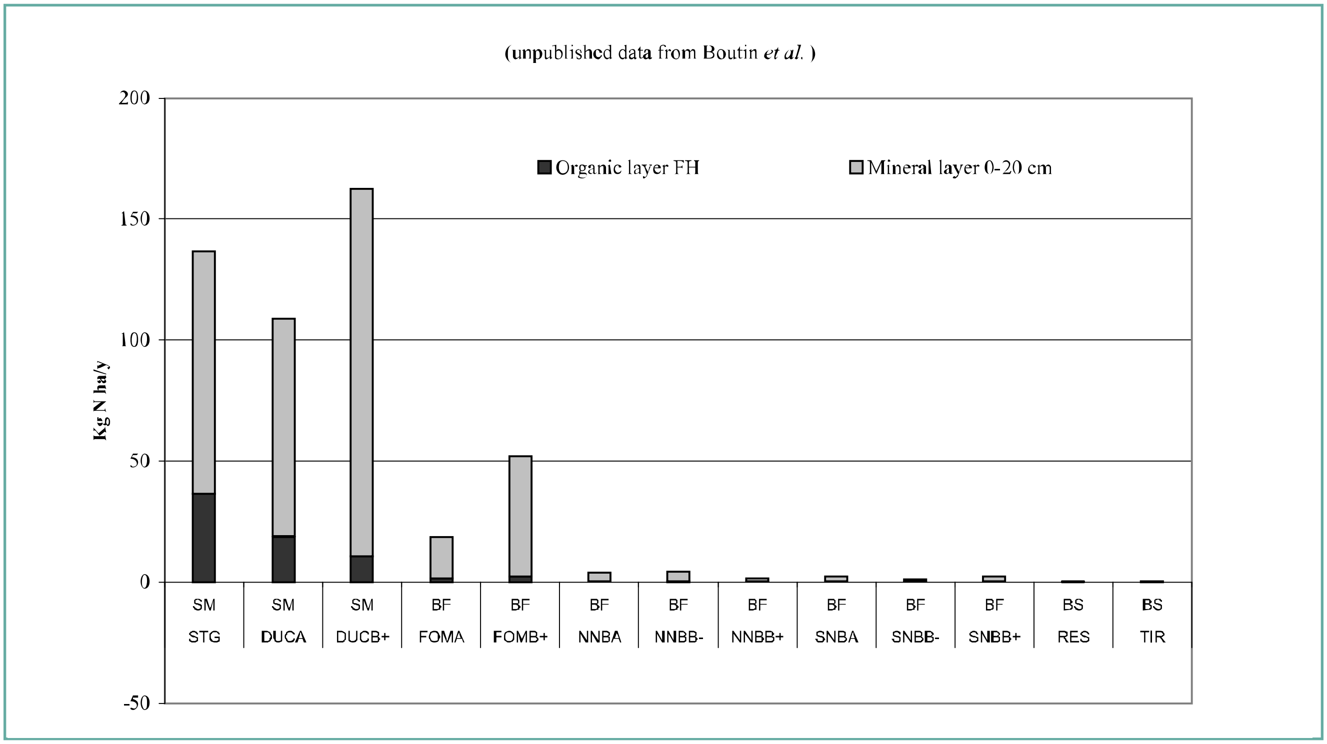

Figure 5.8: Net nitrification (kg/ha/yr) in the organic layer (FH) and the top mineral layer (0-20cm) for 13 eastern Canadian forest sites representing three dominant species. SM= sugar maple; BF= balsam fir; BS = black spruce.

3 kg N/ha/yr in the black spruce sites. It is therefore difficult to tease apart the role of N deposition versus forest types on N cycling. Nevertheless, results suggest that, along a gradient going from sugar maple to balsam fir to black spruce, there is a trend towards systems that are less prone to nitrification, and therefore less sensitive to N losses and N saturation. Because the cycling of N is so different in each of these systems, the impact of N deposition should be studied in each of these systems separately.

5.6.3 Short term N cycling in three contrasting forested catchments

C. Sainte-Marie and D. Houle

In the summer of 2001, an experiment was initiated to assess N dynamics in the organic layer (FH) of three watersheds located in the province of Québec. Each watershed supported different types of vegetation and received different amounts of N deposition (Table 5.4). The study was carried out simultaneously with a chronic N addition experiment in which the three watersheds were subjected to different levels of N addition (see Houle and Moore, Section 5.6.4). The N dynamics study was designed to characterize the internal N cycle in the FH layer of each of the three watersheds. Characterization of the internal N cycle was necessary in order to detect any change in the internal N cycling caused by the addition of N.

In order to assess the N dynamics, gross and net rates of N mineralization and gross rates of mineral N consumption were evaluated. Gross N mineralization and mineral N consumption were evaluated separately by short term isotopic dilutions using ^{15}N, *in situ* and in the laboratory (Davidson et al, 1991). Net rates of N mineralization were measured *in situ* using the buried bag method (Westerman and Crothers, 1980).

Three plots were studied per watershed. For each plot, *in situ* gross rates of N mineralization were measured in six replicates while *in situ* net mineralization rates were measured in three individually incubated and homogenized forest floor samples (three replicates). The results from each plot were then pooled and mean values were used in a statistical analysis. Differences among watersheds were analyzed by performing a one-way ANOVA followed by Tukey's multiple comparisons (HSD). More details about the methodology can be found in Ste-Marie and Houle (2005).

Ambient pool concentrations of mineral N in the FH layers were initially very low in all three watersheds (Table 5.5). Initial mineral N and NH_4^+ were very variable among plots but no statistical differences could be detected among watersheds. The FH layer at the Lake Laflamme watershed (LAF) contained the highest concentration of NO_3^-.

Nitrogen mineralization occurs in two steps: ammonification and nitrification. *In situ* isotopic dilutions on intact FH cores showed that, to some extent, gross N mineralization occurred in these soils but that most mineral N produced in the form of NH_4^+ did not undergo nitrification. In other words, rates of gross ammonification were much higher than rates of nitrification. The highest rate of gross ammonification was measured in the LAF forest floor, which was significantly different from the rates measured at the other two watersheds. Nitrification rates were comparable

Table 5.4 Main characteristics of the three studied watersheds.

Watershed	Location	Elevation (m)	Mean annual temp. (°C)	Mean annual precip. (mm)	Dominant vegetation species	Atmospheric N deposition (kg/ha/yr)
CLAIR	71 40 00 W 46 57 00 N	270-390	3.4	1200	Sugar maple (*Acer saccharum* Marsh.)	9
LAFLAMME	71 14 00 W 47 17 00 N	800	-0.6	1300	Balsam fir (*Abies balsamea*)	6
TIRASSE	73 39 00 W 49 12 45 N	400	0	900	Black spruce (*Picea mariana*)	3

Table 5.5 Mineral N concentrations of the soil FH layers. Mean concentrations are expressed in µg N/g dry soil and are followed by standard errors. Different letters show significant differences between means at the 0.05 level.

Watershed	Nitrate (NO_3^-) µg N/g	Ammonium (NH_4^+) µg N/g	Mineral nitrogen (NO_3^- + NH_4^+) µg N/g
CLAIR	0.91 ± 0.24 B	2.91 ± 0.73	3.81 ± 0.96
LAFLAMME	2.05 ± 0.32 A	4.38 ± 0.31	6.43 ± 0.20
TIRASSE	0.54 ± 0.03 B	6.43 ± 1.67	6.97 ± 1.67

in the three watersheds (Figure 5.9). Compared to rates of gross ammonification, NH_4^+ consumption rates in the forest floor were low at the Lake Clair watershed (CLAIR) and very high at the Lake Tirasse watershed (TIR). Nitrate consumption at CLAIR was lower than in the two other watersheds and lower than gross nitrification. Overall, all rates of gross *in situ* NH_4^+ consumption were higher than rates of gross ammonification suggesting that most of the NH_4^+ produced in these soils is readily consumed by vegetation and very little is left to accumulate in soils. These results agree with the very low NH_4^+ ambient pool concentrations that were measured (Table 5.5). This is also true for NO_3^- with the exception of the soil at CLAIR where lower NO_3^- consumption rates than gross nitrification rates indicates that some nitrate can accumulate in this soil.

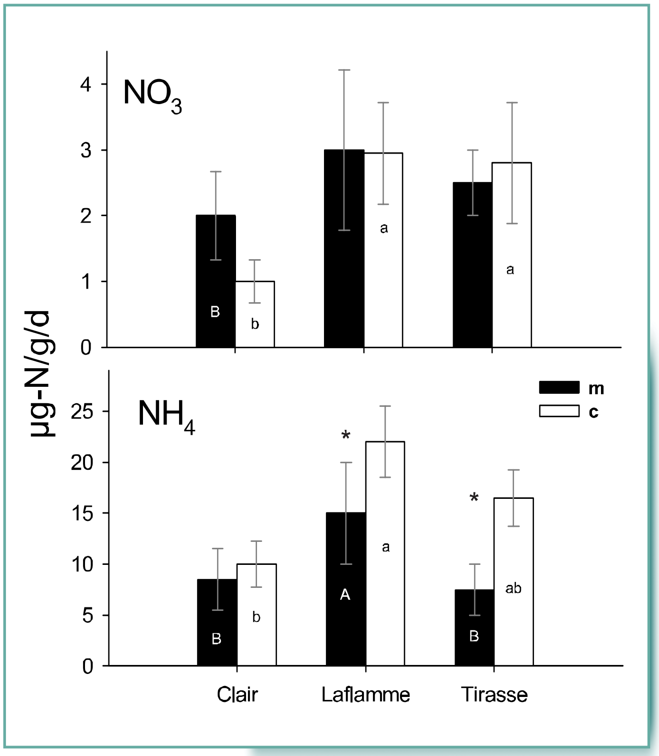

Figure 5.9: Gross N mineralization (m) and inorganic N consumption (c) measured during the *in situ* short term isotopic pool dilution on intact FH cores. Rates are expressed in µg-N/g dry soil/d. Error bars represent standard errors and different letters indicate significant differences between means at the 0.05 level. Stars indicate significant differences between m and c rates.

In the laboratory, isotopic dilutions to evaluate the rates of gross N mineralization and mineral N consumption were performed on sieved and homogenized forest floor samples. These samples were devoid of roots and were more homogeneous than soils in the field. Unlike in TIR, where rates were about the same in the two isotopic dilution experiments, rates of gross ammonification and NH_4^+ consumption for LAF were higher (50 to 60%) in the laboratory than *in situ* and rates of gross nitrification and NO_3^- consumption for CLAIR were higher in the laboratory than *in situ*. This can be explained by the higher activity of the microbial community under laboratory temperatures (20°C) compared to *in situ* conditions (10°C - 15°C). The absence of temperature stimulation in TIR might be the result of a severe N limitation. Once again, as compared to CLAIR and TIR, gross ammonification was significantly higher at the LAF site, where more than 25 µg N were produced per gram of soil within 24h (Figure 5.10). Trends in the rates of NH_4^+ consumption were very similar to what was observed *in situ*. Ammonium consumption was highest in LAF. CLAIR and TIR had similar rates of gross N mineralization, but mineral N tended to be immobilized more readily and to a greater extent by the microbial community in the forest floor of TIR. Rates of gross nitrification were relatively high in the CLAIR forest floor and NO_3^- consumption rates followed gross nitrification rates closely in all three watersheds. Ammonium consumption in the laboratory is the result of microbial immobilization and nitrification. It appears that in the forest floor of CLAIR, all the NH_4^+

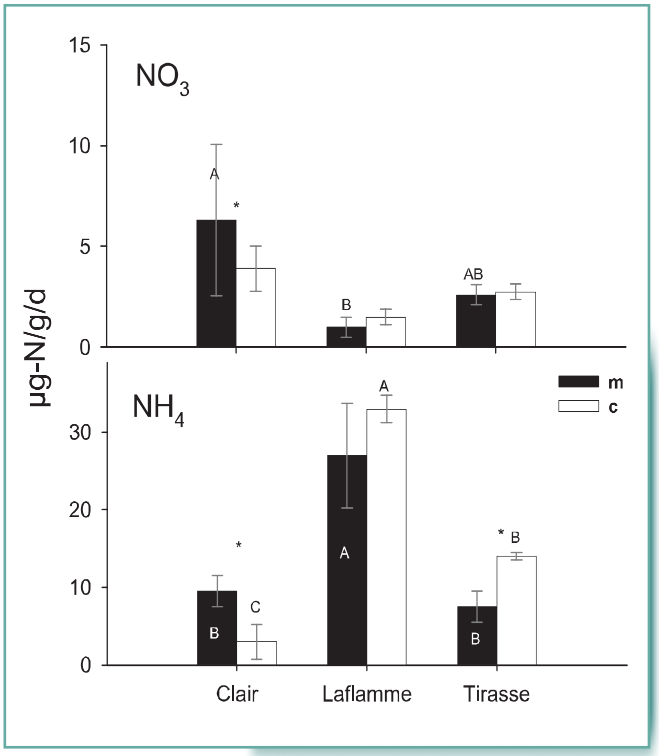

Figure 5.10: Measured gross N mineralization (m) and calculated microbial N consumption rates (c) during laboratory short term isotopic pool dilution. Rates are expressed in µg N/g dry soil/d. Error bars represent standard errors and different letters indicate significant differences between means at the 0.05 level. Stars indicate significant differences between m and c rates.

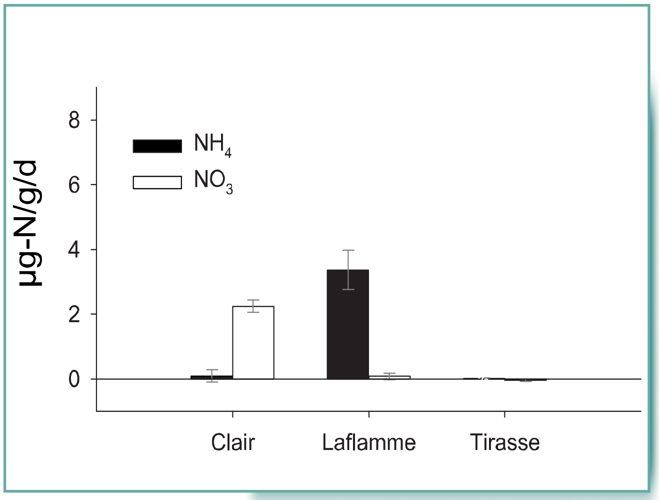

Figure 5.11: Net nitrogen mineralization rates in the forest floor measured *in situ* incubation with the buried bag method. Rates are expressed in µg N/g dry soil/d. Error bars represent standard errors and different letters indicate significant differences between means at the 0.05 level.

produced was consumed by nitrification while in the other watersheds nitrification appeared to account for only a small fraction of NH_4^+ consumption. Overall, the laboratory results corroborated the *in situ* observations.

It is assumed that, at least for a short period of time, small roots are still active in this type of experiment, and therefore intact core and rates of gross consumption measurements include vegetal absorption. Roots were excluded from the soil incubated in buried bags, in turn providing an estimate of net N mineralization under field conditions but in the absence of roots. Net rates of N mineralization reflect the accumulation of mineral N in a given soil (e.g., its production minus its consumption), in this case FH soil. Results from the buried bags showed very different patterns of mineral N accumulation among watersheds (Figure 5.11). LAF experienced the highest net N mineralization with nearly all N accumulating in the form of NH_4^+. Net N mineralization was also relatively high in CLAIR but in this case mineral N was found in the form of NO_3^-. Even with the exclusion of vegetal absorption, no mineral N accumulated in the forest floor of TIR, even though gross rates clearly showed that some N mineralization occured. In fact, NH_4^+ was removed from the soil solution. Mineral N appears to be readily immobilized by the microbial community in the TIR soils. The C:N ratio of this material is very high (49) so the microbial community is very N limited and competition between micro organisms and vegetation is likely fierce in this soil. This could be due to low atmospheric deposition of N (3 kg/ha/yr) observed at TIR.

In conclusion, N dynamics in the forest floor of these three watersheds differs greatly. In the LAF site, a lot of NH_4^+ is produced and very little of it undergoes nitrification. The microbial community immobilizes most of this NH_4^+, and a fraction is left in the soil where it does not accumulate but is readily absorbed by the vegetation. In the CLAIR site, N mineralization is important and almost all the NH_4^+ is in fact dedicated to NO_3^- production, which is not totally immobilized and some is left to the vegetation. In the TIR site, N mineralization is very low and the little inorganic N that is produced is readily immobilized in the FH material.

The patterns of N mineralization in the absence of roots combined with the low pools of inorganic N measured *in situ* strongly suggest that the dominant tree species of the three watersheds have distinct N nutritional requirements. Sugar maple (CLAIR) probably relies on NO_3^-–based N to grow, which prevents NO_3^- accumulation in this nitrifying forest floor. Moreover, sugar maple roots are colonized by arbuscular mycorrhizas fungi, which have a limited capacity to uptake organic N (Aerts and Chapin, 2000). Balsam fir (LAF) appears to absorb mainly NH_4^+ and prevent NO_3^- formation in the forest floor by the liberation of phenolics, which inhibit nitrification. Many conifer species exhibited better growth when supplied with NH_4^+ rather than NO_3^- (Van den Driessche, 1971; Van den Driessche, 1978; McFee and Stone, 1968). Black spruce (TIR) may be able to access organic N with the help of mycorrhizal symbionts allowing them to compete efficiently for N with the soil micro-organisms (Näsholm et al., 1998; Abuzinadah and Read; 1986a, 1986b).

Differences in N transformation patterns are probably more the result of tree species effect than N deposition. Tree species have a strong effect on N transformation (Ste-Marie and Paré, 1999; Vitousek et al., 1982; Thomas and Prescott, 2000; Lovett et al., 2004). The quality of tree litter determines to a great extent many properties of the FH material that are directly associated with N mineralization rates (Scott and Binkley, 1997; Thomas and Prescott, 2000). Soil microbial N transformations vary among tree species and may have consequences for forest N retention and losses (Templer et al., 2003). These results suggest that the effects of tree species on forest floor properties have major consequences on the N retention capacity of forest floors and potentially on their vulnerability to N saturation. Similar results to this experiment were observed at the Catskill Mountains (Templer et al., 2003).

5.6.4 N amendment experiments in three contrasting eastern Canadian forest sites: The first two years of soil solution observations

D. Houle, J.-D. Moore and F. Corbeil-Labonté

In this section, preliminary results of a chronic N addition experiment are presented. The experiment was initiated in the summer of 2001 at three forested watersheds (Clair, Laflamme and Tirasse) that are representative of the main forest stands in Québec. The watersheds were subjected to chronic N addition; their characteristics are described above (Section 5.6.3).

5.6.4.1 *Description of the methodological approach*

In each watershed, nine plots, representative of the forest vegetation, were selected and randomly categorized in triplicates according to three treatments: control (C), low N fertilization (LN) and high N fertilization (HN). Dimensions of the CLAIR plots were 15x15 meters and those of LAF and TIR were 10x10 meters. The quantity of N added annually to the LN and HN plots was equivalent to 3 and 10 times the quantity of humid N naturally deposited on the site annually (CLAIR, LAF and TIR; 8.5, 6.0 and 3.0 kg/ha/yr respectively). No N was added to control plots. Fertilization of the other sites started in June of 2001. Nitrogen vapour was applied monthly, between June and October, in the form of ammonium nitrate (NO_3NH_4), which also contained labelled N ($^{15}NO_3^-{}^{15}NH_4$). The results of the ^{15}N distribution among the forest pools (herbaceous, soil horizons and trees) will be reported in a forthcoming paper. Two tension lysimeters were installed during the fall of 2000 in the center of each plot, at depths of 30 and 60 cm. Water samples were collected weekly between May and October.

The Fisher Exact Test was used to determine the effects of N fertilization (95% confidence interval) on NO_3^- and NH_4^+ concentrations in soil water for each treatment (C, LN and HN) and at each depth (30 and 60 cm). The three sites were treated separately. The correlations between temporal variation of NO_3^- and Ca^{2+} concentrations in soil water were determined using Kendal's Tau (95% confidence interval). This non-parametric correlation is based on the number of pairs of matched and mismatched observations and uses a correction factor for pairs of observations with the same value.

5.6.4.2 *Discussion*

One indicator of N saturation of forest soils is high concentrations of inorganic N in soil solutions compared with non-N saturated soils; inorganic N losses in N-limited ecosystems are usually very low. Concentrations of NO_3^- and NH_4^+ in the soil solution of control plots at 30 and 60 cm were stable and low (Figure 5.12)

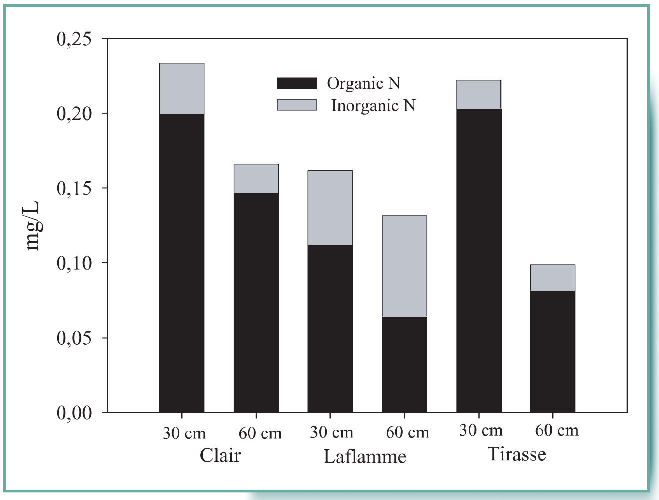

Figure 5.12: Relative concentrations of inorganic (NO_3^- + NH_4^+) and organic N at respective depths of 30 and 60 cm for the three studied sites.

suggesting that these sites are not showing signs of N saturation. Studies conducted on the same watersheds confirm that most of the N coming from atmospheric deposition is retained (Houle et al., 1997; Watmough, Section 5.6.1). These results are also in agreement with short residence times of less than one day observed for inorganic N in the soil solution (St. Marie and Houle, in preparation) and evident through the use of stable isotope methods (Davidson et al., 1991). Also, all three sites showed a high proportion of dissolved organic N (DON) to total dissolved N (Figure 5.12), despite a relatively high value of inorganic N of close to 50% for the LAF site at the 60 cm depth. The proportion of DON to total dissolved N in drainage waters is seen as a good indicator of N limitation in forest ecosystems (i.e. absence of N saturation) because high levels of DON to total dissolved N are characteristic of N limited systems. Perakis and Hedin (2002) reported that DON was the predominant form of dissolved N found in first-order streams at 100 South American unpolluted sites as compared to N saturated sites in the northeastern U.S.

5.6.4.2.1 Effects of fertilization

Treated plots, particularly at a high rate of application, clearly responded to fertilization. Indeed, increases in NO_3^- and NH_4^+ concentrations in soil solution were frequently observed at both lysimeter depths (data not shown). In the case of the TIR site, the increases in NO_3^- (Figure 5.13) and NH_4^+ were observed mostly at 30 cm in the HN application. The temporal variations in increases in NO_3^- concentrations seem to depend on when the fertilizer was applied (vertical dotted lines) and on the timing of rainfall events with respect to fertilizer application.

Generally, the concentrations of NO_3^- and NH_4^+ in soil solution followed the same pattern, but the NO_3^- concentrations were an order of magnitude higher than NH_4^+. Since the N solution used to fertilize the treatment plots is composed of equal quantities of NO_3^- and NH_4^+ (NO_3NH_4) on a molar basis, the lower NH_4^+ concentration observed in soil solution must be explained either by nitrification and/or preferential uptake of NH_4^+ by biota. Any treatment that exhibited a change in the concentrations of NO_3^- and NH_4^+ greater than 1.00 mg/L and 0.05 mg/L respectively, compared with the control (determined by the Fisher Exact Test) was considered to be the result of N fertilization. For the three sites considered, there was a significantly higher probability for a treatment effect to occur at a depth of 30 cm than at 60 cm (both HN and LN) and in HN plots as compared with LN plots.

Despite the high inorganic N concentrations occasionally observed in soil solution and the expected changes in N concentrations in relation to lysimeter depth and treatment intensity, these observed changes were only transitory. Generally, N concentrations returned rapidly to the very low levels typical of the control plots. The removal of N from the soil solution was probably the result of root and/or microbial absorption. The rapid N uptake was also indicative that the sites have not yet reached N saturation after two years of treatment.

5.6.4.2.2 Analysis of a single event

Figure 5.14 shows, in detail, the temporal variability of the soil solution chemistry, sampled with a 60 cm depth lysimeter, at the HN-treated LAF site. Fertilization caused important fluctuations in the concentration of NO_3^- in the soil solution while concentrations of other anions (Cl^- and SO_4^{2-}) stayed constant. In association with the increase in NO_3^-, an increase in base cations (K^+, Mg^{2+} and Ca^{2+}), Al^{3+}, NH_4^+ and H^+ (pH decrease) was observed. The pH decrease was probably caused by the nitrification of the added NH_4^+ as suggested by the molar ratio of NO_3^-

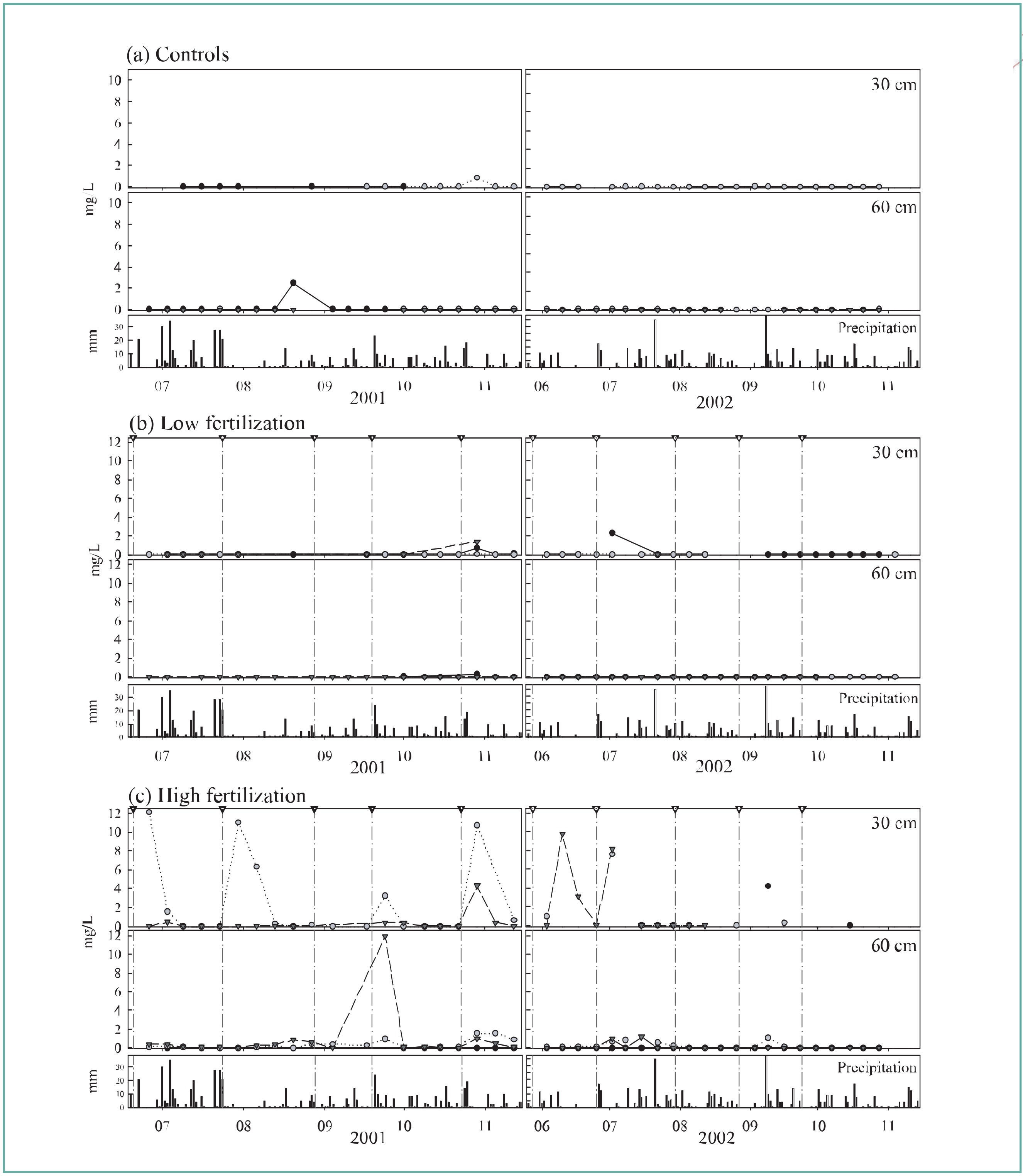

Figure 5.13: Temporal variations of NO_3^- concentration in the lysimeters located at 30 and 60 cm in the control, the low N and the high N fertilization treatments for the Lake Tirasse watershed. The vertical dotted lines indicate the time of N vaporisation. Daily precipitation data were kindly provided by Louis Duchesne (MRNFP-Québec).

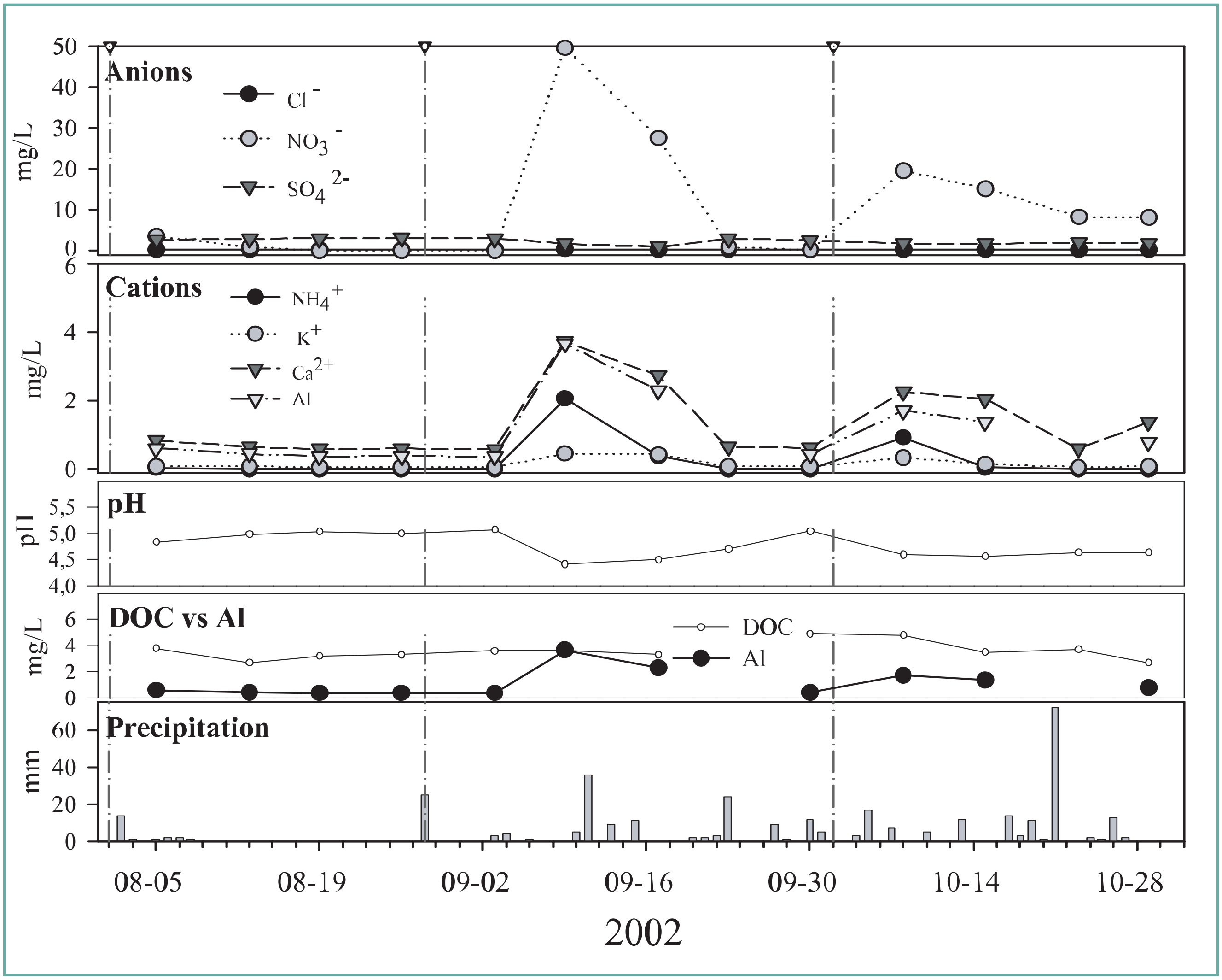

Figure 5.14: Soil solution chemistry at a 60cm depth in the HN treatment plot at the Lake Laflamme watershed.

to NH_4^+ (a high of 12) in the soil solution as compared to that in the added N solution. Of particular interest, is the high Al^{3+} concentration of 3.6 mg/L observed on the same day.

While Al^{3+} concentrations may follow DOC trends in soil solution because of its high affinity for organic matter, during this episode, the Al^{3+} increase was not associated with a DOC increase suggesting that most of the Al^{3+} was bioavailable. Despite the absence of N saturation, short term increases of NO_3^- may thus exert a harmful effect on roots by increasing Al^{3+} bioavailability.

The high NO_3^- concentration treatment was also responsible for increased base cation losses out of the rooting zone. In fact, significant correlations between NO_3^- and Ca^{2+} were frequently observed for HN treatments but not for control sites (data not shown, Houle et al., in preparation). Correlations between NO_3^- and Ca^{2+} indicate that NO_3^-–associated base cation losses were limited to treated plots.

Overall, our observations illustrate the absence of N saturation at the three study sites. The control sites had low inorganic N concentrations in the soil solution and dissolved organic N comprised a large proportion of the total N pool. These attributes are indicative of N limited forest ecosystems. Chronic N addition failed to induce a constant increase in inorganic N in the soil solution (despite transitory increases), which could have been indicative of an experimentally induced N saturation. For the highest treatment (10 times the natural atmospheric loading at a given site), the soil plots have now received the equivalent of 20 years of N deposition; each single addition being the equivalent of 10 years of N deposition. The three study sites are thus apparently still capable of retaining substantial amounts of atmospherically deposited N.

5.6.5 Conclusions of N cycling research

Overall, the data from the watershed N budget study (section 5.6.1) indicate that eastern Canadian forests are not presently showing signs of N saturation with the exception of the Turkey Lakes watershed. This situation, however, contrasts with data from the northeastern U.S. (Stoddard, 1994; Aber et al., 1995; Nodvin et al., 1995) and Europe (Dise and Wright, 1995) where N saturation is more frequently observed.

The experimental work presented in sections 5.6.2, 5.6.3 and 5.6.4 support observations that forested watersheds of eastern Canada have high N retention rates. Despite some site differences, a tight recycling of inorganic N species was observed in the three forest types typical of eastern Canada (sugar maple, balsam fir and black spruce) when using the short term ^{15}N dilution approach (section 5.6.3) which is indicative of a high N demand by the microbes and vegetation. The same sites, when experimentally amended with the equivalent of 20 years of accelerated chronic N addition (section 5.6.4), did not show signs of N saturation (despite transitory increases of inorganic N concentration in soil solution) again indicating that those sites were capable of retaining N additions. Sections 5.6.2 and 5.6.3 generally indicated that the transformation rates of inorganic N were faster in sugar maple sites, followed by balsam fir and black spruce stands. This forest type gradient matches with a superimposed N atmospheric deposition gradient that goes from about 10 to 3 kg N/ha/yr from the south to the north; however, forest types rather than N deposition were probably responsible for the site differences. The sugar maple forest is more likely to be affected by N saturation than coniferous forests in the future because it grows in areas that receive higher levels of N deposition and these forests have higher nitrification rates. Hence, the transformation of N in forest soils is not solely a matter of N deposition at a given site. Climatic and topographic factors, past land use, and tree species must be taken into consideration when interpreting N dynamics of forests in relation to acidic deposition.

5.7 TRANSFER OF ALKALINITY FROM WATERSHEDS TO SURFACE WATERS: THE ROLE OF BASE CATIONS

It is generally accepted that the negative impacts of acid deposition on forests will occur through changes in soil chemistry. While there are localized exceptions where acid aerosols may directly damage trees (Cox et al., 1996), understanding and quantifying biogeochemical processes in forest soils receiving elevated inputs of S and N deposition is vital for predicting both the short-term and long-term impacts of acid deposition on forests. Inputs of strong acid anions (SO_4^{2-} and NO_3^-) to forest soils have led to increased rates of leaching of base cations from soils (Kirchner and Lydersen, 1995; Likens et al., 1996; Watmough and Dillon, 2003a). Export of base cations (Ca^{2+}, Mg^{2+}) from soils can protect downstream lakes against acidification, but if leaching losses exceed the rate of replenishment from mineral weathering and deposition, soils will acidify and ultimately base cation inputs to lakes will decline. Fundamental questions that need to be addressed when considering the impacts of acid rain on forests and surface waters are: 1) To what extent are base cation losses from soils occurring?; 2) What will be the likely impact of changes in soil chemistry on tree health, and what other factors may contribute to forest decline?; 3) How rapidly are these changes occurring?; and 4) How should forests be monitored with respect to acid deposition?

5.7.1. Base cation budgets for eastern Canadian forests

S. Watmough

The net loss of base cations from the exchangeable soil pool will lead to soil acidification. It is therefore imperative to ascertain both the spatial extent and magnitude of base cation losses from the soil. In eastern Canada, base cation budgets (inputs in deposition and outputs in stream water) have been monitored at calibrated forested watersheds receiving differing levels of acid deposition, in some cases for almost 30 years (Beall

et al., 2001; Houle et al., 1997; Watmough and Dillon, 2003c,d, 2004; Yanni et al., 2000). Sites considered in this report are all located in eastern Canada (Figure 5.1), ranging from the Experimental Lakes Area (ELA) in western Ontario to Moose Pit Brook in Nova Scotia. These sites receive differing loads of acid deposition, with highest levels of S and N deposition occurring in south-central Ontario and southern Québec and lowest levels occurring at ELA in northwestern Ontario.
Quantifying fluxes of base cations between deposition and runoff is relatively straightforward at intensively monitored catchments although estimates of base cation inputs through mineral weathering are notoriously difficult to obtain. When base cation budgets are estimated without including estimates of mineral weathering, losses of base cations (Ca^{2+} and Mg^{2+} in particular) greatly exceed inputs in deposition (Figure 5.15). In long-term studies conducted at 15 forested watersheds in eastern Canada, average annual losses of Ca^{2+} in stream water measured in the 1990s exceeded inputs in deposition by between 2.2 kg/ha (ELA) and 26.7 kg/ha (Turkey Lakes).

The inclusion of estimates of mineral weathering does not usually fully balance current losses of Ca^{2+}, indicating that net losses of Ca^{2+} from forest soils are continuing despite reductions in acidifying emissions (Figure 5.15). At most watershed study sites, net annual losses of Ca^{2+} amount to between 1 and 12.7 kg/ha/yr. In some cases, such as the Turkey lakes watershed (S31), Ca^{2+} may be released in weathering reactions from beneath the rooting zone, so estimates of Ca^{2+} losses that consider only the rooting zone will overestimate Ca^{2+} losses from the biologically important upper soil horizons. Mass balance studies conducted in eastern Canada are usually done in undisturbed forests. Net Ca^{2+} (and other base cations) losses, and therefore soil acidification, will be even greater in forests that are harvested because harvesting permenantly removes Ca^{2+} and other base cations incorporated in tree tissues from the ecosystem (Adams, 1999; Federer et al., 1989).

Generally, losses of Mg^{2+} are much smaller than Ca^{2+}, and mineral weathering estimates are able to balance (or almost balance, net loss of < 1 kg/ha/yr) the Mg^{2+} budget at many of the study catchments (Figure 5.16). As well, inclusion of mineral weathering estimates indicates that all the study catchments are retaining K^+ in the soil (Figure 5.17). Trees will take up some of this K^+ at sites where net growth is positive although it is probable that estimates of K^+ weathering may also be slightly less than predicted. Long-term studies indicate that, among all base cations, Ca^{2+} losses appear to be the largest.

The dominant acid anion in runoff, responsible for base cation leaching and therefore soil acidification, is usually SO_4^{2-} (usually accounts for >90 % of acid leaching). Nitrate can also contribute to soil acidification at a few sites, in particular the Turkey Lakes watershed in Ontario (Foster and Hazlett, 2002; Foster et al., 1989). Recent declines in SO_4^{2-} deposition have resulted in lower net

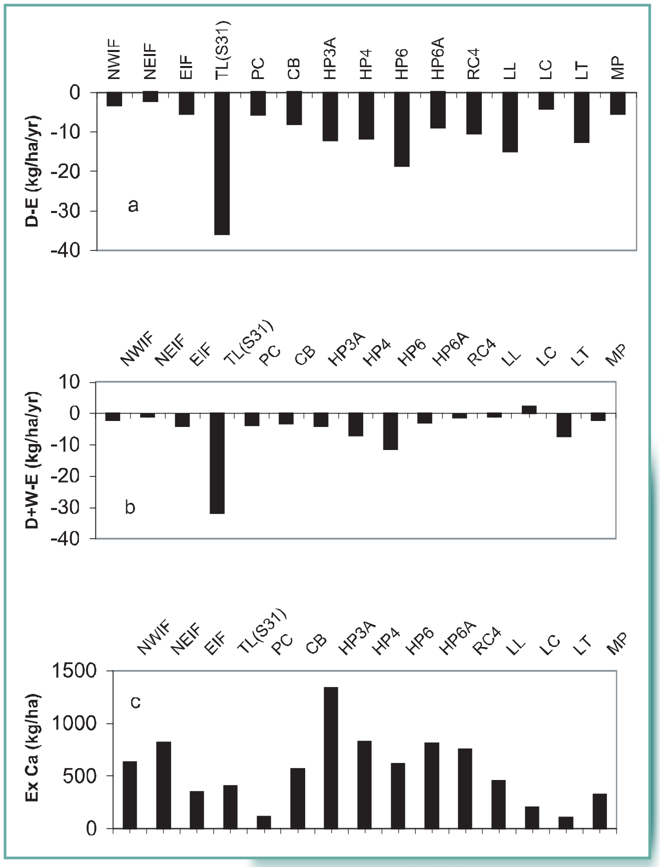

Figure 5.15: Mean annual Ca^{2+} mass balances (bulk deposition – stream output) at 15 forested catchments in eastern Canada during the 1990s (a); annual mass balances with an inclusion of an estimate for Ca^{2+} weathering (b); and current estimated exchangeable Ca^{2+} pool in soil (c). Sites are located in north-western Ontario at the Experimental Lakes Area (NWIF; NEIF and EIF), at Turkey Lakes (TL(S31)) in western Ontario, in south-central Ontario (PC, CB, HP3A, HP4, HP6, HP6A, RC4), in central Québec (LL, LC, LT) and in Nova Scotia (MP). The data used in this compilation are from Watmough et al. (submitted)

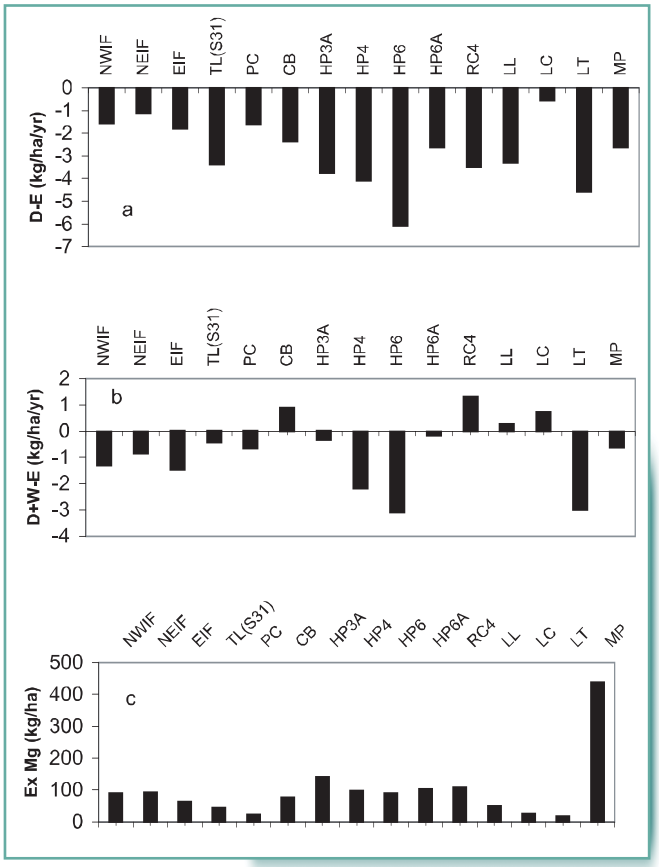

Figure 5.16: Mean annual Mg^{2+} mass balances (bulk deposition – stream output) at 15 forested catchments in eastern Canada during the 1990s (a); annual mass balances with an inclusion of an estimate for Mg^{2+} weathering (b); and current estimated exchangeable Mg^{2+} pool in soil (c). Sites are located in north-western Ontario at the Experimental Lakes Area (NWIF; NEIF and EIF), at Turkey Lakes (TL(S31)) in western Ontario, in south-central Ontario (PC, CB, HP3A, HP4, HP6, HP6A, RC4), in central Québec (LL, LC, LT) and in Nova Scotia (MP).

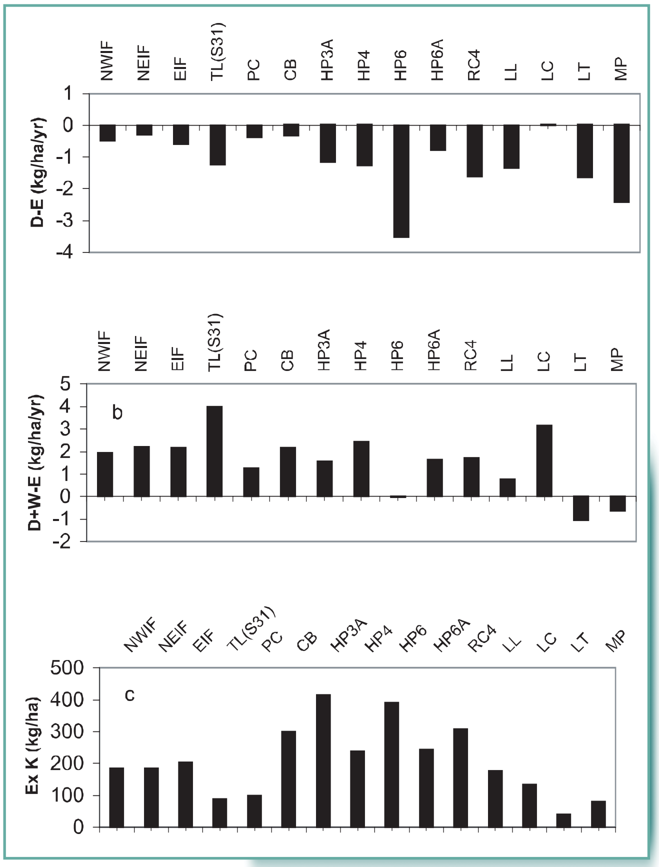

Figure 5.17: Mean annual K^{+} mass balances (bulk deposition – stream output) at 15 forested catchments in eastern Canada during the 1990s (a); annual mass balances with an inclusion of an estimate for K^{+} weathering (b); and current estimated exchangeable K^{+} pool in soil (c). Sites are located in north-western Ontario at the Experimental Lakes Area (NWIF; NEIF and EIF), at Turkey Lakes (TL(S31)) in western Ontario, in south-central Ontario (PC, CB, HP3A, HP4, HP6, HP6A, RC4), in central Québec (LL, LC, LT) and in Nova Scotia (MP).

losses of Ca^{2+} and, in turn, this has slowed down the rate of soil acidification (Likens et al., 1998; Watmough and Dillon, 2003a) although net losses of Ca^{2+} (and in some cases Mg^{2+}) are still occurring. In central Ontario, estimates of Ca^{2+} losses from the soil, obtained from mass balance estimates, were confirmed by repeated soil measurements taken 17 years apart (Watmough and Dillon, 2004). At a site in south-central Ontario, the exchangeable soil pool was reported to have declined by up to 30% since the early 1980s (Watmough and Dillon, 2004). Furthermore, the decline in exchangeable soil Ca^{2+} (and Mg^{2+}) can largely explain why surface water chemistry has not improved as expected from decreasing SO_4^{2-} export (Kirchner and Lydersen, 1995; Watmough and Dillon, 2003a).

A decline in exchangeable Ca^{2+} and Mg^{2+} in soils will lead to a decrease in Ca^{2+} and Mg^{2+} in runoff. In many areas of Canada, the decreases in Ca^{2+} and Mg^{2+} in lakes and streams is one of the factors that have offset the expected benefits to surface water alkalinity from declining SO_4^{2-} deposition (Jeffries et al., 2003). The net loss of base cations (Ca^{2+} in particular) from soils and soil acidification is not restricted to Canada. Losses of base cations from soil and declining soil pH have also been reported in the northeastern U.S. and Europe (Bailey et al., 1996; Drohan and Sharpe, 1997; Friedland and Miller, 1999; Johnson et al., 1994; Johnson et al., 2000; Lawrence et al., 1997; Likens et al., 1996, 1998). Recently, Tomlinson (2003) expressed concern that the decline in forest growth rates at Hubbard Brook, New Hampshire may be a result of Ca^{2+} limitation caused by acid deposition, and suggested that the lack of forest growth in acid stressed regions may have global consequences with respect to climate change.

5.7.1.1 *Base cation dynamics in forest soils*

While there are localized reports of declines in forest health caused by acid deposition, widespread forest decline in eastern North America has not yet occurred (Allen et al., 1992; Bauce and Allen, 1991). In order to understand the potential impacts of acid deposition on forests and determine policy with respect to acid emissions, it is important to consider the time-scale involved. Exchangeable soil base cation pools in glaciated parts of eastern North America have developed over a period of 10 – 12,000 years whereas disturbance caused by acid deposition and forest harvesting is relatively recent (100 years or so). Annual net losses of base cations from soils are usually small relative to the size of the exchangeable pools of base cations (Figures 5.15-5.17). Consequently, acidification of soils can take anywhere from a few decades to several hundred years depending upon: 1) the level of acid and base cation deposition, 2) the rate of mineral weathering, and 3) forest management practices. Dynamic models, currently being developed, generally show that in areas impacted by acid deposition, there has been a gradual decline in soil base cation saturation and soil pH over the course of the 20th century (Cosby et al., 1985; Gbondo-Tugbawa and Driscoll, 2003). Although the rate of soil acidification has slowed down, further reductions in acid deposition are needed to prevent soil base cation saturation from falling below the level considered unsuitable for forest health and productivity (Arp et al., 1996; Ouimet et al., 2001; Watmough and Dillon, 2003b). Base cation levels in soils, unlike stream chemistry, are unlikely to improve in the near future because the recovery of soils from acidification (replacement of base cations lost due of enhanced acid leaching) is extremely slow.

5.7.2 Assessment of base cation reservoirs in the watershed soils of the Québec lake-network and links to lake chemistry

D. Houle and R. Ouimet

As noted in the previous section, acidification of surface waters is widely hypothesized to be related to the size (or decreasing size) of base cation reservoirs in watershed soils. This section presents data describing the linkages between base cation reservoirs in forest soils and lake chemistry. Data describing these linkages are rare in the acid deposition literature because few research programs have the capacity to examine both lake and forest soil chemistry at the same location. In this section, we examine the hypothesis that the concentration of base cations in a lake is proportional to the size of the exchangeable base cation reservoirs present in the surrounding forest soils.

5.7.2.1 *Methodology*

In 2001 and 2002, soils were sampled in 22 watersheds (Figure 5.18) within the Québec lake-network. In each watershed, three 1 m^2 soil pits were dug to a depth of 1 m and a soil profile description was made for each pit. Soil horizons with a thickness greater than 4 cm were sampled individually. The depth of the rooting zone was noted, and an ocular estimate of percent volume of large stones was made. Core samples were taken from each main horizon with a volumetric hammer sampler (diameter: 53 mm, length: 60 mm) to determine bulk density. All soil samples were air-dried and sieved to 2 mm. Exchangeable cations (K^+, Ca^{2+} and Mg^{2+}) were extracted with an unbuffered NH_4Cl (1M, 12 hours) solution, and measured using inductively coupled plasma emission. Soil depth, coarse fragment content, and bulk density were used to convert base cation concentrations to kilograms per hectare in the soil's rooting zone (50 cm). Further details on this study may be found in Houle and Ouimet (in preparation).

5.7.2.2 *Results and discussion*

The exchangeable base cation reservoirs were computed for region 1 to 5 of the Quebec lake network (Figure 5.19). These regions are statistically different in terms of lake pH, alkalinity, mineralization (the sum of the Ca^{2+} and Mg^{2+} concentrations) and SO_4^{2-} concentration (Bobée et al., 1983). We decided to express the soil results in terms of region since the water chemistry was assumed to reflect, to some extent, the nature of the underlying bedrock and surface deposit.

The average size of the exchangeable Ca^{2+} reservoirs varies by one order of magnitude, ranging from 172 (region 1) to 2944 kg/ha (region 5). Regions 2 and 3 have low average values while region 4 exhibited intermediate values. A similar pattern is observed for Mg^{2+} although the absolute sizes of the exchangeable reservoirs are about 10 times lower. The situation is different for K^+, for which the reservoir size is less variable among regions. The patterns for both the Ca^{2+} and Mg^{2+} reservoirs are probably caused by substantial amounts of Ca^{2+}- and Mg^{2+}-bearing minerals in surface deposits in region 5 and, to a lesser extent, in region 4. Proportions of individual base cations that form the exchangeable reservoirs are within the range found in northeastern North America (Figure 5.20). Mg^{2+} shows the least variation in proportion of the total base cation reservoir, representing a median value of 10%, while Ca^{2+} displays the largest variation, followed by K^+.

\With the exception of regions 4 and 5, most of the sites sampled appeared to be susceptible to acidification because the watersheds are composed of soils and rocks with a low capacity to neutralize acids. Regions 1 and 2 are particularly at risk. The average base cation reservoir sizes in these watersheds are among the lowest reported for eastern Canada (see Wathmough, Section 5.7.1) and generally for northeastern North America (18% of the average value). The small exchangeable cation reservoirs found in these regions are due in part to the mineralogical makeup of the underlying granitic bedrock and surface deposits which generate low levels of base cations through weathering. Regions 1 and 2 are very dependent on atmospheric base cation deposition for restoration of base cation pools. Thus, since there has been a decrease in base cation deposition in northeastern North America (Hedin et al., 1994), base cation reservoirs in regions 1 and 2 may continue to decline under current levels of acid deposition.

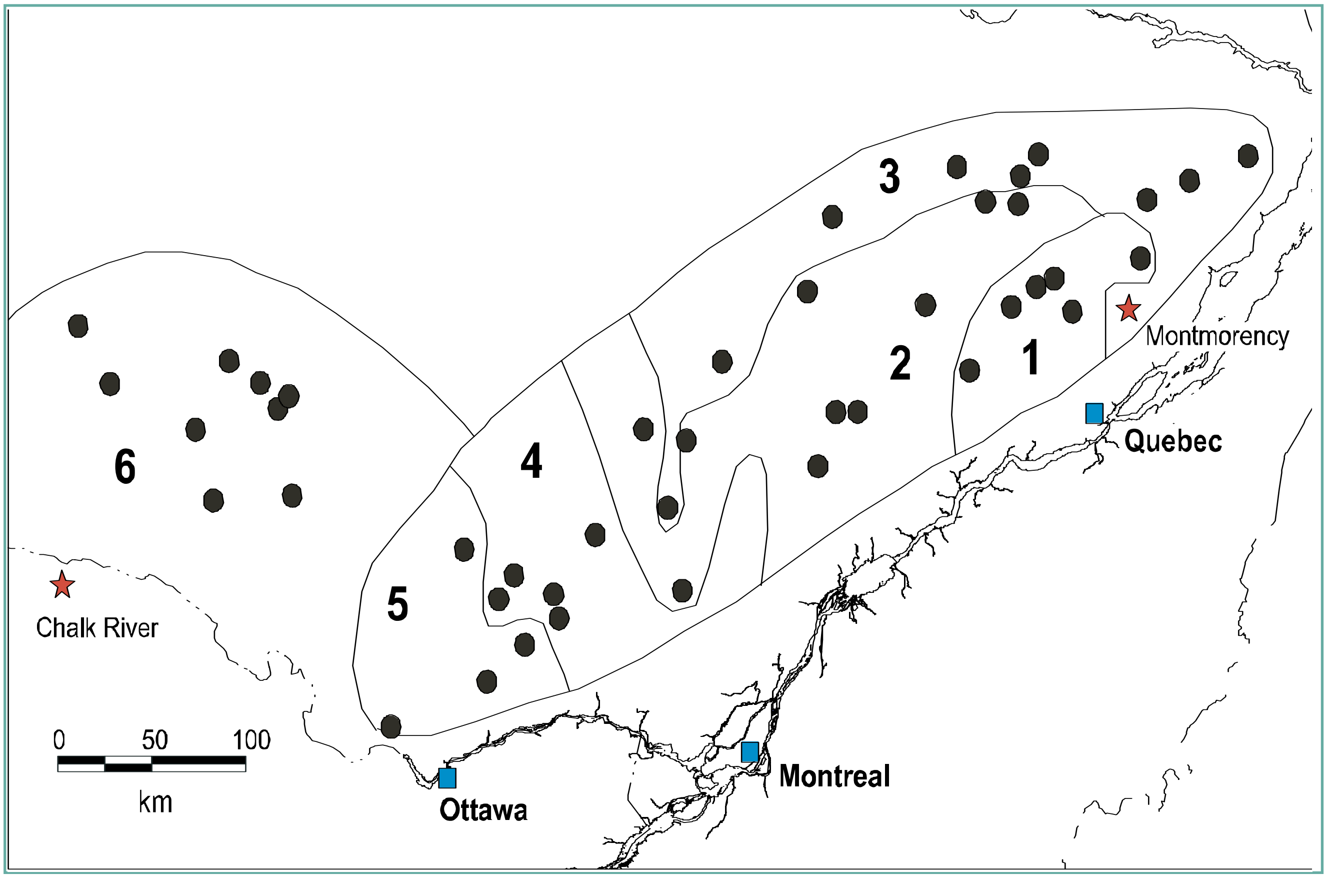

Figure 5.18: Location of the Québec lake-network and boundaries of regions 1 to 6.

Regions 1 and 2 also show the highest proportion of lakes that are either exhibiting no chemical recovery (pH and alkalinity) or that are still acidifying (Houle et al., 2004b). This observation supports the contention that the size of exchangeable base cation reservoirs (which are involved in neutralization of acid inputs) are linked to the capacity of a given lake, not only to resist, but to recover from previous acidification. This relationship between base cation reservoirs in soils and surface water chemistry is supported by the observations in regions 4 and 5. In these regions, which receive high levels of acid deposition, high exchangeable base cation reservoirs, and presumably higher weathering rates, are protecting soils and surface waters from acidification.

The spatial distribution of average Ca^{2+} and Mg^{2+} concentrations in lakes (Figure 5.19) shows an increasing gradient from the northeast to the southwest (from regions 1 to 5). For instance, the mean Ca^{2+} concentration for the lakes in region 1 is the lowest at 1.0 mg/L while the lakes of the Outaouais region (region 5) have the highest values with an average of 8.0 mg/L. The ranking of base cation reservoirs between regions 1 to 5 is in good agreement with the ranking of base cation concentrations (Figure 5.19) and alkalinity (data not shown) of the lakes, suggesting that soil and lake chemistry are closely linked. This link is strong for Ca^{2+} and Mg^{2+} while the link between K^+ in soils and in lakes is weak. This may be due to the fact that K^+ is not as strongly involved in buffering reactions in soils as Ca^{2+} and Mg^{2+}, and is very actively recycled within soils by biota (Likens et al., 1994). Consequently, the soil exchangeable K^+ reservoir would have less impact on surface water chemistry.

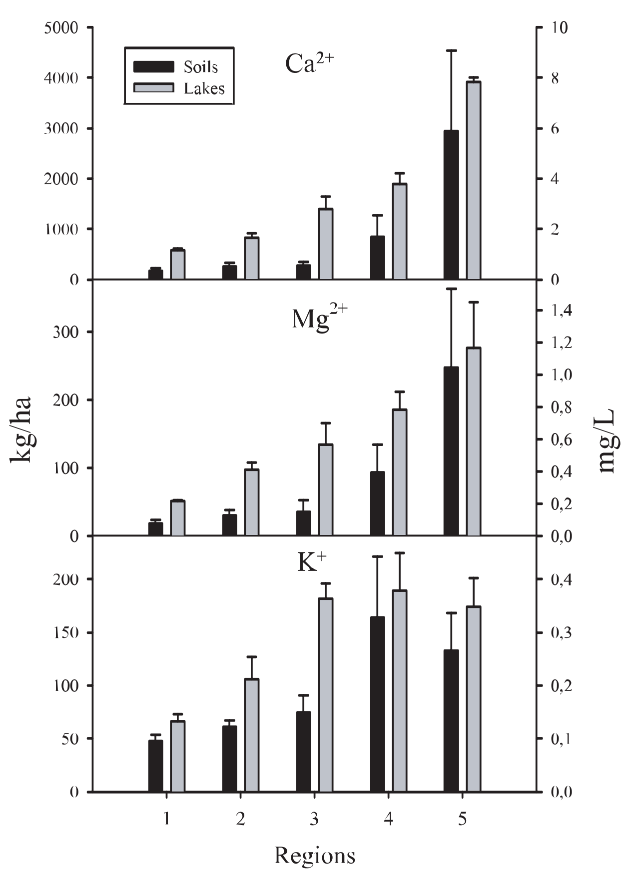

Figure 5.19: Variations of Ca^{2+}, Mg^{2+}, and K^+ soil exchangeable reservoirs and lake concentrations from regions 1 to 5 of the Québec lake-network.

Results of a previous study, using the lake and soil chemistry of a survey of 35 lakes of the Québec lake-network in 1984 and 1985, also revealed strong links between many soil and lake variables (Lachance and Buteau, 1989). Selected variables are shown in Table 5.6. Soil pH, exchangeable Ca^{2+} concentration, and base cation saturation were all significantly and positively

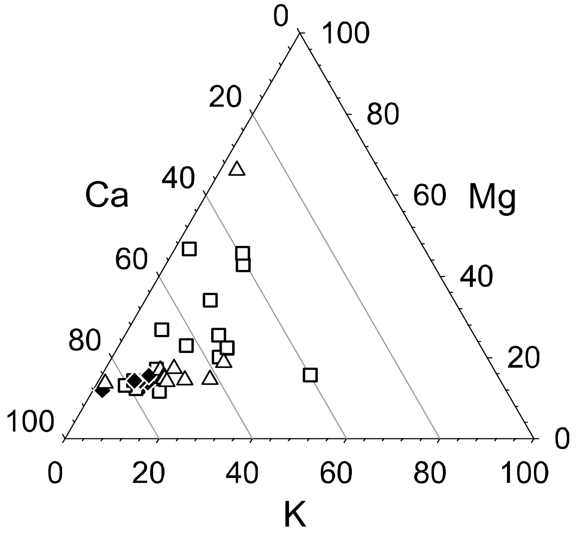

Figure 5.20: Proportion of soil exchangeable basic cation reservoirs in the five regions of the Québec lake-network (diamonds). For comparison, sites of the IFS Study (triangles) (Johnson and Lindberg, 1992) and of the Dorset area, ON (squares) (Watmough and Dillon, 2003) are plotted.

Table 5.6 Relationships between lake and soil chemistry for 35 catchments of the Québec lake-network. All the coefficients shown are significant at a level of 0.05. Data obtained from Lachance and Buteau (1989).

		Lakes		
Variable	**Horizon**	**pH**	**Ca**	**AlkT**
Soil pH H_2O	BHF	0.832	0.848	0.836
	BF + BHF	0.505	0.448	0.487
Soil exch. Ca	BHF	0.787	0.765	0.749
	BF + BHF	0.711	0.695	0.69
Soil Σ Cation	BHF	0.853	0.788	0.809
	BF + BHF	0.683	0.636	0.632
Soil base sat.	BHF	0.828	0.792	0.786
	BF + BHF	0.725	0.695	0.686

correlated to lake pH, Ca^{2+} concentration, and total alkalinity. The strongest correlation coefficients (generally around 0.8) were observed between lake chemistry and the upper mineral soil layer (Bhf horizon) chemistry.

To our knowledge, the strong linkages between the size of the soil exchangeable base cation reservoirs and base cation concentrations in lakes, as well as the linkages between the latter and chemistry of distinct soil horizons, are unprecedented. This finding has important implications because acidification of surface waters as well as absence of recovery from acidification have been widely hypothesized to be related to the size (or decrease in size) of base cation reservoirs in watershed soils (Stoddard et al,. 1999). These data strongly support this hypothesis.

5.8 CONCLUSIONS

In light of the data presented in this chapter, some key conclusions are emerging. First, the report of net base cation losses from eastern Canadian forested catchments (Section 5.7.1) is widespread, showing that weathering inputs of base cations are not sufficient to balance the base cation leaching losses, particularly for Ca^{2+}.

It must be emphasized that the base cation losses in unprotected sites, i.e., subjected to commercial tree harvest, would be higher (because of cation losses through biomass removal) than in research monitoring sites which are, by definition, protected areas. This raises concerns about the long term sustainability of soil fertility, and hence, forest health, particularly for sites with poor buffering capabilities. Furthermore, exchangeable reservoirs of base cations that have been significantly depleted in past decades are not expected to recover rapidly despite the reduction in acid loadings. It has been widely hypothesized that acidification of surface waters, as well as, the absence of recovery of lake pH levels are related to the size (or decreasing size) of base cation reservoirs in watershed soils. The strong link observed in Section 5.7.2 between lakes and soil Ca^{2+} and Mg^{2+} content support this hypothesis. One of the major uncertainties in determination of time to recovery for forest soils and surface waters is the value of weathering rates. For this reason, determination and validation of weathering rates should be a focus of future research.

The negative effects of decreasing soil fertility on forest health are becoming increasingly supported by recent studies. These observations are raising concerns about the productivity of eastern Canadian forests located on poorly buffered soils. Quantification of the relationship between acid deposition and forest health remains difficult, however. Further research is necessary to elucidate this relationship.

This chapter also revealed that most eastern Canadian forested catchments are showing S release in excess of S deposition (Section 5.5). Atmospheric S sources that are currently unaccounted for, including dry S deposition and weathering of S-bearing minerals, do not appear to be sufficient to explain the observed discrepancies between S input and S output at studied catchments. Internal catchment sources, including SO_4^{2-} desorption or SO_4^{2-} release by decomposition of organic matter, remain the likely candidates. Both processes are generating acidity in the soil, and this internal S release simply acts as an additional atmospheric S load for soils and downstream surface waters. The release of excess S may be partly responsible for the lack of recovery observed in surface waters in regions of eastern Canada. Another consequence is that surface water critical load models, which are based on SO_4^{2-} inputs in deposition rather than export in stream water, will underestimate the potential impact of SO_4^{2-} deposition in catchments that exhibit substantial net SO_4^{2-} losses. These findings stress the importance of elucidating the processes governing transformations and exports of S from terrestrial catchments to surface waters in a context of decreasing S deposition. A substantial part of future research efforts should focus on this area.

Finally, based on the results of the N work presented in this chapter (Section 5.6), N saturation does not appear to be a problem for most eastern Canadian sites; however, the capability of forests to accumulate atmospherically deposited N is finite, and leaching of excess N will occur eventually. The question remains as to when this will happen. Research to date cannot answer this question. Detection of N saturation in surface waters must be the subject of an intensive and continued monitoring in the existing Canadian research sites.

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CHAPTER 6

Effects on Aquatic Chemistry and Biology

D. S. Jeffries, D. K. McNicol, and R.C. Weeber

6.1 KEY MESSAGES

- Many lakes in southeastern Canada are still acidified (i.e. have lost some or all of their capacity to neutralize acids) and many do not meet the critical load pH condition of 6; a key threshold for the sustenance of fish and other aquatic biota.
- In many lakes, chemistry is responding to reductions in acidifying emissions (i.e. lakes are becoming less acidic) but several factors are acting to delay or diminish the response.
- Algae, invertebrates and waterbird food chains continue to show acidification effects, particularly in lakes and rivers where fish communities have been impacted. Impacts include direct acidity effects, metal toxicity, loss of prey, and reduced nutritional value of remaining prey.
- Atlantic salmon populations in rivers of the Southern Upland region of Nova Scotia continue to be severely impacted by acidification.
- Overall, the capacity for many lakes to support aquatic biota is improving and increases in waterbirds such as the Common Loon have been observed.

6.2 CONCLUSIONS OF THE 1997 ASSESSMENT

This section reproduces portions of the volume and chapter summaries from the 1997 Canadian Acid Rain Assessment (Jeffries, 1997) and is presented here to establish a starting point for the remainder of this chapter.

The lakes of Atlantic Canada were generally the most sensitive to acidic deposition and exhibited the greatest proportion of acidic systems. In Ontario and Québec, lakes were generally moderately sensitive, while the lakes in western Canada typically exhibited low sensitivity and almost no evidence of anthropogenic acidification. There were exceptions to all these generalizations however.

Sulphate deposition was the primary acidifying agent in Canada, although natural acidification by organic acids occurs in all provinces and is particularly important in Nova Scotia, Newfoundland and eastern Québec. Few lakes in Canadian regions that received low nitrogen (N) deposition (e.g., Newfoundland, Labrador, and Saskatchewan) exhibited evidence of N-based acidification. However, N-based acidification was evident for many lakes scattered throughout southeastern Canada, particularly in southcentral Ontario and southwestern Québec.

In response to reduced SO_2 emissions, sulphate levels declined in most Ontario and Québec lakes, but sulphate levels in most lakes in the Atlantic Region were unchanged. However, only in central Ontario did the acidity decline in the majority of lakes concomitant with a decline in sulphate levels; a result attributed to SO_2 emission control at Sudbury's smelters. Several within-basin biogeochemical processes and/or competing stressors (e.g., drought) moderated the rate of lake response to declining acidic deposition.

Acidic deposition was identified as one of the most serious threats to biodiversity at the ecoregion level. Reduced lake pH negatively affected (directly or indirectly) many species of phytoplankton, zooplankton, benthic invertebrates and fish. Most effects on birds occurred through changes in quality and quantity of foods. Acidification effects may combine with other ecosystem perturbations (e.g., climate change, increased UV-b, mercury) to produce even broader scale, deleterious effects.

Empirical modelling showed that pH was a consistent and significant variable in determining the species richness and occurrence of many taxa in eastern Canadian lakes, even after accounting for other potential confounding factors. Species-specific pH tolerances were generally similar across eastern Canada, and a pH of 6 was confirmed as a threshold below which significant effects occur.

Acidic deposition and mercury contamination of remote aquatic ecosystems appeared to be linked. Lakes and wetlands can be important sources of the most biologically important form of mercury. Wild mammals and piscivorous birds were most at risk from mercury exposure. Fish mercury, cadmium and lead levels were negatively correlated with lake pH.

The loss of dissolved organic carbon in lakes that accompanied acidification permitted a 2- to 3-fold greater penetration of biologically harmful UV-b radiation. This interaction was more important than stratospheric ozone depletion in increasing the exposure of aquatic organisms to UV-b.

6.3 AQUATIC CHEMISTRY

6.3.1 Lake status

6.3.1.1 *Data description*

D. S. Jeffries, D.M. Antoniades, A. Bourne, R. Carignan, L. Cheng, T.A. Clair, S. Couture, P.J. Dillon, M.S.V. Douglas, C. Gagnon, M. Gilliss, M. Hilderman, B. Keatley, W. Keller, M.L. Mallory, P.M. McEachern, D.K. McNicol, N. Michelutti, K.A. Moser, R. Pienitz, B. Raymond, K.M. Ruhland, A.M. Scheuhammer, M.A. Turner, R.C. Weeber, and A.P. Wolfe

Data were compiled from numerous government and university sources to assess the current acidification status of lakes across Canada. Table 6.1 shows the number of lakes provided by each data supplier and citations (when available) which provide more detail on the specific data source. The geographic distribution of lakes contained in this "current status" database is shown in Figure 6.1. Stream and river chemistry was not included in the database except where the sampling station was located at a lake outflow. The terrain of Prince Edward Island is universally insensitive to acid deposition. Consequently, data were not considered in this analysis for the few lakes sampled in that province. Lakes sampled in the other eastern provinces were generally located in acid sensitive terrain (see discussion in Section 6.3.1.2 below). Lakes sampled in western provinces were less likely to be located in sensitive terrain, and in fact, several sensitive areas identified by the National Atlas of Canada (1995) are not accounted for by the available data. Lakes in Nunavut and the Northwest Territories are located in both sensitive and insensitive terrain.

Since the chemistry of many lakes in southeastern Canada is presently changing due to changing levels of acidic deposition (e.g., Jeffries et al. 2003b; see also Section 6.3.2 below), the data compiled for Ontario eastwards were restricted to the most recently available annual average since 1997. In fact, most of the lake records from the eastern provinces reflect sampling that occurred in 2000 or later. However, in order to maximize the data available from the western provinces and territories for this assessment, the temporal restriction was relaxed based on the assumption that there has been little change due to changing deposition throughout these regions. This is the first acid rain assessment to include a substantive northern data set. Most of the samples for the western and northern lakes were collected in the 1990s, although a few were obtained as far back as 1983. An implication of compiling data in this manner is that the sample population is not a statistical subset of the overall population. This and other implications are discussed in Section 6.3.1.3, and noted below whenever appropriate. Nevertheless, this "current status" database is still the best information available for assessment purposes.

The variables requested during the compilation process included the following: pH, calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), potassium (K^+), alkalinity (Alk), sulphate (SO_4^{2-}), chloride (Cl^-), nitrate (NO_3^-), ammonium (NH_4^+), total N (some suppliers provided Total Kjeldahl Nitrogen which when added to NO_3^- yields total N), dissolved organic carbon (DOC), total aluminum (Al), inorganic monomeric aluminum (almost no data for this variable were available except in QC), specific conductance, plus geographic locators and physical

Table 6.1 Number of lakes and sources of chemical data to assess current status and/or statistically significant trends using non-parametric tests. The number of lakes having a ±15% charge balance is in parenthesis in the "status" column. The citation indicates a published use of some or all of the data from the same source(s).

Province Territory	Number of lakes		Originator and/or Supplier	Database Description	Citation
	Status	Trends			
NL	20(16)	21	T.A. Clair	Atlantic Canada Acid Precipitation Monitoring Network	Clair et al. (2002)
NL (Lab)	22(11)		T.A. Clair	Environment Canada Atlantic Region Envirodat database	
NS	69(60)	69	T.A. Clair	Atlantic Canada Acid Precipitation Monitoring Network	Clair et al. (2002)
NB	13(3)		T.A. Clair	Environment Canada Atlantic Region Envirodat database	
NB	119(112)		M. Gilliss	NB Department of Environment and Local Government lake monitoring data	Pilgrim et al. (2003)
QC	38(37)	38	S. Couture	Environment Canada Québec Region Temporal Monitoring Network	Kemp (1999)
QC	46(41)		J. Dupont	QC Ministry of Environment monitoring data	Dupont (1997)
QC	9(8)		A. Scheuhammer	Environment Canada CWS monitoring data	
QC	44(44)		R. Carignan	Personal data collected for Sustainable Forest Management Network	
ON	2(2)	2	D.S. Jeffries	Environment Canada NWRI Turkey Lakes Watershed database	Jeffries et al. (2002)
ON	5(5)	4	M.A. Turner	Fisheries and Oceans Canada Experimental Lakes Area database	
ON	184(144)	41	W. Keller	ON Ministry of Environment Sudbury and NE Region data	Keller et al. (2003)
ON	1086(908)	567	R. Weeber	Environment Canada CWS (Ontario Region) monitoring data	McNicol et al. (1998)
ON	34(34)	24	P.J. Dillon	ON Ministry of Environment Dorset Research Centre database	Dillon et al. (2003)
MB	20(15)		A. Bourne	MB Water Stewardship monitoring data	
SK	27(11)		L. Lechner	SK Department of Environment data	Jeffries (1995)
SK	25(22)		M. Hilderman	SK Department of Environment data	
AB	450(374)		P. McEachern	Several sources compiled by D. Andrews for AB Environment	WRS (2004)
BC	214(194)		B. Raymond	Several sources compiled by Environment Canada (P&Y Region)	Bos & Cumming (2003)
BC	5(5)		A. Scheuhammer	Environment Canada CWS monitoring data	
NT, NU	67, 9		K. Walsh	Environmnet Canada (ECS Yellowknife), pH data only	
NU	31(29)		M. Mallory	Environment Canada (CWS, Iqaluit) data	
NT, NU	35(28), 11(7)		B. Keatley	Personal data (at Queen's University)	
NT, NU	35(35), 56(47)		D. Antoniades	Personal data (3 data sets at University of Toronto)	Antoniades et al. (2003a,b)
NT, NU	70(22), 56(29)		K. Ruhland	Personal data (2 data sets at Queen's University)	Ruhland & Smol (1998), Ruhland et al. (2003)
NT, AB	8(7), 27(26)		K. Moser	Personal data (at University of Utah)	Moser et al. (1998)
NU	72(5)		A. Wolfe	Personal data (2 data sets at Universities of Alberta and Colorado)	Joynt & Wolfe (2001)
NU	38(30), 34(32)		N. Michelutti	Personal data (2 data sets at University of Alberta)	Michelutti et al. (2002a,b)
NT, YK	24(21), 59(16)		R. Pienitz	Personal data (2 data sets at Laval University)	Pienitz et al. (1997a,b)

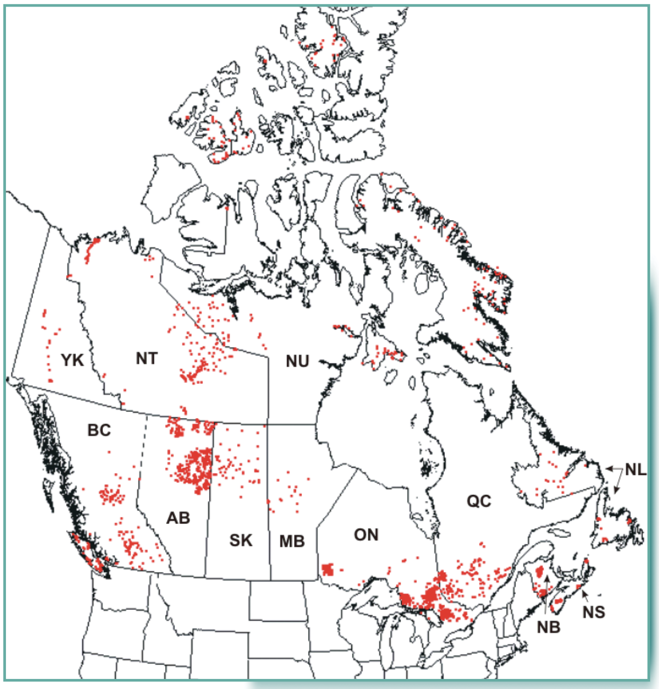

Figure 6.1: Location of lakes contributing data to the current status database. These abbreviations for the provinces and territories are used throughout this assessment: NL = Newfoundland and Labrador, NS = Nova Scotia, NB = New Brunswick, QC = Québec, ON = Ontario, MB = Manitoba; SK = Saskatchewan; AB = Alberta, BC = British Columbia, NU = Nunavut, NT = Northwest Territories and YK = Yukon.

information if available (e.g., lake area, depth, volume, drainage basin area, etc.). Some datasets from NU and NT provided dissolved inorganic carbon (DIC) values rather than Alk, and in such cases, the latter was estimated from the former by assuming that the DIC exists entirely as HCO_3^- (valid up to a pH of nine, Stumm and Morgan, 1981).

The database, compiled from 25 sources, contained information for 3130 lakes distributed as shown in Table 6.1 and Figure 6.1. A large proportion of the lake records (87%) had sufficient chemical variables to calculate a charge balance. Determining the charge balance was the principal method used to identify (and occasionally remove) suspect data, and ultimately, to evaluate overall data quality. In the database, detection limit or "less than" data were substituted by the nominal detection limit value unless that value was inappropriately large, e.g., 10 mg/L for some of the SK SO_4^{2-} data and 3 mg/L for the NT data from Ruhland and Smol (1998). In such cases, the value was set to "missing". Note that there were some cases where the sum of cations balanced the sum of anions even though one or more variables were missing, e.g., the SK records with missing SO_4^{2-} (and also Cl^-) still balanced because of the overwhelming predominance of Ca^{2+}, Mg^{2+} and Alk. In other cases, removing inappropriate values (e.g., the NT SO_4^{2-} detection limit data noted above) prevented use of the charge balance procedure to evaluate the within-record data quality. In some data sets there was evidence of limited analytical (or perhaps reporting) sensitivity, i.e., the data were distributed in distinct concentration steps. Following removal of suspect and inappropriate detection limit values, all the remaining data were included when calculating the distribution statistics used to describe and evaluate current chemical status.

Organic anion (A^-) was an important component of the charge balance for many lakes. There are several models for estimating the A^- component, and even the calibration for a single model varies regionally (Wilkinson et al., 1992). Nevertheless, we adopted a simple strategy for estimating A^- by using the same model for all data sets, i.e., a variant of the Oliver et al. (1983) model in which the "charge density" coefficient in the equation is assigned the value 5 μeq/mg C. This variant of Oliver's model tends to provide reasonable estimates of A^- across a wide geographic range and was employed in previous assessments (RMCC, 1990; Jeffries, 1997). The cation-anion balance agreed within ±15% for 76% of the lakes (cf. numbers in parenthesis in column 2 of Table 6.1). This corresponds to 87% of the records that had sufficient variable coverage to calculate a balance. These were the lake records that were used for predicting future status (see Chapter 7) and calculating critical loads (see Chapter 8).

6.3.1.2 *Current chemical status*

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The general chemical characteristics of the provincial/territorial components of the current status database are summarized by the selected percentile concentrations presented in Table 6.2. These statistics account for the multitude of, and sometimes inter-related, factors and processes that control the chemical

Table 6.2 Fifth, fiftieth and ninety-fifth percentile lake concentrations for provincial and territorial datasets contained in the "current status" database. Consult Table 6.1 for the number of lakes and Figure 6.1 for their geographic distribution. ND indicates no data.

Variable	Percentile	Province or Territory											
		NL	NS	NB	QC	ON	MB	SK	AB	BC	NU	NT	YK
pH	5th	5.15	4.65	5.15	5.14	4.70	7.20	6.22	6.26	6.71	5.99	6.78	6.90
	50th	6.42	5.42	6.88	6.23	6.24	7.65	6.89	7.70	7.61	7.51	7.90	8.10
	95th	7.37	6.58	7.60	7.11	7.37	8.48	7.61	8.86	8.78	8.50	8.63	8.70
Ca^{2+} (μeq/L)	5th	16.5	15.2	24.3	54.2	43.6	441	41.1	133.	87.6	22.3	29.9	294.
	50th	67.4	46.4	103.	89.8	99.8	1100.	185.	708.	534.	983.	240.	913.
	95th	272.	89.7	280.	493.	522.	8670.	885.	2060.	1850.	3220.	1840.	2190.
Mg^{2+} (μeq/L)	5th	14.0	26.4	17.8	18.6	21.5	282.	23.9	41.2	32.9	24.7	32.9	ND
	50th	29.2	41.5	35.3	42.0	47.0	621.	96.2	354.	237.	374.	189.	
	95th	287.	95.3	67.3	225.	222.	1360.	487.	1200.	3530.	3580.	1720.	
Na^+ (μeq/L)	5th	21.5	110.	34.7	18.5	19.1	115.	19.6	21.7	30.4	11.6	13.1	16.8
	50th	52.6	136.	70.	30.4	30.8	146.	62.0	87.0	109.	78.3	35.2	174.
	95th	105.	308.	128.	86.1	95.7	2160.	213.	625.	1600.	3420.	881.	956.
K^+ (μeq/L)	5th	3.33	3.92	2.80	2.82	3.26	25.1	5.75	2.51	3.	5.12	5.12	9.97
	50th	4.61	6.76	6.60	7.97	7.60	35.8	25.6	15.5	23.	13.8	15.4	29.4
	95th	9.27	15.0	13.0	17.9	20.5	73.5	51.2	76.8	224.	245.	67.8	85.4
NH_4^+ (μeq/L)	5th	ND	ND	ND	0.19	0.36	0.56	1.91	0.09	0.29	0.36	0.14	0.36
	50th				1.05	1.52	3.33	3.75	0.86	0.44	0.86	0.64	0.43
	95th				5.12	10.7	20.3	8.66	9.23	9.40	7.87	4.0	2.58
Alk (μeq/L)	5th	-3.36	-28.7	-1.66	2.02	-22.5	888.	68.2	153.	109.	77.5	16.7	174.
	50th	46.2	-1.48	96.0	53.8	41.5	1540.	300.	1030.	774.	1080.	317.	1080.
	95th	294.	42.4	295.	524.	482.	3420.	1240.	3100.	6630.	3080.	2530.	4410.
SO_4^{2-} (μeq/L)	5th	12.1	31.2	36.0	33.9	28.5	45.1	9.12	4.13	10.4	14.6	9.16	16.0
	50th	18.9	45.8	53.7	72.9	103.	149.	20.8	52.1	41.6	70.2	43.7	183.
	95th	77.4	77.8	87.4	161.	208.	699.	72.7	625.	608.	5600.	604.	1730.
Cl^- (μeq/L)	5th	5.62	99.8	10.3	3.04	3.71	32.5	2.94	2.82	4.60	7.57	6.49	8.46
	50th	42.4	132.	29.3	5.64	9.18	70.5	8.45	14.1	36.7	54.7	28.2	56.4
	95th	81.6	357.	94.7	30.0	63.9	386.	45.2	141.	323.	2240.	946.	615.
NO_3^- (μeq/L)	5th	0.16	ND	ND	0.07	0.14	0.71	0.36	0.02	0.03	0.14	0.07	0.73
	50th	0.32			0.48	0.57	0.71	1.43	0.14	0.06	0.71	0.57	0.77
	95th	1.61			2.68	6.65	1.49	7.32	4.81	3.06	5.46	0.71	2.54
Total N (μg/L)	5th	48.9	45.	60.	147.	220.	ND	205.	388.	60.	93.5	79.	217.
	50th	76.7	80.	300.	242.	384.		501.	1000.	340.	238.	355.	497.
	95th	155.	136	535.	601.	775.		1490.	3220.	1460.	1090.	970.	1130.
DOC (mg/L)	5th	1.87	2.37	2.26	2.89	2.16	6.08	3.00	7.32	1.5	0.90	1.70	4.53
	50th	4.06	5.75	5.18	5.36	5.75	9.5	6.60	19.0	6.7	2.90	5.45	10.7
	95th	6.48	12.3	9.96	11.7	15.4	15.7	20.4	36.5	19.9	29.5	14.5	24.5
Total Al (μg/L)	5th	66.2	25.3	11.4	19.8	8.99	31.1	ND	10.	0.4	10.	10.	ND
	50th	124.	134.	61.5	73.0	68.5	220.		35.	60.0	10.	30.	
	95th	208.	305.	262.	275.	301.	1090.		210.	138.	617.	784.	

composition of sample lakes, and they tend to confirm the interpretations of past assessments (i.e., RMCC, 1990; Jeffries, 1997).

Landscape sensitivity to acidic deposition is primarily controlled by soil and bedrock geology, and these factors have been used to produce the national sensitivity map (National Atlas of Canada, 1995; see also http://atlas.gc.ca/site/english/archives/5th_edition/environment/ecology/mcr4157).

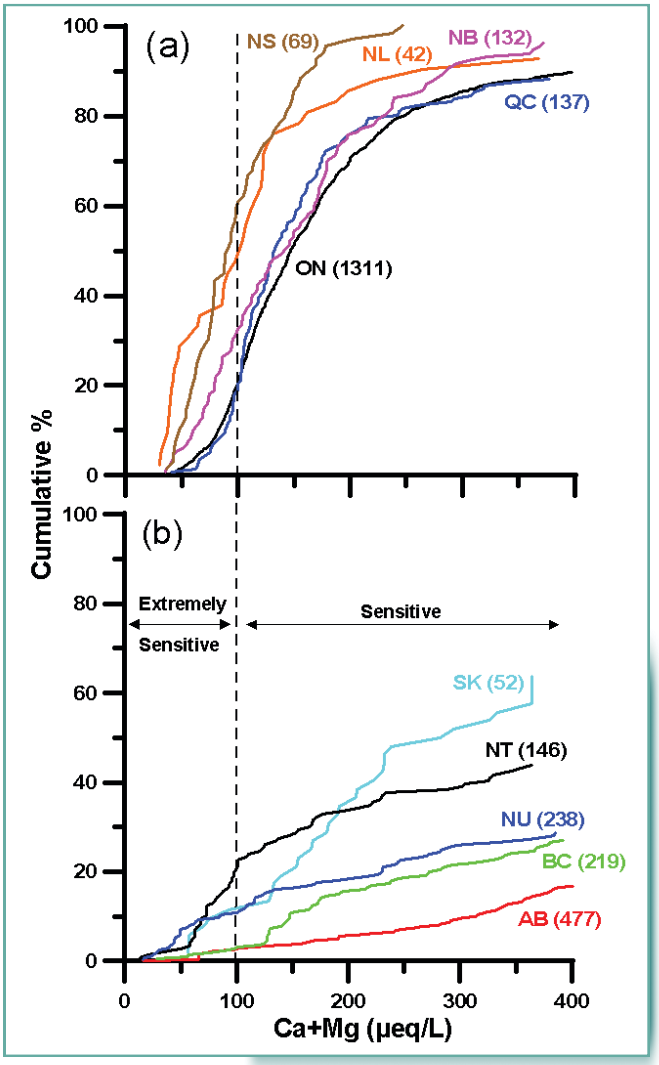


Figure 6.2: Cumulative frequency distributions for base cations (represented by $Ca^{2+} + Mg^{2+}$) from the "current status" data sets for (a) the eastern provinces and (b) the western provinces and northern territories. The number in parenthesis beside each label is the number of data values. Note that the data sets are not statistical subsets of the provincial/territorial lake populations. The dotted line at 100 µeq/L is an arbitrary boundary separating sensitive from extremely sensitive lakes. Base cation values exceeded 400 µeq/L for all MB lakes and there were no data for YK (Mg^{2+} missing throughout entire data set).

The most sensitive terrain (the red areas on the national map) occurs in areas with silicate bedrock, which is not very soluble, and thin, glacially-derived soil deposits. Such terrain is typical of the large, crescent-shaped geological region known as the Canadian Shield, which occurs extensively in Labrador, QC (north of the St. Lawrence River), ON, northern parts of the prairie provinces, and in NU and NT. Although not part of the Canadian Shield, similar terrain is also common in insular NL, large parts NS and lesser parts of NB. Due to the low solubility of the soils and bedrock, surface waters draining sensitive terrain are typically very dilute (i.e., dissolved mineral content is low), and hence, the concentration of base cations can be used as an indicator of aquatic sensitivity. Figure 6.2 presents provincial/territorial cumulative frequency distributions for the base cation data present in our database. Base cations are represented here by the sum of Ca^{2+} and Mg^{2+} for all sample lakes. Note that the cumulative frequencies in Figure 6.2 are only presented for a concentration range relevant to this assessment, i.e., 0 to 400 µeq/L for base cations. Any waters with base cation concentrations >400 µeq/L are not very sensitive to the effects of acidic deposition.

The cumulative frequency distributions for sample lakes in the eastern provinces (upper pane of Figure 6.2) distinctly differ from those for the remainder of the country. Variability in the degree of sensitivity for the regions, as represented by the sample populations, is reflected by the breadth of the cumulative frequency distributions. Virtually all the eastern sample populations exhibit base cation concentrations <400 µeq/L, whereas more than half of the western and northern sample populations (except SK) are >400 µeq/L (i.e., outside the range shown in Figure 6.2). Simply stated, eastern lakes seem to be much more sensitive to acidic deposition than western and northern lakes, with the NS and NL sample populations being the most sensitive of all. Indeed, approximately 50%, 62%, 34%, 24% and 21% of the NL, NS, NB, QC and ON data sets respectively have $Ca^{2+} + Mg^{2+} \leq 100$ µeq/L, a level indicative of extreme sensitivity. Note that even these statistics fail to convey fully the ultra-sensitivity of some NL and NB lakes, and probably all the NS lakes because up to 25% of their $Ca^{2+} + Mg^{2+}$ can originate from wind-blown sea-salt, cf. the Na^+ and Cl^- values for these provinces in Table 6.2.

Some of the data sets used in this assessment are composed of lakes specifically selected to represent the range of regional water chemistry and sensitivity. A good example is from the Québec Regional Temporal Monitoring Network (Kemp, 1999). The 38 lakes are located in a 150 km-wide strip running parallel to the St. Lawrence River between the Ottawa and Saguenay Rivers (see the QC "trend" lakes shown in Figure 6.9 in Section 6.3.2.1). Based on their water chemistry, the lakes were statistically grouped into 6 homogenous sub-regions (Bobée et al., 1983) that represent different degrees of sensitivity. There is a gradient in terrain sensitivity across the overall domain of this monitoring network – from highest in the northeast to lowest in the southwest. This was reflected in the Ca^{2+} and Mg^{2+} concentrations that varied from 265 and 94 µeq/L respectively in the southwest to 51 and 17 µeq/L respectively in the northeast (all values are sub-regional means from 1998-2000). This range almost completely encompasses the QC distribution shown in Figure 6.2.

The base cation cumulative frequencies for the western provinces and territories (except MB and YK, see caption of Figure 6.2) show that all the sample populations exhibit a wide range in sensitivity. A large proportion (>50% for all data sets except SK) must be considered insensitive; however, there are some extremely sensitive lakes as well (ranging from 3% for BC to 16% for NT). As occurs in the Atlantic provinces, it is likely that a portion of the base cations observed in some BC, NU and perhaps NT lakes may have originated from sea-salt (based on the lake locations shown in Figure 6.1). Manitoba has significant portions of sensitive terrain, particularly in the northwest corner (National Atlas of Canada, 1995), so it appears that the MB data set does not include many (if any) lakes from such regions.

Sulphur dioxide (SO_2) has long been acknowledged as the principal air pollutant acidifying eastern Canadian lakes (Jeffries, 1995, 1997), and it is ultimately deposited on aquatic and terrestrial landscapes as SO_4^{2-}. Nitrogen oxides (NO_x) are also potentially acidifying emissions, but at present, they have a lesser effect than SO_2; see Section 6.5. There is only minor biological uptake of SO_4^{2-} and little (though not zero) adsorption of SO_4^{2-} by the young, glacially-derived soils (Rochelle et al., 1987) that are typical of most acid sensitive regions in Canada. Hence, SO_4^{2-} concentrations in the eastern lakes (Table 6.2 and Figure 6.3) reflect variation in the regional magnitude of SO_4^{2-} deposition, i.e., lowest in NL increasing westwards to ON. Spatial variation in deposition rates within NL, NS and NB is comparatively small so that their lake SO_4^{2-} cumulative frequency distributions in Figure 6.3a cover a rather narrow concentration range. The highest SO_4^{2-} concentrations in the Atlantic region distributions (i.e., those above the 80th percentile) reflect, at least in part, situations where wind-blown sea-salt makes a significant (though non-acidifying) contribution to the overall SO_4^{2-} deposition (cf. sea-salt base cation inputs mentioned above). Both QC and ON experience strong gradients in SO_4^{2-} deposition which accounts for the broader frequency distributions of lake SO_4^{2-} levels. For example, lakes in the Québec Regional Temporal Monitoring Network (Kemp, 1999) currently experience a 2-fold variation in wet SO_4^{2-} deposition (from 20 kg/ha/yr in the southwest to 10 kg/ha/yr in the northeast; Environment Canada, 2004), and their corresponding lake SO_4^{2-} concentrations vary from ~100 to ~60 µeq/L. Since both the QC and ON data sets contain lakes located in the vicinity of significant SO_2 sources (i.e., nickel smelters at Rouyn-Noranda and Sudbury, respectively), there is little doubt that such lakes contribute to the high concentration tail of their frequency distributions. While the SO_4^{2-} frequency distributions for the eastern provinces seem to support the assumption of a general direct link between deposition and lake concentration, other factors act to modify the distributions. For example, additional SO_4^{2-} that originates from within lakes' drainage basins via weathering of sulphide minerals (e.g., pyrite) or sulphate minerals (e.g., gypsum) cannot be ruled out. Sulphate reduction occurring at the water-sediment interface of lakes and in anoxic hypolimnia will result in lower lake SO_4^{2-} concentrations (and increased pH and Alk) if the reduced sulphide species remain buried in the sediments. Regional variations in the factors influencing evaporation (precipitation, temperature, etc.) will affect the degree of evaporative concentration, and hence the lake water concentration of many chemical species.

With the exception of SK, the western and northern data sets all show broad SO_4^{2-} distributions (Figure 6.3b) with substantial proportions >200 µeq/L, ranging from 15% (BC) to 41% (YK). While the SK distribution appears

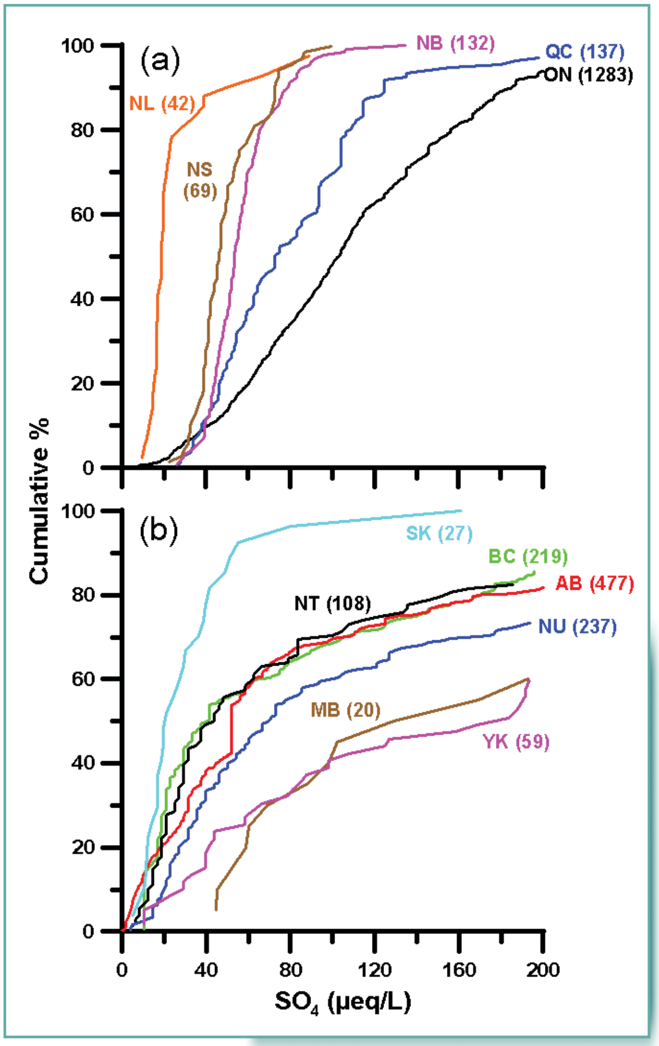


Figure 6.3: Cumulative frequency distributions for SO_4^{2-} from the "current status" data sets for (a) the eastern provinces and (b) the western provinces and northern territories. The number in parenthesis beside each label is the number of data values. Note that the data sets are not statistical subsets of the provincial/territorial lake populations.

similar to the eastern distribution, it should be recalled that 25 of 52 values in that data set were removed because of an inappropriate analytical detection limit (10 mg/L = 208 μeq/L). Analytical sensitivity issues are also obvious in the AB distribution where 60 of the 471 data values have the identical value of 52.08 μeq/L (= 2.5 mg/L). Since SO_4^{2-} deposition in the western and northern provinces/territories is low (with localized exceptions), the high concentrations evident in their lake distributions probably originate from geological sources and/or evaporative concentration as mentioned above.

Many would consider pH to be the obvious chemical indicator of lake acidification. The pH of most "natural, mineral-bearing waters" falls within the range of 6 to 9 (Stumm and Morgan, 1981), and the lower pane of Figure 6.4 shows that the pH distributions for western and northern lakes follow this generalization rather well. Only 0% to 5% of their sample populations have pH <6, and in fact, only the AB and NU populations have more than 2% of their lakes with pH <6. In contrast, the sample populations from the eastern provinces (upper pane of Figure 6.4) all have substantial proportions below pH 6, i.e., approximately 31%, 75%, 27%, 30% and 38% for NL, NS, NB, QC, and ON respectively with minimum values ranging from 4.2 (ON) to 5.1 (NL). Note that pH 6 (vertical dotted line in Figure 6.4) represents more than just the lower end of the natural range suggested by Stumm and Morgan (1981). It has also been identified (and re-confirmed) as a threshold value below which lake biology is detrimentally affected by acidification (Baker et al., 1990; RMCC, 1990; Doka et al., 2003; Holt and Yan, 2003; see also discussion of the aquatic critical load threshold in Chapter 8).

It is tempting to conclude that acidic deposition (which primarily occurs in the south-eastern part of the country) is the reason for the obvious difference between the pH distributions presented in the upper and lower panes of Figure 6.4. In a general way, this is a valid insight. It conforms rather well with the "region of concern" identified in past assessments as that area of overlap of sensitive terrain and elevated acidic deposition which roughly occurs south of 52°N latitude in all provinces east of Manitoba (RMCC, 1990; Jeffries, 1997). There are reasons, other than acidic deposition, for some of the differences however.

The pH distribution can be affected by naturally occurring acids. Dissolved organic matter (represented by DOC in Table 6.2) is composed of a complex mixture of compounds that can contribute organic acidity to the water (Oliver et al., 1983; Wilkinson et al., 1992). Figure 6.5a shows that the eastern provinces have fairly tightly distributed DOC concentrations (NL is skewed to lower DOC than the rest). The highest 95th percentile DOC concentration in the eastern data sets is 15.4 mg/L in ON. DOC concentrations exhibit no longitudinal gradient across the Québec Monitoring Network with sub-regional

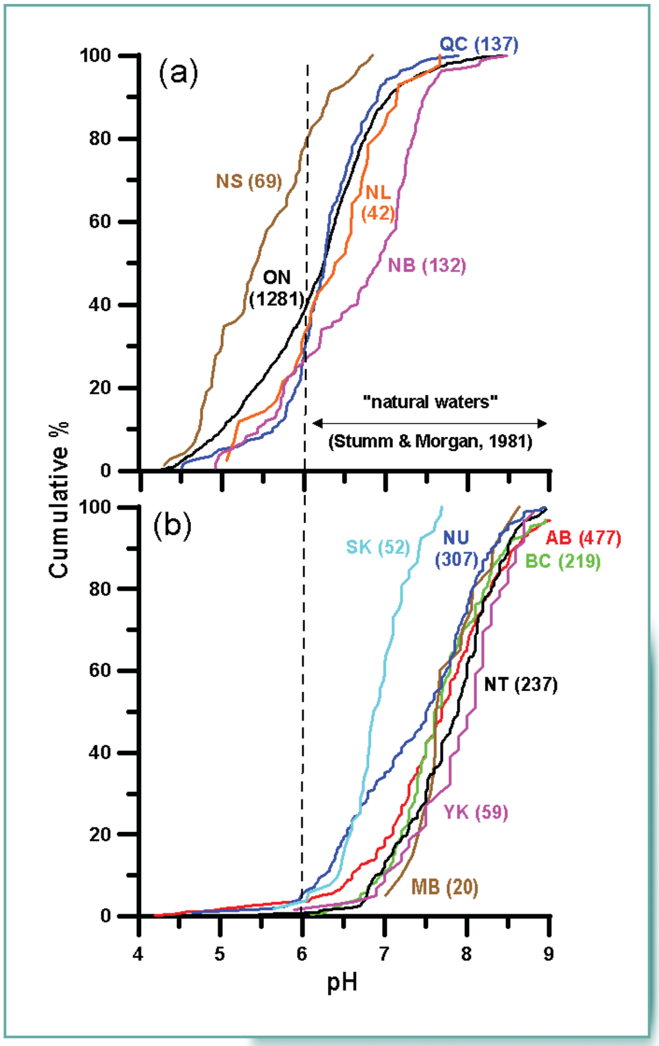


Figure 6.4: Cumulative frequency distributions for pH from the "current status" data sets for (a) the eastern provinces and (b) the western provinces and northern territories. The number in parenthesis beside each label is the number of data values. Note that the data sets are not statistical subsets of the provincial/territorial lake populations.

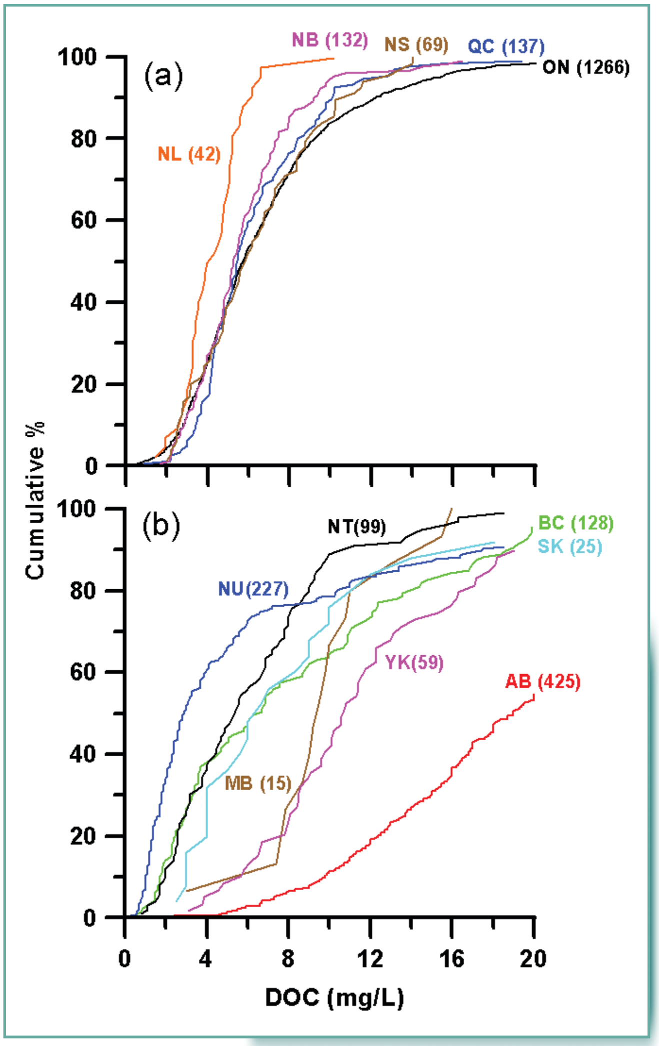


Figure 6.5: Cumulative frequency distributions for DOC from the "current status" data sets for (a) the eastern provinces and (b) the western provinces and northern territories. The number in parenthesis beside each label is the number of data values. Note that the data sets are not statistical subsets of the provincial/territorial lake populations.

average values ranging from ~4 to ~5 mg/L. The relatively low DOC in the Québec Network lakes is not surprising because a selection criterion during program design was a Colour value <75 Hazen units.

Compared to the eastern provinces, DOC concentrations in many western and northern data sets have broader distributions (Figure 6.5b) and some very high concentrations. The lowest and highest 95th percentile DOC values in the western and northern data sets are 15.7 (MB) and 37.0 (AB) mg/L respectively (Table 6.2). A high DOC concentration is not a sufficient condition for lower pH, however. For example, AB has by far the highest DOC concentrations of any of the provincial/territorial data, yet there is little evidence of a suppressed pH in its distribution (Figure 6.4), except perhaps in the low pH tail. It is the coincident occurrence of organic acids and low base cation waters that lead to suppression of pH – hence the "mineral-bearing" caveat included in the statement of the "natural" pH range by Stumm and Morgan (1981). Nova Scotian lakes have the lowest base cation concentrations coincident with moderate (not maximum!) DOC levels, and it is therefore not surprising that 75% of NS lakes have pH <6. Note however, that having naturally low pH does not mean that such lakes are not affected by acidic deposition. For a set of 208 lakes located mostly in southern NS, Jeffries et al. (2000) estimated that approximately 50% would have had pH <6 without acidic deposition (cf. the 75% current status in the NS data set reported here).

Lake pH may be affected by acids introduced by oxidation processes occurring within the lake or in its drainage basin; exceptionally low pH values can result. The two lowest pH values in our current status database (and the only values <4) were from lakes on Axel Heiberg Island in the Arctic Archipelago where there is no acidic deposition (Michelutti et al., 2002a). Schiff et al. (1991) previously used isotopic techniques to identify the source of the acid in one of these lakes (Colour Lake). They showed that oxidation of pyrite in the surrounding basin and oxidation of ferrous iron from an anoxic zone of the lake following spring ice-off and water column overturn caused the observed low pH (3.7) and high SO_4^{2-} concentrations. It is not clear whether the arctic setting of these lakes is an important determinant in this acidification process. Certainly, lakes and rivers in temperate climates that are affected by acid mine drainage become acidic through similar processes. In natural temperate settings, however, acid generation by sulphide mineral oxidation tends to be self-limiting because the iron oxide weathering product coats the mineral surface rendering it less reactive. The occurrence of a naturally occurring, extremely acidic lake such as Colour Lake is, in fact, quite rare. Given the widespread occurrence of sulphide and, to a lesser extent, sulphate minerals, it seems reasonable to assume that some, and perhaps even many, of our lakes have been affected by acid generating oxidation processes. The best evidence of this is probably the SO_4^{2-} data rather than the pH data.

Alkalinity is a measure of water's ability to neutralize acid inputs – a more integrative indicator of lake acidification than pH. It is a unique variable in that it can have a negative concentration. Positive concentrations mean that the water can still neutralize further acid inputs. Negative concentrations mean that the water is already acidic, and the degree of negativity serves to indicate the degree of acidification. A lake can be "acidified" but not acidic, i.e., some of its Alk has been lost to acidic deposition, but it does not yet have a zero or negative concentration. Lakes having Alk concentrations in the range 0 to 200 μeq/L have traditionally been considered sensitive to acidic deposition. Alkalinity data measured using the "Gran" titration procedure (see Stumm and Morgan, 1981) were compiled in our data sets and are reported here. Gran Alk measurements are generally much more reliable than pH measurements due to the multi-point titration used to quantify the former, while the latter is influenced by several factors, e.g., P_{CO2}, temperature, stirred vs. unstirred samples, etc. Hence, Alk data are more commonly used to assess the acidity status of surface waters than pH. Elsewhere in this assessment, an alternate estimate of Alk called the "acid neutralizing capacity" (ANC) is calculated (equivalent sum of base cations minus the equivalent sum of acid anions). Alkalinity and ANC may differ slightly in that measurement of the former operationally includes all the proton accepting chemical species that are titrated during the Gran procedure (most notably bicarbonate but there are others as well; Neal, 2001), whereas the latter depends on which ions are included in the cation and anion sums.

The Alk frequency distributions (Figure 6.6) show that only the eastern data sets contain significant numbers of acidic lakes (10%, 52%, 5%, <1% and 13% for NL, NS, NB, QC and ON respectively have Alk ≤0). Almost all of the remaining eastern lakes fall within the sensitive (0-200 μeq/L) Alk range. Clearly NS stands out from all the rest in the nature of its Alk distribution. The high proportion of NS lakes with negative Alk also emphasizes that organic acidity cannot be the major cause of their low pH values.

Once again, the Québec Regional Temporal Monitoring network provides an instructive example of the spatial variability in Alk that leads to the observed cumulative distributions. Recall that the base cation concentrations decreased from the southwest to the northeast, as did both the SO_4^{2-} deposition and lake SO_4^{2-} concentrations. The same southwest to northeast gradient was observed for Alk that varied from 255 to 15 μeq/L (i.e., covering most of the QC frequency distribution in Figure 6.6a – from the 89th to the 10th percentile). Similarly, pH varied from 7.1 to

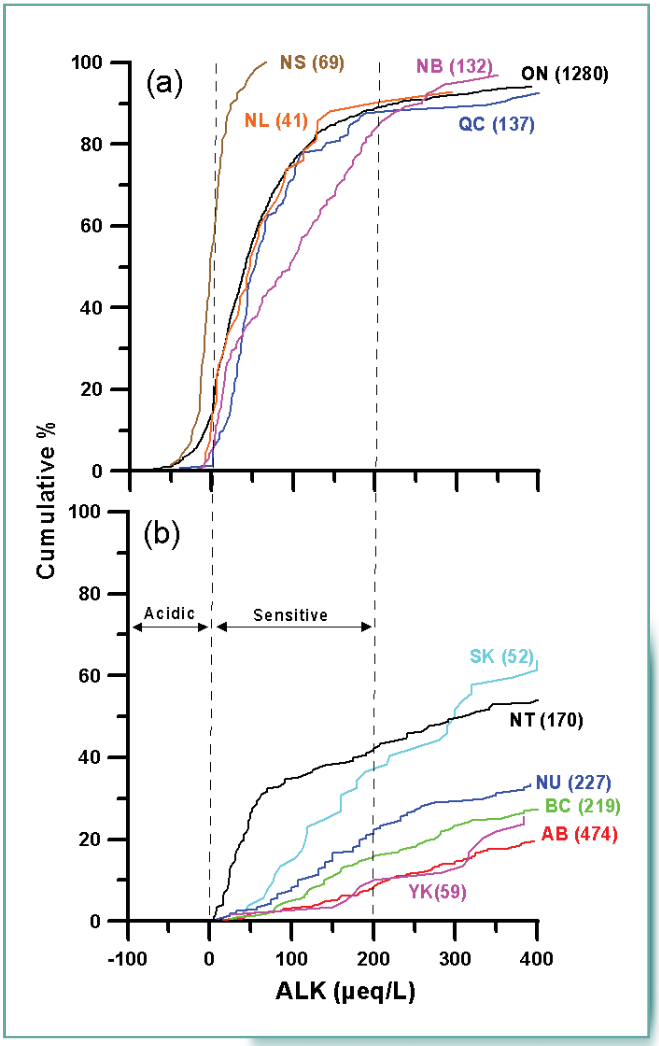


Figure 6.6: Cumulative frequency distributions for Gran Alk from the "current status" data sets for (a) the eastern provinces and (b) the western provinces and northern territories. All MB Alk values were >400 µeq/L. The number in parenthesis beside each label is the number of data values. Note that the data sets are not statistical subsets of the provincial/territorial lake populations.

5.7 (96th to 11th percentile in Figure 6.4a). The fact that Alk was not inversely related to deposition means that the primary determinants of Alk are the same terrain characteristics that determine base cations and sensitivity. Acidic (SO_4^{2-}) deposition is a secondary determinant. The N component of deposition could affect Alk, but NO_3 concentrations in precipitation (typically 20-30 µeq/L) are always higher than in the lakes (commonly below the detection limit - 2.8 µeq/L). Hence, N deposition is strongly retained in the Québec Network watersheds; there is little sign of developing N saturation in the soils; and therefore, it has little affect on the Alk status of the lakes. The only acidic lakes present in the western and northern data sets are found in AB (5 in total) and between 64% (SK) and 100% (MB) of the lakes have Alk >200 µeq/L. Some bimodal and multi-modal Alk distributions are apparent in Figure 6.6, notably NB and NT.

6.3.1.3 *Implications*

D. S. Jeffries

Our lake chemistry assessment is severely limited by the necessity of compiling existing monitoring data without regard to site selection. Ideally, a statistically-based regional survey of lakes such as the stratified random sampling designs that have been employed in the USA (Landers et al., 1987, 1988) and Nordic Europe (Henriksen et al., 1998) would be available to assess current status. Such a lake survey, if occasionally repeated (approximately once per decade) and integrated with an organized hierarchy of temporal monitoring and site-specific research, will provide all the information needed to accurately estimate resource-level status and change, identify the causes of change, and predict future conditions (Nihlgård et al., 1992). As outlined in Section 6.3.1.1, the rapidly changing chemistry of lakes in eastern Canada (Jeffries et al., 2003b; see also Section 6.3.2 below) meant that only fairly recent data could be used to assess current status, and a decision was made to not use any data collected before 1997. In the western and northern provinces/territories, the time-of-sampling restriction was not relevant and therefore relaxed. However, because of the restriction, the only Canadian lake survey statistically designed to represent the lake population (the Québec Lake Survey [QLS] which actually represented the 10 to 2000 ha size fraction; Dupont, 1992a,b) was unsuitable for use in this assessment.

For this assessment there was no alternative but to compile a "current status" database that was composed of data sets provided by willing suppliers that met the conditions set out in Section 6.3.1.1 (see Table 6.1). The available data sets were collected for a number of different reasons, many of them having nothing to do with acidification per se. Hence, substantial between data set differences existed in the physical/chemical information collected, the criteria used to select/include lakes, and the sampling and analytical methodologies employed. Given this reality, the compilation strategy was to obtain data for as many lakes as possible in the hope that this would minimize the influence of the lack of 'representativity' and between data set biases, and still permit discernment of a regional chemical condition.

Table 6.3 compares the provincial/territorial data sets available for this assessment with the datasets available for the 1997 Assessment (Jeffries, 1997) to show the between-assessment differences. The number of lakes now available for assessment in NL and NS is substantially less than before, principally due to reductions in the Atlantic Canada Acid Precipitation Monitoring Network. Spatial coverage focuses on sensitive areas in both provinces, remaining relatively unchanged between assessments in NS, but declining greatly in NL. Lakes present in the 2004 NL and NS data sets were present in the 1997 data sets. The NB data set is slightly smaller than in 1997, but the coverage has improved to represent two sensitive areas rather than one. Gaps in spatial coverage throughout the Atlantic provinces represent all levels of terrain sensitivity.

The number of QC lakes available for assessment is only 10% of what was available in 1997 due to the current unsuitability of data from the QLS survey (Dupont, 1992a,b). Only lakes from the Québec Region Temporal Monitoring Network are common to both the 1997 and 2004 data sets (see Table 6.1). Many lakes in the 2004 data set were not present in the 1997 data set, particularly a cluster surrounding the smelter at Rouyn-Noranda and a group further to the east from the Sustainable Forest Management Network. Exclusion of the QLS segment from the St. Lawrence North Shore has left this part of the province completely unrepresented – an unfortunate situation because, in this area, natural organic acidity plays an important role. This is clearly a major weakness of the QC subset, although it does cover a range of terrain sensitivity and acidic deposition in the southwest part of the province.

In ON, the number of lakes increased for this assessment compared to the 1997 database. The principal data source in 1997 was the Ontario Ministry of Environment's "Acid Lakes Database" (Neary et al., 1990) screened to remove lakes that had been sampled prior to 1985. Since

Table 6.3 Comparison of the "current status" data sets available for the 1997 Assessment (Jeffries, 1997) with those in 2004 (this assessment). See also Table 6.1 and Figure 6.1 for further information on the 2004 data. Note that both the AB and BC data sets are largely compilations of other data sets. Use of the term "federal" or "provincial" implies that the data originated from federal or provincial government organizations.

Province Territory	Number of Lakes		
	1997	2004	Comment (on 2004 data)
NL	101	42	Data clustered at three sites on island; all federal data
NS	150	69	Data clustered in sensitive areas; all federal data
NB	166	132	Data clustered in sensitive areas; 2 sources: mostly provincial data, some federal
QC	1377	137	Data fairly well distributed in SW corner of QC; 4 sources: 2 federal, 1 provincial (clustered around smelter), 1 university
ON	1037	1311	Data largely in 4 clusters (1 in NW and 3 in S-central ON); 5 sources: 3 federal (dominated by CWS monitoring network), 2 provincial
MB	26	20	Data widely distributed in W-central MB; all provincial data
SK	27	52	Data widely dispersed in N SK; all provincial data, but 27 lakes duplicated from 1997
AB	193	450	Data fairly densely distributed in extreme N and NE AB; 2 sources: a provincial compilation dominates, 1 university
BC	6	219	Data largely on Vancouver Island and in 2 dispersed clusters in the central region; 2 provincial sources dominated by a regional compilation; 1 small federal source
NU	-	296	Data distributed in groups in archipelago and on mainland; 7 data sets: 2 federal, 5 university
NT	-	239	Data clustered somewhat, particularly north of Yellowknife; 6 data sets: 1 federal, 5 university
YK	-	59	Data mostly on a N-S transect; 1 source: university

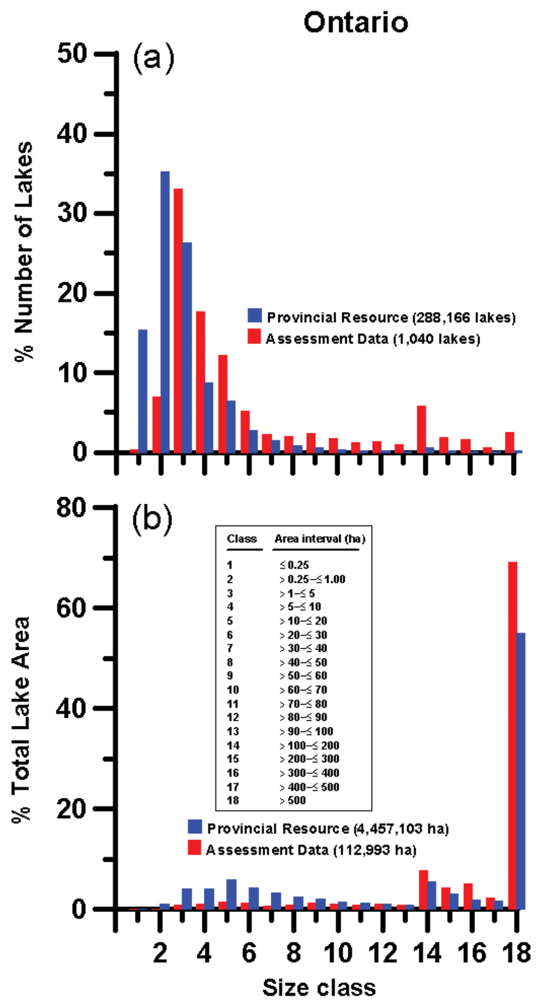
the Acid Lakes Database contains few (if any) results collected since 1997, it was not used at all here. Lakes from the Turkey Lakes Watershed, Experimental Lakes Area, Sudbury and Northeast Region and the Dorset Research Centre (see Table 6.1) were present in the 1997 Assessment as well as now. The ON sources (Table 6.1) yield four regional clusters: Muskoka-Haliburton (M-H), northeastern Ontario-Sudbury-Killarney, Algoma, and northwestern ON surrounding the Experimental Lakes Area (ELA). Another cluster in northwestern ON that was included in 1997 is completely missing here, and in general, there are little data north of Lake Superior. The ON data set is probably the most representative of all the provinces/territories, both in terms of spatial coverage and size distribution (see below). Nevertheless, there are still significant geographic voids (Figure 6.1).

The data set from MB is very limited in size (20 lakes) as it was in 1997, and there is no overlap at all between the two assessments. The sample population is confined to the west-central part of the province, and does not include any lakes from the sensitive areas in the southeast and northwest part of the province. The 52 lakes sampled in SK are located in the sensitive northern part of the province, but 27 of them are the same ones used in 1997 because a more recent survey did not have useful information for several key variables due to unsuitable analytical detection limits. The number of lakes in the AB data set has increased greatly since 1997 (from 193 to 450 with the former included in the latter), thereby providing much denser spatial coverage in the extreme north and northeastern parts of the province. Lakes present in the 1997 database from the west-central part of AB are not included this time, and the northwest corner of the province remains un-surveyed. The agricultural southern regions of all three prairie provinces are not included because of terrain insensitivity. Like AB, the BC data set has expanded greatly for this assessment (from 6 lakes in 1997 to 219 lakes), now including many lakes in the central part of the province (where the terrain is generally not sensitive) and on Vancouver Island; there are few lakes from the sensitive coastal mountain range however.

This assessment is the first to compile data from the territories. Being mostly supplied by university researchers, the data sets occur in clusters in both the Arctic archipelago (on Baffin, Southampton, Ellesmere, Ellef Ringnes, Melville, Victoria and Axel Heiberg Islands), and the mainland (largest cluster between Yellowknife and the coast). The lakes are located in both sensitive and insensitive terrain. While Figure 6.1 shows that there is still no information for large tracts of NU, NT and YK, the lack of acidifying deposition in this area means that the existing data probably give a reasonable overall impression of the chemical status of arctic lakes.

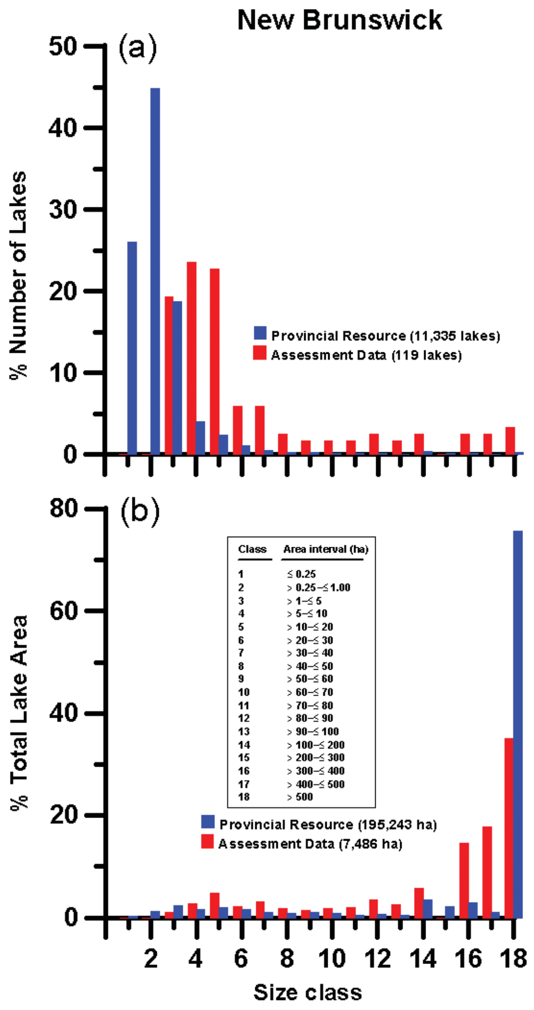
Overall, spatial coverage provided by the current status database is very irregular. Without considering the Arctic, there are large, sensitive regions where either no data exist or where data are too out-of-date to be useful for assessing current chemical status. This is particularly true in NL, QC, ON, MB, SK, and BC. Even where Figure 6.1 seems to show significant regional coverage, sampling density is often very low making extrapolation of sample statistics to the overall lake resource uncertain. For the "region of concern" within the eastern provinces, there has been a steady decline in the amount of survey data available for assessment, i.e., useful data existed for 8505 lakes in 1990 (heavily weighted to ON), for 2779 lakes in 1997, and for 1691 lakes in this assessment (once again heavily weighted to ON). Both the 1990 and 1997 Assessments identified the information gap that this represented, but few surveys have been conducted (or repeated in the case of the QLS) to address the gap. Statistically-based surveys designed to represent the lake resource with a known confidence (e.g., Brakke et al., 1988; Henriksen et al., 1998) have typically sampled from approximately 1%–10% of the overall population. While it is likely that reasonable confidence limits can be obtained from a relatively smaller population sample than was used in those surveys (there are ~800,000 lakes in the region of concern; Hélie et al., 1993), great variability in terrain and climatic/hydrologic characteristics would still necessitate a major effort to obtain a representative data set. At a minimum, new surveys are needed both in areas where there are no data on which to base an assessment, and in some areas of high acidification impact in order to improve extrapolation confidence.

Compilation of a database from multiple sources makes it most unlikely that it will be representative of the lake population. In many cases, lakes present in the



Class	Area interval (ha)
1	≤ 0.25
2	> 0.25–≤ 1.00
3	> 1–≤ 5
4	> 5–≤ 10
5	> 10–≤ 20
6	> 20–≤ 30
7	> 30–≤ 40
8	> 40–≤ 50
9	> 50–≤ 60
10	> 60–≤ 70
11	> 70–≤ 80
12	> 80–≤ 90
13	> 90–≤ 100
14	> 100–≤ 200
15	> 200–≤ 300
16	> 300–≤ 400
17	> 400–≤ 500
18	> 500

Figure 6.7: Size distributions of the ON sample and provincial lake populations shown by (a) number and (b) area. The provincial database and size classes (defined in the inset box) are from Hélie et al. (1993). Note that the Hélie et al. (1993) database in ON only includes lakes located south of ~52° N latitude.



Class	Area interval (ha)
1	≤ 0.25
2	> 0.25–≤ 1.00
3	> 1–≤ 5
4	> 5–≤ 10
5	> 10–≤ 20
6	> 20–≤ 30
7	> 30–≤ 40
8	> 40–≤ 50
9	> 50–≤ 60
10	> 60–≤ 70
11	> 70–≤ 80
12	> 80–≤ 90
13	> 90–≤ 100
14	> 100–≤ 200
15	> 200–≤ 300
16	> 300–≤ 400
17	> 400–≤ 500
18	> 500

Figure 6.8: Size distributions of the NB sample and provincial lake populations shown by (a) number and (b) area. The provincial database and size classes (defined in the inset box) are from Hélie et al. (1993).

provincial/territorial data sets were selected for logistical reasons (e.g., accessibility by road or aircraft) or because they represent specific biological habitat (e.g., for waterbirds or lake trout). In other cases, lakes were selected to cover a range of terrain sensitivity and/or deposition, which does not necessarily make them representative of the regional population. Comparison of the size distributions of the sample and resource populations confirms that the former is unrepresentative. The sample and provincial size distributions for ON and NB are presented in Figures 6.7 and 6.8 respectively (of the eastern data sets, ON and NB have the most complete information on lake size). When considered in terms of numbers (upper panes), these Figures show that the sample populations are skewed to larger lakes. The ON data set is somewhat less skewed than the NB set because a large proportion of the ON lakes are from a program that monitors the small lake habitat preferred by waterfowl (McNicol et al., 1998). On an areal basis (lower panes of Figures 6.7 and 6.8), the sample and resource distributions compare more favourably, although the largest proportion of total lake area of both falls in the

>500 ha size class. For the sample populations, the >500 ha size class is composed of 26 of the 1040 lakes in ON, and 4 of 119 lakes in NB. Similar observations were made for the 1997 Assessment database (Jeffries, 1997; Jeffries et al., 2000). In order to improve the 'representativity' of the sample populations, surveys that sample lakes according to their size frequency must be conducted. This recommendation was also made in the 1997 Assessment, but it was never implemented.

6.3.2 Changes in lake chemistry

6.3.2.1 *Trend analyses*

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The scientific consensus on aquatic effects, developed in previous assessments, was largely responsible for the initial political action to reduce sulphur dioxide (SO_2) emissions. In response to various policy initiatives, (see Jeffries et al., 2003a), total North American emissions are now ~40% less than in 1980 and further reductions are expected (see Chapter 2). While both Canada and the U.S. have monotonically reduced emissions for over two decades, the timing of the maximum rate of reduction differed between them. The magnitude of SO_2 reductions in eastern Canada was greater during the 1980s than the 1990s, whereas the largest U.S. reductions occurred in the early 1990s.

Nitrogen oxide emissions (NO_x) are also a potentially acidifying pollutant, but SO_4^{2-} deposition is still considered by far the predominant regional agent responsible for the acidification of waters in southeastern Canada. Domestic policy initiatives to reduce NO_x emissions in both Canada and the U.S. are intended to address local smog issues. Compared to SO_2, total North American NO_x emissions have changed relatively little.

Concentrations of SO_4^{2-}, measured in precipitation in eastern Canada and the U.S. over the last two decades, have shown a general downward trend (see Chapter 3), with the largest regional changes occurring near the source areas that contributed the greatest emission reductions. In Canada, southern and central ON, and southwestern QC have undergone the greatest reduction in regional SO_4^{2-} deposition. Areas directly influenced by the Sudbury and Rouyn-Noranda smelters have experienced the most extreme reductions in deposition (55% of the total eastern Canadian emission reductions required by the 1985 domestic 'Acid Rain Control Program' was attained from these two smelters).

Surface waters are among the first receptors to respond to decreases in acidifying emissions and deposition. During the last decade, the expected changes in water chemistry generated many publications analyzing the trends present in monitoring records from the preceding 10-20 years. For this assessment, we have evaluated chemical trends that occurred during the 1990s, considering them within the context of the previously reported analyses. The evolution of the trend results, as additional data were added to monitoring records or different time windows were analyzed, provides an ever clearer indication of the long term changes that will occur in response to declining deposition.

Seven hundred and forty-two eastern lakes from federal and provincial data sets that contributed to the "current status" database described in Section 6.3.1.1 had temporal data records suitable for evaluation of chemical trends. These lakes are identified in the "Trends" column of Table 6.1 and their location is shown in Figure 6.9. The trend analyses results compiled for this assessment had the following characteristics:

- Lakes with suitable data were from NL, NS, QC and ON. The NL, NS and QC data were all collected within regional monitoring programs of Environment Canada. The ON information was also from Environment Canada monitoring programs, but supplemented by monitoring data collected by Fisheries and Oceans Canada and the Ontario Ministry of Environment.
- The chemical data, analyzed for trends, were collected within the 1990-2001 time period, had data from at least 8 of the 12 years and had no breaks in the data record that prevented the use of trend procedures. These trend results are slightly more contemporary than those reported by Jeffries et al. (2003b) because all the data records used here include the late 1990s.
- Statistically significant monotonic trends ($p \leq 0.05$) were identified using non-parametric methods such

as the Seasonal Kendall procedure (Hirsch and Slack, 1984) or other related procedures (several suppliers used the program "DETECT" which contains a suite of non-parametric procedures; Cluis et al., 1989; McNicol et al., 1998).

- The trend magnitudes were estimated from the associated linear regression slopes. The distribution (overall percentages) of positive and negative regression slopes was also recorded.
- The chemical variables analyzed included:
  - SO_4^{2-} and NO_3^- - the acid anions of acidic deposition. Trends in the concentrations of these anions reflect recent trends in deposition (especially SO_4^{2-}) and in ecosystem response to long-term deposition (e.g., NO_3^-). Note that no NO_3^- trends are available for NL, NS and QC for the reasons outlined in a footnote to Table 6.4.
  - Base cations (either sum of $Ca^{2+}+Mg^{2+}+Na^{+}+K^{+}$ or $Ca^{2+}+Mg^{2+}$ as available), which are mobilized by weathering reactions and cation exchange processes that neutralize acids in watersheds. Base cations will respond indirectly to changes in SO_4^{2-} and NO_3^-.
  - pH and Gran Alk – acidity variables which reflect the outcome of interactions between changing concentrations of acid anions and base cations.
  - DOC, which is a surrogate for organic acidity. Organic acids are common natural sources of acidity in surface waters.

The trend results are summarized in Table 6.4.

6.3.2.1.1 Atlantic region

Analysis of monotonic SO_4^{2-} trends for the period of 1983-1997 for 63 lakes in NL and NS showed 34 cases (54%) where there was a significant ($p \leq 0.05$) decline in concentrations (Clair et al., 2002). These results qualitatively agreed with those obtained using a more sophisticated statistical procedure on a combined Maine/Atlantic Canada data set (Stoddard et al., 1999). However, both of these results were a decided shift from those of an earlier analysis of the 1983-1991 period which

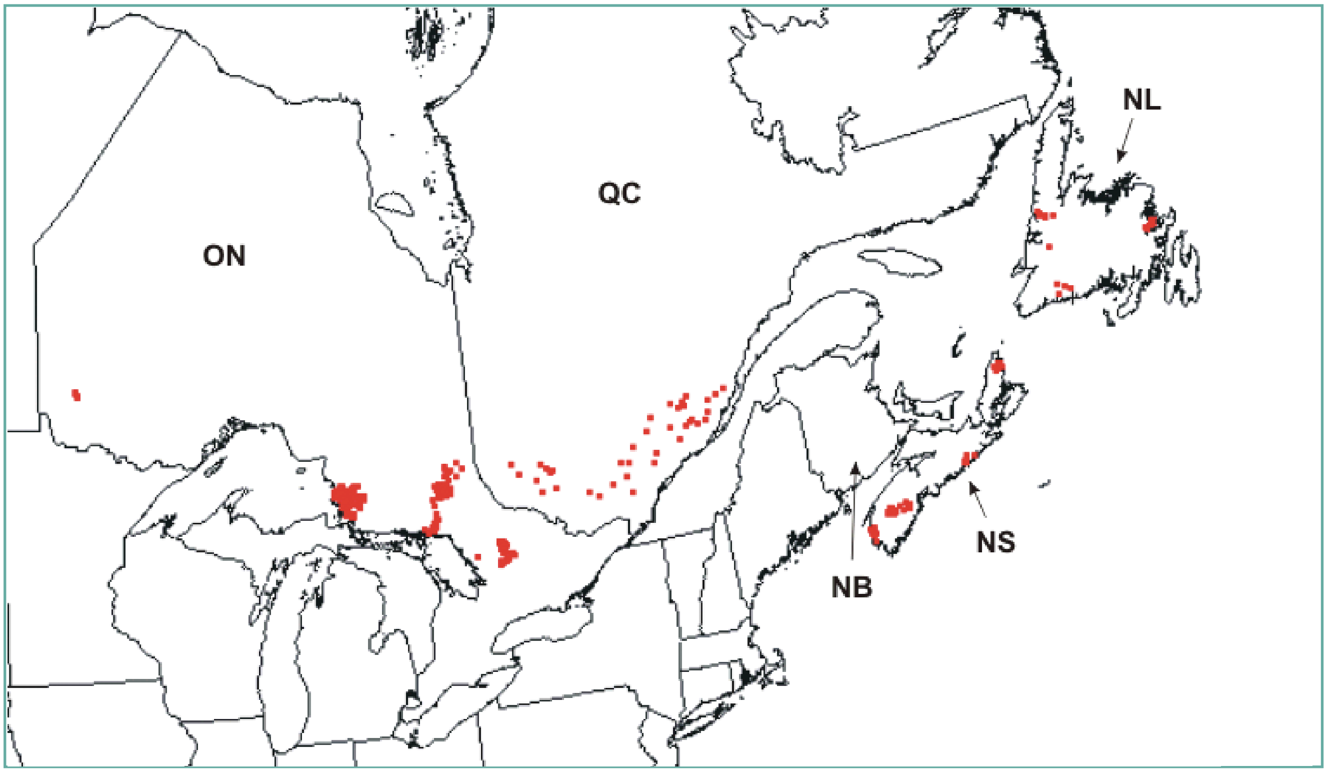

Figure 6.9: Location of lakes having temporal data sets suitable for trend analyses.

Table 6.4 Summary of significant chemical trends ($p \leq 0.05$) in eastern Canadian lakes within the period 1990 to 2001 detected using non-parametric statistical procedures (see text). The numbers in parentheses (% columns) are the overall percentage of positive or negative regression slopes regardless of statistical significance. The annual magnitude of increasing and decreasing trends was estimated from the median of all significant linear regression slopes.

		Newfoundland (21 lakes)			Nova Scotia (69 lakes)			Quebec (38 lakes)			Ontario (638 lakes[5])		
		n	%	Sig. Slope	n	%	Sig. Slope	n	%	Sig. Slope	n	%	Sig. Slope
Sulphate[2] (µeq/L)	Increasing Trends	0	0 (0)		0	0 (3)		0	0 (3)		5	1 (17)	4.65
	Decreasing Trends	9	43 (100)	-0.75	32	46 (97)	-0.97	28	74 (97)	-2.10	182	29 (83)	-5.01
	No Significant Trends	12	57		37	54		10	27		451	71	
Nitrate[3] (µeq/L)	Increasing Trends	NA			NA			NA			26	4 (57)	0.19
	Decreasing Trends	NA			NA			NA			23	4 (43)	-0.36
	No Significant Trends	NA			NA			NA			576	92	
pH	Increasing Trends	0	0 (57)		4	6 (72)	0.02	18	47 (89)	0.03	74	12 (74)	0.06
	Decreasing Trends	0	0 (43)		4	6 (28)	-0.02	0	0 (11)		7	1 (26)	-0.04
	No Significant Trends	21	100		61	88		20	53		557	87	
Alkalinity (µeq/L)	Increasing Trends	0	0 (14)		1	1 (16)	0.77	17	45 (84)	1.32	94	15 (70)	3.10
	Decreasing Trends	1	5 (86)	-0.88	24	35 (84)	-1.04	0	0 (16)		10	2 (30)	-1.66
	No Significant Trends	20	95		44	64		21	55		533	84	
Base Cations[2,4] (µeq/L)	Increasing Trends	0	0 (43)		0	0 (35)		0	0 (5)		4	1 (12)	11.9
	Decreasing Trends	0	0 (57)		3	4 (65)	-1.26	26	68 (95)	-2.07	198	34 (88)	-5.10
	No Significant Trends	21	100		66	96		12	32		388	66	
DOC (mg/L)	Increasing Trends	2	10 (90)	0.11	13	19 (80)	0.18	10	26 (58)	0.07	45	7 (57)	0.13
	Decreasing Trends	0	0 (10)		1	1 (20)	-0.37	3	8 (42)	-0.08	17	3 (43)	-0.23
	No Significant Trends	19	90		55	80		25	66		571	90	

[1] Minimum, tenth percentile and median record length within the twelve-year time window was 8, 9 and 11 years respectively.

[2] Sulphate and base cations were sea-salt corrected for NL and NS lakes.

[3] Analyses of nitrate trends not performed for NL and NS due to high incidence of detection limit values and for QC due to varying analytical detection limits during the period of record.

[4] Base cations equal Ca+Mg for NL, NS and QC, and Ca+Mg+Na+K for ON.

[5] Differences between overall number of Ontario lakes and the number of trends analyzed for a given variable was due to missing values.

showed few SO_4^{2-} declines (only 8% of the 71 lakes), and in fact, 27% had increasing SO_4^{2-} levels (Clair et al., 1995). A subsequent re-evaluation of the 1983-1991 data set showed that selection of the time window for analysis had a profound effect on how the lakes were distributed among 'increasing', 'decreasing' and 'no trend' categories (Ehrman and Clair, 1995).

In the analysis of the period of 1983-1997, 'no trend' was by far the predominant response for pH, Alk and base cations. The earlier analysis of the 1983-1991 period (Clair et al., 1995) also predominantly showed 'no trend' for pH and base cations, but 44% of the lakes exhibited increasing Gran Alk. An increase in organic ion buffering can result in the coincident occurrence of increasing Alk trends and no pH trends, but Clair et al. (1995) reported only 16% of their monitored lakes had increasing Colour trends (water Colour is a surrogate variable for DOC or organic anions; no lakes had decreasing Colour trends). Hence the apparently contradictory trend results were ascribed to the fact that the length of the monitoring record available for trend analysis was relatively short in ecological terms - a limitation noted in the 1997 Assessment (Jeffries, 1997). Despite ample evidence that the chemistry of Canadian Shield lakes can be responsive to changes in acidic deposition (e.g., Kelso et al., 1992), Atlantic Region lakes were clearly in a state of disequilibrium (with respect to atmospheric deposition) such that trend interpretation was anything but straightforward.

Trend results for the 1990s (i.e., for the 1990-2001 period presented in Table 6.4) confirmed that increasing SO_4^{2-} levels are no longer observed in the monitored NL and NS lakes. In fact, 100% of NL lakes and 97% of NS lakes had negative SO_4^{2-} regression slopes, although only 43% and 46% respectively had statistically significant decreasing concentrations. The rate of SO_4^{2-} decline was low (median decreasing slopes were -0.75 and -0.97 μeq/L/yr) compared to other regions. The declining SO_4^{2-} did not engender much improvement in lake acidity – the predominant pH and Alk response was 'no significant trend' in both NL and NS. Where pH and/or Alk trends were detected, they indicated continuing acidification rather than improvement. No NL lakes showed significant increasing pH or Alk, and the single identified trend was in fact negative. Similarly, only 4 and 1 significant positive trends for pH and Alk respectively were detected in NS lakes, whereas 4 and 24 negative pH and Alk trends were identified. The distribution of positive and negative regression slopes for Alk reflected the occurrence of significant trends (negative slopes predominated), but this was not the case for pH where positive regression slopes predominated. The predominant base cation and DOC response was 'no significant trend' in both NL and NS, although, where trends were detected (virtually all cases occurred in NS), base cations declined and DOC almost always increased. These significant trends once again mirrored the overall distribution of positive and negative regression slopes.

Among the four provincial data sets presented in Table 6.4, the scale of continuing acidification for NS lakes is unique (35% had decreasing Alk). This result corroborates the findings of Skjelkvåle et al. (in press). Out of 12 regional data sets from Europe and North America, only the Maine/Atlantic Canada data set (composed of 18 lakes from Maine and NS) had a median Alk slope that was negative (statistically significant). Although not obvious from Table 6.4, the cause of the continuing acidification most likely rests with the response of mitigating variables - base cations and/or DOC (organic acids), or perhaps the slow release of sulphur stored in the soils. The concentrations of acidifying variables are either declining (SO_4^{2-}) or are so low (NO_3^-) as to preclude trend analysis. Skjelkvåle et al. (in press) did not identify a significant NO_3^- trend in their Maine/Atlantic Canada data set, but did find significantly declining base cations.

Waters that may not appear to be chronically acidified, based on annual average chemistry, can nevertheless exhibit episodes of low pH/Alk during snowmelt- or rainfall-induced hydrological events. Such episodes can be produced by natural factors (e.g., dilution, organic acids) and/or anthropogenic factors (e.g., SO_4^{2-}, NO_3^-). Laudon et al. (2002) used the "Boreal Dilution Model" of Bishop et al. (2000) to assess the factors contributing to acidification episodes observed in two NS streams from 1983 to 1998. They found that the anthropogenic contribution to episodic ANC declines was strongly correlated with the decline in SO_4^{2-} deposition.

6.3.2.1.2 Québec region

Analysis of the 1983-1991 records for 29 lakes in southwestern QC showed that declining SO_4^{2-} was a predominant chemical response (Clair et al., 1995). There were no cases of increasing pH or Alk, nearly equal numbers of increasing (6) and decreasing (7) base cation trends, and 11 increasing NO_3 trends (2 decreasing). A re-analysis of the data, with the inclusion of eight additional lakes using the 1985-1993 sampling period, confirmed the SO_4^{2-} response but showed changes in other variables (Bouchard, 1997). Nine of the 37 lakes now had significant increases in pH and/or Alk in this analysis. In addition, there were now no cases of increasing base cations (17 were declining), fewer increasing NO_3 trends (5), and 17 lakes exhibited decreasing DOC trends. These results corroborated the trends identified in a Québec-Vermont data set (Stoddard et al., 1999).

During the 1990s, declining SO_4^{2-} was the predominant significant trend in QC, occurring in 74% of the 38 monitored lakes (Table 6.4; 97% of all regression slopes were negative as well). There were no significant increasing SO_4^{2-} trends. Over the 12-year period, the reductions in SO_4^{2-} varied from 9.6 to 55.3 μeq/L between lakes, with a median annual decline of -2.1 μeq/L/yr. These results match the findings of Skjelkvåle et al. (in press) for their Vermont/Québec group of lakes. The consistent reduction in SO_4^{2-} concentrations shows that the lakes and watershed soils represented by the Québec Regional Temporal Monitoring Network are responding in a fairly uniform fashion to significant decreases in SO_4^{2-} deposition. It also suggests that the lake-watershed systems are rapidly reaching a new steady-state with regard to the changing SO_4^{2-} deposition. For example, at Lac Laflamme toward the eastern end of the Québec Network, SO_4^{2-} concentrations decreased 23% between 1990 and 2001, while the precipitation SO_4^{2-} concentration measured at the Montmorency meteorological station within the Laflamme watershed decreased by 28% between 1985 and 2000. Sulphate adsorption-desorption reactions in the forest soils have been shown to control mid-term SO_4^{2-} fluxes and to reach a new steady state within four years in response to various scenarios of changing SO_4^{2-} deposition at Lac Laflamme (Houle and Carignan, 1995). The soil in this watershed is humo-ferric podzol type found throughout most of the Network domain.

The fairly uniform significant declines in SO_4^{2-} were not reflected in equivalently uniform significant trends in pH or Alk, although positive regression slopes did predominate for both variables. Slightly less than half of the Québec Network lakes showed significantly increasing pH or Alk, and slightly more than half exhibited 'no significant trend'. For the QC data set, pH and Alk are the variables most sensitive to the choice of time-window for analysis. Jeffries et al. (2003b) reported trends for the slightly narrower 1990-97 time window for 43 Québec Network lakes, and in this case 12% of the lakes had declining pH and 19% had declining Alk. Considering the Québec Network as a whole, no significant Alk or pH decrease was identified during the 1990-2001 period. Skjelkvåle et al. (in press) reported the same result. The high degree of inter-annual variability present in the pH and Alk data for many lakes limits the ability of the statistical procedures to recognize significant trends.

Declines in base cation (Ca^{2+} + Mg^{2+}) concentrations are the most likely explanation for the limited pH/Alk increases (Houle et al., 2004). Sixty-eight percent of the 38 lakes in the Network exhibited significantly declining trends (95% had negative regression slopes), but 12 of the lakes showed 'no significant trend'. For the 12-year period, the reductions varied between 7.5 μeq/L and 50 μeq/L with a median annual decline of -2.1 μeq/L/yr. Of the 28 lakes with significant decreasing SO_4^{2-} trends, 20 of them also had decreasing base cation trends; and the median annual trend magnitude is virtually identical for these two variables (Table 6.4). However, Skjelkvåle et al. (in press) did not find such a close correspondence in the two trend magnitudes for their Vermont-Québec data set (SO_4^{2-} was greater than base cations), probably because their data set contained no lakes from the Québec sub-region exhibiting the steepest base cation declines (S. Couture, pers. comm.). The concomitant occurrence of declining SO_4^{2-} and base cation trends seems fairly ubiquitous, being present in three of the four provincial data sets in Table 6.4 and in nine of 12 European and northeastern North American regions (Skjelkvåle et al., in press), and having been reported in many other studies (e.g., Driscoll et al., 1995; Likens et al., 1996, 1998; Mallory et al., 1998; Stoddard et al., 1998). Since the SO_4^{2-} anion acts as a carrier for cations (Galloway et al., 1983), less SO_4^{2-} leaching from soil means less cation leaching and therefore decreasing Ca^{2+} and Mg^{2+} concentrations in surface waters.

Ten of the 38 lakes in the Network showed a significant increasing trend in DOC at a median annual rate of 0.07 mg/L/yr (3 other lakes decreased and 25 exhibited 'no significant trend', Table 6.4). The DOC regression slopes were more evenly distributed. The ten lakes were distributed mainly within a sub-region north of Québec City, but the significant increasing DOC trend identified by Skjelkvåle et al. (in press) for their Vermont-Québec region shows this to be a wider-spread phenomenon. Indeed, Skjelkvåle et al. (in press) reported significantly increasing DOC trends in seven of 12 regions covering most of Europe and northeastern North America. DOC increases may have been caused by variations in temperature and precipitation (Molot and Dillon, 1997), but other process interactions may have been influential as well.

Variations in analytical detection limits for NO_3^- prevented statistical identification of trends for the Québec Network lakes. From an empirical inspection of the data, most of the Network lakes showed no NO_3^- trend during the 1990s (S. Couture, pers. comm.).

6.3.2.1.3 Ontario region

Trend analyses in ON must be considered in two groups: those for lakes directly influenced by the Sudbury smelters, and those for lakes affected only by long-range emissions.

Study of the chemistry and biology of lakes in the vicinity of Sudbury has a long history (in North American terms). Indeed, it was loss of fish species from lakes in the La Cloche Mountains (Killarney) of ON (Beamish and Harvey, 1972) that spurred the initial scientific interest in deposition-induced lake acidification. With particularly early and large SO_2 emission reductions occurring at Sudbury (see Potvin and Negusanti, 1995), many papers have focused on lakes in the surrounding region. Where chemical changes were detected, such studies (e.g., Dillon et al., 1986; Keller et al., 1992; Mallory et al., 1998; Keller et al., 2003) produced a generally consistent picture of predominantly decreasing SO_4^{2-}, base cation, Al and base metal concentrations, and increasing pH and/or Alk. The rate (slope) of these chemical changes was often steeper in the 1970s and 1990s than in the 1980s, apparently reflecting the SO_2 emission history at local smelters. The lake population being monitored and the time window being analyzed also influenced the nature of the reported recovery response. For example, 36 of 38 relatively large lakes (14.5 – 1315 ha) sampled by the Ontario Ministry of Environment exhibited increasing pH between 1981 and 1989 (Keller et al., 1992), while only 26 of 161 smaller lakes (0.1 – 350 ha) sampled by the Canadian Wildlife Service (CWS) showed increasing pH between 1983 and 1995 (2 were decreasing and the rest showed no change; Mallory et al., 1998). At present, SO_4^{2-} in Sudbury area lakes is influenced by local sulphur sources out to a distance of ~45 km (Keller et al., 2001a). Beyond 45 km, SO_4^{2-} from long-range sources appears to be more important determinant of changes in lake chemistry. The potential increase in lake pH and/or Alk has been partially reduced by declining base cation concentrations (Keller et al., 2001b). The measured rate of Ca^{2+} decline in Sudbury lakes was less in the 1980s than the 1990s. Despite the remarkable recovery of Sudbury area waters, several studies (e.g., Mallory et al., 1998; Keller et al., 2003) still conclude that many lakes remain too acidic (pH <6) and/or metal-degraded to support sensitive aquatic biota.

Eleven ON lakes were included in the 1983-91analysis by Clair et al. (1995) and 17 lakes were included in the broader analysis of North American regions by Stoddard et al. (1999) covering the 1980s through to 1995. All were located outside Sudbury's influence. These studies suggested that decreasing SO_4^{2-} and base cation trends became more prevalent and/or steeper in magnitude in ON from the 1980s to the 1990s, while trends for other variables were few or inconsistent between sites. Trends for an early-1980s to mid-1990s time frame for a larger ON compilation (Jeffries, 1997) indicated that 60% of the lakes had increasing pH and/or Alk, but the results were greatly influenced by a sizeable Sudbury component in the sample population (38 of 90 lakes). Data from repeated surveys of 56 headwater lakes in Algoma (Kelso et al., 1992) suggested that initial improvements in their acidity (median pH increased 0.5 units between 1979 and 1985) had been lost by 1994 (Jeffries, 1997). The CWS monitored 216 and 235 small water bodies in the Muskoka region (southeast of Sudbury) and the Algoma region (west of Sudbury) respectively (McNicol et al., 1998). The CWS focus on small water bodies (median size for the two data sets was 4.2 and 3.8 ha, respectively) yields sample populations that are more representative of the regions' actual lake population than other monitoring networks. For the CWS Muskoka and Algoma data sets, 47-56% and 51-57% of the lakes showed significant declining trends for SO_4^{2-} and base cations respectively between 1988 and 1996. Increasing pH and Alk trends occurred in only 12% and 21-23% of the lakes however.

The ON data set of 638 lakes used here for analysis of 1990s trends (Table 6.4) is nearly the same as the set of 662 lakes employed by Jeffries et al. (2003b), although the time windows differ slightly. Neither data set explicitly excluded Sudbury lakes, although the fraction of the sample population within the 45 km region of smelters influence (Keller et al., 2001a) is small. The data set was compiled from five sources (Table 6.1), one of which dominates in terms of numbers (i.e., the CWS data;

McNicol et al., 1998). The CWS data component of the overall ON data set includes many of the relatively small water bodies (median lake size = 5.2 ha) that are the preferred habitat of waterfowl. In contrast, the median lake size for the other four sources ranged from 25 ha (ELA) to 122 ha (Ontario Ministry of Environment Sudbury and NE Region). The importance of discriminating the ON data sources becomes apparent when it is noted that only 29% of the full compilation showed significantly declining SO_4^{2-} although 83% of the regression slopes were negative. However, when the CWS component was excluded, 91% of the remaining lakes (now with 41 of 70 from the Sudbury region) showed significant SO_4^{2-} reductions. Clearly, landscape elements that are particularly important to small lakes and wetland water bodies influence SO_4^{2-} export, most likely via the retention and mobilization processes influenced by climatic variations discussed in Section 6.3.2.5.

The ON data set was the only one suitable for analysis of NO_3^- trends (frequent occurrence of detection limit values precluded analysis of the other data sets). 'No significant trend' was the overwhelming response (92%) with almost equal numbers of increasing and decreasing trends observed in the remaining lakes. The distribution of NO_3^- regression slopes was also fairly evenly split (57% positive, 43% negative). Jeffries et al. (2003b) noted that the 1990-99 CWS data set used in that paper showed increasing NO_3^- in 17% of the cases, so the inclusion of two years to the data records analyzed here has affected the trend detection rather substantially. Nitrogen deposition is a potentially important acidifying input to lakes; however, whether or not the N is actually acidifying depends on whether it is being retained by terrestrial ecosystems or exported as NO_3^- (see Section 6.5). These trend results for NO_3^- provide little evidence that N-based acidification has developed any further than was reported in the 1997 Assessment.

'No significant trend' predominated the pH and Alk response of ON lakes (87% and 84% of the 638 lakes respectively), although increasing values clearly predominated the regression slope distribution (74% for pH and 70% for Alk). Most of the remainder (12% and 15%) exhibited increasing pH and Alk trends respectively, although 1% and 2% were decreasing which seems to mirror the small incidence of increasing SO_4^{2-} (or perhaps NO_3^-). The median increasing Alk slope (3.1 μeq/L/yr) was smaller (in absolute terms) than the median declining SO_4^{2-} slope (-5.0 μeq/L/yr). Once again, the data sets from the different ON sources exhibited different trend behaviour. The factors influencing variability in SO_4^{2-} concentrations in the CWS "small lake" data set that reduced detection of declining trends (as noted above) likely also limited detection of positive pH and Alk trends. When the CWS trend results are excluded from the ON compilation, 53% and 60% of the remaining 70 lakes showed significantly increasing pH and Alk trends respectively. Jeffries et al. (2003b) also noted these differences among data sets, but exclusion of the CWS results from their ON compilation only increased the occurrence of significant positive pH and Alk trends to 39% and 41% respectively. Addition of two years to the data sets analyzed here has greatly increased the incidence of positive pH and Alk trends in the CWS data set. Finally, it is noteworthy that the majority of decreasing Alk trends occurred outside of both the "small lake" CWS data set and the Sudbury and NE Region data set.

Whether or not declines in acid anions translate into increasing pH or Alk trends depend on the response of other mitigating variables, primarily base cations and perhaps DOC (i.e., organic anions). Declining base cation trends were half as prevalent in the ON data as they were in QC, although the predominance of negative regression slopes was more similar. When the CWS results were excluded, the ON and QC distributions of significant base cation trends were more similar, but still of greater magnitude in ON, i.e., 76% of the remaining 70 ON lakes had significant decreases in base cations with a median slope of -3.9 μeq/L/yr. 'No significant trend' was by far the predominant response for DOC in ON, but once again this was strongly influenced by the "small lake" CWS data set. A much higher proportion of ON lakes (32%) exhibited significant increases in DOC when the CWS results were excluded, and the proportion of significant declines in DOC was 0%. The latter observation means that all cases of decreasing DOC identified for the entire ON data set (Table 6.4) were contained in the generally higher concentration CWS component. The climatic variability that influenced SO_4^{2-} and probably pH and Alk trends, undoubtedly influenced other chemical trajectories as well. Hudson et al. (2003) showed that solar radiation and winter precipitation (i.e., not acidic deposition) best explained the annual DOC variation in nine relatively larger lakes in the M-H region of ON.

Overall, lake chemistry trends observed during the 1990s show that SO_4^{2-} is declining throughout southeastern Canada in response to declining North American SO_2 emissions. This generalization is only now becoming commonplace in the Atlantic provinces and is constrained in ON by the effect of landscape elements that are particularly important to small lakes and wetland water bodies. While increasing pH and/or Alk is becoming increasingly prevalent (relative to earlier assessments), the predominant acidity response is still 'no significant trend' primarily due to base cation declines compensating the SO_4^{2-} declines. Increasing DOC (organic anions) and possibly increasing NO_3^- (in a few cases) may be mitigating pH or Alk increases for a small number of lakes.

6.3.2.2 *Analyses of repeated surveys*

D.S. Jeffries, M. Gilliss and J. Dupont

Some lake surveys have been repeated over time in ways that make them unsuitable for the type of non-parametric test procedures used in the previous section, e.g. single repetitions or repetitions but at irregular intervals. Nevertheless, they can provide useful information on how lake chemistry has changed through time.

A survey of 39 lakes in a sensitive portion of southwestern NB was irregularly repeated five times between 1986 and 2001 (Pilgrim et al., 2003). Evaluation of the chemical changes occurring between adjacent samplings, using analysis of variance and paired t-tests, generally corroborated observations made in the NL and NS trend analyses presented above. Between 1986 and 1993, sea-salt corrected SO_4^{2-}, Ca^{2+}, Alk and Total Organic Carbon (TOC – similar but not identical to DOC) decreased significantly. Despite the reduced concentration of the primary acidifying anion, the lakes (further) acidified over this seven-year period due to a marked reduction in base cations (1986 mean Ca^{2+}= 62 µeq/L, 1993 mean Ca^{2+} = 53 µeq/L). Sulphate did not significantly change between 1993 and 2001, but nevertheless, it was significantly lower over the entire period ($p = 0.03$; 1986 mean = 61 µeq/L, 2001 mean = 54 µeq/L). There was a non-significant increase in Ca^{2+} between 1993 and 2001 that led to a non-significant pH increase and a highly significant Alk increase ($p = 0.0001$; 1993 mean = 22 µeq/L, 2001 mean = 32 µeq/L). While NO_3^- composed 37% of the acidic deposition within the region, it was not detectable in the lakes throughout the study period. It was found that significant changes in water chemistry occurred only within the most acid sensitive lakes in the survey (lake with Alk <40 µeq/L), corroborating a similar conclusion from a more broad-based study (Skjelkvåle et al., 2001). These lakes still have pH <6 – the critical load threshold condition.

A cluster of 46 headwater lakes in north-central NB was surveyed in 1984, 1998 and 2001. Using the same methods and variables as Pilgrim et al. (2003), overall and between sampling changes were evaluated (M. Gilliss, pers. comm.). Sulphate significantly decreased between 1984 and both 1998 and 2001; however, it significantly increased between 1998 and 2001. The same pattern occurred for Ca^{2+} and Alk. The concentration increases over the short period from 1998 to 2001 were particularly notable (1998 mean Ca^{2+} and Alk were 118 and 117 µeq/L respectively; 2001 means were 168 and 183 µeq/L respectively), resulting in a significant increase in pH as well. Total organic carbon significantly increased between 1984 (mean = 4.5 mg/L) and 1998 (mean = 7.6 mg/L), and significantly decreased between 1998 and 2001 (mean = 5.8 mg/L). The lakes were separating into four Alk classes. While all classes exhibited similar concentration changes in terms of direction, the most sensitive class (Alk <50 µeq/L) behaved differently from the other three in that the 2001 values for Alk, Ca^{2+} and pH were lower than in 1984. The other three (less sensitive) classes all exhibited 2001 values that exceeded their 1984 values.

The smelter located at Rouyn-Noranda, QC is responsible for a large portion of that province's SO_2 emissions, and a large emission reduction (~90% relative to 1980) was implemented, mostly in the early 1990s. Water quality has been measured in 36 lakes surrounding Rouyn Noranda in 1982, 1991, 1996 and 2001 (Dupont, 2004). This is a subset of the 64-lake survey described by Dupont (1996) - 28 lakes having been removed from the sampling program in 1996 because of high pH, seasonal anoxia or distance from the smelter. The lakes are of two types: those located to the south and east of Rouyn-Noranda on the Laurentian Highlands are deep, clear and sensitive to acidification, while those located on the Abitibi Lowlands near and north of the city are shallow, DOC-rich lakes.

The non-parametric Wilcoxon Signed Ranks Test was used to identify significant change in variable concentrations between paired samples. Over the entire period (1982 to 2001) the tests showed that SO_4^{2-}, base cation (Ca^{2+} + Mg^{2+}) and DOC concentrations significantly declined ($p \leq 0.05$), while Alk and NO_3^- significantly increased. No significant change in pH was detected. There were several variations in the direction of significant change between adjacent sampling dates. For example, significant declines in Alk and pH accompanied declines in SO_4^{2-} and base cations between 1982 and 1991. However, these changes in Alk and pH reversed during the following period (1991 to 1996) when SO_4^{2-} showed no significant change and base cations actually increased. A further significant Alk increase between 1996 and 2001 yielded the overall 1982-2001 trend noted above, while the lack of significant pH change between 1996 and 2001 resulted in no significant pH trend being detected over the entire period. The highly significant and large DOC decrease that occurred between 1982 and 1991 was sufficient to produce a statistically significant decline over the entire 1982-2001 period despite the fact that there was no significant change between 1991 and 1996, and a significant (although small) increase between 1996 and 2001.

The increasing NO_3^- concentrations identified in the Rouyn-Noranda data are of particular interest because there has been no increase in N deposition or land-use change to explain them, and they are spatially restricted to a zone within 50 km of the smelter. Other reported cases of increasing NO_3^- in QC (Clair et al., 1995; Bouchard, 1997; Stoddard et al., 1999) were outside this zone and were more numerous in the 1980s than the 1990s. In fact, the increasing NO_3^- trend identified in this data set is almost entirely due to concentration changes that occurred between 1991 and 1996.

The zone of direct smelter influence at Rouyn-Noranda extends ~125 km from the smelter (Dupont, 1996). Within this zone, 9 clear water lakes were added to the 1991 and all subsequent surveys. The mean pH of this subset was 5.4 in 1991 (range=4.9 to 5.7), 5.84 in 1996, and 6.04 in 2001 (range=5.8 to 6.3).

Overall, the evidence of chemical change offered by analyses of repeated surveys generally agree with the trend results presented in the previous section. Repeated surveys are an economical alternative to the frequent sample collection needed to perform trend analyses; however they generally do not provide the information needed to define the cause of change, e.g., whether it is due to declining acidic deposition, climatic variation, etc.

6.3.2.3 *Paleolimnology*

A.M. Paterson and J.P. Smol

In the absence of historical or monitoring data, paleolimnological techniques can be used to quantify long-term changes in water quality resulting from the deposition of strong acids, as well as other stressors (Smol, 2002). Over the past two decades, the paleolimnological approach has been used throughout North America and Europe to track changes in lakewater acidification and recovery (Charles et al., 1989; Smol et al., 1998; Battarbee et al., 1999; Smol, 2002). Research activity peaked in the late 1980s, but has since dropped off considerably. Below, we review the paleolimnological research that has been completed in Canada (with some comparisons to lakes in the northeastern USA) since publication of the 1997 report.

The recovery of aquatic ecosystems following reductions in the deposition of strong acids has become a focus of many recent paleolimnological studies. These patterns are commonly measured relative to pre-disturbance or background conditions. For example, a comparison of acidified lakes in Adirondack Park, New York and Sudbury, ON indicated that there were differences in the rate and degree of recovery across regions, with lakes near Sudbury showing more recovery than those in Adirondack Park (Smol et al., 1998; Majewski and Cumming, 1999; Snucins et al., 2001). These differences were attributed primarily to a larger decrease in sulphate deposition in the Sudbury area, as well as higher pre-industrial pH levels in Sudbury lakes, suggesting that lakes with higher natural buffering capacities may recover more quickly with declines in deposition (Smol et al., 1998).

Chemical recovery of lakes may be complicated by interactions between climatic variability and previously deposited acids stored in wetlands. Faulkenham et al. (2003) examined the sediment record of two central-Ontario lakes with similar basin characteristics but different wetland areas in their watersheds. Diatom assemblages over the past ~200 years were significantly more variable in the lake with greater wetland area. Furthermore, water chemistry explained the largest portion of variation in diatom communities examined at annual resolution over the past 20 years. Complex interactions among water chemistry, acidic deposition, and climatic variability explained an additional 10% and 1% of the variation in the lakes with high and low wetland areas, respectively. Thus, drought-related re-acidification and its effect on water chemistry may impact algal communities in lakes with modest wetland coverage (Faulkenham et al., 2003).

In addition to pH, recent studies have examined the impact of acid deposition and recovery on other water quality variables. Despite evidence of recovery in the acidity of many Sudbury lakes, Ca^{2+} levels have remained low relative to long-term pre-disturbance concentrations (Keller et al., 2001b). Paleolimnological reconstructions of Ca^{2+} in six Sudbury lakes suggested that declines in concentrations began in the early to mid-1900s (ground-level ore roasting in the Sudbury area began in the late-1800s). Long term decreases have been large in comparison to pre-industrial concentrations, averaging 75 μeq/L or 46%. In addition to depletion of base cations in catchment soils as a result of long-term and sometimes extreme acidic deposition, other factors may have contributed to the Ca^{2+} patterns, including climate change, and forest harvesting and regeneration (Keller et al., 2001b).

Paleolimnological techniques have also been used to reconstruct levels of dissolved organic carbon (DOC) in lakes since pre-industrial times. Using a diatom-based model calibrated from 80 lakes in the Sudbury region, Dixit et al. (2001) inferred DOC concentrations in three lakes in Killarney Park, ON. Following decades of acidification, significant decreases in DOC concentrations, and consequently increases in UV-b penetration, were recorded in two of the lakes (Dixit et al., 2001).

The impact of acidification on whole-lake algal communities has also been studied recently using paleolimnological methods. In six acidified lakes in Killarney Park, and an experimentally-acidified lake in the ELA, ON, ecological changes in algal communities were measured using sedimentary pigment analysis (Leavitt et al., 1999; Vinebrooke et al., 2002). Despite differences in the scale of the studies, and in the mechanism of disturbances, some interesting similarities were found. In both studies, changes were consistent with a reduction in DOC and increased water clarity, resulting in an increased biomass of deep-water phytoflagellates. In the experimentally-acidified lake, the combined effects of change in pH and irradiance accounted for 20% of the variance in sedimentary pigments (Leavitt et al., 1999).

Improvements have also been made to predictive models for reconstructing environmental variables related to acidification and recovery. In the Sudbury region, the addition of 33 lakes to the existing calibration set improved the ability of models to infer lakewater pH from sedimentary diatom and scaled chrysophyte assemblages (Dixit et al., 2002). In central ON, models for reconstructing lakewater pH now exist for diatom (Hall and Smol, 1996), chrysophyte cyst (Wilkinson et al., 1999), and scaled chrysophyte assemblages (Paterson et al., 2002). Paterson et al. (2001) also tested the use of a multi-indicator model for reconstructing pH from several phycological indicators simultaneously. The model performed as well or better than the individual models when used to predict the present-day pH of 53 study lakes in central ON.

6.3.2.4 Relationship of trend occurrence to deposition trends

D.S. Jeffries

Regulatory action has resulted in substantial reductions in SO_2 emissions in both Canada and the U.S.A. (Chapter 2; Jeffries et al., 2003a). Total North American emissions are now ~40% less than in 1980 – a reduction level greater than the targets specified in the Canada-U.S. Air Quality Agreement. In 1997, Canadian SO_2 emissions were 18% and 24% below the national and eastern targets respectively. Similarly, U.S. SO_2 emissions were 23% below the allowable level in 1997, and further reductions are expected as Phase II of the U.S. Acid Rain Program is implemented. While nitrogen oxide (NO_x) emissions are also a potentially acidifying pollutant, policy initiatives to control NO_x in both Canada and the U.S.A. have focused on reducing local smog levels. Compared to SO_2, total North American NO_x emissions have changed little (in fact increased slightly) over the last two decades.

Changes in acidifying emissions are generally reflected by changes in precipitation chemistry. Environment Canada (1997) evaluated chemical trends for the Canadian Air and Precipitation Monitoring Network (CAPMoN) stations that are east of Manitoba (monitoring period from the early 1980s to 1994). Twelve of 14 stations exhibited statistically significant declines in SO_4^{2-} concentrations, while NO_3^- showed mixed responses (five declining trends, three increasing and six with no trend). Including more recent data in the trend analyses presented in Chapter 3 confirmed these generalities.

Since SO_4^{2-} deposition is the predominant acidifying agent in Canada, concentration reductions in precipitation leading to declines in the receiving surface waters will be the first step towards chemical recovery. However, it remains an open question as to whether the changes in SO_4^{2-} deposition directly translate into equivalent surface water changes. One cannot expect that absolute changes in precipitation SO_4^{2-} concentrations will be comparable to changes in surface water concentrations because dry deposition and evapotranspiration yield higher concentrations in the latter. Skjelkvåle et al. (in press) attempted to adjust for this effect by comparing the percent change of the SO_4^{2-} trend slopes in precipitation and lakes for 12 regions of Europe and northeast North America. They reported that the rates of SO_4^{2-} decline are smaller in surface waters than in deposition for all North American and European regions (except one) indicating a lagged response. These researchers hypothesized that this result reflects desorption of SO_4^{2-} that accumulated in catchment soils over the past century due to atmospheric deposition. Desorption of stored sulphur has the effect of damping the trends in surface water SO_4^{2-} and slowing the rate of decline. The single exception to the pattern was the Upper Midwest region of the U.S. where most lakes are seepage lakes and where soils consequently have only a minor effect on SO_4^{2-} concentrations.

Desorption of the SO_4^{2-} anion from soil particle surfaces is caused by the shifting electrochemical equilibrium that results from declining SO_4^{2-} input (see Chapter 5). However, sinks of reduced S forms are also present in catchments, e.g., the organic S compounds that are present in soil or wetland organic matter, or iron/manganese sulphide minerals that have precipitated in anaerobic compartments. Development of conditions suitable for oxidation of the reduced S and mobilization of the resulting SO_4^{2-} is another process that would lead to damping of surface water SO_4^{2-} trends relative to deposition trends. In fact, isotopic studies suggest that the SO_4^{2-} exported from catchments, more often than not, has undergone geochemical transformations that involve reduction and re-oxidation (Caron et al., 1986; Schiff et al., in press). The occurrence of such re-oxidation processes is commonly driven by climatic events (some observations are discussed in Section 6.3.2.5 below).

Dillon et al. (2003) compared the temporal patterns in SO_4^{2-} concentrations from nine lakes in the M-H region of south-central ON with patterns in both deposition and climate observed during the 1980s and 1990s. They found that the nine lakes statistically separated into two groups that had synchronous chemical patterns. Water replenishment time seemed to be a characteristic that classified many but not all lakes. Theoretically, a lake with a long replenishment time should respond more slowly to changes in atmospheric deposition than one with rapid water replacement. Even so, the average SO_4^{2-} pattern was very similar for both lake groups. The response of both lake groups to decreasing SO_4^{2-} deposition was independent of degree of or sensitivity to acidification. Models were developed to determine what factors were important in determining the lakes' SO_4^{2-} concentration patterns. Dillon et al. (2003) found that inclusion of regional/global climate indices (i.e., the El Niño Southern Oscillation Index and the North Atlantic Oscillation Index) in addition to SO_4^{2-} deposition gave the best predictive models. Large-scale climatic factors play a major role in the response of aquatic systems to changes in SO_4^{2-} deposition. Observations discussed in the following section suggest that such climatic factors tend to affect lake or catchment processes so as to delay the response to reduced deposition.

6.3.2.5 *Factors other than deposition that influence trends*

D.S. Jeffries, T.A. Clair, S. Couture, P.J. Dillon, J. Dupont, W. Keller, D.K. McNicol, and M.A. Turner

In many Canadian lakes, part or all of the ionic compensation for declining SO_4^{2-} concentrations is declining base cations instead of increasing pH and/or Alk (Mallory et al., 1998; Keller et al., 2001b; Jeffries et al., 2002), a phenomenon also observed in Europe and the U.S.A. (Stoddard et al., 1999; Lawrence et al., 1999; Skjelkvåle et al., in press). In such cases, the lakes are not only failing to recover, but they are likely becoming more dilute. There are even a few cases where lakes with declining SO_4^{2-} continue to acidify, at least in part, because the rate of base cation decline exceeds the rate of SO_4^{2-} decline (Couture, 1995; Jeffries et al., 2002; Houle et al., 2004; Skjelkvåle et al., in press).

The observations of declining base cations correspond to a part of the chemical trajectory described by a generally accepted conceptual model of ecosystem acidification (see Norton and Veselý, 2003). In the absence of acidic deposition, stream base cation concentrations reflect the steady-state that exists between catchment supply mechanisms (mostly from primary weathering – a kinetically slow process – but also from atmospheric deposition) and removal mechanisms (leaching by percolating precipitation water). The concentration of base cations in stream water typically varies inversely with discharge. The soil pool of easily exchanged base cations is of central importance to this steady-state because it is usually very large relative to the magnitude of the supply and export fluxes. Introduction of the strong acids in acidic deposition causes leaching of the easily exchanged base cation pool (Likens et al., 1996, 1998). Hence, more often than not, runoff waters exhibit increasing base cation concentrations with the onset of acidic deposition rather than declining pH or alkalinity. Only ecosystems with extremely small base cation pools (e.g., those with very thin or no soil cover) acidify immediately (runoff waters have high H^+ and aluminum concentrations). If acidic deposition continues long enough, the pool of exchangeable bases will eventually be leached to the extent that stream cation concentrations will decline and the water will become acidic.

It appears that most Canadian aquatic ecosystems fall somewhere between these endpoints. Many are acidified (alkalinity depleted relative to the original) but not yet acidic (alkalinity ≤0; see Section 6.3.1.2), and the declining base cation trends are in response to declining acid inputs. Their soil base cation pools have been leached but are not yet exhausted. Therefore, an important question is what will base cation concentrations in runoff be once acidic deposition declines even further. Our only direct information on this question comes from paleolimnological reconstruction of long-term Ca^{2+} patterns in six Sudbury-area lakes (Keller et al., 2001b). The study showed that following some small initial increases, Ca^{2+} concentrations have been declining since the early to mid 1900s (local SO_2 emissions began in the late 1800s) to levels that are approximately half of what they were in pre-industrial times. The conceptual acidification model predicts that the concentrations will decrease below their pre-acidification levels and only return when the soil pool of exchangeable bases is replenished by weathering. Since weathering is a slow process, it is unrealistic to expect that pre-industrial chemical conditions in runoff waters can be re-established in the short term (decades to centuries). Finally it should be noted that the chemical trajectories described by the conceptual model are necessarily simplistic. Several other factors introduce variability into the base cation-SO_4^{2-} relationship, e.g., the glacial origin of Canadian Shield soils, soil thickness and profile maturity, occurrence of wetlands, declining base cation deposition (Sirois et al., 2001) and other external stressors like climatic and land-use changes.

The time required for lakes to re-equilibrate to lower SO_4^{2-} deposition differs from lake to lake. Lakes with long water replenishment times obviously take longer to reach a new steady-state than those with short replenishment times. However, SO_4^{2-} mass budgets show that even when accounting for the effect of water replenishment, terrestrial basin (stream) inputs and lake output generally exceed SO_4^{2-} deposition (Eimers and Dillon, 2002; Eimers et al., 2004). Additional sources of SO_4^{2-} in the terrestrial basin are indicated, e.g., SO_4^{2-} desorbed from forest soils or mobilized by mineralization of organic compounds; SO_4^{2-} produced by oxidation and mobilization of reduced S stored in wetlands, stream margins, etc.; and possibly SO_4^{2-} produced by oxidation of sulphide minerals present in the bedrock (Evans et al., 1997; Mitchell et al., 2001b; Eimers et al., 2004). These sources depend on spatially variable basin characteristics such as topography, forest type, soil type, depth and chemistry, percentage of wetlands, etc. Major watershed disturbance may also play a role, e.g., stream SO_4^{2-} concentrations at Rawson Lake increased following forest fires in the late 1970s and early 1980s (see Figure 6.10). Whether or not the movement towards new SO_4^{2-} input-output equilibria translates into discernible recovery trends also depends on the magnitude of the deposition reduction. Where it is large, e.g., near Sudbury and Rouyn-Noranda, both lake SO_4^{2-} and pH change quickly leaving little doubt that recovery is occurring in direct response (e.g., Clearwater Lake in Figure 6.10). Where the magnitude of deposition reduction is smaller, the other factors influencing the input-output equilibrium may obscure chemical trends and probably delay recovery for years if not decades.

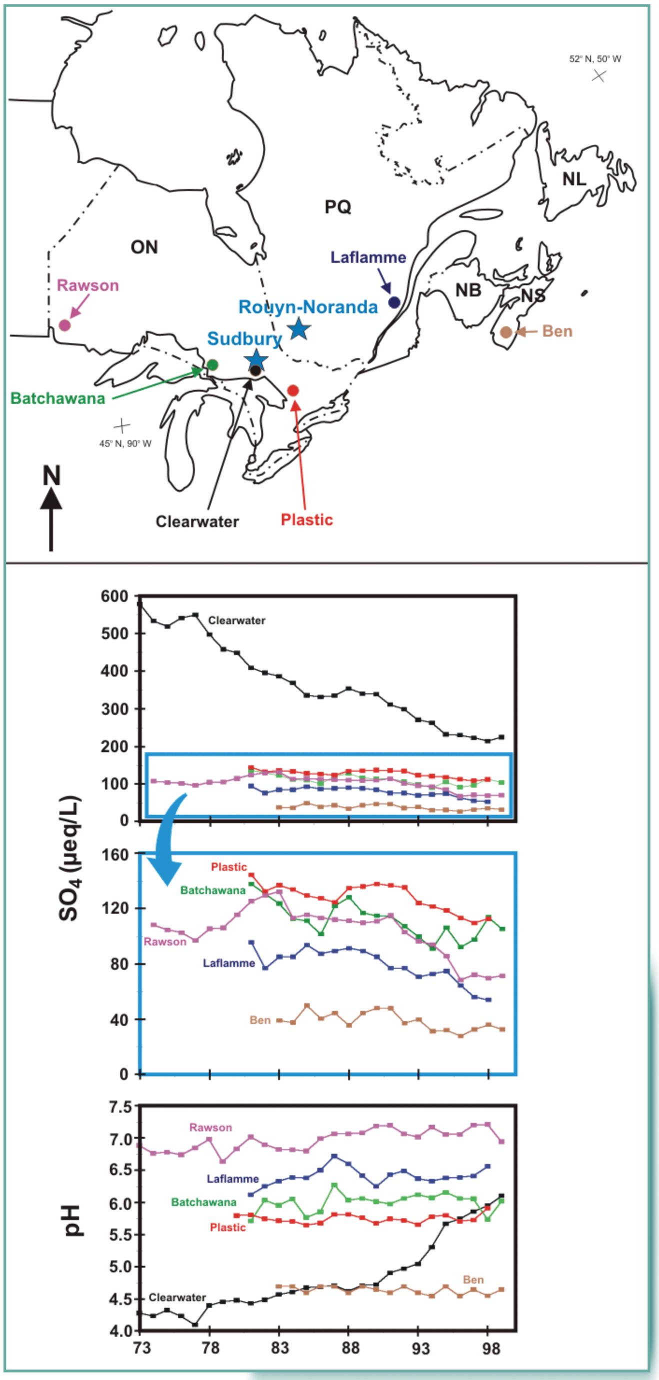

Figure 6.10: Annual average SO_4^{2-} and pH measured in six lakes in southeastern Canada. Lake locations are shown on the accompanying map as are the location of the Sudbury, ON and Rouyn-Noranda, QC smelters. Adapted from Jeffries et al. (2003b).

Drought has particularly influenced SO_4^{2-} export from ON lakes (Yan et al., 1996; Dillon et al., 1997; Jeffries et al., 2002). It is hypothesized that water table or lake level draw-down allows wetland soils and/or littoral zone sediments to dry thereby producing conditions where reduced S species may be oxidized. Evaluation of the sulphur and oxygen isotope geochemistry in stream SO_4^{2-} at the Turkey Lakes Watershed (TLW) has confirmed that post-drought concentration pulses are a result of this process (Schiff et al., in press). When the systems re-wet, export of the resulting mobile SO_4^{2-} has produced both occasions of episodic acidification when H^+ was an important co-exported cation, and extended periods of elevated SO_4^{2-} (relative to pre-drought levels) when Ca^{2+} was typically a more important compensating cation. Increases in the annual average SO_4^{2-} concentration during the mid-1970s in Clearwater Lake and during the late 1980s and late 1990s in Batchawana, Clearwater and Plastic Lakes (Figure 6.10) were all attributed to the drought effect (Jeffries et al., 2003a). Drought events delay lake recovery and work is underway to quantify the nature and size of the reduced S pool and its accessibility in order to assess the long-term potential of this stressor interaction. In the Plastic and Batchawana Lake catchments (see Figure 6.10 for location), Eimers et al. (2003) showed that peat deposits in lowland areas and the forest floor in upland areas are the most likely sources of the stream water SO_4^{2-} peaks that occur following droughts.

Drought also influences episodic acidification. Laudon et al. (2004) applied the "ANC Dilution Model" (Laudon and Bishop, 1999) to 311 rainfall-induced, hydrological episodes observed in nine headwater streams from the Dorset and Turkey Lakes research sites in ON. They showed that SO_4^{2-} was by far the predominant driving mechanism of the associated ANC declines. There was a strong correlation between ANC decline and antecedent stream discharge, meaning that episodic acidification during rain events is strongly associated with preceding drought.

As SO_4^{2-} deposition declines, the relative importance of acidification by N deposition increases. Between 1982 and 1992, Lac Laflamme in QC had declining ANC despite the fact that SO_4^{2-} trend changed from increasing to decreasing around 1986 (Figure 6.10), and this was attributed to the combined effect of declining base cations and increasing NO_3^- (Couture, 1995). In the TLW in ON (cf. Batchawana Lake in Figure 6.10), increasing NO_3^- was observed in ground water and some surface water sites although its influence on acidity status was minor (Jeffries et al., 2002). At both Lac Laflamme and Turkey Lake, increasing NO_3^- was probably more related to changing forest condition (and perhaps climatic variation) than atmospheric deposition. However, no such explanation is apparent for the NO_3^- increases observed in lakes near the Rouyn-Noranda smelter between 1982 and 1996 (see Section 6.3.2.2). Whether or not N deposition in southeastern Canada is moderating pH and/or Alk trends in lakes remains an open question.

Factors that affect internal Alk generating processes may profoundly influence lake acidification or recovery. The importance of internal Alk generation (IAG) in lakes generally increases with the water replenishment time. Typically the most important processes underlying IAG include SO_4^{2-} reduction (Evans et al., 1997), denitrification, ion exchange at the water-sediment interface (Cook et al., 1986), and DOC assimilation. Depletion of the iron needed to form insoluble sulphide compounds has also been shown to reduce the IAG (Carignan, 1989). Impairment of IAG appears to depend partly on the severity of the acidification. For example, reducing the pH below 5 as was the case in the ELA Lake 302S experiment impaired the lake's IAG, whereas lowering the pH of Lake 223 to only 5.1 did not. The impairment of a lake's biogeochemical ability to internally buffer acids means that the efficiency of acidifying inputs is greater during the recovery period than it was during acidification.

6.4 AQUATIC BIOLOGY

The 1997 Assessment presented a wide range of acidification effects on freshwater ecosystems, reaffirming and extending previously documented findings (Schindler, 1988; Longcore et al., 1993; RMCC,1990). The acidification effects highlighted in the previous assessment included reduced algae and invertebrate taxonomic richness, reduced fish and amphibian abundance and distribution, and impacts to waterbirds through disruption of their food webs. Food webs in acid-damaged lakes are usually altered to become more simple and dominated by acid-tolerant biota. Along with chemically inhospitable conditions, the extirpation of acid-sensitive taxa, loss of preferred prey species, reduced nutritional value of remaining prey, and eco-toxicological effects (e.g., metal toxicity) often combine to extend acidification effects from primary producers (e.g., algae) through to higher trophic levels (e.g., fish, waterbirds).

In this assessment, we summarize recent work updating or refining previously observed consequences of lake and wetland acidification. Topics reviewed in this chapter include acidity effects on invertebrates, waterbirds and Atlantic salmon (*Salmo salar*), and the mercury toxicity consequences for aquatic wildlife in acidified habitats. New observations of acidity responses by littoral crustacean communities and several individual macroinvertebrate taxa are also presented. Temporal trends in waterbird population indices, and habitat modelling results for small fish and waterbirds, provide context for understanding both acidification effects and likely recovery patterns. Biological topics addressed in this chapter are those which identify acidification effects on biota or evaluate tools for assessing biological indicators for acidification and recovery. The following chapter (Recovery of Aquatic Ecosystems) includes a discussion of several of the same biological groups but with the focus on concurrent chemical and biological change.

6.4.1 Benthic algae

R.C. Weeber

Benthic algae include the periphyton, epipelon and metaphyton assemblages and are often important contributors to the overall primary production of acid sensitive Canadian Shield lakes. Benthic algae grow attached to plants, stones, wood and sediments, and are an important food resource for the herbivorous invertebrates, amphibian larvae and fish that in turn support higher trophic levels. Generally dominated by diatoms, green algae, and cyanobacteria, these communities play a role in nutrient cycling and food web support, and are often responsive to changes in acidity, nutrient availability, grazing, and light penetration (Kalff, 2002).

Working in Killarney (northeastern ON), Vinebrooke (1996) showed that acidification suppresses edible algal biomass and diversity in the otherwise highly productive and diverse littoral fringe of Canadian Shield lakes. Grazing pressure was important as an additional factor affecting algal biomass and community composition only in circumneutral lakes, a pattern confirmed by Graham and Vinebrooke (1998). Vinebrooke (1996) reported that periphyton growth was suppressed for algae transplanted from low to high acidity (pH 6.3 to pH<5, respectively). The reverse was not observed, however. Algae transplanted from high to low acidity continued to show inhibited growth even after one month in low acidity conditions. When algae were transplanted to lakes of differing acidity, overall biomass did not change but the taxonomic composition of the transplanted community quickly shifted to resemble the community already resident in the lake (Vinebrooke, 1996). These results, corroborated by subsequent work (Vinebrooke and Graham, 1997; Graham and Vinebrooke, 1998), suggest that periphyton colonization across the acidity gradient does not appear to be limited by dispersal but rather by habitat conditions in the colonized lake. Acidification-induced impairment of benthic algae primary production appears to be related to competition for DIC, which tends to decline with acidification (Vinebrooke and Graham, 1997; Graham and Vinebrooke, 1998). Along with acidity, buffering capacity and aluminum (Al^{3+}), the availability of DIC and DOC are important influences on the species composition of periphyton along the littoral fringe of boreal lakes (Vinebrooke and Graham, 1997) (Figure 6.11).

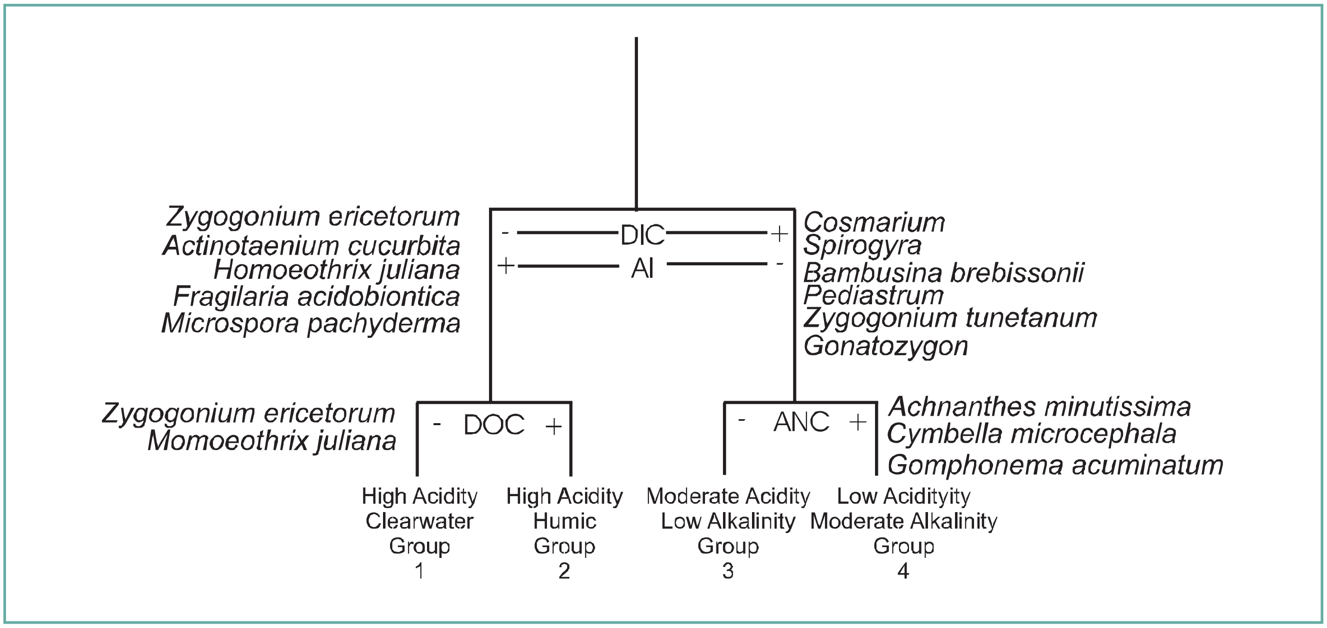

Figure 6.11: Classification of lake groups and identification of periphyton indicator taxa and key discriminating environmental variables based on a COINSPAN analysis of $\log_{10}$-transformed taxa biovolumes with $\log_{10}$-transformed water chemistry data. Data were collected in 1992 from 15 low pH (3.9 – 6.3) lakes in Killarney, northeastern ON. Adapted with permission from Vinebrooke and Graham (1997).

In contrast to the patterns observed in the chronically acidified Killarney lakes, periphytic algae in Lake 302S, an experimentally acidified lake in the Experimental Lakes Area (ELA), showed compensatory species shifts resulting in stable total biomass despite a decline in pH from 6.8 to 4.5 and nearly a 70% loss of species richness (Vinebrooke et al., 2003). Increasing acidity and loss of DOC, however, suppressed photosynthesis in Lake 302S, suggesting that the stability in biomass may not have been sustainable under long-term high acidity conditions (see also 7.4.3.3.1).

Sediment cores from Killarney lakes suggested that decades of acidification may have caused a fundamental spatial shift in whole-lake algal community structure (Vinebrooke et al., 2002). Chronic acidification appears to have increased the dominance of metaphytic algae in shoreline habitats while shifting the algal communities of deepwater habitats towards dominance by phytoflagellates. These shifts may have been due to a reduced DOC as acidity increased, which in turn led to an increased light availability in deepwater zones. Reductions in certain acid-sensitive algal grazers (e.g., copepods, cladocerans) and the subsequent release from grazing pressure may also have played a role in algal community shifts.

Recent evidence indicates that lake acidification and related chemical and physical changes are likely to have strong impacts on the composition and growth of benthic algal communities. Impairment of this important community of primary producers is likely to be particularly strong if acidification is extreme or chronic.

6.4.2 Invertebrates

R.C. Weeber, M.F. Bowman, R.W. Brook, L. Champoux, W. Keller, D.A. Kirk, S. Légaré, S. MacPhee, D.K. McNicol, R.A. Reid, E. Snucins, and K.M. Somers

The 1997 Assessment reported acidification effects on a broad set of invertebrate taxa and communities. Lake acidification is associated with lower zooplankton and macroinvertebrate species richness and the elimination of many calcium-rich macroinvertebrate taxa. Although lake acidity is often a dominant stressor for invertebrate communities, specific responses to acidity are also influenced by lake physical characteristics, toxic metal concentrations, nutrient status, and fish presence and community composition. Fish presence has a particularly strong effect on invertebrate communities, with acidity-related elimination of fish associated with shifts in dominance to large predatory insects, acid-tolerant species and shredder rather than grazer functional groups.

In this section we summarise recent observations of acidification effects on invertebrates and review promising methods for estimating taxa- and assemblage-level responses to continued acid stress or the recovery of aquatic habitats.

6.4.2.1 Nektonic

Work summarised in the previous assessment identified pH 6 as an important threshold for several groups of biota. This was recently confirmed as a threshold for zooplankton community change by Holt et al. (2003) based on an analysis of zooplankton data collected from 47 lakes in central ON. Zooplankton richness and correspondence analysis scores were used to remove spatial and lake morphometric influences on community and lake acidity relationships with the results identifying pH 6 as a point of greatest taxonomic change (Figure 6.12).

Planktonic crustaceans have proven to be useful indicators of lake acidification and recovery, but crustaceans occupying the littoral zones of acidified lakes have only recently been considered for their potential role in understanding biological responses. Walseng and Schartau (2001) sampled planktonic and littoral crustacean species composition in Killarney ON (n=22 lakes) and Østfold, Norway (n=15 lakes) to compare species composition and the pH affinity of individual species between the two areas. They collected 83 and 69 species in Killarney and Østfold, respectively; 35 species occurred in both areas. Species ordinations were used to define, for each study area, a first Detrended Correspondence Analysis (DCA) axis that was strongly correlated with pH (correlation r^2 =0.80 and 0.72 for Killarney and Østfold, respectively) and sampled species were grouped according to their position along the axis for each area. The authors defined five species assemblages representing a gradient from acid-

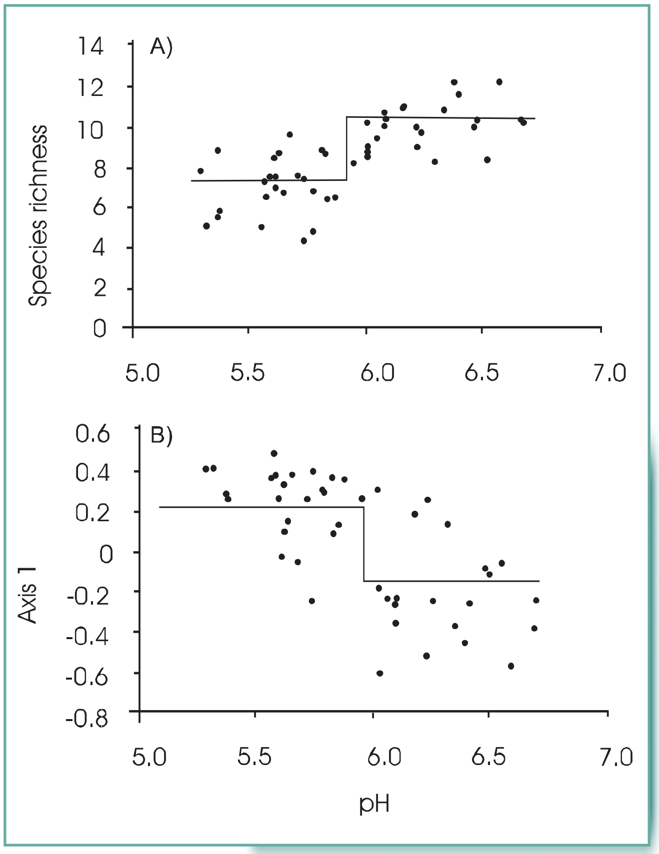

Figure 6.12: Step function plots modelling the relationship between pH and zooplankton a) species richness and b) species abundances based on correspondence analysis scores (n=47 lakes in central ON). Used with permission from Holt et al. (2003).

associated to acid-sensitive (i.e., acidic, weakly acidic, indifferent, weakly sensitive, and sensitive), noting that many of the species in common between the two study areas were located near the acid-associated end of the DCA axes. After screening for the species occurring in at least 10% of sites in a particular study area (n=54 species in each area), the full range of the DCA axes were represented, with 14 species occurring in both study areas (Table 6.5). As a further exploration of the use of littoral crustaceans as acidification recovery indicators, Walseng et al. (2003) evaluated qualitative and quantitative sampling techniques in Killarney (n=21 lakes) and Dorset (n=18), ON. They identified littoral cladocerans and copepods of potential use as lake acidification indicators and evaluated taxa with respect to variations in sampling intensity and method. They found that species richness was positively correlated with pH for both the simple qualitative and more intensive quantitative sampling methods and that regression slopes were similar between the methods (Figure 6.13). Although many species occurred across the pH gradient and were therefore poor acidification indicators, about 41 species appeared to be good candidates as acidity indicators. One species (*Acanthocylops vernalis*) was restricted to lakes of pH<6 and about 40 acid-sensitive species were common only in less acidic lakes. Of particular value for future monitoring activities was their conclusion that the two sampling protocols they employed were complementary; the methods resolved community patterns with respect to acidity but did so by sampling somewhat different species assemblages. The species richness of littoral crustaceans, their responsiveness to lake acidity, the potential for geographic similarities in species occurrence and acid-sensitivity, and the availability of both simple and intensive sampling methods suggest that this group may be a promising bioindicator for littoral habitat responses to acidification and chemical improvements.

Leeches play important roles as predators, parasites and prey in many freshwater systems and have been shown to be sensitive to pH declines. Using samples from 79 lakes in the Muskoka, Sudbury and Algoma regions, Schalk et al. (2001) evaluated the occurrence and relative abundance of leech species with regard to their potential

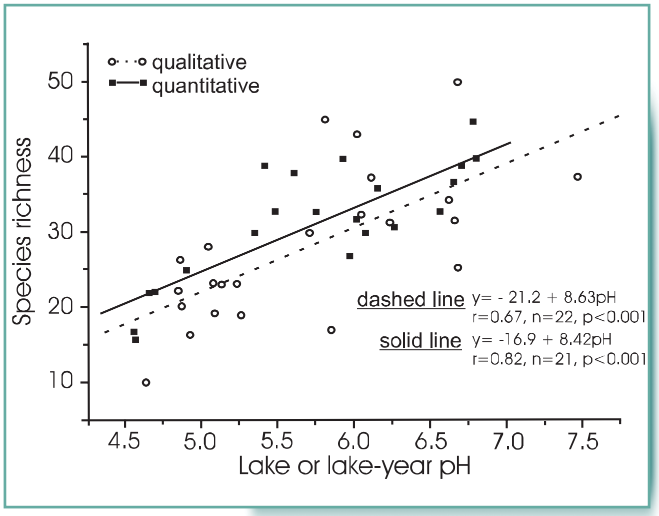

Figure 6.13: Total microcrustacean species richness in 22 Killarney lakes (northeastern ON), as sampled by qualitative and quantitative methods, regressed on lake pH. Adapted with permission from Walseng et al. (2003).

Table 6.5 Crustacean taxa occurring in at least 10% of the sites in both Østfold, Norway and Killarney, ON (n=54 for each) grouped according to their association with lake acidity. Adapted from Table 1 in Walseng and Schartau (2001), copyright 2001 Kluwer Academic Publishers and used with kind permission of Springer Science and Business Media.

	Østfold, Norway		Ontario, Canada	
	axis1	N	axis1	N
CATEGORY I (acidic)				
Acantholeberis curvirostris (O.F.M.)	3.50	14	4.55	16
Ceriodaphnia quadrangula (O.F.M.)	3.30	11		
Alona rustica (Scott)	3.23	14	3.90	8
Alona intermedia (Sars)			3.70	11
Ilyocryptus spinifer (Herrick)			3.22	7
Eucyclops prionophorus (Kiefer)			3.17	20
Orthocyclops modestud (Herrick)			3.10	10
Macrocyclops fuscus (Jur.)	2.50	14		
Ophryoxus gracilis (Sars)			2.33	42
Chydorus piger (Sars)			2.18	44
Steblocerus serricaudatus (Fisch.)	2.17	14		
Paracyclops affinis (Sars)	1.94	14	2.17	13
Alonella excisa (Fischer)	1.94	19		
Latona setifera (O.F.M.)	1.94	3	2.87	21
Alona guttata (Sars)	1.64	23		
Alona affinis (Leydig)	1.23	24	2.57	33
CATEGORY II (weakly acidic)				
Alonella exigua (Fischer)			2.01	44
Bosmina tubifen (Brehm)			1.83	9
Eucyclops neomacruroides (Dussart)			1.59	22
Macrocyclops fuscus (Jur.)			1.51	9
Alona guttata (Sars)			1.45	28
Leptodiaptomus minutus (Lillj.)			1.44	56
Bosmina longispina (Leydig)			1.23	35
Alonella nana (Baird)	1.18	28		
Acroperus harpae (Baird)	1.16	27	1.61	54
Rhynchotalona falcata (Sars)	1.13	17		
Alonella acutirostris (Birge)			1.11	25
Scapholeberis mucronata (O.F.M.)	1.11	28		
Bosmina freyi (De Melo)			1.01	45
Macrocyclops albidus (Jur.)	1.02	26	1.86	31
Chydorus piger (Sars)	1.01	6		
Alona bicolor (Frey)			1.00	16
Eucyclops serrulatus (Fisch.)	0.99	29	1.70	35
Bosmina longispina (Leydig)	0.91	30		
Polyphemus pediculus (Leuck.)	0.91	30	1.30	56
Daphnia longispina (O.F.M.)	-0.55	13		
Bosmina liederi (De Melo)			-0.57	21
Daphnia cristata (Sars)	-0.60	18		
Eucyclops speratus (Lillj.)	-0.61	10		
Epischura lacustris (S.A. Forbes)			-0.63	24
Thermocyclops oithonoides (Sars)	-0.73	18		
Diaphanosoma brachyurum (Liev.)	-0.77	11		
Disparalona rostrata (Koeh)	-0.81	6		
CATEGORY V (sensitive)				
Daphnia retrocurva (S.A. Forbes)			-0.68	9
Daphnia galeata mendotae (Birge)			-0.74	19
Skiptodiaptomus oregonensis (Lillj.)			-0.81	13
Eucyclops denticulatus (A.Graet.)	-0.95	4		
Alonopsis elongata (Sars)		0.91	30	
Eurycercus lamellatus (A.F.M.)	0.73	25		

	Østfold, Norway		Ontario, Canada	
	axis1	N	axis1	N
Acanthocyclops robustus (Sars)	0.67	12		
Chydorus sphaericus (O.F.M.)	0.67	28	1.80	52
CATEGORY III (indifferent)				
Streblocerus serricaudatus (Fisch.)			0.89	9
Daphnia catabwa (Coker)			0.68	7
Diaphanosoma sp			0.61	39
Graptoleberis testudinaria (Sars)	0.64	9		
Cyclops bicucpidatus thomasi (S.A. Forbe)			0.59	39
Alonella excisa (Fischer)			0.58	13
Bythoptrephes longimanus (Leydig)	0.58	11		
Acanthocyclops robustus (Sars)			0.57	14
Paracyclops fimbriatus poppei (Rehberg)			0.52	8
Eudiaptomus gracilis (Sars)	0.38	26		
Scapholeberis kingi (Sars)			0.38	27
Holopedium gibberum (zaddach)	0.38	20	0.75	42
Daphia ambigua (Scourfield)			0.24	24
Cyclops varicans rubellus (Lillj.)			0.21	7
Megacyclops viridis (Jur.)	0.17	7		
Cyclops scutifer (Sars)	0.12	24		
Mesocyclops leuckarti (Claus)	0.10	17		
Megacyclops gigas (Claus)	-0.05	7		
Ophryoxux gracilis (Sars)	-0.05	16		
Pleuroxus truncatus (O.F.M.)	-0.02	22		
Ceriodaphnia megops (Sars)	-0.88	3		
CATEGORY IV (weakly sensitive)				
Mesocyclops edax (S.A. Forbes)			0.18	34
Chydorus bicornutus (Doolittle)			0.13	9
Pleuroxus striatus (Schodler)			-0.05	8
Tropocyclops extensus (Kiefer)			-0.08	25
Pleuroxus hastatus (Sars)			-0.12	11
Cyclops scutifer (Sars)			-0.12	9
Sida crystallina (O.F.M.)	-0.13	22	-0.02	32
Leptodora kindti (Focke)	-0.34	13	-0.52	13
Heterocope appendicalata (Sars)	-0.34	18		
Pseudochydorus globosus (Baird)	-0.46	5		
Eucyclops denticulatus (A.Graet.)	-0.95	4		
Daphnia longirernis (Sars)			-1.03	10
Eucyclops maeruroides (Lillj.)	-1.08	3		
Alona setulosa (Megard)			-1.24	8
Ceriodaphnia pulchella (Sars)	-1.34	11		
Leptodiaptomus sicilis (S.A. Forbes)			-1.35	6
Bosmina longirostris (O.F.M.)	-1.41	10		
Camptocercus rectirostris (Schoedler)	-1.45	5		
Pleuroxus trigonellus (O.F.M.)	-1.55	3		
Bosmina coregoni (Baird)	-1.93	4		
Alona costata (Sars)	-2.24	4	-0.68	13
Limnosida frontosa (Sars)	-2.24	4		
Eucyclops macrurus (Sars)	-2.36	3		

as acidity indicators. The occurrence and abundance of some leech species were related to acidity (i.e., pH, conductivity, ANC, SO_4^{2-} and base cations) and were marginally associated with lake nutrient status (i.e., TN, TP and DOC). However, models including pH, conductivity, TN, DOC, and lake depth explained only 10-13% of the overall variance in leech relative abundance. Despite improving chemistry trends for many Sudbury area lakes, the species richness, occurrence and relative abundance of leeches in this study area declined from 1987 to 1996. Based on the low resolution of acidity-related models and the lack of relationship between trends in lake chemistry and leech community measures, the authors suggested that leeches may not be suitable indicators for chemical recovery of acidified lakes.

Open water zooplankton assemblages continue to be important for understanding the ecological effects of lake acidification and recovery (see also Section 7.4). Recent evidence reinforces pH 6 as an important threshold for changes to open water zooplankton community structure. Littoral crustaceans are also taxonomically rich, have measurable affinities across a wide range of acidity conditions, and are promising bioindicators for assessing continuing acid-stress or recovery in lake and wetland littoral zones. Although leeches are sensitive to low pH, their occurrence and relative abundance do not appear to be strongly associated with lake acidity, suggesting that these measures may not be effective as direct indicators of acidification or recovery.

6.4.2.2 *Benthic*

Benthic invertebrates are important food items for waterbirds, fish and predatory invertebrates and respond to lake acidity at both the species and community levels (see below and 6.4.2.3). Due in part to the relative ease of sampling, work with benthic invertebrates of lakes and wetlands has tended to focus on the soft sediments rather than the rocky littoral zones. However, Carbone et al. (1998) sampled benthic invertebrates from the rocky shorelines of 17 Sudbury area lakes to evaluate the utility of this group for measuring lake acidification and recovery. The 17 lakes ranged widely in acidity (pH 4.7 to 7.3) and surface area (10 to 10,000 ha) and 11 lakes contained fish; five of the seven lakes below pH 5.5 were fishless. Two of the lakes had been limed (see also Section 7.4.2). Four insect orders comprised 95% of the total insects captured. Among the mayfiles (O. Ephemeroptera), three taxa were significantly more abundant above than below pH 5.5 (Table 6.6), with *Stenonema femoratum* being the most acid-sensitive and occurring only at or above pH 5.6. In contrast, three acid-associated species of dragonfly (O. Odonata) larvae were identified, occurring in significantly greater abundance below than above pH 5.5. Similarly, three acid-associated fly (O. Diptera) taxa were observed to occur in greater abundances below pH 5.5. A direct relationship with pH was observed for only one caddisfly (O. Trichoptera) genus. Multivariate ordinations corroborated these results and also indicated that the relative abundance of a dragonfly species (*Basiaeshna janata*) was related negatively to acidity. Although the species composition differed across the pH gradient, total species richness and total abundance did not correlate with lake pH and averages of these metrics did not differ above and below pH 5.5. The authors concluded that lake acidity and fish species richness were major influences on the composition of rocky littoral benthic invertebrate communities. Acidic lakes (< pH 5.5) tended to have more of certain acid-tolerant dragonfly, diptera, and caddisfly species but also had fewer mayflies and an acid-sensitive dragonfly species.

Table 6.6 Mean insect abundance per cage for Sudbury, ON lakes above (n=10) and below (n=7) pH 5.5. Statistically significant ($p<0.05$) differences, denoted with an asterisk, were assessed using an analysis of variance comparison of mean log(x+1) insect abundance between acidity classes. Adapted with permission from Carbone et al. (1998).

Taxa		pH	
		< 5.5	≥ 5.5
O. Ephemeroptera			
	Eurylophella	0.06	0.65*
	Stenonema femoratum	0.00	11.27*
	Stenacron interpunctatum	3.07	22.02*
O. Odonata			
	Aeshna eremita	0.85*	0.00
	Aeshna interrupta	0.70*	0.02
	Leucorrhinia glacialis	2.99*	0.00
O. Diptera			
	Ceratopogonidae	4.81*	0.03
	Psectrocladius	2.72*	0.29
	Stackelbergina	0.69*	0.00
O. Trichoptera			
	Banksiola	0.30*	0.00

Proportions and other metrics quantifying the composition and dominance patterns in macroinvertebrate communities are commonly used to describe aquatic biota and estimate the impacts of pollution or other stressors. Although most frequently applied to lotic habitats (e.g., Barbour et al., 1999; Sandin and Johnson, 2000), metrics and biological indices have also been used to describe lake and wetland macroinvertebrate communities (e.g., Eriksson, 1999). These measures range in complexity from simple metrics such as taxonomic dominance and species richness to those that incorporate species composition, relative abundance and, for indices of biotic integrity, species' sensitivity to particular stressors.

Bowmans et al. (unpublished) reported temporal trends in chemistry and benthic macroinvertebrate metrics for eight nutrient-poor, acid-sensitive, headwater lakes located in Muskoka, central ON. Lakes were sampled at least monthly each year from 1988 through 2002 and trends were estimated for annual, ice-free season, averages of SO_4^{2-}, Alk, and pH (Table 6.7). Benthic macroinvertebrates were collected in October or November in at least 11 of the 15 years with five sample sites per lake, each representative of littoral substrate types (Reid et al., 1995). At each site, a ten-minute kick-and-sweep method was used along a series of transects aligned perpendicular to shore and originating at 1 m depth. Collected dipterans were classified to family and most other invertebrates were classified to order. Taxonomic richness and the numerical dominance of several taxa were calculated as a percentage of the total number of individuals sampled. Trends in chemistry and invertebrate metrics were estimated using the non-parametric Mann-Kendall test and the Sen's slope calculation (U.S.Environmental Protection Agency, 2000). Lakes were moderately acid-stressed, with mean pH values ranging from 5.58 to 6.67. Although SO_4^{2-} declined in seven of the eight lakes, Alk and pH improvements were observed in only two lakes and one lake, respectively (Table 6.7). Despite the moderate degree of acid stress relative to many other studied lakes (e.g., see Section 7.4.2) and the limited chemical improvements, two metrics responded in the direction expected for a reduction in environmental stress. The percent of mayflies increased in half of the lakes and the percent of midges (F. Chironomidae) decreased in six lakes (Table 6.7, Figure 6.14) with significant changes occurring in lakes across the acid sensitivity gradient. Mixed trends were observed in the percent of amphipods, with significant changes observed in two moderately acidic lakes (Table 6.7). The percent of molluscs changed only in the lake where declining SO_4^{2-} and improving acidity were both observed (Heney Lake, Table 6.7). Overall

Table 6.7 Mean, range and median change per year for chemical parameters and benthic macroinvertebrate metrics in eight acid-sensitive Muskoka, ON lakes sampled in 1988 – 2002. Statistically significant ($p<0.05$) and marginally significant ($0.05<p<0.10$) trends are indicated by an asterisk and underline, respectively. Lakes are arranged from left to right by increasing mean pH.

Parameter / Metric	All lakes (n = 8) Mean (min., max.)	Crosson	Plastic	Hamer	Clear	Heney	Westward	Harp	BlueChalk
		median change per year (Sen's slope)							
SO_4^{2-} (mg/L)	5.8 (3.2, 7.9)	-0.23*	-0.13*	-0.12	-0.16*	-0.21*	-0.10*	-0.12*	-0.10*
Alk (mg/L)	1.8 (0.1, 4.5)	-0.01	-0.01	0.04	0.01*	0.08*	-0.02	-0.02	0.00
pH	6.0 (5.5, 6.8)	0.01	-0.01	0.04	0.01	0.03*	0.02	0.00	0.01
% Chironomids	28.8 (1.0, 78.8)	-2.04*	-4.34*	-1.46*	-1.17	-4.36*	-2.32*	-1.91	-2.13*
Taxa richness	14.2 (8, 18)	-0.60*	-0.25*	-0.36	-0.21*	-0.29*	-0.20	-0.18*	-0.33*
% Mayflies	19.8 (1.3, 67.3)	1.60*	2.36*	2.41*	0.31	1.27	0.53	0.87*	1.23*
% Dominant taxon	42.8 (25.3, 78.8)	-0.23	-2.56*	1.19	-0.62*	-3.25*	-0.24	-1.09*	0.47
% Amphipods	28.6 (2.4, 54.9)	-0.33	0.86	-1.04	-0.62	-0.48	2.32*	-1.95*	0.99
% Insects	61.8 (28.1, 91.6)	0.41	-0.35	1.25	0.58	-1.30	-1.91*	0.49	-0.73
% Mollusks	4.9 (0, 43.1)	-0.05	-0.20	-0.05	-0.03	0.14*	-0.17	0.75	-0.04
Mean pH		5.58	5.70	5.81	5.83	5.96	6.28	6.31	6.67

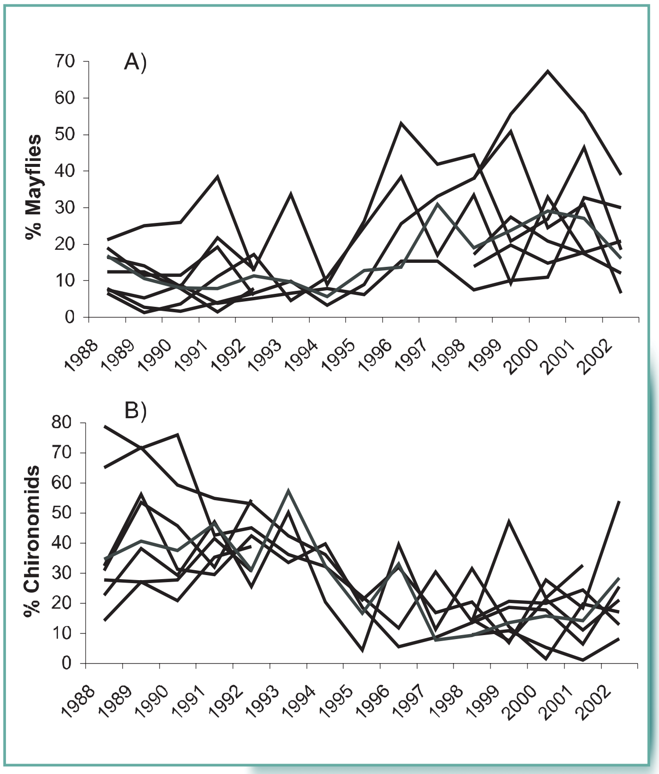

Figure 6.14: Change over time in the percent of (A) mayfly and (B) chironomid taxa in eight acid-sensitive Muskoka, ON lakes from 1988-2002.

taxonomic richness declined in six lakes due primarily to a reduction in abundance of several acid-tolerant dipterans.

6.4.2.3 Macroinvertebrates as waterfowl foods

Macroinvertebrates are important components of breeding waterfowl diets and are particularly important for nesting females and their young (Krapu and Reinecke, 1992; Bendell and McNicol, 1995a). Wetland breeding waterfowl and ducklings often prey on conspicuous macroinvertebrates in both nektonic and benthic habitats. A collective treatment of the effects of acidity related stressors on large benthos and nekton, therefore, provides a tool for understanding how the major animal component of breeding waterfowl food webs responds to acidification and chemical recovery. Waterfowl species can adjust their diets to make use of abundant prey, providing some flexibility in their response to changes in their macroinvertebrate prey base (Krapu and Reinecke, 1992). This flexibility is constrained, however, by their foraging efficiency (Bendell and McNicol, 1995a) and reliance on prey which are difficult to catch or nutritionally suboptimal; reliance on these prey is likely to have physiological costs (Krapu and Reinecke, 1992; Scheuhammer et al., 1997).

The importance of fish presence to the composition and relative abundance of macroinvertebrates is well documented; hence, accounting for fish is clearly important for estimating lake acidity effects on invertebrates (e.g., McNicol et al., 1995a). Additional factors that influence the structure of macroinvertebrate communities may include the functional composition of fish communities. For example, the predation pressures exerted by small-gaped minnows (e.g., dace (*Phoxinus*) species) and their allies differ from the pressures exerted by the larger-gaped predators such as yellow perch (*Perca flavescens*) and white sucker (*Catostomus commersoni*) (McNicol and Wayland, 1992; Bendell and McNicol, 1995a).

Benthic and nektonic macroinvertebrate data were combined to broadly characterise the macroinvertebrate prey available to breeding waterfowl in four acid-sensitive regions of ON (Muskoka, Sudbury, Algoma, and ELA) and to evaluate these resources with respect to fish community structure and lake chemical and physical attributes (Weeber et al., in prep.c). Macroinvertebrate data from 1987-2003 samples were screened and counted. Counts for some related taxa were grouped to define a dataset of reliably and consistently sampled and identified taxa. Two approaches were used to summarize acidity effects in the context of lake fish status and other potentially important chemical and physical lake attributes. Simple metrics of individual taxa dominance and species richness were used to focus on taxonomic groups with particular sensitivity to lake acidity or fish presence and to provide estimates of these and other habitat-related effects. Ordinations were used to evaluate acidity and other habitat effects while explicitly and simultaneously considering all macroinvertebrate taxa (Weeber et al., in prep.c).

Benthic and nektonic macroinvertebrate counts were available for 166 lakes in four regions of ON (Muskoka, Sudbury, Algoma, ELA), with approximately 39 percent of lakes (n=64) sampled in multiple years during the 1987 – 2003 period (Weeber et al., in prep.c). Portions of these data have been summarised elsewhere (e.g., McNicol et al., 1995a; Doka et al., 2003) and in the 1997 Assessment (Jeffries, 1997). Lakes were classified as fishless if fish were never captured and were classified as large-gaped if any one of several species had been sampled which had large mouth gapes according to Scott and Crossman (1973). Other lakes with fish were classified as small-gaped fish lakes. The large-gaped lake group was strongly dominated by yellow perch, white sucker and creek chub (*Semotilus atromaculatus*). Small-gaped lakes were dominated by *Phoxinus* dace species, pearl dace (*Semotilus margarita*) and brook stickleback (*Culaea inconstans*), with a moderate level of occurrence of fathead minnow (*Pimephales promelas*). A full suite of data on selected chemical attributes (pH, SO_4^{2-}, DOC, Ca^{2+} and TP) and morphological or landscape characteristics (lake area, shoreline complexity, riparian area, lake depth, and the number of islands, streams and nearby wetlands), along with fish status were available for 131 lakes (Table 6.8).

Regional level mean values were similar for pH, TP, lake area and depth, and the number of wetlands within 500m. Concentrations of SO_4^{2-} were highest in Sudbury and lowest in the ELA, and some regional differences were also observed for DOC and Ca^{2+}. Lakes in Muskoka, Sudbury and Algoma tended to have similar shoreline complexity and proportions of riparian area but both attributes were lower in the ELA set of lakes. Relative to the other study areas, more Sudbury lakes were classified as either fishless or large-gaped lakes. Counts for 299 taxa were available for analysis, with the majority classified to the species (n=182 taxa) or genus (n=111) level and the remainder to family (n=3) or order (n=3) level. Seventy-three invertebrate taxa were globally common, occurring in at least 10 percent of lakes in the four study areas (Table A6.1).

Table 6.8 Means and 95% confidence limits of lake-level median chemistries and lake morphological and landscape attributes for 131 ON lakes in four regions (Muskoka, Sudbury, Algoma, Experimental Lakes Area) sampled for macroinvertebrates, 1987-2003. Different letters within rows indicate differences between mean values based on non-overlapping confidence limits. The number and percent of lakes assigned to one of three fish classes is also shown. Shoreline development index (SDI) was calculated as (Shoreline length)/(2*SquareRoot(π*Lake area)).

	Muskoka (n = 28)	Sudbury (n = 63)	Algoma (n = 35)	ELA (n = 5)	All (n = 131)
pH	5.87 (5.741, 5.999)a	5.81 (5.598, 6.017)a	6.03 (5.840, 6.212)a	6.29 (5.865, 6.711)a	5.90 (5.780, 6.015)
SO_4^{2-} (mg/L)	5.22 (4.898, 5.545)a	8.45 (8.055, 8.847)b	4.22 (3.911, 4.522)c	2.01 (1.173, 2.854)d	6.38 (5.964, 6.803)
DOC (mg/L)	5.08 (4.324, 5.828)a	5.08 (4.493, 5.673)a	7.97 (6.893, 9.043)c	7.39 (5.059, 9.715)ac	5.94 (5.448, 6.432)
Ca^{2+} (mg/L)	1.65 (1.506, 1.797)a	3.31 (2.752, 3.861)b	2.28 (1.889, 2.670)c	1.50 (0.967, 2.026)ac	2.61 (2.297, 2.922)
Total phosphorous (µg/L)	6.71 (5.797, 7.613)a	6.20 (5.672, 6.732)a	6.49 (5.877, 7.099)a	6.68 (4.920, 8.440)a	6.40 (6.041, 6.767)
Lake area (ha)	6.6 (5.43, 7.84)a	7.7 (5.43, 9.87)a	7.1 (5.93, 8.16)a	6.9 (4.24, 9.64)a	7.3 (6.11, 8.38)
Shoreline development index	1.9 (1.69, 2.02)a	1.9 (1.72, 2.10)a	1.8 (1.67, 1.99)a	1.5 (1.24, 1.66)b	1.9 (1.75, 1.97)
Percent riparian area	24.4 (17.0, 31.9)a	26.5 (22.2, 31.0)a	31.2 (24.6, 37.7)a	2.2 (0, 6.39)b	26.4 (23.1, 29.7)
Depth (m)	9.4 (7.51, 11.4)a	7.1 (5.83, 8.45)a	7.4 (4.55, 10.3)a	4.7 (0.16, 9.29)a	7.6 (6.52, 8.70)
# of islands	0.4 (0.04, 0.75)a	1.3 (0.86, 1.81)b	0.5 (0.18, 0.74)a	0.4 (0, 1.18)a	0.9 (0.60, 1.13)
Total # of streams	2.0 (1.42, 2.51)ab	1.3 (1.10, 1.50)b	2.2 (1.63, 2.83)a	1.2 (0.81, 1.59)b	1.7 (1.46, 1.92)
# wetlands within 500m	1.8 (1.44, 2.20)a	2.4 (2.05, 2.72)a	1.9 (1.39, 2.44)a	2.2 (1.24, 3.16)a	2.1 (1.90, 2.36)
No fish	12 (42.9%)	23 (36.5%)	11 (31.4%)	1 (20.0%)	47 (35.9%)
Small gaped fish only	7 (25.0%)	9 (14.3%)	11 (31.4%)	4 (80.0%)	31 (23.7%)
Large gaped fish	9 (32.1%)	31 (49.2%)	13 (37.2%)		53 (40.4%)

6.4.2.3.1 Macroinvertebrate metrics

Simple metrics relating particular invertebrate taxa or groups of taxa to environmental stressors of interest can provide efficient measures of biotic responses to changes in stress. Counts of nektonic and benthic macroinvertebrates were used to calculate two general types of metrics for individual lake-years and to generate lake-level averages. The proportional representation of several families and orders, and one class, were calculated by expressing the counts at each classification level as a proportion of all individuals captured in each year. Community metrics including several calculations of taxonomic richness and diversity (Shannon-Wiener, Simpson's) were also calculated. Lake-level averages for those metrics that were well distributed (e.g., not based on extremely rare taxa) were evaluated to identify those with broad geographic relevance and with easily measurable responses to acidity and other acidity-related lake attributes.

Multiple regression models were fit for data collected from Muskoka, Sudbury and Algoma (habitat data available for 151 lakes sampled 1987-2003) and from ELA (5 lakes sampled in 2002). Separate regression analyses were also conducted for 33 lakes along the north shore of the St. Lawrence River in QC sampled between 2001 and 2003. Relatively few QC lakes were fishless (n=4, 12% versus n=52, 33% for ON lakes). Regression analyses were used to test for the effects of the terms in the full model statement (i.e., fish presence, pH, DOC, lake surface area and shoreline complexity) and, for the more intensively sampled Muskoka, Sudbury and Algoma lakes the analyses controlled for geographic region. Regressions were screened to include only results for those terms with good model fit (i.e., Pearson Chi-square dispersion estimates between 0.7 and 3.0).

After controlling for the other model terms, four types of responses by macroinvertebrate metrics to fish presence and pH were observed (Table 6.9). For the ON data, 14 metrics showed pH effects after accounting for a statistically significant positive or negative effect of fish presence. Five metrics responded to fish presence but showed no additional pH effects. Three metrics responded to pH but did not show additional fish presence effects. Finally, four metrics showed statistically ambiguous relationships with both fish presence and pH.

Four types of responses were also observed for metrics calculated for macroinvertebrates collected from the southern QC lakes. Two metrics, the proportions of sampled invertebrates that were predaceous diving beetles (dytiscids) or backswimmers (notonectids), occurred in the fishless, low pH group for both the ON and QC datasets (Table 6.9). An additional 11 metrics calculated for the QC data showed responses to fish presence and/or pH but the specific effects differed from the ON dataset, due perhaps to the smaller proportion of fishless lakes in the QC dataset. Given that low pH lakes are often fishless, all but one of these 11 metrics showed acidity effects consistent with those observed for the ON lakes. Although the pH effect was marginally significant (p=0.14), dragonfly and damselfly richness (Rich_Odonata) tended to be greater in high pH QC lakes but was highest in fishless ON lakes (p<0.0001). Several of the calculated metrics are potentially useful as indicators of waterfowl food web responses to lake or wetland acidification and recovery, particularly if the fish status of the waterbody is known. With further refinement of the estimates of effect sizes (e.g., through more intensive modelling), these metrics could be used to identify efficiencies in data collection and to help predict waterfowl food web support relative to emission and water chemistry scenarios.

6.4.2.3.2 Macroinvertebrate ordinations

The dataset described above (Section 6.4.2.3) was used to evaluate macroinvertebrate responses to lake acidity along with fish gape-size and other habitat effects (Weeber et al., in prep.c). A Detrended Correspondence Analysis (DCA) based on the macroinvertebrate composition and relative abundance indicated that sampled lakes in the Muskoka, Sudbury and Algoma regions of ON (n=28, 69 and 64 lakes, respectively) were similar in terms of the invertebrates sampled (Figure 6.15). Although zoogeographic differences are a possible cause, the somewhat distinct position of four ELA lakes in the DCA may have also been due to the fact that the single sampling of the five ELA lakes may have been more subject to annual effects than the more intensively sampled lakes in other regions. Taxa positively associated with the left side of the ordination included *Valvata tricarinata* (C. Gastropoda), *Halipus* (O. Coleoptera), *Orconectes propinquus* (O. Decapoda) and *Libellula incesta* (O. Odonata) and those with the right side included

Table 6.9 Summary of observed fish presence and pH effects for macroinvertebrate metrics calculated using data from ON lakes sampled between 1987 and 2003 in four areas (Muskoka, Sudbury, Algoma, Experimental Lakes Area) and QC lakes sampled between 2001 and 2003 (north shore of St. Lawrence River). The table summarises the directions of statistically significant fish presence and pH effects after control for geographic location (ON data only) and lake DOC, area and shoreline complexity. The criteria for classifying effects as statistically significant ($p<0.05$) was relaxed ($p<0.1$) for the smaller QC data source in an effort to compare response patterns between data sources. Metrics are grouped by column according to the positive (+) or negative (–) multiple regression slopes on fish presence and pH effects. Metrics represent taxonomic richness (i.e. "Rich_") or the proportion (denoted with a "p") of all individuals captured within a particular family or other classification. Indices at the order or family level are preceded by the order to which they belong (i.e. A=Amphipoda, H=Heteroptera, C=Coleoptera, O=Odonata, E=Ephemeroptera, T=Trichoptera, D=Diptera) or at the Class level (i.e. Biv=Bivalvia).

ata source	Fish presence effects						No observed effects of fish presence		
	pH effect				No observed pH effect		pH effect		No observed pH effect
	Fish (—)		Fish (+)		Fish (—)	Fish (+)			
	pH (—)	pH (+)	pH (—)	pH (+)			pH (—)	pH (+)	
ON = 156 lakes)	H-pCorixidae H-pNotonectidae C-pDytiscidae	Rich_Families pCrustacea A-pAmphipoda	O-pOdonata O-pCorduliidae C-pGyrinidae	pGastropoda Biv-pPisidiidae Biv-pPlanorbidae E-pEphemeroptera E-pCaenidae	Rich_Insecta Rich_Odonata D-pCeratopogonidae	A-pCrangonyctidae H-pGerridae	O-pLibellulidae T-pPhryganeidae	A-pHyalellidae	Rich_Heteroptera O-pLestidae T-pLeptoceridae T-pLimnephilidae
QC n = 33 lakes)	C-pDytiscidae H-pNotonectidae D-pCeratopogonidae	Biv-pPlanorbidae	Biv-pPisidiidae	A-pAmphipoda	C-pGyrinidae	pGastropoda		Rich_Families Rich_Ephemeroptera Rich_Odonata pCrustacea E-pEphemeroptera E-pCaenidae	Rich_Coleoptera Rich_Heteroptera O-pOdonata O-pLestidae O-pCorduliidae H-pGerridae H-pCorixidae T-pHydroptilidae T-pLeptoceridae T-pLimnephilidae

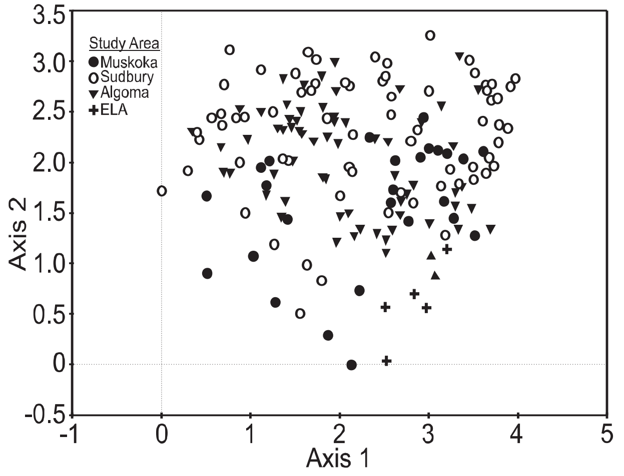

Figure 6.15: Detrended Correspondence Analysis site ordination based on average macroinvertebrate counts for lakes sampled between 1987 and 2003 in the Muskoka (n=28 lakes), Sudbury (n=69), Algoma (n=64) and Experimental Lakes Area (n=5) regions of ON.

Ptilostomis ocellifera (O. Trichoptera), *Llybius* (O. Coleoptera), *Sphaerium occidentale* (C. Bivalvia) and *Ranatra fusca* (O. Heteroptera). On axis 2, positively associated taxa were *Gammarus* (O. Amphipoda), *Haliplus connexus* (O. Coleoptera), *Graphoderus liberus* (O. Coleoptera), *Peltodytes* (O. Coleoptera) and *Lestes dryas* (O. Odonata), and negatively associated taxa included *Orthotrichia* (O. Trichoptera), *Simocephalus* (O. Cladocera), *Ferrissia fragilis* (C. Gastropoda), and *Choroterpes* (O. Ephemeroptera).

The 131 lakes with available environmental data, along with the average counts for 287 macroinvertebrate taxa, were entered into a Canonical Correspondence Analysis (CCA) to evaluate the importance of fish status and other lake attributes to macroinvertebrate communities, and to identify taxa with particularly strong affinities for acidity, fish or other habitat variables. Forward selection was used to assign statistical significance ($p<0.05$) to explanatory variables. In an effort to connect the results of this analysis with an intensive modelling of waterfowl habitat associations, the variables included in the CCA to represent chemical, fish and habitat conditions were the same as those described in Section 6.4.4.2 (see also Weeber et al., in prep.a). After controlling for study region, a partial CCA identified two major gradients influencing macroinvertebrate communities. The first CCA axis represented a gradient from fishless to small-gaped to large-gaped fish lakes, a chemical gradient of increasing pH and Ca^{2+}, and increasing lake area (Area) and depth (Depth) (Figure 6.16). The second CCA axis had negative loadings for pH, Ca^{2+}, TP, DOC and percent riparian area (PRiparian), and positive loadings for lake area, depth and the number of nearby wetlands (NWet500m). The statistically significant terms in the ordination were lake pH (Lamda=0.2, p=0.001), Ca^{2+} (0.1, 0.002), TP (0.07, 0.016), surface area (0.12, 0.001), and small- and large-gape fish classes (SmGape: 0.1,0.001 and LgGape: 0.27, 0.001, respectively) (Figure 6.16).

Among the globally common taxa (Table A6.1), the CCA suggested two groups responsive to lake acidity and tolerant of fish. Taxa with a strong affinity for higher pH and tolerant of fish presence included three of the four common snail taxa (*Gyraulus* spp., G. *deflectus* and *Helisoma anceps*) and one common mayfly genus (*Siphlonurus*) (Figure 6.16: acid/fish1). Taxa with a moderate affinity for higher pH and also tolerant of fish presence included an amphipod (*Hyallela azteca*), a caddisfly genus (*Limnephilus*), one water strider species (*Trepobates inermis*), two odonates (*Leucorrhinia intacta* and *Enallagma hageni*), three mayfly taxa (*Caenis* spp, C. *diminuta* and C. *youngi*), and two clam taxa (the Pisidiid family and *Musculium partumeium*) (Figure 6.16, inset: acid/fish2).

Two groups of common taxa were associated with fishless conditions but with some variation in their tolerance of low pH conditions. The taxa associated with low pH, fishless conditions (Figure 6.16, inset: acid/fish3) included backswimmers (*Notonecta* spp. and N. *undulata*), beetles (*Hydroporus* and *Coptotomus* spp.), dragonflies (L. *glacialis/hudsonica* combined), and a caddisfly (*Triaenodes*). The location of several other taxa suggested their relative abundance was strongly influenced by the absence of fish but very little by pH (i.e., near the pH vector origin in Figure 6.16, inset: fish1). This group included several large conspicuous beetles (*Graphoderus*, *Dystiscus*), true bugs (Hemiptera: Corixidae spp., *Sigara*, *Buenoa*, and N. *insulata*) and a damselfly genus (*Lestes*).

Two groups of macroinvertebrate taxa displayed strong affinities in the CCA for lakes assigned a particular fish gape size but had only weak associations with lake

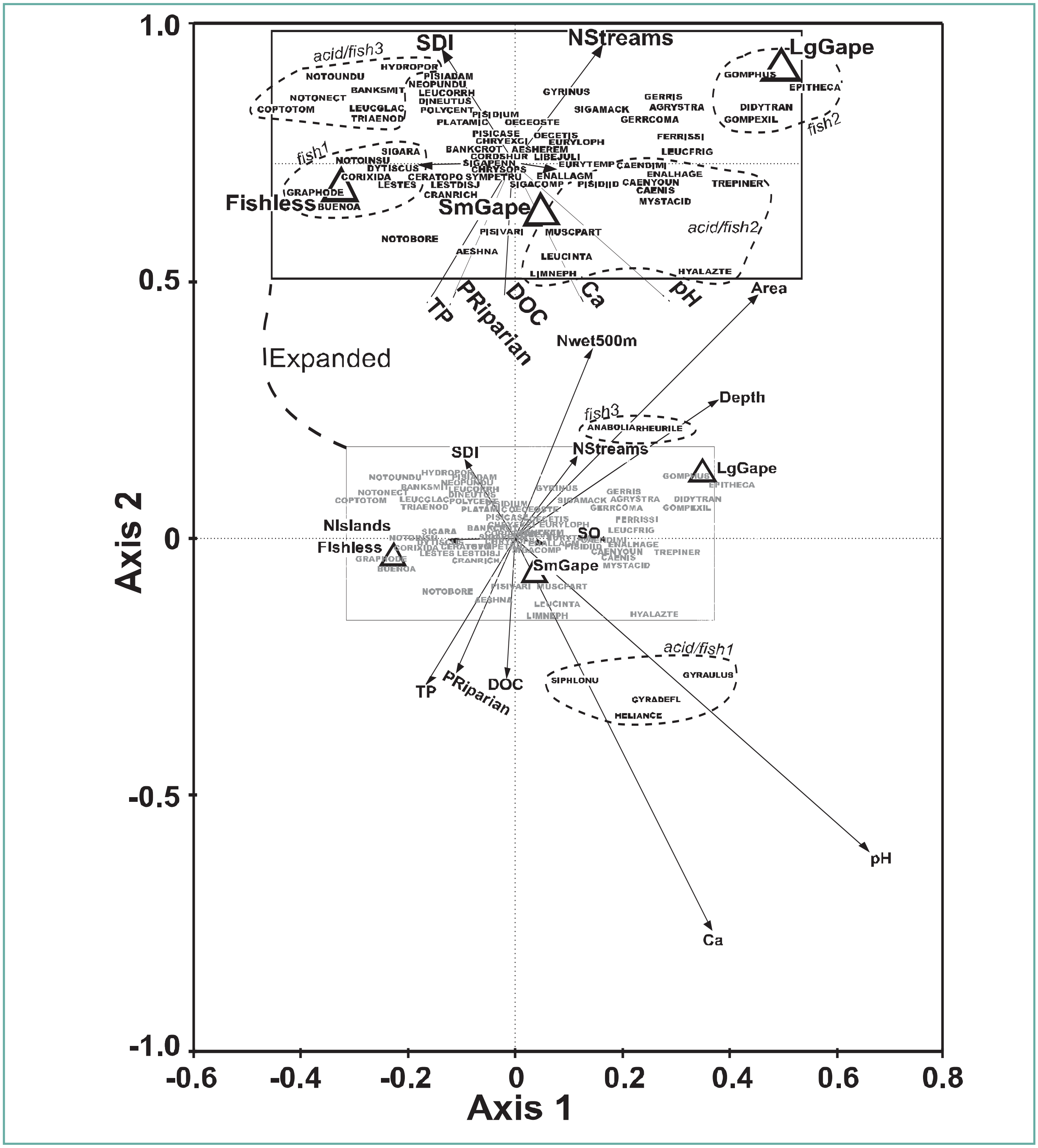

Figure 6.16: Partial Canonical Correspondence Analysis taxa ordination for 131 lakes sampled during the period 1987 - 2003 in the Muskoka, Sudbury, Algoma and Experimental Lakes Area of ON. Although the ordination space was defined using 287 taxa, only those taxa occurring in at least 10% of lakes are shown to improve the figure clarity. Labelled polygons refer to groups of taxa discussed in the text; polygon boundaries were arbitrarily drawn. The ordination was controlled for geographic region and was based on average macroinvertebrate counts and median values for explanatory variables. The statistically significant terms were lake pH, Ca^{2+}, TP, surface area, and small- and large-gape fish classes. The vector labels for the number of islands and SO_4^{2-} were removed from the left and right of the origin, respectively, to improve the clarity of the figure inset. See Table 6.8 for details on explanatory variables and Table A6.1 for macroinvertebrate taxa codes, classification and occurrence summaries.

acidity. Four dragonfly taxa showed a tolerance for the presence of large-gaped fish and minimal association with pH (*Gomphus* spp., *G. exilis*, *Epitheca* spp., and *Didympops transversa*) (Figure 6.16, inset: fish1). A caddisfly (*Anabolia* spp.) and water strider (*Rheumatobates rileyi*) were also tolerant of large-gaped fish presence but displayed an affinity for larger lakes (Figure 6.16: fish2).

Generally, the macroinvertebrate community is likely to be most taxa-rich in fishless and small-gaped fish lakes (Figure 6.16; McNicol and Wayland, 1992) but both fish status and acidity are important influences on macroinvertebrate dominance patterns and taxonomic composition (see also, McNicol and Wayland, 1992; Bendell and McNicol, 1995b). Fishless lakes are more likely to have macroinvertebrate communities dominated by conspicuous taxa with certain true bugs, beetles and dragonflies dominating in low pH conditions and other bug and beetle taxa, along with Lestid damselflies, tending to be more numerous across a wider range of pH. Lakes with fish which are not strongly acidic (e.g., approximately pH$\geq$6) are likely to be dominated by a mix of taxa including certain molluscs, mayflies, dragonflies, caddisflies and particular amphipod and water strider species. Among lakes with fish, the distinct effects of small- and large-gaped fish on the macroinvertebrate community may be due to several attributes of large-gaped species including the wider range of prey sizes available, shifts in prey base associated with increasing body size, and their flexibility in feeding in either benthic or nektonic habitats (Scott and Crossman, 1973; Saint-Jacques et al., 2000; Sherwood et al., 2002).

Although the acidity relationships of many taxa were modified by the inclusion of other habitat attributes in the CCA model, the pH responses of several taxa appeared to be robust to the simultaneous consideration of acidity, other environmental variables and geographic region. Because these acidity responses remained after accounting for these other influences, these taxa are likely to be particularly useful bioindicators for estimating the quality of waterfowl food webs in the small, acid-sensitive lakes and wetlands used by breeding ducks. Further work to assess these relationships in other regions would extend the utility of these taxa in assessing the food base for waterfowl and other macroinvertebrate predators.

Recent evidence confirms that lake and wetland acidification affects the composition and relative abundance of invertebrate communities. Zooplankton of open water and littoral habitats are good illustrations of the taxonomic diversity of invertebrate communities and their responsiveness to aquatic chemical conditions. Several aquatic macroinvertebrate taxa respond to acidity in similar ways across studies, geographic regions and analytical approaches. Fish presence and fish gape size have strong influences on invertebrate community structure and modify invertebrate responses to acidity and other habitat attributes. General acidity responses included an association with high pH conditions for some mayflies, molluscs and amphipods. Groups with taxa resistant to low pH conditions included dipterans, dragonflies, true bugs and beetles. Responses by individual species or genera, however, provide the strongest resolution on community level effects and the consequences for higher trophic levels.

6.4.3 Freshwater fish

R.C. Weeber, R.W. Brook, and D.K. McNicol

Freshwater fish communities in acid sensitive lakes are ecologically important in terms of their influence on macroinvertebrates, as a food source for piscivorous fish, birds and other wildlife, and as a resource base for recreational fishing. Large regions of acid-sensitive landscape in southeastern Canada contain watersheds with high fish species richness, particularly in ON (Chu et al., 2003). Many fish species are sensitive to acidification and responses to increased acidity often include lower recruitment and growth rates, increased accumulation of toxic metals, and impaired anti-predator responses. The 1997 Assessment reported acidity-related reductions in fish species richness in lakes across southeastern Canada (see also, Doka et al., 2003). Although fish responses to acidity varied somewhat geographically and lake size and DOC were important modifiers, pH 5.9 was identified as a generally optimal acidity level for the largest number of fish species and pH 5.0 as an approximate lower threshold for many species. The probability of occurrence of several fish species (i.e., northern pike (*Esox lucius*), pumpkinseed (*Lepomis gibbosus*) and brook trout (*Salvelinus fontinalis*)) increased with increasing pH, although other factors such as lake area and average air temperature were also important.

This section summarises a portion of the recent work pertaining to acidification effects on freshwater fish. The majority of recently collected, available and relevant data for freshwater fish relates to sport fish, recovery of acidified ecosystems (i.e., concurrent fish and chemistry changes) or both (see Sections 7.4.3.3.3 and 7.5). The work presented in this section was based entirely on data collected in Ontario because, except for the information summarised in the next chapter, there were no data pertaining to freshwater fish and acidification which were more recent than those contained in Doka et al. (2003).

Data on typical waterbird prey fish (i.e., small perch (*Perca flavesens*), suckers, cyprinids and allies) in small, primarily headwater lakes and wetlands in three regions in ON (Muskoka, Sudbury, Algoma, n= 591 lakes) were available for the sample years 1981-2002 (see Bendell and McNicol, 1995b). Sampled lakes were moderately acidic (median pH=5.9, range=4.3 to 7.5) and small (median size=4.3 ha, range=0.2 to 112.4), with the majority sampled in a single year (n=420, 71.3%). Lakes were classified as fishless only if fish were never observed otherwise lakes were identified as with fish. Logistic regressions were used to update and refine models relating the probability of small fish occurrence with respect to lake chemical and physical characteristics. Information-theoretic model selection and averaging techniques (Burnham and Anderson, 2002) were used to identify a parsimonious model. Multiple logistic regression analysis was used to estimate the effects of selected explanatory variables (see also 6.4.4.2; Weeber et al., in prep.a). Modelling results indicated a higher probability of small fish occurrence with increased lake size, pH, DOC or Ca^{2+} concentrations and lower predicted occurrence with high TP or Al^{3+} levels (Table 6.10). Similar results relating lake size, DOC and pH to fish occurrence were previously observed for these lakes (McNicol, 2002; Doka et al., 2003) as were positive associations with Ca^{2+} (Bendell and McNicol, 1987) and many of these variables have proven useful for other efforts to predict fish community composition (e.g., Olden, 2003). However, a curvilinear effect of pH and the importance of Al^{3+}, Ca^{2+} and TP have not been previously reported for these lakes. When DOC and pH effects are examined together (Figure 6.17), the curvilinear effect of pH on the probability of fish occurrence tends to occur at moderate and lower DOC values. For pH values above pH ~5, fish occurrence is likely to increase with increasing

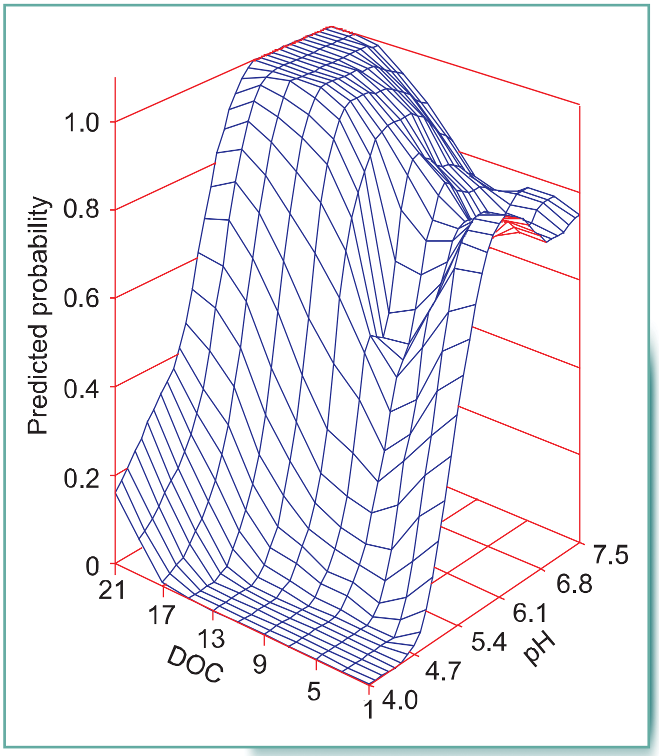

Figure 6.17: Predicted probability of small fish occurrence in small lakes and wetlands in Muskoka, Sudbury and Algoma regions of ON, expressed relative to lake DOC concentrations (mg/L) and pH.

Table 6.10 Parameter estimates, 95% confidence limits, and model concordance for logistic regression models predicting the presence of small fish (cyprinids, yellow perch and white sucker) for small lakes and wetlands in the Muskoka, Sudbury and Algoma regions of ON (n=591 lakes).

Constant	pH	pH^2	DOC	Lake area	Ca	TP	Al	Percent concordance
-105.3	35.14	-2.92	0.35	0.04	0.53	-0.27	-0.01	86.6
(-140.73, 69.82)	(23.139, 47.131)	(-3.949, -1.896)	(0.230, 0.471)	(0.013, 0.075)	(0.209, 0.846)	(-0.358, -0.176)	(-0.013, -0.004)	

DOC. As illustrated in both the previous and following Sections (6.4.2 and 6.4.4) the fish status of acidified and recovering lakes and wetlands is a very important contributor to the response of aquatic invertebrates and breeding waterbirds. Additional data on the presence and composition of small fish communities in other acid sensitive regions of eastern Canada would provide the means to refine and geographically extend modelling results. Along with efforts to restore and manage freshwater sport fish populations (see 7.5), improved estimates of small fish responses to the acidification and recovery of small lakes and wetlands would enhance our ability to understand and predict biological responses to acidifying emissions controls (see 7.6.3.2.1).

6.4.4 Breeding waterbirds

R.C. Weeber, R.W. Brook, N. Burgess, L. Champoux, D. Masse, and D.K. McNicol

Ducks, loons, herons and gulls (hereafter, waterbirds) tend to respond to lake acidification through the indirect influences of acidity on the availability and quality of their foods and through changes to their habitats. The 1997 Assessment identified acidification effects on food web structure, specifically on fish communities, as a major pathway by which acidification effects were transferred to breeding waterbirds. Modelling indicated that acidification alone could not sufficiently explain the variation in habitat use for many waterbirds and that acidification responses were influenced by other wetland chemical and physical attributes (e.g., DOC, TP, wetland size) or with factors not directly related to acidification (e.g., weather, winter mortality, predation). The previous assessment summarized the strong relationships between lake acidity and Common Loon breeding success, with food chain disruption and bioaccumulation of toxic metals, such as mercury, implicated in lower chick production in acidified systems. Here, we summarise observed temporal trends in breeding waterbird pair counts and productivity measures; present modelling results estimating the associations of waterbirds with the chemical, physical and fish status attributes of their breeding lakes and wetlands; and review the impacts of acidification-related mercury contamination on waterbirds and their food webs.

6.4.4.1 *Temporal trends*

6.4.4.1.1 Breeding pairs

Temporal trends in waterbird pairs breeding in acid sensitive landscapes help provide context for observations of responses to the acidity of their habitats. Trends were analyzed for breeding waterbird data collected by: surveys for Common Loons (*Gavia immer*) in La Mauricie National Park, QC; waterbird breeding pair surveys conducted as part of the CWS – Ontario Region Acid Rain Biomonitoring Program in the Muskoka, Sudbury and Algoma areas in ON (McNicol et al., 1996); the volunteer Canadian Lakes Loon Survey (CLLS) (McNicol et al., 1995b); and the waterbird breeding pair surveys conducted in eastern Canada as part of the Black Duck Joint Venture of the North American Waterfowl Management Plan (Ross, 1985; North American Waterfowl Management Plan, 1986). Results from these analyses show positive or no discernable trends in breeding pairs for most common waterbird species.

Aerial and ground-based survey data from 76 lakes in La Mauricie National Park, QC were available for each year between 1987 and 2002. The surveyed lakes tended to be moderately acidic (mean pH=6.08, range=5.45 to 6.85) with an average surface area of 54 ha (range=2.1 to 396.2 ha). Linear regression indicated there was no observable trend in the number of Common Loon pairs establishing territories (mean=25.2, range=18 to 32) or the number attempting to breed (mean=14.4, range=11 to 20) (Masse and Champoux, 2003). However, more extensive aerial surveys of waterbird pairs in the Muskoka, Sudbury and Algoma areas of ON (respectively, 1988-2002, n=226 lakes; 1993-2002, n=156; 1989-2001, n=234) provide evidence of trends for several waterbirds, including the Common Loon and Common Merganser (*Mergus merganser*) (Brook et al., unpublished). Average annual rates of change, along with their 95% confidence intervals, were calculated for counts of piscivores and other waterbirds in the three ON regions using the Estimating Equations (Link and Sauer, 1994) module in the WILDSPACE Decision Support System (Wong et al., 2003). When data were pooled regionally and Common Loon and Common Merganser considered together as a piscivore guild, the greatest rate of increase for pair counts occurred in the heavily damaged but chemically recovering Sudbury area (11.7% annual increase, 95%CI=6.4-17.3). Lower rates of increase for piscivore pairs occurred in Algoma (3.7%, 95%CI=1.9-5.6) and Muskoka (3.3%, 95%CI=1-5.7). Diving duck (Hooded Merganser (*Lophodytes cucullatus*), Common Goldeneye (*Bucephala clangula*), Ring-necked Duck (*Aythya collaris*)) pair counts also increased at the greatest rate in the Sudbury area (4.8%, 95%CI=1.2-8.5). Diving ducks also increased in Algoma (2.4%, 95%CI=1.2-3.7) but there was no trend in Muskoka (-0.3%, 95%CI=-2.9-2.5). Dabbling duck (Mallard (*Anas platyrhynchos*), American Black Duck (*Anas rubripes*), and Wood Duck (*Aix sponsa*)) pair counts increased in Algoma (6.7%, 95%CI=3.7-9.7), but trends for dabblers in Sudbury (1%, 95%CI=-6.2-8.7) and Muskoka (2.6%, 95%CI=-0.8-6.1) were not statistically significant.

When waterbird pair data for Muskoka, Sudbury and Algoma were partitioned by lake pH classes (low: <5.3, medium: 5.3 to 6.0 and high: >6.0), piscivorous waterbirds increased in medium pH Muskoka lakes, all three pH classes in Sudbury, and in medium and high pH Algoma lakes; the largest observed average trend occurred in the most acidic Sudbury lakes (Figure 6.18). Diving ducks increased significantly in low pH Sudbury lakes and in medium and high pH Algoma lakes. Dabbling duck pairs increased in low and medium pH Sudbury lakes and in medium and high pH Algoma lakes. An unexplained statistically significant decline in dabbler pairs in high pH Muskoka lakes contrasts with the pattern in the other regions and with other guilds. Based on an analysis of a portion of the Sudbury data (1985-1989), McNicol et al. (1995c) reported an increasing trend for Common Loon pair counts overall and increasing trends for moderately acidic (pH 5.5-6.3) and slightly- or non-acidic (pH>6.3) lakes. At the time of those analyses, a trend in very acidic lakes (pH<5.5) was not evident. In the current analyses, the recent increases in piscivore pair occupation of low pH lakes may indicate a response to habitat quality improvements associated with a broader regional chemical recovery of acidified Sudbury lakes (see Sections 6.3.2.1.3 and 7.4.2.1; McNicol et al., 1995c)). Overall, these results suggest that increased numbers of breeding waterbird pairs, particularly piscivores, are using lake habitats that were previously unoccupied. Increasing occupation of previously under-utilized breeding habitats may occur from a shift in the distribution of potential breeders from adjacent areas (see McNicol et al., 1995c). Whether or not food resources and other habitat attributes of these lakes and wetlands have improved sufficiently to support more breeding pairs is currently unclear.

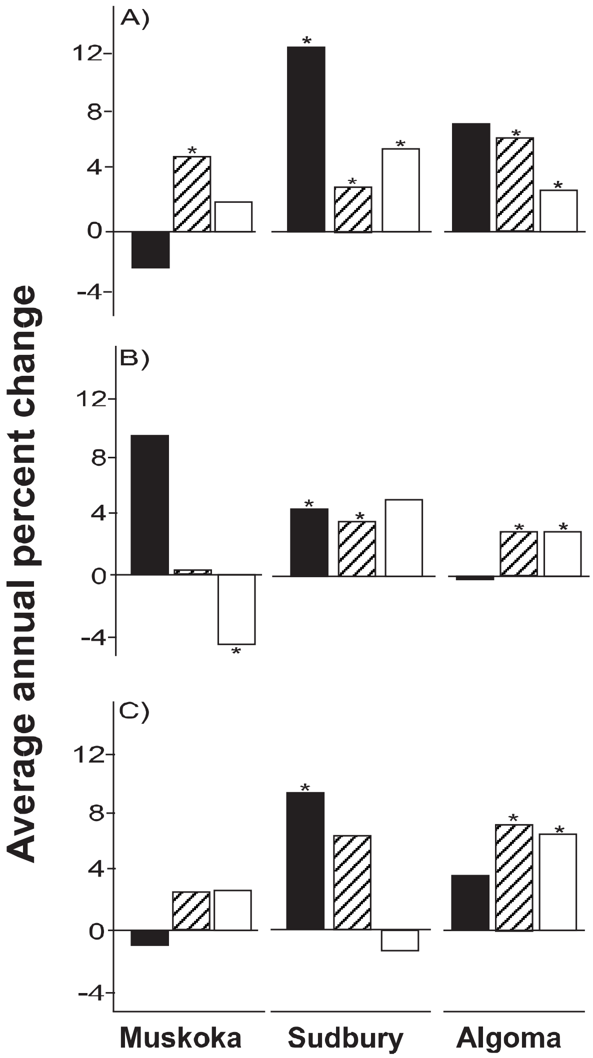

Figure 6.18: Average annual percent change in the number of breeding pairs for three waterbird guilds observed on lakes in the Muskoka, Sudbury and Algoma regions of ON. Trends are shown by region and are classified according to three lake pH classes (solid (pH < 5.3), hatched (5.3 – 6.0), open (pH > 6.0)). Trends by pH class are shown for A) piscivores (Common Merganser and Common Loon), B) divers (Hooded Merganser, Common Goldeneye and Ring-necked Duck) and C) dabblers (Mallard, American Black Duck and Wood Duck). Asterisks indicate statistically significant trends (i.e., 95% confidence intervals on trend estimates do not include zero).

Common Loon pair counts collected during the eastern Canadian Black Duck Joint Venture Surveys also indicated increases during the 1990s (1990-2003) (N. Burgess and

B.T. Collins, Canadian Wildlife Service, Environment Canada, pers. comm.). Statistically significant trends were observed for ON (4.7% annual increase, 95%CI=2.2-7.1), QC (5.8%, 95%CI=2.6-9.1) and NL (6.8%, 95%CI=2.1-11.7). No statistically significant trend was observed in NB (1.8%, 95%CI= -7.6-12.3). Although not statistically significant at the 5% level, a decline in loon pair counts was suggested by the results for NS (-4.0% annual decline, 95%CI = -8.5-0.7). It will be important to determine if this apparent decline strengthens in coming years.

6.4.4.1.2 Breeding productivity

The links between waterbird breeding productivity and lake acidification are more direct and effects are likely to be larger than for breeding pairs because nesting adults and their young typically are strongly dependent on the habitat and food chains of nesting and natal lakes. Changes in the distribution, composition, availability and quality of waterbird foods in acidified lakes have direct consequences on the growth and survival of young waterbirds. The toxicological effects of acidification-related increases in mercury also have implications for waterbird breeding productivity (see 6.4.4.3). Lake acidification is associated with lower breeding productivity for Common Loons (Wayland and McNicol, 1990; Kerekes et al., 1996; Doka et al., 2003), Common Mergansers (McNicol, 2002), American Black Ducks (Haramis and Chu, 1987), and tree swallows (Blancher and McNicol, 1988). Although factors such as metapopulation dynamics and juvenile and adult survival rates are important population influences, widespread chemical change in acidified lakes has the potential to affect waterbird populations and distributions through changing rates of recruitment.

Common Loons monitored in La Mauricie National Park, QC between 1987 and 2002 (n=76 lakes; see also 6.4.4.1.1 above) laid an average of 1.79 eggs per nest (Masse and Champoux, 2003). Average reproductive success was lower for lakes smaller than 25 ha, lakes with pH below 5.5 and/or Alk below 40 μeq/L, and lakes with low shoreline complexity and those without islands. Human presence was also associated with lower reproductive success, with lower productivity observed on lakes having >15 person-years/ha. There was no temporal trend in the average number of breeding pairs in the park or in the number of eggs laid over the entire time period. Nesting success declined over the time period (slope = -1.78, p=0.03, r^2=0.29), dropping by 15% between the two halves of the survey period (i.e., 1987-1994 vs. 1995-2002) and shifting from an average of 69% of nests successful during the 1987-1994 period to 54% during the 1995-2002 period. Similarly, breeding productivity, expressed as the total number of young produced on surveyed lakes, declined from 1987 to 2002 (slope = -0.49, p=0.02, r^2=0.33) (Figure 6.19). Both the average lake area and pH of lakes used for breeding tended to be higher than the size and pH of lakes not used for breeding (Figure 6.20). The average size and pH of lakes used for breeding also increased slightly from 1987 to 2002 (Figure 6.20), indicating that the productivity decline was not simply due to a shift by loons toward the poorer breeding habitats of acidic or small lakes. Although human disturbance tended to reduce loon productivity, there were also indications of declining success for lakes not used by park visitors (n=13, slope = -0.20, p=0.07, r^2=0.21), suggesting that productivity declines were not driven by human disturbance.

The CLLS is a national survey of breeding Common Loons, conducted primarily by volunteer observers (McNicol et al., 1995b; see http://www.bsc-eoc.org/cllsmain.html). The ON (Weeber et al., in prep.b), QC

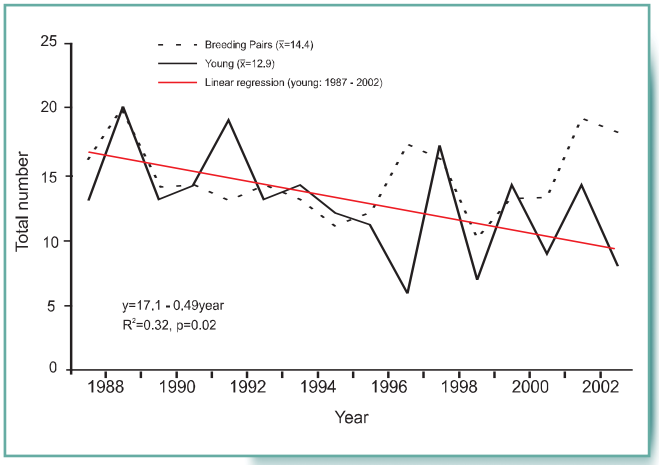

Figure 6.19: The total number of Common Loon breeding pairs (dashed line) and young (solid line) observed during surveys of 76 lakes in La Mauricie National Park, QC between 1987 and 2002. The regression line represents a statistically significant (p=0.02) trend for the total number of young observed in the park.

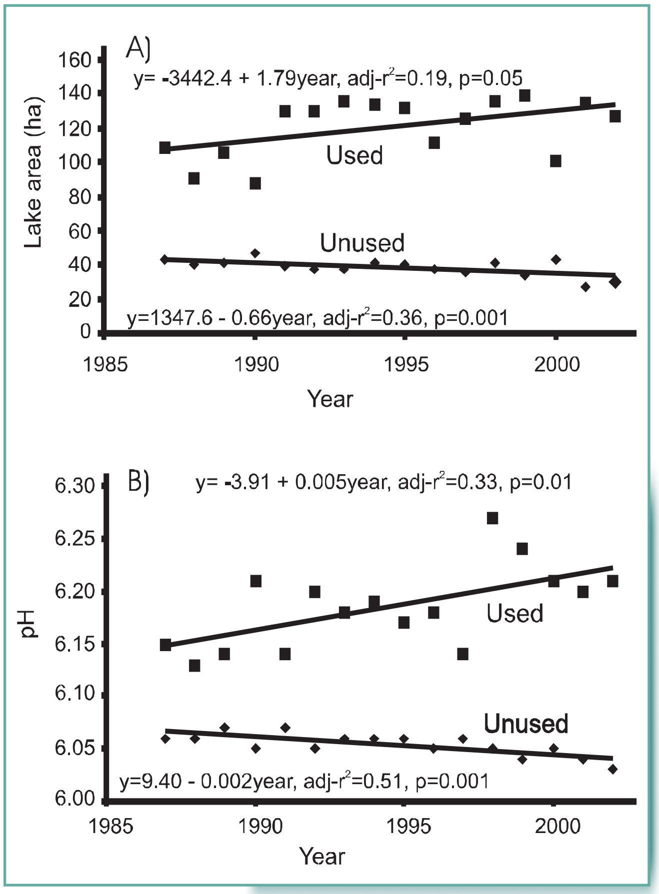

Figure 6.20: The average lake area (A) and pH (B) for those lakes used and not used by Common Loon breeding pairs in La Mauricie National Park, QC between 1987 and 2002 (n=76 lakes). Regression equations, adjusted r^2 and statistical significance levels are shown for each trend.

(Timmermans et al., 2004) and NS (Badzinski and Timmermans, submitted) portions of the CLLS data were evaluated to identify temporal patterns and the effects of lake acidity and human activity stressors on loon breeding success. Breeding success for a pair was defined as at least one observation with one or more chicks that was at least 6 weeks of age (i.e., Large Young (LY)). Three indices of breeding success were evaluated. Two statistically independent proportions were calculated: the number of successful pairs (i.e., with at least one LY) was expressed as a proportion of all pairs observed (hereafter, “successful pairs”) and the number of pairs with two or three LY expressed as a proportion of the number of successful pairs (hereafter, “very successful pairs”). The number of LY per territorial pair, a commonly applied success measure often used for population modelling purposes, was also calculated for each data source.

A total of 962 ON lakes were available for analysis over the 1981-1999 period with 63% surveyed in multiple years (Weeber et al., in prep.b). Similar to the La Mauricie National Park data, average lake pH (6.8, SD=0.86) was higher for the CLLS – ON data than for many other types of biological data summarised in this chapter; the proportion of surveyed lakes which were acid-stressed (pH<6) (13.2%) was very small relative to the proportion of circumneutral (pH 6-7; 46.6%) or non-acidic (pH>7; 40.2%) lakes. These lakes also tended to be larger (mean=195 ha, SD=246.6) than many of the lakes surveyed for waterfowl (see 6.4.4.1.1). Habitat effects evaluated included lake pH and surface area, and volunteer-reported estimates of the intensity of lake-based human activity and the percent of shoreline developed with cottages and other structures. The mean number of LY per pair ranged from 0.47 to 1.08 with an overall mean of 0.71. The proportion of successful pairs ranged from 0.34 to 0.76 (mean=0.5) and varied significantly among years (p=0.0001). The proportion of very successful pairs ranged from 0.28 to 0.55 (mean=0.41) but did not vary significantly among years. After controlling for annual variation, both lake area and pH had significant positive effects (p<0.0004 and p=0.03, respectively) on the proportion of successful pairs, but only lake pH had a significant positive influence on the proportion of very successful pairs (p=0.0002). After controlling for annual variation, lake area and pH, neither the percent of shoreline developed nor the intensity of lake-based human activity had a discernable effect on either of the two breeding success measures. Finally, after controlling for lake area and pH, there was a significant declining trend for the proportion of successful pairs (slope= -0.0627, p<0.0001) over the entire time period and a stronger decline from the peak success in 1987 onward (slope= -0.1183, p<0.0001, Figure 6.21).

Loon breeding success estimates were available for 277 QC lakes surveyed at least once over the 1992-2003 period (Timmermans et al., 2004). Relative to the ON data summarised above, a larger portion (60%) of the surveyed lakes in QC were at least moderately acidic (pH<6) and most (63%) were between 20 and 400 ha in size. The average number of LY per territorial pair ranged

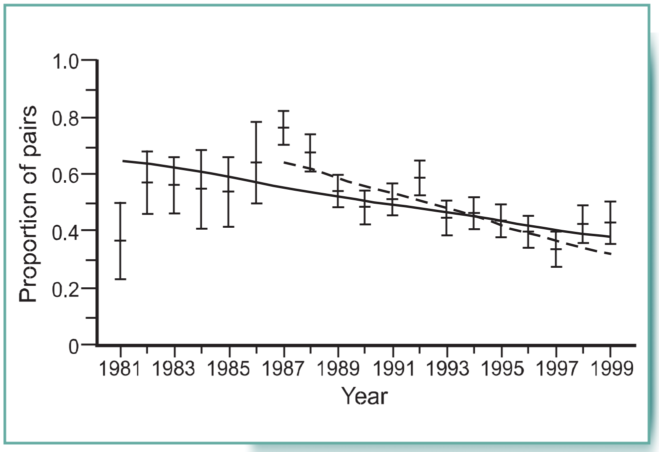

Figure 6.21: The annual average (with 95% confidence intervals; middle horizontal dash with vertical erro bars) proportion of Common Loon pairs with at least one young estimated to have fledged from ON lakes surveyed between 1981 and 1999 (solid line; n=962 lakes). Also shown is the estimated trend, after controlling for lake area and pH, in the probability of breeding success for the entire time period and for the 1987-1999 period (dashed line).

from 0.45 to 0.83 with an overall average of 0.59. The estimates of breeding success, the proportion of successful and very successful pairs, averaged 0.42 and 0.44 respectively, but neither showed a trend over the 12-year period. Although the effect was not particularly strong (p=0.11), the proportion of successful pairs varied among years. Lake pH, area, human activity and shoreline development data were available for 94 lakes. Models controlling for annual variation indicated that the proportion of successful pairs was positively associated with pH (p=0.01) but there was no evidence of pH effects on the proportion of very successful pairs. After controlling for annual variation and lake size, no effects on either measure of breeding success were observed for lake-based human activity. The proportion of successful pairs had a positive association with the percent of lake shoreline with cottages or other structures (p=0.04), perhaps due in part to the fact that attributes which attract humans to lakes (e.g., robust sport fish populations) also benefit breeding loons.

Loon breeding success estimates were available for 180 NS lakes surveyed between 1991 and 2000 (Badzinski and Timmermans, in press). Only a small proportion (<10%) of surveyed lakes were very acidic (pH<5.5); the majority (approximately 70%) were moderately- or non-acidic (6.5<pH<7.5). Lakes had DOC concentrations that ranged from 1.6 to 7.9 mg/L and the majority of lakes (78%) were between 20 and 400 ha in size. There was no discernable trend and no discernable annual variation for either the proportion of successful pairs or the proportion of very successful pairs. When controlling for both annual variation and lake area, however, there were marginally significant effects of annual variation and pH for the proportion of successful pairs and stronger pH effects for the proportion of successful pairs with two young (Table 6.11, Badzinski and Timmermans, in press). Although DOC is a particularly important contributor to lake acidity in many eastern Canadian lakes (see Section 6.3), there was no detected effect of lake DOC for loons raising at least one chick. There was a positive correlation, however, for loons raising two chicks (Table 6.11). The authors attributed the negative effect of pH on productivity to the relatively low number of acidified lakes (< 10% of lakes had pH < 5.5, mean pH = 6.2) in the NS sample. Further, Badzinski and Timmermans (In press) suggested the possibility that interactions among lake chemical factors may have influenced the resolution of acidity effects. There was no indication that human activity or boating disturbance had an effect on loon productivity after controlling for lake area.

In summary, waterbird surveys over approximately the last decade indicate general increases in trends in surveyed lakes in ON, QC and NL for pair counts of piscivores (Common Loon, Common Merganser). Evidence from the Sudbury, ON region suggests an increasing use of low-pH (pH<5.5) lakes by piscivorous waterbirds, possibly a result of generally improving conditions in the Sudbury area. Survey data from ON show increasing pair counts for some diving waterbirds (Hooded Merganser, Common Goldeneye, Ring-necked Duck) but limited or stable trends in surveyed lakes for dabbling ducks (Mallard, American Black Duck, Wood Duck). In contrast, there is some evidence for declines in breeding productivity for Common Loons in ON and La Mauricie National Park, QC. Although the observed declines were not simply attributable to lake acidification, the known sensitivity of loon breeding success to lake acidity and associated food web impacts, and the observation that productivity declines were not correlated with human disturbance indices, suggests that the potential remains that these declines could relate indirectly to acidification issues. For Common Loons, the seemingly counterintuitive results of increasing pair

Table 6.11 Annual variation, lake area, pH and DOC effects on the breeding success of Common Loons in NS lakes surveyed between 1991 and 2000 (n=180). Adapted with permission from Badzinski and Timmermans (in press).

Response variable[a]	Explanatory variables	Effect estimate ± SE[b]	*n*	*df*	χ^2	P[c]
P_{s1}	Year	—	42	9	16.20	0.06
	Lake area (ln(ha))	-0.17 ± 0.23		1	0.46	0.50
	pH	-0.74 ± 0.36		1	3.06	0.08
P_{s2}	Year	—	34	8	14.17	0.08
	Lake area (ln(ha))	+0.02 ± 0.20		1	1.21	0.27
	pH	-1.06 ± 0.39		1	5.04	0.03
P_{s1}	Year	—	42	9	16.21	0.06
	Lake area (ln(ha))	-0.09 ± 0.21		1	0.16	0.69
	DOC	+0.16 ± 0.19		1	0.73	0.39
P_{s2}	Year	—	34	8	15.61	0.05
	Lake area (ln(ha))	+0.49 ± 0.22		1	4.42	0.04
	DOC	+0.68 ± 0.20		1	6.03	0.01

[a] P_{s1} = "successful pairs" (proportion of breeding pairs successfully rearing at least one large young)

P_{s2} = "very successful pairs" (proportion of successful pairs rearing two large young)

[b] Parameter estimates from Generalized Estimating Equations (GEE) shown as logit-transformed values. Year effects are not presented, as they were included only to account for annual variation.

[c] Based on score statistics from Type III GEE analysis.

counts and decreasing breeding success could be due to dynamics such as population age-structure shifts or to differing consequences of habitat change for pairs establishing territories and those raising chicks. Although trends do not provide direct evidence for waterbird population responses to acid deposition effects or habitat recovery, they provide some indirect evidence important for guiding research and refined analyses. Research directly linking population vital rates (e.g., breeding success, survival) to habitat characteristics would help quantify the effects of acidification on waterbird populations and productivity.

6.4.4.2 *Habitat associations*

The 1997 Assessment stressed the importance of multiple factors in shaping the observed responses of waterbirds to lake and wetland acidity. For the current assessment, additional data and information-theoretic model selection and averaging techniques (Burnham and Anderson, 2002) were used to develop and evaluate models for waterbird pair and brood occurrence (Weeber et al., in prep.a). The candidate models that were evaluated included the effects of pH, DOC, Al and lake area, as in the previous assessment, but also considered the influence of shoreline complexity and fish presence. Modelling was based on breeding pair and brood data collected from aerial surveys conducted in the Muskoka, Sudbury and Algoma regions of ON between 1988 and 2003 (n=613 lakes). Surveyed lakes with available explanatory variables (n=584) tended to be only moderately acid-stressed (mean pH=5.9, range=4.3 to 7.5) and small (mean area=7.8 ha, range=<1 to 112) and approximately half (55%) of the lakes were fishless.

Regression models with acceptable estimates of predictive strength (i.e., average concordance ≥70%) were developed for predicting pair occurrence of piscivores as a guild (i.e., Common Loon, Common Merganser, Great Blue Heron (*Ardea herodias*) and Herring Gull (*Larus argentatus*)), and Common Merganser, Common Loon, Common Goldeneye and Hooded Merganser at the species level. A somewhat weaker (concordance=68.3%) model was developed for predicting pair occurrence for diving ducks as a guild (i.e., Hooded Merganser, Common Goldeneye, Ring-necked Duck). Although modelling was attempted for dabbling ducks (Mallard, American Black Duck, Wood Duck) (Weeber et al., in prep.a), those results are not reported here. Observations of Mallard and Wood Duck pairs and young were uncommon (often <10% of lake-years) relative to the piscivore and diver species

(12% to 35% of lake-years). Observations of American Black Duck pairs were sufficiently common (20% of lake-years) but the performance of the models was poor (concordance<63%), suggesting their habitat associations were poorly represented by the set of explanatory variables considered.

The predicted presence of piscivore pairs was positively influenced by lake pH, area and fish presence and was negatively affected by DOC concentrations. Estimated model strength declined from 83.3% (Table 6.12) to 78.9% (not shown) when fish presence was removed from the model statement, emphasizing the importance of fish prey information for predicting acidity responses for this group. Species level models with good predictive strength were developed for Common Loon pairs (concordance=83.6%) and Common Merganser pairs (concordance=79.1%, Figure 6.22). Concordance for merganser pair models dropped to 72.1% when fish presence was removed from the model statement (not shown). Both species were predicted to occur more frequently with increasing lake pH and area but the likelihood of loon pairs was inversely related to DOC levels. In addition, predicted Common Merganser pair occurrence was strongly associated with fish presence and was also positively influenced by the complexity of lake shorelines (SDI). Previous work has shown both positive effects of lake pH and area for both loons and mergansers (e.g., McNicol, 2002; Doka et al., 2003) and the presence of loons on clear lakes has been associated with their dependence on visual detection of prey during pursuit (McIntyre and Barr, 1997). Although the magnitude of pH effects on the predicted occurrence of piscivorous waterbird pairs (Table 6.12) was small relative to previous reports based on a portion of these data (e.g., McNicol, 2002), this was due, for some species, to the inclusion of fish presence observations in the models presented here because fish presence tended to be positively associated with both pH and DOC (see 6.4.3).

Habitat association models for diving duck pairs as a guild (i.e., Hooded Merganser, Common Goldeneye, Ring-necked Duck) were not as strong as those for piscivores (Table 6.12) and the estimated effects of pH and DOC were in opposite directions from those observed for piscivores. Diver pairs were more likely to occur in lakes with complex shorelines and, after controlling for other modelled variables, divers were more likely to occur in Algoma and Muskoka than in the Sudbury area. Within the diver group, models for Common Goldeneye pairs and their young had strong predictive power (concordance=83.6% for each). Common Goldeneye pairs and young were more likely to occur in small, acidic and fishless lakes (Figure 6.22) and, after controlling for modelled lake chemical and physical attributes, were more likely to occur in Algoma than in Sudbury. In addition, the presence of Common Goldeneye young was more likely in lakes with complex shorelines. An affinity of insectivorous ducks for naturally fishless lakes (e.g., due to hydrological isolation) lakes was noted in the 1997 Assessment and a particularly pronounced association has been noted for Common Goldeneye in central ON (McNicol, 2002). Although highly acidic conditions have the potential to cause chronic difficulties for breeding goldeneye and may have effects on breeding productivity, goldeneye are also likely to benefit from the increased invertebrate prey availability in fishless lakes (see 6.4.2.3).

Simple habitat association models for Hooded Merganser pairs and young were relatively weak (concordance=64.7% and 64.3%, respectively). More complex models that included the positive effects of lake pH, TP, and shoreline complexity, and the negative effects of DOC and fish gape class had estimated predictive power above 70% (Weeber et al., in prep.a).

The results of these recent habitat association analyses underscore that breeding waterbird responses to the acidity of the small lakes and wetlands they use for breeding are also influenced by the presence of small fish, lake morphology and other chemical attributes. Small fish are important food sources for some waterbird species (e.g.,, loons, mergansers) and have strong influences on macroinvertebrate prey of several waterbird species and their young (e.g., Section 6.4.2.3). After fish presence and habitat attributes such as lake area, shoreline complexity and DOC are taken into account, piscivorous waterbird pairs are more likely to occur in higher pH lakes. Although insectivorous diver species such as the Common Goldeneye have a positive association with lake acidity, a greater likelihood of pair and brood presence does not necessarily indicate the absence of acidification effects on duckling growth, fledging success or other life history dynamics of importance to population regulation.

Table 6.12 Guild and species-specific models summarising estimates of waterbird habitat associations for the Muskoka, Sudbury and Algoma regions of ON surveyed between 1988 and 2003 (n=613 lakes). Modelled effects are those identified by model selection and are statistically significant if their 95% confidence intervals (in parentheses) exclude zero. Average concordance was calculated with a leave-one-out jackknife using lake-level observations and predicted values (i.e. 1000 iterations of 1000 paired observations) (e.g. Olden and Jackson, 2000). Common Goldeneye models used only Algoma and Sudbury data because Muskoka is at the southern edge of their breeding range. The shoreline development index (SDI) was calculated as (Shoreline length)/(2*SquareRoot(π*Lake area)).

Species	LH[a]	Constant	pH	DOC	Lake area	Fish presence	SDI	Algoma	Muskoka	n[b]	C[c]	Freq[d]
Piscivore guild	pairs	-2.05 (-3.222, -0.869)	0.03 (0.162, 0.226)	-0.10 (-0.136, -0.061)	0.14 (0.105, 0.166)	1.32 (1.031, 1.613)				3162	83.3	28.5 (34.8)
Common Loon	pairs	-3.02 (-4.332, -1.706)	0.21 (0.004, 0.420)	-0.09 (-0.144, -0.038)	0.10 (0.073, 0.128)					3162	83.6	19.3 (20.1)
Common Merganser	pairs	-5.07 (-6.740, -3.395)	0.15 (-0.131, 0.423)		0.03 (0.017, 0.045)	2.04 (1.555, 2.524)	0.21 (-0.065, 0.487)			3162	79.1	11.1 (12.4)
Diver guild	pairs	2.82 (1.766, 3.879)	-0.72 (-0.894, -0.540)	0.02 (-0.014, 0.051)			0.46 (0.276, 0.638)	0.96 (0.639, 1.284)	0.12 (-0.180, 0.419)	3162	68.3	45.1 (49.7)
Common Goldeneye	pairs	2.65 (1.246, 4.044)	-0.58 (-0.855, -0.303)		-0.002 (-0.014, 0.010)	-1.47 (-1.882, -1.061)		1.24 (0.861, 1.611)		2179	83.6	32.4 (33.8)
Common Goldeneye	young	-0.05 (-1.675, 1.579)	-0.36 (-0.618, -0.104)		-0.04 (-0.058, -0.013)	-1.27 (-1.676, -0.860)	0.48 (0.187, 0.765)	1.31 (0.946, 1.664)		2153	83.6	10.4 (10.4)

[a] LH=Life history stage.

[b] n=Number of lake-years available for analysis.

[c] C=Mean percent concordance.

[d] Freq.=Mean percent of years (lake-years) occurring

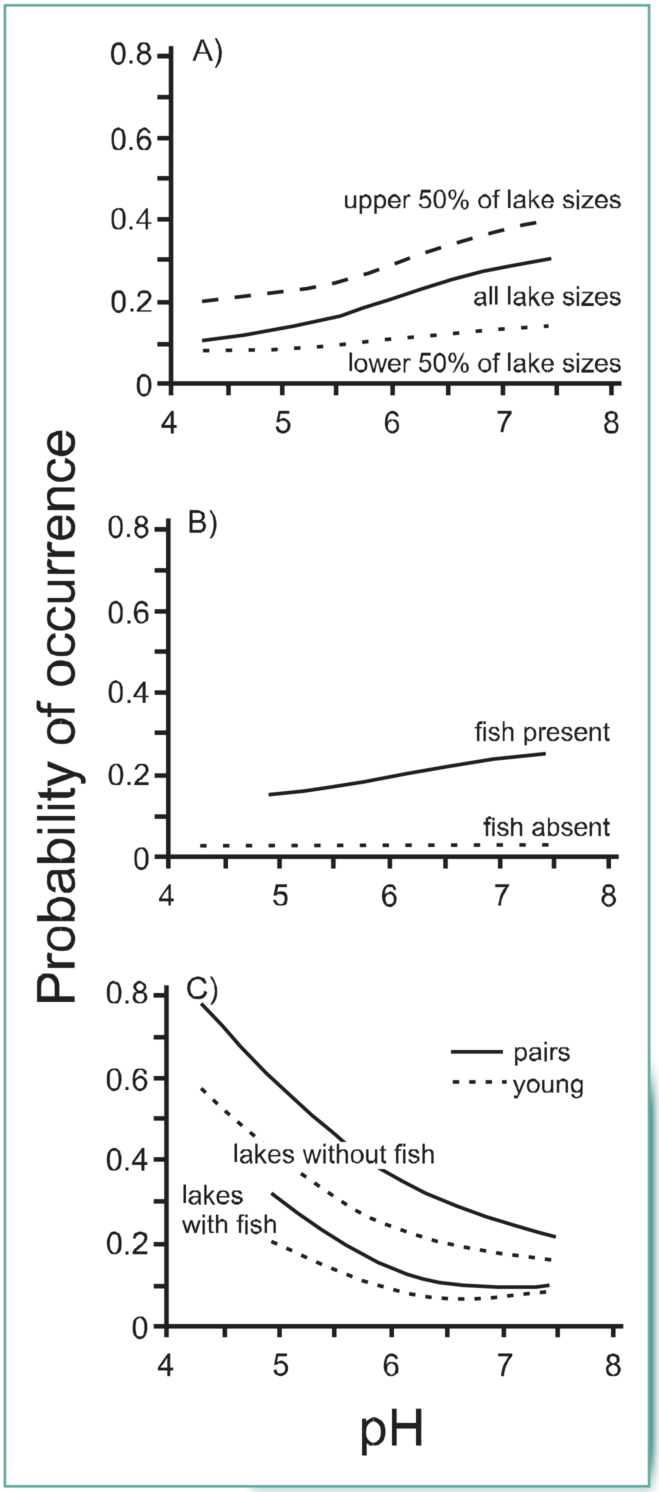

Figure 6.22: Predicted probability of occurrence for three waterbird species relative to lake pH. Calculated probabilities are shown for A) Common Loon pairs based on all lakes and the lower and upper 50% of lake sizes; B) Common Merganser pairs for lakes with and without fish; and C) Common Goldeneye pairs and young in lakes with and without fish. Probabilities were calculated using the model expressions in Table 6.12.

6.4.4.3 *Mercury*

The 1997 Assessment presented evidence that methylmercury (MeHg) is the most biologically toxic of the chemical species of mercury (Hg) in the environment. Anthropogenic sources of inorganic Hg include atmospheric deposition of air pollution from coal-fired power plants, municipal, medical and hazardous waste incinerators, metal smelters, and cement kilns. Inorganic Hg is converted to MeHg in aquatic ecosystems by several chemical and biological processes, but primarily by sulphate-reducing bacteria in lake sediments and bogs. Fish accumulate higher concentrations of MeHg under low pH (<6.7) and ANC (<60 μeq/L) conditions (Spry and Wiener, 1991), probably due to an increase in microbial production of MeHg in these chemical conditions (Gilmour et al., 1992). The Hg content of blood in adult and young Common Loons is negatively correlated with lake pH (Meyer et al., 1995) and positively correlated with fish Hg levels. Declines in loon reproduction are associated with fish Hg levels of 0.3-0.4 μg/g (Barr, 1986). These fish Hg levels were estimated to occur in 5-30% of ON lakes (Scheuhammer and Blancher, 1994), depending on the fish species present. The degree of bioaccumulation of MeHg appears to vary across taxa and trophic levels; the variation in MeHg bioaccumulation is evident in the low MeHg concentrations in leeches from acidified lakes (McNicol et al., 1997).

Mercury contamination remains a major environmental problem in lakes and rivers in eastern Canada. Government agencies have issued warnings advising the public to limit consumption of freshwater fish due to Hg contamination in every province in eastern Canada except Prince Edward Island (Anonymous, 2004).

Acidification of lakes increases the rate of conversion of inorganic Hg to MeHg, thus increasing MeHg concentrations in water, sediment, and biota (Frost et al., 1999). MeHg concentrations in freshwater fish are negatively correlated to lake pH in southern ON (Scheuhammer et al., 1998a), in NB and NS (Burgess et al., 1998a; Carter et al., 2001; Rencz et al., 2003; Drysdale et al., in press), and generally across northeast North America (Kamman et al., 2005). MeHg is highly bioavailable, bioaccumulates in most aquatic animals, and biomagnifies in aquatic food webs (Wiener et al., 2003). Reproduction in birds and mammals is sensitive to impacts from MeHg, since it is highly toxic to developing embryos and young animals (Scheuhammer, 1991). The developing nervous, endocrine and immune systems can all be adversely affected by MeHg in fish and wildlife (Pollard and Hultman, 1997; Faustman et al., 2002; Drevnick and Sandheinrich, 2003).

Acidification can also reduce the species diversity and biomass of phytoplankton and zooplankton in lakes (see Sections 6.4.2 and 7.4). This reduction in biomass at lower trophic levels results in higher MeHg concentrations in the remaining algae and invertebrates, leading to higher MeHg concentrations at the top of the food web (Pickhardt et al., 2002). Acidification often reduces growth rates of fish, resulting in higher concentrations of MeHg in small fish than would occur under higher pH conditions (Carter et al., 2001; Drysdale et al., in press), and consequently, an increase in MeHg exposure for fish-eating wildlife.

Common Loons have been studied as indicators of Hg contamination and impacts in aquatic ecosystems. There is a general eastward trend of increasing Hg levels in Common Loon eggs and blood from ON to NS (Scheuhammer et al., 1998b, 2001; Burgess et al., 1998a, 2005; Champoux et al., in press). The same trend is also observed in the northern United States (Evers et al., 1998; Evers et al., 2003). In study lakes across eastern Canada, Hg concentrations in the blood of adult and young Common Loons, loon eggs and their fish prey are generally negatively correlated with lake pH (Scheuhammer et al., 1998a, 1998b; Burgess et al., 1998a; Burgess and Hobson, in press; Champoux et al., in press; Drysdale et al., in press). In QC, NS and NB, Hg concentrations in loon adult and chick blood and fish prey were both negatively associated with lake pH (Figure 6.23). After controlling for this correlation, adult loons had the highest concentrations of blood Hg and loon chicks had lower concentrations than adults but higher concentrations than small prey fish (Figure 6.23). In Atlantic Canada, Hg concentrations were higher in fish and Common Loons in low pH lakes, despite an indication from stable-nitrogen isotope ratios that the length of aquatic food chains may have been shorter in acidic lakes (Burgess et al., 1998a; Burgess and Hobson, in press).

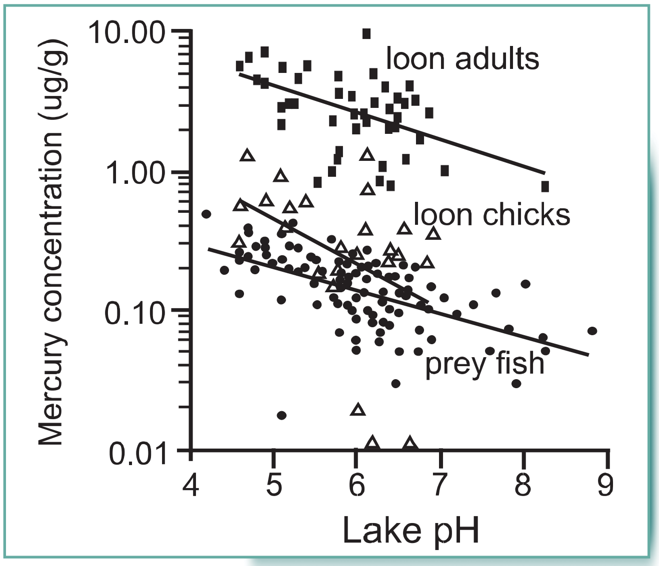

Figure 6.23: Mercury concentrations in Common Loons and their fish prey in relation to lake pH across eastern Canada. Mean blood Hg concentrations were determined for adult Common Loons (solid square) captured in QC, NS and NB (n=24, 9 and 12 lakes, respectively) and loon chicks (open triangles; n=16, 7 and 7 lakes, respectively). Mean Hg concentrations in whole prey fish (solid circles; 10-15 cm in length) were measured from samples taken from the same lakes as loon samples and additional lakes in QC, NS and NB (n=56, 23 and 24, respectively). Regression equations (standard errors) and statistics for loon adults, chicks and prey fish were: log(adult Hg) = 1.57 (0.295) – 0.19 (0.049) lake pH ($n=45$, $p<0.001$, $r^2=0.26$); log(chick Hg) = 1.23 (0.760) – 0.32 (0.129) lake pH ($n=30$, $p=0.020$, $r^2=0.18$); log(fish) = 0.13 (0.148) – 0.17 (0.024) lake pH ($n=103$, $p<0.001$, $r^2=0.32$).

Where Hg levels were moderate in loon blood and fish (i.e., QC and NB) there was no association between Hg levels and loon productivity, but where Hg levels were high (i.e., NS), loon productivity was reduced (Burgess et al., 1998b; Champoux et al., in press). A similar association between high loon Hg levels and low productivity was found in Wisconsin (Meyer et al., 1998).

Elevated Hg levels have also been associated with impacts on loon behaviour and growth. Changes in the behaviour of downy (i.e., < 3 weeks old) Common Loon young in Kejimkujik National Park, NS were associated with elevated blood Hg concentrations (Nocera and Taylor, 1998). Loon young with high Hg concentrations spent less time back-riding on adult loons and more time preening. The fledging rate of young loons appeared to be positively related to the amount of time spent back riding, suggesting the potential for observed behavioural effects to influence breeding productivity (Nocera and Taylor, 1998). In a controlled mercury-dosing experiment with captive loon young, growth rates were not affected by increased dietary doses of MeHg (Kenow et al., 2003). However, loons raised from eggs taken from low-pH lakes ($pH \leq 6.3$) grew slower than loons raised from eggs from neutral-pH lakes ($pH > 6.3$). The authors suggested that this difference might be caused by the elevated Hg levels found in eggs from low-pH lakes. Finally, high Hg levels in adult loons and their fish prey were associated with low rates of nest initiation in NS (Burgess et al., 1998b) and ON (Barr, 1986).

Many fish-eating predators can demethylate Hg in their liver and other organs to the less toxic inorganic form, particularly in the presence of selenium. This is true for Common Loons, Mergansers (Scheuhammer et al., 1998b; Daoust et al., 1998), river otters (*Lontra canadensis*) and mink (*Mustela vison*) (Evans et al., 2000). The antagonistic relationship between Se and Hg is well studied in adult animals (Cuvin-Aralar and Furness, 1991) and selenium-mercury complexes are much less toxic and more stable than MeHg in sea mammals (Honda et al., 1983) and presumably other mammals and birds. Therefore, much higher concentrations of total Hg may be present in organs bound in selenium complexes without causing apparent toxicity than would be the case if the Hg were methylated (Wiener et al., 2003). Thus, demethylation of methylmercury and binding of the resultant inorganic mercury with selenium are physiological adaptations that many adult fish-eating birds and mammals use to reduce the toxicity of methylmercury in their diet. However, the ability to demethylate Hg and the associated beneficial effects of selenium found in adult birds and mammals do not extend to developing embryos in the same species. About 87 – 99% of the Hg in Common Loon eggs is MeHg (Scheuhammer et al., 2001; Evers et al., 2003), indicating that methylmercury transferred from maternal tissues is not demethylated by developing embryos. In Mallards, eggs dosed with MeHg and selenium had poorer hatching success and more embryo deformities than eggs dosed with MeHg or selenium alone (Heinz and Hoffman, 1998). In contrast, adult Mallards were dosed in the same study with MeHg, selenium or both, and the birds receiving both metals were healthier than the ones receiving one or the other. The embryo's lack of ability to demethylate mercury and bind it with selenium partially explains the reproductive impacts of mercury, at exposure levels far below those that impair the health of adult animals, as noted by Scheuhammer (1991).

Developing a cause-and-effect linkage between Hg in aquatic food webs and adverse effects on top predators such as Common Loons (e.g., changes in behaviour, growth, productivity or survival) is particularly difficult because there are many other environmental stressors that can potentially cause similar effects in field studies (Meyer et al., 1998). The only way to develop a scientifically defensible assessment of Hg risks to fish-eating wildlife is to use a combination of laboratory and field studies (Kenow et al., 2003). Mercury concerns have been raised not only for Common Loons, but also for other fish-eating predators like river otter, mink, bald eagle (*Haliaeetus leucocephalus*) and osprey (*Pandion haliaetus*) (Evans et al., 1998; DesGranges et al., 1999; Laperle et al., 1999).

It is encouraging to note that recent studies in Wisconsin have documented significant declines in atmospheric SO_4^{2-} and Hg deposition (Watras et al., 2000), which are associated with declines in fish Hg concentrations (Hrabik and Watras, 2002). These changes in fish have led to recent declines in Hg levels in Common Loons (Fevold et al., 2003). Data from an experimentally acidified lake in Wisconsin permit an estimate of the relative contribution of decreased SO_4^{2-} versus decreased Hg deposition towards declining fish Hg levels (Hrabik and Watras, 2002). These findings suggest that management of both SO_4^{2-} and Hg emissions may contribute to downwind improvements in fish Hg concentrations.

6.4.5 Atlantic salmon

P.G. Amiro, R.W. Brook, and R.C. Weeber

Atlantic salmon (*Salmo salar*) populations have declined globally over the past 30 years and the species has been extirpated from some rivers in Europe and Canada (WWF, 2001; DFO, 2002). The previous acid rain assessment (Jeffries, 1997) reported that the status of Atlantic salmon populations in acidified rivers of NS had declined since the 1990 review of the acid rain problem (RMCC, 1990). Jeffries (1997) noted that the most severe impacts were occurring in the Southern Upland region of the province.

In 63 rivers assessed, salmon populations were extirpated from 14 rivers (pH<4.7), had declined by 90% in 20 partially impacted rivers (4.7<pH<5.0), were reduced by about 10% in 16 lightly impacted rivers (5.1<pH<5.4) and were considered less affected in 13 rivers with mean annual pH>5.4 (DFO, 1996). Chronic and episodic acidification of rivers and their tributaries were also implicated in reductions of adult fish returning to rivers and in the numbers of juvenile salmon produced (Watt, 1997). Acidification has also been implicated in the decline of the endangered Atlantic whitefish (*Coregonus huntsmani*). Remnant populations of the whitefish occur in two Southern Upland rivers which also contained historical salmon populations (Edge and Gilhen, 2001). Because less is known about the specific effects of acidification on Atlantic whitefish, recent information on this species, with a focus on their prospects for recovery, is summarised in the next chapter (see 7.5.2). In this section, we summarise recent assessments of Atlantic salmon stocks, with a particular emphasis on rivers in the Southern Upland region of Nova Scotia. We also review results of modelled projections for stocks in some of these rivers.

6.4.5.1 *Status and trends*

Canadian Atlantic salmon populations declined by at least 75% from 1970 to 2000 (WWF, 2001). Despite closures of Canadian net fisheries (in 1985, 1992 and 2000) for Atlantic salmon and restrictive recreational fishing regulations since 1983, populations in many rivers continue to decline. Approximately 550 Canadian rivers are considered to have contained Atlantic salmon historically (ICES, 2000; WWF, 2001). Sixty-five rivers in the Southern Upland region of NS, historically known to have Atlantic salmon, are the most severely affected by acidification (Amiro, 2000; DFO, 2000).

Recent reports indicate that chemical conditions and the salmon stock status of rivers in the Southern Upland region of NS have not improved despite progress in reducing outputs from many acidifying emission sources (Watt et al., 2000; DFO, 2002; DFO, 2003). Current salmon assessments in the Southern Upland region do not include all historic salmon rivers but instead focus on indicator rivers for each of three pH classes (DFO, 2003). Heavily acidified rivers (pH<4.7) can no longer support wild salmon and the most recent introduction of hatchery smolts to one assessed river in 2002 re-confirmed that hatchery enhancements to these rivers are unlikely to be successful. The East River, a partially acidified indicator river (4.7<pH<5.0), had smolt return rates generally below 1% from 1974 to 2002 (DFO, 2003). The outlook for the East River was that returns were inadequate for conservation objectives and are not expected to improve. Two low or non-acidified rivers (pH>5.1), the St Mary's and LaHave rivers, were also not expected to have returning salmon in numbers sufficient for conservation targets in 2003 (DFO, 2003). Other rivers in this category are expected to be similar or worse than the index rivers due in part to the more intensive stocking of hatchery smolts in the index rivers. Stocking of hatchery smolts in some rivers of the Southern Upland region of NS was considered ineffective in maintaining viable populations (Amiro, 2000) and was discontinued for many rivers (DFO, 2002).

Amiro (2000) modelled salmon populations on a subset of the 65 rivers (n=47) and suggested Atlantic salmon would become extirpated from a further 26 rivers, based on an assumption of 10% marine survival. Forty rivers were predicted to become extirpated given a 5% survival rate. However, measured survival rates have been below 5% since 1996 (e.g., 3% average survival for wild salmon (DFO, 2003)) and extirpations are therefore expected to increase at rates greater than modelled in 2000.

Although the acidity of some Southern Upland rivers may not be at lethal levels for adult or juvenile salmon, sublethal effects and increasing mortality after salmon leave the rivers could render populations unsustainable, particularly for rivers with pH between 5.0 and 5.4 or for rivers subjected to seasonal pulses of low pH (Amiro, 2000). Rivers in the Southern Upland region of NS continue to be of concern and Atlantic salmon populations will probably continue to decline (DFO, 2000). An electrofishing survey of Southern Upland rivers in 2000 (Amiro, 2000) indicated that about 50% of the rivers were likely devoid of juvenile salmon. Furthermore, in 2003 only trace populations of juvenile salmon were found in rivers that were classified as threatened in the 1999 prognosis (Amiro and Jefferson, in prep.).

6.4.5.2 *Habitat*

Major threats to Canadian Atlantic salmon populations include pollution effects and habitat modification through hydroelectric projects and river engineering

(WWF, 2001). A combination of geochemistry, local weather patterns, thin soils and low ANC resulted in severe acidification of rivers in the Southern Upland region of NS (Watt et al., 2000). Although juvenile salmon survival varies annually, there has been little or no evidence of a broad scale temporal trend in recovery from acidification (Watt et al., 2000). Atlantic salmon have a pH tolerance level between pH 5.0-5.4 depending on other river variables (Watt et al., 2000). For rivers in this pH range, there was a positive correlation between juvenile salmon abundance and pH ($p<0.05$) and a positive correlation between fish species diversity and pH (Watt et al., 2000).

Rivers with pH in the borderline toxicity range (pH 5.0 to 5.4) are at high risk of Atlantic salmon extirpation for several reasons. Sublethal effects at this pH range reduce feeding and growth, increase gill damage, and cause endocrine and osmoregulatory disruption. All these effects are associated with a reduction in the numbers of returning adult salmon (see Magee et al., 2003 for review).

Aluminum (Al) levels increased in Southern Upland rivers from 1982 to 1996. Total Al increased 0.019 mg/L ($p<0.001$; Watt et al., 2000), resulting in increasing exposure to this toxic metal for juvenile salmon in these rivers (e.g., Poléo et al., 1997). However, very little Al is in a free ionic state (the most toxic form at about 1 μeg / L of Al^{3+}) in the presence of organic acids which are commonly present in the drainages of the Southern Upland region. Aluminum is therefore not thought to be a health problem for salmon in most rivers (see Watt et al., 2000).

In summary, the concern for the national population of Atlantic salmon has increased since the last acid rain assessment (Amiro, 2000; DFO, 2000; DFO, 2003). However, only rivers in the Southern Upland region of NS have been shown to be affected by acidic deposition. Salmon stocks in the Southern Upland region continue to decline because the acidity of these rivers is not recovering in response to declines in SO_4^{2-} deposition, and marine survival of salmon remains low. Even non-lethal effects in moderately-acidified rivers have placed once-viable populations at risk of extinction by way of reduced freshwater productivity that affects juvenile survival and results in increased susceptibility to low marine survival (Amiro 2000). Population models developed since the last assessment predict salmon from most of the Southern Upland rivers (40 of 47 rivers modelled) will become extinct if adult survival rates remain at current levels (<5%). Unfortunately, pH recovery in response to reduced sulphate depositions experienced in other regions is not expected to occur in these rives for 50 to 70 years (Clair et al., 2004). The complex organic chemistry, low cation sources and high cation debts produce this expectation. The optimistic view is that given recent trends in depositions and population extirpations, we may have reached the trough of acidification effects on Atlantic salmon in the Southern Upland region.

6.5 NITROGEN-BASED ACIDIFICATION

D.S. Jeffries

Jeffries (1995, 1997) presented a preliminary assessment of the potential for and evidence of N-based acidification of Canadian fresh waters noting the following:

- Because N exists in many chemical forms and is a major biological nutrient, the environmental chemistry of N is much more complex than that of sulphur.
- If a lake's terrestrial catchment is or becomes N saturated (i.e., has little need for additional input of the nutrient), NO_3^- becomes a mobile anion, runoff waters show elevated NO_3^- concentrations, and N deposition acts as an acidifying agent just like SO_4^{2-} deposition. Such an occurrence will undermine the ecological benefits expected to accrue from SO_2 emission control.
- Catchment mass balance studies showed that saturated ecosystems tend to occur where N deposition is elevated, but non-saturated ecosystems can be found there also. Catchment saturation is generally not observed when deposition is less than approximately 10 kg N/ha/yr. Other natural factors (e.g., forest age, soil conditions, etc.) and interactions with other ecosystem perturbations (e.g., SO_4^{2-} deposition, climate change, etc.) may influence N saturation as well.
- Based on classification of survey NO_3^- data, few lakes with concentrations indicative of developing or existing N saturation occurred in Canadian regions receiving low N deposition, except where there was an alternative N source such as agricultural runoff.

- For lakes only affected by long range transport, N-based acidification was indicated for many lakes scattered throughout southeastern Canada, particularly in south-central ON and southwestern QC.
- Records of episodic, seasonal, or annual variations in nitrate concentrations provide superior information on the degree of N saturation (Stoddard, 1994), but Canadian data of this type were limited. Examination of four such data sets showed little evidence of N saturation in the Plastic (ON) and Kejimkujik (NS) catchments, while the waters of Lac Laflamme (QC) and especially Turkey Lake (ON) experienced seasonal variations indicative of incipient N saturation.
- Trend analyses of NO_3^- in waters from both southeastern Canada and northeastern USA showed that during the 1980s and early 1990s, there were many cases of either no or increasing trends, and only a few cases of decreasing trends.

Overall, the preliminary assessment in 1997 concluded that there was a clear potential for N-induced acidification of Canadian ecosystems. It recommended that further work be conducted to define both the status of Canadian lakes and their catchments with respect to N saturation and the factors that control it. Indeed, the only effects-based issue explicitly mentioned in the federal-provincial-territorial acid rain agreement that grew out of the 1997 Assessment (i.e., the Canada-Wide Acid Rain Strategy for Post-2000, see http://www.ec.gc.ca/acidrain/strat/strat_e.htm) was to assess the role of N in acidification.

Surveys of lakes affected only by atmospheric deposition have not been conducted to identify regional occurrences of elevated NO_3^- (see Section 6.3.1.3). The multi-source, annual average data set used in Section 6.3.1.2 showed that the median NO_3^- level was <1 μeq/L (defining the "growing season" low concentration class used by Jeffries, 1995, 1997) for all provincial/territorial data sets except SK (Table 6.2). However, some elevated NO_3^- levels were also found; notably 14% of the ON data set, 25% of SK data, and surprisingly, 11% of the NU data set were >2.5 μeq/L (defining the "growing season" high concentration class). Between 2% (AB and NT) and 6% (BC) of the remaining provincial/territorial data sets had NO_3^- concentrations >2.5 μeq/L (excluding NS and NB where the lack of NO_3^- data precluded calculation of percentile concentrations). This analysis seems to confirm the 1997 conclusion that some lakes in south-central ON may be affected by N-based acidification, but does not confirm that same conclusion for lakes in southwestern QC (perhaps excepting some lakes near Rouyn-Noranda, see Section 6.3.2.2). At present it is not possible to determine whether the "high" NO_3^- concentrations present in the multi-source database are due to incipient N saturation in the lakes' catchments, sugar maple forest types that tend to have higher rates of nitrification and NO_3^- leaching (Lovett and Mitchell, 2004), or a local anthropogenic N source.

An important change in NO_3^- trend behaviour in southeastern Canada has occurred since the last assessment. While some instances of positive NO_3^- trends during the 1980s to early 1990s were cited in 1997, most of these have become "no trend" during the 1990s (see Sections 6.3.2.1 and 6.3.2.2). The limited provincial/territorial occurrence of elevated mean NO_3^- concentrations and the apparent disappearance of many formerly positive NO_3^- trends in southeastern Canada suggest that N-based acidification has, if anything, declined since the last assessment although the potential still clearly exists. No reason is immediately obvious for this shift in detectable trends. Certainly atmospheric N deposition has not declined, but it must be recognized that many environmental perturbations can affect the N cycle. For example, Aber et al. (2002) evaluated dissolved inorganic nitrogen (DIN) export from a reference watershed that has been monitored since the mid-1960s in the Hubbard Brook Experimental Forest (NH, U.S.A.) – a northern hardwood forest similar to that found in southern QC and ON. They noted that the most widely accepted theories of N behaviour in forested ecosystems predict a decadal-scale increase in NO_3^- export from the watershed, whereas in reality, the opposite has been observed. It was necessary to consider the full range of other perturbations experienced by the watershed (i.e., interannual climate variation, changes in atmospheric chemistry and deposition, forest harvests, hurricane salvage, and insect defoliation) before the pattern of NO_3^- export could be accurately reproduced. Clearly, continued monitoring of Canadian ecosystems will be needed in order to resolve N-based responses within normal ecosystem variability and perturbation.

The importance of N in atmospheric, forest, agricultural and aquatic environments has given rise to a prodigious and still rapidly expanding scientific literature. It is composed of everything from a general assessment of nutrients in Canada (i.e., Chambers et al., 2001) to the topic-specific papers that emanate from N-focused conferences (e.g., see the more than 100 papers contained in *Environmental Pollution*, Volume 102, Supplement 1, 1998). Summarizing even the information associated with aquatic environments is beyond the scope of this assessment. Reference to a few important papers provides an impression of current scientific thought.

A concept gaining increasing prominence is the "nitrogen cascade" (Galloway et al., 2003; Driscoll et al., 2003). Of all the elements necessary for life (N, C, P, O and S), N has the greatest total abundance in the earth's atmosphere, hydrosphere and biosphere. Yet >99% of it exists in a form unusable by most organisms (N_2 gas). Some natural mechanisms such as lightning or N-fixing bacteria do convert N_2 to inorganic or organic N forms, but it is the human production of food and energy that are presently the dominant continental processes performing this function. The <1% of the total N pool that exists in the inorganic and organic forms is collectively known as "reactive nitrogen". Reactive N can cause multiple effects in the atmosphere, terrestrial, freshwater and marine ecosystems and human health as it moves along biogeochemical pathways - hence the term "nitrogen cascade". For example, the same molecule of reactive N can contribute to air quality degradation, acidification of soil and surface waters, disruption of forest processes, and eutrophication of coastal waters. The cascade does not proceed at the same rate through different environmental compartments. The terrestrial compartment has a large capacity for short- to long-term storage of reactive N, which causes a lag in the cascade. In comparison, the capacity of freshwater ecosystems to store reactive N is rather small (wetlands would have the greatest capacity of any aquatic systems) so that they tend to act as a fairly efficient conduit for moving reactive N from the terrestrial to the marine environment. This does not diminish the fact, however, that the aquatic N cycle is strongly affected by changes in the input of reactive N. Based on modelling results, Driscoll et al. (2003) concluded that NO_x emission reductions beyond those required by the U.S. Clean Air Act will be needed to mitigate the effect of high N deposition on sensitive ecosystems in the northeastern U.S.A. This likely applies to sensitive systems in southeastern Canada as well.

A consequence of significant terrestrial storage of reactive N is the development of "nitrogen saturation". Although the term has been defined in several ways, all definitions of N saturation include the notion that "increases in N availability over time... result in the alleviation of N limitations on rates of biological function and increases of NO_3^- mobility in soils" (Aber et al., 1998). Aber et al. (1989) set forth a conceptual model composed of an integrated set of hypotheses describing the effects of elevated N deposition on temperate forest ecosystems, specifically emphasizing increased NO_3^- and Al mobility in soils, soil and stream acidification, nutrient-nitrogen imbalances in trees and forest decline. An important implication of the hypotheses was that the forest response to N deposition would not be linear, and in fact was expected to be highly non-linear with critical threshold points. Discussion of the associated forest soil processes is beyond the scope of this chapter (see Chapter 5), but it should be noted that field experiments designed to test the hypotheses sometimes confirmed them and sometimes found them to be wanting. This led Aber et al. (1998) to revise their hypotheses slightly and to propose an additional mechanism (mycorrhizal assimilation) for retaining DIN inputs in forest soils.

While complex N biogeochemistry in its terrestrial basin principally determines if and by how much a lake is being affected by N deposition, the commonly used indicator of N saturation (and hence N-based acidification) is simply the presence of elevated NO_3^- concentrations in runoff. With respect to this indicator, large-scale experiments in European coniferous forests suggest that N saturation can be induced (or reversed) in only a few years (Wright et al., 1995). Study of three hardwood ecosystems in the Adirondack Region of New York with similar soils and vegetation showed that their N biogeochemistry can differ substantially (Mitchell et al., 2001a). Responses of the Adirondack forests to N deposition were a function of a suite of interactions that included hydrological, soil and biotic processes. The long-term history of N deposition and the temporal patterns of precipitation were considered important factors governing the amount and temporal patterns of NO_3^- export.

Stoddard (1994) empirically defined the NO_3^- concentrations and seasonal patterns in drainage waters that can be used to classify watersheds into one of four stages of N saturation (Stages 0 to 3). This was the approach used by Jeffries (1997) to conclude that the coniferous, boreal watershed of Lac Laflamme (QC) and the mixed hardwood ecosystem at the Turkey Lakes Watershed (TLW) (ON) may be experiencing incipient N saturation (Stage 1 and Stage 2 respectively). Since 1997, work on N-based acidification in QC and ON has largely focused on defining and understanding the biogeochemical processes controlling the NO_3^- export. The QC studies have been primarily terrestrial and the results are presented in Chapter 5. The ON results are summarized here. Most of the ON studies have been conducted at intensive research sites in Muskoka-Haliburton (M-H), the TLW, or the ELA. They tend to group into (1) those assessing topographic influences on catchment N export, (2) those inferring biogeochemical processes from catchment manipulation experiments or mass budgets, and (3) those employing isotope geochemistry.

Stream NO_3^- concentrations commonly vary greatly among adjacent catchments that have the same deposition input, forest type and age, etc. (e.g., streams draining into Harp Lake in M-H, Schiff et al., 2002) and may even exhibit differing trend behaviour (e.g., headwater streams in the TLW, Beall et al., 2001). Vegetative uptake and denitrification in riparian zones may play an important role in attenuating N export (Cirmo and McDonnell, 1997), but Schiff et al. (2002) found that terrain slope, till/soil stratigraphy and hydraulic conductivity were more important factors controlling NO_3^- concentrations in waters draining the Harp Lake catchments. Similarly, Hazlett and Foster (2002) showed that NO_3^- concentrations in subsurface throughflow draining towards Little Turkey Lake in the TLW varied greatly in relation to slope position. This largely reflected the soil horizons through which the water had passed. Higher concentrations occurred in the upper, well-drained hillslope that has more acidic, better-developed podzols; whereas, lower concentrations occurred in the wetter, less well-drained, less well-developed podzolic soils present at lower positions on the hillslope.

Creed and Band (1996) observed that headwater catchment export of DIN (mostly NO_3^-) in the TLW varied ±50% from the catchment-average response while export of dissolved organic nitrogen (DON) varied ±25%. They determined that variation in DIN export was linked to variation in catchment “flushing” behaviour (i.e., catchments with short flushing times exported less DIN than catchments with long flushing times) and concluded that in order to accurately predict DIN export, the influences of topographic complexity must be considered. These findings lead to development of a NO_3^- export model that (among many features) combined water flushed from high concentration source zones (i.e., near surface soil layers, including riparian zones) with deeper groundwater base flow (Creed et al., 1996). Subsequently, Creed et al. (2002) showed that static topographic factors such as slope, aspect and elevation were important determinants of spatial patterns of potentially mineralizable N in the soils at the TLW. It should be noted that Creed and Band (1996) also concluded that the mechanisms controlling DON export at the TLW were too poorly understood to make accurate predictions. An additional factor potentially complicating DON dynamics at the TLW, Morrison and Foster (2001) showed that only N (of all the elements considered) accumulated in the forest floor organic matter over a fifteen-year monitoring period. Hill et al. (1999) had previously shown that the organic Ae soil horizon in some M-H catchments was a sink for NO_3^-.

The two plant/soil communities that dominate the rocky ridge terrain at ELA exhibited contrasting responses to artificial additions of NO_3^-. Forest “islands” were N limited and they strongly retained all added NO_3^- (Lamontagne and Schiff, 1999). In fact, even when forest islands covered only a small proportion of a catchment area, they still had a strong impact on overall catchment export of N because most water had to pass through at least one island before exiting. In contrast, the rock surfaces that are covered only by intermittent patches of lichens, mosses and grasses appeared to be intrinsically N saturated. Within one year, NO_3^- additions to these ecosystem components were no longer retained. Based on the fate of ^{15}N-labelled NO_3^- additions, N storage appeared to primarily occur in the soil organic horizons (27%; cf. conclusion of Hill et al., 1999 mentioned above), although a significant proportion of the added ^{15}N could not be accounted (Lamontagne et al., 2000).

Mass budgets measured for seven catchments in M-H showed that most exported N was organic N, although NO_3^- export varied 10-fold between catchments and between years (Watmough and Dillon, 2003a). The total N export was a fraction of the atmospheric N input, i.e., all catchments showed net N accumulation with a significant retention component being tree uptake (Watmough and Dillon, 2003b). Hill et al. (1999) had previously shown that even during autumn storm events, N export was dominated by DON. They concluded that the biogeochemistry of organic soil horizons can regulate patterns of DIN loss in subsurface runoff. The differences in NO_3^- export noted by Watmough and Dillon (2003a) appeared to be due to differences in catchment characteristics (cf. discussion above) and climate variations. Watmough et al. (2004) observed that the pattern of annual NO_3^- concentration was similar among many M-H streams. A variance coherence analysis for 16 M-H catchments identified two stream groupings: first, catchments with shallow soils, moderate slopes, large wetland components, and low NO_3^- concentrations, and second, catchments with deeper soils, steeper slopes, smaller wetland components, and higher NO_3^- concentrations. The second grouping has the characteristics of upland sites (cf. Hazlett and Foster, 2002 cited above). Patterns of NO_3^- concentration in wetland-influenced catchments were related to summer drought and cumulative frost depth, while patterns in upland catchments were related to mean annual temperature and summer drought.

Stable isotope analyses have been used to assess the source and processing of N in the TLW, the most N saturated of all the research basins in southeastern Canada (Stoddard's Stage 2). The studies used a newly developed "dual NO_3^- isotope technique" (quantification of the isotopic ratios for both the nitrogen and oxygen atoms in the NO_3^- ion; Spoelstra, 2004). Low $\delta^{18}O$ values in the NO_3^- exported from undisturbed, first-order stream basins indicated that the NO_3^- was predominantly produced by microbial nitrification of ammonium in forest soils (Spoelstra et al., 2001). The contribution of an atmospheric source of NO_3^- in streams was greatest during the snowmelt period, but even then, never exceeded 30%. Therefore, the detrimental effects of NO_3^- export during snowmelt, such as episodic acidification, cannot be solely attributed to atmospheric nitrate accumulated in the snowpack. France and Schlaepfer (2000) also used N isotope ratios to show the prevalence of microbially modified N dynamics in an ephemeral, humic wetland in northwestern ON.

Forest harvesting occurred in some TLW stream basins in 1997, producing, in effect, short-term N saturation. Removal of N uptake by the trees from a basin's N cycle results in dramatic increases in NO_3^- export, and NO_3^- concentrations in excess of the drinking water standard (10 mg N/L) were briefly observed. Once again, low $\delta^{18}O$ values showed that the NO_3^- exported from the harvested basins was a two-source mixture, i.e., predominately NO_3^- produced by microbial nitrification plus a small atmospheric NO_3^- component. There was no indication of isotopic modification by other processes. Nitrate produced in the forest floor was very depleted in ^{15}N compared to NO_3^- in groundwater and streams. Spoelstra (2004) hypothesized that immobilization and assimilation of forest floor NO_3^- in the mineral soil were responsible for the disappearance of the depleted forest floor NO_3^- signature. Since the $\delta^{15}N$ values of microbial NO_3^- in groundwater did not change as a result of harvest, the rates of the unknown immobilization/assimilation mechanisms responsible for the change in NO_3^- $\delta^{15}N$ must have also increased to compensate for the increased leaching of ^{15}N-depleted NO_3^- from the forest floor. Finally, an extremely small, mid-basin wetland was very effective in retaining the high NO_3^- concentrations produced following forest harvest (Spoelstra et al., submitted). If the wetland were located closer to the catchment outlet, the degree of stream NO_3^- attenuation would have been even more dramatic.

In summary, the 1997 Assessment concluded that there was a clear potential for nitrogen-based lake acidification, particularly in southern QC and ON. Lake NO_3^- data present in the survey data set compiled for this assessment continue to support this conclusion (at least for southern ON). However, some lakes with elevated NO_3^- concentrations occur in regions with very low NO_3^- deposition (e.g., SK and NU) so that work needs to be conducted to determine the N source and lake dynamics that contribute to these observations. What lake NO_3^- trends have been detected suggest that N-based effects are, if anything, declining, but this must be related to other ecosystem factors (e.g., topography, climate, forest type, other perturbations, and interactions among them) since N deposition has not declined. The "nitrogen cascade" concept demonstrates how N deposition can have multiple ecological effects that extend beyond the acidification issue. Finally, organic soil horizons play an extremely important role in controlling catchment storage, cycling and release of N. Isotopic analyses have definitively shown that most of the NO_3^- exported from forested catchments (in ON) has been produced by microbial nitrification. Atmospheric N inputs are biogeochemically processed prior to mobilization and export as NO_3^-.

6.6 SUMMARY

The chemical and biological effects of acidic deposition on surface waters in southeastern Canada have been documented since the 1970's (reviewed in Schindler, 1988; RMCC, 1990; Longcore et al., 1993), with the most recent assessment summarised in Jeffries (1997) and Doka et al. (2003). Such reviews have recognised that changes in chemistry can generate cascading effects through aquatic ecosystems which produce measurable ecological responses. Here, we summarise our assessment of recent information concerning acidic deposition effects on aquatic chemistry and biology in Canada.

A water chemistry database was assembled as a foundation for the assessment of aquatic effects.

- Water chemistry data were compiled for 3130 lakes from all the Canadian provinces and territories (except PEI) to assess their current status. In the eastern provinces (defined as ON and eastwards) where lake chemistry is changing due to reductions in acidic deposition, the sampling period for these "current status" lakes was 1997 or later. This restriction was relaxed for the western provinces and northern territories. Where data were available, the assembled database contained the full suite of major ions, plus other chemical or physical variables important to acidification assessment.
- The compiled databases provide a sample population that is not a representative subset of the overall lake resource. Geographically, the lakes are irregularly distributed; they often occur in clusters. There are numerous areas across the country where sample data are unavailable. Lake samples in the eastern provinces tend to be located in acid sensitive terrain since they were more often than not specifically selected for acidification monitoring. The western and northern lakes were sampled for a variety of reasons, and therefore occur in both sensitive and insensitive terrain.

The acid sensitivity and current chemical status of sampled lakes across Canada was evaluated.

- The eastern sample lakes are generally sensitive to acidic deposition having low base cation and Alk concentrations (<400 and <200 μeq/L respectively). The NS and NL lakes are the most sensitive of all. Almost all acidic sample lakes (i.e., those having no buffering capacity; Alk is zero or negative) occur in eastern Canada, and in particular, more than half of the NS subset is in this category. Between 27% (NB) and 75% (NS) of eastern lakes have pH <6 – a level below the "normal" pH range and a value commonly used as a threshold for protecting the structure and function of aquatic ecosystems (i.e., the aquatic critical load). Some but not all of these low pH values are due to naturally occurring organic acids (reflected by high DOC concentrations).
- Western and northern sample lakes exhibit very broad base cation and Alk distributions; a large fraction of them are insensitive to acidification. The small MB sample population is unique in that it contains no sensitive lakes at all (base cation and Alk concentrations always >400 μeq/L); acid sensitive terrain in MB was not represented in the current status database. Very few western and northern lakes have pH <6 even though some have high DOC levels.
- The highest SO_4^{2-} concentrations in eastern sample lakes generally occur where atmospheric deposition is high. However, this relationship is sometimes modified by climatically-influenced catchment processes that temporarily store or release S. Broad SO_4^{2-} distributions observed in western and northern sample lakes, where deposition is generally low, indicate the existence of geological sources of S.

The compilation of an assessment database from existing data sets carries with it implications concerning the regional representativeness of the sample information.

- The database compiled to assess chemical status has important limitations. Without considering the northern Territories, there are large, sensitive regions where either no data exist or where data are too out-of-date to be useful for evaluating current status. This is particularly true in NL, QC, ON, MB, SK, and BC. Moreover, the available sample populations were skewed to larger lakes, and it is likely that many aquatic effects occur in the small, generally underrepresented size fraction. Lake surveys that collect a sample representative of the regional population are recommended.

Data records for a subset of lakes from the current status database could be analyzed to determine whether their chemistry is changing through time. In many cases it was also possible to assess the cause of identified changes (or lack of changes).

- There were 742 eastern lakes (638 in ON) that had sufficiently complete temporal records over the 1990-2001 period to allow statistical analysis of monotonic trends. Analyses of this "trends" database showed that SO_4^{2-} is declining throughout southeastern Canada in response to declining North American SO_2 emissions. This generalization is only now becoming commonplace in the Atlantic provinces (relative to previous assessments) and was constrained in ON lakes, mostly because climatically-induced variations in SO_4^{2-} export obscured their trends (SO_4^{2-} declines were statistically significant in only 29% of ON lakes, although their regression slopes were overwhelmingly negative). Many of the significant ON declines were in the Sudbury region, an area affected by emission reductions at local smelters. Analysis of variance coherence among nine lakes in the M-H region of ON confirmed both the direct relationship between SO_4^{2-} deposition and lake concentration declines, and the importance of climatically-induced modifications to this relationship.
- Increasing trends for lake pH and/or Alk are becoming more prevalent relative to previous assessments. Nevertheless, the predominant acidity response for lakes in the "trend" database was still "no significant trend" (89% for pH and 83% for Alk), primarily due to the fact that base cation declines counterbalance the SO_4^{2-} declines. Increasing DOC (organic anions) is likely mitigating pH or Alk improvements for some lakes. There are few NO_3^- trends and little evidence that N is influencing the acidity trends. Analyses of chemical change using repeated surveys from NB and the Rouyn-Noranda region of QC generally agree with the above trend conclusions.

Nitrogen-based acidification may be a future problem, but sulphur-based acidification is still the primary concern in Canada.

- A conclusion from the previous assessment that there is a clear potential for nitrogen-based lake acidification was supported by the "current status" NO_3^- data, at least for southern ON. The NO_3^- trends detected, however, suggest that N-based effects are, if anything, declining, even though N deposition has not declined. Some lakes with elevated NO_3^- concentrations do occur in regions with very low NO_3^- deposition (e.g., SK and NU). The N sources and lake dynamics that contribute to these observations need to be more fully evaluated. Finally, the "nitrogen cascade" concept demonstrates how N deposition can have multiple ecological effects that extend beyond the acidification issue.

Ecosystem stressors beyond atmospheric deposition influence aquatic acidification.

- As an issue, surface water acidification does not occur in isolation. There are strong interactions between acidification and other ecosystem stressors such as climate change, UV radiation, metal and organic contaminants, etc. The nature of many of these interactions remains very uncertain.

Biota in acidified aquatic systems are impacted by chemically inhospitable conditions, loss of preferred prey species, reduced nutritional value of remaining prey, and eco-toxicological effects (e.g., metal toxicity). These impacts often combine to extend acidification effects from primary producers (e.g., algae) through to higher trophic levels (e.g., fish, waterbirds).

- The taxonomic composition and growth of benthic algae, which grow attached to plants, stones, wood and sediments, is strongly impacted by acidification and related chemical and physical changes. Extreme or chronic acidification reduces algal biomass and diversity (e.g., up to 70% species richness loss under extreme acidification) and may lead to a shift in dominance from deepwater algae to floating taxa (e.g., metaphyton).

Open water (nekton) and benthic invertebrates are important primary consumers and are prey for higher trophic levels such as fish and waterbirds.

- Recent evidence reinforces pH 6 as an important threshold for changes to open water zooplankton (e.g., Daphnia, copepods) community structure. Similar to the well-studied open water zooplankton (see Chapter 7), crustaceans of littoral zones of lakes are taxonomically rich and have measurable species-level affinities across a wide range of acidity. These attributes make littoral crustaceans promising bioindicators for assessing continuing acid-stress or recovery in sensitive aquatic systems.
- Benthic invertebrate species composition and abundance is strongly influenced by acidity, with fish presence an important modifier of species responses. Certain acid-tolerant species (e.g., some dragonflies, flies) are more abundant at higher acidity but the abundance of other invertebrates, particularly mayflies and molluscs, is reduced under acidic conditions. Among the benthic invertebrate community, pH 5.5 is an important threshold for changes in composition and abundance.

Macroinvertebrates (e.g., dragonflies, caddisflies) from both nektonic and benthic habitats are important foods for breeding waterbirds and are particularly important for nesting females and their young. The acidity effects on benthic and nektonic macroinvertebrates provide a tool for understanding how waterbird food webs respond to acid stress.

- Measures of taxonomic richness and numerical dominance of macroinvertebrates are commonly used to estimate the impacts of pollution or other stressors on aquatic ecosystems. This assessment shows that several macroinvertebrate community metrics respond to lake acidity with fish presence also an important modifier of particular responses. Several groups of beetles and true bugs (e.g., corixids, dytiscids) dominate in acidic (e.g., pH<6), fishless lakes. Dragonflies and other beetles (e.g., gyrinids) tend to dominate in acidic lakes with fish. Relative to acidic lakes, circumneutral lakes typically have more macroinvertebrate families and stronger dominance by crustaceans (e.g., amphipods), mayflies, snails and clams.
- The simultaneous consideration of lake chemical, fish predation and other habitat attributes on macroinvertebrate community structure and composition provides a way to estimate acidity effects in the context of other important constraints on macroinvertebrates. After controlling for lake chemical and physical characteristics, this assessment shows that snails, mayflies and an amphipod (*Hyallela azteca*) respond to lake acidity and are also tolerant of fish. Backswimmers, a caddisfly genus (*Triaenodes*), and certain beetles and dragonflies were associated with low pH, fishless conditions. Other dragonflies, another caddisfly genus (*Anabolia*) and a water strider (*Rheumatobates rileyi*) were tolerant of fish presence across a range of pH. Because these acidity responses remained after accounting for other habitat influences, these taxa are particularly useful bioindicators for estimating the quality of waterbird food webs in the small, acid-sensitive lakes and wetlands used for breeding.

The fish status of acid sensitive lakes and wetlands is clearly an important influence on how the structure and composition of aquatic food webs respond to acid stress. Most new information available for this assessment relates to the restoration and management of sport fish populations (see Chapter 7).

- Modelling results presented in this assessment confirm that the small fish (e.g., perch, minnows) typical of small, acid-sensitive lakes and wetlands are more likely to occur with increasing pH. Small fish occurrence is also positively influenced by lake size, DOC and Ca^{2+} concentrations and negatively associated with TP and Al levels.

Waterbirds (e.g., ducks, loons, herons and gulls) are ecologically important and are also a valuable cultural and economic resource. Waterbirds respond to lake acidification through the acidity-induced changes in the availability, nutritional value and toxicity (e.g., mercury contamination) of their foods and impacts to the suitability of their breeding habitats.

- This assessment reports increasing trends in the number of breeding piscivorous waterbirds (Common Loon, Common Merganser) in much of southeastern Canada (i.e., ON, QC and NL). In particular, evidence from the Sudbury, ON region suggests an increasing use of low-pH (pH<5.5) lakes by piscivorous waterbirds, possibly a result of generally improving conditions in the region. Breeding numbers are also increasing for some diving waterbirds (Hooded Merganser, Common Goldeneye, Ring-necked Duck) but pair counts remain stable for dabbling ducks (Mallard, American Black Duck, Wood Duck).
- Loon breeding success is strongly associated with lake acidity and associated food web impacts. This assessment summarises evidence that productivity for Common Loons breeding in parts of ON and QC declined during the last two decades. A continuing and widespread decline in loon productivity would be a cause for concern.
- This assessment underscores that breeding waterbird responses to acidity are also influenced by the presence of small fish, lake morphology and other chemical attributes. Fish-eating waterbird pairs are more likely to occur in higher pH lakes even after accounting for fish presence and other important habitat attributes (i.e., lake area, shoreline complexity and DOC). An insectivorous diving duck, the Common Goldeneye, has a positive association with lake acidity, although the potential for acidification effects on productivity or survival remain.
- Methylmercury (MeHg) is highly bioavailable, bioaccumulates in most aquatic animals, biomagnifies in aquatic food webs and is highly toxic to developing embryos and young animals. This assessment reaffirms that the acidification of aquatic systems leads to increased MeHg concentrations in water, sediment, and biota, and often results in elevated levels in the prey of fish-eating wildlife. Mercury concentrations are negatively correlated with lake pH for Common Loon adults, eggs, young and their fish prey, with increasing Hg concentrations observed from west to east across southeastern Canada. High Hg levels are associated with impacts to loon breeding productivity and include reduced breeding success, modified chick behaviours which may increase mortality, and reduced chick growth rates.

Atlantic salmon (*Salmo salar*) populations have declined over the past 30 years and their decline has had important ecological, economic and cultural impacts in Canada and elsewhere.

- This assessment reaffirms that Atlantic salmon populations in rivers of the Southern Upland region of NS are severely impacted by acidification. Salmon in rivers with pH in the borderline toxicity range of pH 5.0 to 5.4 are at high risk due to sub-lethal effects at this pH range which reduce feeding and growth, increase gill damage, and cause endocrine and osmoregulatory disruption. Salmon stocks continue to be at risk due to continued river acidity, reduced survival of smolts, and insufficient numbers of adult fish returning to spawn. Model predictions indicate that salmon from most Southern Upland rivers will become extinct if adult survival rates remain at current low levels and pH recovery continues to be delayed.

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appendix 6.1

Table A6.1 Classification, taxonomic codes and names, and the frequency and mean occurrence of common (>10% of lakes) macroinvertebrates sampled from four regions of ON (Muskoka, Sudbury, Algoma and the Experimental Lakes Area) between 1987 and 2003. Taxa are sorted by Order or, for molluscs, by Class.

Order/Class	Taxa Code	Taxa Name	Number (%) of lakes occurring	Mean count
Bivalvia	PISIDIID	Pisidiidae	112 (67.5)	13.25
	PISIDIUM	*Pisidium*	32 (19.3)	3.00
	MUSCPART	*Musculium partumeium*	23 (13.9)	0.78
	PISIADAM	*Pisidium adamsi*	24 (14.5)	0.81
	PISICASE	*Pisidium casertanum*	47 (28.3)	2.29
	PISIVARI	*Pisidium variabile*	34 (20.5)	1.86
Gastropoda	FERRISSI	*Ferrissia*	23 (13.9)	0.15
	GYRAULUS	*Gyraulus*	22 (13.3)	0.86
	GYRADEFL	*Gyraulus (s. s.) deflectus*	24 (14.5)	0.45
	HELIANCE	*Helisoma (s. s.) anceps*	34 (20.5)	0.82
Coleoptera	COPTOTOM	*Coptotomus*	20 (12)	0.25
	DYTISCUS	*Dytiscus*	16 (9.6)	0.08
	GRAPHODE	*Graphoderus*	63 (38)	7.82
	HYDROPOR	*Hydroporus*	32 (19.3)	0.32
	NEOPUNDU	*Neoporus undulatus*	20 (12)	0.08
	DINEUTUS	*Dineutus*	77 (46.4)	0.99
	GYRINUS	*Gyrinus*	73 (44)	1.64
Diptera	CERATOPO	Ceratopogonidae	80 (48.2)	1.65
	CHRYSOPS	*Chrysops*	53 (31.9)	0.37
	CHRYEXCI	*Chrysops excitans*	31 (18.7)	0.18
Ephemeroptera	CAENIS	*Caenis*	78 (47)	6.78
	CAENDIMI	*Caenis diminuta*	33 (19.9)	3.71
	CAENYOUN	*Caenis youngi*	21 (12.7)	1.04
	EURYLOPH	*Eurylophella*	30 (18.1)	0.54
	EURYTEMP	*Eurylophella (s. s.) temporalis*	20 (12)	0.29
	SIPHLONU	*Siphlonurus*	19 (11.4)	0.65
Hemiptera	CORIXIDA	Corixidae	97 (58.4)	11.64
	SIGARA	*Sigara*	49 (29.5)	0.91
	SIGAPENN	*Sigara (A.) penniensis*	24 (14.5)	0.19
	SIGACOMP	*Sigara (Ph.) compressoidea*	20 (12)	0.21
	SIGAMACR	*Sigara (Ph.) macropala*	33 (19.9)	0.80
	SIGAMACK	*Sigara mackinacensis*	22 (13.3)	0.26

Table A6.1 cont.

Order/Class	Taxa Code	Taxa Name	Number (%) of lakes occurring	Mean count
	GERRIS	*Gerris*	24 (14.5)	0.20
	GERRCOMA	*Gerris comatus*	39 (23.5)	0.69
	RHEURILE	*Rheumatobates rileyi*	31 (18.7)	2.40
	TREPINER	*Trepobates inermis*	24 (14.5)	0.63
	BUENOA	*Buenoa*	41 (24.7)	4.33
	NOTONECT	*Notonecta*	39 (23.5)	1.14
	NOTOINSU	*Notonecta (P.) insulata*	49 (29.5)	2.90
	NOTOBORE	*Notonecta (s. s.) borealis*	24 (14.5)	0.45
	NOTOUNDU	*Notonecta undulata*	47 (28.3)	1.18
Odonata	AESHNA	*Aeshna*	27 (16.3)	0.25
	AESHEREM	*Aeshna eremita*	30 (18.1)	0.13
	EPITHECA	*Epitheca*	27 (16.3)	0.22
	CORDSHUR	*Cordulia shurtleffii*	128 (77.1)	4.57
	GOMPHUS	*Gomphus*	56 (33.7)	1.44
	GOMPEXIL	*Gomphus (s. s.) exilis*	20 (12)	0.24
	LEUCORRH	*Leucorrhinia*	16 (9.6)	0.30
	SYMPETRU	*Sympetrum*	22 (13.3)	0.17
	LEUCGLAC	*Leucorrhinia glacialis/hudsonica*	101 (60.8)	12.93
	LEUCFRIG	*Leucorrhinia frigida*	25 (15.1)	0.21
	LEUCINTA	*Leucorrhinia intacta*	37 (22.3)	0.39
	LIBEJULI	*Libellula julia*	134 (80.7)	5.83
	DIDYTRAN	*Didymops transversa*	21 (12.7)	0.19
	ENALLAGM	*Enallagma*	46 (27.7)	0.56
	ENALHAGE	*Enallagma hageni*	16 (9.6)	0.10
	LESTES	*Lestes*	46 (27.7)	1.12
	LESTDISJ	*Lestes disjunctus*	18 (10.8)	0.15
Trichoptera	MYSTACID	*Mystacides*	24 (14.5)	0.36
	OECETIS	*Oecetis*	86 (51.8)	3.08
	TRIAENOD	*Triaenodes*	29 (17.5)	1.36
	OECEOSTE	*Oecetis (Ps.) osteni*	25 (15.1)	0.36
	ANABOLIA	*Anabolia*	21 (12.7)	0.11
	LIMNEPH	*Limnephilus*	63 (38)	1.31
	GLYPIRRO	*Glyphopsyche irrorata*	30 (18.1)	0.53
	LIMNINFE	*Limnephilus cf. infernalis*	30 (18.1)	0.81
	PLATAMIC	*Platycentropus amicus*	47 (28.3)	0.37
	AGRYSTRA	*Agrypnia straminea*	25 (15.1)	0.18
	BANKCROT	*Banksiola crotchi*	30 (18.1)	0.14
	BANKSMIT	*Banksiola smithi*	38 (22.9)	0.57
	POLYCENT	*Polycentropus*	69 (41.6)	1.51
Decapoda	HYALAZTE	*Hyalella azteca*	60 (36.1)	9.14
	CRANRICH	*Crangonyx richmondensis*	55 (33.1)	5.75

CHAPTER 7

Recovery of Aquatic Ecosystems

R.C. Weeber, D.S. Jeffries and D.K. McNicol

7.1 Key messages

- Declining sulphur dioxide emissions are leading to declining trends in lake sulphate, the primary acidifying agent. Expected declines in lake acidity are less widespread, however, due in part to declines in base cations, drought-induced release of stored S and impairment of within-lake processes that generate alkalinity.
- Encouraging signs of biological recovery are being observed but complete recovery to a regionally representative biological community is rarely being observed. Biological recovery will lag behind chemical improvements, will be complex and may eventually lead to biological communities that differ from their pre-acidification state.
- A large proportion of previously acidified lakes in southeastern Canada are expected to remain chemically and biologically damaged following implementation of currently planned emission reductions. Lower sulphur dioxide emissions will likely be needed to accelerate the reversal of the chronic ecosystem stress associated with acidification.
- The nature and degree of recovery is influenced by climatic, chemical, physical and biological factors. Understanding and predicting ecosystem change in a multiple-stressor environment requires information from broad-scale, integrated monitoring programs conducted in concert with intensive investigations of ecosystem stressors and recovery processes.

7.2 Conclusions of the 1997 Assessment

The following observations and conclusions were presented in the 1997 Assessment (Jeffries, 1997). The occurrence of and factors influencing the recovery of aquatic ecosystems were documented at sites of intensive research and monitoring in southeastern Canada. Evidence of recovery in the form of declines in lake sulphate (SO_4^{2-}) were observed almost everywhere although, where deposition was lowest (Kejimkujik, Nova Scotia (NS)), the change was minimal. Associated increases in lake pH or alkalinity (Alk) were only widespread near Sudbury, Ontario (ON). Large reductions in deposition achieved by emission controls at Rouyn-Noranda, Québec (QC) in 1989 were just beginning to induce an increase in pH/Alk in local lakes. Sulphate declines at the remaining sites across southeastern Canada were mostly compensated by declines in lake base cations reflecting a decline in the acidification of catchment soils. Increases in pH/Alk observed in Algoma, ON lakes during the 1980s were lost in the 1990s so that their acidity status was very similar to that of 15 years prior.

Several factors were identified as influencing the course of recovery. Improvements in acidity were negated by increases in other acid anions, e.g. natural organic anions at Kejimkujik and both organic anions and nitrate (NO_3^-) at Lac Laflamme, QC. Drought-induced increases in SO_4^{2-} export from the drainage basins of lakes delayed recovery at 3 sites in central ON. The presence of wetlands in the drainage basins is an important factor influencing the rate of lake recovery. Whole-lake acidification and recovery experiments conducted at the Experimental Lakes Area (ELA), in northwestern ON showed that recovery of a severely acidified lake (Lake 302S, pH=4.5) was not as reversible as it was for a moderately acidified lake (Lake 223, pH=5.0). Damage to the internal Alk-generating mechanism of the severely acidified lake did not seem recoverable in the short term, and in fact, the lake appeared to be moving to a chemical/biological state that differed from the original. The 1997 Assessment concluded that chemical recovery of lakes is a long-term process and recommended continued monitoring.

Paleolimnological studies of microfossils stored in lake sediments provided inferences of past acidification and recovery trajectories of lakewater pH and fish status. Clear evidence was presented showing that lake acidification and fish loss near Sudbury, ON had occurred since 1850. These studies also provided evidence of striking chemical and biological recovery in recent years in response to local emission reductions. Monitoring evidence of biological recovery in southeastern Canada primarily came from studies in the Sudbury region. Increases or reinvasion of acid-sensitive phytoplankton, zooplankton, benthic macroinvertebrates and fish populations were observed in some Sudbury area lakes. Increases in local populations of breeding waterbirds, notably fish-eating species such as Common Loons (*Gavia immer*) and Hooded Mergansers (*Lophodytes cucullatus*), were also observed.

Outside of the Sudbury region, recovery of aquatic biota affected by acid deposition was not observed in any substantive way. Monitoring reproduction and survival of Atlantic salmon (*Salmo salar*) and brook trout (*Salvelinus fontinalis*) in NS rivers during the 1980s and early 1990s showed great interannual variation and no overall trend. Through the 1980s, some crayfish populations in the Muskoka region of ON actually declined. Studies of the Common Loon show that reproductive success remained low for those breeding pairs nesting on acid-stressed lakes, particularly in the Maritimes, and breeding success in ON and QC may have actually declined.

Experimental studies also addressed biological recovery. Placing limestone gravel in a NS stream resulted in a small pH increase; however, no recovery trend in either salmon or brook trout was observed over eight years although the fish seemed to cope better with episodic acidification. Annual liming of four NS lakes induced pH increases in downstream rivers sufficient to allow a return of Atlantic salmon to normal densities; however, model simulations suggested full recovery of Atlantic salmon populations might require several decades beyond the time required to restore natural chemical conditions. The model also indicated that strategies resulting in river pH increases of only 0.2-0.4 units would lead to large relative increases in salmon smolt production and to population recovery in some rivers. Biological recovery observed at the ELA lagged behind chemical recovery. Recovery in a lake acidified to pH 4.5 was slower than that in a lake acidified only to pH 5.0. The pH of 5.0 appeared to be an important threshold governing the rate and nature of the recovery of biological communities. The 1997 Assessment concluded that while chemical reversal of acidification could be achieved in relatively short periods of time (probably decades), the reversibility of biological effects was much more in doubt. The original ecosystems might never be re-attained.

7.3 WHAT IS RECOVERY?

D.S. Jeffries and R.C. Weeber

Why ask this question? The dictionary definition of recovery ("a return to a normal state of health"; Pearsall, 1998) contains two elements – process (i.e., returning) and outcome (i.e., normal state of health). Human nature seems to focus on outcome. Consequently, reports of improvements of acidified ecosystems lead some to mistakenly assume that ecosystem acidification is no longer of concern or in need of amelioration. Observations summarised in this chapter generally relate to the processes, rather than the endpoints, of recovery; they focus on the trajectory through time of various chemical and biological components of aquatic ecosystems. While there are (very) few cases where it may be argued that certain ecosystem components (chemical and biological) have reached an endpoint resembling a "normal state of health", a fully recovered aquatic ecosystem has not yet been physically observed. Hence, analyses of recovery outcomes generally rest in the realm of prediction (modelling) or informed speculation.

Acidification recovery must also be considered within a whole-ecosystem perspective. Lake chemistry effects were first reported in the 1950s in the Sudbury-Killarney region of ON (Gorham and Gordon, 1960) and in the Halifax region of NS (Gorham, 1957). The fact that acidification has been a decades-long process must surely mean that recovery will also be a long-term process. Second, resilience (i.e., the capacity to rebound from damage; Holling, 1973) is likely to vary among ecosystem components (chemical, physical and biological), meaning that we should expect there will be an inherent complexity to recovery, e.g., similar entities (lakes or biotic groups within lakes) may recover at different rates and proceed to different endpoints. Third, during the multi-decade acidification process, many other atmospheric changes have occurred and continue to occur, e.g., increasing CO_2 levels (probably affecting vegetation growth), increasing climatic variability (e.g. changes in temperature, wind and precipitation patterns), higher levels of UV radiation due to stratospheric ozone depletion (affecting certain aquatic biota and dissolved organic carbon – DOC), a general increase and circulation of reactive nitrogen compounds, expanding occurrences of elevated ground-level ozone concentrations, etc. (Schindler et al, 1996; Arnott et al., 2003; Dillon et al., 2003). All of these factors (and more) will affect the recovery process and endpoint. Therefore, expectations of being able to re-attain a pre-acidification ecosystem or even a stable ecosystem should be muted accordingly. The study of ecosystem change in a multiple-stressor environment demands that the kind of integrated, hierarchical monitoring program described in Chapter 6 (Section 6.3.1.3) be maintained in the long term.

Chemical changes are the first response of aquatic ecosystems to the ~40% reduction in North American sulphur dioxide (SO_2) emissions that have occurred over the last two decades (see Jeffries et al., 2003a for an account of the scientific and political milestones that led to these reductions). In contrast to SO_2, North American nitrogen oxide (NO_x) emissions (the other potentially significant acidifying pollutant) have changed little over the same time period. The desired chemical response of lakes to the resulting decline in SO_4^{2-} deposition is a reduction in lake acidity, commonly quantified as an increase in pH and/or Alk. As discussed below (see Chapter 6 also), the observed response usually differs greatly from this simple chemical response, largely due to a number of confounding, interacting biogeochemical processes that must play out before increasing pH and Alk predominate. Many of these processes are sensitive to physical factors such as climatic variation. This does not mean that the lakes are not undergoing the process of chemical recovery. It does mean that the expectation held by some of an immediate and direct lake acidity response to deposition reduction is naïve. Equally naïve is the expectation that lake chemistry will return to its original (i.e., pre-acidification) state in a time-frame of any relevance to us who are observing the recovery.

The recovery of aquatic biota necessarily occurs only after improvements in chemical conditions. Biological recovery is influenced by many factors beyond water quality and is therefore comparatively more complex (see Section 7.4; Keller and Yan, 1998; Depledge, 1999; Power, 1999; Keller et al., 1999; Gunn and Sandøy, 2001; Schindler, 2001; Vinebrooke et al., 2004). Some of the factors are outright bottlenecks, including for example, an inadequate supply of colonists to re-establish a biological community and community-level impediments to recovery dynamics (see Yan et al., 2003). Re-establishing populations of extirpated species that have low mobility (e.g., some benthic invertebrates) or whose availability from nearby sources is prevented by physical barriers (e.g., waterfalls) may require direct intervention (e.g., fish stocking) (e.g., Bilton et al., 2001; see 7.5). Even if colonisation is successful, factors such as water quality that differ from the original, the order of species' arrivals, predatory and competitive interactions among colonists and existing species, modified food web dynamics, and variation in species' tolerance to stressors will further influence the taxonomic composition and abundance of the resulting biological communities (e.g., see 7.4.2.2 and 7.4.3.3; Vinebrooke et al., 2004). With some exceptions, the information summarised below indicates that biological communities in chemically recovered lakes are likely to be permanently altered from their pre-acidification state. This has led some authors to conclude that it is best to define a recovered biological community as one that is "normal" or "typical" for a region, using reference data collected from comparable but circumneutral lakes (Keller and Yan, 1998; Keller et al, 1999; Gunn and Sandøy, 2001, 2003). Although recent progress has been made (e.g., see 7.4.3.3), the consequences of biological recovery for ecosystem function (e.g., nutrient storage and cycling) are not sufficiently understood to predict whether a return to a functional "normal state of health" is possible.

To summarise, this chapter will present evidence to date that aquatic ecosystems are (or are not) recovering from acidification, and that recovery endpoints have not yet been reached. In recovered ecosystems, chemical conditions may, and biological conditions most likely will, differ from the original, although they should resemble un-acidified systems typical of the surrounding region.

7.4 RECOVERY OBSERVATIONS

Expectations that lake ecosystems will be showing evidence of recovery are prompted by the fact that total North American emissions are now ~40% less than in 1980 (see Chapter 2). While both Canada and the United States (U.S.) have monotonically reduced emissions for over two decades, the timing of the maximum rate of reduction differed between them. The magnitude of SO_2 reductions in eastern Canada was greater during the 1980s than the 1990s, whereas the largest U.S. reductions occurred in the early 1990s.

Data on levels of SO_4^{2-} in precipitation in eastern Canada and the U.S. over the last two decades have shown a general downward trend (see Chapter 3), with the largest regional changes occurring near the source areas that contributed the greatest emission reductions. In Canada therefore, southern and central ON, and southwestern QC have undergone the greatest reduction in regional SO_4^{2-} deposition, with the areas directly influenced by the Sudbury and Rouyn-Noranda smelters experiencing the most extreme reductions.

Observations of recovering lake ecosystems fall into three categories, i.e., those from (1) lakes in regional monitoring programs where inferential evidence is available from trend analyses, (2) lakes situated near large point sources that have experienced exceptionally large reductions in acid deposition, and (3) experimentally acidified lakes at the ELA that have been progressing through a chemically managed recovery. These will be dealt with in turn in the following sections.

7.4.1 Lakes from regional monitoring programs

7.4.1.1 *Chemical recovery*

D.S. Jeffries, T.A. Clair, S. Couture, P.J. Dillon, W. Keller, D.K. McNicol, and R.C. Weeber

A review of the numerous analyses of chemical trends conducted over the last decade that cover various time periods and sets of eastern Canadian lakes plus a new analysis focusing on the 1990s has been presented in Chapter 6 (see Sections 6.3.2.1 and 6.3.2.2 for details; see also Jeffries et al., 2003b). Two important findings emerged. First, lake chemistry trends observed during the 1990s show that SO_4^{2-} is declining throughout southeastern Canada in response to declining North American SO_2 emissions. However, this generalization is only now becoming commonplace in the Atlantic provinces and is constrained in ON (see discussion below). Second, increasing Alk and/or pH trends indicate that chemical recovery is proceeding, and this response is becoming increasingly prevalent relative to earlier assessments. Positive regression slopes for Alk and pH in monitored lakes predominate in most eastern provinces (except decreasing Alk in Newfoundland (NL) and NS), and this is taken as an early sign of recovery. Nevertheless, the predominant *statistically-significant* acidity response is still 'no significant trend' as was the case in previous assessments.

Dillon et al. (2003) have shown that the SO_4^{2-} trends are predominantly, but by no means exclusively, influenced by declining SO_4^{2-} deposition. Many factors contribute to muting the Alk/pH recovery responses relative to the SO_4^{2-} trends. They include, among others, declining base cations, episodic or chronic release of SO_4^{2-} stored in the lakes' catchments or sediments, impairment of the lakes' internal Alk-generating mechanisms, and possibly an increase in the importance of nitrogen-based acidification (see Chapter 6, Sections 6.3.2.4 and 6.3.2.5 for detailed discussion, citations, etc.).

Ionic compensation of declining SO_4^{2-} concentrations in lakes by declining base cations instead of increasing pH and/or Alk is the most important factor impeding or at least delaying aquatic recovery. Lakes experiencing both declining SO_4^{2-} and base cations are not only failing to recover, they are also likely becoming more dilute. There are even a few cases where lakes with declining SO_4^{2-} continue to acidify at least in part because the rate of base cation decline exceeds the rate of SO_4^{2-} decline (see Table 6.4 in Chapter 6).

Declining base cations is an expected phenomenon, being a part of the chemical trajectory described by a generally accepted conceptual model of ecosystem acidification (see Norton and Veselý, 2003). In the absence of acid deposition, stream base cation concentrations reflect the steady-state that exists between catchment supply mechanisms (mostly from the kinetically slow process of primary weathering) and removal mechanisms (leaching by percolating precipitation water). The concentration of base cations in stream water typically varies inversely with discharge. The soil pool of easily exchanged base cations is of central importance to this steady-state because it is usually very large relative to the magnitude of the supply and export fluxes. Introduction of the strong acids in acid deposition causes leaching of the easily exchanged base cation pool (Likens et al., 1996, 1998). Hence, runoff waters usually exhibit increasing base cation concentrations with the onset of acid deposition rather than declining pH or Alk. Only ecosystems with extremely small base cation pools (e.g., those with very thin or no soil cover) acidify immediately (runoff waters have high hydrogen ion (H^+) and aluminum (Al) concentrations). If acid deposition continues long enough, the pool of exchangeable bases will eventually be leached to the extent that stream cation concentrations will decline and the water will become acidic.

Most Canadian aquatic ecosystems fall somewhere between these extremes. Many are acidified (Alk depleted relative to the original) but not yet acidic (Alk ≤ 0; see Chapter 6), and the declining base cation trends are in response to declining acid inputs. Their soil base cation pools have been leached but are not yet exhausted. Therefore an important question is what will runoff base cation concentrations be once acid deposition declines even further. Our only direct information on this question comes from paleolimnological reconstruction of long-term calcium (Ca^{2+}) patterns in six Sudbury area lakes (Keller et al., 2001). The study showed that following some small initial increases, Ca^{2+} concentrations have been declining since the early to mid 1900s (local SO_2 emissions began in the late 1800s) to levels that are approximately half of what they were in pre-industrial times. The conceptual acidification model predicts that the concentrations will decrease below their pre-acidification levels and only return when the soil pool of exchangeable bases is replenished by weathering. Since weathering is a slow process, it is unrealistic to expect that pre-industrial chemical conditions in runoff waters can be re-established in the short term (decades to centuries). Finally, it should be noted that the chemical trajectories described by the conceptual model are necessarily simplistic. Several other factors introduce variability into the base cation-SO_4^{2-} relationship, e.g., the glacial origin of Canadian Shield soils, soil thickness and profile maturity, occurrence of wetlands, declining base cation deposition and other external stressors like climatic and land-use changes. Work is needed to assess (on a regional basis) the scale of base cation depletion from catchment soils so that its affect on the chemical recovery of lakes can be better predicted.

Calculations of lake mass budgets for SO_4^{2-} show that terrestrial basin (stream) inputs and lake output generally exceed deposition (Eimers and Dillon, 2002) and this excess SO_4^{2-} export can prevent or delay recovery. Additional sources of SO_4^{2-} in the terrestrial basin are indicated; for example, SO_4^{2-} desorbed from forest soils, SO_4^{2-} produced by oxidation and mobilization of reduced S stored in wetlands, stream margins, etc., and occasionally, SO_4^{2-} produced by oxidation of sulphide minerals present in the bedrock. These sources depend on spatially variable basin characteristics such as topography, bedrock geology, forest type, soil type, depth and chemistry, percentage of wetlands, etc. Major watershed disturbance may also play a role, e.g., a SO_4^{2-} increase observed in Rawson Lake at ELA during the late 1970s and early 1980s followed two forest fires.

Drought has particularly influenced SO_4^{2-} export from ON lakes (Yan et al, 1996a; Dillon et al., 1997; Jeffries et al., 2003a). Water table or lake level draw-down allowed wetland soils and/or littoral zone sediments to dry, thereby producing conditions where previously reduced sulphur (S) species could be oxidized. When the systems re-wetted, export of the resulting mobile SO_4^{2-} produced both occasions of episodic acidification when H^+ was an important co-exported cation, and extended periods of elevated SO_4^{2-} (relative to pre-drought levels) when Ca^{2+} was typically a more important compensating cation. Drought events delay lake recovery and work is needed to quantify the size of the reduced S pool and its accessibility in order to assess the long-term potential of this stressor interaction.

As SO_4^{2-} deposition declines, the relative importance of acidification by N deposition increases. There have been limited reports of increasing NO_3^- concentrations at some Environment Canada monitoring sites (e.g., Couture, 1995; Jeffries et al., 2002), but in both cases they were probably more related to changing forest condition (e.g., attaining climax status and perhaps climatic variation increasing soil nitrification rates) than atmospheric deposition. No such explanation is appropriate for NO_3^- increases observed in lakes near the Rouyn-Noranda smelter in QC nor the limited instances present in a Canadian Wildlife Service (CWS) data set from ON that was analyzed in Chapter 6 (see Section 6.3.2.1). Chapter 6 concluded that there is little evidence that N-based acidification is presently affecting Canadian lakes. By extension, therefore, it is unlikely that N deposition is presently delaying recovery. However, N differs from S in that most of the deposition is stored in the terrestrial catchment (most SO_4^{2-} deposition is mobile and passes through), and N-based acidification begins once the accumulated storage reaches the point that it can satisfy the forest's nutritional requirement for N (called N saturation). The potential certainly exists in the future, if elevated N deposition continues and catchment N saturation develops (Stoddard, 1994), for NO_3^- to become mobile like SO_4^{2-}, allowing N-based acidification to prevent or delay recovery.

Changes in organic anions (reflected in DOC concentrations) may also influence recovery, i.e., increasing organic anions could compensate for a SO_4^{2-} decline so that there is no change in acidity variables. 'No trend' in DOC concentrations was by far the dominant observation reported in Chapter 6, although there were some instances of both decreasing and increasing levels. As mineral acid deposition decreases, the influence of organic acids will increase due to their amphoteric nature (i.e., capable of acting either as an acid or base), even without an increase in DOC (Clair et al., 1992). This effect may be a cause for some of the apparently contradictory Alk and pH responses observed in NL and NS (Chapter 6, Section 6.3.2.1.1) wherein regression slopes for monitoring records of pH were more often than not positive while slopes for Alk were more often than not negative. The Gran Alk variable used in Chapter 6 is influenced by any organic anions that will accept protons above a pH of about 5.

Factors that affect internal Alk-generating processes may influence lake recovery. The importance of internal Alk generation in lakes generally increases with the water replenishment time. Typically the most important processes underlying internal Alk generation include SO_4^{2-} reduction, denitrification, ion exchange at the water-sediment interface (Cook et al., 1986), and DOC degradation (P.J. Dillon, pers. comm.). Whole-lake acidification studies conducted at the ELA have indicated that internal Alk generation can be impaired such that the pH trajectory during recovery differs from the acidification trajectory (Jeffries, 1997). At a minimum, there is a lag in the pH recovery relative to the SO_4^{2-} decline, and a significant likelihood that the chemical condition of the lakes is proceeding to a different state than the original (cf. movement to more dilute systems noted above). Impairment of internal Alk generation may be related to reduced availability of organic carbon to power the microbially driven SO_4^{2-} reduction, and/or depletion of the iron (Fe) needed to form insoluble sulphide compounds (Carignan, 1989). Impairment of internal Alk generation also appears to depend partly on the severity of the acidification. For example, reducing the pH below 5, as was the case in one ELA experiment, impaired the lake's internal Alk generation while lowering the pH to only 5.1 in another experiment, did not. The impairment of a lake's ability to internally buffer acids means that the efficiency of acidifying inputs is greater during the recovery period than it was during acidification.

Overall, evaluation of regional lake chemistry trends in terms of recovery shows that the primary acidifying agent (SO_4^{2-}) is generally declining in response to declining SO_4^{2-} deposition. This is the good news – reduction of precursor SO_2 emissions is having an observable effect in southeastern Canada. Deviations from this generalization arise from mobilization of (most likely) previously deposited and stored S. Determining how long this "old" S will continue to influence lake recovery is a subject of current research. Direct evidence of significant lake recovery (increasing Alk and/or pH) is much less widespread, being principally muted by declining base cations; however, the mobilization of stored S and alterations of in-lake mechanisms that generate Alk also play a role. The direction of change in Alk and/or pH (see Chapter 6) is encouraging, and similar evaluations in Scandinavia where there is a longer history of reduced deposition (e.g., see Stoddard et al., 1999) suggest that in time, Alk and pH improvements will begin to predominate over base cation declines. Nevertheless, it is likely that the lakes will ultimately recovery to a different chemical state (more dilute) than their original, pre-industrial condition.

7.4.2 Lakes near large point sources

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Lakes located near smelters at Sudbury, ON and Rouyn-Noranda, QC deserve special attention in this chapter. They have been influenced by acid deposition originating from both local and long-range sources. Reductions in smelter emissions at both locations have reduced the scale of local deposition to a much greater degree than in adjacent regions. Such lakes present a unique setting in Canada for evaluating recovery. In particular, there has been intense study of aquatic ecosystems in the Sudbury area for many years, particularly the extremely sensitive lakes in Killarney Provincial Park southwest of the smelters. The information provides one of the best (and probably the best) documented case studies of ecosystem recovery following reductions in acid deposition available anywhere in the world (e.g., Gunn, 1995; special volumes in the Canadian Journal of Fisheries and Aquatic Science, 1992 (Vol. 14, Supplement 1) and Ambio, 2003 (Volume 23)).

Over a century of operations by the metal smelters in the Sudbury, ON area have resulted in atmospheric pollution impacts to aquatic ecosystems within a large zone (roughly 17,000 km^2) around the city. Lakes near the smelters received chronic, high deposition of acidifying pollutants and metal particles, and their chemistry, physical characteristics and biota have been the most severely affected. Large SO_2 emission reductions occurred at Sudbury particularly early (1970s) (Gunn, 1995) (Figure 7.1), and now, local SO_4^{2-} deposition is similar to regional sites 200 km to the southeast (Keller et al., 2003). The commission of the so-called "superstack" in 1972 provided a large and instantaneous decrease in acid deposition (mostly dry) in the local Sudbury region, due to both large emission reductions and greater dispersion of pollutants. Following these emission reductions and additional emission reductions in the late 1970s (Figure 7.1), and some observations of improving water chemistry and recovering biological communities, the emphasis of Sudbury area monitoring programs shifted from assessing damage to tracking recovery. The 1997 Assessment (Jeffries, 1997) singled out the Sudbury area as the only region where widespread recovery was observed, due in part to both the extreme historical acidification and the dramatic reduction in local emissions, notably S.

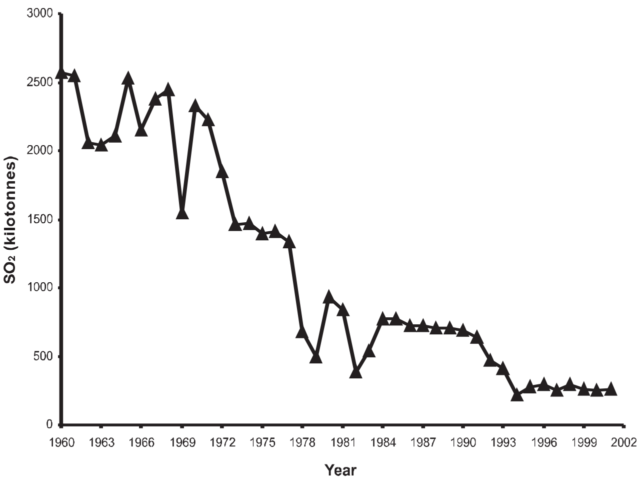

Figure 7.1: Sulphur dioxide emissions for smelters in the Sudbury, ON area from 1960 to 2001.

7.4.2.1 *Chemical recovery*

Over the years, many papers have reported changes in chemistry for lakes in the Sudbury region (e.g., Dillon et al., 1986; Keller et al., 1992; Mallory et al., 1998; Keller et al., 2003). Such studies produced a generally consistent picture of predominantly decreasing SO_4^{2-}, base cation, Al and base metal concentrations, and increasing pH and/or Alk. Although patterns vary among lakes, intensively monitored lakes in the Sudbury area show increasing pH and decreasing SO_4^{2-} concentrations (Figure 7.2) The rate of SO_4^{2-} changes was often steeper in the 1970s and 1990s than in the 1980s, apparently reflecting the local SO_2 emission history. The sample lake population and the choice of time period for analysis influenced the nature of the reported recovery response. For example, 36 of 38 relatively large lakes (14.5 to 1315 ha) monitored by the Ontario Ministry of the Environment (MOE) exhibited increasing pH between 1981 and 1989 (Keller et al., 1992), while only 26 of 161 smaller lakes (0.1 to 350 ha) sampled by the CWS had increasing pH between 1983 and 1995 (2 were decreasing and the rest showed no change; Mallory et al., 1998). The potential increase in lake pH and/or Alk has been partially reduced by declining base cation concentrations (Keller et al., 2001). Specific departures from these recovery trends were usually readily explained, e.g., short-term, drought-induced trend reversals as described above (Keller et al., 1992; Yan et al., 1996a; see Section 6.3.2.5). Despite the observed and paleolimnologically-inferred improvements of Sudbury area waters, several studies (e.g., Mallory et al., 1998; Keller et al., 2003; see Section 6.3.2.3) still conclude that many lakes remain too acidic (pH <6) to support sensitive aquatic biota (see Section 7.4.2.2). Despite the water quality improvements, many of the lakes closest to Sudbury continue to have high copper (Cu) and nickel (Ni) concentrations in their water and sediments. Recovery in the sensitive Killarney lakes has been accompanied by decreased Ca^{2+} concentrations, increased transparency and altered thermal regimes that may affect these ecosystems. Keller et al. (2003) concluded that even in these lakes that offer our best evidence of chemical recovery, the recovery process is incomplete (see also Larssen et al., 2003) and continued surveillance within a multi-stressor framework is needed.

The smelter located at Rouyn-Noranda, QC is responsible for a large portion of that province's SO_2 emissions, and the emission reduction was initially implemented mostly in the early 1990s (i.e., much later than at Sudbury) with a 90% reduction goal to be achieved by 2010. Study of lakes in the Rouyn-Noranda region has been much less intense than at Sudbury. Dupont (2004) evaluated chemical changes that occurred in 36 lakes sampled in 1982, 1991, 1996 and 2001 (see Chapter 6, Section 6.3.2.2 for more details). Over the entire period, SO_4^{2-}, base cations and DOC concentrations significantly declined, while Alk and NO_3 significantly increased. No significant change in pH was detected however, although a subset of nine clear water lakes did show increasing pH between 1991 and 2001. The increasing NO_3^- concentrations are particularly interesting because there has been no increase in N deposition or land-use change to explain them, and they are spatially restricted to a zone within 50 km of the smelter. Lakes surrounding the Rouyn-Noranda smelters are clearly in a very early stage of recovery and an increased level of surveillance is warranted.

7.4.2.2 *Biological recovery in the Sudbury region*

In general, the previous assessment indicated that biological recovery for Sudbury area lakes lagged behind chemical recovery, with the lag time dependent in part on the severity and duration of acidification. Several acid-sensitive phytoplankton, zooplankton and benthic invertebrate species reinvaded many Sudbury lakes during the 1980s and 1990s. Long-term liming of acidified lakes often enhanced zooplankton and fish recovery but the degree of recovery declined with the strength of acidification (e.g., pH≤4.5) and metal contamination. Although continued local emission reductions have led to improvements in aquatic habitats, evaluating lake responses to emission controls has been

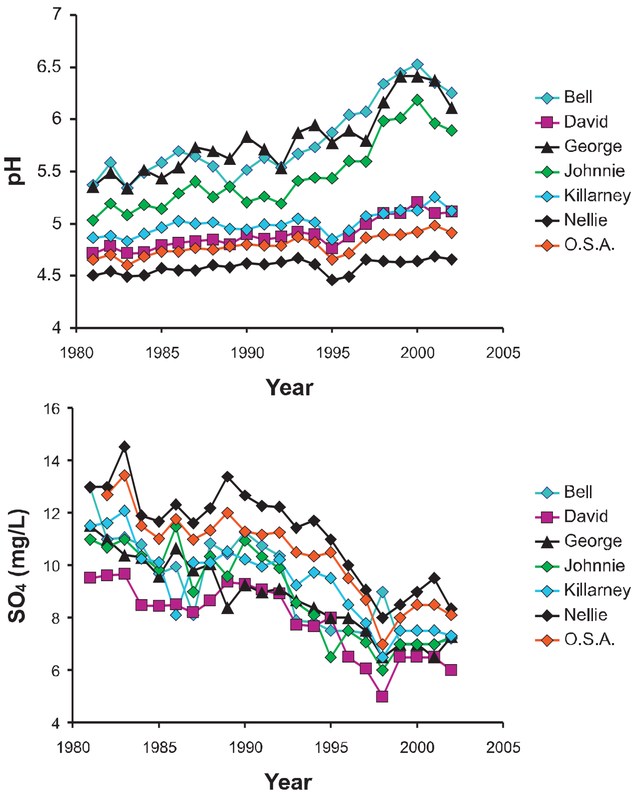

Figure 7.2: Patterns of pH and SO_4^{2-} concentrations in seven lakes in the Sudbury, ON area during the period 1981 to 2002.

challenging due to the complex interactions of lake acidity with toxic metals and other factors. Severely damaged biological communities have been slow to recover naturally, probably reflecting both continuing habitat impairment and restricted dispersal opportunities.

The following sections summarise recent observations of biological recovery for the Sudbury ON region only; recent biological monitoring information was unavailable for the Rouyn-Noranda, QC area.

7.4.2.2.1 Algae

7.4.2.2.1.1 *Planktonic*

The previous assessment summarised the positive influence of lake pH and Alk on phytoplankton species richness. Along with lake morphological features, nutrient status and other chemical characteristics, lake acidity status was indicated as an important factor in the recovery of phytoplankton communities in acidified lakes. Despite improving acidity conditions, phytoplankton community richness continued to be less than in reference lakes near Dorset, ON (approximately 200 km southeast of Sudbury), perhaps due to continued stresses of high metal concentrations.

Findlay (2003) sampled 22 Killarney lakes southwest of Sudbury to assess the recovery of phytoplankton relative to historical information and to the status of planktonic algae communities in Lake 302S, an experimentally acidified lake in ELA in northwestern ON (see also 7.4.2). Phytoplankton species richness was strongly correlated with lake pH for the 22 Killarney lakes and for Lake 302S at four stages of the experiment (Figure 7.3). Correspondence analysis of phytoplankton community structure differentiated lakes above and below pH 6 and indicated several of the most acidic lakes had undergone a partial recovery in phytoplankton community composition. Phytoplankton biomass was not correlated with pH for Killarney lakes but was negatively correlated for Lake 302S, suggesting that biomass relationships with pH may be lake-specific and be influenced by factors such as water renewal times and phosphorus availability. Findlay (2003) suggested acid tolerant species may continue to fill niches as pH increases, a process likely to slow the recovery of acid sensitive competitor species.

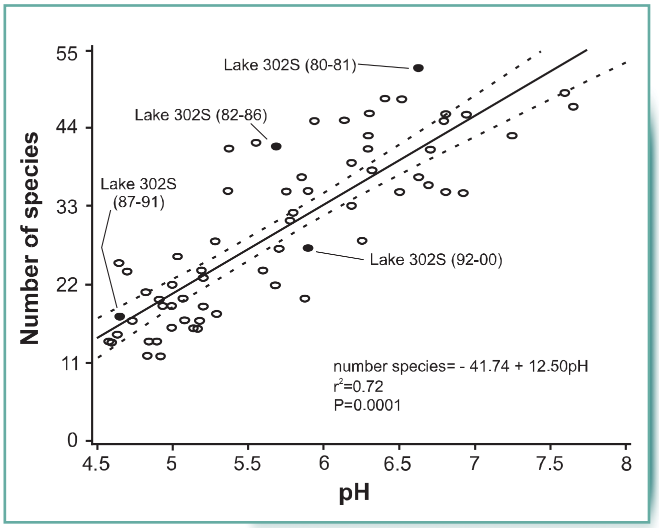

Figure 7.3: Linear regression of the number of phytoplankton species present relative to the pH of 22 Killarney lakes (1998 – 2000) (open circles) and average pH of ELA's Lake 302S (1980 – 1981, 1982 – 1986, 1987 – 1991, 1992 – 2000) (solid circles). Adapted with permission from Findlay (2003).

Although metal concentrations declined with decreasing acidity, residual concentrations may have also impeded phytoplankton recovery.

Although phytoplankton communities can recover with chemical improvements, recent observations indicate that re-acidification events can have important and lasting impacts on algal recovery. The acidified Swan Lake near Sudbury was showing signs of chemical and biological recovery in the early 1980s but drought conditions in 1986 and 1987 led to a drop in pH from near 6 to 4.5 (Arnott et al., 2001). Dissolved organic carbon concentrations also declined and metal concentrations, water clarity, oxygen concentration and bottom water temperature increased. Arnott et al. (2001) reported the impacts of the re-acidification event on the phytoplankton, rotifers and crustacean zooplankton of Swan Lake (fishless since the 1950s). During the 1980s, changes to the phytoplankton community suggested recovery. Although taxonomic richness and diversity did not change, dinoflagellates were replaced by chrysophytes as the dominant phytoplankton, a pattern similar to the chrysophyte dominance of phytoplankton in Dorset, ON reference lakes. The re-acidification of the lake was associated with a single year reduction in chrysophytes and a decline in richness and diversity.

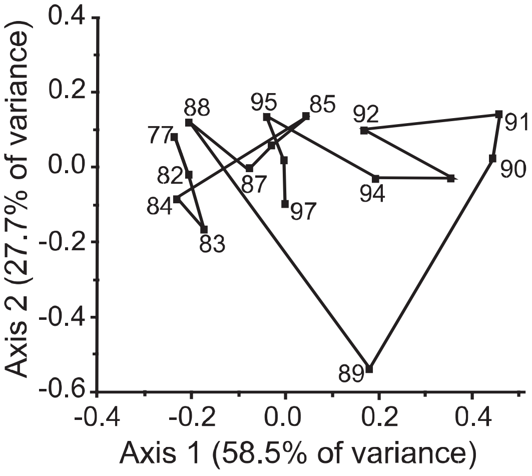

Figure 7.4: Scatterplot summarising the temporal change in phytoplankton community biomass sampled in Swan Lake near Sudbury, ON between 1977 and 1997. The position of Swan Lake phytoplankton communities is shown for each sample year relative to the first two Correspondence Analysis axes. Adapted with permission from Arnott et al. (2001).

Chrysophytes recovered as the dominant group by 1989 but richness and diversity did not recover to values similar to reference lakes until the late 1990s. Ordinations of the phytoplankton community illustrated that community structure was dramatically altered by the re-acidification event and the disturbance persisted for seven years (Figure 7.4). As of 1997, acidity effects were still observed in Swan Lake phytoplankton with the absence of diatoms being one of the most obvious continuing effects. This paper demonstrated the important and persistent influence of drought-induced acidification events on recovering phytoplankton and zooplankton communities in acid-damaged boreal lakes.

Working in Clearwater Lake, a severely acidified lake within the Sudbury city limits, Winter et al. (unpublished) assessed phytoplankton community recovery from acidification. In the early 1970s, after decades of severe acid stress, the lake had a pH of about 4.2 and contained elevated levels of Cu, Ni, Al and other metals. All fish were extirpated, and there were large reductions in the diversity of phytoplankton, macrophytes, zooplankton, and benthic invertebrates (Scheider and Dillon, 1976; Yan and Miller, 1984). Following dramatic reductions in local S deposition, there was an improvement in many aspects of the physical and chemical conditions in the lake with pH reaching > 6 in the 1990s (Girard et al., 2003). Winter et al. (unpublished) compared temporal changes in the Clearwater Lake phytoplankton community from 1973 to 2001 relative to the community composition of three reference lakes beyond the influence of Sudbury smelters (Yan et al., 1996b) near Dorset, ON sampled from 1981 to 2001. Annual ice-free mean pH for each reference lake was > 6 throughout the study. Phytoplankton samples were collected through the euphotic zone in the deepest part of each lake once or twice a month during the ice-free season and the samples were pooled to obtain one sample per lake for each year. Most of the identifications were made to the genus level. A Correspondence Analysis (CA) based on relative abundance indicated a three-stage temporal shift in the taxonomic composition of the phytoplankton community in Clearwater Lake towards that of the reference lakes (Figure 7.5). The first two CA axes explained most (i.e., 23%) of the variance captured by the ordination, and Clearwater Lake phytoplankton samples shifted in time from positive to negative positions on both axes 1 and 2. The phytoplankton genera positively associated with CA axis 1 included unidentified (naked) dinoflagellates, chlorophytes (*Xanthidium* and *Mougeotia*), euglenophytes (*Trachelomonas*), and the tribophyte genus *Isthmochloron*. Genera negatively associated with axis 1 included the chrysophyte *Uroglena*, several diatoms (*Tabelleria*, *Cyclotella* and *Rhizosolenia*) and the haptophyte (*Chrysochromulina parva*). As indicated by the shifts in ordination space, Clearwater Lake phytoplankton changed from being quite distinct from the communities in the three Dorset lakes during the earliest period (i.e., the 1970s and early 1980s) and the mid- to late-1980s to being similar in the 1990's and in 2000, 2001. The single exception to this recovery pattern was in 1988 when the phytoplankton community shifted briefly towards an earlier composition, primarily due to an increase in the abundance of dinoflagellates. Although the 1988 re-acidification event in another Sudbury area lake (Swan Lake, described earlier) impaired phytoplankton recovery (Arnott et al., 2001), Clearwater Lake did not experience a dramatic drop in pH that year, indicating re-acidification was not the cause for the temporary shift in the phytoplankton response. The overall change in phytoplankton composition in Clearwater Lake indicates recovery of the community over the last 30 years.

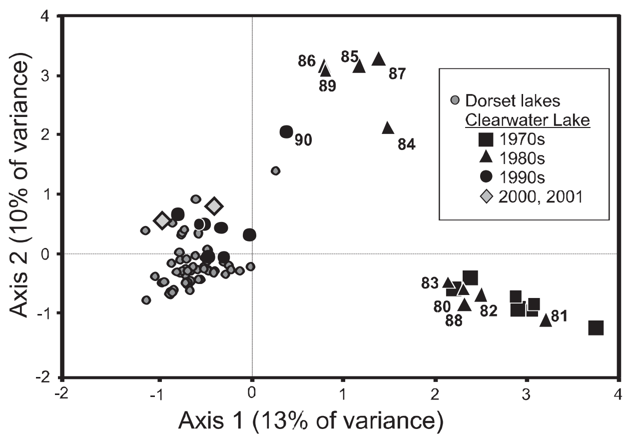

Figure 7.5: Scatterplot summarising the temporal change in the relative abundance of phytoplankton taxa sampled from Clearwater Lake near Sudbury, ON between 1973 and 2001. The position of Clearwater Lake phytoplankton communities in the first two Correspondence Analysis (CA) axes are shown relative to phytoplankton sampled from three reference lakes (pH>6) near Dorset, ON (eigenvalues for axis 1 and 2 were 0.53 and 0.37, respectively) (shaded circles). Clearwater Lake CA scores are labelled by year from 1980 to 1990; data were unavailable from Clearwater Lake for 1992 and 1997.

7.4.2.2.1.2 Benthic

Relative to phytoplankton, much less information is available on the responses of benthic algae to the acidification and recovery of Sudbury area lakes. This group, which includes filamentous and cellular algae in association with bottom substrates, was not included as a topic in the previous assessment. Detailed work on benthic algae was conducted in the ELA (see 7.4.3.3.1) and one recent study included a focus on lakes in the Killarney area. Working in Killarney and ELA's Lake 302S, Vinebrooke et al. (2003a) investigated the influence of the spatial and temporal scale of acidification on the resilience of epilithic algae. Increases in DOC, dissolved inorganic carbon (DIC) and calcium (Ca^{2+}) best explained the temporal variability of epilithic species abundance in recovering lakes. The authors defined resilience as the distance travelled through time by lakes in ordination space. In the case of Lake 302S, resilience was defined as movement toward pre-acidification algal composition as represented in ordination space. Although the chemical conditions of many Killarney lakes improved between 1992 and 2002, the distances moved by Killarney lakes and Lake 302S in ordination space indicated that epilithic algae assemblages responded weakly in Killarney but quite strongly in Lake 302S (Figure 7.6). A delay of algal recovery relative to chemical improvement was more pronounced in Killarney lakes than in Lake 302S, perhaps due to the consequences of long-term regional acidification in the Sudbury, ON area. The authors suggested the low resilience of many Killarney lakes relative to Lake 302S may have been due to factors related to the spatial extent and temporal scale of acidification. Recovery in Killarney lakes may have been impaired by factors including the regional extirpation of algal and other beneficial colonizers, the establishment of acid-tolerant competitors and grazers, and more extreme abiotic conditions due to chronic acidification. The observed delay in algal response to chemical improvements agrees with many other reports of lagging biological recovery and also suggests that, relative to an example of extreme but simplified experimental acidification (i.e., Lake 302S at ELA), the long-term acidification of a region may result in a higher degree of biological impairment.

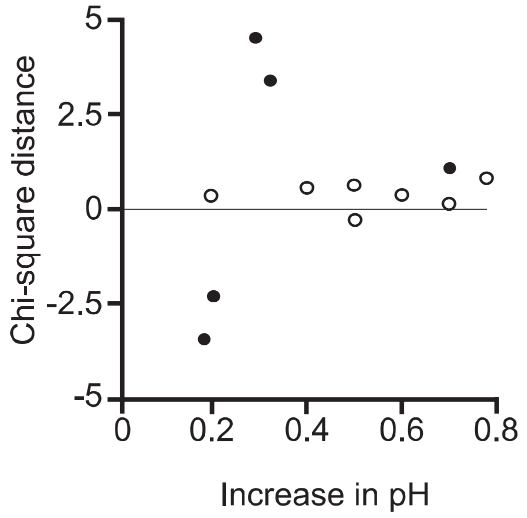

Figure 7.6: Net chi-square distance traveled by site scores in Canonical Correspondence Analysis ordination space towards coordinates for pre-acidification ELA's Lake 302S (1981) as a function of pH recovery in Lake 302S (1990 – 1995) and 7 Killarney lakes (1992 – 2000). Ordinations were of $\log_{10}$ transformed biovolumes of epilithic algae taxa in Lake 302S (solid circles) and Killarney lakes (open circles). Adapted with permission from Vinebrooke et al. (2003a).

7.4.2.2.2 Invertebrates

7.4.2.2.2.1 Planktonic

The previous assessment highlighted evidence from Sudbury area studies showing the potential for acid-sensitive zooplankton species to reinvade acidified lakes following chemical improvements. The previous assessment pointed out that zooplankton recovery is a function of species and community responses to chemical improvements; physical, biological and other habitat quality attributes of lakes; the availability and success of colonizers; and the extent and severity of habitat damage. Recent work supports those conclusions (e.g., Keller and Yan, 1998; Doka et al., 2003). Zooplankton recolonisation requires that habitat quality improvements have been sufficient to ensure the survival of colonists which have invaded from refugia within the lake, expanded from existing populations, or dispersed from other lakes (Keller and Yan, 1998; Pollard et al., 2003). Conditions that promote recolonisation include high degrees of physical connection between recovering and source lakes; control of invertebrate predators (e.g., *Chaoborus*) by fish; and high species mobility, fecundity, wide distribution and acid-tolerance. Depending on the severity of acidification, colonisation sources and the current habitat conditions, zooplankton communities may not recover to their pre-acidification states but to some alternative state with different dominance patterns among the species groups. Although recovery patterns are complex, several general patterns have been observed. Improving lake pH is often associated with increasing zooplankton species richness and increasing dominance by acid-sensitive species. Zooplankton recovery may be delayed if acidification has been chronic and severe, if fish are absent and predatory invertebrates are common, or if chemical recovery is interrupted.

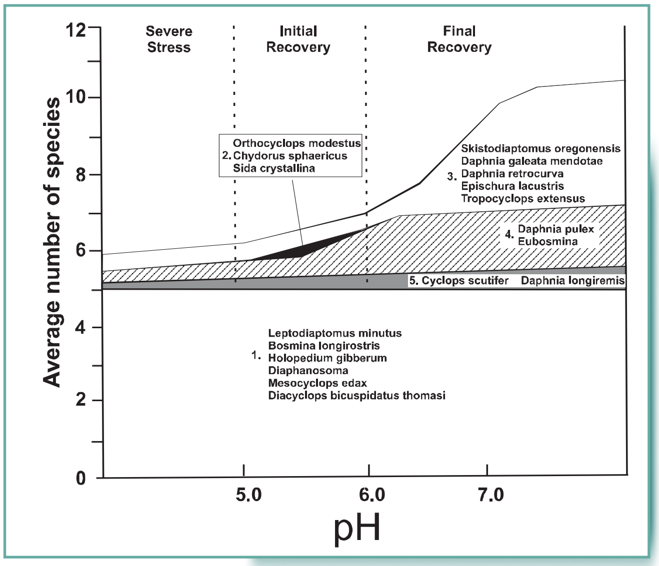

Figure 7.7: Schematic showing the general sequence of change for species composition of crustacean zooplankton communities during recovery of lakes near Sudbury, ON. The areas under each curve indicate the general change in average species richness per collection along the pH gradient. The species most likely to contribute to increased species richness are shown and are classified as (1) acid-tolerant, (2) littoral, (3) highly acid-sensitive, (4) moderately acid-sensitive and (5) hypolimnetic. Adapted with permission from Keller and Yan (1998).

Zooplankton species richness often increases as lake acidity levels decline. Work in the Sudbury area indicates that the species contributing to increases in species richness are generally predictable (Figure 7.7) (Keller and Yan, 1998). Several taxa tend to occur across a range of pH values (i.e., groups 1 and 5 in Figure 7.7) while the contribution of moderately and highly acid-sensitive species to overall richness tends to increase between pH 5.5 and 6.5 with maximum richness occurring above pH 7. Snucins et al. (2001) sampled crustacean zooplankton in 11 Killarney lakes between 1972 and 1998. By 1998, the pH of several lakes had improved to near the pre-industrial levels predicted by diatom microfossil estimates. Although mean zooplankton species richness did not change in lakes that were never acidified, richness increased in the chemically improving lakes, with 1998 mean values similar to those in unacidified lakes.

The patterns of recovery in Sudbury's Clearwater and Middle lakes provide encouraging examples of zooplankton response to chemical improvements in severely acidified water bodies. As described previously (see 7.4.2.2.1.1), the composition of Sudbury's Clearwater Lake phytoplankton community recovered soon after the lake reached pH 6. Several fish species also reinvaded the lake (J. Gunn, pers. comm.). Zooplankton sampling in Clearwater Lake began in 1973 and has been conducted monthly during the ice-free season using standardized sampling and counting protocols (since 1979) (Scheider and Dillon, 1976; Yan and Strus, 1980). The time series of change in the zooplankton community offers evidence both of severe initial damage and substantial progress towards recovery. The Clearwater Lake zooplankton community of the 1970s was quite different from the communities of 22 non-acidic (pH>6) reference lakes sampled near Dorset, ON between 1983 and 1988 (Yan et al., 1996b) (Figure 7.8a). In particular, the Clearwater Lake community was dominated by *Cyclops vernalis*, *Bosmina longirostris* and *Chydorus sphaericus* to the virtual exclusion of all other taxa commonly found in non-acidic lakes (Figure 7.8b). As the pH of Clearwater Lake increased, however, the community changed substantially. Abundance of the three acididophilic taxa fell by orders of magnitude. Other species, particularly *Diaphanosoma birgei* and *Leptodiaptomus minutus* became permanent in the lake, while several other common species of larger Cladocera (*Daphnia* spp. and *Holopedium*) also appeared, albeit with small and variable populations. As of 2001, the zooplankton community of Clearwater Lake was still damaged relative to the 22 reference lakes but was clearly recovering toward the community structure found in the non-acidic reference lakes.

Although patterns of zooplankton recovery in Sudbury's Middle Lake have been promising, the responses of copepods and cladocerans to changes in acidity were dramatically different (Yan et al., 2004). Located near the centre of Sudbury, Middle Lake was first acidified in the 1950s and by the mid-1970s was severely damaged with severe acidity (pH 4.2) and high Ni and Cu concentrations. After additions of neutralising bases between 1973 and 1975, lake pH increased to above 6, metal concentrations declined, and light attenuation and temperature regimes improved. Fish returned to the lake in the mid-1980s and the community was strongly dominated by the planktivorous yellow perch (*Perca flavescens*) by the early 1990s. With the exception of a single year missed (1980), zooplankton were sampled approximately monthly during the ice-free season of each year between 1973 and 2002. Yan et al. (2004) summarised temporal changes in Middle Lake's zooplankton community and assessed recovery with respect to the zooplankton in 22 non-acidic Dorset reference lakes. Average crustacean richness in Middle Lake increased from 2.6 species to between six and eight taxa after 2000 (Figure 7.9). Although a strong improvement, recent taxonomic richness was usually below the target of eight to 12 taxa defined based on the reference lake communities. During the 1970s, the copepod assemblage of Middle Lake was very distinct from those in the 22 reference lakes. After 1996, however, the Middle Lake and reference lake copepod communities were almost indistinguishable (Figure 7.10). The

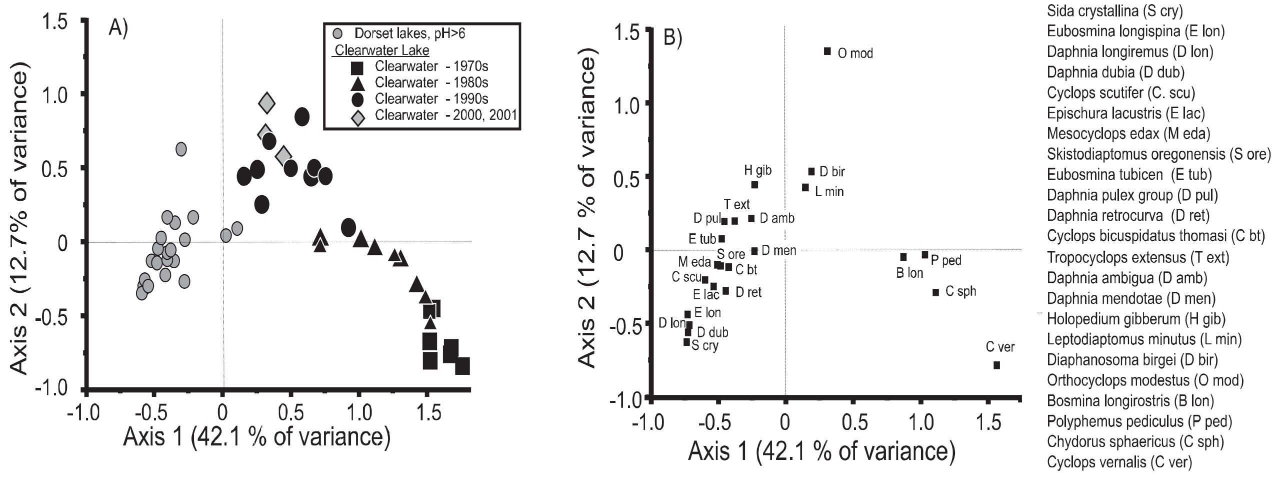

Figure 7.8: Scatterplots summarising temporal change in zooplankton community composition based on Correspondence Analysis (CA) of the relative abundance of species sampled from Clearwater Lake near Sudbury, ON between 1973 and 2001. A) The positions of Clearwater Lake zooplankton communities are shown relative to the first two CA axes and the zooplankton sampled from 22 non-acidic reference lakes near Dorset, ON (shaded circles). B) The location of zooplankton species collected from Clearwater Lake and Dorset reference lakes relative to the first two CA axes.

cladoceran community of Middle Lake was also quite different in the 1970s from the community in the reference lakes. Although some shifts in cladoceran composition occurred during the 1980s, the recovery of cladocerans in Middle Lake was essentially stalled by 1990 (Figure 7.10).

Working with a set of 32 damaged but chemically improving lakes in the core of the Sudbury area, Keller et al. (2004) also reported evidence that copepod communities may recover more completely and more quickly than the cladoceran zooplankton. For both 1990 and 2003 samples, the cladoceran species composition of most sampled Sudbury lakes was quite different from the 22 non-acidic Dorset reference lakes used by Yan et al. (2004) (Figure 7.11a). In contrast, copepod communities in many of the 1990 and 2003 Sudbury lakes were more similar to those in the reference lakes (Figure 7.11b). Yan et al. (2004) suggested the strong copepod recovery was due to colonists responding favourably to suitable habitat conditions and unsaturated food webs. The limited cladoceran recovery was not likely due to dispersal problems or food scarcity but more likely to either the predation pressure exerted by an abundant yellow perch population, continuing toxicity from residual metal concentrations or a combination of both these factors. Although cladoceran recovery may require additional declines in metals and shifts toward a more balanced fish community, both Keller et al. (2004) and

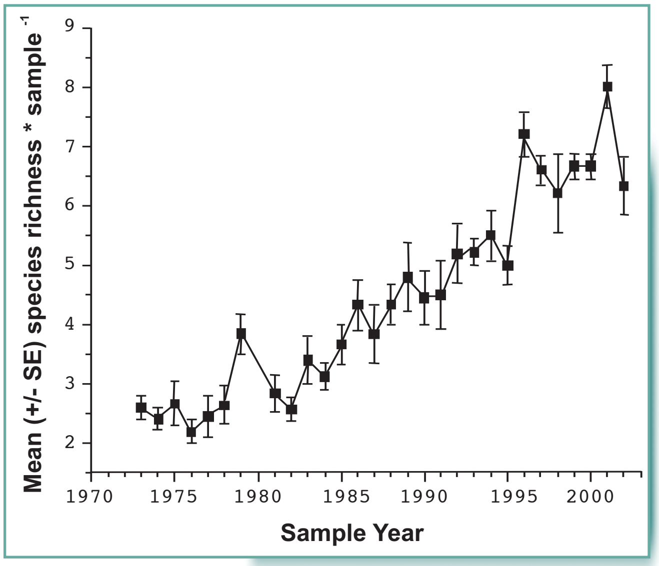

Figure 7.9: Long-term changes in ice-free season average crustacean zooplankton species richness identified in standard counts of monthly samples collected in Middle Lake near Sudbury, ON between 1973 and 2002. Only individuals identified to the species level are included. Adapted with permission from Yan et al. (2004).

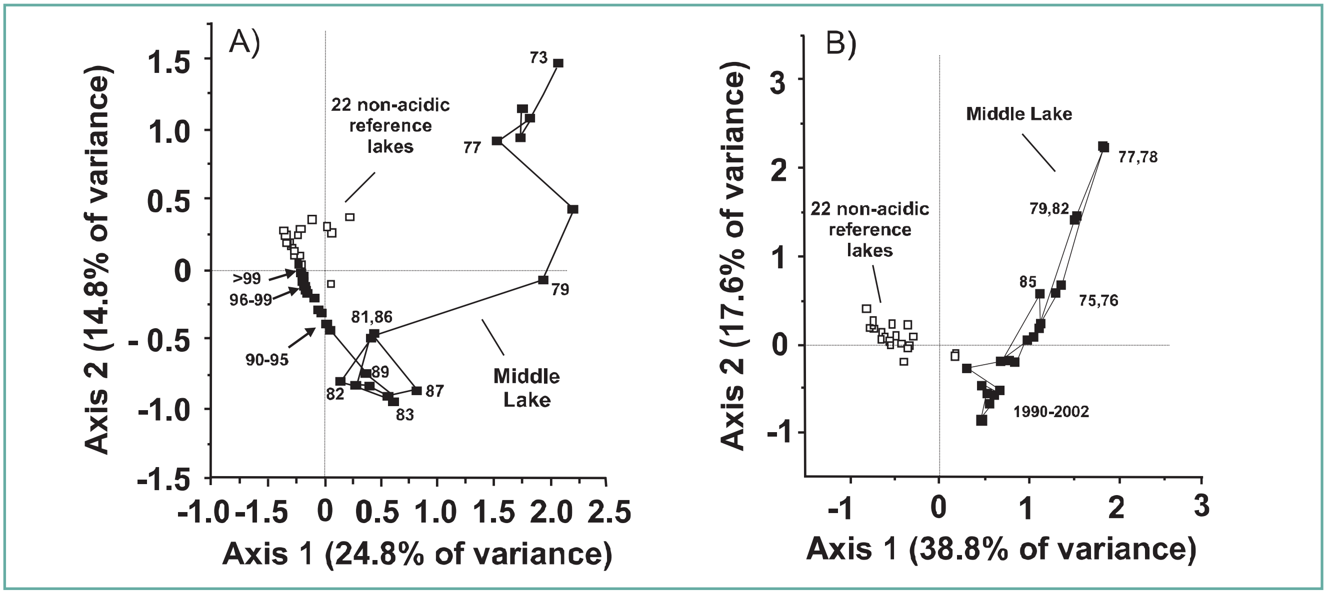

Figure 7.10: Scatterplots summarising temporal change in the log(x+1) transformed, ice-free season mean abundance of (A) Copepoda and (B) Cladocera zooplankton sampled from Middle Lake, near Sudbury, ON between 1973 and 2002. Temporal change for Middle Lake copepods and cladocerans (solid squares) are shown relative to the species composition of samples from 22 non-acidic reference lakes near Dorset, ON (open squares). Each point in the Middle Lake trajectories represents a sample year. Lake-year scores are shown relative to the first two Correspondence Analysis axes. Adapted with permission from Yan et al. (2004).

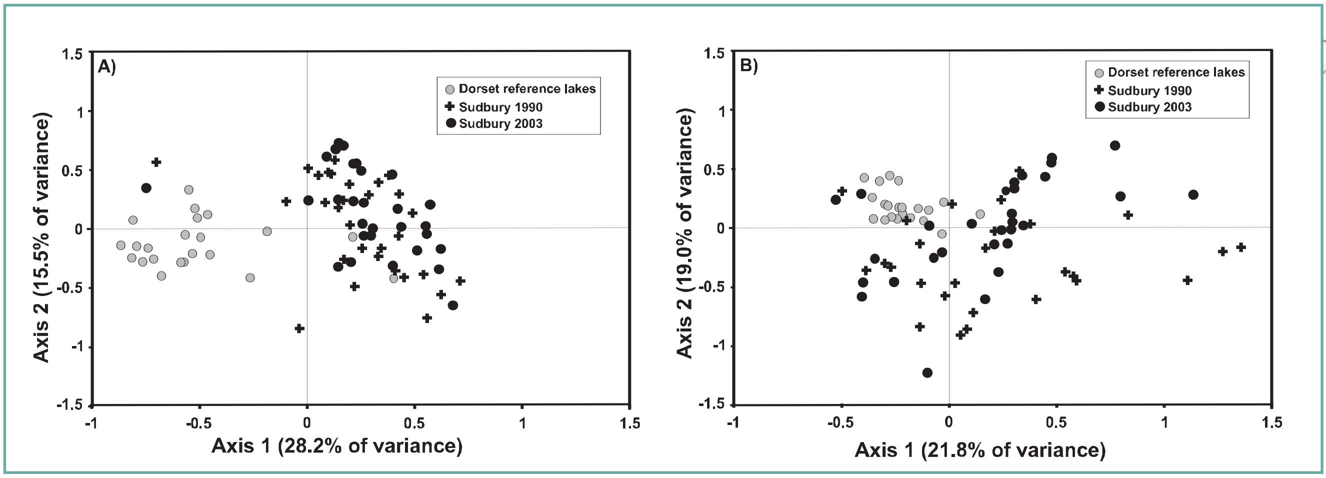

Figure 7.11: Scatterplots summarising the taxonomic composition of A) Cladoceran and B) Copepod zooplankton sampled from 32 Sudbury, ON lakes in 1990 (solid cross) and 2003 (solid circles), and from 22 non-acidic reference lakes near Dorset, ON (shaded circles). Lake scores are shown relative to the first two Correspondence Analysis axes. Adapted with permission from Keller et al. (2004).

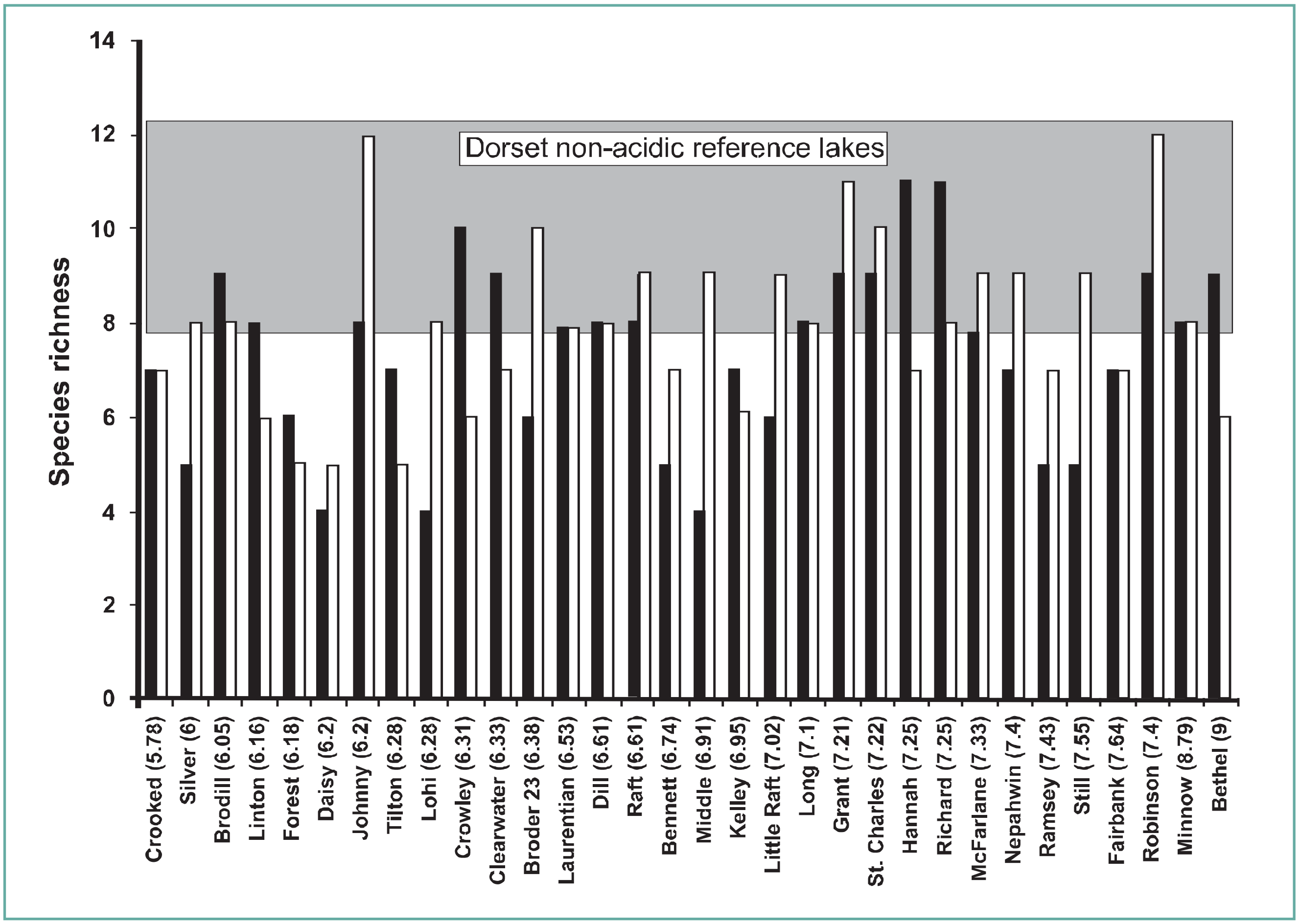

Figure 7.12: Number of crustacean zooplankton species sampled from 32 Sudbury, ON lakes in 1990 (solid bars) and 2003 (open bars). Lakes are ordered by increasing current pH (in brackets). The species richness (mean +/- 2 SD) of 22 non-acidic reference lakes near Dorset, ON (shaded area) is shown for comparison. Adapted with permission from Keller et al. (2004).

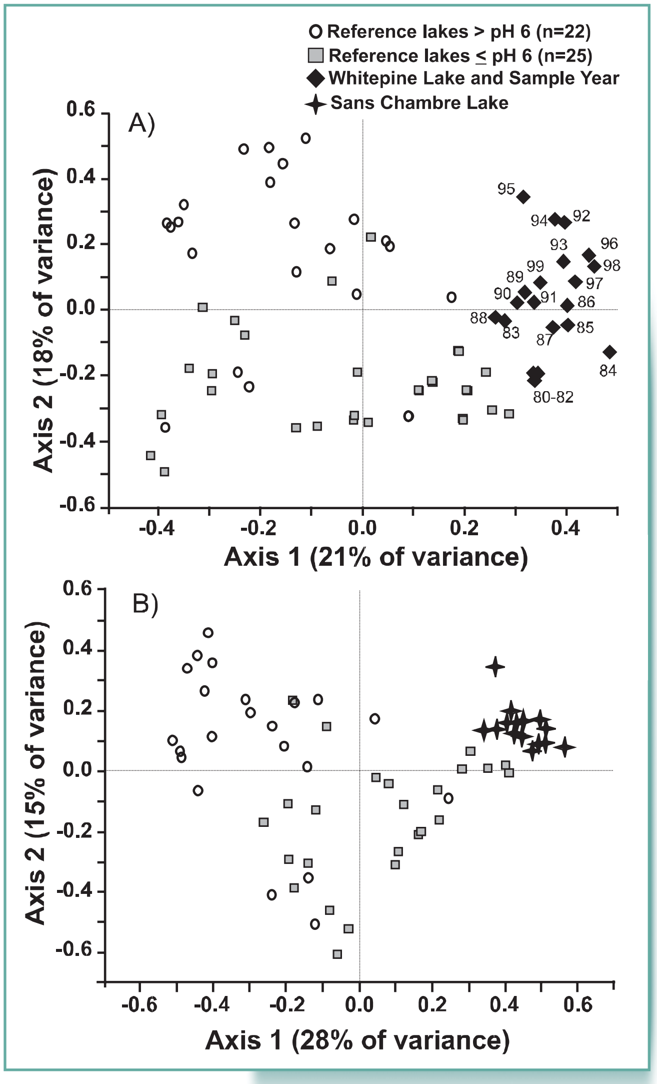

Figure 7.13: Site scores from a Correspondence Analysis (CA) of zooplankton abundance for two lakes near Sudbury, ON: A) Whitepine Lake (solid diamonds) and B) Sans Chambre Lake (solid crosses), sampled between 1980 and 1999. Lake-year scores are shown relative to the first two CA axes and to 25 acidic (pH<6, shaded squares) and 22 non-acidic (pH>6, open circles) reference lakes near Dorset, ON sampled between 1983 and 1988. Adapted with permission from Keller et al. (2002).

Yan et al. (2004) highlighted the strong copepod recovery as an encouraging sign for acidified but chemically recovering lakes.

Despite promising signs of recovery for some lakes in the large deposition zone around Sudbury, many severely acidified lakes near the smelters continue to be biologically impaired (Keller et al., 1999). Relative to the 22 non-acidic Dorset reference lakes used by Yan et al. (2004), Sudbury lakes tended to have a lower species richness based on both 1990 and 2003 sampling (Figure 7.12) (Keller et al., 2004). This pattern was probably due to the continued inhospitable chemical and biological conditions in these lakes and limited nearby sources of zooplankton colonists.

Using data collected between 1980 and 1999, Keller et al. (2002) compared the zooplankton community structure and species richness of two chemically recovering lakes near Sudbury, ON to 47 circumneutral reference lakes near Dorset, ON. The Sudbury lakes, Whitepine and Sans Chambre, had average pH values below 5.5 in 1980 but were above pH 6 by the late 1990s. Zooplankton species richness recovered to within two standard deviations of the Dorset lakes and some acid sensitive species became established. Overall community structure in the two Sudbury lakes, however, had not truly recovered relative to Dorset lakes (Figure 7.13). Community change in Whitepine Lake suggested a change toward non-acidic (pH>6) reference lakes (i.e., increasing Axis 2 scores through time in Figure 7.13a) but signs of recovery were much more limited in Sans Chambre (i.e., little change in Axis 1 or 2 scores in Figure 7.13b). The differing patterns between the lakes may have been related to the abundance of the zooplankton predator *Chaoborus* that was much higher in Sans Chambre than Whitepine Lake.

Re-acidification events have the potential to impair the recovery of algal communities (see 7.4.2.2.1.1), but observations from Swan Lake in the Sudbury area indicate that an interruption of chemical recovery can also delay the recovery of planktonic invertebrate communities (Arnott et al., 2001). The response of planktonic invertebrates to re-acidification varied taxonomically. During chemical recovery, the rotifer community had been shifting in composition toward an assemblage similar to less acidic reference lakes; the dominance of acid-tolerant species had been decreasing, and relative abundance of several acid-sensitive taxa and overall species richness were increasing. Following the re-acidification event of 1988, the rotifer community reverted to 95% dominance by a single acid-tolerant species (*Keratella taurocephala*). Changes to species richness could not be detected but diversity estimates declined sharply and overall community composition changed from its previous temporal trajectory (Figure 7.14a). By 1990, when sample processing for rotifers was discontinued, there was no evidence for resumption in recovery for this community. The composition of the crustacean zooplankton was very dynamic during both the chemical recovery period of the early 1980s and following re-acidification in 1988 (Figure 7.14b); the community was frequently dominated by a single taxonomic group and did not include any large cladocerans. Unexpectedly, species richness peaked in the high acidity of 1988, but soon declined to levels previously observed. The authors attributed the slow and incomplete recovery of crustacean zooplankton, and the lack of apparent re-acidification effects, to the small degree of chemical recovery achieved prior to the 1988 acidity increase and to the continued toxicity of the habitat for acid-sensitive zooplankton colonisers. In addition, the absence of fish in Swan Lake and the associated dominance of predatory *Chaoborus* may have also limited the invasion of many zooplankton species.

7.4.2.2.2.2 Benthic

The response of several benthic macroinvertebrates to acidification was summarised in the previous assessment and an updated and expanded summary is provided in Sections 6.4.2.2 and 6.4.2.3 of this assessment. Along with phytoplankton, zooplankton and fish, the previous assessment highlighted benthic invertebrates as one of the groups for which some recovery had occurred following chemical improvements in Sudbury area lakes.

The rate and magnitude of dispersal and colonisation are important dynamics in the recovery of biota in damaged but recovering systems (e.g., Bilton et al., 2001). One of the few studies to explicitly focus on colonisation rates was recently conducted in Killarney Park, southwest of Sudbury, ON (Snucins, 2003). Extensive (n=77 or 119 lakes) and intensive (n=4 lakes) sampling for three common benthic invertebrates was conducted between 1995 and 2001. One hundred and nineteen lakes were sampled for the amphipod *Hyalella azteca* and 77 lakes were sampled for the mayflies *Stenonema femoratum* and *Stenacron interpunctatum*. The distributions of these acid-sensitive species were also mapped for two chemically recovering acidified lakes. Distribution mapping was conducted in each of five years in Partridge Lake, a relatively small (area=11 ha, perimeter=1.6 km) lake with measured pH increasing from a low of 5.1 in 1986 and 1987 to a high of 5.9 in 2000. Mayfly and amphipod distributions were also mapped in each of six years in George Lake, a larger (area=189 ha, perimeter=13.5 km) lake with pH levels increasing from a low of about 5.3 in 1981 to a peak of almost 6.5 in 1999.

Stenacron interpunctatum occurred more frequently (n=53 lakes, 69% of sampled lakes) and at lower pH (5.3) than S.

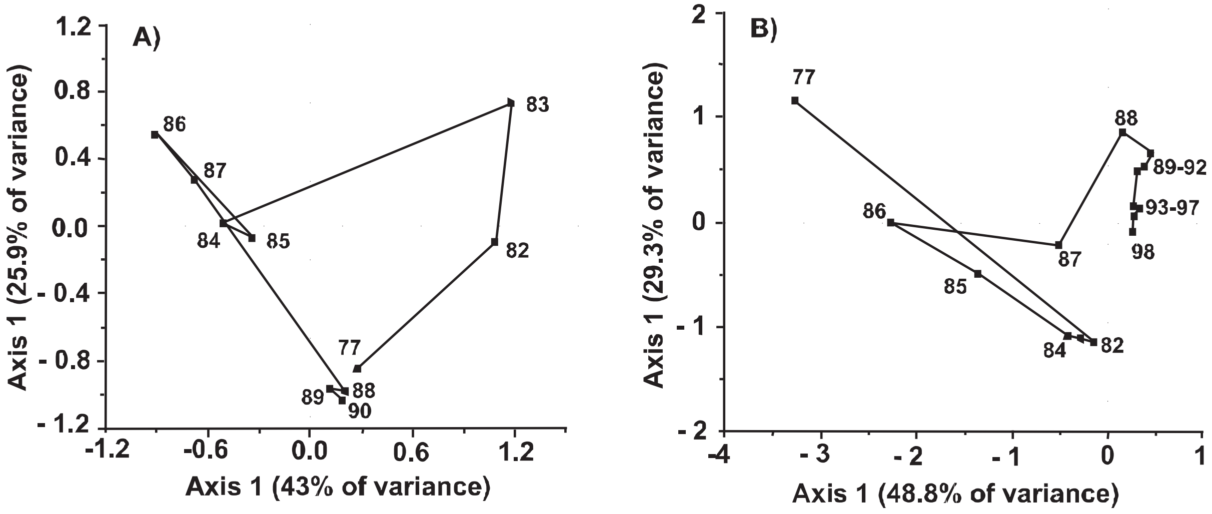

Figure 7.14: Scatterplot of year scores summarising the temporal change in A) rotifer and B) crustacean zooplankton community biomass sampled in Swan Lake near Sudbury, ON between 1977 and 1997, as defined by the first two Correspondence Analysis axes. Adapted with permission from Arnott et al. (2001).

femoratum (n=45, 58%) and H. *azteca* (n=51, 43%) which did not occur in lakes below pH 5.6. George Lake pH values were above the lower threshold (pH 5.3) from 1980 onward and the higher threshold (pH 5.6) was achieved and maintained after 1993. These thresholds were estimated to have occurred later in Partridge Lake, with pH of 5.3 achieved in approximately 1990 and pH 5.6 in 1994. In both George and Partridge lakes, the number of sites at which S. *interpunctatum* occurred increased rapidly through the sampled time series but saturation of available sites occurred only in the much smaller Partridge Lake (Figure 7.15). In contrast, the two more acid-sensitive taxa occurred at a small and temporally stable number of sites in George Lake.

Hyalella azteca occurred in Partridge Lake at a similar number of sites during each of the three sampled years but S. *femoratum* did not occur. The estimated density of S. *interpunctatum* in both George and Partridge lakes tended to increase with the number of years since their presence had been first detected (Figure 7.16). Sites where this species were established for at least five years had higher average density estimates than sites colonised for only one or two years. Densities of S. *interpunctatum* at George Lake sites that were colonised for at least six years were significantly ($p<0.05$) higher than densities in the two reference lakes, Helen and Low.

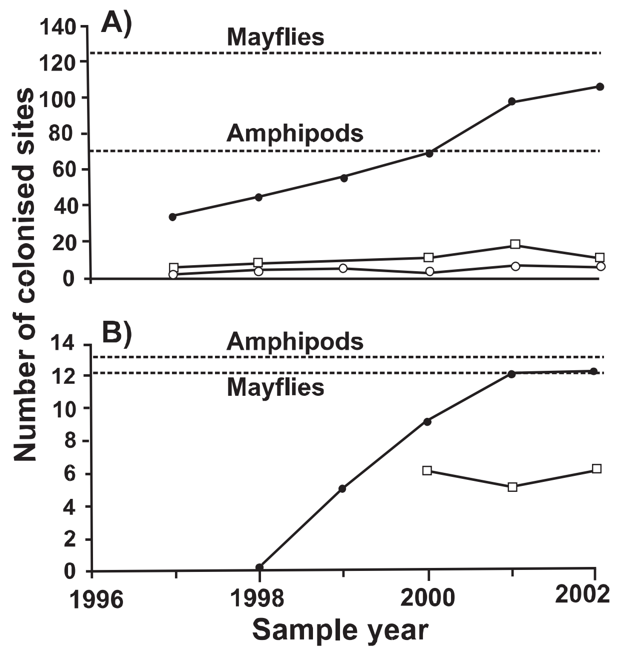

Figure 7.15: Number of sites colonised by the mayflies *Stenacron interpunctatum* (solid circles) and *Stenonema femoratum* (open circles) and the amphipod *Hyalella azteca* (open box) in A) George Lake and B) Partridge Lake near Killarney, ON sampled between 1997 and 2002. The annual surveys of Partridge Lake began in 1998 for mayflies and in 2000 for amphipods. The total number of surveyed sites available for colonisation by each group is indicated by the dashed lines. Adapted with permission from Snucins (2003).

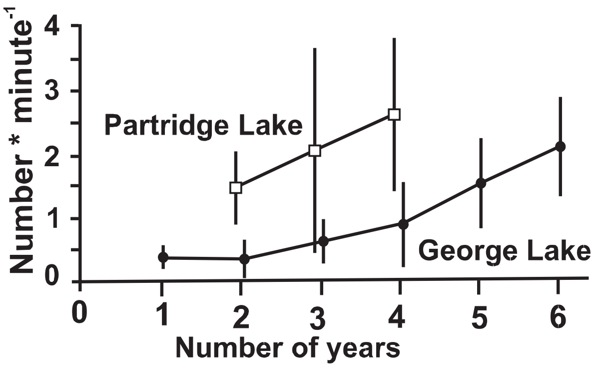

Figure 7.16: Estimated density (mean +/- 2 standard errors) in 2002 of the mayfly *Stenacron interpunctatum* relative to the number of years since their presence was first detected at appropriate sites in two recovering acidic lakes near Killarney, ON, Partridge Lake (open squares) and George Lake (solid circles). Adapted with permission from Snucins (2003).

Although colonisation of chemically recovering lakes by the mayfly S. *interpunctatum* occurred rapidly in the small lake (Partridge), full colonisation of suitable sites was still incomplete in the larger George Lake after six years. The estimated delay between the time each lake achieved suitable pH levels and complete colonisation was 11 years for Partridge Lake and appeared likely more than 22 years for George Lake. The increasing densities of S. *interpunctatum* with increasing colonisation time and the relatively modest colonisation of S. *femoratum* illustrate the potential for differing stressor tolerances, competitive dynamics, and dispersal abilities to affect the recovery patterns among related species. Snucins (2003) speculated the high densities of S. *interpunctatum* at sites colonised for six or more years may be a temporary condition associated with recent colonisation. His suggestion is supported by the dynamic nature of recovery and colonisation observed for other taxonomic groups (e.g., see Sections 7.4.2.2.2.1 and 7.4.3.3.2).

The addition of lime to acidified lakes as a means for improving habitat conditions has been successful for some biota (e.g., Yan et al., 1995), including benthic invertebrates (e.g., Raddum and Fjellheim, 2003). Carbone et al. (1998) compared benthic invertebrate communities in 17 Sudbury area lakes, two of which were limed. Seventeen lakes were sampled during the 1987 to 1989 period and three of these (Whitepine, Little Whitepine and Whirligig lakes) were sampled for an additional five years, through 1994. Whitepine Lake was not manipulated and had a pH of 4.9 to 5.1 over the 1987 to 1994 period. As part of an effort to improve the habitat suitability for the endangered aurora trout (*Salvelinus fontinalis timagamiensis*) (Snucins et al., 1995; see 7.5.1), liming was used in the fall of 1989 to increase the pH of Little Whitepine and Whirligig lakes to above 6. Little Whitepine remained above pH 6 but, after re-acidifying to pH 5.5 by 1992, Whirligig Lake required a second lime treatment to increase pH above 6.

Table 7.1. Loadings on the first Principal Component Analysis axis for 11 benthic invertebrate taxa sampled from 17 Sudbury, ON area lakes between 1987 and 1994. Adapted with permission from Carbone et al. (1998).

Order	Taxa	Component 1 Loadings
Trichoptera	*Banksiola*	0.86
Odonata	*Leucorrhinia glacialis*	0.84
Diptera	*Stackelbergina*	0.80
Diptera	Ceratopogonidae	0.79
Diptera	*Psectrocladius*	0.76
Odonata	*Aeshna eremita*	0.74
Odonata	*Aeshna interrupta*	0.70
Odonata	*Basiaeshna janata*	-0.58
Ephemeroptera	*Eurylophella*	-0.63
Ephemeroptera	*Stenonema femoratum*	-0.72
Ephemeroptera	*Stenacron interpunctatum*	-0.80

Table 7.2. Statistically significant (p<0.05) Pearson correlation coefficients between lake environmental variables, number of fish species, and scores on the first Principal Component Analysis axis for 17 Sudbury, ON area lakes sampled for benthic invertebrates between 1987 and 1994. Adapted with permission from Carbone et al. (1998).

Parameter (units)	Correlation with Component 1
Number of fish species	-0.90 **
Area (ha)	-0.80 **
pH	-0.76 **
Magnesium (mg/L)	-0.76 **
Alkalinity (mg/L)	-0.71 *
Potassium (mg/L)	-0.69 *
Calcium (mg/L)	-0.66 *
Sodium (mg/L)	-0.60 *
Mean depth (m)	-0.58 *
Total aluminum (ug/L)	0.73 **

* p<0.01; ** p<0.001

A Principal Components Analysis ordination of the most common benthic invertebrate taxa was used to summarise the sampled community and define a first component axis that captured 31.4% of the variance in taxa relative abundance. Seven taxa were positively associated with this first component and four taxa were negatively loaded (Table 7.1). This first ordination component was correlated with several acidity-related environmental factors with high component scores associated with acidic conditions (Table 7.2). The initial liming treatment and aurora trout reintroductions in Whirligig Lake were associated with both an increase in pH and a movement of the sampled benthic invertebrate community composition toward that of more circumneutral lakes (Figure 7.17). These changes in ordination scores were driven by a decrease in the occurrence and relative abundance of several acid-tolerant dragonfly and dipteran taxa and the increase of acid-sensitive mayflies.

7.4.3 Experimental Lakes Area: Manipulation experiments

M.A. Turner, D.L. Findlay, R.H. Hesslein, D.S. Jeffries, D.K. McNicol, K.H. Mills, M.J. Paterson, V.L. St. Louis, C.G. Trick, R.D. Vinebrooke, and R.C. Weeber

Beginning in the early 1970s, researchers at the Experimental Lakes Area (ELA) in northwestern ON (see lake cluster in Chapter 6, Figure 6.1), began a program to investigate the effects of acidification on lakes of the boreal shield in a region of low background H^+ deposition (Jeffries et al., 2003b). Several lakes (Lake 223, Lake 114 and the southern basin of Lake 302 (Lake 302S, hereafter)) and a wetland (239Fen) were acidified according to various experimental designs. This program provided scientific evidence identifying the sulphur emission reductions required to protect acid-sensitive

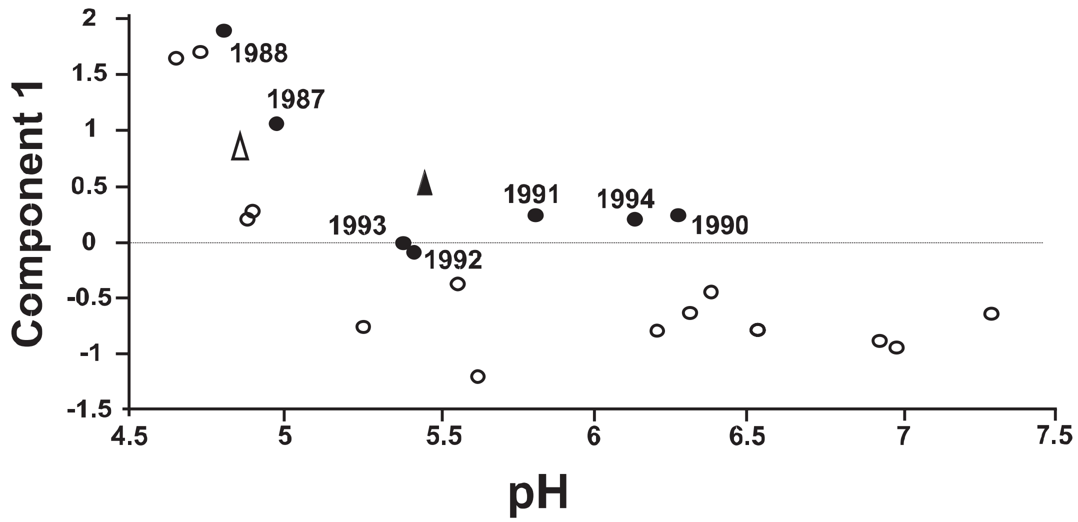

Figure 7.17: First Principal Component Analysis axis scores from an ordination of benthic invertebrate relative abundance plotted against lake pH for 17 Sudbury, ON area lakes. Lake-year component scores and pH are plotted for Whirligig Lake (1987, 1988, 1990 to 1994; solid circles), average values are indicated for two other intensively sampled lakes (Whitepine Lake (open triangle) and Little Whitepine Lake (solid triangle)), and open circles represent values for 14 lakes sampled once between 1987 and 1989. Adapted with permission from Carbone et al. (1998).

aquatic ecosystems that was instrumental in the development of the 1991 Canada-U.S. Air Quality Agreement.

To better understand the natural recovery potential of boreal lakes, ELA researchers and their collaborators have continued to study ecosystems that had previously been experimentally acidified. The general goal of these acidification recovery studies has been to evaluate the ability of boreal forest lakes to recover from acidification without deliberate intervention in the recovery process. To achieve this goal, two experimental lakes have been studied in terms of their physical, chemical and biological properties, as their target pH has been relaxed following years of experimental acidification.

Principal physical features of the study lakes (Lake 302S and Lake 223) are described in Table 7.3. Studies were pH press experiments during which annual pH targets were established (Figure 7.18) and sufficient sulphuric acid was added to the epilimnion to achieve the target pH. Lake 223 acid press started in 1976, resulting in a decline in pH from about 6.8 (1973 – 1975) until the minimum target pH of 5.0 was reached during 1981 – 1983. During the pH recovery phase, pH targets were increased in Lake 223 to 5.4 (1984 – 1987), 5.8 (1988 – 1990), 6.1 (1991 – 1993); pH was uncontrolled as of 1994. Lake 302S pH was reduced from an average of 6.7 in 1980 – 1981 to 4.5 during 1988 – 1991 (Rudd et al., 1990). Beginning in 1992, the pH was allowed to increase stepwise thereafter (Figure 7.18) to pH targets of 5.1 (1992 – 1993), 5.8 (1994 – 1997), 6.2 (1998 – 2000); pH was uncontrolled as of 2001. Rudd et al. (1990) described the details of sulphuric acid additions to the lake's epilimnion.

These whole ecosystem studies at the ELA provide an opportunity to understand the potential of aquatic boreal ecosystems to recover from acidification. Perturbations associated with these case studies are typically simpler than is usually the case for lakes in regions chronically acidified by increased acid deposition such as those described earlier in the Sudbury region (see Section 7.4.2). With experimental acidification, only the lake was acidified meaning chemical changes occurred only as a result of within-lake acidification rather than as a result of watershed acidification; for example, Al concentrations were lower than in regionally acidified lakes. There was no history of chronically increased deposition of nutrients, nitrogen-based acidifying compounds, or metals. The ELA is located in a region receiving

Table 7.3. General watershed and physical characteristics of the two acid recovery study lakes (Lake 223 and Lake 302S) located in the Experimental Lakes Area (ELA) in northwestern ON.

Parameter	Lake 223	Lake 302S
Latitude	49° 41′ 53.85″ N	49° 40′ 36.22″ N
Longitude	93° 42′ 27.77″ W	93° 45′ 38.80″ W
Lake order	3	1
Watershed area (ha)	260	54.3
Lake surface area (ha)	27.27	10.9
Mean depth (m)	7.1	5.4
Water renewal (yr^{-1})	3	5.1
Background phase	1974-1975	1980-1981
Acidification phase	1976-1983	1982-1991
pH Recovery phase	1984-1998	1992-2003

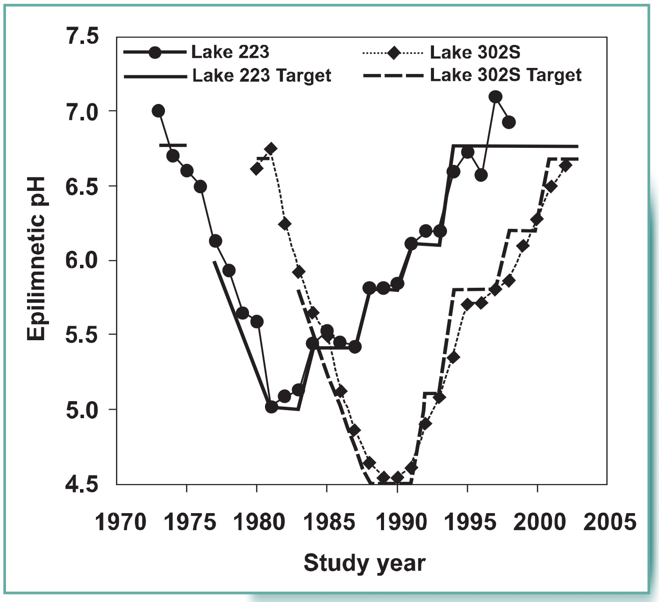

Figure 7.18: History of target and achieved epilimnetic pH in the experimentally acidified study lakes, Lake 223 and Lake 302S, during the acidification (1982 – 1991) and recovery (1992 – 2001) phases.

background, rather than more severe, acid deposition (Jeffries et al., 2003b). Unlike chronically acidified lakes where biotic extirpations can be regionally widespread, a source of biological invaders existed adjacent to the experimentally acidified lakes. One result of these differences is that the ELA acidification studies are biased to exhibit more rapid recovery than is typical of regionally acidified systems. Another result is that we better understand the consequences of reducing SO_4^{2-} and acid inputs to lakes only, without the complicating influences of watershed differences, and other sources of pollution. Because of these differences with lakes recovering from chronic regional acidification, the ELA acidification experiments have contributed valuable insight into the mechanisms underlying the potential for recovery of boreal lakes from acidification.

Climatic changes also occurred during the course of the studies. For example, in Lake 302S, pH recovery occurred during both a wetter and cooler decade (1992-2004) relative to the acidification years (1982-1991). For this reason it was essential to understand the changes seen in the study lakes in the context of regional climate-related changes in nearby reference lakes (principally Lake 239).

The 1997 Assessment (Jeffries, 1997) summarised the incomplete nature of recovery for the experimentally acidified Lake 223 and Lake 302S in the ELA. Lake 302S, which was acidified to pH < 4.7, was not proceeding on a recovery trajectory similar to Lake 223 (acidified to pH 5.0), suggesting that within-lake Alk generation capabilities were diminished when pH was depressed beyond 5.0. There were indications, however, the carbon and nitrogen cycles were recovering in these lakes. Although concentrations of the metals Al, manganese (Mn) and zinc (Zn) were in decline, Fe concentrations had increased, possibly due to reoxidation of previously reduced iron-S compounds. An important conclusion highlighted in the 1997 Assessment was that acidification of lakes below pH 5.0 may damage their internal Alk generation capabilities (see 7.4.1.1), resulting in their increased sensitivity to acidifying inputs and related implications for the timing and nature of recovery. Biological recovery lagged behind chemical recovery for both lakes and was slower for the severely acidified Lake 302S. Although biotic recovery appeared to be returning to the pre-acidification state in Lake 223, Lake 302S seemed to be recovering more slowly and to a rather different state than pre-acidification. Given the Lake 223 recovery study had largely concluded by the 1997 Assessment, Lake 302S is the primary focus of the following sections unless otherwise specified.

7.4.3.1 *Chemical*

During Lake 302S's recovery, SO_4^{2-} concentrations generally declined monotonically during the open-water period and pH increased (Jeffries et al., in prep.). During the early stages of pH recovery, it appeared that growths of metaphytic algae interfered with internal S-based neutralization processes (SO_4^{2-} reduction; Kelly et al., 1995). Thus rates of SO_4^{2-} reduction were lower during the pH recovery phase than during the acidification phase. Although pH values in unperturbed ELA lakes typically increase during summer, the pH in Lake 302S decreased during open water periods (Turner et al., 2002; Jeffries et al., in prep.), probably due to re-oxidation of previously reduced S compounds. As reported in the 1997 Assessment, in addition to hydrological factors, impairment of within-lake Alk generation continued to occur during much of the pH recovery phase. For example, only 15% of the acid was needed to maintain the target pH during the first decade of pH recovery phase compared to that needed during the acidification phase. At least two processes may be responsible for disrupting Alk generation, i.e. re-oxidation of previously reduced S similar to the drought responses reported by Arnott et al. (2001), and depleted supplies of the sedimentary reduced carbon that normally fuels SO_4^{2-} reduction (algal composition changed and rates of lake respiration increased; Jeffries et al., 2003b; Jeffries et al., in prep.)).

Nitrification, which was disrupted when pH declined below 5.4 (Rudd et al., 1988), restarted as the pH increased above 5.4 (Jeffries et al., in prep.). This reduced the ammonium (NH_4^+) concentrations that had been very high during the early stages of pH recovery. Epilimnetic NO_3^- concentrations that began to increase as Lake 302S was acidified to pH 4.5 also remained elevated until the pH increased above 5.4. No major change in the phosphorus cycle was observed and metal concentrations declined during recovery (except for Fe that continued to increase during the early stages of pH recovery (Jeffries et al., in prep.)).

Concentrations of DOC that had declined during the acidification phase of the experiment due to both acidification (Schindler et al., 1996) and climatically-induced reductions (Hesslein et al., in prep.) increased with pH recovery as both factors reversed (Jeffries et al., in prep.; Hesslein et al., in prep.). The character of the DOC also differed during the early stages of pH recovery, likely because of increased photodegradation. This would have further enhanced the penetration of ultraviolet (UV) radiation during that time period (Schindler et al., 1996; Donahue et al., 2003).

7.4.3.2 *Physical*

Several physical properties were influenced by the pH- and climate-mediated changes in DOC seen in Lake 302S. There was increased transmissivity of UV in the water column due to DOC concentrations that were lower during the pH recovery phase than at the same pH during the acidification phase (Turner et al., 2002). Increased UV resulted in increased metabolic costs for biota in the littoral zone (Watkins et al., 2001; Weidman et al., in revision), and possibly for others. Lower DOC concentrations also increased the penetration of radiant energy, leading to increased deep-water heating such as occurred in both study lakes (Hesslein et al., in prep.). Such deep-water heating can compress habitat availability for cold-water fishes (Jansen and Hesslein, 2004), such as lake whitefish (*Coregonus clupeaformis*) in Lake 302S (Turner et al., 2002) and lake trout (*Salvelinus namaycush*) in Lake 223 (R. Hesslein, pers. comm.). However, it does not appear that habitat compression altered either their growth or survivorship during the pH recovery phases of the respective studies (K. Mills, pers. comm.).

7.4.3.3 *Biological*

7.4.3.3.1 Algae

7.4.3.3.1.1 Planktonic

Although expected to recover rapidly with chemical recovery, phytoplankton community structure remained disturbed despite full pH recovery of Lake 302S. Acidification had resulted in elevated phytoplankton biomass because of increases in dinoflagellates, the proportion of which remained persistently elevated until the pH increased above 5.5 (Findlay et al., 1999; Turner et al., 2002; Findlay, 2003; Turner et al., in prep.a). Although whole-lake area-normalized rates of phytoplankton productivity were unrelated to pH, biomass-normalized rates of phytoplankton productivity declined with pH and were even lower during much of the pH recovery phase because of the higher dinoflagellate biomass (Turner et al., 2002; Turner et al., in prep.a). For unknown reasons, the fraction of planktonic productivity that occurred in the hypolimnion fluctuated substantially during the study, and was elevated during the latter stages of pH recovery (Turner et al., 2002; Turner et al., in prep.a).

During acidification, lake whitefish abundance declined dramatically. It had been postulated that dinoflagellate blooms had killed the lake whitefish population in Lake 302S during the acidification phase of the experiment (Mills and Chalanchuk, 1992). Subsequent research discovered that even during the pH recovery phase of Lake 302S, bacteria associated with the dinoflagellates had the potential to produce toxins capable of killing cyprinids (and possibly other biota) (Rooney, 1995; Murphy, 1995; Ray, 1997). The lethality of the bacteria was dependent on rapid dinoflagellate growth, moderately high Fe concentrations and the availability of certain forms of DOC (C. Trick, pers. comm.).

Recovery of planktonic taxonomic richness lagged during pH recovery, remaining about 20% lower after full pH recovery than at the outset of the experiment (Turner et al., in prep.a).

7.4.3.3.1.2 *Benthic*

Benthic community composition was influenced strongly by pH, DIC and DOC (Vinebrooke et al., 2003a,b; Turner et al., in prep.b). Filamentous cyanobacteria remained lower during pH recovery while diatoms remained persistently elevated (Findlay et al., 1999; Turner et al., in prep.b). The resulting recovery trajectory of benthic algal composition has been moving to a different state than its pre-acidification departure point, partly because of the influence of DOC, which did not recover as quickly as it had declined during acidification (Vinebrooke et al., 2003a,b; Turner et al., in prep.b).

Benthic photosynthesis was controlled largely by the availability of DIC (Donahue et al., 2003; Turner et al., 1991), and as a result its recovery was largely a mirror image of acidification-caused decline (Turner et al., 2002; Turner et al., in prep.b). The increase in rates of epilithic respiration that had occurred during acidification (Turner et al., 1995; Turner et al., 2002), persisted during the pH recovery phase for undetermined causes, although the correlation with UV intensities, which remained elevated, was suggestive of a UV influence (Turner et al., in prep.b). Ultraviolet radiation has been shown to affect both epilithic structure and function (Watkins et al., 2001; Weidman et al., in revision.).

The annual abundance of metaphyton (filamentous green algae that are benthic but are really neither suspended nor attached), which had appeared during acidification, became highly variable during the severe acidification phase; this variability was at least partly related to climatic conditions (Turner et al., 2002; Turner et al., in prep.b). Although they failed to bloom after the pH exceeded 6.3, metaphyton persisted to a much higher pH than their onset pH of about 5.5 (Turner et al., 2002; Turner et al., in prep.b).

7.4.3.3.2 Invertebrates

7.4.3.3.2.1 *Planktonic*

The structure of the zooplankton community was a variable function of pH. Patterns of recovery were both group and time dependent, and were not mirror images of the patterns with pH seen during the acidification phase (Turner et al., in prep.b).

Rotifer biomass increased during acidification, and remained elevated through the early phase of pH recovery (Turner et al., 2002; Turner et al., in prep.b; Paterson et al., in prep.). Calanoid copepods, which decreased severely during acidification below pH 5, reappeared when the pH increased above 5.9, and then recovered rapidly to pre-acidification abundances (Turner et al., in prep.b). Cyclopoid copepod densities were relatively stable until pH 4.5 when they virtually disappeared. Cyclopoid numbers rebounded as the pH increased and, as the pH increased above 5.5, became persistently more abundant than before acidification (Turner et al., in prep.b). Cladoceran biomass, which was severely depressed as the pH declined to 4.5, became very high during the early stages of pH recovery, and then declined to pre-acidification values despite considerable among-year variability (Turner et al., in prep.b; Paterson et al., in prep.). In contrast to phytoplankton, changes in crustacean and rotifer species richness closely tracked changes in pH. Although they were measured only during the pH recovery phase, *Chaoborus* spp. declined quickly during the early stages of pH recovery, likely due to increased predation by reinvading fish (Turner et al., in prep.b).

These contrasting patterns, involving adjacent trophic levels within the plankton community, strongly suggest the importance of trophic interactions (i.e., trophic cascade effects) to biological recovery in lakes. Specifically, increases in planktivorous minnows were correlated with declines in herbivorous cladocerans and increases in omnivorous copepods that were better able to evade the visually-feeding fish during recovery.

7.4.3.3.2.2 *Benthic*

The nature and patterns of recovery differed strongly among the various benthic invertebrate groups. Recovery of chironomid abundance was essentially the reverse of acidification for the period of the recovery record available (i.e., to pH 5.7 in 1997) (Turner et al., in prep.b). In contrast, the abundance of littoral microcrustacea was negatively influenced by the reinvasion of cyprinids (Hann and Turner, 1999; Hann and Turner, 2000; Turner et al., in prep.b). A similar pattern was seen for *Chaoborus* (Turner et al., in prep.b; Paterson et al., in prep.).

Insects (notonectids, corixids, and Trichoptera), which had been especially abundant during severe acidification, declined during pH recovery coincident with the reinvasion of cyprinids (Vinebrooke et al., 2001; Turner et al., in prep.b). Leeches, which had been extirpated by acidification, reinvaded successfully following several years of unsuccessful attempts (Turner et al., in prep.b). Sponges, which had not been abundant prior to acidification, flourished during the period that pH increased from ~5.8 to 6.6, although they have since declined substantially (Turner et al., in prep.b).

Amphibians like tadpoles of the green frog (*Rana clamitans*) and the American toad (*Bufo americanus*), which had previously been extirpated, appear to have successfully reinvaded Lake 302S (Turner et al., in prep.b). Crayfish (*Orconectes virilis*) were extirpated from both Lake 302S and Lake 223 during the acidification phases of the experiments. Although they have not yet reinvaded Lake 302S (Turner et al., in prep.b), they are re-established in Lake 223 (K. Mills and M. Turner, unpublished data), likely invading via a stream connecting Lake 223 to an upstream lake containing crayfish. However, *Mysis relicta* is still absent from Lake 223 despite its presence in the immediately upstream lake.

7.4.3.3.3 Vertebrates

7.4.3.3.3.1 *Fish*

All fish species that were present in Lake 302S prior to acidification were again present in 2000 (pH 6.3). Although all species had persisted to pH 4.6 at least in low abundance (Turner et al., 2002; Turner et al., in prep.a), recovery patterns varied among the species. The small number of pearl dace (*Margariscus margarita*) that survived during severe acidification thrived in terms of condition as the pH increased above 5; reproduction was also successful by 1994 (pH 5.4). The other minnow species (fathead minnow (*Pimephales promelas*), finescale dace (*Phoxinus neogaeus*) and northern redbelly dace (*Phoxinus eos*)) were opportunistic invaders; finescale dace showed especially forceful recruitment (Turner et al., in prep.a). Most of the previously extirpated species likely reinvaded from the northern basin of Lake 302 (i.e., Lake 302N), which had acted as a biological reservoir.

In the fall of 1999, 308 adult lake whitefish were taken from Lake 302N and added to Lake 302S to re-establish the whitefish population in the study lake at a density that existed before acidification. These stocked whitefish suffered high mortality (about 82% versus 31% during 1982-1985; K. Mills, pers. comm.; Turner et al., 2002; Turner et al., in prep.a), which was unexpected (Rask et al., 1995) given the relatively high pH (about 6.1) and low Al concentrations (0.5 µM) at the time of addition. The lower condition of the Lake 302N whitefish may have been a contributing factor given that higher than normal mortality was observed in the host basin (K. Mills, pers. comm.). However, the whitefish that survived in Lake 302S spawned, and subsequent recruitment was very successful, with 2002 and 2003 year classes being unusually abundant for this lake when in an undisturbed state (K. Mills, pers. comm.).

Fish reinvasions, especially by cyprinids, likely restructured the food web of Lake 302S. For example, insect abundance declined (Vinebrooke et al., 2001) and *Daphnia catawba* swarms disappeared from the littoral zone (M. Turner, unpublished data), and the reappearance of cyprinids correlated with declines of *Chaoborus* in the pelagic zone and microcrustacea in the littoral zone (Hann and Turner, 1999, 2000; Turner et al., 2002).

Recovery of several fish populations in Lake 223 was also delayed beyond original expectations, and occurred only after several years of circumneutral pH. For example, abundance of both fathead minnow and white sucker (*Catostomus commersonii*) abundance only stabilized after several years of erratic population abundance (K. Mills, pers. comm.). In contrast, populations of brook stickleback (*Culaea inconstans*) that had entered and become abundant during acidification, persisted during pH recovery despite substantially decreased abundance (Mills et al., 2000). Slimy sculpin (*Cottus cognatus*) were extirpated during acidification and their reappearance, likely from upstream Lake 224, occurred more than 18 years after the start of recovery from acidification (K. Mills, pers. comm.).

Lake trout in Lake 223 exhibited slow rates of recovery (Mills et al., 2002a) as would be expected given their natural population dynamics (Mills et al., 2002b), but achieved pre-acidification abundance as of 2003 (K. Mills, pers. comm.). Low rates of recruitment for much of the pH recovery phase (Mills et al., 2000, 2002a) slowed the rebuilding of the population (Mills et al., 2002a). The inherently slow rates of recovery of lake trout (and of other biota) could put these populations at further risk if additional stresses, such as increased competition from invading warm water species during a climatic warming period, were to occur during acidification recovery (Turner et al., in prep.a).

7.4.3.3.3.2 *Swallows*

Among insect-eating birds, a negative influence of wetland acidity was observed on the reproductive success of tree swallows (*Tachycineta bicolor*) nesting near experimentally acidified lakes at ELA (St. Louis and Barlow, 1993). These observations corroborated the results of an earlier study conducted in the Sudbury area (Blancher and McNicol, 1988). Both the foraging behaviour of adult tree swallows and the diet of nestlings varied markedly in relation to the acidity of the lake near where the birds nested (St. Louis et al., 1990; Blancher and McNicol, 1991). The inadequacy of emerging and other available insect prey over and around acidic lakes and wetlands was implicated in reduced breeding success.

Following several years of unsuccessful attempts by young swallows during much of the pH recovery phase, tree swallows in Lake 302S began reproducing successfully in 1998 at a pH of about 5.9 (St.Louis et al., in prep.). Attempts to establish the cause of failed reproduction were unsuccessful (V. St. Louis, pers. comm.); neither metal burdens nor calcium insufficiency in food were explanations.

7.4.3.4 *Ecosystem-level interpretation*

The ELA study ecosystems displayed considerable resiliency and ability to recover once the stress of acidification was reduced. However, full pH recovery did not result in complete ecosystem restoration within the timeframe of these experimental pH recovery studies even though they were simpler and biased towards faster recovery than are chronically and regionally acidified lakes. As a result, it is necessary in many cases to adjust expectations of the rate of recovery of aquatic habitat in many cases to understand that habitat and biotic recovery will lag pH recovery, and in some cases for considerable periods. In those cases where ecosystem resilience has been exceeded, or biota important to food webs are unable to recolonise, ecosystems will recover to an alternate state.

Recovery of the ELA study ecosystems also diverged from expectations in ways that have implications for understanding and predicting recovery elsewhere. Recovery of these study ecosystems was incomplete and often diverged from expectations predicted by our understanding of pH-dependent acidification effects. Many ecosystem features of acidification recovery were complex and indirect, in part because the forces acting on the ecosystems were more complex than those associated purely with pH decline. This means that predictions of the recovery of aquatic habitat and biota should not be made solely on the pH-dependent reversal of acidification impacts. Similarly, attainment of specific pH thresholds was limited as a way of characterizing and assessing aquatic recovery.

There were multiple forces affecting the nature of recovery in the ELA study lakes. These forces included the important interaction between pH and DOC, which further increased the complexity of relationships among the physicochemical and biological properties of the study systems. In particular, there were periods of increased UV intensity, increased deep-water heating, and likely altered dynamics of both nutrients and metals. Other physicochemical forces included summer reacidification events, complexity due to altered chemical cycles, and toxins of biological origin, all of which had the potential to interfere with food-web recovery.

During our ELA studies, we learned that a changing climate further complicates our ability to forecast recovery from acidification. In response to climate changes, recovering lakes would likely receive altered terrestrial yields of nutrients and dissolved organic material. For example, climate change may result in lowered inputs of DOC to lakes, which will both affect the availability of nutrients and metals, and enhance the transmissivity of radiant energy to the deeper waters of lakes. In lakes with shallower hypolimnia, this could result in compression of habitat for stenotherms (i.e., species surviving only within a very narrow temperature range; Jansen and Hesslein, 2004), which may be further exacerbated by greater oxygen depletion at the lake bottom caused by the increased heating. Such anoxia would likely be worse if the ecosystem were subjected to the additional stressor of increased nutrient loading. Hence, an implication of our studies is that disturbance of terrestrial habitats in acid-sensitive areas must avoid reduction of inputs of DOM / DOC, especially where there are slow-recruiting fish (e.g., lake trout); such cases will require precautionary management.

Recolonisation of biota extirpated during our ELA studies was aided by the proximity of biological reservoirs, which contrasts with areas where acidification has been chronic and regional (see 7.4.2.2). However, despite the supposedly relative ease of biotic recolonisation in our studies, recovery of biodiversity varied among groups of biota and sometimes occurred in unpredictable ways. For example, although we might have expected phytoplankton to have recovered most quickly of all biota, there was an unexpected lag in recovery of planktonic taxonomic richness (Turner et al., 2002; Turner et al., in prep.a); in contrast, diversity of zooplankton and benthic algae was more resilient (Vinebrooke et al., 2003b; Turner et al., in prep.a). Moreover, we found that our reintroduction of lake whitefish was initially less successful than expected.

Our ELA studies point to several research needs. Continued monitoring of the recovery of Lake 223 and Lake 302S would help to distinguish whether the hysteresis observed during recovery represented lags in combination with stochastic events, or alternate endpoints for the study systems. Because we found that ecosystem recovery from acidification occurs in the presence of other forces (potentially including climate warming, biotic invasions, eutrophication, and other types of contamination), it is essential to better understand which forces are likely to interact with recovery, and the extent and nature of these interactions. To this end, the establishment of parallel case studies that vary geographically (e.g., across ecozones), in degree (pH) and duration of prior acidification, and in the complexity of additional stressors will help us to understand and to predict the recovery of acidified aquatic ecosystems. Further quantification of delays in the recovery of biota is needed to enable effective modelling of recovery.

We have also found that we need to better understand the link between altered ecosystem structure and recovery of ecosystem function. Similarly, it remains to be confirmed that functional instability and structural variability were greater during pH recovery than during acidification. From a trophic perspective, because food web changes also shaped the character of recovery, fluctuating abundances during initial reestablishment of taxa potentially intensifies ecosystem fluctuations and instability. However, it remains uncertain how persistent loss of biodiversity will influence ecosystem function. In the interim, Vinebrooke et al. (In prep.) concluded that changes in several ecosystem processes (e.g., primary and secondary production) were better explained by environmental factors (e.g., loss of DOC and altered food web structure) than by the loss of taxonomic richness. Note that because littoral and pelagic responses often differed within equivalent functional groups, generalizations cannot be made from one to the other (e.g., between phytoplankton and benthic algae or between zooplankton and zoobenthos).

7.5 RESTORATION AND MANAGEMENT OF FISH POPULATIONS

7.5.1 Sport fish in acidified Ontario lakes

E. Snucins

Observations from lakes near Sudbury, ON responding to pollution reductions and from experimentally acidified

Lake 223 in the ELA (see 7.4.3.3.3.1) indicate that remnant sport fish (e.g., salmonids, bass) populations can recover naturally when water quality improves (Gunn and Keller, 1990; Gunn and Mills, 1998; Mills et al., 2000). Recruitment resumes at about the same pH that it ceased during acidification but some sparse populations have become extirpated despite improved water quality.

Extirpated fish species can return to acid-damaged lakes without human assistance if stream connections to source populations exist (Mills et al., 2000; Snucins and Gunn, 2003). Re-colonisation of headwater or otherwise isolated acidified lakes, however, is dependent largely on the transfer of wild fish from healthy lakes or the introduction of hatchery-reared fish to initiate recovery. Lake trout and smallmouth bass (*Micropterus dolomieu*) are the sport fish species most affected by acidification in ON and both have been stocked into recovering lakes in northeastern ON (lake trout being the primary focus of restoration).

Research indicates that lake trout recovery can be inhibited by species losses and shifts in fish communities that occurred during acidification. Mills et al. (2000) felt the absence of key acid-sensitive food species in ELA's Lake 223 may have been a factor in retarding the return of lake trout abundance to pre-acidification levels during the lake's chemical recovery. This suggests the reintroduction of food web components may be a potential management option. Fish community composition also strongly influences the success of lake trout reintroductions. Lake trout in particular do poorly in species-rich lakes and the presence of potential competitors such as cisco (*Coregonus artedi*), rock bass (*Ambloplites rupestris*) and smallmouth bass results in slower growth, lower survival and delayed recruitment (Snucins and Gunn, 2003). These fish community interactions may delay recovery of lake trout for many decades. Acid-tolerant prey species tend to expand when lake trout populations are depressed or absent. Some of these prey species (e.g., yellow perch) serve as an abundant food source that is reduced by predation once lake trout recovery occurs. Other prey species exhibit more complicated interactions with lake trout. For example, cisco serve as an abundant food source for large lake trout, but may inhibit recovery through competition for food with young lake trout (Gunn and Mills, 1998). The introduction of large adult lake trout that feed on the abundant prey fish, rather than small yearlings that must compete with them for food, is being tested as a rehabilitation method in lakes that contain cisco (Snucins and Gunn, 2003).

In contrast to lake trout, smallmouth bass re-introductions can succeed in species-rich communities. Snucins and Gunn (2003) found the biomass of natural smallmouth bass recruits increased to reference lake levels within 5 years following water quality recovery and spawning by stocked fish. The biomass of natural lake trout recruits, however, remained well below reference levels 5-15 years after water quality recovery and spawning by adults. These differences among species may be related to life history characteristics (e.g., fecundity, age of maturity) and the effects of interspecific competition and predation on recruitment. The smallmouth bass, a warm-water species, may also have benefited from warmer than average weather in recent years. That is not necessarily the case for cold-water species such as lake trout. For example, the warmer water temperatures associated with the 1998 El Niño event caused the loss of all hatchery-reared juvenile lake trout stocked in a shallow recovering lake (Gunn, 2001).

Long-term shifts in water temperature have the potential to influence sport fish responses to the recovery of acidified lakes. Climate warming and water temperature increases may benefit smallmouth bass and other warm water species, potentially to the detriment of lake trout and other cold-water fish. Invasion of lake trout lakes by warm water species is in fact occurring, as evidenced by recent surveys that found new populations of smallmouth bass, rock bass, pumpkinseed (*Lepomis gibbosus*) and walleye (*Sander vitreus*) in recovering lakes, some of which had not contained those species prior to acidification (E. Snucins, pers. comm.). In many cases the appearance of new species has been due to unauthorized transfers, both intentional and unintentional, by anglers. These introductions may change the food web structure and alter recovery endpoints for lake trout. For example, invasions by rock bass and smallmouth bass lead to an energetic bottleneck that reduces lake trout growth by forcing them to shift their diet towards feeding primarily on zooplankton in lakes that lack pelagic prey fish (Vander Zanden et al., 1999). Protecting lakes from introduction of non-native species is one of the challenges facing resource managers.

Lake trout populations are also very vulnerable to angler exploitation. A chemically recovering lake near Sudbury was closed to fishing for seven years; when a normal open season and catch limit was begun, the lake suffered a 72% decline in adult abundance within a few months (Gunn and Sein, 2000). The rapid collapse of that fishery suggests resource managers need to consider regulation of angler harvest when restoring damaged lake trout populations.

The liming of lakes to reverse acidification, a rehabilitation technique used routinely in Scandinavia, has been largely restricted in North America to experimental applications in a few lakes. An exception is the repeated liming done to improve and maintain the habitat suitability for the aurora trout (*Salvelinus fontinalis timagamiensis*), a type of brook trout native to only two lakes in the world and classified as an endangered species (Snucins et al., 1995; **http://www.speciesatrisk.gc.ca**). Both of the native lakes are located about 110 km north of Sudbury, ON. The fish were extirpated from those lakes during the 1960s by acidification from atmospheric deposition. The aurora trout was saved from extinction by a captive breeding program and successfully reintroduced after liming in 1989. To maintain suitable water quality, it was necessary to repeat the treatment twice during the 1990s. Recent episodic depressions to pH 5.0, the threshold for aurora trout reproduction, occurred in 2001 and 2002, indicating that the lakes could potentially require liming again in the future. The preservation of the aurora trout is an endangered species success story, but the continued need for human intervention to preserve water quality in the native lakes highlights their vulnerability to acidification.

Successful recovery of sport fish in acidified ON lakes will require chemical improvements as well as targeted active management (e.g., stocking). Improved understanding of how prey and competitor fish will respond to lake recovery, particularly in the context of other environmental stressors, will be required to identify the most promising recovery strategies and to accurately predict their effectiveness.

7.5.2 Atlantic salmon in Nova Scotia's southern upland

P.G. Amiro, R.W. Brook, and R.C. Weeber

Acidification of historical Atlantic salmon (*Salmo salar*) rivers has been particularly severe in the Southern Upland region of NS (see Section 6.4.5). Due to chronic acidification and extremely limited base cation buffering capacity, chemical recovery for lakes and rivers in this region is projected to require decades even under optimistic emission reduction scenarios (see Sections 6.3 and 7.6.4). Clair et al. (2004) modelled acidity conditions for 40 streams in 35 NS rivers which historically had viable Atlantic Salmon populations (see also 7.6.4). They estimated pH, ANC and Ca^{2+} under pre-acidification conditions and for three scenarios of acid deposition relative to the year 2000: no change, and 10% or 20% reductions per decade. Modelled pH for each river was used to classify the acidity impacts on Atlantic salmon populations: populations not significantly affected by acidity (pH 5.4), stocks depleted (pH 5.0 to 5.4), reduced to residual populations (pH 4.7 to 5.0.), and extirpated (pH < 4.7) (see Watt et al., 2000). All but two rivers were predicted to have had pH > 5.4 under pre-acidification conditions early in the 20th century. Model predictions indicate that acidification effects likely began in the 1950s, reached their peak in the mid-1970s and early-1980s and, although still acidified, predicted pH increased slightly between 1980 and 2000. Simulations based on decadal 10% and 20% reductions from 2000 deposition levels indicated that predicted pH in all rivers would be sufficient to sustain salmon by 2100 and 2070, respectively. Calcium, a cation of physiological importance for fish osmoregulation and bone maintenance, was predicted to remain below pre-industrial levels for at least the next 100 years. The recovery of salmon rivers in NS's Southern Upland is likely to be long and slow and the continued low Ca^{2+} concentrations are likely to have negative impacts on the physiological health of remnant or reintroduced Atlantic salmon.

As described in Section 6.4.5, Atlantic salmon in NS's Southern Upland are impacted by river acidification, reduced survival of young fish migrating from their natal rivers to the sea (i.e., smolts), and poor marine survival. Natural recovery of Southern Upland salmon populations is unlikely given the long time required for pH recovery, continued reductions in Ca^{2+} levels (see above), and marine survival at levels below 5% (see Section 6.4.5.2). A recent review (DFO, 2000) emphasised the importance of continued and substantial reductions in SO_2 emissions and identified four options for protecting the Atlantic salmon stocks remaining in the region: 1) neutralisation of acidified rivers, 2) stocking to replace or supplement natural reproduction, 3) gene banking to protect or enhance genetic diversity, and 4) fisheries restrictions. The degree to which these approaches may be effective for protecting, recovering and/or enhancing Southern Upland Atlantic salmon stocks remains a topic of open discussion among scientists and other stakeholders and is explored further in the remainder of this section. Both increased smolt production and improved marine survival are essential for restoring salmon populations (Amiro, 2000).

1. Neutralisation of acidified waters usually involves the addition of limestone, with river discharge rates and acidity levels important determinants of the timing and magnitude of lime releases. Lime application methods include spreading on lake surfaces, installing limestone gravel as submerged bars or inside revolving drums, powdered lime dispensers and 'diversion wells' which use upwelling water to abrade limestone chips. Liming techniques can be successful in improving pH and Ca^{2+} conditions for salmon, reducing dissolved metal concentrations, moderating low pH episodes and improving physical and chemical conditions for spawning and eggs (e.g., Watt et al., 1983; Lacroix, 1996). However, due to the dendrite (tree like) structure of rivers and the propensity for salmon to occupy smaller tributaries, many treatment methods do not effect significant portions of upper watersheds where most salmon are produced. Basin area coverage methods, which have not been widely researched in North America, may therefore be more applicable to the case of Atlantic salmon than main-stem liming.

   The effectiveness of liming acidified rivers as a technique for improving full life-cycle closure for Southern Upland salmon populations has not yet been demonstrated. Liming-derived improvements to spawning, egg development and smolt production have not been established as a general technique across the range of river types and acidification damage. Also, it has not been demonstrated in North America that increased smolt production following liming results in sustainable return of spawning adults. Important questions remain concerning the specific chemical and physical consequences of liming. These questions include possible genetic effects of low pH on survivorship, as has been shown for brook trout (*Salvelinus fontinalis*; Hurley et al., 1989) and brown trout (*Salmo trutta*; Battram, 1990), and long term dependence on the delivery system, the spatial and temporal scale required, the most efficient methods, and the economic viability of liming at the required scale. An economic valuation of liming for the restoration of Atlantic salmon indicated that applications costs at CD $50/ ton, low to medium productivity and 10% marine survival, resulted in cost estimates of CD $6.40 to $29.60/adult (Power, 1998). The scalability of this analysis to current marine survival rates, wider basin areas and current costs is unknown. Research into these and other important questions are necessary to fully evaluate liming as a restorative technique for Southern Upland salmon rivers.

2. Stocking of hatchery-reared salmon can be used to supplement or replace naturally reproducing stocks during times of average or better marine survival. Although smolts are the most acid-sensitive stage, their short residency in freshwater suggest they may be the most effective stage for stocking. Smolts stocked to most Southern Upland rivers would likely be subjected to at least short periods of acidity. The effects on the physiology and marine survival of smolts exposed to acidity, and the chemical conditions associated with those effects, are areas of active investigation (e.g., Fivelstad et al., 2004; Magee et al., 2003). Rivers with low or partial acidification impacts (pH 4.7 to 5.0 and pH >5.0 to pH 5.4, respectively) are good candidates for stocking but return rates by released smolts tend to be low, exceptionally so in the partially-impacted rivers (DFO, 2000). Salmon population models do not currently incorporate the effects on smolt mortality of short exposures to acidity; this refinement is required to evaluate the effectiveness of hatchery smolt additions to acidified rivers (Amiro, 2000). Further complications for supplementation are the scarcity of donor populations and the critically low

numbers of adults in residual populations. These conditions necessitate actions that reduce domestication selection, loss of genetic diversity and that do not artificially induce genetic drift, both known effects associated with supplementation in small populations.

3. Gene banks involve protecting or enhancing naturally reproducing or captive populations through selective breeding where the proposed use is to maintain the genetic diversity of a species through a period of extreme population restriction. A promising method is to establish captive populations of broodstock that contain the breadth of genetic diversity represented by remaining wild salmon. Variations of these methods use juveniles obtained from residual wild populations to produce adult salmon in captivity for release back to the wild. Protecting productive habitats for salmon is an important part of this approach. To date, these methods have only been applied to natural residual populations. The eventual effectiveness of this approach depends not only on careful selection of genetic stock and good husbandry but also on continued or improved suitability of salmon habitats in Southern Upland rivers.
4. Restrictions on the taking and retention of Southern Upland Atlantic salmon by recreational, commercial and Aboriginal fisheries has been practised since the early 1980s. Current harvest controls are quite stringent and few opportunities exist to fish Southern Upland salmon. Additional harvest restrictions are unlikely to be effective in improving Southern Upland Atlantic salmon stocks.

Residual populations of Atlantic salmon in non-impacted rivers of the Southern Upland as well as salmon populations southwest of the Southern Upland in Canada and in the United States are threatened with extirpation from high marine mortality coupled with relatively low to medium productivity (ICES CM, 2004; DFO, 2003, Amiro, 2000). The numbers of smolts produced per spawning adult salmon cannot keep pace with recent low marine survival and more extirpations are expected. If maintaining a variety of Atlantic salmon populations on the Southern Upland is desired, then the preceding review indicates that a form of supplementation that is sensitive to the genetic constraints is required. Even if acid deposition was reduced, non-impacted rivers would remain threatened from low marine survival. Under the current low marine survival, the time frame for persistence in non-impacted rivers may be as short as 30 years (P. Amiro, unpublished analysis; Legault, in press) and the time frame for recovery of base cations may be 70 to 100 years (Clair et al., 2004). Certainly, reduced acid deposition will lessen these threats by increasing habitat productivity and availability. In the mean time, over the next 30 to 70 years, diverse habitat restoration for important residual populations can only be considered as last-resort precautionary actions possibly leading to recovery. Increased marine survival, to levels observed prior to 1990, would render some of these methods viable as well as decrease the sensitivity to undesirable genetic consequences. Now, above any other period in the history of industrialization, careful biological and habitat management of residual Atlantic salmon populations is required.

7.5.3 Atlantic whitefish

R.G. Bradford, R.W. Brook, and R.C. Weeber

Atlantic whitefish (*Coregonus huntsmani*) are endemic to Canada and occur only in the province of NS (Edge and Gilhen, 2001). At the time of their first description in 1922, Atlantic whitefish were limited in distribution to the Tusket-Annis and Petite Riviére drainages in southern NS (Bradford et al., 2004a). Genetic and demographic factors indicate the species must have occupied a broader contiguous distribution at an earlier time (DFO, 2004). The Tusket-Annis population appears to have been entirely anadromous (i.e., spend their adult life in saltwater and return to freshwater to reproduce) whereas both anadromous and wholly freshwater resident fish have been reported from the Petite Riviére (Bradford et al., 2004a). Atlantic whitefish were assessed by the Committee on the Status of Endangered Wildlife in Canada (COSEWIC) as “endangered” in 1984 and 2000 on the basis of elevated risk to survival within a restricted global distribution, decline in abundance leading to possible loss of individual spawning populations, and susceptibility of the species to further decline from river acidification, invasive species, impediments to fish passage, and poaching (RENEW, 2004). The Atlantic whitefish is currently listed and protected as endangered under the Canada *Species at Risk Act* (SARA).

Atlantic whitefish, reportedly common on the Tusket-Annis rivers until the early 1970's (Bradford et al., 2004a), have not been observed in the river system since 1982 (Edge and Gilhen, 2001; Bradford et al,. 2004a). Concerted attempts to assess the status of the population in 2001 and 2002 failed to capture a single specimen (Bradford et al., 2004a). The species is now considered extirpated from the Tusket-Annis rivers (DFO, 2004).

Atlantic whitefish still occur in the tidal portions of the Petite Riviére but in low abundance (Bradford et al., 2004a). These are likely strays from the freshwater resident population; there is no evidence that anadromous members contribute to production (Bradford et al., 2004a). Life-cycle closure is now certain only for the freshwater resident members occurring in three semi-natural lakes which total no more than 16 km^2 of aquatic habitat (DFO, 2004). The lakes have not been accessible from the sea owing to the presence of a dam which lacks a proper fishway, and the infilling of a sluiceway in 1968 that offered fish passage around the dam during periods of high water flow (Bradford et al., 2004b). A recent illegal introduction of smallmouth bass (*Micropterus dolomieu*) into one of the three lakes, and their likely colonization into the remaining lakes, creates uncertainty as to the future status of resident Atlantic whitefish, and by extension, of the species and potential for recovery (DFO, 2004).

Acidification is one of several stressors implicated in the decline of Atlantic whitefish (Edge and Gilhen, 2001) and is an important consideration in the determination of recovery feasibility and recovery objectives (DFO, in prep.). The Tusket River is quite acidic (pH about 4.5 to 5.2) and the Annis River tributary is only slightly less acidic (pH about 5.0 to 6.0) (Edge and Gilhen, 2001). River pH tends to decline during the high flow winter periods and increase during low-flow summer months. For example, the mean pH of Tusket River samples collected between 1965 and 1974 was below 4.6 from December to March, increased to nearly 5.0 by September and then declined to about 4.5 in December. Acidification has been less extreme in the Petite Riviére but some locations within the watershed are consistently or seasonally (i.e., fall, winter) below pH 5 (Edge and Gilhen, 2001). Acidity effects on population drivers are not known but are the subject of current research (DFO, in prep.). Spawning appears to occur during low pH periods of December-January, and eggs and larvae may be particularly vulnerable to seasonal declines in pH and episodic events. The pH tolerance trials are expected to be complete by March, 2006. Results will be applied to assessment of habitat requirements, likelihood of successful repatriation of the species to the Tusket-Annis rivers, and identification of alternate stocking sites.

7.6 RECOVERY PREDICTIONS

D.S. Jeffries, J. Franklyn, D.C.L. Lam, D.K. McNicol, M.D. Moran, F. Norouzian, R.C. Weeber and I. Wong

7.6.1 Data and modelling

Chemical and biological responses to scenarios of reduced acid deposition were modelled using the provincial lake chemistry data sets compiled for the "current status" assessment presented in Chapter 6 (see Section 6.3.1). Since the deposition scenarios were only available for ON eastwards (see Section 7.6.2 below), predictive modelling was restricted to this part of the country. The lake chemistry data were limited to the most recent annual mean after 1997, and only chemical records that charge balanced within ±15% were included in the modelling runs. The locations of the lakes included in this analysis are shown in Figure 7.19.

As for the 1997 Assessment, the Integrated Assessment Model (IAM; Lam et al., 1998) was used to predict chemical and biological responses for various scenarios of SO_2 emission reductions. The IAM is not a single model but rather a framework of sub-models and/or cause-effect relationships. For this chapter, three IAM components have been used, an atmospheric source-receptor relationship linked to an expert system of water chemistry models linked in turn to biotic response models (see 7.6.3.2 for biological models). Several components of the IAM have been updated and improved from the version that was used for the 1997 Assessment.

The atmospheric source-receptor relationship (SRR) was used to predict sea-salt-corrected wet SO_4^{2-} deposition received by all the lakes. It was obtained from runs of the continental-scale source-receptor model of Olson et al. (1983) using SO_2 emission data for 40 North American

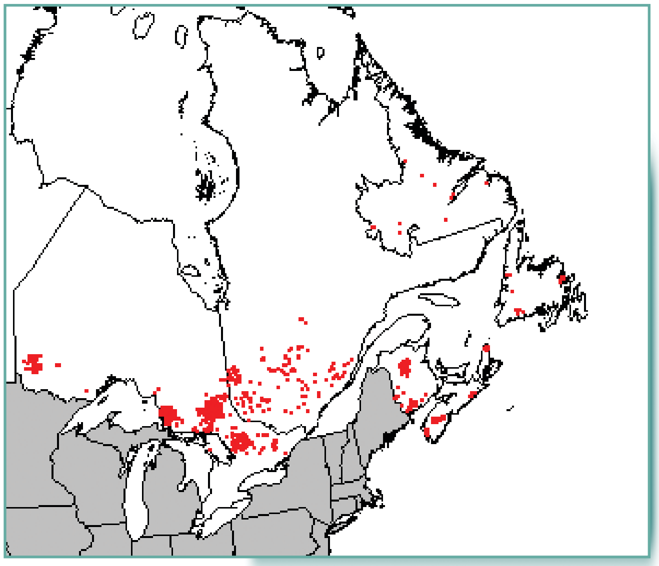

Figure 7.19: Location of lakes with data sufficient to permit water chemistry modelling. The data are the subset of the "current status" data set (see Chapter 6, Section 6.3.1) that charge balance within ±15% (including organic anions).

source regions and meteorological information from either 1980 or 1985. The IAM's single source-receptor relationship is an optimal combination of the annual source-receptor matrices for the two meteorological years. The source-receptor relationship estimates wet SO_4^{2-} deposition, however total (wet + dry) SO_4^{2-} deposition is required to run the water chemistry models. Total deposition was obtained by adding an estimate of dry deposition (quantified in Chapter 3) to the wet component. In the 1997 Assessment, the dry component was assumed to be 15% of total deposition in most regions. Chapter 3 of this assessment shows that the dry component is in fact larger than this – sometimes as much as two-fold larger.

The total SO_4^{2-} deposition estimates were input to the IAM's expert system of water chemistry models to predict lake pHs. The expert system uses one or more of four steady-state models to compute lake acid neutralizing capacity (ANC, the difference between acid anions including organic anions and base cations). Lake pH is subsequently estimated from a pH–Alk relationship (modified after Small and Sutton, 1986). The automated choice of model(s) to predict ANC is based on a set of rules that use measured sample Alk and DOC levels as selection criterion. The rules were established using both knowledge of which model is most appropriately applied to a given lake chemistry and testing to optimize prediction accuracy – hence the term "expert" system. Water flux (runoff) required by the model was interpolated for every lake from a digital version of the national runoff map (see insert map in the national stream flow map at **http://atlas.gc.ca/site/english/maps/archives/5thedition/environment/water/mcr4178**). The IAM uses steady-state water chemistry models because the required input data are modest compared to time-dependent models, and their predictions have a common frame of reference, i.e., after equilibration to a given SO_4^{2-} deposition. Propagation of error through the IAM's sub-models and determination of the overall error have been evaluated (see Lam et al., 1992, 1998 for details). Lam et al. (1992) showed that the expert system simulated observed Alk and pH distributions with an overall relative error in the median pH of 20-30%.

Neither the effect of nitrogen deposition nor decreasing base cation deposition was considered in the model runs. At present, nitrogen-based water acidification is of minor regional importance (see Chapter 6). Decreasing base cation deposition may be of potentially greater regional significance than nitrogen since declining trends have been identified (see Chapter 3), but with no means of projecting future levels, base cation deposition was held constant throughout the scenario simulations.

Time dependent models provide a temporal dimension to the predictions that is not available in the IAM's steady-state predictions. Such models are relatively data intensive, however, so that they cannot be applied to most of the lakes modelled by the IAM. Nevertheless, the Model of Acidification of Groundwater in Catchments (MAGIC; Cosby et al., 1985, 2001) has been applied to selected river and lake systems across southeastern Canada, and the results of these studies are summarised below (see Section 7.6.4).

7.6.2 Deposition scenario definition

Four emission control scenarios were considered for use with the IAM. These scenarios correspond to a "base" situation, and nominally to the years 2010, 2020, and 2060. Broadly, the first emission scenario, the base scenario, corresponds to a recent period when both deposition and aquatic measurements are available

(1994-97 for the former and 1997 and later for the latter). The second and third scenarios are based on realistic estimates of what emission levels will be in 2010 and 2020 given both existing and planned emission control measures in Canada and the United States (U.S.). The last scenario is a hypothetical scenario arbitrarily assigned to the year 2060 that assumes additional emission reductions beyond those expected over the next 15 years. Throughout the remainder of this chapter, the four deposition scenarios will be called "base", "s2010", "s2020" and "s2060" scenarios, respectively. Details concerning assumptions and the regional distribution of emissions for each scenario are given below. Finally, the effect of these scenario emission levels on aquatic ecosystems will be compared to their original condition estimated by the IAM using background SO_4^{2-} deposition as the driving input.

The IAM requires a total SO_4^{2-} deposition value for every lake to model its steady-state water chemistry for each scenario. In general, the deposition value for each lake is derived by interpolation from the kriged deposition field (map) defined by the IAM's 15 deposition receptor sites. The deposition at these 15 sites was specified in one of three ways depending on the scenario. Measured wet and dry SO_4^{2-} deposition estimates were available for the 15 sites for the 1994-97 time-period, and they were used directly to derive the IAM deposition input values for the base scenario. Using s2020 emissions, wet/dry deposition predictions were available from the Acid Deposition and Oxidant Model (ADOM; Venkatram et al., 1988; Fung et al., 1991). These estimates were deemed the best available, and therefore, they were used to derive the s2020 deposition values for the lakes.

No ADOM deposition predictions were available for the s2010 and s2060 scenarios, and hence, the SRR component of the IAM was used. In order to increase the reliability of the SRR estimates, the SRR was used to estimate base and s2020 deposition so that the results could be compared to the measured or ADOM-predicted values respectively. Where differences existed, the s2010 and s2060 SRR estimates were scaled so that they more closely followed the spatial variability present in the more reliable data sets, i.e. measured deposition for the base scenario and ADOM-predicted for the s2020 scenario.

The measured or estimated SO_2 and NO_x emission levels for these four scenarios for various Canadian and U.S. jurisdictions are presented in Table 7.4, and the following summaries provide more details about each scenario.

Scenario 1 (or "base")

This scenario is based on SO_2 and NO_x emissions reported by province in the 1995 Canadian national criteria air contaminant (CAC) emissions inventory and by state in the 1996 U.S. national CAC inventory. In terms of the impact of emission control legislation, these inventories include the impact of SO_2 emission reductions in Canada due to the 1985 Eastern Canada Acid Rain Plan and SO_2 and NO_x emission reductions in the U.S. by 1996 due to various provisions of the 1990 U.S. Clean Air Act Amendments (CAAA). On a North American basis, SO_2 emissions for this scenario are 31% lower than 1980 SO_2 levels but NO_x emissions are 5% higher than 1985 levels (see Table 7.4; Moran and Makar, 2001; U.S. EPA, 2001).

Scenario 2 (or "s2010")

This realistic scenario incorporates both expected emission increases due to population and economic growth in Canada and the U.S. that has already occurred or is expected to occur between 1995/96 and 2010, and emission reductions in Canada and the U.S. due to implementation of both current and planned emission control legislation. Canadian legislation considered for this scenario includes (a) the new Canadian regulations on light-duty and heavy-duty vehicle emission standards and fuel standards that have been passed recently under the 1999 Canadian Environmental Protection Act (CEPA) and (b) the Canada-Wide Acid Rain Strategy for Post-2000. U.S. legislation considered for this scenario includes (a) full implementation of the 1990 CAAA, including the provisions of Title IV related to electrical generating units, (b) the NO_x State Implementation Plan (SIP) Call reductions, (c) the new light-duty and heavy-duty vehicle emission standards and fuel standards that have been passed recently under the U.S. Clean Air Act, (d) the proposed program for non-road diesel engines and fuel (i.e., the "Non-road Rule"), and (e) 2010 levels in the proposed 2003 Clear Skies Initiative. Compared to the base scenario, North American SO_2 emissions are 33% lower for this scenario and NO_x emissions are 33% lower. See Chapter 4, Section 4.5.2.1.1.S6 for more details

Table 7.4. Annual SO_2 and NO_x emissions for North American jurisdictions as reported for 1995/96 and estimated for 2010, 2020 and 2060 (see scenario descriptions in the text). Standard postal abbreviations for states are used in the table where required.

Source		SO_2 Emissions (ktonnes SO_2)				NO_x Emissions (ktonnes NO_2)			
Regions	**Description**	**1995/96**	**2010**	**2020**	**2060**	**1995/96**	**2010**	**2020**	**2060**
NMN 10	Northern Manitoba	360	438	437	328	10	12	12	9
SMN 11	Southern Manitoba	5	3	3	2	86	55	41	31
NOW 12	NW Ontario	5	3	3	2	10	9	8	6
NEO 13	NE Ontario	25	15	15	11	13	12	10	8
SUD 14	Sudbury area	262	215	168	126	20	19	17	13
SWO 15	SW Ontario	282	190	175	131	608	403	344	258
SEO 16	SE Ontario	50	34	31	23	107	71	61	46
SLV 17	St. Lawrence Valley (QC)	153	111	113	85	360	243	236	177
NQU 18	Northern Québec	174	99	101	76	13	17	17	13
GBY 19	Gaspé & North Shore (QC)	46	3	3	2	21	14	13	9
NBK 20	New Brunswick	114	81	48	36	73	68	65	49
NSP 21	Nova Scotia & PEI	169	98	22	17	93	85	77	58
NFL 22	Newfoundland & Labrador	65	49	50	37	50	51	48	36
ASK 23	Alberta & Saskatchewan	740	703	713	535	953	1,061	1,091	818
BCA 24	BC & Yukon	184	195	209	157	346	287	275	207
OHO 50	Ohio	1,777	729	608	456	1,155	527	398	299
ILL 51	Illinois	956	492	487	365	982	612	481	361
PEN 52	Pennsylvania	1,161	438	343	258	964	598	451	338
IND 53	Indiana	1,001	498	461	346	768	379	272	204
KEN 54	Kentucky	691	386	268	201	668	320	248	186
MCH 55	Michigan	508	497	458	344	784	557	461	346
TEN 56	Tennessee	675	406	250	188	720	411	300	225
MSU 57	Missouri	479	373	370	278	478	261	187	140
WVR 58	West Virginia	701	330	279	209	465	192	162	121
NYK 59	New York	558	373	339	254	670	411	279	209
ALA 60	Alabama	698	489	426	320	591	377	289	217
WIO 61	Wisconsin & Iowa	560	547	524	393	742	531	390	292
MIN 62	Minnesota	133	118	125	94	417	297	209	157
VNC 63	Virginia & North Carolina	824	666	508	381	1,176	725	538	403
FLD 64	Florida	741	320	306	230	936	564	380	285
GSC 65	Georgia & South Carolina	783	737	330	247	1,005	640	452	339
MDJ 66	Maryland, Delaware, NJ	582	280	226	170	812	459	347	261
ALM 67	Arkansas, Louisiana, MS	720	665	572	429	1,312	1,084	902	676
MCR 68	Massachusetts, CT, RI	240	107	100	75	473	281	187	140
MAN 69	Maine	40	33	34	26	82	56	40	30
VNH 70	Vermont & New Hampshire	152	108	110	82	127	77	54	40
WNE 71	ND, SD, NE, MT, WY	600	453	460	345	869	624	496	372
WSE 72	KS, OK, TX, CO, NM	1,504	1,137	1,060	795	3,377	2,527	2,070	1,552
WNW 73	Washington, Oregon, ID	203	138	145	109	665	499	362	272
WSW 74	CA, Nevada, Utah, Arizona	426	326	347	261	2,103	1,476	1,211	908
E.Canada	(including Manitoba)	1,710	1,339	1,169	877	1,466	1,058	949	712
East U.S.	(incl. MN, IA, MO, AR, LA)	13,979	8,592	7,126	5,344	15,328	9,360	7,025	5,269
	Canada Total	2,634	2,237	2,091	1,568	2,764	2,406	2,316	1,737
	U.S. Total	16,712	10,646	9,138	6,854	22,342	14,486	11,165	8,374
	North America Total	**19,346**	**12,883**	**11,229**	**8,422**	**25,106**	**16,892**	**13,481**	**10,111**

concerning the various control programs, and Canada-United States Air Quality Committee (2004) for more details about how the projected emission levels given in Table 7.4 were obtained.

Scenario 3 (or "s2020")

This realistic scenario corresponds to the "NOX3P" ADOM scenario discussed in Chapter 4, Section 4.5.2.1.1.S6. It makes the same assumptions as s2010, except that (a) population and economic growth is extended to 2020, (b) the impact of the clean vehicle and clean fuel legislation in both countries is greater than in Scenario 2 (due to greater vehicle fleet turnover and clean-vehicle penetration), and (c) the impact of the 2003 U.S. Clear Skies Initiative is greater (due to the more stringent caps that come into force by 2018). Compared to the base scenario, North American SO_2 emissions are 42% lower for this scenario and NO_x emissions are 46% lower. See Chapter 4, Section 4.5.2.1.1.S6 and Canada-United States Air Quality Committee (2004) for more information about this scenario.

Scenario 4 (or "s2060")

This hypothetical "roll-back" scenario is based directly on s2020 in which SO_2 and NO_x emissions for each jurisdiction are scaled by a factor of 0.75, that is, reduced by 25%. Compared to the base scenario, North American SO_2 emissions are 56% lower for this scenario and NO_x emissions are 60% lower.

Overall, the four scenarios represent 31%, 54%, 60% and 70% reductions in North American SO_2 emissions respectively relative to 1980. The differences in emission levels between s2010, s2020 and s2060 are relatively small compared to the difference between base and s2010. Finally, as a point of reference, a zero-anthropogenic or background emission/deposition scenario was defined and the resulting "original" pH and ANC estimates termed pH_0 and ANC_0 respectively.

7.6.3 Steady-state predictions

7.6.3.1 *Water chemistry*

The cumulative frequency distributions predicted for ANC and pH for the four emission scenarios, plus the estimated original condition (ANC_0 and pH_0 distributions), are shown by province in Figures 7.20 to 7.24. Note that these are steady-state predictions. The data sets available for modelling reflect (a) choices made when compiling the current status database (i.e., the 1997 and later restriction), and (b) a general reduction in monitoring principally due to funding reductions. The lakes that remain after monitoring programs are reduced are predictably the most sensitive to acid deposition. These factors have resulted in a massive reduction in the number of lakes available for modelling compared to the 1997 Assessment. For example, the southern NS cluster in 1997 had 211 lakes while the NS data set now has only 60 lakes and many geographic gaps. Only in ON has the number of modelling lakes not changed greatly, although the data are strongly clustered and significant spatial voids still remain. The implications of the reduced quantity of data available for assessment have been discussed in Chapter 6, Section 6.3.1.3.

For NL, the four scenarios and even the predicted original distributions virtually overlap for both ANC (upper pane of Figure 7.20) and pH (lower pane). This is not surprising since NL is on the edge of the deposition field where emission reductions made mostly in the central part of the continent will effect the least absolute change in deposition. The greatest divergence occurs in the 5 to 6 range of the pH distributions with a shift to higher values for each successively higher level of emission reduction. The scheduled or hypothetical emission reductions will have only a small effect on the water chemistry of NL lakes. Note that the large proportion of originally acidic lakes (predicted steady-state ANC_o <0 μeq/L) in NL (and NS below) arises from the combination of extremely low base cation concentrations and significant organic anion concentrations. Without a way of estimating the historic DOC concentrations, we were obliged to use the present-day levels in the model runs.

Like NL, the NS ANC and pH distributions show only minor differences among the four scenarios although all of them are clearly shifted to lower ANC/pH values compared to the original condition (Figure 7.21). The pH distributions have the sharp inflection in the 5 to 6 range that is typical of titration curves of very poorly buffered waters. The IAM predicts that deposition reductions will result in small increases in ANC relative to the "base" or mid-1990s situation and very small increases in pH.

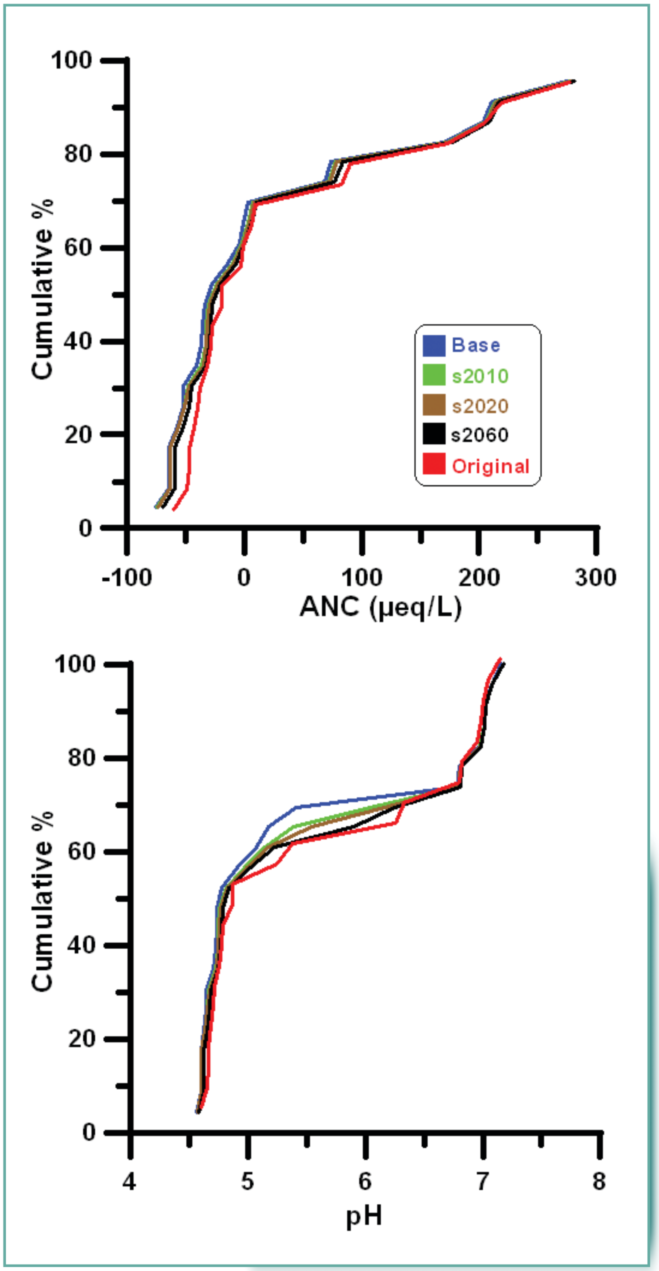

Figure 7.20: Cumulative frequency distributions for steady-state ANC (µeq/L) and pH predicted by the IAM for 23 "modelling" lakes in NL. Distributions are shown for the four deposition scenarios described in Section 7.6.2 plus the estimated pre-acidification (original) distribution.

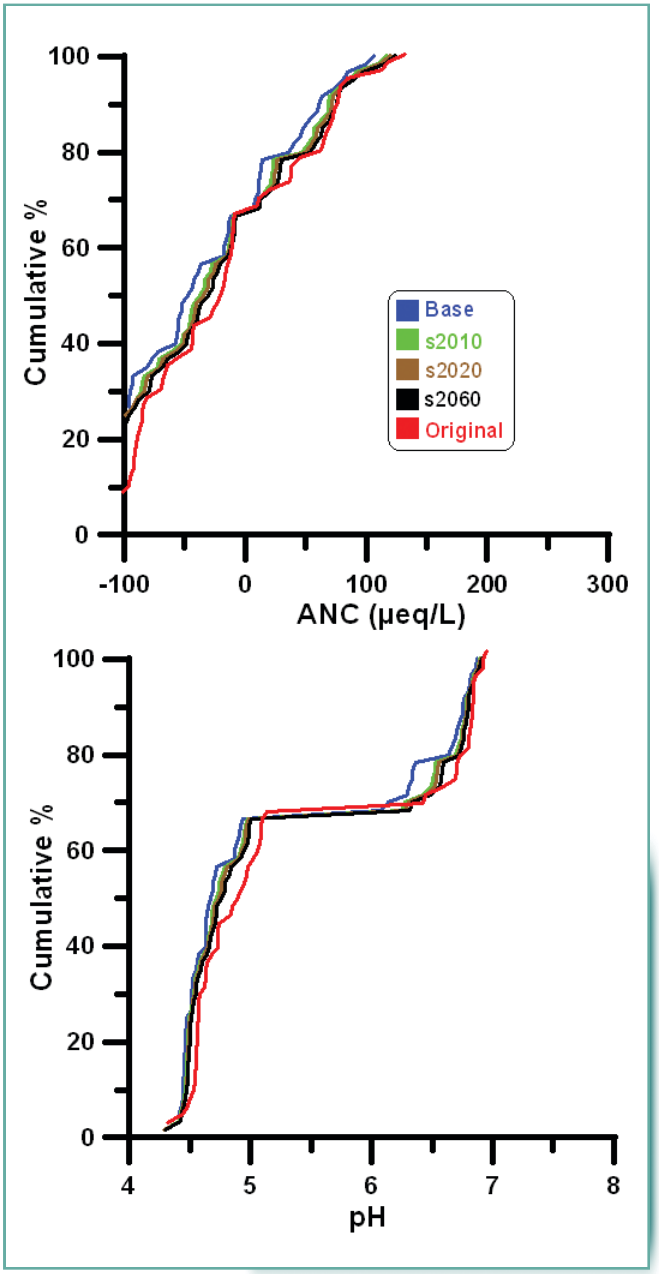

Figure 7.21: Cumulative frequency distributions for steady-state ANC (µeq/L) and pH predicted by the IAM for 60 "modelling" lakes in NS. Distributions are shown for the four deposition scenarios described in Section 7.6.2 plus the estimated pre-acidification (original) distribution.

In NB there is a significant separation between the base and other 3 scenarios, and an even clearer separation of all of them from the estimated original distribution (Figure 7.22). The breadth of the distributions reflect the much lower sensitivity of the NB modelling data set compared to the NL and NS sets. The part of the NB pH distributions below 5 should be disregarded. Four percent of NB's modelling data have virtually identical pH values (4.92-4.95) that cause a problem when developing a pH-Alk relationship which covers the entire observational range. This results in the sharp discontinuity in the pH distributions at approximately pH 4.8. The future deposition reduction scenarios (s2010, s2020 and s2060) all result in some lake recovery relative

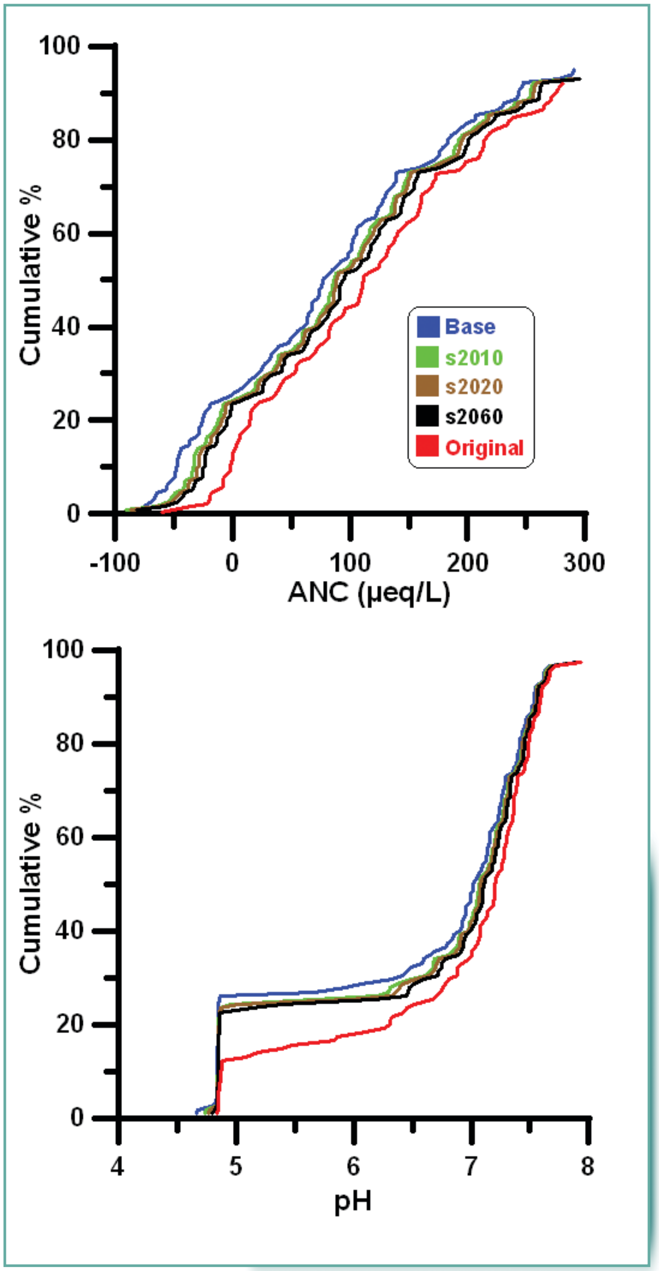

Figure 7.22: Cumulative frequency distributions for steady-state ANC (μeq/L) and pH predicted by the IAM for 115 "modelling" lakes in NB. Distributions are shown for the four deposition scenarios described in Section 7.6.2 plus the estimated pre-acidification (original) distribution. The discontinuity in the pH distributions should be ignored (see text).

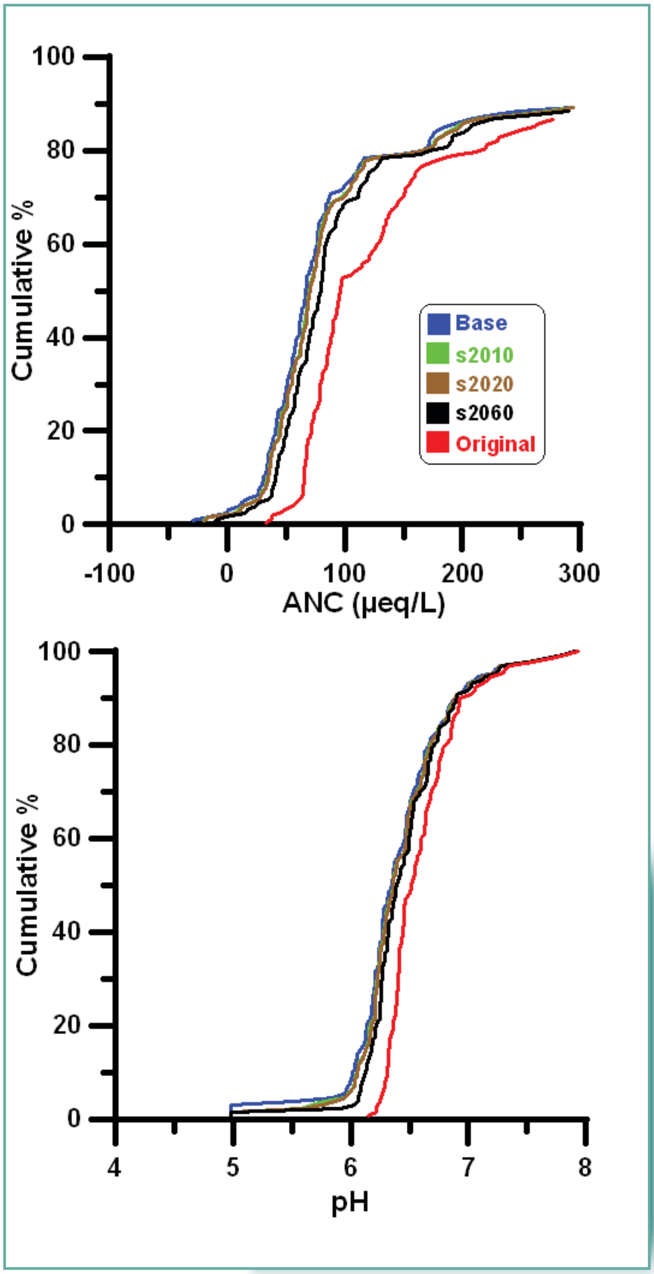

Figure 7.23: Cumulative frequency distributions for steady-state ANC (μeq/L) and pH predicted by the IAM for 130 "modelling" lakes in QC. Distributions are shown for the four deposition scenarios described in Section 7.6.2 plus the estimated pre-acidification (original) distribution.

to the base scenario, but there is little difference between the three of them.

The QC distributions reflect a data set that is somewhat more sensitive than NB's, but less sensitive (i.e. generally higher ANCs) than NL's or NS's (Figure 7.23). The base, s2010 and s2020 scenario distributions virtually overlap, while the s2060 scenario shows identifiable recovery (shifts in ANC and pH to higher values). However, none of the deposition scenarios come close to the estimated original ANC and pH distributions. Monitoring reductions in QC resulted in removal of lakes from the

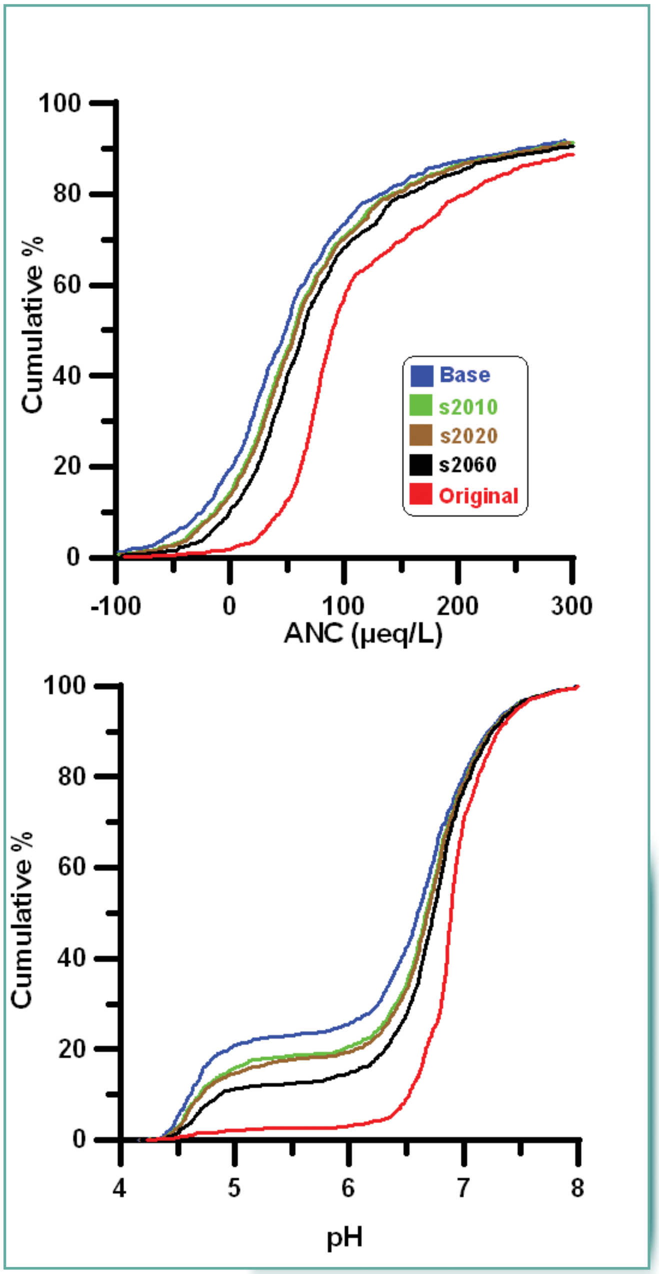

Figure 7.24: Cumulative frequency distributions for steady-state ANC (µeq/L) and pH predicted by the IAM for 1041 "modelling" lakes in ON. Distributions are shown for the four deposition scenarios described in Section 7.6.2 plus the estimated pre-acidification (original) distribution.

St. Lawrence north-shore region. This region contains some of the most sensitive and acidic lakes in QC, and they are no longer represented in the modelling data set.

The ON data set is by far the largest of all the provincial sets. It represents a sensitivity range comparable to QC's, but also contains substantially more acidic lakes. Except for s2010 and s2020, there is clear separation of the ANC/pH responses to the different levels of deposition reduction and a big difference from the estimated original condition (Figure 7.24). Deposition reduction will clearly promote recovery in ON lakes, albeit within a rather narrow range based on the scenarios employed here.

The ON modelling data set is sufficiently large that it can be separated into components to assess spatial variability in the lake chemistry predictions. As shown in Figure 7.19, the ON modelling lakes are clustered, and this fact was used to define three ON subsets. These were as follows: (1) 239 lakes situated in secondary watershed 2B which roughly corresponds to the Algoma region of central ON, (2) 250 lakes situated in secondary watershed 2D (roughly equivalent to the Sudbury region), and (3) 201 lakes situated in secondary watershed 2E (roughly equivalent to the Muskoka region of south-central ON) (see also Figure 7.26). The cumulative frequency distributions for these ON subsets are presented in Figure 7.25.

The three regions in ON exhibit fairly similar "original" ANC and pH distributions for the modelling lakes; very few were acidic (ANC_O <0 µeq/L) or had pH_O <6 (the few present in the distributions are almost all located in Algoma (2B)). These subsets are not normally distributed; they are clearly multi-modal. In all cases, the scenario distributions are substantially shifted towards lower ANC and pH values. Separation between the scenario ANC distributions was slightly greater for Muskoka (2E) than for either Sudbury (2D) or Algoma (2B). The two scenarios representing the most realistic future deposition levels (s2010 and s2020) yield almost identical ANC distributions, which is not surprising given the rather small difference in their SO_2 emission levels (see Table 7.4). The pH distributions show greater separation between scenarios compared to ANC. Of the three regions, the Muskoka (2E) subset shows by far the largest pH improvements, and in particular, the IAM predicts that the additional emission reductions expected by 2010 will render a significant pH recovery in Muskoka lakes. The predicted pH response of Algoma (2B) lakes to the reduction scenarios is less than for Muskoka, but nevertheless, still quite substantial. The Sudbury (2D) subset is the least responsive of the three regions to

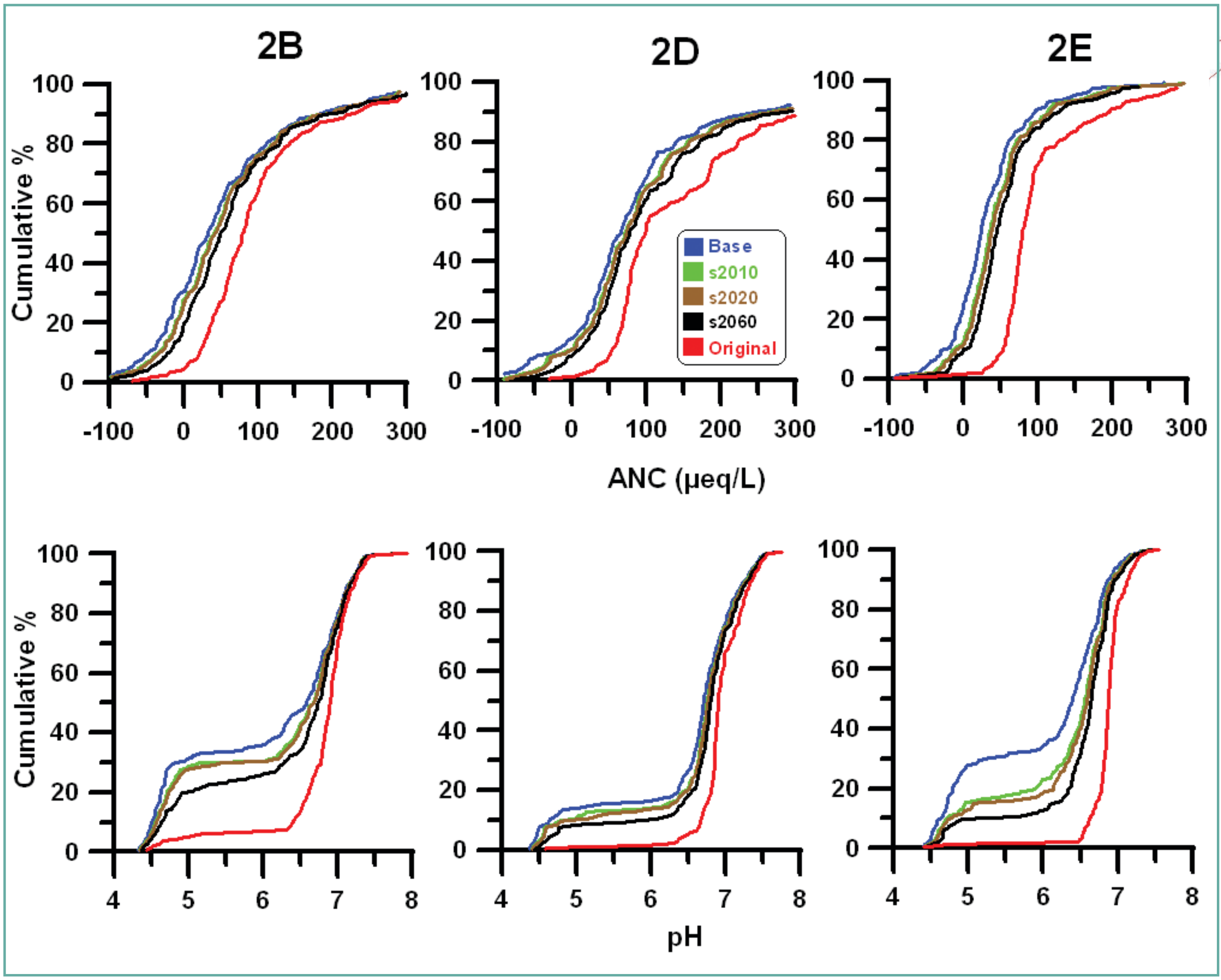

Figure 7.25: Cumulative frequency distributions for steady-state ANC (μeq/L) and pH predicted by the IAM for "modelling" lakes in the 2B (Algoma, n=239), 2D (Sudbury, n=250) and 2E (Muskoka, n=201) secondary watersheds of ON. Distributions are shown for the four deposition scenarios described in Section 7.6.2 plus the estimated pre-acidification (original) distribution.

the reduction scenarios, probably because it has the highest proportion of lakes with base (or contemporary) pH >6. This may be surprising to some, but it must be remembered that most of the lakes in the 2D subset actually reside to the northeast of Sudbury, well outside the area of direct smelter impact.

A number of Alk and pH values have been suggested as thresholds for determining critical loads of acidity for aquatic ecosystems (see Chapter 8, Section 8.3.2). Among them are values of 0, 15 and 40 μeq/L for Alk and 5.0, 5.5 and 6.0 for pH. The proportion of lakes damaged by acid deposition can be judged relative to these thresholds (as was done in the 1997 Assessment; Jeffries, 1997; Jeffries et al., 2000). In the critical load chapter of this assessment (Chapter 8), 40 μeq/L of ANC and a pH of 6.0 were selected as the most appropriate chemical thresholds for Canadian aquatic ecosystems. The effectiveness of the four emission/deposition scenarios in achieving these and the other chemical threshold values for the modelling data sets is shown in Table 7.5.

The Atlantic provinces have many lakes that are naturally acidic due to very low base cation concentrations in combination with organic acidity from DOC. The fraction of such lakes in the modelling data sets is apparent from the estimated percent of lakes that had "Original" ANC (or ANC_O) >0 μeq/L, i.e., 45%, 33% and 91% for NL, NS

Table 7.5. Estimated percent of modelled lake populations meeting specified pH and ANC criteria under the deposition scenarios described in the text. "Original" indicates the estimated pre-acidification values. The values in parentheses for NF, NS and NB are the same percentages for the subset of modelled lakes having ANC$_O$ >0 μeq/L (rounded to closest 5% for NF due to the small number of lakes in that subset).

Province	Deposition Scenario	Percent of Modelled Lakes					
		pH			ANC (μeq/L)		
		>5.0	>5.5	≥6.0	>0	>15	≥40
Newfoundland 23 lakes (11 ANC$_o$ >0)	Original	48 (100)	40 (85)	37 (80)	45	31 (65)	30 (65)
	Base	43 (90)	31 (65)	29 (65)	35 (75)	30 (65)	29 (60)
	2010	44 (95)	35 (75)	32 (70)	39 (85)	31 (65)	29 (60)
	2020	45 (95)	37 (80)	33 (70)	40 (85)	31 (65)	29 (65)
	2060	46 (100)	39 (85)	35 (75)	40 (90)	31 (65)	29 (65)
Nova Scotia 60 lakes (20 ANC$_o$ >0)	Original	44 (100)	33 (100)	32 (100)	33	32 (100)	27 (85)
	Base	33 (100)	33 (100)	32 (100)	32 (100)	21 (68)	18 (59)
	2010	33 (100)	33 (100)	32 (100)	33 (100)	29 (90)	20 (64)
	2020	34 (100)	33 (100)	32 (100)	33 (100)	29 (91)	21 (65)
	2060	35 (100)	33 (100)	32 (100)	33 (100)	29 (92)	21 (66)
New Brunswick 115 lakes (105 ANC$_o$ >0)	Original	88 (94)	85 (93)	82 (90)	91	82 (90)	74 (81)
	Base	74 (81)	73 (80)	72 (79)	75 (82)	71 (78)	64 (71)
	2010	76 (83)	75 (82)	74 (82)	76 (83)	74 (81)	66 (73)
	2020	76 (83)	75 (83)	75 (82)	76 (84)	75 (82)	68 (75)
	2060	77 (85)	76 (83)	75 (82)	77 (84)	75 (82)	70 (77)
Québec 130 lakes	Original	100	100	100	100	100	99
	Base	97	96	93	98	95	81
	2010	99	98	94	98	96	83
	2020	99	98	94	98	96	84
	2060	99	98	97	99	98	92
Ontario 1041 lakes	Original	97	97	97	98	97	91
	Base	79	77	74	80	73	54
	2010	84	81	79	85	78	60
	2020	85	82	80	86	79	62
	2060	88	87	85	89	84	68

and NB respectively. In contrast, virtually all QC and ON modelling lakes had ANC$_O$ >0 μeq/L. Therefore in Table 7.5, the subset of modelling lakes in each of the three Atlantic Provinces that had ANC$_O$ >0 was identified and the percentages re-calculated for the subset only. These re-calculated values (in parentheses in the NL, NS and NB rows of the table) show the effect of the different scenarios on lakes that were not originally acidic.

In NL, the percentage of non-acidic lakes (ANC >0 μeq/L) increases from 35% for the base scenario to 40% for the s2060 scenario (from 75% to 90% when the originally non-acidic subset is considered). The percentages meeting the ANC critical load threshold used in Chapter 8 (≥40 μeq/L) remains constant at 29% across all scenarios and increases marginally from 60% to 65% for the subset. The pH response is slightly greater, e.g., the percentage of modelled lakes meeting the critical load pH threshold (pH ≥6) increases from 29% for the base scenario to 35% for the s2060 scenario (65% to 75% for the originally non-acidic subset). These values demonstrate that the emission reductions will have a positive effect in NL, but the magnitude is small.

In NS, there is little response by the modelling lakes to reduced levels of deposition. The largest percent changes are for the ANC >15 and ≥40 categories, e.g., for the latter category, an increase from 18% for the base scenario to 21% for the s2060 scenario (or 59% to 66% when the originally non-acidic subset is considered; 85% of the subset originally had ANC ≥40). This minimal response in NS is undoubtedly due to the nature of the modelling data set. For example, all the lakes in the ANC_O >0 subset had pH >6 – hence the complete lack of pH response from scenario to scenario with respect to the pH thresholds in Table 7.5. The NS data set appears to be bimodal, being composed of many naturally acidified, low pH lakes and some high pH lakes. The NS pH and ANC distributions modelled by Clair et al. (2003) support this conclusion. Hence a better, larger modelling data set for NS is needed to properly assess the impact of the deposition reduction scenarios.

The response of NB lakes to the scenario reductions is slightly larger than it was for NL. The percentage of lakes meeting the ANC critical load threshold increased from 64% for the base scenario to 70% for the s2060 scenario (71% to 77% for the subset in which 81% originally exceeded the threshold). The pH values tell the same story, e.g., 72% had pH ≥6 for the base scenario and this increased to 75% for the s2060 scenario (79% to 82% for the subset where 90% originally exceeded the threshold).

Both the QC and ON modelling data sets contained few naturally acidic lakes so there was no need to identify a subset with ANC_O >0 μeq/L. The QC lakes showed pH improvements that almost attain their original condition, e.g., increasing from 93% with pH ≥6 for the base scenario to 98% for the s2060 scenario when 100% originally exceeded this threshold. Similarly, the QC lakes showed improvements in ANC although the s2060 value for the ≥40 category (92%) still falls short of the original value (99%). Clearly, deposition reduction will induce significant improvement in QC lakes. Unfortunately, the modelling data set does not include sensitive and possibly naturally acidified lakes from the region of the St. Lawrence north shore, so that the picture presented here may be too positive.

The size of the ON data set probably makes it the most representative of all the provincial sets. Marked improvements will occur as deposition decreases. For example, the percentage of lakes exceeding the pH 6 threshold increases from 74% for the base scenario to 85% for the s2060 scenario, however this still falls very short of the 97% that originally exceeded the threshold. The ANC categories also show large improvement (e.g., from 54% to 68% for the ≥40 μeq/L category).

The level of damage reported in the 1997 Assessment was quantified in terms of the number of lakes having pH <6. Clearly it is only appropriate to consider those lakes that were originally capable of exceeding this threshold. We predict that 37% , 32%, 82%, 100% and 97% of the lakes in our NL, NS, NB, QC and ON modelling data sets respectively were originally capable of exceeding this pH threshold (Table 7.5). If it is assumed that our data sets are representative of the provincial inventories of sensitive lakes south of 52°N latitude (Hélie et al., 1993; sensitive lakes are categorized as occurring in terrain having “a low potential to reduce acidity” in this document), then it is possible to directly extrapolate the subset percentage values in Table 7.5 to determine the damage levels associated with each scenario. Performing this calculation suggests that approximately 86,000 lakes in southeastern Canada capable of having pH ≥6 will in fact have a steady-state pH <6 under the base scenario. These numbers decline as deposition is reduced, i.e., ~71,000, ~69,000 and ~48,000 lakes for the s2010, s2020 and s2060 scenarios respectively. These numbers correspond to ~15%, ~12%, ~12% and ~8% respectively of the ~580,000 sensitive lakes in southeastern Canada capable of having pH ≥6. The 1997 Assessment estimated that ~95,000 lakes would have pH <6 once all emission reductions required by the Canada-U.S. Air Quality Agreement were fully implemented. This is equivalent to the s2010 scenario reported here. Not too much should be made of the difference between the two estimates, i.e., 71,000 lakes vs 95,000 lakes. The estimates were derived using very different data sets and the assumption of representativeness is no doubt incorrect. Only collection of statistically representative data sets will yield extrapolations that have a known level of uncertainty. The important message from these calculations is that large numbers of lakes will remain damaged after currently planned emission reductions are implemented, and even a further 25% reduction (i.e., our hypothetical s2060 scenario) will not reduce damage below the 5% level that is commonly used when determining aquatic critical loads.

7.6.3.2 Biology

This section provides estimates of habitat suitability for three groups of biota that illustrate the range of expected responses to the predicted pH changes discussed above (see Section 7.6.3.1). Habitat suitability, represented as a probability of occurrence, was estimated using predicted pH values for five scenarios (i.e. base, s2010, s2020, s2060, original). Habitat suitability was estimated for small fish (i.e. cyprinids and allies, yellow perch (*Perca flavesens*) and white sucker (*Catostomus commersoni*)), breeding pairs of fish-eating waterbirds (e.g. Common Loon (*Gavia immer*), Common Merganser (*Mergus merganser*)), and breeding pairs and young of the diving duck Common Goldeneye (*Bucephala clangula*). Model terms other than pH were based on the database assembled to describe the current (i.e. since 1997) chemical status of sampled lakes in eastern Canada (see Section 6.2.1) and these values were held constant among the five scenarios. As described in Chapter 6 and Section 7.3 above, biological responses to acidity are often modified by other chemical or physical stressors, species' dispersal and colonisation rates, and competition and predation. Predicting habitat suitability changes solely on pH changes is useful for estimating the relative impact of emission reduction scenarios but are necessarily simplistic because estimates of current and future values of the habitat attributes driving biological recovery are not yet available.

Habitat association models were derived using small fish and waterbird data collected between 1988 and 2003 in three regions of ON (Muskoka, Sudbury, Algoma). Sections 6.4.3 (small fish) and 6.4.4.2 (waterbirds) describe the models resulting from an intensive model selection exercise and discuss the biological relationships represented by the model terms. Observed values were not widely available for certain terms (i.e., total phosphorus, Al, and observed fish presence). The objectives in this recovery section were to identify patterns in habitat suitability relative to predicted change in steady-state pH, rather than to a broad set of habitat attributes. For these reasons, regression and concordance estimates were recalculated using subsets (see Table 7.6) of the models described in Chapter 6. All regression models included estimates for lake area and pH and all had high estimates of predictive strength (i.e., concordance >70%). In general, models applied to IAM chemical results suggested that small fish and fish-eating waterbirds would be expected to respond positively to pH increases (i.e., reduced acidity). An opposite response, however, would be expected for the strongly insectivorous Common Goldeneye (Table 7.6), which often benefits during the breeding season from the available prey base in many lakes and wetlands with low fish predation (see 6.4.4.2).

Habitat suitability predictions for each scenario were generated for lakes with available IAM-derived pH predictions and the lake physical and chemical values identified in Table 7.6 (see also 7.6.1 above). Patterns in habitat suitability were driven by four interrelated factors: the estimates of effects summarised in Table 7.6, the prevalence of predicted pH change (i.e., how many lakes were predicted to change), the magnitude of those predicted pH changes, and the degree to which predicted pH change was correlated with other terms in the model statements of Table 7.6. Patterns were summarised by province and by secondary watershed for four provinces in eastern Canada (NL was excluded due to small sample size). Interpretation of predicted habitat suitability changes was strongest and most straightforward for the ON portion of the dataset due to the higher number of

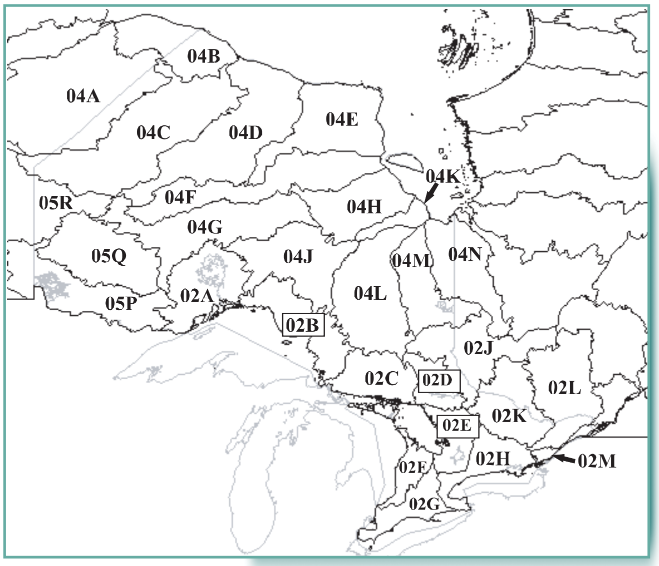

Figure 7.26: Location of secondary watersheds in ON. The three watersheds discussed in the text (2B, 2D, 2E) are highlighted.

Table 7.6. Biological models used to estimate predicted habitat suitability changes in response to Integrated Assessment Model (IAM) predictions of pH change under four scenarios of acidifying emission reductions. Guild and species-specific habitat association models were derived using data from the Algoma, Sudbury and Muskoka regions of ON and are subsets of those described in Sections 6.4.3 (minnows and other small fish) and 6.4.4.2 (waterbirds) (see 7.6.3.2 text for further details). Modelled effects are considered statistically significant if their 95% confidence intervals (in parentheses) exclude zero. Average concordance was calculated with a leave-one-out jackknife using lake-level observations and predicted values (i.e. 1000 iterations of 1000 paired observations) (e.g. Olden and Jackson, 2000). Common Goldeneye models, which excluded data below the southern edge of their breeding range (i.e. approximately 46° north latitude), include a term for Algoma, ON region to account for their greater probability of occurrence in that region. The shoreline development index (SDI) was calculated as (Shoreline length)/(2*SquareRoot(π *Lake area)).

Species	LH[a]	Constant	Lake area	pH	DOC	SDI	Algoma	n[b]	C[c]	Freq[d]
Small fish		-12.2 (-14.57, -9.73)	0.05 (0.027,0.079)	1.95 (1.559, 2.342)	0.10 (0.028,0.162)			591	79.9	55.0
Piscivore waterbirds	pairs	-3.51 (-4.634, -2.380)	0.15 (0.123, 0.187)	0.36 (0.184, 0.539)	-0.07 (-0.101, -0.029)			3162	78.9	28.5 (65.3)
Common Goldeneye	pairs	4.30 (2.994, 5.602)	-0.01 (-0.026, 0.004)	-0.97 (-1.222, -0.717)			1.19 (0.814, 1.571)	2179	79.4	32.4 (63.9)
Common Goldeneye	young	1.54 (-0.084, 3.160)	-0.05 (-0.079, -0.020)	-0.74 (-0.983, -0.487)		0.53 (0.226, 0.839)	1.31 (0.946, 1.672)	2153	80.0	10.4 (58.7)

[a] LH=Life history stage.

[b] n=Minnows: Number of years available for analysis; Waterbirds: Number of lake-years available for analysis.

[c] C=Mean percent concordance.

[d] Freq.=Minnows: Percent of lakes occurring; Waterbirds: Mean percent of years (lake-years) occurring

available lakes relative to other eastern provinces and the likelihood that model estimates captured geographic variation in species' habitat associations. Cumulative frequency plots were used to summarise the patterns in predicted habitat suitability for small fish and fish-eating waterbirds in NS, NB, QC and ON. In these figures, lines located toward the left side of the plot indicate better habitat suitability than those nearer the right side of the plot (i.e., lines to the left side indicate a smaller proportion of modelled lakes were required to achieve similar levels of predicted probability of occurrence). To illustrate one method of summarising patterns according to geophysical boundaries, habitat suitability patterns were plotted for three secondary watersheds in ON (2B, 2D, 2E) where sample sizes were relatively large (i.e., >100 lakes) (Figure 7.26).

7.6.3.2.1 Small fish

Predicted habitat suitability patterns for minnows and other small fish varied among the four eastern provinces modelled. The probability of occurrence lines rose more slowly for the cumulative frequency plot of NS than for the other provinces, indicating generally lower estimated probabilities of small fish occurrence for modelled lakes in this province relative to those in NB, QC and ON (Figure 7.27). Habitat suitability predictions for small fish in the NS lakes used for modelling were similar among the emission reduction scenarios (Figure 7.27a). Divergence among scenarios was also small for NB lakes but some improvements were predicted with future emission reductions (i.e., s2010, s2020 and s2060 lines shifted to left of base line; Figure 7.27b). The modelled QC lakes had generally high suitability for small fish (i.e., lines grouped near far left of plot), leaving little opportunity for divergence among the scenarios (Figure 7.27c). Divergence among the scenario lines was greatest for the modelled ON lakes with predicted habitat suitability best under pH_O and worst under the base pH conditions. This pattern occurred across a wide range of habitat suitability, from <0.1 to nearly 0.9 probability of occurrence, and habitat suitability was predicted to improve with emission reductions for nearly 40% of modelled lakes (i.e., range on horizontal axis for which base differed from s2010, s2020 and s2060 lines).

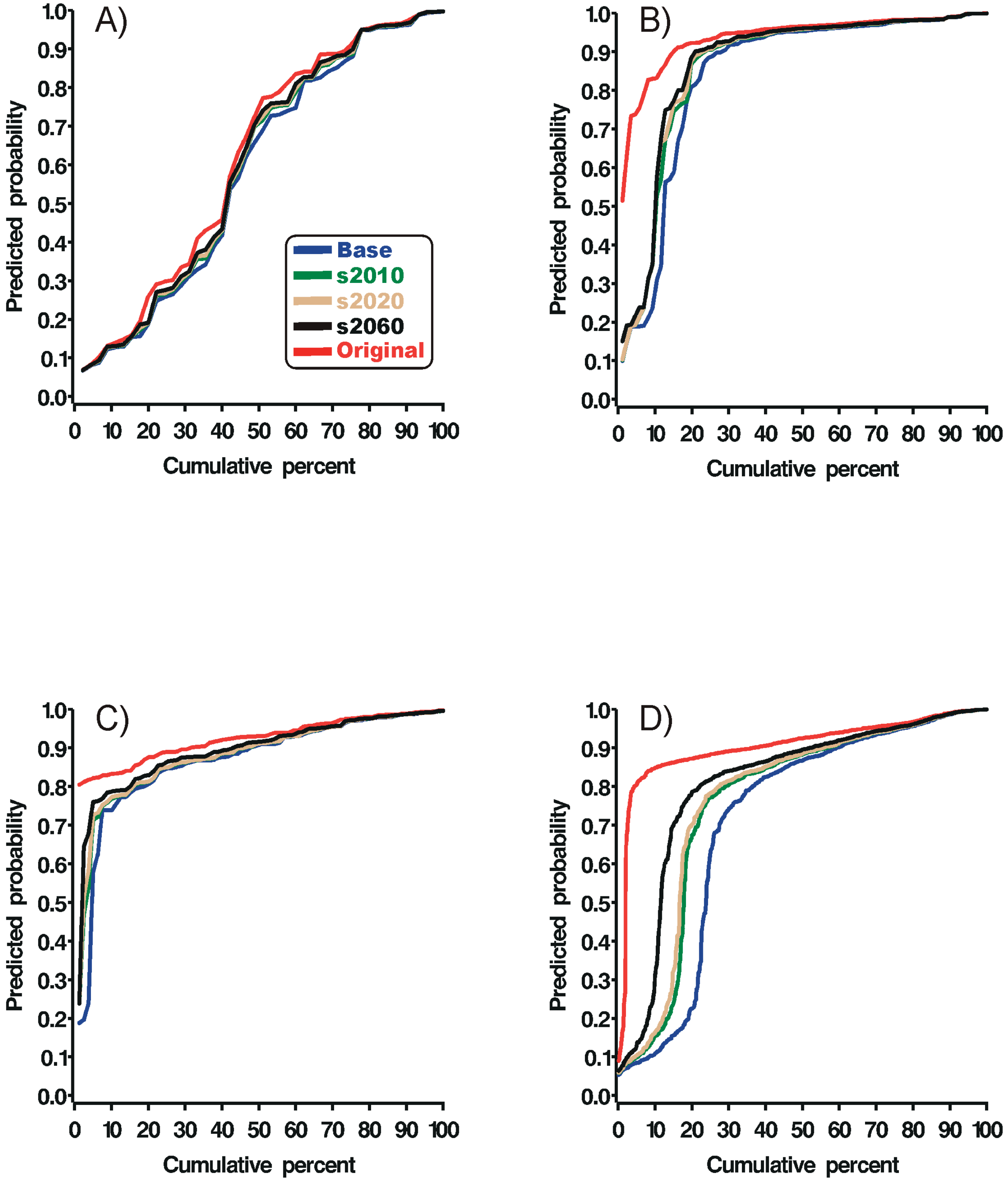

Figure 7.27: Predicted probability of small fish (i.e. cyprinids and allies, perch, sucker) occurrence relative to the cumulative percent of modelled lakes in the provinces A) NS (n=45 lakes), B) NB (n=86), C) QC (n=76) and D) ON (n=672). Lake size was restricted to the range included in generating the model estimates (i.e. 2 to 110 ha). Probabilities were based on the predicted original pH (red) and the predicted pH under four emission scenarios: base (blue), s2010 (green), s2020 (tan) and s2060 (black). Lines to the left indicate improved habitat suitability relative to lines near the right side of the plot.

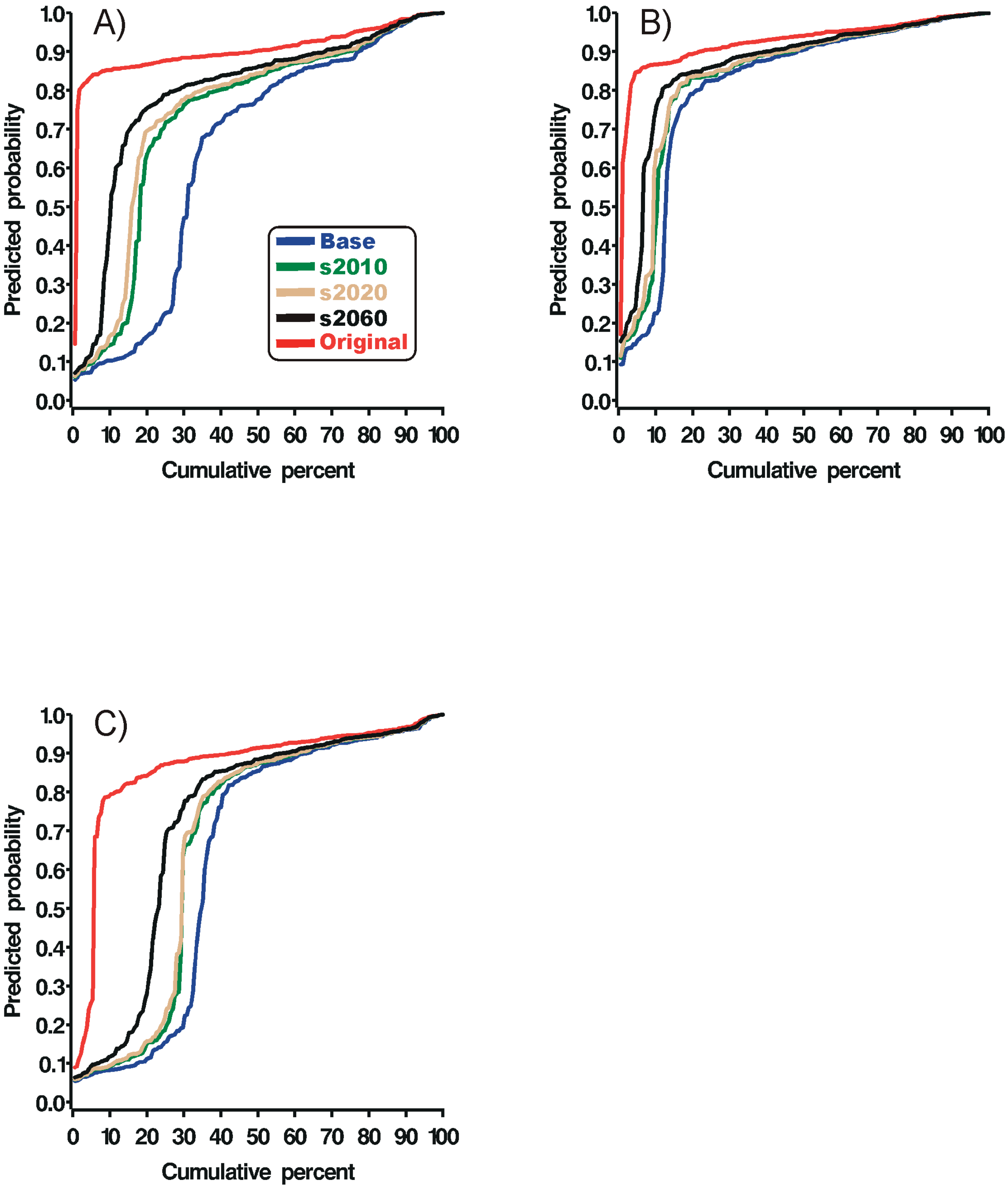

Figure 7.28: Predicted probability of small fish (i.e. cyprinids and allies, perch, sucker) occurrence relative to the cumulative percent of modelled lakes in secondary watersheds A) 2E (Muskoka; n=163 lakes), B) 2D (Sudbury; n=175) and C) 2B (Algoma; n=185) in ON. Lake size was restricted to the range included in generating the model estimates (i.e. 2 to 110 ha). Probabilities were based on the predicted original pH (red) and the predicted pH under four emission scenarios: base (blue), s2010 (green), s2020 (tan) and s2060 (black). Lines to the left indicate improved habitat suitability relative to lines near the right side of the plot.

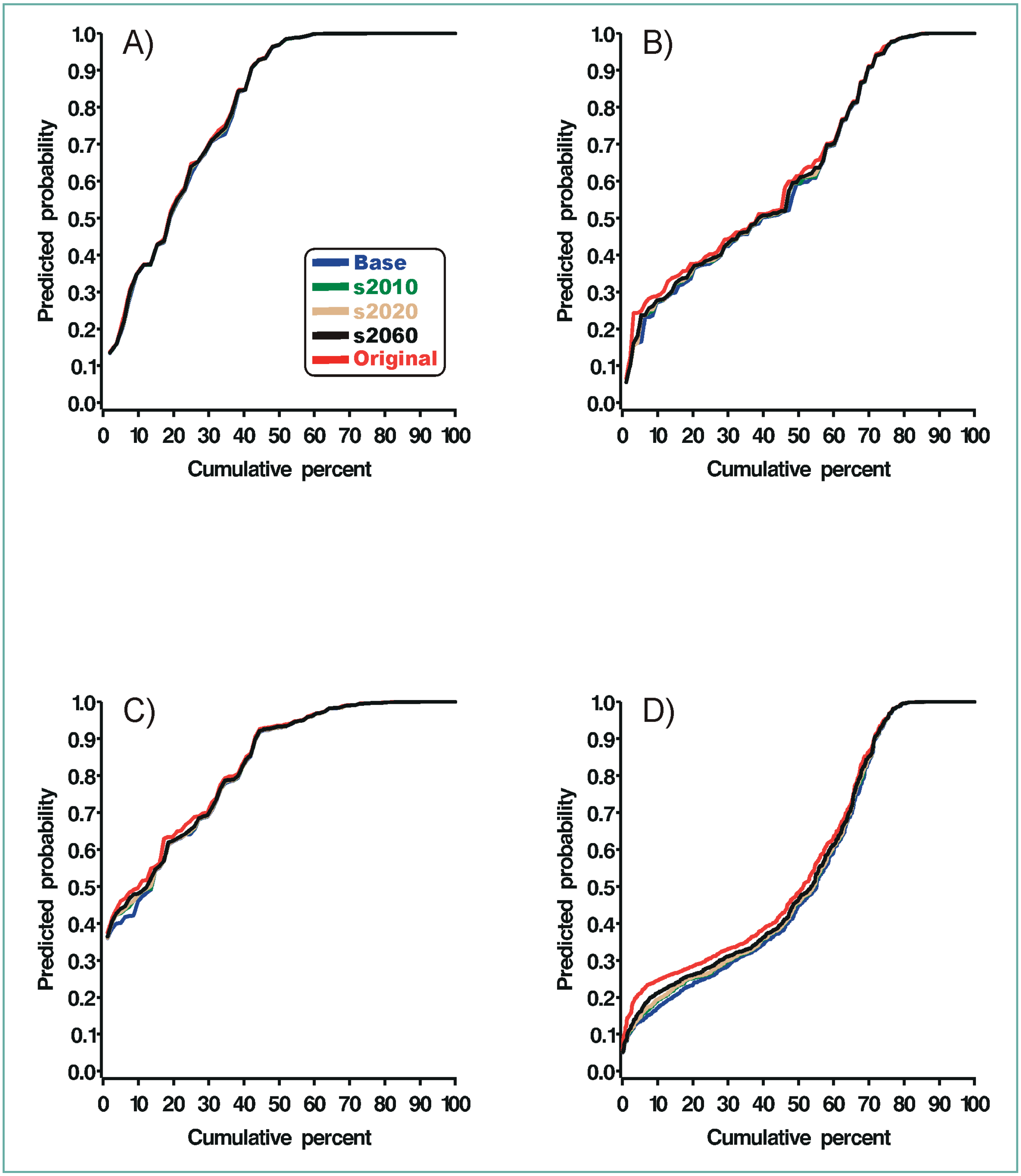

Figure 7.29: Predicted probability of occurrence for breeding pairs of piscivorous waterbirds relative to the cumulative percent of modelled lakes in the provinces A) NS (n=52 lakes), B) NB (n=93), C) QC (n=81) and D) ON (n=737). The range of lake sizes included was extended somewhat (i.e. 2 to 500 ha) in recognition that the species in this guild frequently occur on lakes larger than the 110 ha maximum included in model derivations (see also McNicol, 2002; Doka et al., 2003). Probabilities were based on the predicted original pH (red) and the predicted pH under four emission scenarios: base (blue), s2010 (green), s2020 (tan) and s2060 (black). Lines to the left indicate improved habitat suitability relative to lines near the right side of the plot.

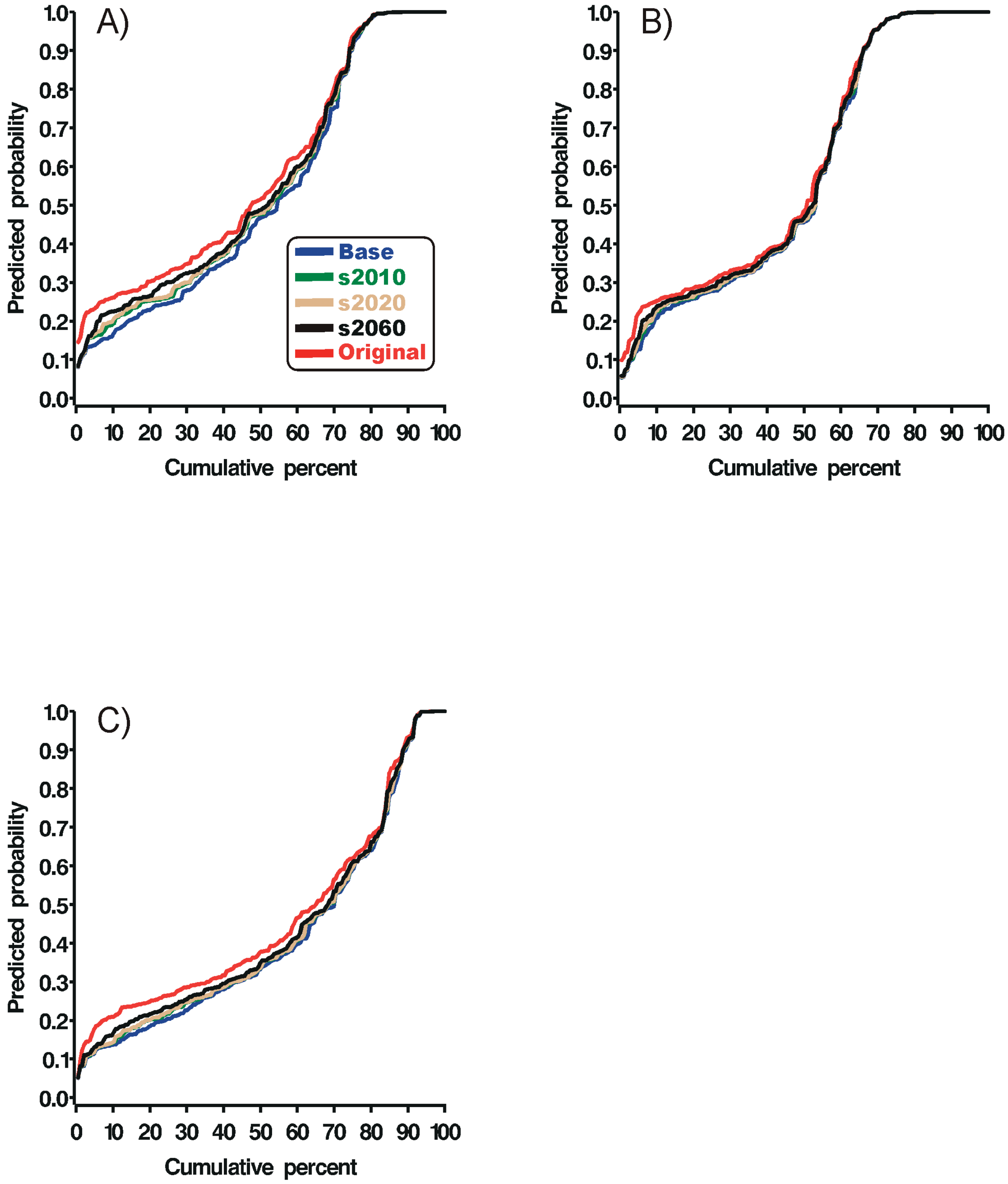

Figure 7.30: Predicted probability of occurrence for breeding pairs of fish-eating waterbirds relative to the cumulative percent of modelled lakes in secondary watersheds A) 2E (Muskoka; n=175 lakes), B) 2D (Sudbury; n=196) and C) 2B (Algoma; n=186) in ON. The range of lake sizes included was extended somewhat (i.e. 2 to 500 ha) in recognition that the species in this guild frequently occur on lakes larger than the 110 ha maximum included in model derivations. Probabilities were based on the predicted original pH (red) and the predicted pH under four emission scenarios: base (blue), s2010 (green), s2020 (tan) and s2060 (black). Lines to the left indicate improved habitat suitability relative to lines near the right side of the plot.

Although actual recovery will also be influenced by other factors, these patterns suggest that emission reductions will promote substantial improvements in small fish habitat suitability for a large number of lakes in ON like those modelled here (e.g., generally small, moderately acidic; see Section 6.4.3). Because predicted pH changes were small (see Figure 7.24), there was very little difference between s2010 and s2020 lines (Figure 7.27d).

Patterns in predicted habitat suitability varied among the three ON secondary watersheds with sufficient numbers of lakes available for modelling (Figure 7.29). As for the provincial summary, habitat conditions were best under pH_O and worst under base pH conditions. Scenarios diverged much more in watersheds 2E (Muskoka) and 2B (Algoma) than in the Sudbury area watershed 2D, a pattern reflected in the predicted pH change (Figure 7.25). Relative to the base scenario, habitat suitability was improved with emission reductions for about 70% of 2E lakes and 50% of the 2B lakes (Figure 7.28a and c, respectively), with the divergence among scenarios spanning a wide range of probabilities from <0.1 to about 0.85.

7.6.3.2.2 Waterbirds

Relative to the patterns for small fish, habitat suitability estimates for breeding pairs of fish-eating (i.e., piscivorous) waterbirds were generally more similar among the emission reduction scenarios (Figure 7.29). Probability lines were fairly similar among provinces but the probability of piscivorous bird occurrence was slightly higher in modelled QC lakes relative to those in the other three provinces. Where divergence among the probability lines occurred, the original predicted pH was associated with better habitat suitability conditions. Divergence among the emission scenarios was evident only for the ON lakes that were modelled (Figure 7.29d), with the differences occurring from probabilities of 0.15 to about 0.6 and including about 35% of the modelled lakes.

Although the magnitude of change was less than for small fish, habitat suitability predictions for fish-eating waterbirds showed more divergence among scenarios when summarised for three secondary watersheds in ON (Figure 7.30). Emission reductions were associated with improved habitat suitability for the 2E (Muskoka) and 2B (Algoma) watersheds, where substantial changes in pH were predicted (Figure 7.25). Although the magnitude of the predicted improvements were relatively small, some of the patterns of divergence from the base scenario occurred across a wide range of probability of occurrence (e.g., about 0.15 to 0.75 for watershed 2E) and for a substantial portion of the modelled lakes (e.g., about 70% in 2E). Given the complexity of waterbird responses to the quality of their breeding habitats and the relative simplicity of the models used here, these results suggest the potential for emission reductions to result in habitat improvements despite the small magnitude of predicted change, particularly if the types of lakes showing improvements are strongly represented in regions of acidity declines such as the 2E and 2B watersheds.

Summaries of predicted habitat suitability for Common Goldeneye are presented only for the two ON watersheds 2D (Sudbury) and 2B (Algoma) with at least 100 lakes available for modelling (Figure 7.31). Extrapolations were not made beyond the southern edge of the breeding range (approximately 46° north latitude) of this diving duck, which typically breeds in northern boreal forests. General patterns indicated that goldeneye pairs were predicted to occur more frequently than young and, due in large part to the strong positive association with the Algoma region, the predicted habitat suitability was generally better in watershed 2B than 2D. In contrast to small fish and piscivorous waterbirds, habitat suitability for Common Goldeneye tended to decrease with emission reductions and was much lower for the original predicted pH scenario, particularly for modelled lakes in 2B (Figure 7.31b and d). Divergence among scenarios was small for modelled lakes in the 2D watershed but was substantial in 2B. For breeding pairs, the base and 2060 probability lines diverged over the range of about 0.25 to 0.7; differences between these lines were restricted to a maximum probability of about 0.6 for Goldeneye young in 2B (Figure 7.31b and d). These patterns suggest that pH increases are likely to lead to a decline in habitat suitability for Common Goldeneye, with the most substantial change occurring in the Algoma region. As noted elsewhere (e.g., Section 6.4.4.2 and in this section), acidity responses by insectivorous fish (e.g., dace species) and their impact on aquatic invertebrate food sources are likely to be very strong influences on the consequences of emission reductions for breeding Common Goldeneye and their young.

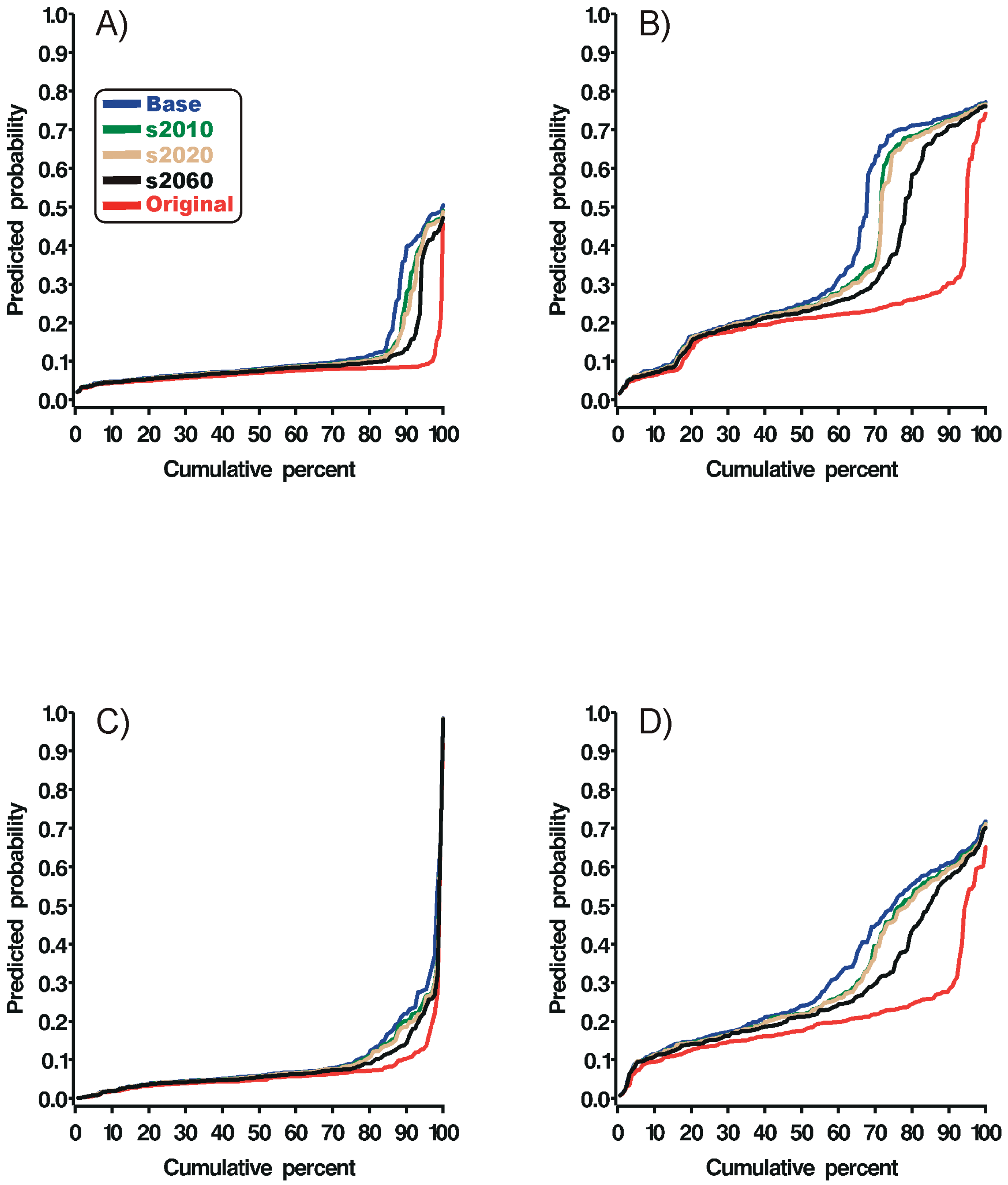

Figure 7.31: Predicted probability of common goldeneye breeding pair occurrence relative to the cumulative percent of modelled lakes in secondary watersheds A) 2D (Sudbury; n=174 lakes) and B) 2B (Algoma; n=185) in ON. Similar plots for lakes in C) 2D (n=132) and D) 2B (n=155) are shown for common goldeneye young. Lake size was restricted to the range included in generating the model estimates (i.e. 2 to 110 ha). Probabilities were based on the predicted original pH (red) and the predicted pH under four emission scenarios: base (blue), s2010 (green), s2020 (tan) and s2060 (black). Lines to the left indicate improved habitat suitability relative to lines near the right side of the plot.

Table 7.7. Provincial summaries of the estimated percent of modelled lake populations in which small fish (e.g., minnows, perch and sucker) and piscivorous waterbird breeding pairs would likely occur (i.e. probability of occurrence >0.6) under the deposition scenarios described in the text. Sample sizes vary between small fish and piscivorous waterbirds because a somewhat smaller range of modelled lake sizes was included for small fish (i.e. 2 to 110 ha) relative to piscivorous waterbirds (i.e. 2 to 500 ha). "Original" indicates the estimated percent of suitable lakes assuming predicted pre-acidification pH values.

	Deposition	Province			
Taxa	Scenario	NS	NB	QC	ON
	n lakes	*45*	*86*	*79*	*672*
	Original	58	99	100	98
Small fish	Base	56	85	95	76
	2010	56	88	96	82
	2020	56	90	96	83
	2060	56	90	99	88
	n lakes	*52*	*93*	*81*	*737*
Piscivorous waterbird pairs	Original	77	52	84	43
	Base	77	47	83	40
	2010	77	49	83	40
	2020	77	51	83	41
	2060	77	51	83	41

Table 7.8. Estimated percent of modelled lake populations in which Common Goldeneye pairs and young would likely occur (i.e. probability of occurrence >0.6) under the deposition scenarios described in the text. The percent of lakes is shown for the secondary watershed 02B (Algoma region) in ON. This watershed is located within the Common Goldeneye breeding range and there was a sufficient number of modelled lakes available. Results for the Sudbury area (watershed 02D) are not shown because almost all probabilities were <0.6. The range of lake sizes included in modelling was 2 to 110 ha. "Original" indicates the estimated percent of suitable lakes assuming predicted pre-acidification pH values.

Life History Stage	Deposition Scenario	Percent of Modelled Lakes[1]
	Original	5
	Base	31
Pairs	2010	28
	2020	26
	2060	18
	Original	2
	Base	13
Young	2010	10
	2020	10
	2060	7

[1] The number of modelled lakes in the watershed was 185 and 155 for pairs and young, respectively.

Predicted changes in the percent of lakes which would likely have (i.e., probability of occurrence ≥ 0.6; hereafter, "suitable") small fish, piscivorous waterbird pairs, or Common Goldeneye pairs or young generally reflected the patterns observed in the cumulative frequency plots (Tables 7.7 and 7.8). Emission reductions under the 2060 scenario were generally predicted to increase the percent of lakes suitable for small fish relative to the percent of lakes suitable under the base scenario (Table 7.7). Relatively small increases in the percent of lakes suitable for piscivorous waterbird pairs were predicted for NB and ON. Emission reductions under the 2060 scenario were associated with a decrease in the percent of lakes suitable for Common Goldeneye in ON watershed 2B (Algoma) relative to the base scenario conditions (Table 7.8).

The magnitude of changes in habitat suitability were related to the estimate of pH effect size (i.e., slope on pH in Table 7.6), prevalence and magnitude of predicted pH change, and the degree to which predicted pH change is correlated with other terms in the Table 7.6 models. For the lakes modelled here, the summaries show improved habitat suitability for small fish with the selected emission reduction scenarios and small improvements for breeding pairs of piscivorous waterbirds. The reduced habitat suitability for Common Goldeneye pairs and young is best explained by their dependence on invertebrate food items more commonly available in moderately acidic, fishless lakes. Predicted habitat suitability patterns were consistent with the scale and direction of the predicted pH changes by province and watershed (see Section 7.6.3.1) but were modified by the effects in each biological model (Table 7.6) and influenced by patterns in the characteristics of lakes predicted to show acidity changes. For the ON lakes modelled, the magnitude of predicted pH changes was negatively related to lake surface area (slope= -0.0002, $p<0.0001$, dfe=842); the greater divergence in habitat suitability for Common Goldeneye, a species associated with small lakes, than for piscivores, which generally use larger lakes, is therefore not surprising.

As emphasised in the introduction to this section, the objective of these analyses was to compare the relative impact of changes in steady-state pH on habitat suitability rather than attempt to capture the full chemical and biological complexity of ecosystem recovery. The small changes predicted for piscivorous waterbird pairs do not necessarily indicate they are insensitive to the recovery of acidified lakes. Waterbird breeding productivity (e.g., number of young fledged) is strongly associated with the trophic and habitat quality of the natal lake or wetland (e.g., Sedinger, 1992), a relationship particularly true for piscivorous waterbirds which require a large biomass of fish to sustain growing chicks (e.g., Barr, 1996). Common Loon breeding productivity has been shown to be strongly associated with lake acidity (e.g., Doka et al., 2003; see also Section 6.4.4.1.2). Although loon breeding success estimates are available from a large scale monitoring program (see http://www.bsc-eoc.org/cllsmain.html), recent habitat data for monitored lakes was limited at the time of this assessment, precluding the development of loon breeding productivity and emission scenario models. Important next steps should include the integration of breeding productivity measures for loons and other waterbird species in addition to Common Goldeneye.

Future chemical and biological changes are likely to be broadly influenced by other factors, a conclusion supported by information presented elsewhere in this Assessment. Acidity changes do not occur in isolation from other chemical, hydrological and physical changes (e.g., Sections 6.3.2.5 and 7.6.3.1) and many of these ecosystem characteristics play a role in shaping biological responses (e.g., see Sections 6.4 and 7.4). Important cautions in the interpretation of the habitat suitability patterns presented here include the reduced predictive power associated with small sample sizes (e.g., < 100 lakes) and, as mentioned above, the potential for geographic variation in habitat associations. As pointed out elsewhere (e.g., Section 6.4.4.2), habitat conditions which promote a species' presence do not necessarily imply benefits to their breeding success, survival or other population dynamics. Certain further developments of these predictive models, supported by targeted research into critical population and community regulators (e.g., colonisation, predation, competition, adult and young survival), are needed to help develop recovery predictions which provide a more complete picture of potential future biological communities. For example, refinements such as estimates of food quality and fledging success (e.g., for Goldeneye and loons) would help to associate the predicted presence of breeding pairs on particular lakes or wetlands with their eventual breeding success. Improved predictions about the effects of emission reductions on the status and composition of biological communities will require models, supported by observational data, that capture the important but complex relationships that species and populations have with the chemical, physical and biological characteristics of their habitats.

7.6.4 Time-dependent chemical predictions

Several dynamic process-oriented models have been developed to investigate water quality responses to acid deposition. Among them, MAGIC (Cosby et al., 1985, 2001) has been recently applied to several sites in southeastern Canada. MAGIC is a lumped-parameter, easily-modified model of intermediate complexity, developed to predict the long-term effects of acid deposition on soil and surface water chemistry. Once calibrated with current water chemistry, it hindcasts and forecasts monthly and annual major ion concentrations using time-series inputs of deposition, hydrology, climate and various catchment abiotic (e.g., weathering) and biotic (e.g., forest uptake) processes. Using historic and current S emission inventories, the SO_4^{2-} deposition sequence that drives the model generally increases from background levels in 1850 to maximum values in the 1970s, followed by declines so that the 2010 value is ~50% of the 2000 value and constant thereafter.

Aherne et al. (2003) modelled a set of 25 lakes in the Muskoka-Haliburton region of south-central ON. MAGIC predicted that reductions in acid deposition have had and will have a significant impact on water chemistry; by 2050, concentrations recovered to levels predicted for the early 1900s. Nevertheless, it also predicted that soils will continue to acidify through loss of Ca^{2+} from the exchangeable base cation pool. It is this depletion of the pool that is ultimately buffering runoff waters against the effects of acid deposition. As the pool becomes depleted, lake base cation levels are expected to decline below current levels.

One of the lakes in the above set (Plastic Lake) has been modelled by a new version of MAGIC, modified to include a "wetland" component that contains redox processes driven by climatic events (Aherne et al., 2004). The modified version was successful in simulating the delayed recovery response associated with drought-induced mobilization of S stored in wetlands (see Section 7.4.1.1 above).

Larssen et al. (2003) applied the MAGIC model to three lakes from Killarney Provincial Park in ON. The lakes were chosen to represent cases of fast, intermediate and slow recovery from acidification. The model reasonably simulated observed data and the differing response times of the three lakes. Despite the recovery that has already occurred in these Killarney lakes (see Section 7.4.2.1 above), MAGIC predicts that there is still a large potential for further improvement in the lakes' chemistry (higher ANC and pH). For the lake having the slowest response time, several decades will be needed to obtain stable water quality.

Clair et al. (2003) used MAGIC to determine whether a 50% reduction from 2000 deposition levels would be effective in promoting the recovery of lakes in NB, NS and NL. The model confirmed that at present, lake chemistry is significantly affected by acid deposition, but nevertheless, it is considerably better than it was in the 1970s when deposition levels were greatest. A 50% reduction in deposition was not sufficient to return the lakes to original conditions. Moreover, the model runs predicted that base cation concentrations will decline below historic levels (cf. the soil pool depletion as noted above) which would be of particular concern since the lakes of this region are already among the most dilute in Canada.

Clair et al. (2004) also modelled the chemistry of 35 Nova Scotian Atlantic salmon rivers to estimate pre-industrial water chemistry and predict the effect of three scenarios of deposition reduction (0%, 10% and 20% per decade decline in SO_4^{2-} deposition from the 2000 level). They showed that the rivers' water chemistry remained relatively unchanged until the 1950s and had the lowest pHs during the 1970s. The decline in pH was accompanied by an initial increase in base cations as ion exchange processes in soils released them into the water, followed by declines as the soil pools are depleted. Scenario predictions suggest that the faster deposition declines, the faster the rivers will recover. Even though recovery in terms of water acidity is predicted to occur in a few decades, base cations are expected to remain low and not recover to pre-industrial levels within 100 years. Extremely low base cation levels in these rivers may be just as problematic for fish survival as high acidity (see 7.5.2). Mitigation in the form of base cation addition to either the rivers or their catchments might be considered.

7.7 SUMMARY

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D.K. McNicol and M.A. Turner

The notion of ecosystem recovery involves both process and outcome. A two-decade decline in acidifying emissions and acid deposition can encourage a focus on the outcomes of recovery (e.g., restored lakes). In reality, however, only the process of recovery can be observed within this time frame.

- The final outcome of recovery is largely unknown. Due to a rapidly changing continental environment and permanently altered ecological context, recovered aquatic ecosystems will likely differ from their pre-acidification state.
- Acidification has been a decades-long process and recovery will also be a long-term process. Biological recovery will necessarily lag behind chemical recovery.
- Resilience, the capacity to rebound from damage, will vary among ecosystem components (chemical, physical and biological). Recovery will therefore be inherently complex. Recovery rates and endpoints are likely to differ among ecosystems (e.g., lakes with differing acidification histories) and among ecosystem components (e.g., biotic groups within lakes).

Observations of aquatic recovery come from three sources: (1) General chemical and biological monitoring conducted to detect regional changes, (2) more detailed monitoring conducted near specific emission sources (e.g., Sudbury) where past reductions have fostered more pronounced, localized recovery, and (3) controlled, whole-ecosystem experiments (e.g., ELA). The Sudbury area monitoring and ELA experimental acidification research provide important and complementary perspectives on the recovery of acidified lakes. Sudbury monitoring provides information from a region affected by very large and long-term local acid inputs to both aquatic and terrestrial habitats. The relative simplicity of the ELA studies facilitates a strong focus on within-lake acidification and recovery processes.

- Lake chemistry trends show that the primary acidifying agent (SO_4^{2-}) is generally declining in response to declining SO_2 emissions. Corresponding declines in acidity (quantified as increasing pH or Alk) are much less widespread, however. There are several reasons for the muted acidity response, most notably declining base cations, but also drought-induced release of stored S, increasing organic anions, damaged in-lake Alk-generating mechanisms, and others. The observed responses generally agree with currently accepted conceptual models of the acidification/recovery process.
- Ecosystems and their biota display resilience when acidic inputs are reduced. However, the nature and degree of recovery are affected by climatic, physicochemical and biological factors. Although encouraging signs of biological recovery were often observed, complete recovery to a regionally representative biological community was rarely observed.
- Recent findings confirmed that: biological recovery lagged behind chemical recovery, pH recovery rarely resulted in complete restoration of biotic communities within the timeframe of the studies, and recovery patterns often involved surprises and diverged from expectations.
- Phytoplankton showed encouraging signs of recovery with shifts in dominance from acid-tolerant to acid-sensitive algal groups in both chemically recovering Sudbury lakes and in ELA's Lake 302S. However, phytoplankton recovery in Lake 302S remained incomplete even after full pH recovery, due largely to persistently suppressed taxonomic richness.
- Although benthic algae assemblages also responded quickly, changes in taxonomic composition and function persisted after reductions in acidity. Benthic algae responded more quickly in experimentally acidified Lake 302S than in Killarney (Sudbury area) lakes, supporting the conclusion that large-scale chronic acidification will tend to increase recovery times relative to those seen in the experimental acidification studies.
- Zooplankton species richness tended to increase following declines in acidity, with generally predictable patterns of species dominance during recovery. Zooplankton in several Sudbury area lakes, including some with severe damage, became more similar to non-acidic reference lakes with chemical improvements. Although rapid recovery was observed, both Sudbury and ELA results showed that patterns of recovery varied among the major zooplankton groups.
- In contrast, there was less evidence of recovery of benthic invertebrates, although colonisation and increased abundance of certain acid-sensitive mayflies were observed in response to improved lake acidity.
- Fish recovery in ELA's experimentally acidified lakes was generally successful but some species exhibited delayed or incomplete recovery to pre-acidification levels. Fish recovery was also seen to have trophic consequences.
- Observations summarised here provide encouraging signs of biological recovery but also suggest that acidification may have permanently altered many lakes and their biological communities.

Recent evidence indicates that remnant sport fish populations in acidified ON lakes can recover after the water quality improves but prospects for recovery are less promising for Altantic salmon and Atlantic whitefish in NS.

- Lake trout and smallmouth bass recover well in lakes with few strong competitors or predators, although the ELA Lake 223 study showed that natural recovery can be slow. Captive breeding, liming of their acidified Sudbury area lakes, and reintroductions have been critical to saving the endangered aurora trout. Recovery can also be enhanced with human assistance (e.g., stocking, angling restrictions) and a good understanding of the trophic structure of recovering lakes.
- Atlantic salmon rivers in the Southern Upland region of NS are projected to remain chemically damaged for many decades. Calcium, a cation of physiological importance for fish, will likely remain below pre-

industrial levels for at least a century. Reduced river acidity, increased production of young fish, and improved marine survival are essential for restoring salmon populations. Options for protecting remaining Southern Upland Atlantic salmon stocks include: 1) neutralisation of acidified rivers, 2) stocking, 3) gene banking, and 4) fisheries restrictions. The degree to which these approaches may be effective for protecting and enhancing Southern Upland Atlantic salmon stocks remains a topic of open discussion among scientists and other stakeholders.

- Acidification is one of several stressors implicated in the decline of Atlantic whitefish, an endangered species endemic to Canada and occurring only in NS. Full lifecycle closure is now certain only for fish in three semi-natural lakes. The effects of acidity on population drivers are the subject of current research and the recovery of acidified habitat is an important consideration in defining recovery objectives.

The recent monitoring and research in ELA and the Sudbury area provides additional insight into the multiple influences on chemical and biological recovery.

- Results from ELA highlight that there are multiple forces affecting recovery. For example, pH and DOC interactions can lead to several dynamics (e.g., increased UV intensity, deep-water heating), which along with summer re-acidification events and the possibility of biological toxins, all have the potential to impair biological recovery.
- A changing climate further complicates recovery from acidification. Sudbury area studies showed that re-acidification events (e.g., due to drought) in chemically recovering lakes can have strong and lasting impacts on biota. The ELA studies showed that climate change will likely alter terrestrial inputs of nutrients and dissolved organic material to recovering lakes. In lakes with shallow hypolimnia, reduced inputs of DOC to lakes will enhance the transmissivity of radiant energy to the deeper waters of lakes, resulting in compression of habitat for stenotherms (i.e., species surviving only within a very narrow temperature range).
- Although metal concentrations have declined in many acidified lakes, evidence from the Sudbury area suggests that biotic recovery in some lakes will continue to be impaired by residual toxic metal concentrations.
- Predatory fish are strong influences on the recovery of planktonic and benthic invertebrates and illustrate the importance of trophic relationships to biological recovery. Accounting for the sensitivity of colonising species to predation and competition will improve our ability to predict biological responses to chemical improvements.
- Recovery of benthic invertebrates was enhanced by nearby sources of colonists and by good dispersal abilities. These two factors will be important determinants of the rate and taxonomic composition of biological recovery patterns, particularly in regions subjected to large-scale chronic acidification.

The Integrated Assessment Model (IAM), a framework of sub-models and cause-effect relationships, was used to predict chemical and biological responses for various scenarios of SO_2 emission reduction for a "modelling" set of 1369 lakes located throughout southeastern Canada but predominantly (1041) occurring in Ontario (described in Chapter 6).

- A zero-anthropogenic emission/deposition scenario and four SO_2 emission reduction scenarios, representing 31%, 54%, 60% and 70% cuts relative to 1980, were used as input to the IAM. The scenarios corresponded to a recent period when both deposition (1994-1997) and aquatic (1997) measurements are available ("base"), realistic estimates of what emission levels will be in 2010 and 2020 given both existing and planned emission control measures in Canada and the United States ("s2010" and "s2020", respectively), and a hypothetical scenario that assumes an additional 25% emission reduction beyond s2020 (arbitrarily termed "s2060").

- In the Atlantic provinces, the IAM predicts that there will be only small changes in the steady-state lake ANC or pH distribution patterns across the four emission reduction scenarios, and all of the scenario distributions are shifted to lower values relative to their predicted original condition.

- In QC, only the hypothetical (s2060) scenario showed an obvious recovery (ANC and pH distributions shifted to higher values), and this did not come close to the predicted original distribution.
- The deposition reductions associated with the four scenarios are expected to promote recovery in ON lakes, albeit within a rather narrow range. Predicted improvements vary spatially. Modelling lakes in a Muskoka subset show by far the largest pH increase, followed by an Algoma subset, with a Sudbury subset showing the least response.
- Overall, large numbers of eastern lakes will remain chemically damaged after currently planned emission reductions are implemented, and even a further 25% reduction (cf. the hypothetical s2060 scenario) will not reduce damage below the 5% level that is commonly used when determining aquatic critical loads.
- Modelled lakes showed generally improved habitat suitability for small fish with the selected emission reduction scenarios and small improvements for breeding pairs of piscivorous waterbirds. Habitat suitability predictions for fish-eating waterbirds showed more divergence among scenarios when summarised for three secondary watersheds in ON.
- Emission reductions were associated with reduced habitat suitability for Common Goldeneye pairs and young, a pattern best explained by their dependence on invertebrate foods that can be more commonly available in moderately acidic, fishless lakes.

The information presented in this chapter indicates that programs to study and monitor the physicochemical and biological properties of acidified ecosystems must be continued and reinvigorated. Without the resulting information, it will be impossible to properly assess and predict the regional status of aquatic ecosystem recovery in Canada.

- Predictions based entirely on reversal of pH declines are insufficient. Predictive models, and the observed data supporting them, should continue to be refined and broadened to take better account of the multiple forces affecting chemical and biological recovery.
- It is essential to understand which forces (e.g., climate warming, biological invasions, eutrophication, and contaminants) are likely to interact with recovery, and the extent and nature of these interactions. Along with broad scale monitoring, parallel case studies that vary geographically, in the degree and duration of acidification, and in the complexity of additional stressors will improve our understanding and prediction of acidification recovery.
- Much of the emphasis of biological acidification recovery work thus far has been on understanding and predicting the occurrence and relative abundance of species. Much less is known about how the composition and abundance of species will affect the basic ecological functions (e.g., nutrient transfer and storage) of recovering lakes and wetlands.
- In some cases it is clear that keystone taxa (e.g., fish) will be extirpated for considerable periods without management intervention. Research is needed to help make reintroductions of previously extirpated species more effective and to anticipate the consequences of the invasion or introduction of new species.
- Further developments of predictive biological models, supported by targeted research into critical population and community regulators (e.g., colonisation rates, predation, competition, adult and young survival), are needed to help develop recovery predictions which provide a more complete picture of potential future biological communities.
- Declines in Ca^{2+} concentrations may have important effects on biological recovery. Reduced Ca^{2+} concentrations could affect the distributions of organisms with relatively high Ca^{2+} requirements, and could increase the sensitivity of some biota to other stressors including acid, metals and UV light.

The recent information summarised here shows that a large proportion of previously acidified lakes in southeastern Canada will remain chemically and biologically damaged following the achievement of current emission reduction targets. As a result, lower S-deposition targets will likely be needed to accelerate the reversal of chronic acidic pressure. Understanding and predicting ecosystem change in a multiple-stressor environment requires the long-term maintenance of a hierarchical program that integrates information from a broad-scale, national monitoring framework coupled with intensive investigations of ecosystem stressors and recovery processes (see also Chapter 6).

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CHAPTER 8

Critical Loads: Are They Being Exceeded?

D.S. Jeffries and R. Ouimet

8.1 KEY MESSAGES

- Critical loads (CLs) of acidity (sulphur + nitrogen) were determined for sample lakes and upland forest soils using steady-state models. Critical load exceedances (difference between level of acidifying deposition and critical load) were determined using two different estimates of current levels of acidifying deposition: “Nitrogen-leaching” (current situation) and “Steady-state” (potential future situation).
- The highest current Nitrogen-leaching exceedances for sample lakes were identified for 11% of the mapped area in eastern Canada, which included southern Nova Scotia and New Brunswick and central and south-central Ontario. The highest Nitrogen-leaching exceedances for forest soils in the eastern provinces included areas of Newfoundland and Labrador, Nova Scotia, Quebec and Ontario.
- Very high Steady-state exceedances of critical loads for sample lakes occurred in all eastern provinces except the Labrador region of Newfoundland and Labrador. Fifty-two percent of the mapped area in southeastern Canada (932,300 km^2) exceeded Steady-state critical loads for upland forest soils. The Steady-state exceedances clearly indicate that if present-day levels of nitrogen deposition eventually lead to the development of nitrogen saturation, the effect on CL exceedances will be profound.
- Combined aquatic-terrestrial CL and exceedance maps were produced for the first time in North America. In eastern Canada, CLs are being exceeded in 21-75% of the mapped area according to the Nitrogen-leaching and Steady-state methodologies, respectively.
- Regardless of the methodology used to calculate critical loads, further reductions in acid deposition are needed to protect Canada’s ecosystems.

8.2 INTRODUCTION

D.S. Jeffries and R. Ouimet

Within the context of the North American acid rain issue, critical loads (CLs) were first discussed (with significant controversy) by the U.S. and Canada in the Memorandum of Intent on Transboundary Air Pollution (U.S.-Canada, 1983) – the earliest bilateral acid rain assessment and a document originally expected to form the basis for an agreement between the two countries to mitigate the problem. The values suggested at that time were based largely on empirical associations between observed aquatic effects and measured deposition, and correctly termed “target loads”. Water and soil chemistry modelling were soon being used to refine the empirical values (see Section 8.2.1).

During the mid-to-late 1980s, European countries that signed the United Nations Economic Commission for Europe (UN ECE) Convention on Long-Range Transboundary Air Pollution (Canada had signed in 1979) embarked on an ambitious program to develop a critical load basis to guide continent-wide emission reductions. Several aquatic and soil acidification models were developed and refined for this purpose, mapping protocols established, and manuals produced (e.g., see Nilsson and Grennfelt, 1988; Grennfelt and Thörnelöf , 1992; Posch et al., 1995, 2003).

Using an “expert” system of steady-state water chemistry models (Lam et al., 1989), regional aquatic CLs and exceedances were determined for southeastern Canada in the 1990 Assessment (RMCC, 1990a; Jeffries and Lam, 1993). The 1997 Assessment employed the same system (now refined and in the structure of an Integrated Assessment Model [IAM]; Lam et al., 1992, 1994, 1998) to refine the values for several eastern lake clusters and to extend the analysis to northern Alberta lakes (Jeffries, 1997; Jeffries et al., 1999). In both cases, sulphur-only CLs were reported. More recently, some aquatic CL evaluations have employed steady-state models that were originally developed and used in Europe (Henriksen and Posch, 2001). The Steady-State Water Chemistry Model (SSWC) has been applied to regional data sets in Ontario (ON) (Henriksen et al., 2002; Watmough and Dillon, 2002), to data sets from the other eastern provinces and the New England states of the U.S.A. (Dupont et al., in press), and to lakes in the oil sands region of northern Alberta (WRS, 2004). A more complex model, the First-Order Acidity Balance Model (FAB), has been applied in ON as well (Hindar et al., 2000, 2001; Aherne et al., 2004). The SSWC and FAB models consider both sulphur and nitrogen when determining CLs and/or exceedances (see discussion in Section 8.4 below). Note that throughout the remainder of this chapter, the term "S-CL" will be used for sulphur-only CLs, whereas the term "CL" will imply the critical load for acidity which considers both sulphur (S) and nitrogen (N) components.

For the most part, CLs of acidity and exceedances for upland forests in eastern Canada have been determined using the UN ECE approach (Posch et al., 1995), usually at specific locations (Arp et al., 1996; Oja and Arp, 1998; Moayeri, 2001; Ouimet et al., 2001; Watmough and Dillon, 2003). The 1997 Assessment (Hall et al., 1997) principally used the results from Arp et al. (1996). The New England Governors and Eastern Canadian Premiers Environment Task Group (NEG/ECP, 2001) extended these analyses into the New England states of the U.S.A. The Forest Mapping Group of the NEG/ECP Acid Rain Action Plan is in the process of refining the critical load for soil acidification for the provinces east of and including Quebec (QC) plus several eastern U.S. states (NEG/ECP, 2003). Forest CLs account for both sulphate (SO_4^{2-}) and nitrate (NO_3^-) deposition and are intended to prevent harmful changes to soil chemistry.

This Assessment chapter will present aquatic CLs and exceedances for all provinces using data sets that are described in Chapter 6. Comparisons with other recent CL analyses (as noted above) will be made when appropriate. Critical loads of acidity for upland forests and current exceedances will be presented for ON, QC, New Brunswick (NB), Nova Scotia (NS), Prince Edward Island (PEI) and Newfoundland (NL) (protocols and working groups to estimate terrestrial CLs for other Canadian provinces are currently in progress). This new terrestrial analysis combines and expands on the information presented in the recent papers cited above. Finally, combined (aquatic-terrestrial) CL and exceedance maps will be presented.

8.2.1 History

A legacy of acid rain assessment activities in Canada has been the specification of critical or target deposition values for acidifying pollutants (Jeffries et al., 2003). U.S.-Canada (1983) reviewed aquatic chemical and biological responses related to wet SO_4^{2-} deposition and concluded that regions receiving ~17 kg/ha/yr did not exhibit detrimental chemical or biological effects. This S-CL inference was refined further through the application of water chemistry models (e.g., Thompson, 1982) resulting in the conclusion that a loading of 15-20 kg/ha/yr wet SO_4^{2-} would maintain annual average pH >5.3 in moderately sensitive waters (base cation concentrations ~200 μeq/L). U.S.-Canada (1983) qualified the CL range by noting that it would in fact be spatially variable, that very sensitive basins would not be protected and that future re-evaluation was to be expected as more information was obtained. Based on this information, in 1983, the Canadian Council of Resource and Environment Ministers recognized a 20 kg/ha/yr wet SO_4^{2-} target load for southeastern Canada. Reductions in acid deposition to this level in sensitive regions of southern ON and QC became the goal for a Canadian SO_2 emission control program. Note that while both S and N pollutants were recognized as acidifying agents, the overwhelming predominance of the former in acidifying Canadian waters led to specification of a S-only target load.

As further lake data were obtained and water chemistry models evolved and improved (e.g., Marmorek et al., 1990), CL estimates declined. RMCC (1986) concluded that S-CLs for sensitive aquatic ecosystems would be <12 kg/ha/yr sea-salt corrected wet SO_4^{2-}. The 1990 Assessment (RMCC, 1990a; see also Jeffries and Lam, 1993) performed a much more comprehensive analysis, specifying the level of SO_4^{2-} deposition that would maintain pH 6 in 95% of lakes in 21 regions of southeastern Canada. Values ranged from <8 to >20 kg/ha/yr sea-salt wet SO_4^{2-}, the lower value reflecting modelling limitations of that time and the fact that background SO_4^{2-} deposition was deemed to be ~4 kg/ha/yr, and the upper limit reflecting the target load. RMCC (1990b) mapped the results in 4 kg/ha/yr classes. Results from the 1990 Assessment plus review and assessment work in the U.S.A. (e.g., Irving, 1991) provided the scientific underpinning for the Canada-U.S. Air Quality Agreement (AQA, see **http://www.ijc.org/rel/agree/air.html**).

The 1997 Assessment further refined some aquatic S-CL values (Jeffries, 1997), discussed exceedances (Jeffries et al., 1999; Environment Canada, 1997), and presented some comparable CL values for forest soils (Hall et al., 1997). Aquatic values ranged from <6 to >18 kg/ha/yr wet SO_4^{2-} while terrestrial values ranged from ~90 to ~2900 eq/ha/yr total S + N deposition (see below). Findings presented in the 1997 Assessment were used in developing a new domestic SO_2 emission control policy in Canada – the "Canada-Wide Acid Rain Strategy for Post-2000" (see **http://www.ec.gc.ca/acidrain/strat/strat_e.htm**).

8.2.2 Conclusions of the 1997 Assessment

For determining aquatic S-CLs, the 1997 Assessment used pH 6.0 in 95% of a region's lakes to define a damage threshold. Less protective thresholds (lower pH and lower percentages) were also considered to determine less restrictive target loads. The S-CLs were determined for 4 lake clusters in southeastern Canada and 1 cluster in northern Alberta using the IAM to estimate steady-state lake pH distributions. S-CLs ranged from <6 kg wet SO_4^{2-}/ha/yr for the Kejimkujik, NS and Fort McMurray, Alberta (AB) clusters to 13.2 kg/ha/yr for the Sudbury, ON cluster. S-CLs for the Montmorency, QC and Algoma, ON clusters were 6.9 and 8.0 kg/ha/yr respectively. These S-CL estimates were considered overestimates for a number of reasons. Wet SO_4^{2-} deposition in the early 1990s exceeded the CLs at all eastern Canadian clusters by ~7 to 12 kg/ha/yr and was expected to continue to exceed them by ~6 to 10 kg/ha/yr after all emission controls required by the AQA are finally implemented. The Aquatic Effects volume (Jeffries, 1997) concluded that a further reduction in SO_4^{2-} deposition would be needed to reduce the magnitude of the exceedances and/or provide protection for a higher proportion of aquatic ecosystems. It was estimated that ~95,000 lakes in central ON, southern QC and much of the Atlantic provinces would still receive SO_4^{2-} deposition in excess of their S-CLs, even after all emission reductions required under the Canada-U.S. AQA are fully implemented. It was further estimated that this degree of exceedance would result in a net loss of ~162,000 fish populations (relative to estimated original population levels) in the affected lakes.

The Atmospheric Science volume (Environment Canada, 1997) estimated current or predicted future S-CL exceedances across southeastern Canada by comparing measured or modelled deposition values with the aquatic S-CL map produced for the 1990 Assessment. Both the AES-LRT model and Eulerian ADOM model were used. The S-CL map, which was originally presented in the form of aggregated drainage basins, was converted to a grid format in order to facilitate comparison with gridded model output. Exceedance of the geographically uniform 20 kg/ha/yr wet SO_4^{2-} target load was also evaluated. Environment Canada (1997) concluded that full implementation of AQA SO_2 emission reductions will succeed in lowering wet SO_4^{2-} deposition below the 20 kg/ha/yr target load at almost all locations in southeastern Canada. Furthermore, it estimated that those areas with aquatic S-CLs >14 kg/ha/yr will also exhibit zero (or negative) exceedance. However, this still leaves a large area (~800,000 km^2) where the aquatic S-CLs will have a positive exceedance – sometimes by as much as 10 kg/ha/yr.

The forestry effects volume (Hall et al., 1997) evaluated CLs of acidity (S + N) for soils located at Acid Rain National Early Warning System (ARNEWS) plots. Forest soils that have a high sensitivity to acidification were identified in northern ON, QC, Saskatchewan (SK) and Manitoba (MB) (defined by those ARNEWS sites having a CL <500 eq/ha/yr, see the following section for unit conversions). Plots with greatest exceedance were found in central ON and southern QC. Such plots were prone to forest decline, e.g., a 500 eq/ha/yr exceedance was associated with a 10% annual productivity loss, and a 1,000 eq/ha/yr exceedance contributed to an 8±2% increase in mortality over an 11-year period. Because S and N dry deposition was not included when exceedance was calculated, the forest soil exceedance values reported in 1997 were considered underestimates.

8.3 DEFINITIONS, CHEMICAL THRESHOLDS AND METHODS

D.S. Jeffries, R. Ouimet, and I. Wong

8.3.1 Definitions

The CL definition used here is that employed by the UN ECE, i.e. "a quantitative estimate of an exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge" (Nilsson and Grennfelt, 1988). An important implication of the definition is that as "present knowledge" increases, CL estimates may require revision. This expectation was certainly borne out by the changes in the minimum aquatic S-CL values reported by assessments conducted in the 1980s compared to those conducted in the 1990s. For several reasons outlined below, further changes will be evident in this assessment also.

The CL exceedance is total acidifying deposition minus the CL. Since S has little biological reactivity and SO_4^{2-} acts almost entirely as a mobile anion, it is generally assumed that all S deposition is acidifying. On the other hand, N has a large biological reactivity and large quantities are stored in various catchment compartments. The significant retention of N deposition in lake catchments means that only a part of the deposition is acidifying, namely that part currently exported as NO_3^-. Hence one method of specifying total acidifying deposition is to add an estimate of current NO_3^- export to total (wet + dry) S deposition (Henriksen and Posch, 2001). Throughout the remainder of this chapter, exceedances calculated in this way will be termed "N-leaching". Another method of specifying total acidifying deposition is to assume that ecosystems will eventually reach a steady-state with N deposition, meaning that they are N saturated and all N deposition is acidifying. The exceedance calculated using this assumption simply uses the sum of all wet and dry S and N deposition as the total acidifying deposition, and henceforth in this chapter, it will be termed the "Steady-state" exceedance. Exceedances can be positive or negative with positive values indicating sensitive ecosystems, elevated acidifying deposition, or both. Negative values indicate that the ecosystems can buffer more acidity than the amount they receive.

In earlier assessments, aquatic CLs were expressed in terms of SO_4^{2-} deposition only. The nitrogen-based component of acidic deposition was implicitly assumed (with some observational justification) to be of minor significance. Moreover, these S-CLs were expressed as *wet* SO_4^{2-} deposition. This approach was used because wet deposition was the most accurately measured regional response to SO_2 emissions (dry deposition estimates were considered highly uncertain), and the models used to simulate the effect of hypothetical emission reductions also produced output in terms of wet deposition. Hence design of national or regional emission reduction programs (the ultimate reason for specifying CLs) was made simpler by specifying their target in wet deposition units. This did not change the fact that aquatic ecosystems respond to total acidic deposition. To account for this, a dry deposition component (assumed to be 15% of total) was added to the wet component for the model runs that determined S-CLs for the 1990 and 1997 Assessments. The dry component was subsequently removed to express the results in the desired wet deposition units.

The current situation has changed. First, the uncertainties associated with estimating dry deposition have become much more manageable (see Chapter 3) so that it is now more reasonable to report aquatic CLs in terms of total (wet + dry) deposition. Second, this assessment will combine for the first time both aquatic and terrestrial CL estimates in a single CL map. Since terrestrial CLs have always been reported as total deposition, common units will be required. Third, the nitrogen component cannot be dismissed for terrestrial ecosystems. Hence CLs for both terrestrial and aquatic ecosystems must be expressed in terms of the sum of both (i.e., sulphur and nitrogen) acidifying components. Since S and N have different atomic weights, it is impossible to report combined CL values on a mass basis (e.g., kg/ha/yr), but instead, they must be reported on a charge equivalency basis. Both eq/ha/yr and meq/m^2/yr are extensively used in the scientific literature, and we will use the former in this chapter. In order to alleviate some of the confusion that will no doubt arise from the shift in CL units from past assessments to this one, Table 8.1 provides unit conversion factors for various S and N species. For example, 20 kg SO_4^{2-}/ha/yr is the same as 416 eq/ha/yr or 41.6 meq/m^2/yr.

Table 8.1. Relationships among the units for atmospheric deposition used in this Assessment to quantify CLs and exceedances. Multiply or divide by the appropriate factor to convert from one unit to another.

Chemical species	kg/ha/yr	eq/ha/yr	meq/m^2/yr
SO_4^{2-}	1.00	20.8	2.08
S	1.00	62.4	6.24
NO_3^-	1.00	16.1	1.61
NH_4^+	1.00	55.4	5.54
N	1.00	71.4	7.14

8.3.2 Chemical thresholds

Determination of CLs requires identification of "significant harmful effects on specified sensitive elements of the environment". Biotic health and sustainability would be the appropriate measure for both lake and forest ecosystems were they not concepts that are difficult to define precisely, let alone quantify. Therefore, chemical indicators have been adopted as surrogate measures of biotic health and threshold values established which define the onset of harmful effects.

Based principally on largely subjective evaluations of relationships between water chemistry and biological presence-absence, past assessments (e.g., RMCC, 1990a; Baker et al., 1990; Jeffries, 1997; Doka et al., 2003) concluded that maintaining lake pH ≥6 would ensure a reasonable level of protection across a wide range of aquatic biota. Of course, pH sensitivity does vary among species. Consideration of sports fish yields lowers threshold pHs, typically in the 5.0 to 5.5 range, whereas consideration of species lower in the food chain (e.g., plankton, crayfish, minnow species) yields values in the 5.5 to 6.0 range. In addition, other geographic and morphometric factors can influence species presence-absence. For zooplankton communities in ON, Holt et al. (2003) were able to separate the influence of such physical factors and objectively confirm the pH 6 threshold for that biotic group. Finally, it should be recognized that pH values discussed heretofore are "averages", and in at least some cases are not sufficient to prevent the biological damages that can occur during low pH episodes (see Wigington et al., 1996a,b for further discussion of episodic acidification).

An acid neutralizing capacity (ANC) threshold concentration has been extensively used to calculate CLs in Europe and North America. Note that there are many instances in the literature where alkalinity and ANC are used interchangeably. In this Chapter, however, we will maintain the distinction that the former is a directly measured quantity while the latter is a calculated variable (difference between base cations and strong acid anions). One of the advantages of using an ANC threshold is the fact that this variable not only reflects hydrogen ion (H^+) toxicity (as does pH) but also biotic toxicity associated with some other elements, notably ionic aluminum. Lien et al. (1992) found that brown trout populations in Norway were generally intact above 20 μeq/L (corresponding to a pH of ~5.5), prompting several groups to use that value as a threshold for CL computations (e.g., Henriksen et al., 1992; Posch et al., 1997; Hindar et al., 1998). However, as noted above, several other aquatic species are already negatively affected when pH is <6. Hence others have adopted higher ANC threshold concentrations, and in particular, Henriksen et al. (2002) opted for a threshold value (termed "ANC_{limit}") of 40 μeq/L when using the SSWC to assess aquatic CLs in south-central ON. Dupont et al. (in press) also used this ANC_{limit} value for lakes in Canada's Atlantic provinces, QC and the New England states of the U.S.A. Dupont et al. (in press) also noted that the pH-alkalinity relationship developed by Small and Sutton (1986) predicts that a 40 μeq/L alkalinity value corresponds to a pH 6 for QC lakes. WRS (2004) derived an ANC_{limit} of 75 μeq/L for Alberta lakes employing much the same method as that used for Norwegian lakes. This is the highest (most protective) ANC threshold reported in the literature, but WRS (2004) noted that using even the lowest Norwegian value (20 μeq/L) had only a small effect on the number of exceeded lakes for various SO_4^{2-} deposition scenarios.

Specification of a pH or ANC threshold concentration has the implicit problem that certain lakes may not be capable of attaining that value. Extremely dilute lakes may never have had an ANC ≥40 μeq/L, and the presence of even moderate levels of natural organic acids may have rendered their historical pHs <6. While this results in a methodological problem (see below), the fact remains that such dilute lakes must be very sensitive to acidic inputs and have minimum CL values.

There are several chemical criteria recommended as indicators of potential damage to forest ecosystems (Posch et al., 1995). In a CL analysis, the objective is to set a chemical threshold related to the ANC of soil water that will protect the forest ecosystem. Models such as the one described in Section 8.3.3.2 below, which determine CLs for upland forest soils, employ a critical alkalinity leaching rate (termed $ANC_{le(crit)}$). The most widely used approach for estimating $ANC_{le(crit)}$ is based on a calcium or base cation to aluminum ratio $(Bc:Al)_{crit}$ in soil water which reflects the connection between soil chemical status and plant response. The base cations considered in the ratio (Ca^{2+}, Mg^{2+} and K^{+}) are all tree nutrients whereas dissolved ionic Al is toxic. Calcium uptake by tree roots is compromised in soils with a low Bc:Al ratio. Strongly acidic soils generally have high Al (and H^{+}) concentrations, while soils with high base cation concentrations are generally not acidic and have low Al concentrations. Many threshold values for $ANC_{le(crit)}$ have been suggested in the literature, and derivation of the value used in this assessment is provided in Section 8.3.3.2.

8.3.3 Methods for determining critical loads

8.3.3.1 *Aquatic*

Critical loads were calculated for provincial lake data sets that were compiled for the "current status" assessment presented in Chapter 6 (see Section 6.3.1). In the provinces experiencing significant declines in acidic deposition (ON and east), the data were limited to the most recent annual mean after 1997. This time-of-collection restriction was relaxed for western lakes, but nevertheless, many of them also met this criterion. Individual lake records that did not charge balance within ±15% (including organic anion contributions) were screened out of this CL analysis. The locations of the lakes included in the CL analysis are shown in Figure 8.1.

Two water chemistry models were used to estimate aquatic CLs and exceedances – the Expert Model (an updated version of Lam et al., 1992, 1994) and the SSWC model (Henriksen et al., 2001, 2002). The expert system uses one or more of four steady-state models to compute lake ANC, taking into consideration organic anion contributions to the charge balance. Steady-state water chemistry models are used because the input data requirements are modest compared to time-dependent models. The automated choice of model(s) to predict ANC is based on a set of rules that use measured sample alkalinity and DOC levels as selection criterion. The rules were established using both knowledge of which model is most appropriately applied to a given lake chemistry and testing to optimize prediction accuracy – hence the term "expert" system. In order to use a pH threshold criterion

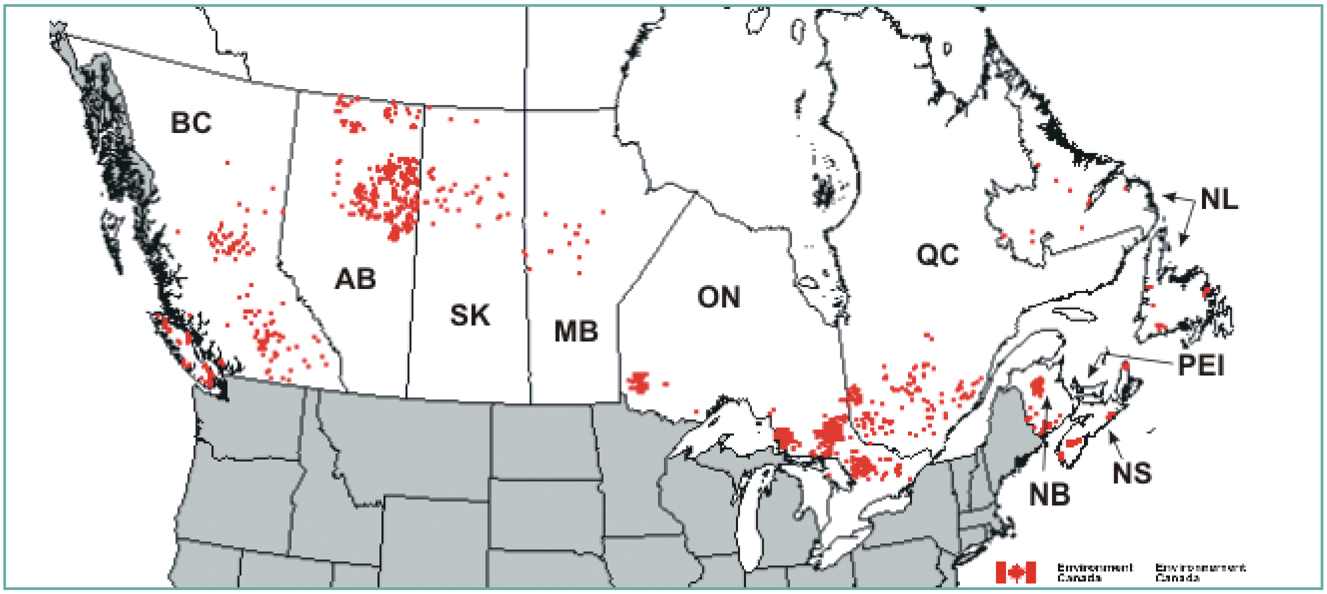

Figure 8.1: Location of lakes with data sufficient to permit water chemistry modelling. The data are the subset of the "current status" data set (see Chapter 6, Section 6.3.1) that charge balance within ±15%. These abbreviations for the provinces are used throughout this assessment: NL = Newfoundland and Labrador, NS = Nova Scotia, NB = New Brunswick, PEI = Prince Edward Island, QC = Québec, ON = Ontario, MB = Manitoba; SK = Saskatchewan; AB = Alberta, BC = British Columbia.

for defining the CL, lake pH is subsequently estimated from region-specific, non-linear pH–alkalinity relationships (modified after Small and Sutton, 1986). Lam et al. (1992) showed that the expert system accurately simulated observed alkalinity and pH distributions for several regional data sets when contemporary SO_4^{2-} deposition was used as the driving input and that the overall relative error in the median pH (estimated for regional subsets of lakes) was 20-30%. A S-CL value for each lake was obtained using an iterative process to determine the total SO_4^{2-} deposition (in the range 2 to 100 kg/ha/yr) that yielded pH 6. While it is possible to calculate a negative CL (i.e., for lakes incapable of achieving the threshold pH or ANC), this is clearly not a realistic outcome and such lakes were deemed to have a CL value equivalent to background deposition.

The effect of N deposition was not explicitly considered in the Expert Model runs to calculate CLs. At present, N-based water acidification is of minor regional importance (see Chapter 6, Section 6.5), e.g., provincial median lake NO_3^- is <1% of the median SO_4^{2-} concentration in all provinces except NL (2%) and Saskatchewan (7%). However, calculations of *current* or N-leaching exceedances did include N-based acidification by adding an estimate of the NO_3^- export flux to the total (i.e., wet + dry) SO_4^{2-} deposition (cf. the procedure used to calculate SSWC exceedances, Henriksen et al., 2002). Wet SO_4^{2-} deposition estimates (1994-98 averages) were provided by R. Vet (Meteorological Service of Canada, Environment Canada, pers. comm.) from the Meteorological Service of Canada (MSC) for a 127 km x 127 km grid that covered most lakes in Figure 8.1 east of and including Manitoba. MSC also provided gridded dry deposition estimates for S species that covered most lakes east of and including ON. For lakes falling outside the MSC grids in western Canada, wet deposition levels interpolated from the closest CAPMoN monitoring station (see Chapter 3) were used, and dry deposition was considered to be 30% of total deposition. The nitrate export flux for calculating N-leaching exceedances was estimated as the product of measured lake concentration and long-term, annual average surface runoff as interpolated from a digital version of the national runoff map (see insert map in the national stream flow map at **http://atlas.gc.ca/site/english/maps/archives/5thedition/environment/ecology/mcr4157**). Wet and dry N deposition gridded in the same way as for S deposition was supplied by MSC and was only available for southeastern Canada so that Steady-state exceedances could only be calculated for this part of the country. Even then, the dry component of N deposition was underestimated since the NH_3, NH_4^+, NO_2, and PAN components were not included. In addition, the organic-N component of wet deposition was not included. Hence the Steady-state exceedance values will be underestimated accordingly.

Runoff values interpolated from the runoff map were in fact deemed the best, *readily available* estimates for either of the models. Direct runoff measurements would of course increase the reliability of the calculated CLs, but such measurements were available for only a small number of the “current status” lakes. Measured runoff was available for 8 lakes in south-central ON (Henriksen et al., 2001) ranging from 490 to 558 mm/yr (mean = 523 mm/yr). The value interpolated from the runoff map was 500 mm/yr in all cases, a 4% error on average. Henriksen et al. (2001) read values from a provincial runoff map that had a higher resolution than the national map used here. Their values averaged 505 mm/yr (i.e., almost identical to those interpolated here) leading them to conclude that it was safe to use runoff values read from maps. The measured average annual runoff at Lac Laflamme, QC is 851 mm/yr (S. Couture, Environment Canada, Québec, pers. comm.), and the map-interpolated value was 700 mm/yr, an 18% error. Measured runoff for the Mersey River was 982 mm/yr (T.A. Clair, Environment Canada, Atlantic Region, pers. comm.) and the map-interpolated value for the nearby group of lakes in and around Kejimkujik National Park in southern NS was 900 mm/yr, an 8% error. Based on this very limited comparison, the error associated with map interpolation of runoff appears to be within the modelling error suggested above. However, the potential error arising from map interpolation may be greater where there is high spatial variability in precipitation. For example, measured average runoff at Turkey Lake in central Ontario is 810 mm/yr (Semkin et al., 2001), whereas the map-interpolated value was 500 mm/yr, a 38% error. The magnitude of this error arises from the fact that Turkey Lake is strongly influenced by localized lake-effect precipitation that is not captured on the national map. Errors in interpolated runoff may be greatest in British

Columbia (BC) due to its terrain and climatic complexity, but at present we have no comparative data for assessment. In general, interpolated runoff that underestimates the true value for a lake results in an underestimated CL, and conversely, overestimated runoff yields an overestimated CL value.

Decreasing base cation concentrations in lakes (see Chapter 6, Section 6.3.2) may be of greater regional significance than N since base cations are used in Expert Model estimations of ANC. However, with no means of projecting future levels, base cation concentrations were held constant at the "current status" level throughout the model runs. If reduced base cation levels had been considered during modelling, the resulting Expert Model CL estimates would be lower.

A detailed description of the version of the SSWC used here is given in Henriksen and Posch (2001). It works on the principle that a lake's CL of acidity is equal to the weathering rate in its catchment (quantified by the pre-acidification base cation flux) less a buffer amount that maintains chemical conditions acceptable to aquatic organisms. The "buffer amount" is the ANC_{limit} threshold used by the SSWC. It was assigned a value of 40 μeq/L for this analysis. Henriksen et al. (2002) and Dupont et al. (in press) used the same value for ANC_{limit} in their applications of the SSWC to eastern Canadian lakes (see discussion above). As with the Expert Model, a lake incapable of attaining this threshold value (i.e. one with a negative, calculated CL) was assigned background deposition as its CL. An alternative way of dealing with negative CLs would be to derive variable, catchment-dependent ANC_{limit} values (Henriksen et al., 1998). Their modification of the SSWC does not allow a lake to have a zero or negative CL; however, using a fixed ANC_{limit} value was considered more convenient for the analysis presented here. A necessary outcome of this decision was accepting background deposition for the CL of some lakes. Future CL assessment should consider development of lake-specific threshold values, although this will not change the fact that those lakes assigned background deposition for CL here will still have extremely low CL values.

Since the SSWC requires a value for the pre-acidification base cation flux (and there are no measurements), it must be estimated from the present-day flux, i.e., from the product of base cation concentrations and runoff interpolated from the national runoff map as described above. However, it is recognized that acidic deposition elevates the present-day flux by stripping base cations from ion exchange sites in catchment soils. Hence, in order to correct (reduce) the present-day flux to estimate long-term weathering, Henriksen introduced the so-called "F-factor". It relates the present-day excess production of base cations to the long-term changes in inputs of acidifying anions. Terrestrial catchments with an F-factor of zero do not neutralize any incoming acidity so that surface waters are directly acidified, whereas catchments with an F-factor of one neutralize all incoming acidity and the water does not acidify, i.e. only the soil is acidified. Henriksen (1984) empirically estimated that the F-factor for sensitive terrain is in the range 0.2 to 0.4. Several equations have been proposed for calculating the F-factor (reviewed in Henriksen and Posch, 2001), most of them involving a relationship with the present-day base cation concentration. Using sub-catchment mass budget measurements, Watmough and Dillon (2002) estimated the weathering inputs of base cation for three lakes in the Muskoka-Haliburton area of ON. The SSWC-calculated CLs for these lakes were 13% to 48% lower when these mass budget-determined base cation fluxes were substituted for the F-factor-estimated fluxes. Hence, the SSWC CLs determined here are, if anything, overestimated.

In order to show regional variation, CL and both exceedance values were determined for the same grid as employed by the MSC. The MSC grid was laid over the individual lake CLs, and the lower 5th percentile value, computed by either the Expert or SSWC models for all lakes falling within a given grid square, was selected as that square's CL value. This grid square CL value was then used to calculate both the N-leaching and Steady-state exceedances as described above. Using the 5th percentile CL value (or the 95th exceedance value; both imply 95% protection) maintains the practice used in past Assessments.

Whether or not the 5th percentile value accurately represents the CL for a given grid square depends on both the representativity of the associated sample population of lakes, modeling assumptions, and/or the procedures to estimate necessary input data (e.g., runoff and base cation flux estimates as discussed above). The lake data subsets are generally not representative of the overall lake population (see Chapter 6, Section 6.3.1), most often not including the smaller size fractions. The number of lakes sampled in some provinces (see Figure 8.1) is clearly too small or too patchy to represent the broader lake population. Lake chemistry data are not available for some sensitive terrain in some provinces, most notably MB, SK and BC. Hence for these three western provinces, the results presented below are unlikely to accurately represent the regional situation, and there are no other independent CL analyses to support (or refute) these CL values. They are simply the best that could be produced given the data and procedural constraints associated with this assessment. In the Georgia Basin of BC, work is already underway to improve the representativity of the lake chemistry database and to reconsider how some of the key model inputs (e.g., runoff and SO_4^{2-} deposition) may be refined.

8.3.3.2 Terrestrial

In this assessment, CLs for forest soils were calculated using the Simple Mass Balance (SMB) model (originally formulated by Sverdrup and De Vries, 1994):

$$CL(S + N) = BC_{dep} - Cl_{dep} + BC_w - Bc_u + N_i + N_u + N_{de} - ANC_{le(crit)} \qquad (1)$$

where

BC_{dep} = base cation (Ca, Mg, K, Na) wet + dry deposition;
Cl_{dep} = chloride wet + dry deposition;
BC_w = base cation weathering;
Bc_u = net base cation (Ca, Mg, K) uptake by trees;
N_i = net nitrogen immobilisation rate in soil;
N_u = net nitrogen uptake;
N_{de} = net denitrification rate;
$ANC_{le(crit)}$ = critical alkalinity leaching rate.

All variables are expressed in eq/ha/yr. Dry and wet deposition estimates of base cations and chloride are based on deposition data provided by the MSC (Ro and Vet, 2002; Vet and Shaw, 2004; see also Chapter 3). Base cation weathering was estimated following the soil substrate type approximation and texture method (Sverdrup et al., 1990). In the current assessment, harvesting removals were not considered in the calculations, i.e., Bc_u and N_u were set to zero. In addition, N_i and N_{de} were assumed to be negligible. Further details on the SMB model are given by UBA (1996) and the NEG/ECP (2001).

In ecosystems at steady state, the rate of anion input equals the rate of anion output. To respect the law of electro-neutrality, the rate of cation output from soil leaching must equal the rate of anion leaching. A key component of the CL calculation is the critical base cation leaching rate (the $ANC_{le(crit)}$ parameter). This critical chemical criterion ultimately determines the acceptable level of base saturation in forest soils. Among the many chemical criteria proposed in the European modelling exercise, the UN-ECE developed a model to calculate the critical $ANC_{le(crit)}$ for forest soils based on two criteria: 1) the molar BC/Al ratio in soil leachate, and 2) the gibbsite dissolution constant which controls Al solubility (UBA, 1996). The following equation summarises the calculation of $ANC_{le(crit)}$:

$$ANC_{le(crit)} = 1.5 \times \left(\frac{BC_{dep} + BC_w - Bc_u}{(Bc / Al)_{crit}}\right) + Q^{2/3} \times \left(1.5 \times \frac{BC_{dep} + BC_w - Bc_u}{(Bc / Al)_{crit} \times K_{gibb}}\right)^{1/3} \qquad (2)$$

where Bc = K + Ca + Mg (the subscripts *dep*, *w*, and *u* represent deposition, weathering, and net uptake, respectively); Na is excluded since it provides no protection against Al toxicity for plants, $(Bc/Al)_{crit}$ = soil solution threshold criterion; Q is the runoff rate (m^3/ha/yr); and K_{gibb} = gibbsite dissolution constant criterion. A range of threshold values have been proposed for Bc/Al and K_{gibb}; the current assessment is based on a Bc/Al = 10 and $\log_{10}(K_{gibb}) = 9.0$ (NEG/ECP, 2001). These values were chosen with the overall objective of maintaining soil base saturation at an acceptable level for forest health and productivity.

The application of this steady-state model within the geographic mapping context has been described in detail by the NEG/ECP Environment Task Group (2001) and Arp et al. (2001). Critical loads for upland forests and related exceedances were compiled and mapped separately for PEI, NS, NB (DeMerchant et al., 2004), QC (Ouimet, 2004), and ON (Watmough et al., 2004), based on various data sources according to data availability in each province. At this stage, these maps assess CLs and exceedances for upland forest soils without taking into account forest harvesting or fire. The CL values and related maps thus reflect the situation where soils and forests are basically at steady state, without harvesting or fire adding to local soil acidification. Forest harvesting, particularly, removes base cations from ecosystems which is an acidifying process in the long term, but also removes nitrogen which is a neutralising process in the long term. Thus, the magnitude of acid input caused by forest harvesting is dependent on the base cations/ nitrogen ratio of the biomass harvested, which is a function of forest growth rate, tree species, and type of biomass harvested (stem, bark, branches and foliage). Forest harvesting can represent a major acid input in northern hardwood ecosystems, while it can cause a minor acidification effect in boreal coniferous ecosystems in the case where only stem wood is harvested. For instance, forest harvesting in the boreal coniferous forests in QC would represent on average about 10% of the incoming acidity input in these ecosystems (Ouimet, 2004). However acidity caused by forest logging and harvesting can vary from 0 to more than 300 eq/ha/yr (Ouimet, 2004; Watmough and Dillon, 2003). Including the effects of harvesting and fire would result in lower calculated CLs and higher exceedances. Therefore the maps and tables presented here underestimate the impact of acid deposition on the forest resource.

Both N-leaching and Steady-state exceedances were calculated for forest soils. The N deposition component of the current N-leaching exceedance was estimated for every soil polygon by multiplying a median NO_3^- concentration for each province by polygon-specific runoff values read from the national runoff map. The Steady-state exceedance was calculated using the sum of the wet and dry components of S and N deposition supplied by MSC. As noted above, several components of N deposition have not been quantified so that the Steady-state exceedances are underestimates.

8.3.3.3 Combining aquatic and terrestrial exceedance estimates

In order to provide as extensive regional coverage as possible, aquatic and terrestrial N-leaching and Steady-state exceedance estimates were combined into single maps. Combining them was complicated by their differing nature – the aquatic values effectively corresponding to points in geographic space and the upland forest soil values corresponding to polygons of varying size in geographic space. Adoption of the grid-style presentation already used for the lake CLs and exceedances was deemed the simplest way of combining the two sources of information. To do this, the polygon information in the soil CL map was “re-sampled” at a 1 km^2 resolution, the 127 km x 127 km MSC grid overlaid, and the 5th percentile re-sample value within a given grid square taken as the terrestrial CL for that square. The exceedance associated with this 5th percentile CL re-sample value was taken as the terrestrial exceedance for that square. The re-sampling procedure gives greater weight to larger soil polygons thereby providing percentile statistics akin to area-weighted values. When both an aquatic and a terrestrial CL value existed for a given square, the lower of the two was selected as the overall value for that grid square. There were many instances where only one of the CL estimates was available for a given square, particularly forest soil estimates in northern ON and QC, and lake estimates in the provinces west of ON. Finally, combined exceedance grid maps (i.e., N-leaching and Steady-state) were produced by using the exceedance value associated with each square according to which CL type (i.e., aquatic or terrestrial) had been selected for the combined CL map. The combined exceedance maps are the first such maps ever produced in North America.

8.4 CRITICAL LOAD VALUES AND EXCEEDANCES

D.S. Jeffries, R. Ouimet, J. Aherne, P.A. Arp, V. Balland, I. Demerchant, J. Dupont, J. Franklyn, D.C.L. Lam, F. Norouzian, S. Watmough, and I. Wong

8.4.1 Aquatic critical load values

Statistics for the aquatic CLs calculated for each province are summarized in Table 8.2. The 5th percentile value (shaded columns in Table 8.2) is taken as the provincial CL value to allow for uncertainties in the determination. Note, however, that even these values must be used with caution since the lake data sets are compilations of existing monitoring data and not statistically representative of the provincial lake populations. Given the nature of the biases in the data sets (see discussion in Chapter 6, Section 6.3.1), the CL values in Table 8.2 are probably overestimated. A negative S-CL value occurs when the models predict that no level of SO_4^{2-} deposition is sufficient to attain the chemical threshold

Table 8.2. Number of lakes (n), range, 5th and 50th percentile CL values (eq/ha/yr) calculated for each province using the "current status" lake chemistry database (see Figure 8.1). Results from application of both the Expert and SSWC models in this Assessment are presented. The 5th percentile values (shaded columns) are considered the regional CL values. Negative CLs are indicated as "Bkd" (= background deposition) implying that the lake can never attain the chemical threshold used for calculating the CL. Critical load values determined from other databases using the SSWC model are presented for comparison.

	Provincial CLs (eq/ha/yr) calculated by this Assessment								Provincial CLs (eq/ha/yr) calculated by other Assessments				
	Expert Model				Steady-State Water Chemistry Model				Steady-State Water Chemistry Model				
			Percentile				Percentile				Percentile		
Province	n	Range	5th	50th	n	Range	5th	50th	n	Range	5th	50th	Reference
NL	23	Bkd – >2080	Bkd	Bkd	23	Bkd – 6950	Bkd	530	29	Bkd – 5930	Bkd	824	Dupont et al. (in press)
NS	60	Bkd – >2080	Bkd	Bkd	60	Bkd – 2920	50	444	97	Bkd – 16000	Bkd	344	Dupont et al. (in press)
NB	115	Bkd – >2080	Bkd	942	115	79 – 9260	205	1000	94	Bkd – 7640	104	806	Dupont et al. (in press)
QC	130	147 – >2080	345	734	130	175 – 6670	311	619	1351	Bkd – 10100	184	575	Dupont et al. (in press)
ON	1041	Bkd – >2080	126	832	1081	47 – 18900	177	542	1469	Bkd – 15600	337	607	Henriksen et al. (2002)
MB	Not Analyzed				15	1070 – 8810	1620	2870					
SK					11	93 – 1630	148	465					
AB					319	Bkd – 7040	307	1760	460	Bkd – 4720	47	961	WRS (2004)
BC					196	410 – 110000	1220	4570					

concentration in a given lake. Such lakes have no capacity to neutralize any anthropogenic acidifying input from the atmosphere. "Bkd" indicates these situations in Table 8.2. Background, sea-salt corrected SO$_4^{2-}$ deposition in southeastern Canada is approximately 40 to 60 eq/ha/yr (or ~2-3 kg/ha/yr). The maximum S-CL reported for applications of the Expert model was >2,080 eq/ha/yr (or >100 kg SO$_4^{2-}$/ha/yr) since model iterations were stopped at this level even though the pH threshold had not been reached.

The 5th percentile CL values range from background deposition levels in NL, NS and NB (Expert Model value only for the latter two provinces) to 1620 eq/ha/yr for the very small MB data set. For all eastern provinces except QC, the CL values determined by the Expert Model were lower than the SSWC estimates, largely because the former considers the effect of natural organic acids on lake pH while the latter does not. The QC data set tends to have low DOC (see Chapter 6, Section 6.3.2). The effect of natural organics on lake pH is most important for those lakes with low base cation concentrations, i.e., precisely those acid sensitive lakes that are most likely to define the regional CL value.

The SSWC was recently applied to several Canadian data sets, i.e., by Henriksen et al. (2002) in ON, by WRS (2004) in AB, and by Dupont et al. (in press) in NL, NS, NB and QC (see the right-hand columns of Table 8.2). Differences between their CL values and the SSWC values calculated for this assessment can be attributed to several factors. For example, very different sample populations were sometimes evaluated (particularly in QC and ON); different data collection periods were sometimes used (cf. the effect of chemical trends noted above); different methods were used to specify some

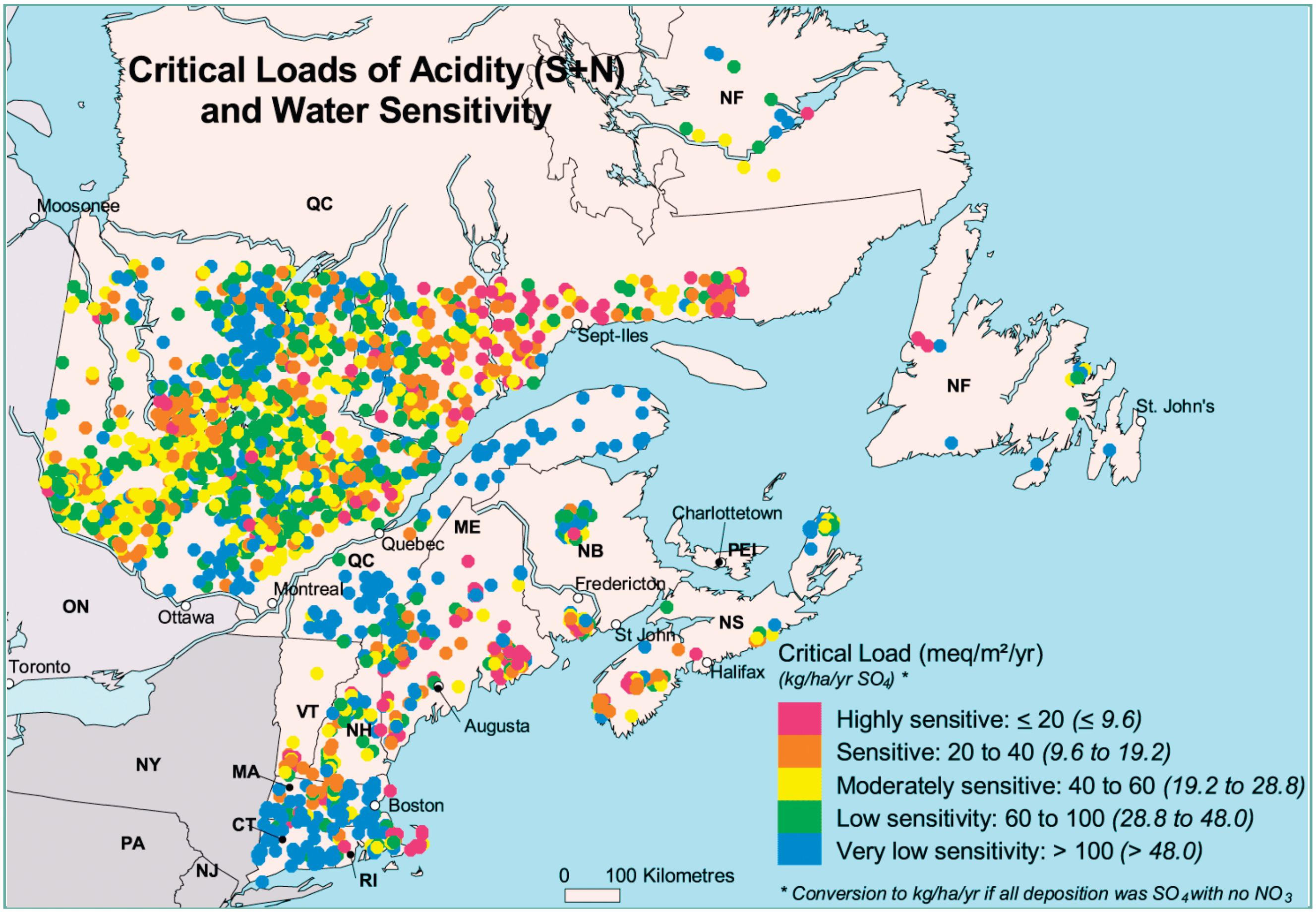

Figure 8.2: Critical loads of acidity determined for lakes in the NEG-ECP region by Dupont et al. (in press). Note that the CL classes shown on the map are expressed as meq/m^2/yr (multiply by 10 for eq/ha/yr) and the equivalent sulphur-only values (kg SO$_4^{2-}$/ha/yr) are shown in parentheses.

important input data such as runoff; and finally, slightly different constants or coefficients internal to the SSWC model were sometimes used. This last factor was particularly important for the AB analyses since WRS (2004) used a much more stringent value for ANC_{limit} (75 μeq/L) than ours (40 μeq/L), thereby resulting in a much lower 5th percentile CL value (47 eq/ha/yr) than ours (307 eq/ha/yr). Apart from these AB results and given the factors noted above, the CL values calculated for this assessment are comparable to those of Henriksen et al. (2002) for ON and Dupont et al. (in press) for QC and the Atlantic provinces.

Critical load values typically show a high degree of spatial variability due to the natural variability in terrain characteristics that control them (principally bedrock and surficial geology). This was well illustrated by Dupont et al. (in press; see Figure 8.2), particularly in southern QC, north of the St. Lawrence River, where the QC Lake Survey database (QLS; Dupont, 1992a,b) provided rather dense spatial coverage. Both high and low CL values are distributed throughout Dupont et al.'s map – often in close proximity to each other. Within the Canadian portion of the map, lakes with very low CLs occur with greater frequency in northwestern QC (near Rouyn-Noranda), QC northeastern shore, southwestern NS and NB, and western NL. High CL lakes occur more frequently east of Ottawa, the Chibougamau area, and the St. Lawrence lowlands in QC, in southern NL and western Cape Breton. The most acid sensitive lakes (i.e., those having the lowest CLs) are generally located on igneous or silicate metamorphic bedrock, or some other carbonate-poor types of geology. Insensitive (high CL) lakes mostly occur where limestone and sedimentary rocks are present.

Spatial variability in the aquatic CL values determined using this assessment's lake chemistry database is shown in Figure 8.3. The grid CL value was determined as described in Section 8.3.3.1 and subsequently classified as defined in the Figure legend. The grid is composed of 127 km x 127 km squares, and the tilted appearance arises from laying a Polar Stereographic grid over a Lambert Conformal map.

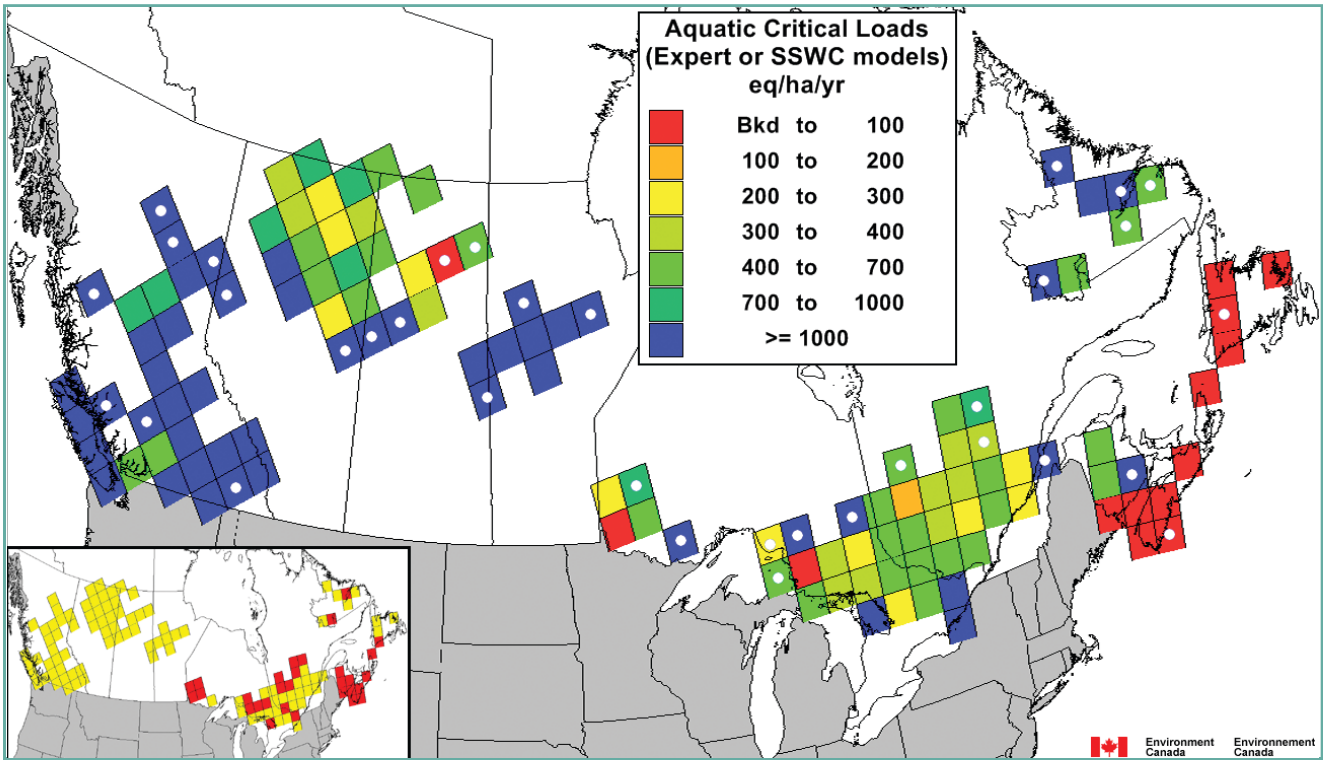

Figure 8.3: Aquatic CLs (wet + dry deposition in eq/ha/yr) for acidity (S + N) calculated using either the Expert or SSWC models according to the selection protocol described in Section 8.3.3.1. "Bkd" in the legend implies background deposition which is ~40-60 eq/ha/yr. The index map (lower left) specifies the model selected for each grid square: red = Expert, yellow = SSWC. The CL value of a given square is the 5th percentile value for all lakes located within the square. Grid squares containing only one lake are indicated by a white dot.

The grid format presented here has the advantage of suppressing the small-scale (lake-to-lake) variability evident in Dupont et al.'s NEG/ECP map, but the disadvantage of obscuring the amount of data contributing to a square's value. Of the 2054 lakes with chemical records suitable for calculating CLs, the number of lakes located within a given grid square ranged from one to 280 (mean = 15.9, median = 3.5). Grid square values based on only one lake are the most uncertain, and this occurred for 34 of the 125 grid squares shown in Figure 8.3. Some of the "one-lake" squares no doubt resulted where only a fraction of a grid square covered terrain that could contain sampled lakes – the remainder covering open ocean, portions of the Great Lakes, or U.S. territory.

Past assessments adopted an approach that underestimated the number of lakes and geographic area having low CLs. The unrepresentative nature of the lake data sets combined with the methodology used here in assigning a CL value to each square seems to have continued to overestimate regional CLs here. Of the 34 "one-lake" grid squares in Figure 8.3, 29 were classified as having a CL >400 eq/ha/yr (approximately >20 kg SO_4^{2-}/ha/yr) and 22 of them were >1000 eq/ha/yr. This occurred despite the fact that at least some of the squares cover sensitive terrain according to the national sensitivity map (National Atlas of Canada, 1995). Conversely, squares that contain large numbers of lakes such as those associated with the four lake clusters in ON (see Figure 8.1) tend to be classified in the lower CL categories (two in the 0-100 eq/ha/yr class and two in the 200-300 class). Only three of the "one-lake" grid squares were in the lowest (most sensitive) CL class (0-100 eq/ha/yr), and two of them (one in NS and one in NL) were adjacent to similarly classified squares where the CL value was based on data from 4 to 14 lakes. The third, "one-lake", low-CL square is located in north-central Saskatchewan where the terrain is sensitive according to National Atlas of Canada (1995). The pH and base cation concentration for the single lake in that square fall in the 3rd percentile of Saskatchewan's "current status" data set (see Chapter 6).

Grid squares covering the 1983 target load (20 kg wet SO_4^{2-}/ha/yr) are represented by the lowest four CL classes in Figure 8.3 (i.e. those ≤400 eq/ha/yr). They occur in all provinces except MB and BC, and in fact, they all contain squares with CLs ≤300 eq/ha/yr.

The lowest, most sensitive CL class (Bkd – 100 eq/ha/yr; red squares in Figure 8.3) occurs in 13 (~21%) of the eastern grid squares. Eleven of them are in NL, NS and southern NB which is consistent with findings from previous assessments and the extreme sensitivity of their waters (see Chapter 6). The other two squares with an extremely low CL occur in the vicinity of the Experimental Lakes Area in northwestern ON and the Algoma region of central ON (east of Lake Superior). The CL value for both of these squares is based on lots of data – 85 and 267 sample lakes occur in each square respectively.

The moderately low CL classes (100-400 eq/ha/yr; orange, yellow and yellow-green squares) occur in 20 squares that are irregularly distributed throughout QC, ON, SK and AB. Their distribution pattern generally reflects terrain sensitivity (cf. National Atlas of Canada, 1995).

The less sensitive, moderate to high CL classes (>400 eq/ha/yr; green, blue green and blue squares) actually predominate the map, occurring in 70% of the 125 squares in Figure 8.3. These squares occur in all provinces except NS and approximately twice as often in the west as in the east. Thirty-seven of the 87 higher CL squares are from MB and BC. This reflects their water chemistry data sets that do not adequately include lakes from the sensitive parts of those provinces. One should not use Figure 8.3 to conclude that acidic deposition will not affect aquatic ecosystems in MB and BC. Lake surveys that include sensitive areas of these provinces are needed to deal with this limitation.

In ON, CLs for lakes in the Sudbury-Killarney area and the Muskoka River Catchment have been evaluated using the more complex FAB model (Hindar et al., 2000, 2001; Aherne et al., 2004). The FAB model is a steady-state model that accounts for the sources and sinks of N in a lake's terrestrial catchment as well as retention of S and N within the lake. The model does not produce a unique CL value but rather a "critical load function" for each lake that explicitly includes both the S and N components. The advantage of using the FAB model is that it shows how reductions in S or N deposition (individually or in combination) can be used to reduce exceedances. The limitation of using it rests with the greater input data required to run it (relative to the Expert or SSWC models). The FAB model applications in ON have shown that further reductions in S deposition will be required to eliminate CL exceedances (reducing only N deposition will not be sufficient), and that accounting for N retention in upstream lakes yields significantly higher CL values in downstream lakes.

8.4.2 Terrestrial critical load values

In eastern Canada, the median CL for upland forests reaches 559 eq/ha/yr (area-weighted median), ranging from 135 up to 7980 eq/ha/yr. The highest median critical load is found in PEI and the lowest in QC (Table 8.4 located in Section 8.4.4). The 5th percentile CL for terrestrial ecosystems is below 400 eq/ha/yr for the majority of the eastern Canadian provinces, and generally higher than the corresponding aquatic 5th percentile values (Table 8.2).

As shown in Figure 8.4, CLs are generally highest where the soil substrate is calcareous, and are generally high where soils are deep. Southern parts of ON, therefore, are well buffered against acid deposition. On the other hand, shallow and coarse-textured upland soils mainly derived from felsic or granitic bedrock such as those found in southwest NS and on the Canadian Shield have low CLs. Note that the forest soil CLs shown in Figure 8.4 assume neither forest harvesting nor fire. If the forests are harvested, the base cation net removal associated with the removed timber greatly increases their sensitivity to acidic deposition (Watmough and Dillon, 2003).

While the analysis of terrestrial CLs presented here was limited to southeastern Canada, CLs have been determined in AB (summarized by Foster et al., 2001). Sandy soils supporting a jack pine forest exhibited a median CL of 440 eq/ha/yr (range 210 to 690 eq/ha/yr). Consideration of this information plus aquatic CL information led Foster et al. to propose 250 eq/ha/yr as a suitable CL for all sensitive terrain in AB.

8.4.3 Aquatic critical load exceedance

Aquatic exceedances were calculated for every sample lake in the provincial data sets as the difference between total (wet + dry) S deposition and the CL (cf. Figure 8.3) with the N-based component estimated either by adding the present-day NO_3^- leaching (for the N-leaching exceedance) or by adding wet + dry N deposition (for the Steady-state exceedance). The 95th percentile N-leaching and Steady-state exceedance values for each province are given in Table 8.3. The larger of the Expert and SSWC model estimates for the eastern provinces were selected (only SSWC N-leaching values were available for the western provinces). All of the eastern provincial N-leaching exceedances were positive, ranging from 132 eq/ha/yr (QC which had the highest provincial CL, see Table 8.2) to 379 eq/ha/yr (NB which had a very low CL). The extremely low CLs in NL and NS result in substantial N-leaching exceedance values (219 and 317 eq/ha/yr respectively) even though deposition is relatively low. They are not that different from ON's N-leaching exceedance (323 eq/ha/yr) where moderate CLs combine with relatively higher deposition. None of the western provinces exhibit positive N-leaching exceedances, although the only slightly negative value for SK raises the concern that even a small increase in deposition could result in positive values. Once again, the extremely negative N-leaching exceedance values for MB and BC no doubt reflect the unrepresentative nature of their data sets (lakes in sensitive terrain not or inadequately sampled), and do not justify permitting increases in deposition.

As expected, the aquatic Steady-state exceedances for the eastern provinces are much higher than the N-leaching exceedances, the difference being that part of N deposition that is not exported as NO_3^- in surface runoff. Note also that even these high numbers must be underestimates because several N species were not included in the estimates of wet + dry N deposition.

The variation among provinces in the 95th percentile Steady-state exceedance (Table 8.3) reflects low CLs in the Atlantic provinces in combination with moderate N deposition, and higher CLs in QC and ON in combination with higher deposition. The Steady-state exceedances clearly point out the need to avoid development of N saturation due to persistently high N deposition.

Spatial variation in the N-leaching and Steady-state exceedances is shown in Figures 8.5a and 8.5b respectively. Figure 8.5a represents the current exceedance situations while Figure 8.5b represents a potential future situation if ecosystem N saturation develops.

With respect to the current situation, the 7 red-orange

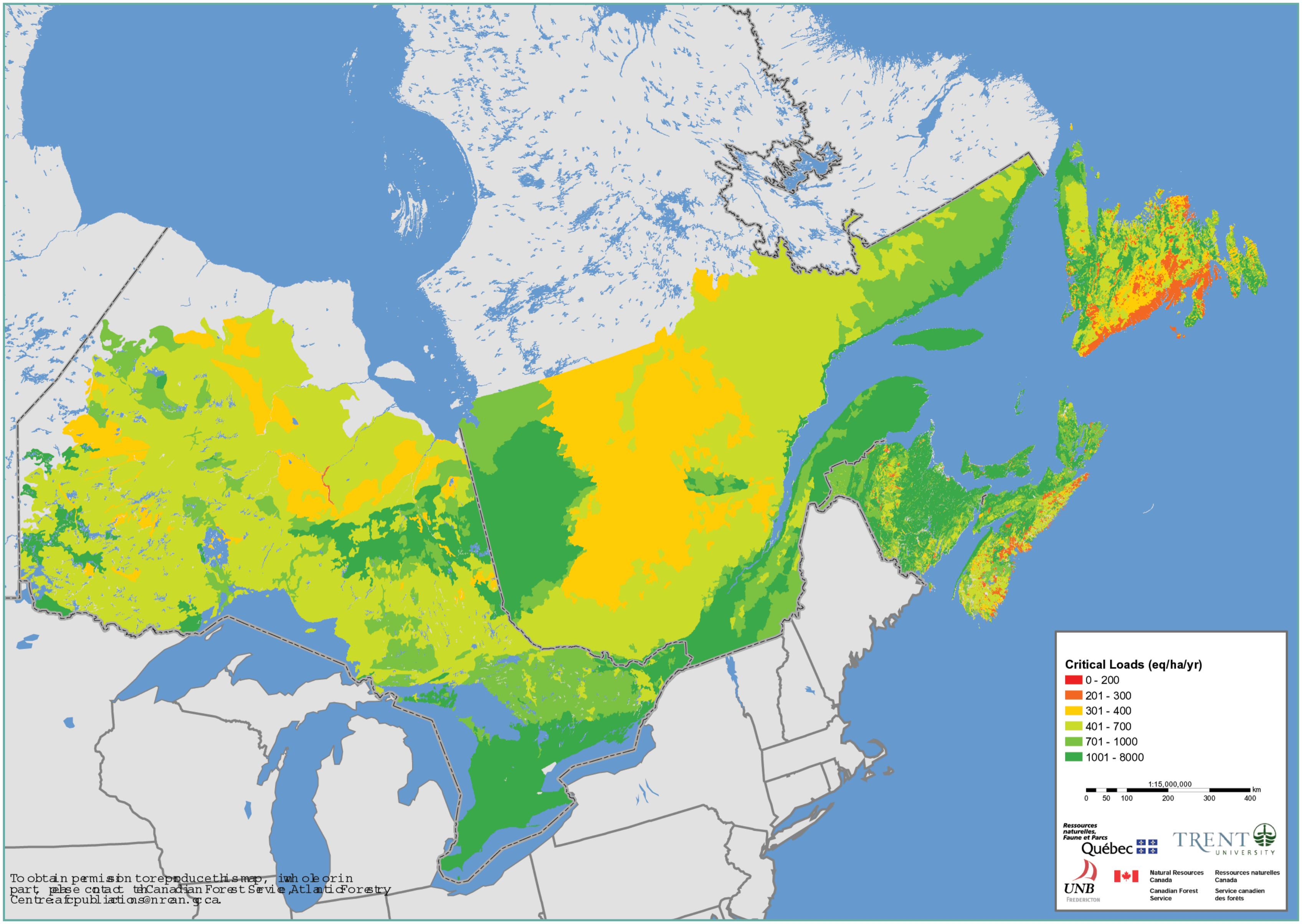

Figure 8.4: CLs for upland forest soils in southeastern Canada in eq/ha/yr assuming no forest harvesting.

Table 8.3. Aquatic N-leaching CL exceedances (95th percentile value) for provincial data sets (cf. Table 8.2) calculated by the indicated model. Equivalent Steady-state exceedances for the eastern provinces are shown also.

Province	N- leaching Exceedance (eq/ha/yr)	Steady-state Exceedance (eq/ha/yr)	Model
Newfoundland	219	429	Expert
Nova Scotia	317	677	Expert
New Brunswick	379	749	Expert
Quebec	132	617	SSWC
Ontario	323	1070	SSWC
Manitoba	-1520	-	SSWC
Saskatchewan	-53	-	SSWC
Alberta	-242	-	SSWC
British Columbia	-953	-	SSWC

grid squares in Figure 8.5a represent the highest aquatic N-leaching exceedances (300 to 600 eq/ha/yr, equivalent to 14.4 to 28.8 kg SO_4^{2-}/ha/yr). They occur in three locations: 5 squares in southern NS/NB, one square in central ON east of Lake Superior, and one square in south-central ON east of Georgian Bay. The first two locations have very low CLs (see Figure 8.3) while the last has a moderate CL and higher deposition. Seventeen orange squares in Figure 8.5a indicate moderate N-leaching exceedances (100 to 300 eq/ha/yr). They occur in NL (but not in Labrador), NS, southwestern QC, and central and south-central ON. Seven low exceedance squares (0 to 100 eq/ha/yr, yellow squares in Figure 8.5a) occur irregularly throughout southwestern QC and ON. The extremely low CL found in the vicinity of the Experimental Lakes Area in northwestern ON (red square in Figure 8.3) results in a low (yellow) but positive N-leaching exceedance in Figure 8.5a even though atmospheric deposition is low. Aquatic CLs are not exceeded (N-leaching assumption) in half (32 of 63) of the eastern grid squares and their spatial distribution reflects either lower terrain sensitivity (a higher CL) or low deposition. Overall, the widespread occurrence of positive N-leaching exceedances for lakes in southeastern Canada means that further reduction in acidic deposition is needed.

No positive N-leaching exceedances were determined in western Canada, i.e. there are no western yellow to red squares in Figure 8.5a. The single lake in the extremely low CL square in north central SK (red square in Figure 8.3) had an N-leaching exceedance of -2 eq/ha/yr so that even a tiny increase in deposition will switch this lake into a positive exceedance class. Exceedance results for western Canada should be treated with caution because the sample lakes do not adequately represent extensive areas of sensitive terrain in northern and southeastern MB, northern SK and in the coastal mountain range of BC. In addition, the spatial variation in current S deposition used to calculate the exceedances is much more uncertain in western Canada than in the east.

Very high aquatic Steady-state exceedances 300 to >600 eq/ha/yr occur in all eastern provinces (Figure 8.5b) except Labrador. Thirty-nine of 63 squares occur in the two highest exceedance classes (compare to the 31 squares in all positive exceedance classes in Figure 8.5a). If the present-day levels of N deposition eventually lead to development of N saturation, then this will have a profound effect on CL exceedances.

8.4.4 Terrestrial critical load exceedance

As with the aquatic exceedances, we considered two types of terrestrial CL exceedance. The “N-leaching” exceedance considers that all current S deposition is acidifying plus only that component of N deposition leached as NO_3^- (cf. the procedure for estimating current exceedance for aquatic ecosystems). The N-leaching exceedance is more representative of the current state of terrestrial ecosystems since evidence of N saturation in terrestrial ecosystems is still uncommon (see Chapter 5).

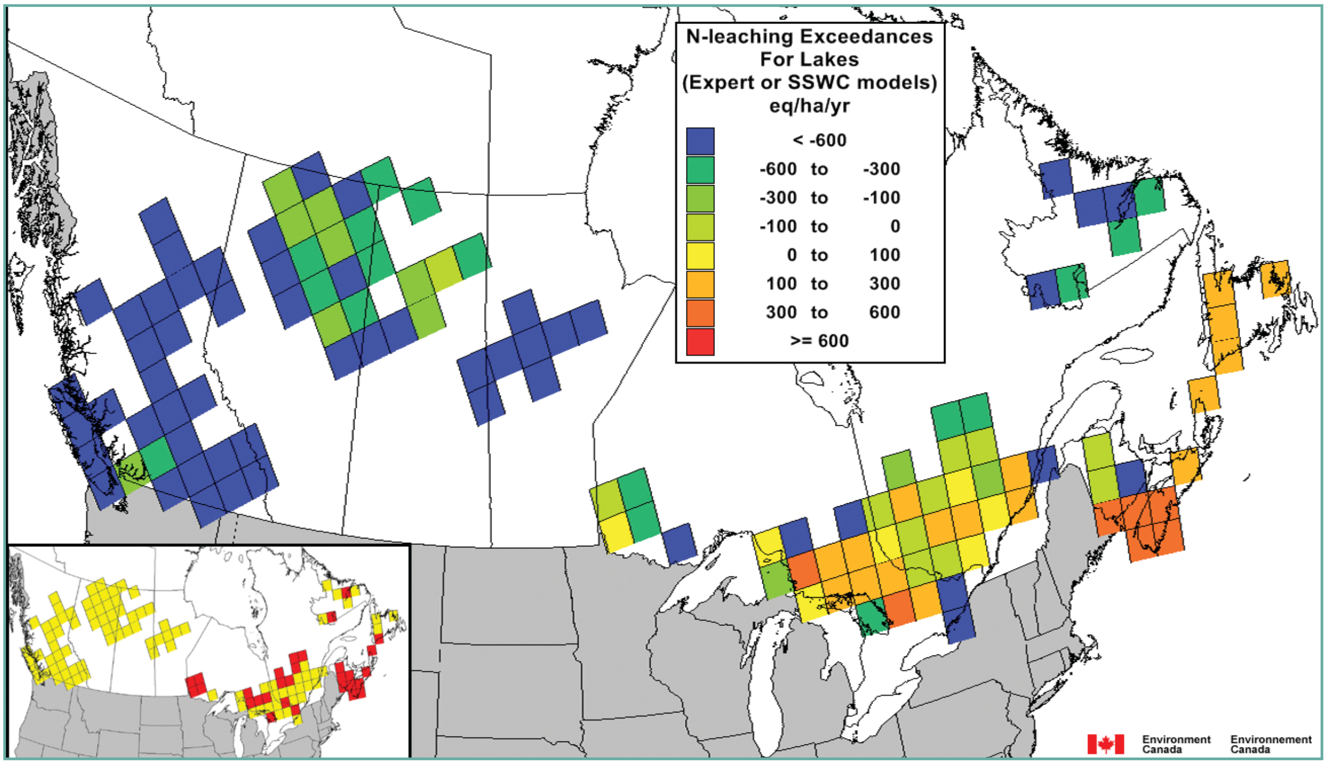

Figure 8.5a: Current or N-leaching aquatic CL exceedances (eq/ha/yr) for acidity (S + N) calculated using either the Expert or SSWC models. The index map (lower left) specifies the model selected for each grid square: red = Expert, yellow = SSWC.

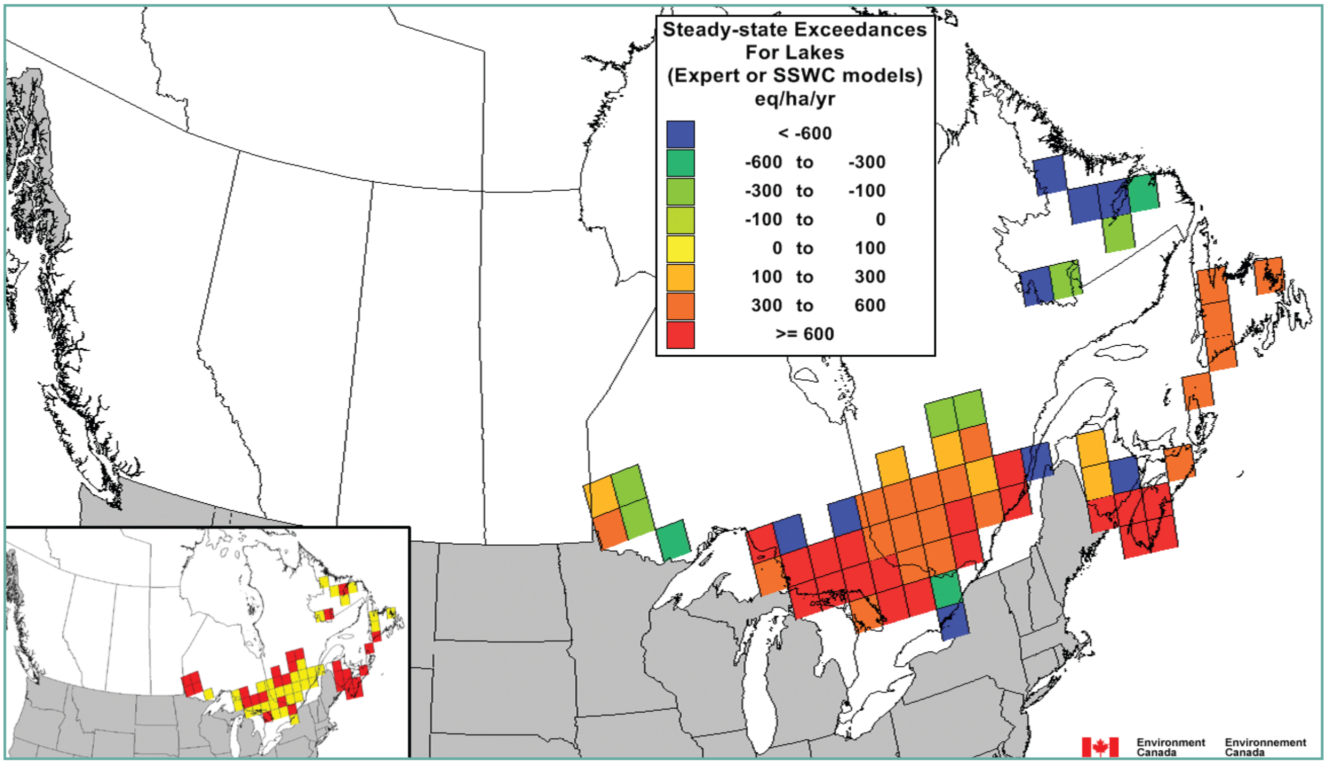

Figure 8.5b: Steady-state aquatic CL exceedances (eq/ha/yr) for acidity (S + N) calculated using either the Expert or SSWC models. Steady-state exceedances could only be calculated for the eastern provinces. The index map (lower left) specifies the model selected for each grid square: red = Expert, yellow = SSWC.

However, it underestimates the acidifying impact of episodic soil nitrification of ammonia (see Chapter 5) and forest harvesting, ignores the cumulative potential for developing N saturation as N deposition remains elevated, and therefore, probably represents an overly optimistic estimate of terrestrial exceedance.

The "Steady-state exceedance" considers all current N + S atmospheric deposition to be acidifying to terrestrial ecosystems in the long term. "Steady-state" means that soils are in equilibrium with incoming deposition implying N saturation, and therefore, all N deposition would be exported from the forest to lakes as NO_3^-. Since N saturation is not currently occurring to any great degree, the Steady-state exceedance can be considered the more pessimistic estimate of the current terrestrial exceedance. Nevertheless, European nations have assumed that the Steady-state exceedance is the most reasonable one to use when assessing long-term acidification and designing emission control programs to reduce it (e.g., UBA, 1996).

The upland forest terrain exhibiting N-leaching exceedance represents <5% of the mapped area of southeastern Canada (Table 8.4; Figure 8.6a). The 95th percentile values for PEI and NB are less than or equal to -197 eq/ha/yr, meaning that most of the territory in these provinces can neutralize the present-day acidity inputs (assuming no harvesting or forest fire). However, current acidity inputs in pristine forest ecosystems in NL, NS, QC and ON are currently close to the buffering capacity limits in nearly 5% of their territory. If additional acidifying inputs such as nitrification of current ammonia deposition and forest harvesting are considered, these current exceedances would be much higher and more widespread, probably resulting in an upwards shift of at least one exceedance class in Figure 8.6a. The acid-generating input of these two phenomena needs to be quantified accurately in order to assess more adequately the current exceedance status of the forests.

In the Eastern Canadian provinces, the median and 95th percentile Steady-state exceedances of soil CLs and percentage of mapped area with Steady-state exceedance increase from east to west with the highest average exceedance occurring in QC (Table 8.4). On average, areas with Steady-state exceedance cover 52.1% of the mapped area in southeastern Canada. Mapped terrestrial Steady-state exceedances are highest where atmospheric acid deposition rates are high and soil CLs are low (Figure 8.6b). Approximately two-thirds of the mapped area in ON and half in QC currently receives acid deposition in excess of the long-term forest soil CL. The lowest percentage area of exceedance is in PEI, where only 3.5% of the province exceeds the Steady-state CL. Highest exceedances are projected to occur in eastern

Table 8.4. Forest soil critical loads by province in Eastern Canada and their exceedances considering 1) all atmospheric S and N atmospheric depositions are acidifying in the long term (Steady-state exceedance), and 2) all atmospheric S deposition and NO_3 leaching[1] are acidifying in the short term (current or N-leaching exceedance). Values are area-weighted.

	Critical Load		Steady-state exceedance			Current (N-leaching) exceedance		
Province	Median	5th percentile	Median exceedance	95th percentile exceedance	Area mapped in exceedance	median exceedance	95th percentile exceedance	Area mapped in exceedance
			(eq/ha/yr)		(%)	(eq/ha/yr)		(%)
NL	572	247	-134	235	35.4	-357	-15	0.4
NS	817	277	-135	423	39.9	-479	54	8.8
PEI	2063	715	-1486	-126	3.5	-1772	-417	1.2
NB	1169	559	-455	175	14.6	-795	-197	1.7
QC	519	358	-15	568	48.6	-293	-3	4.6
ON	548	388	42	695	62.3	-281	8	5.2
Total	559	358	15	678	52.1	-298	-5	4.6

[1] NO_3^- leaching flux based on provincial median lake NO_3^- concentrations (see Chapter 6, Table 6.2). It was assumed that median lake NO_3^- concentration in NB, NS and PEI was the same as in NL.

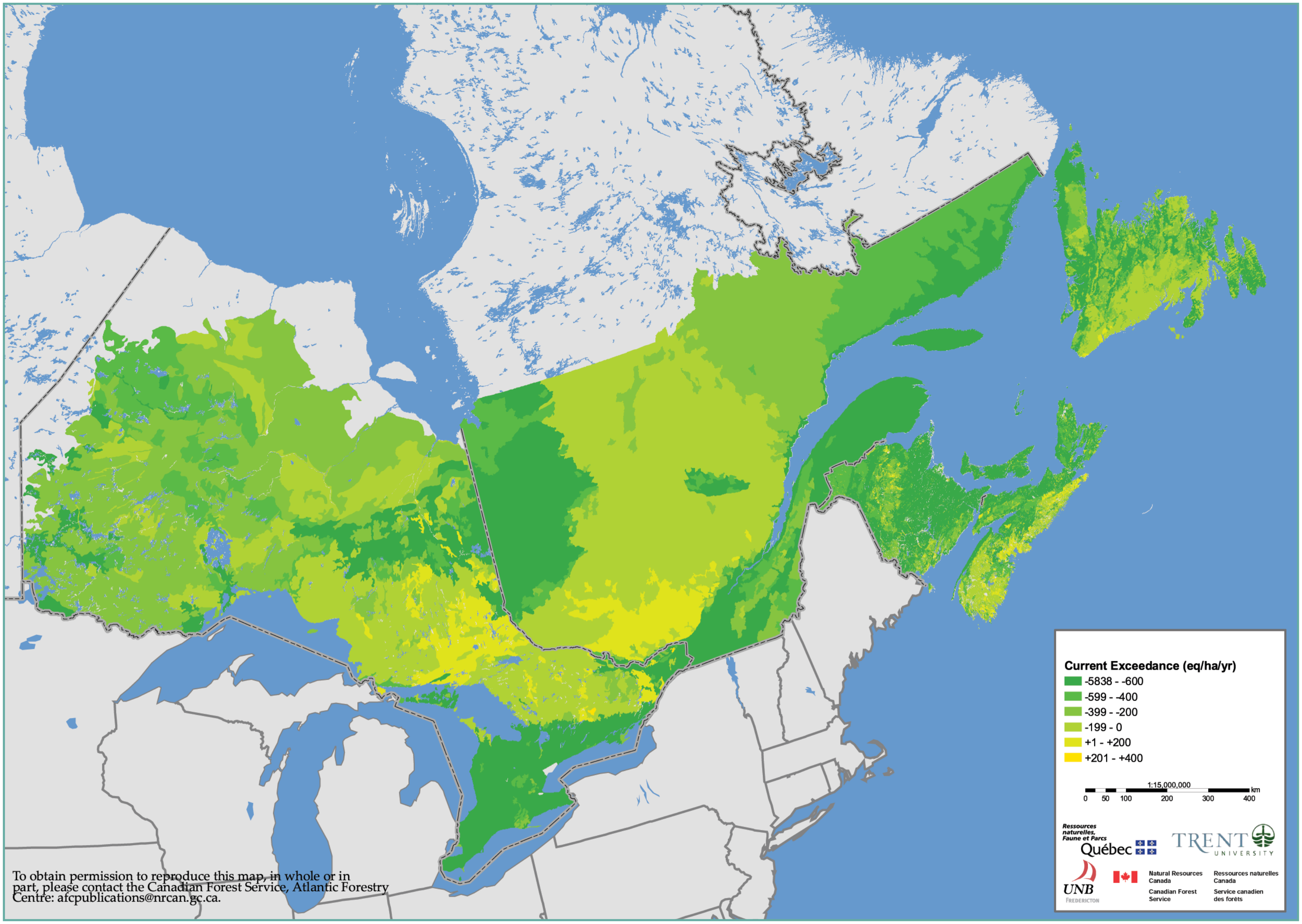

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Figure 8.6a: Upland forest soil current or N-leaching exceedances for southeastern Canada in eq/ha/yr assuming no forest harvesting.

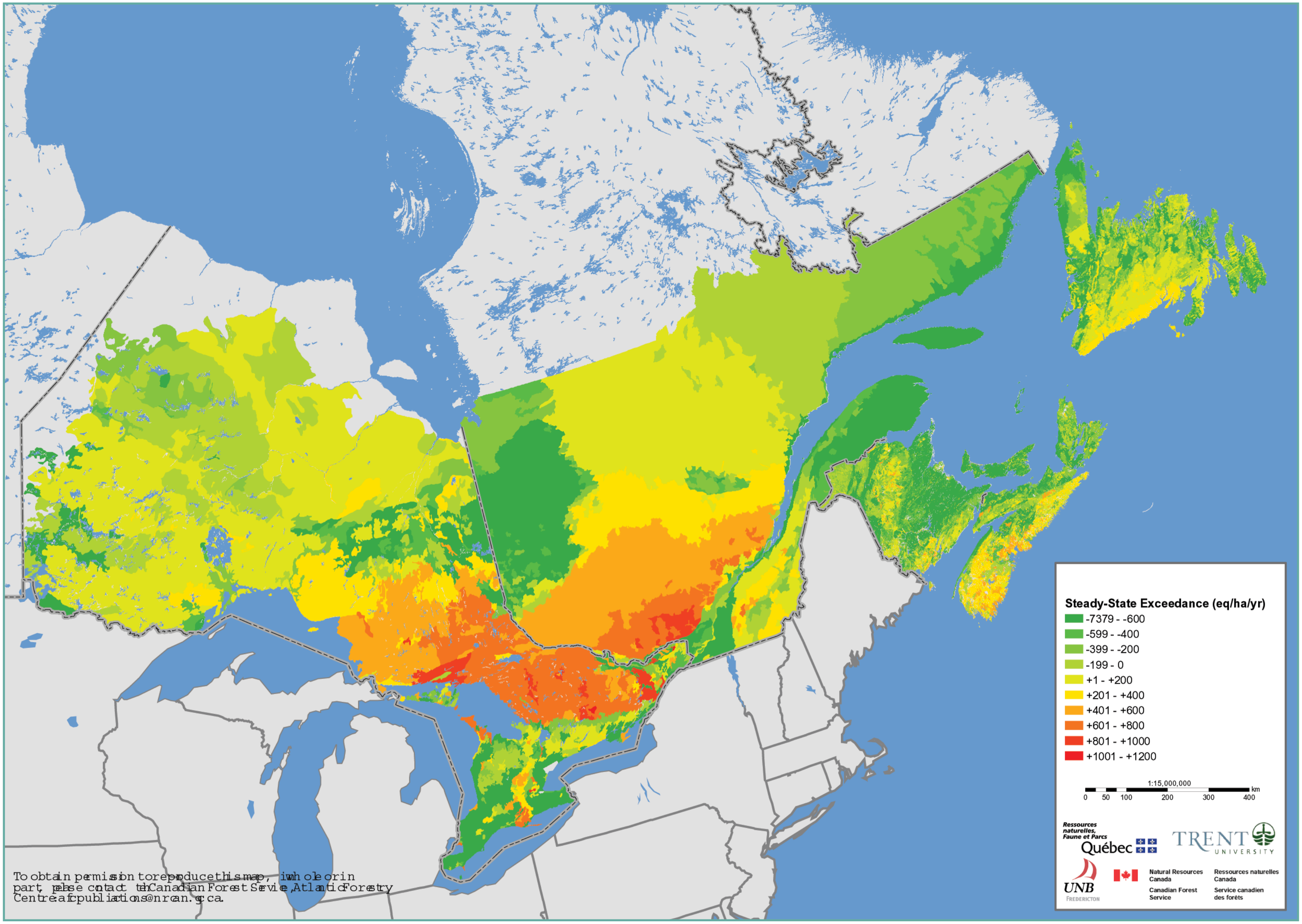

Figure 8.6b: Upland forest soil Steady-state CL exceedances for southeastern Canada in eq/ha/yr assuming no forest harvesting.

ON and southern QC, especially in the Lower-Laurentides north of the St. Lawrence River.

Locations with high Steady-state exceedances likely identify areas where forests are stressed because of past acid- and base-cation losses from soils, and where water that percolates through these soils may have a low bicarbonate to SO_4^{2-} ratio. They may also have a high Al and low Ca^{2+} content. The possibility that high Steady-state exceedances leads directly or indirectly to poor forest health appears strong because calculated Steady-state exceedance values generally correlate significantly with plot-specific canopy transparencies, mortalities, and forest productivities (see Chapter 5).

8.4.5 Combined critical load and exceedance maps

The aquatic and upland forest soil CL maps were combined in Figure 8.7 using the grid square format as described in Section 8.3.3.3. This map is the first of its kind ever produced in North America. It provides far greater spatial coverage and detail than in past assessments. Note the index map (lower left corner of Figure 8.7) that identifies which CL analysis specified the value in a given square. Only aquatic CLs were calculated in the western provinces, and there were many squares in eastern Canada where only a forest soil value was available. The lowest (red) CL squares occur predominantly in Atlantic Canada, although there are also two squares in ON and one in SK; they were all contributed by the aquatic analysis. Both the aquatic and forest soil analyses contributed squares to all of the other CL classes in Figure 8.7. There were some squares in Figure 8.7 where forest soil CLs were selected because they had lower values than the corresponding aquatic CLs. The terrain in such squares is probably characterized by shallower soils.

The four lowest classes in Figure 8.7 (red, orange, yellow and yellow-green grid squares) roughly cover the 1983 target load of 20 kg wet SO_4^{2-}/ha/yr (400 eq/ha/yr = 19.2 kg SO_4^{2-}/ha/yr) although recall that the CL values shown here are expressed as total (wet + dry) deposition. Grid

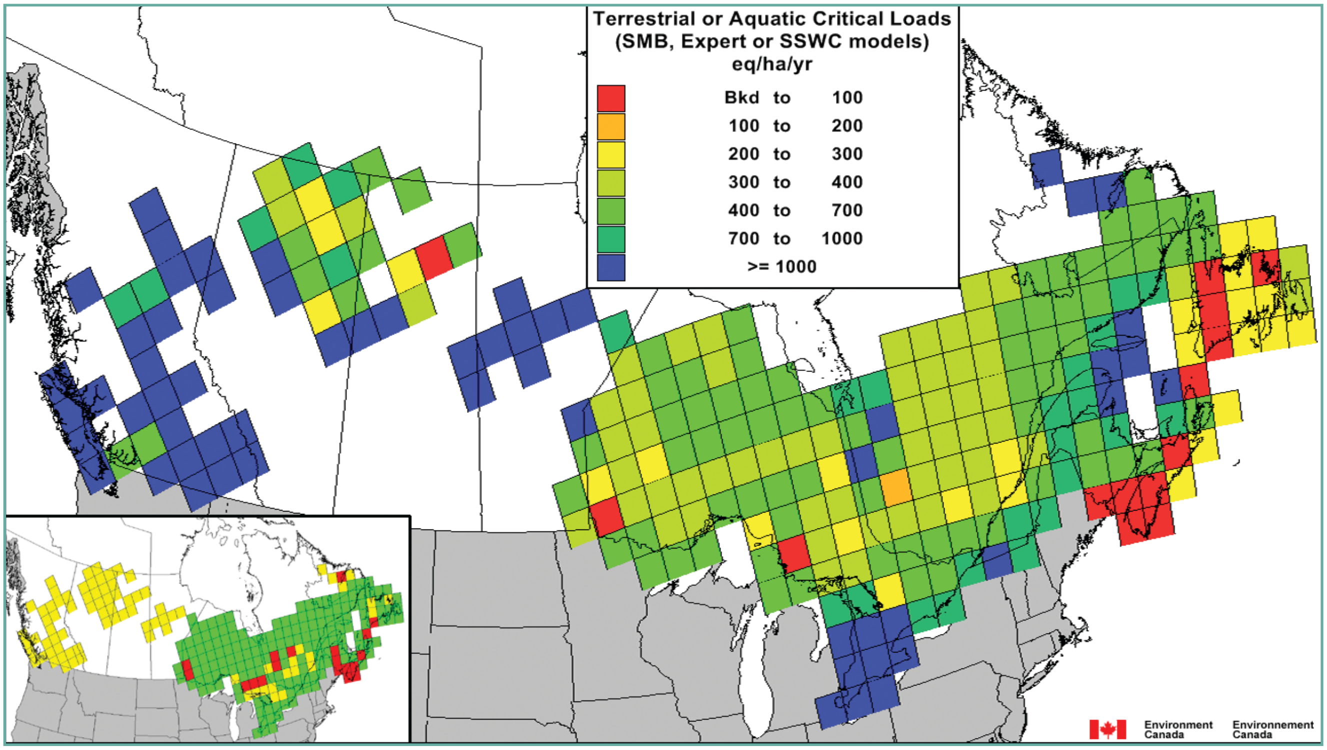

Figure 8.7: Aquatic or upland forest soil CLs (wet + dry deposition in eq/ha/yr) for acidity (S + N) calculated using either the Expert or SSWC or SMB models according to the selection protocol described in Section 8.3.3.3. The index map (lower left) indicates the model selected for each grid square: red = Expert, yellow = SSWC, green = SMB. The CL value for a given square is either the 5th percentile lake value or the 5th percentile soil polygon value. The forest soil component was obtained by laying the grid over the soil polygon CL map shown in Figure 8.4.

squares from these classes occur throughout all of the eastern provinces and in northern SK and AB as well. The map could be improved by determining forest soil CLs in western Canada and conducting new lake surveys in both the east and west to improve the spatial coverage and representativeness of the lake chemistry database.

The combined current or N-leaching exceedance map is shown in Figure 8.8a and the percent of mapped grid area in each province by exceedance class is given in Table 8.5. Approximately 0.5 million km^2 (some in all eastern provinces) currently receives acidic deposition in excess of forest soil or lake CLs. This corresponds to 21% of the mapped area in eastern Canada (~2.4 million km^2) or 15% of the country-wide mapped area (3.3 million km^2). In fact, 14% of the eastern grid area is exceeded by >100 eq/ha/yr (equivalent to >4.8 kg SO_4^{2-}/ha/yr). Fifteen percent of the eastern mapped area has only slightly negative exceedances (-100 to 0 eq/ha/yr class). Hence, even a small increase in runoff NO_3^- concentrations due to the cumulative effect of N deposition or the influence of some other ecosystem interaction (e.g., climate change) could greatly increase the size of the exceeded area. Further reductions in S deposition would prevent this from happening. Squares showing maximum N-leaching exceedance (300-600 eq/ha/yr class in Figure 8.8a) are all defined by aquatic ecosystems. That is, almost all ecosystems with *extremely* low CLs (and therefore higher exceedances) are lakes rather than forest soils. This may not have been the case if the soil CLs had included forest harvesting and/or fire.

These N-leaching exceedance values are numerically larger than those presented in past assessments. This is primarily due to the fact that they are expressed here in terms of total (wet + dry) deposition and the dry component is now considered much larger than before (see Chapter 3). No N-leaching exceedances were found in western Canada, but the information available to make this conclusion does not properly represent much of the sensitive terrain known to exist in the west.

If it is assumed that all N deposition will eventually become acidifying (i.e., the Steady-state assumption), then the eastern exceedance grid has a dramatically different appearance (Figure 8.8b). Note that the second figure in the pairs of numbers in Table 8.5 is the percent of mapped area for Steady-state exceedance. Positive Steady-state exceedances occur over ~1.8 million km^2 (75%) of the mapped area in southeastern Canada. Maximum exceedance (>600 eq/ha/yr equivalent to >29 kg SO_4^{2-}/ha/yr) occurs over 0.33 million km^2 in southern NS and NB, southwestern QC and south-central ON (equivalent to 14% of the mapped area). Red squares showing maximum Steady-state exceedance originate from both aquatic and forest soil ecosystems. Expansion of the Steady-state exceeded area relative to the current

Table 8.5. Percent of mapped grid area in each province for the N-leaching exceedances shown in Figure 8.8a. For the eastern provinces only (i.e., Ontario east), the second number is the percent of mapped grid area for Steady-state exceedances shown in Figure 8.8b. PEI's N-leaching exceedance falls 100% within the –600 to –300 class, and its Steady-state exceedance falls 100% within the –300 to –100 class. Grid area located over open water (e.g., the ocean, Great Lakes, etc.) or U.S. territory was excluded from the percent calculation, as was area in a given province derived from lakes falling entirely outside that province's boundary (applicable to the western provinces only).

Exceedance Class (eq/ha/yr)	BC (%)	AB (%)	SK (%)	MB (%)	ON (%)	QC (%)	NB (%)	NS (%)	NL (%)	Overall (%)	East (%)
< -600	93	49	34	100	4, 1	9, 5	14, 2	0, 0	16, 16	25	8, 4
-600 to -300	4	23	34	0	9, 1	20, 9	14, 2	0, 0	34, 16	16	17, 6
-300 to -100	3	28	21	0	48, 2	39, 11	20, 12	32, 0	17, 18	32	39, 8
-100 to 0	0	0	11	0	16, 5	13, 10	41, 12	0, 0	16, 8	11	15, 7
0 to 100	0	0	0	0	9, 23	10, 22	0, 0	5, 0	0, 9	6	8, 20
100 to 300	0	0	0	0	11, 34	10, 14	0, 61	23, 32	18, 16	8	11, 25
300 to 600	0	0	0	0	3, 16	0, 17	10, 0	40, 28	0, 18	2	3, 17
> 600	0	0	0	0	0, 18	0, 12	0, 10	0, 40	0, 0	0	0, 14

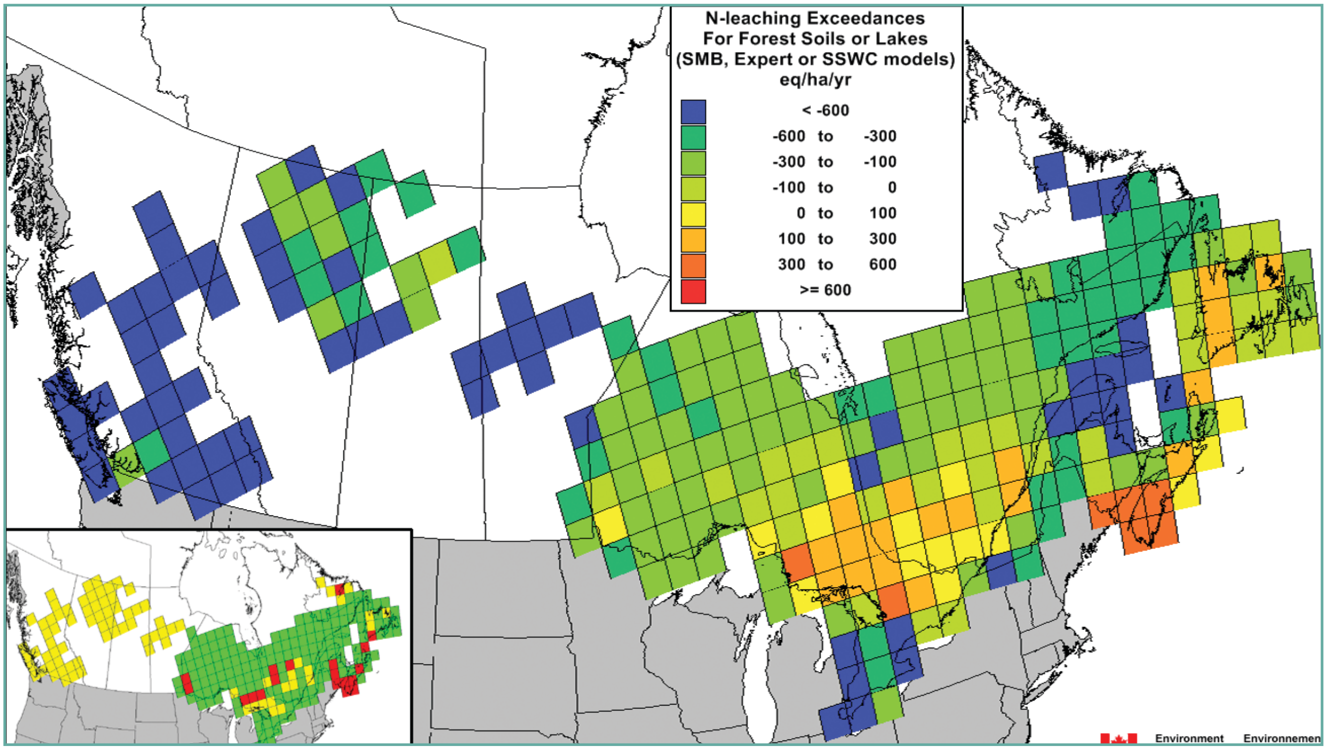

Figure 8.8a: Aquatic or upland forest soil N-leaching exceedances (eq/ha/yr) for acidity (S + N) calculated using either the Expert or SSWC or SMB models. The index map (lower left) indicates the model selected for each grid square: red = Expert, yellow = SSWC, green = SMB. The forest soil component was obtained by laying the grid over the soil polygon exceedance map shown in Figure 8.6a.

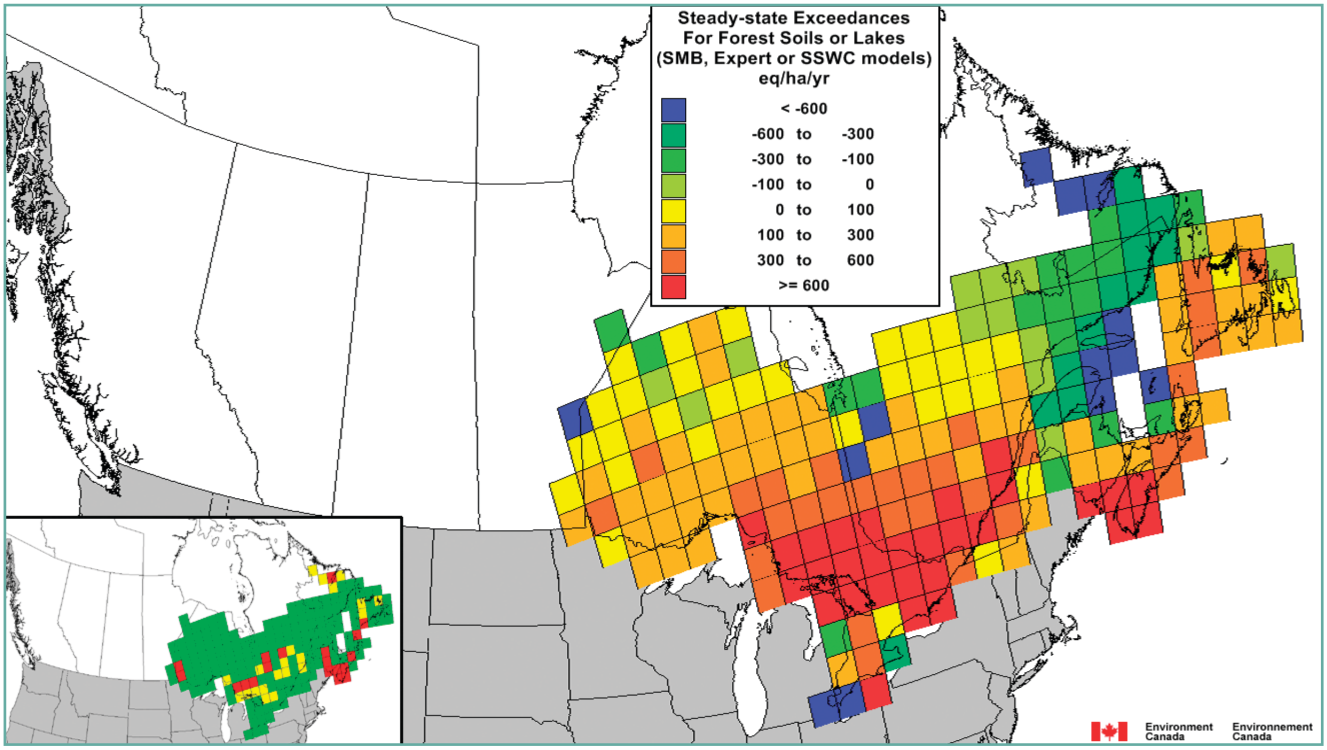

Figure 8.8b: Aquatic or upland forest soil Steady-state exceedances (eq/ha/yr) for acidity (S + N) calculated using either the Expert or SSWC or SMB models. The index map (lower left) indicates the model selected for each grid square: red = Expert, yellow = SSWC, green = SMB. The forest soil component was obtained by laying the grid over the soil polygon exceedance map shown in Figure 8.6b.

or N-leaching area occurred principally in ON, southwestern QC and NL (not Labrador).

Whether considering N-leaching or Steady-state exceedances, the answer to the question posed in the title of this chapter is that aquatic and forest soil CLs are currently being exceeded throughout southeastern Canada. Further reductions in deposition will be needed to reduce them.

8.5 SUMMARY

The following points summarize the important components and conclusions of our assessment of aquatic and forest soil CLs and their present exceedances:

- For more than 20 years Canada has used ecosystem CLs in the eastern provinces to set deposition targets for emission control programs. Originally considering only S-based acidification of aquatic ecosystems, the original 1983 "target" load of 20 kg wet SO_4^{2-} was reduced by both the 1990 and 1997 Assessments as information and knowledge increased.
- Present-day CLs need to consider both the S and N components of acidic deposition. In this assessment, CLs of acidity (S+N) were determined for both lakes and upland forest soils using steady-state models. Because both acidifying pollutants are included, the CLs and their exceedances must now be expressed as eq/ha/yr or related unit (1 kg SO_4^{2-}/ha/yr = 20.8 eq/ha/yr). Readers who are familiar with the "old" reporting units (kg/ha/yr) must always keep in mind this shift in reporting units from past practice. In addition, the CLs determined in this chapter are expressed in terms of total (wet + dry) deposition. Previous assessments had expressed aquatic CLs in terms of wet SO_4^{2-} deposition only.
- In order to determine a CL, two quantities must be selected: a chemical threshold that defines the onset of ecosystem damage, and the desired degree of ecosystem protection. For aquatic ecosystems, pH = 6 and/or alkalinity = 40 μeq/L were selected as threshold values. Some lakes (predominantly located in Atlantic Canada) were unlikely to have ever met these threshold conditions. In the CL analysis presented here, such lakes were assigned background deposition as their CLs (approximately 40-60 eq/ha/yr). For forest soils, a critical alkalinity-leaching rate was used as the threshold. It was estimated from the base cation to aluminum ratio in the soil water. For both aquatic and terrestrial ecosystems, a 95% protection level was used when calculating the CLs.
- A lake chemistry database was assembled for all provinces except PEI and CLs calculated using one or both of two water chemistry models. When both models were used, the lower CL value was selected to represent the lake. The CL data were mapped by overlaying the MSC deposition grid and selecting the 5th percentile value of all lakes falling within a given grid square. The CL exceedance was calculated as the difference between a lake's acidifying deposition and its CL. The acidifying deposition was estimated in two ways: first, by the sum of wet + dry S deposition plus N-based acidification estimated by NO_3^- leaching; second, by the sum of all wet + dry S and N deposition. The former was termed the "N-leaching" exceedance and corresponds to the current exceedance. The latter was termed the "Steady-state" exceedance since it assumes a N saturated steady-state in which all N deposition is acidifying.
- Terrestrial ecosystem CLs were calculated for the eastern provinces using a steady-state mass balance model that considers the acid producing and consuming processes operating in upland forest soils. Forest harvesting and fire were not considered when calculating the CLs. Both would reduce the CL values, and therefore, the CLs determined here are overestimates. Existing databases of soil information were used as model inputs and a CL value determined for every soil polygon present in the databases. The two exceedance estimates as described above were also calculated. This information was mapped using GIS technology, and subsequently gridded for combination aquatic CL data.
- Provincial aquatic CL values range from background deposition in NL, NS and NB to 1620 eq/ha/yr in MB. These results agree well with other CL analyses conducted since the 1997 Assessment. Critical load values that are less than the old target load

occur in all provinces except MB and BC (their lake chemistry databases do not adequately cover acid sensitive terrain, however).

- Upland soil CLs in the eastern provinces range from 135 to 7980 eq/ha/yr. Lowest values occur where soils are shallow, coarse-textured and derived from felsic or granitic bedrock as commonly occurs on the Canadian Shield. Calcareous soils have high CL values.
- Current (N-leaching) exceedances were determined for sample lakes. Highest exceedances (>300 eq/ha/yr) were identified for 11% of the mapped grid squares in eastern Canada (located in southern NS/NB, central ON and south-central ON). Moderate exceedances (100-300 eq/ha/yr) occurred in 27% of the grid squares distributed across all eastern provinces except NB. Low exceedance squares (0-100 eq/ha/yr) were identified in QC and ON, including one in the relatively low deposition area in northwestern ON. No CL exceedances were identified among sample lakes in western Canada.
- The 95th percentile of the Steady-state exceedances for forest soils in the eastern provinces ranged from -126 eq/ha/yr (PEI) to 695 eq/ha/yr (ON). On average, positive Steady-state exceedances covered ~52% of the mapped area of upland forest soils in southeastern Canada.
- The current (N-leaching) exceedances for forest soils in the eastern provinces suggest that concern focus on NL, NS, QC and ON in the short term. The majority of PEI and NB soils can currently buffer the incoming acidity in the short term. However, these exceedance values do not include acidification associated with forest harvesting and nitrification of ammonia deposition. These factors must be better quantified in order to more accurately assess current exceedances for upland forest soils.
- Combined aquatic-terrestrial CL and exceedance maps were produced for the first time in North America. Positive N-leaching exceedances occur in 21% of the mapped grid area of eastern Canada, corresponding to ~0.5 million km^2. This estimate best represents the present situation. Positive Steady-state exceedances occur in 75% of the mapped area in eastern Canada, corresponding to ~1.8 million km^2. This estimate represents a future situation at current levels of acid deposition where ecosystems are N saturated. Either way, further reductions in acidic deposition are needed to reduce the extent of these exceedances.
- Future assessments of CLs and exceedances would benefit from: using base cation weathering estimates rather than the F-factor in aquatic models, improving the representativeness of lake chemistry data sets (particularly in western and northern Canada), including the effects of fire and harvesting in the soil models, and extending the forest soil analyses to western Canada.

8.6 ACKNOWLEDGEMENTS

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CHAPTER 9

The Effects of Acid Deposition on Human Health

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9.1 KEY MESSAGES

- Recent epidemiological studies generally found small but significant associations between ambient aerosol acidity and the following outcomes: respiratory symptoms, impaired lung function, hospital admissions and emergency room visits, and premature mortality. Susceptible sub-populations were identified for the different health outcomes. It is possible that some of the toxicity of particulate matter (PM) might be attributable to aerosol acidity, however a strong colinearity was generally observed between measured components of PM. This colinearity confounded the attribution of specific components of PM to observed effects.
- New clinical studies indicate that subjects with asthma or allergies may be particularly sensitive to short-term exposure to acid aerosols alone, or to sequential exposure to sulphuric acid and ozone, compared with normal subjects. However, exposure levels in clinical studies were generally higher than levels measured in Canadian cities.
- Results from recent toxicological studies suggest that exposure to acid aerosols can produce effects on host-defence related endpoints at concentrations close to those observed in eastern Canada. The effects of pollutant mixtures on health endpoints can either increase or decrease compared with the effects of exposure to individual pollutants depending on the pollutants studied, the relative concentrations of individual pollutants in mixtures and, the endpoints measured.

9.2 INTRODUCTION

This chapter is a follow-up to the 1997 Canadian Acid Rain Assessment (Volume 5: The Effects on Human Health) (Environment Canada, 1997). This previous assessment investigated the direct and indirect health effects of sulphur dioxide (SO_2) and its derivatives — sulphate (SO_4^{2-}), particulate matter (PM) and acid aerosols (H^+) — and included studies up to 1995; it also indicated future research directions. The present document includes all relevant peer-reviewed scientific literature published from 1995 to June 2003 on the direct health effects of SO_4^{2-} and particle and gaseous H^+, and attempts to identify new key findings. Tables summarizing the location, time frame, variables, design, results and comments of studies referenced in the present chapter are available upon request from Environment Canada **(downsview.library@ec.gc.ca)**.

9.3 CONCLUSIONS OF THE 1997 ASSESSMENT

The 1997 Canadian Acid Rain Assessment (Volume 5: The Effects on Human Health) reached the following conclusions:

1. Epidemiological studies provided strong evidence that ambient particle pollution was associated with increased human respiratory and cardiovascular mortality. It stated that aerosol acidity may contribute to the associations between PM and human mortality, but the key reactive component(s) of PM responsible for ambient particle-induced increases in mortality remained undetermined.
2. Epidemiological studies were suggestive of acute and chronic effects from PM pollution (on respiratory and cardiac hospital admissions, respiratory symptoms and pulmonary function) that appeared to be larger in infants, elderly people and in symptomatic groups such as asthmatics. In some studies, strong acidity of aerosols appeared to contribute significantly to the effects observed, while in others H^+ seemed to have a threshold in initiating respiratory illness. It stated that the effects of PM

and of aerosol acidity were difficult to separate, due to a strong colinearity between the pollutants measured.

3. In response to acid aerosol exposure, the only effects seen in clinical studies were mild decrements in pulmonary function in asthmatics (a susceptible subgroup). Elderly subjects and subjects with Chronic Obstructive Pulmonary Disease (COPD) did not appear to be at higher risk than younger subjects, even while doing mild exercise.
4. Toxicological investigations showed that very high concentrations of acid aerosols (in the range of mg/m^3) were required to induce animal mortality and acute morphological alterations. Biological mechanisms of sulphuric acid (H_2SO_4) effects were characterized as immunosuppression, bronchial hyperreactivity and changes in mucociliary movement. Short-term exposure to 75 μg/m^3 H_2SO_4 aerosol attenuated the release of reactive mediators involved in maintaining the reactivity of pulmonary alveolar macrophages.
5. Toxicological studies indicated that the type of interaction between acid species and other air pollutants depended on the endpoint measured and the duration of the exposure.

9.4 EPIDEMIOLOGICAL STUDIES

Recent epidemiological studies investigating the association between aerosol acidity and human health effects have generally looked into the effects of SO_4^{2-} and/or H^+ as part of a broader analysis involving multiple PM components. It is therefore noteworthy that not all studies measured both SO_4^{2-} and H^+. A majority of these studies took place in eastern North America, using measured concentrations of pollutants compatible or relevant to Canadian situations. Data from many of the time-series studies were reanalyzed and included in this document, due to reported problems with the use of the Generalized Additive Models (GAM) with non-parametric smoothing functions to adjust for confounding by time trends and weather. The use of GAM can lead to biased estimates of regression coefficients and standard errors, and substantially overstate the risk estimate. The basic conclusions of the original studies were generally unchanged following reanalysis (unless stated otherwise in this chapter).

9.4.1 Association with mortality

Overall, small but significant associations between ambient SO_4^{2-} and total and cardio-respiratory mortality, without apparent threshold, were found in new publications. These findings support conclusions drawn in the previous assessment. Few studies investigated the effects of H^+ on mortality; no obvious threshold was observed. However, a strong colinearity was generally seen between the pollutants measured, making it difficult to separate the effects of the multiple PM components (Gauderman et al., 2002; Anderson et al., 2001; Goldberg et al., 2001,2000; Gwynn and Thurston, 2001; Gauderman et al., 2000; Gwynn et al., 2000; Hoek et al., 2000; Lipfert et al., 2000; Lippmann et al., 2000; Shwartz and Neas, 2000; Stieb et al., 2000; Honma et al., 2000; van der Zee et al., 2000, 1999; Fairley, 1999; McConnell et al., 1999; Naeher et al., 1999; Neas et al., 1999, 1996, 1995; Peters et al., 1999a, 1999b, 1996; Burnett et al., 1988, 1997, 1995; Korrick et al., 1998; Tanaka et al., 1998, 1996 ; Delfino et al., 1997; Peters et al., 1997a, 1997b; Thurston et al., 1997; Dockery et al., 1996; Raizenne et al., 1996; Schwartz et al., 1996; Stieb et al., 1996; Hoek and Brunekreef, 1995; Studnicka et al., 1995).

Six cities in the eastern U.S. were considered in a study on mortality and fine particulates between 1979 and 1987. In single-pollutant models, a 5th to 95th percentile increment of 17 μg/m^3 in SO_4^{2-} (1 μg/m^3 SO_4^{2-}=0.0961 nmol/m^3 SO_4^{2-}) was associated with a 3.8% (95%CI= 2.2-5.5) increase in daily deaths, while the association between a 5th to 95th percentile increment of 57.3 nmol/m^3 in H^+ and mortality was not statistically significant (1.2%, 95%CI=-2.0-4.3). SO_4^{2-} concentrations were not directly measured, as they were estimated from the measured SO_2 concentrations. Mortality stratified by age and cause of death was not analyzed (Schwartz et al., 1996; Schwartz, 2003).

In another study, the association between acidic PM and mortality between 1988 and 1990 was investigated in the Buffalo, New York region. Relative risks (RRs) for each pollutant's most significant lag were computed for the maximum minus mean increment (H^+=345.5 nmol/m^3, SO_4^{2-}=328.8 nmol/m^3). Pollutants most strongly associated with respiratory mortality in single-pollutant models were H^+ (RR=1.54, 95%CI=1.09-2.20) and SO_4^{2-}

(RR=1.24, 95%CI=1.01-1.52). H^+ and SO_4^{2-} were not significantly associated with circulatory mortality, but were associated with total non-accidental mortality. Those associations were still statistically significant in two pollutant models with carbon monoxide (CO), nitrogen dioxide (NO_2), ozone (O_3) or SO_2. This study used non-parametric smoothing in GAM, but results were not reanalyzed (Gwynn et al., 2000).

Lippmann and coworkers included two periods in their analysis (1985-1990 and 1992-1994) in order to study various fractions of PM and their relation to daily mortality in Detroit. For the 1992-1994 period, during which both H^+ and SO_4^{2-} were measured, no significant associations were seen between 5th to 95th percentile increments of 40 nmol/m^3 for H^+ and 165 nmol/m^3 for SO_4^{2-} and mortality (Lippmann et al., 2000; Ito, 2003).

In Philadelphia, the association between different PM fractions and mortality between 1992-1995 was investigated. Mean concentrations were 55.5 nmol/m^3 for SO_4^{2-} and 8.3 nmol/m^3 for H^+. Associations were seen between SO_4^{2-} and cardiovascular mortality (RR=1.0406, t=3.27; t_{crit}=1.96) and H^+ and cardiovascular mortality (RR=1.0271, t=2.66; t_{crit}=1.96); however, those values were no larger than for other particles investigated (Lipfert et al., 2000).

Some studies included measures of SO_4^{2-}, but not of H^+, in their analysis. For example, in an attempt to identify subgroups at greater risk from exposure to particulates, a time-series study of daily ambient air pollutant concentration and mortality rate between 1984 and 1993 in Montreal was conducted. Associations were found between daily measures of SO_4^{2-} and a number of conditions, including respiratory and cardiovascular diseases, diabetes and total mortality. Associations were generally stronger among people over 65 years of age. The original analysis used the non-parametric GAM; reanalysis was performed on subgroups in the original study that showed associations with particles. Reanalysis with natural splines to control for weather had a profound effect on these associations, which were attenuated (compared to the original study) and generally became non-significant (Goldberg et al., 2000; Goldberg et al., 2001; Goldberg and Burnett, 2003).

A time-series study was conducted to study the association between ambient CO levels and daily mortality in Toronto between 1980 and 1994; it found associations between a 5th to 95th percentile increment of 13.3-µg/m^3 in SO_4^{2-} and non-accidental mortality in single-pollutant model (RR=1.024, 95%CI=1.011-1.038) and in two-pollutant models with CO (RR=1.018, 95%CI=1.004-1.031). The study used non-parametric GAM, but results were not reanalyzed (Burnett et al., 1998).

A time-series study in California including data from 1989-1996 found associations between SO_4^{2-} (mean ± standard deviation (SD)= 1.8 ± 1.3 µg/m^3) and total (RR=1.05, $p<0.05$) and respiratory (RR=1.15, $p<0.05$) mortality in single-pollutant models. The association for total mortality was stronger in the summer (RR=1.11, $p<0.05$) than in other seasons, but was not significant in two pollutant models with $PM_{2.5}$ or nitrate (NO_3) (Fairley, 1999, 2003).

Data from 1994 to 1996 for the United Kingdom showed that a 5.8 µg/m^3 increment in SO_4^{2-} was not associated with total, respiratory and cardiovascular mortality in an all-year analysis, but all-cause mortality showed a positive effect in the warm season (p=0.001). It is unsure if the effects estimates and standard errors are affected by the issues identified with the use of non-parametric smoothing functions in GAM (Anderson et al., 2001).

A time-series analysis for the Netherlands between 1986 and 1994 found significant associations between the sum of NO_3^- and SO_4^{2-} (approximate ranges of 25 and 35 µg/m^3, respectively) and total daily mortality (RR=1.043, 95%CI=1.014-1.073) and SO_4^{2-} and total mortality (RR=1.032, 95%CI=1.006-1.059) in single-pollutant models, with larger associations seen in the summer than in the winter months. The associations were still significant in several two-pollutant models with O_3, CO, PM_{10} or black smoke (BS). The association with cause-specific mortality (cardiovascular, COPD and pneumonia) was not statistically significant for SO_4^{2-}, but was significant for the sum of SO_4^{2-} and NO_3^- and pneumonia (RR: 1.175, 95%CI=1.006-1.372) (Hoek et al., 2000; Hoek, 2003).

9.4.2 Association with morbidity

The following conclusions of the previous assessment remain unchanged: exposure to elevated ambient PM concentrations has been related to increased hospital admissions for respiratory and cardiac diseases, increased incidence and duration of respiratory symptoms, and declines in lung function. It is likely that the toxicity of the PM mixture might be attributable in part to aerosol acidity, although it was stated in the 1997 Assessment that the effects of PM and of aerosol acidity were difficult to separate, due to a strong colinearity between the pollutants measured. The results of recent studies are suggestive of increased respiratory and cardiac hospital admissions, particularly in susceptible subpopulations such as infants and the elderly in response to exposure to acid aerosols. In general, larger effects in children than in adults were observed in recent studies on lung function and respiratory symptoms. No obvious threshold was observed in morbidity effects (Gaulderman et al., 2002; Anderson et al., 2001; Goldberg et al., 2001,2000; Gwynn and Thurston, 2001; Gauderman et al., 2000; Gwynn et al., 2000; Hoek et al., 2000; Lipfert et al., 2000; Lippmann et al., 2000; Shwartz and Neas, 2000; Stib et al., 2000; Honma et al., 2000; van der Zee et al., 2000, 1999; Fairley, 1999; McConnell et al., 1999; Naeher et al., 1999; Neas et al., 1999, 1996, 1995; Peters et al., 1999a, 1999b, 1996; Burnett et al., 1988, 1997, 1995; Korrick et al., 1998; Tanaka et al., 1998, 1996 ; Defino et al., 1997; Peters et al., 1997a, 1997b; Thurston et al., 1997; Dockery et al., 1996; Raizenne et al., 1996; Schwartz et al., 1996; Stieb et al., 1996; Hoek and Brunekreef, 1995; Studnicka et al., 1995).

9.4.2.1 *Association with hospital admissions and emergency department visits*

Burnett and coworkers conducted a longitudinal analysis for Toronto, and found associations between increases in the interquartile ranges (IQR) of H^+ (5.25 nmol/m^3) and SO_4^{2-} (40.00 nmol/m^3) on respiratory and cardiac admissions in 1992-1994. The relationships were no longer significant in multi-pollutant models including O_3, NO_2, SO_2 or CO (Burnett et al., 1997).

A time-series analysis conducted for the summers of 1992-1993 in Montreal found an association between an increase in mean H^+ (4.0 nmol/m^3) and emergency room visits for respiratory illnesses in children under 2 years of age (5%, 95%CI=0.4-9.6%). The association was still significant when SO_4^{2-} was added in the model. An association was also seen between an increase in mean SO_4^{2-} (34.8 nmol/m^3) and emergency room visits for respiratory illnesses in patients over 65 years of age (6.1%, 95%CI=0.8-11.5%) (Delfino et al., 1997).

A study in Saint John, New Brunswick looked at daily emergency department (ED) visits in 1992-1996 for cardiorespiratory conditions. In single-pollutant models, SO_4^{2-} was associated with increases in respiratory ED visits for all-year (mean ± SD= 31.1 ± 29.7 nmol/m^3; p=0.034) and summer (mean ± SD= 38.7 ± 37.5 nmol/m^3; p=0.032) analyses and with decreases in cardiac ED visits in all-year (p=0.001) and summer (p=0.014) analyses. All-year (mean ± SD= 25.7 ± 36.8 nmol/m^3) and summer (mean ± SD= 38.6 ± 47.0 nmol/m^3) H^+ were also associated with decreases in respiratory (all year: p=0.0005; summer: p=0.0004) and cardiac (all-year: p=0.010; summer: p=0.008) ED visits in single-pollutant models. In the final multi-pollutant model, constructed using a backward stepwise procedure, an association was seen between mean SO_4^{2-} and a decrease in cardiac ED visits for the summer months (-7.3%, 95%CI=-12.2 to -2.1%). When all-year analyses were stratified by specific diagnosis, H^+ and SO_4^{2-} were both associated with increases in dysrhythmia and asthma ED visits; SO_4^{2-} was also associated with increases in COPD, respiratory infection and total respiratory ED visits. No reanalysis was performed for the use of non-parametric GAM (Stieb et al., 2000).

The association between acidic PM and hospital admissions in 1988-1990 was also investigated in the Buffalo, New York region. Maximum minus mean increment of H^+ (345.5 nmol/m^3) and SO_4^{2-} (328.8 nmol/m^3) showed coherent associations with respiratory (H^+: RR=1.31, 95%CI=1.14-1.51; SO_4^{2-}: RR=1.178, 95%CI=1.09-1.28), but not circulatory hospital admissions. These associations were still statistically significant in two-pollutant models with CO, O_3, SO_2 or NO_2. It is noteworthy that the same study also found statistically significant associations between H^+ and SO_4^{2-} and total and respiratory mortality. No reanalysis was performed for the use of non-parametric GAM (Gwynn et al., 2000).

Another study, by the same team of investigators taking place in New York City during the same period, found a positive association between a 340.9 nmol/m^3 maximum minus mean increase in SO_4^{2-} levels and respiratory hospital admissions for non-whites (RR=1.072, 95%CI=1.011-1.136). The association between a 251 nmol/m^3 maximum minus mean increase in H^+ and respiratory hospital admissions for non-whites was not statistically significant. The authors concluded that within-race analyses suggested that most of the apparent differences in air pollution effects found between races were explained by socio-economic and/or health care disparities. No reanalysis was performed for the use of non-parametric GAM (Gwynn and Thurston, 2001).

Lippmann and coworkers included hospital admissions in their analysis of 1992-1994 data in Detroit. While they found no association between any PM metric and mortality, they did find associations for H^+ and pneumonia in the elderly (RR=1.060, 95%CI=1.005-1.118), SO_4^{2-} and pneumonia in the elderly (RR=1.156, 95%CI=1.050-1.273), H^+ and COPD (RR=1.067, 95%CI=1.000-1.138), and SO_4^{2-} and heart failure (RR=1.091, 95%CI=1.012-1.176). Those associations were still significant in several two-pollutant models with O_3, SO_2, NO_2 and CO. No significant associations were found for H^+ and SO_4^{2-} and ischemic heart disease, stroke and dysrhythmia (Lippmann et al., 2000; Ito, 2003).

Some studies included measures of SO_4^{2-} but not H^+ in their analysis. For example, a time-series analysis was conducted in southern Ontario in order to study the association between daily admissions for cardiac and respiratory illnesses and ambient SO_4^{2-} in 168 hospitals between 1983 and 1988. A 13 µg/m^3 increase in SO_4^{2-} recorded on the day prior to admission was associated with increases in respiratory admissions of 3.5% (95%CI=2.3-4.7) and cardiac admissions of 3.3% (95%CI=1.7-4.8) for the entire sample when adjusted for O_3 and temperature. Increases were observed for all age groups, and were higher in males than in females (Burnett et al., 1995).

However, another Canadian study showed no significant association between SO_4^{2-} (mean=5.5 µg/m^3, max=14 µg/m^3) and ED visits for asthma in Saint John, New Brunswick between 1984 and 1992. Since the number of sampling days for SO_4^{2-} was limited, the authors indicated that an association between particles and asthma ED visits could not be ruled out (Stieb et al., 1996). Furthermore, a time-series analysis of emergency hospital admissions and environmental data for 1994-1996 was conducted in the UK. A 10th to the 90th percentile increment of 5.8 µg/m^3 in SO_4^{2-} was not significantly associated with respiratory or cardiovascular admissions for the entire sample, or for admissions stratified by age. It is unsure if the results were biased due to non parametric GAM (Anderson et al., 2001).

A cohort study of naturally-occurring fog and hospital admissions in 102 asthmatic patients was performed in Japan in 1992-1993. Fog (pH range=3.32-6.91) occurred in 378 out of 731 days. Hospital visits for asthma increased on foggy days in 8.8% ($p<0.05$) of the adult asthmatics in the study population (Tanaka et al., 1996). Associations between fog (yes *vs.* no) and asthma hospital admissions were seen in both atopic (odds ratio (OR)=1.66, 95%CI=1.09-2.51) and non-atopic (OR=2.50, 95%CI=1.26-4.93) patients (Tanaka et al., 1998).

9.4.2.2 *Association with lung function and respiratory symptoms*

9.4.2.2.1 *Children*

As part of the Harvard/Health Canada 24-City Study, where 18 sites throughout the United States and 6 sites throughout Canada were investigated, cross-sectional analyses of lung function and respiratory symptoms in children aged 8 to 12 (n=10,251) were performed between 1988 and 1991. A 52 nmol/m^3 increase in particle strong acidity (PSA) (1) was associated with decreases in forced vital capacity (FVC) (-3.5%, 95%CI=-4.9 to -2.0), forced expiratory volume in 1 second (FEV_1) (-3.1%, 95%CI=-4.6 to -1.6), forced expiratory volume in 0.75 seconds ($FEV_{0.75}$) (-3.0%, 95%CI=-4.5 to -1.5), forced expiratory flow between 25 and 75% FVC ($FEF_{25-75\%}$) (-3.5%, 95%CI=-6.5 to -0.3) and peak expiratory flow rate (PEFR) (-3.7%, 95%CI=-7.1 to -0.2). Controlling for daytime O_3 had little effect on the association between PSA and FVC. A 6.8 µg/m^3 increase in SO_4^{2-} was also associated with decreases in FVC (3.0%, 95%CI=1.6-4.5), FEV_1 (2.6%,

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[1] The amount of strong acidity equivalent (H_2SO_4) available in the fine particle component (<2.5 µm) of the atmospheric aerosol

95%CI=1.1-4.2) and $FEV_{0.75}$ (2.5%, 95%CI=1.0-4.1) (Raizenne et al., 1996). The same investigators also found associations between increases of 6.8 μg/m^3 in SO_4^{2-} and 52 nmol/m^3 in PSA and a higher reporting of bronchitis in the previous year (SO_4^{2-}: OR=1.65, 95%CI=1.12-2.42; PSA: OR=1.66, 95%CI=1.112.48), as well as between a 2.7 ppb increase in gaseous acids (the sum of nitrous (HNO_2) and nitric (HNO_3) acids) and a higher reporting of asthma in the previous year (OR=2.00, 95%CI=1.14-3.53) (Dockery et al., 1996).

As part of this cohort, the relationship between air pollution and respiratory function in 4th and 5th grade children (n=83) from Pennsylvania communities were also investigated in the summer of 1990. Increases of 125 nmol/m^3 in SO_4^{2-} and PSA were associated with increases in incidence of evening cough episodes (SO_4^{2-}: OR=1.64, 95%CI=1.08-2.50; PSA: OR=1.75, 95%CI=1.23-2.49) and with decreases in PEFR (SO_4^{2-}: -2.81 l/min, 95%CI=-5.08 to 0.54; PSA: 2.44 l/min, 95%CI=-4.06 to -0.83) when adjusted for time spent outdoors during the previous 12 hours. The association between PSA and PEFR was still significant when O_3 was added to the model (Neas et al., 1995). This study was replicated a year later in 4th and 5th grade children (n=108). No significant associations were seen for pulmonary function parameters when the whole study period was considered, but when the analysis was restricted to the 4 weeks when the only major episode of acid aerosol pollution occurred, a 125 nmol/m^3 increment in daytime PSA was associated with a decrease in evening PEFR (-1.0 l/min, 95%CI=1.9 to -0.2). When the whole study period was considered, increments of 125 nmol/m^3 in 12-hour daytime PSA and total SO_4^{2-} particles were associated with the incidence of cough (SO_4^{2-}: OR=1.26, 95%CI=1.00-1.60; PSA: OR=1.19, 95%CI=1.01-1.39) and cold (SO_4^{2}: OR=1.53, 95%CI=1.17-2.00; PSA: OR=1.35, 95%CI=1.14-1.61) episodes (Neas et al., 1996). In a reanalysis of these two previous studies to examine the relative contributions of fine ($PM_{2.1}$) and coarse (PM_{10}-$PM_{2.1}$) particles on children's health effects, an IQR increment of 125 nmol/m^3 for SO_4^{2-} was associated with a decrease in evening PEFR (-1.14 l/min, 95%CI=1.77 to -0.51). SO_4^{2-} was more closely associated with decreases in PEFR (Schwartz and Neas, 2000) than coarse or fine particle mass.

A panel study of children aged 6-11 (n=156) attending two non-residential summer camps in Philadelphia in 1993 found an association between an 8 μg/m^3 increase in 24-hour average SO_4^{2-} and reductions in subsequent morning PEFR (2.44 l/min, 95%CI=-4.51 to -0.36). An increase of 1.5 μg/m^3 of PSA had no effect on PEFR (Neas et al., 1999).

Three panels of children aged 7-13 (n=52, 58, 56) with moderate to severe asthma participating in summer asthma camps in Connecticut during the summers of 1991-1993 were investigated. Mean levels of H^+ of 53.9 nmol/m^3 and of SO_4^{2-} of 7.0 μg/m^3 were not associated with children's daily variation in PEFR, but were associated with children's chest symptom counts (H^+: t=3.44, SO_4^{2-}: t=3.86; t_{crit}=1.65). When temperature was added to the model, the association between H^+ and children's chest symptoms was no longer significant (Thurston et al., 1997).

A 10-year prospective cohort study involving 4th-, 7th- and 10th-grade children from 12 communities in California (selection based on their historical air pollution levels) was initiated in 1993. Several cross-sectional evaluations were conducted throughout the study period in order to explore the effects of air pollutants on lung function parameters (n=3,293) and respiratory symptoms (n=3,676). Inorganic (nitric (HNO_3) and hydrochloric (HCl) acids) and/or organic (formic (CH_2O_2) and acetic (CH_3CO_2H) acids) acid vapour concentrations (2) were estimated for the 1986-1990 period, and measured during the study period starting in 1993. Children in the most polluted communities were compared with children in the least polluted communities. Associations were found between increases in the IQR (1.7 ppb) of inorganic acid vapour and the prevalence of wheeze in males for the 1986-1990 (OR=1.55, 95%CI=1.03-2.32) and 1994 (OR=1.44, 95%CI=1.12-1.87) periods (Peters et al., 1999b). Increases in the IQR of inorganic acid vapour levels for 1994 were also associated with lower regression coefficients for FVC (-44.0, p<0.05), FEV_1 (-36.2, p<0.01), PEFR (139.7, p<0.05) and maximal mid-

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[2] Measured on a mole basis of the specific acids

expiratory flow (MMEF) (-75.5, $p<0.05$) in females in single-pollutant models, with larger effects for girls spending more time outside (Peters et al., 1999a). An association was also found for the 1994 period between an increase of 1.8 ppb in inorganic acid vapour and phlegm in children with asthma (OR=1.9, 95%CI=1.03.6) (McConnell et al., 1999).

Average growth of lung function over a 4-year period in children who were in 4th (n=1,498), 7th (n=802) and 10th (n=735) grade in 1993 was measured as part of a prospective cohort study in California. When children in the most polluted communities were compared to children in the least polluted communities, a 4.3 ppb increase in annual average of inorganic acid vapour levels was associated in 4th grade children with significantly lower annual growth rates for FVC (0.57%, 95%CI=1.06 to -0.07), FEV_1 (0.73%, 95%CI=-1.42 to -0.03) and forced expiratory flow at 75% of expired FVC (FEF_{75}) (-1.47%, 95%CI=-2.87 to -0.05). The association between acid vapours and FEV_1 was still significant after adjustment for daily O_3 levels (Gauderman et al., 2000). A second cohort of 4th-graders (n=1,678) enrolled in 1996 was followed for 4 years. An increase of 9.5 ppb in annual average of inorganic and organic acid vapours resulted in lower annual growth rates for FEV_1 (-0.63%, 95%CI=-1.21 to 0.05), MMEF (1.28%, 95%CI=-2.16 to -0.40) and MMEF/FVC (-0.96%, 95%CI=1.77 to -0.14). These associations did not qualitatively change following adjustment for O_3, NO_2, PM_{10}, $PM_{2.5}$ or elemental carbon in two-pollutant models (Gauderman et al., 2002). In both studies, the strength of the effects was generally greater in children who reported spending more time outside. Of all the pollutants studied, acid vapour showed the most consistent effect on lung function growth across both studies; however, it was impossible to identify the independent effects of pollutants in the studies because of strong correlations seen between acid vapours and other pollutants, especially NO_2.

Three consecutive panels of children, 7 years or older (n=47, 45, 41), participating in a summer camp in the Austrian Alps in 1991 were investigated. Given the markedly different exposure levels and patterns among panels, each panel was analyzed separately. In Panel 1 (where mean H^+ was 32.2 nmol/m^3 – almost twice as high as in the other two panels), a decrease of 2.99 ml in FEV_1 per nmol/m^3 H^+ ($p=0.004$) was found for the mean H^+ exposure during the previous 4 days. This association was still significant in two-pollutant models with O_3. Ambient H^+ exposure was not associated with lung function decrements in Panels 2 and 3 (Studnicka et al., 1995).

A time-series analysis of respiratory symptoms and air pollutants in the summer of 1989 in children aged 7-11 (n=300) in the Netherlands found no association between SO_4^{2-} (range=027 µg/m^3) and any respiratory symptoms (Hoek and Brunekreef, 1995). Another study based in the Netherlands investigated the effects of air pollution from urban and non-urban areas in children aged 7-11 (n=633) in winter 1992-1995. In children without chronic respiratory symptoms, the only association seen was between a 15 µg/m^3 increase in SO_4^{2-} and an increase in cough in non-urban areas (OR=1.17, 95%CI=1.01-1.35). In symptomatic children, a 15 µg/m^3 increase in SO_4^{2-} was associated with a decrease in evening PEFR in urban areas (OR=1.99, 95%CI=1.18-3.34), symptoms of the lower respiratory tract in urban (OR=1.83, 95%CI=1.162.87) and non-urban (OR=1.30, 95%CI=1.01-1.67) areas, cough in non-urban areas (OR=1.14, 95%CI=1.00-1.31), and use of bronchodilator in urban (OR=1.77, 95%CI=1.10-2.84) and non-urban (OR=2.76, 95%CI=1.345.70) areas (van der Zee et al., 1999). The aerosol acidity levels were below the detection limit throughout these two studies, and were therefore not analyzed.

In a panel of asthmatic subjects in former German Democratic Republic and Czech Republic cities between 1990 and 1992, 5-day mean SO_4^{2-} (IQR=8.9 µg/m^3) and PSA (IQR=0.36 µg/m^3) were associated with decreases in PEFR (SO_4^{2-}: -1.11%, 95%CI=-1.65 to -0.56; H^+: -0.52%, 95%CI=-0.89 to -0.16) in children aged 7-15 (n=155). SO_4^{2-} and PSA were not significantly associated with acute respiratory symptoms (Peters et al., 1996). In Sokolov, Czech Republic, a panel study of medication use and respiratory morbidity in asthmatic children aged 6-14 (n=89) was instigated during the winter 1991-1992. An increase of 6.5 µg/m^3 in 5-day mean SO_4^{2-} was associated with decreases in morning (-1.49 l/min, 95%CI=-2.78 to -0.20) and evening (1.88 l/min, 95%CI=-3.08 to -0.67) PEFR, while an increase of 0.3 µg/m^3 in

PSA was associated with a decrease in evening (-1.22 l/min, 95%CI=2.06 to -0.38) PEFR. Several associations were also seen for 5-day mean SO_4^{2-} and PSA and parent-reported cough, phlegm, dyspnoea, runny nose, fever, school absence, and β-agonist and theophylline use. The associations between SO_4^{2-} and respiratory symptoms were generally weaker when fever was included in the model (Peters et al., 1997b). In another study in Sokolov during the same period, 5-day mean SO_4^{2-} was associated with a decrease in PEFR (-5.62 l/min, 95%CI=-9.93 to -1.30), and increases in cough (OR=1.16, 95%CI=1.00-1.34), fever (OR=2.26, 95%CI=1.11-4.61) and β-agonist use (OR=1.46, 95%CI=1.08-1.98) in the 51 out of 82 children who used asthma medication during the period of analysis (Peters et al., 1997a). In all three studies, PSA was low and/or below the detection limit on most sampling days.

9.4.2.2.2 Adults

The association between air pollutants and lung function was studied in healthy non-smoking volunteers hiking Mount Washington during the summers of 1991 and 1992. An increase of 1.3 µg/m^3 or 26.5 nmol/m^3 across the IQR of aerosol acidity (reported as H_2SO_4 equivalent) was associated with a decrease in PEFR (-0.4%, 95%CI=-0.7 to -0.1) that persisted but was no longer significant after adjustment for mean O_3. The study used non-parametric GAM and results were not reanalyzed (Korrick et al., 1998).

The relationship between ambient air pollution and daily change in PEFR was further studied in healthy non-smoking women in Virginia during the summers of 1995 and 1996. An increase of 50 nmol/m^3 in H^+ was related to a decrease in morning PEFR (-0.89 l/min, 95%CI=-1.57 to 0.21), association that disappeared in models with PM_{10} or $PM_{2.5}$. The study used non-parametric GAM and results were not reanalyzed (Naeher et al., 1999).

In July 1995 (foggy season) and May 1996 (non-foggy season), a panel study in Kushiro, Japan, investigated the effects of naturally-occurring acid fog (pH range=3.0-3.2) on asthmatic adult patients (n=44). Decreases in PEFR (p=0.05) and FEV_1 (p=0.04) and a tendency of increased sputum eosinophils cationic protein (ECP) (p=0.1) and interleukin-8 (p=0.08) were seen in asthmatics in the foggy season compared to the non-foggy season. Patients that had >10% lower PEFR in the foggy season also had increased sputum ECP (p=0.007) compared to the non-foggy season. Fog acidity did not induce bronchial hyper-responsiveness. No other environmental or socio-economic factors were taken into account in the analyses (Honma et al., 2000).

In a panel of asthmatic adults (n=102) in former German Democratic Republic and Czech Republic cities between 1990 and 1992, an association was found between 5-day mean PSA (IQR= 0.36 µg/m^3) and a 10.6% increase in respiratory symptom score in symptom questionnaire (95%CI=1.4-19.7). No association was seen between SO_4^{2-} and PEFR or respiratory symptoms. PSA was mostly below the detection limit throughout the study. The study did not investigate if the results remained significant in multi-pollutant models (Peters et al., 1996).

A panel study of adults aged 50-70 years old (n=489) assessed the effects of urban and non-urban air pollution during three consecutive winters on lung function and respiratory symptoms in the Netherlands. In symptomatic subjects, an association was seen between a 15 µg/m^3 increase in 5-day mean SO_4^{2-} in urban areas and a large decrease (>20%) in morning PEFR (OR=3.56, 95%CI=1.0212.48) and upper respiratory tract symptoms (OR=1.46, 95%CI=1.06-2.01). Associations were seen in non-symptomatic subjects between SO_4^{2-} and the prevalence of >10% decrease in morning PEFR in urban areas (OR=1.87, 95%CI=1.11-3.15) and in non-urban areas (OR=0.13, 95%CI=0.04-0.50). In this study, the aerosol acidity levels were below the detection limit and therefore not analyzed (van der Zee et al., 2000).

9.5 CLINICAL STUDIES

Overall, recent human clinical studies are consistent with the conclusions of the 1997 Assessment, in that they indicate that healthy subjects are not particularly sensitive to short-term exposure to acidic aerosols alone, or to sequential exposures to H_2SO_4 aerosol and O_3, and that subjects with asthma or allergy may represent a susceptible population. However, concentrations to which the subjects were exposed in recent clinical studies were generally higher than levels observed in ambient air in eastern Canada (Tunnicliffe et al., 2001; Linn et al., 1997; Beckett et al., 1995; Frampton et al., 1995; Leduc et al., 1995).

For example, healthy (n=30) and asthmatic (n=30) volunteers were exposed for 3 hours to 100 µg/m^3 H_2SO_4 (mass median aerodynamic diameter (MMAD)=0.6 µm) or saline aerosols, followed 24 hours later by exposure to 0.08, 0.12 or 0.18 ppm O_3 for 3 hours with intermittent exercise. In healthy subjects, lung function parameters (FVC and FEV_1) post-exposure were comparable to baseline values. In asthmatics, pre-exposure to H_2SO_4 enhanced the decrements in FVC and FEV_1 that occurred both immediately and 4 hours after O_3 exposure (Frampton et al., 1995).

Exposure of healthy children (n=15) to a mixture of 0.1 ppm O_3, 0.1 ppm SO_2 and 100 µg/m^3 H_2SO_4 (MMAD=0.6 µm) for 4 hours had no statistically significant effects on spirometry, overall discomfort while exercising, and symptoms scored in questionnaires compared with healthy children exposed to clean air. The same exposure regimen in children suffering from allergy or mild asthma (n=26) was associated with an increase in symptom score (p=0.01), but not with lung function parameters (Linn et al., 1997).

The effect of exposure of adult mild asthmatics (n=13) to 100 or 1000 µg/m^3 H_2SO_4 (mass median diameter (MMD)=0.3 µm) for 1 hour, followed 14 hours later by a fixed dose of pollen allergen (established for each subject in order to produce a 15% decrease in FEV_1), was studied. Compared to air exposure, the exposure regimens induced dose-dependent decreases in FEV_1 of 16.7% following the 100 µg/m^3 H_2SO_4 and pollen allergen exposure (p=0.051), and of 18.4 % following the 1000 µg/m^3 H_2SO_4 and pollen allergen exposure (p=0.013) (Tunnicliffe et al., 2001).

A single 3-hour exposure to 700 ppm HNO_2 with intermittent exercise in mild asthmatics (n=11) resulted in a decrease in FVC (p=0.017), but not in FEV_1 or MMEF. The aggregate score of self-reported respiratory and mucous membrane symptoms in questionnaire was higher on HNO_2 exposure days than on control days (p=0.038) (Beckett et al., 1995).

Asthmatic volunteers (n=24) were exposed at rest for 1 hour to 500 µg/m^3 H_2SO_4 (pH 2.5, MMAD=9µm, osmolarity=300mOsm) or to a simulated artificial acid fog (pH 3.5, MMAD=7µm, osmolarity=300mOsm) containing 15 mEq/liter SO_4^{2-} and 12 mEq/liter NH_4^+. The exposures did not result in any significant changes in FEV_1 (p=0.14), specific airway resistance (p=0.87) or bronchial responsiveness to metacholine (p=0.36) compared to baseline values (Leduc et al., 1995). A possible explanation for the lack of effects in asthmatic volunteers in this study is the size of the particles administered. Discrepancies in deposition sites between coarse and fine aerosols might explain the differences in effects seen between studies.

9.6 Toxicological studies

The time frames of exposure of the different studies investigating the effects of acid exposure ranged from a single exposure of a few hours to continuous or intermittent exposures for up to more than 2 years, with most of the studies being short-term. The acid species investigated included H_2SO_4, HNO_3, ammonium bisulphate (NH_4HSO_4) and SO_4^{2-} from the conversion of SO_2 on carbon black aerosols (CBA) at 85% relative humidity. Acid was studied either alone, in combination with O_3, or in mixtures with other pollutants such as carbon particles, NO_2 or neutral sulphites (SO_3^{2-}). Since different mixtures of pollutants were studied in different species, it is difficult to identify the agent(s) responsible for the toxicity seen in animals.

In recent toxicological studies, the most common endpoints assessed included pulmonary macrophage-associated defense capacity (e.g., Fc-receptor binding, phagocytic activity, oxidative defense and intrapulmonary bactericidal activity), cell content of broncho-alveolar lavage fluid (BALF) (e.g., total protein, total and differential cell counts and viability), respiratory tract clearance, breathing patterns and morphological changes. Generally consistent signals were seen for alveolar macrophage (AM) Fc-receptor binding and phagocytic activity, with decreased activity observed with increasing doses of acid (Jakab et al., 1996; Kleinman et al., 1999; Clarke et al., 2000; Ohtsuka et al., 2000a, 2000b; Mautz et al., 2001). Full re-establishment of phagocytic potential was seen within 7-14 days after the end of exposure in the studies that assessed this parameter (Jakab et al., 1996; Clarke et al., 2000; Ohtsuka et al., 2000a, 2000b). Total and differential cell counts and viability, as well as total protein content of the broncho-alveolar lavage fluid, were generally unaffected by acid exposure (Chen et al., 1995; Jakab et al., 1996; Zelikoff et al., 1997; Heyder et al., 1999; Kleinman et al., 1999; Clarke et al., 2000; Ohtsuka et al., 2000a, 2000b; Mautz et al., 2001), with the exception of one study in guinea pigs, a particularly sensitive species (Lee et al., 1999). Signals for other endpoints were less consistent, mostly because of the limited number of studies that investigated them (Mautz et al., 2001; Clarke et al., 2000; Ohtsuka et al., 2000a, 2000b; Heyder et al., 1999; Kleinman et al., 1999; Lee et al., 1999; Sindhu et al., 1998; Kimmel et al., 1997; Last and Pinkerton, 1997; Zelikoff et al., 1997; Jakab et al., 1996; Wong et al., 1996; Chen et al., 1995; el-Fawal et al., 1995).

9.6.1 Short-term studies

It has been postulated that acid particles may affect the functional state of AM by altering their intracellular pH. The effects of a single 3-hour exposure of rabbits to 125 µg/m^3 H_2SO_4 alone or in concomitance with 0.1, 0.3 or 0.6 ppm O_3 were investigated. Synergistic interactions were seen between H_2SO_4 and O_3 for the intracellular pH regulation and maximal rate of pH recovery. The intrinsic buffering capacity of the cells was increased following exposure to 50 µg/m^3 H_2SO_4 alone, but was decreased following exposure to the mixture of 50 µg/m^3 H_2SO_4 with 0.6 ppm O_3, suggestive of an antagonistic interaction for this endpoint (Chen et al., 1995).

Mice were exposed for a single 4-hour exposure to CBA (MMAD=0.3 µm) and SO_2 alone or in mixtures at either 10% or 85% relative humidity. At 85% relative humidity only, conversion of SO_2 to SO_4^{2-} on CBA was significant, and macrophage phagocytosis and intrapulmonary bactericidal activity were depressed transiently, returning to normal after at least 5-6 days (Jakab et al., 1996; Clarke et al., 2000).

In order to study if genetic background has an important role to play in susceptibility to acid exposure, different genetic strains of mice were exposed for 4 hours to a combination of CBA (MMAD=0.3 µm) and SO_2 at 85% relative humidity. An interstrain variation in mice in the effects on AM phagocytic response was found (Ohtsuka et al., 2000b). A follow-up study indicated that two unlinked genes on chromosomes 11 and 17 were responsible for the responsiveness to AM phagocytic dysfunction after acid-coated particle exposure in mice, and that these quantitative trait loci overlap those identified for responsiveness to O_3 and acute lung injury (Ohtsuka et al., 2000a).

A study was undertaken in order to compare the immunotoxic effects of an acute inhalation of 1000 µg/m^3 H_2SO_4 (MMAD=0.88 µm) for 3 hours in rabbits with those produced in exposed human volunteers. The capacity to phagocytose latex particles was significantly increased only in rabbit macrophages following H_2SO_4 exposure. Acid exposure also suppressed bacterial uptake and intracellular killing of bacteria in rabbit cells, while data for human cells were inconclusive. Lactate deshydrogenase levels were elevated in the BALF of rabbits only. No effects were seen in either species following H_2SO_4 exposure on total protein in BALF, cell number and viability, neutrophil infiltration, modulation of Fc receptors or the index of phagocytosis of latex particles. The production of reactive species by the macrophages was generally unaffected by acid exposure, except for a decrease in stimulated production of superoxide anion by rabbit and human macrophages (Zelikoff et al., 1997).

The effects of acid exposure on pulmonary surfactant activity were compared in rats and guinea pigs, which were exposed to approximately 100 and 50 mg/m^3 H_2SO_4, respectively, for a single 4-hour exposure. While no significant effects were seen in rats, guinea pigs appeared to be a particularly sensitive species to the effects of H_2SO_4 insult. Surfactant parameters were altered in guinea pigs, as shown by histopathological changes of the trachea and lung parenchyma. Surface tension properties and film compressibility parameters of the BALF were increased, compared with control pigs. Phospholipid concentrations were similar between control and exposed groups of guinea pigs, but macrophages and neutrophils/eosinophils were increased in the BALF compared with controls (Lee et al., 1999).

Rabbits were exposed to 50, 75 or 125 µg/m^3 H_2SO_4 (MMAD=0.3 µm) and 0.1, 0.3 or 0.6 ppm O_3 alone or in mixture for 3 hours. Exposure to all levels of O_3 alone, to 75 µg/m^3 H_2SO_4 in mixtures with all levels of O_3 and to

125 µg/m^3 H_2SO_4 alone resulted in bronchial hyperresponsiveness to acetylcholine. The concomitant exposures produced effects that were less pronounced than the effects of the pollutants alone, suggesting an antagonistic interaction between the pollutants (el-Fawal et al., 1995).

In order to determine if particle size influences toxic effects of H_2SO_4, rats were exposed for 4 hours per day on 2 consecutive days to 0.6 ppm O_3 and 500 µg/m^3 fine (MMD=0.3 µm) or ultrafine (MMD=0.06 µm) H_2SO_4 alone or in mixture. Acid exposure alone did not produce any significant morphological changes or cellular proliferation in the pulmonary parenchyma, and no changes in ventilatory parameters were noted. Synergistic interactions were found between O_3 and ultrafine H_2SO_4 for the volume percentage of markedly to severely injured pulmonary parenchyma, and between O_3 and fine H_2SO_4 for the cell proliferation in the periacinar region subsequent to cell injury. The discrepancies in deposition sites of fine (deposition in or proximal to the periacinal region) and ultrafine (deposition distal to the periacinal region and the periacinal region itself) H_2SO_4 aerosols may explain in part the type of interaction seen with O_3 (Kimmel et al., 1997).

Intermittent exposure of rats to O_3 alone or a mixture containing carbon, 0.2 or 0.4 ppm O_3, and 100 or 500 µg/m^3 H_2SO_4 (MMAD=0.3 µm) for one or 5 days was studied. Single and repeated exposures to the high-concentration mixture suppressed AM Fc-receptor binding and increased lung inflammatory response relative to controls. The effects seen for AM Fc-receptor binding were greater for the high-concentration mixture than for the low-concentration mixture or O_3 alone. Breathing patterns and lung inflammatory response were affected by exposure to 0.4 ppm O_3 on Day 1, but not on Day 5, suggestive of adaptive mechanisms that seem to be altered following concomitant exposure to O_3 and H_2SO_4 (Kleinman et al., 1999).

9.6.2 Medium-term studies

Repeated intermittent exposure of rats to fine particle mixtures (MMAD=0.3 µm) containing carbon, NO_2, 50, 100 or 200 µg/m^3 NH_4HSO_4, 0.15, 0.30 or 0.60 ppm O_3, and 25, 50 or 100 µg/m^3 HNO_3 vapour for 4 weeks resulted in dose-dependent (generally becoming statistically significant in mid- and/or high-particle mixture exposure groups only) decreases in AM Fc-receptor binding and phagocytosis, increases in cells containing carbon inclusion, and increases in epithelial cell proliferation at all levels of the respiratory tract. Exposure to the high-concentration mixture only resulted in increased epithelial permeability. Breathing patterns were also altered by the exposures, while respiratory tract clearance was not (Mautz et al., 2001).

Intermittent or continuous exposure of rats to 20, 100 or 150 µg/m^3 H_2SO_4 (MMAD=0.4-0.8 µm) in combination with 0.12 or 0.20 ppm O_3 for up to 90 days was investigated. Exposure to O_3 resulted in increased lung 4-hydroxyproline and elicited tissue and cellular changes at the bronchiole-alveolar duct junction, while no effect was seen following H_2SO_4 exposure alone. No interactive effects were noted between H_2SO_4 and O_3 (Last and Pinkerton, 1997).

9.6.3 Longer-term studies

Healthy beagle dogs were exposed to clean air for 29 months, or to clean air for 16 months followed by intermittent exposure to a mixture containing 1.53 µg/m^3 neutral SO_3^{2-} particles (MMAD=1 µm) and 5.66 µg/m^3 acidic SO_4^{2-} particles (MMAD=1 µm) for 13 months. Antagonistic interactions were generally seen following exposure to the mixture, with effects on functional and structural responses of the lungs less pronounced or even reversed when compared with results of exposure to sulphur (IV) alone from a previous study by the same authors (Heyder et al., 1992). The elevation of the activity of alkaline phosphatase and the proliferation of type II pneumocytes were attributed solely to acid exposure (Heyder et al., 1999).

Episodic exposure of rats for 40 weeks to 50 µg/m^3 HNO_3 vapour or 0.15 ppm O_3 elevated the levels of stress-inducible HSP70 in the respiratory tract, compared with controls, while the increase following their combined exposure was less than the increases of either pollutant alone, suggesting an antagonistic interaction (Wong et al., 1996). Following the same exposure pattern, the lung content of putrescine (exhibiting anti-oxidant and anti-inflammatory activities) in rats was increased 28%

following O_3 alone, decreased 21% following HNO_3 alone, and increased 56% following a combination of O_3 and HNO_3 vapour, compared with controls (Sindhu et al., 1998).

9.7 SUMMARY

Recent epidemiological studies investigating the association between aerosol acidity and mortality have found small but significant associations between ambient SO_4^{2-} and total and cardio-respiratory mortality. Few studies investigated the effects of H^+ on mortality; no obvious threshold was observed. Recent studies have also found associations between exposure to elevated ambient PM concentrations and increased hospital admissions for respiratory and cardiac diseases, particularly in susceptible sub-populations such as infants and the elderly, and increased incidence of respiratory symptoms and declines in lung function, with larger effects in children than in adults. It is possible that some of the toxicity of PM might be attributable to aerosol acidity, although a strong colinearity was generally seen between the pollutants measured, making it impossible to separate the effects of PM components.

New clinical studies indicate that healthy subjects are not particularly sensitive to short-term exposure to acid aerosols alone or to sequential exposures to H_2SO_4 aerosol and O_3, but that subjects with asthma or allergy may represent a susceptible population. However, exposure levels in clinical studies are usually higher than what is normally measured in ambient air in Canadian cities.

Overall, results from recent toxicological studies suggest that acid exposure can produce effects, mainly on host-defence related endpoints, at concentrations close to what can be expected in ambient air in Eastern Canada. There also appear to be inter-species differences in sensitivity to H_2SO_4, with guinea pigs being particularly sensitive to acid exposure. Genetic background may also have a role to play in susceptibility to acid exposure. The potential interaction(s) following concomitant or sequential exposure to acid species and O_3 has been described as synergistic, additive or antagonistic, while in some cases no interaction was seen at all. It has been postulated that O_3 and acid particles act independently and at different sites in the respiratory tract. Depending on the relative concentrations of the agents in the mixture and the endpoint measured, the effects of mixtures could be increased or decreased compared with the effects of pollutants alone.

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CHAPTER 10

Socio-Economic Benefits and Costs of Acid Deposition Abatement

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10.1 KEY MESSAGES

- There are considerable socio-economic benefits to reducing acid deposition, and work is ongoing to quantify them, but at present many of these benefits are not well quantified.
- The direct socio-economic benefits of reducing acid deposition include increased forest growth and forestry production, benefits for recreational and commercial fishing due to reduced lake acidification and increased number of fish, and decreased rates of corrosion for historical buildings and electrical towers.
- Reductions in emissions that cause acid deposition (SO_x, NO_x, etc.) would also have significant socio-economic benefits in the form of lower particulate matter and ground-level ozone concentrations (a.k.a. smog). Lower levels of smog would result in increased visibility, increased agricultural production, and lower levels of sickness and mortality.

10.2 INTRODUCTION: THE ROLE OF ECONOMICS IN ACID DEPOSITION ABATEMENT STRATEGY

Socio-economic benefit and cost analyses support the decision making process by assessing the impacts of policy implementation in common terms. Economic approaches and techniques, as well as the use of a common scale, dollars, can allow for a more thorough appreciation of the extent of acid deposition impacts and provide policy makers with a way to objectively compare the costs and benefits of various abatement options.

This is the first time that a Canadian acid deposition assessment has included a chapter on socio-economics. Until recently, the availability of the underlying science upon which to base Canadian economic valuation was limited. Recent work clarifying scientific links between acid deposition and environmental effects is making economic analysis of abatement strategies more practical. In addition, new economic research is making the economic analysis of acid deposition more feasible. Consequently, economists are becoming increasingly able to provide information to help policy makers understand the full effects of acid deposition.

This chapter is intended to outline recent economic developments in acid deposition abatement analysis and identify the main gaps that still exist in our knowledge. The chapter is divided into three main sections. Section 10.3 looks at the benefits of reducing acid deposition and assesses our current ability to value the effects of acid deposition on various endpoints. Section 10.4 outlines some of the main tools and approaches that are, or could be, used for evaluating the costs of abatement options. The final section summarizes the main points of this chapter.

10.3 VALUING ACID DEPOSITION DAMAGES AND ESTIMATING ABATEMENT BENEFITS

This section attempts to value the benefits of acid deposition abatement. Several endpoints are considered, including corrosion, agriculture, forestry (timber), visibility and non-market resources in general, and human health. For each endpoint, we examine the work that has been conducted and is being conducted to develop economic valuations. We also examine gaps in our knowledge and identify sources of difficulty for accurately quantifying the costs and benefits of acid deposition. We start this section with a brief review of the underlying theory of benefit valuation.

10.3.1 Economic valuation of environmental endpoints

Economic valuation aims to estimate the value of a particular choice to society. Valuation techniques are designed to capture the *relative* value that society places on an option. That is, they measure the value of one option in terms of another, using dollars as a common reference. These values can be used to assess the pros and cons of implementing different options.

In order to facilitate the comparison of costs and benefits of acid deposition abatement options, it is convenient to use a common measure such as monetary currency. A common measure assists policy makers in comparing and choosing between alternative policies. For instance, an acid deposition abatement policy that increases electricity costs by 150%, but at the same time reduces building corrosion by 20% and saves 10,000 acres of forest, would be hard to evaluate without some means to compare these outcomes on a common scale. By using economic valuation techniques, the various endpoints mentioned above can be expressed in dollar terms, making the costs and benefits of the policy easier to compare and assess.

In the last decade, economic valuation of acid deposition has lagged behind efforts to evaluate the economic impacts of other environmental issues. In Canada, economic valuation efforts have focussed largely on the impact of particulate matter (PM) and ozone on human health. Economic approaches and tools developed for PM and ozone impacts could be expanded to account for acid deposition impacts. In addition, PM and ozone abatement efforts result in co-benefits by reducing acid deposition precursors (see Chapter 11). For example, reductions in SO_X to achieve PM reduction targets are likely to have the added benefit of reducing acid deposition. In the following sections, we therefore examine valuation work that has been conducted not only to assess the direct impacts of acid deposition, but the areas that could have direct or indirect relevance to the issue.

10.3.1.1 *Steps involved in valuation*

In order to value the effects of pollution, it is necessary to trace the environmental impact in two directions; backwards to the initial pollution emission; as well as forwards, to human activities that are affected by the environmental impact. There are four steps in this sequence: pollution is emitted; pollution changes ambient air quality; ambient air quality has physical effects on humans and the environment; and physical effects are assigned monetary value based on their links to human beings.

In order to fully evaluate an abatement option, each step in the valuation process must be linked with the preceding step using a model that allows a quantifiable, functional relationship to be established between each step (see Figure 10.1). Quantifying each relationship enables the analyst to link specific emission levels to predicted damages in dollar terms. In order to quantify the relationships, the following techniques can be used:

- The emission of pollution (SO_X and NO_X) must be linked to changes in environmental conditions. This relationship can be made using a source-receptor tool.
- The change in environmental conditions (acid deposition) needs to be linked with environmental effects, such as corrosion or lake acidification. This link is typically made using a dose-response function (DRF), also called a concentration-response function (CRF), or exposure-response function (ERF).
- Once the environmental effects are identified, the impacts of these effects on humans have to be characterized (reduction in recreational fishing, loss of endangered species, etc.). Subsequently, human impacts are valued using economic valuation and modeling techniques.

This approach to valuation replicates the approach that has commonly been used in models such as the Air Quality Valuation Model (AQVM) and in studies such as MacMillan (2001). The approach considered in this chapter also includes one additional step not commonly found in the literature. In our discussion, the step that links environmental effects to human activity, connecting the science with the economics, is considered explicitly. This step includes identifying the population affected by acid deposition, acid deposition impacts on human behaviour (through avoidance activity or induced activity), impacts on human perception and the attitude

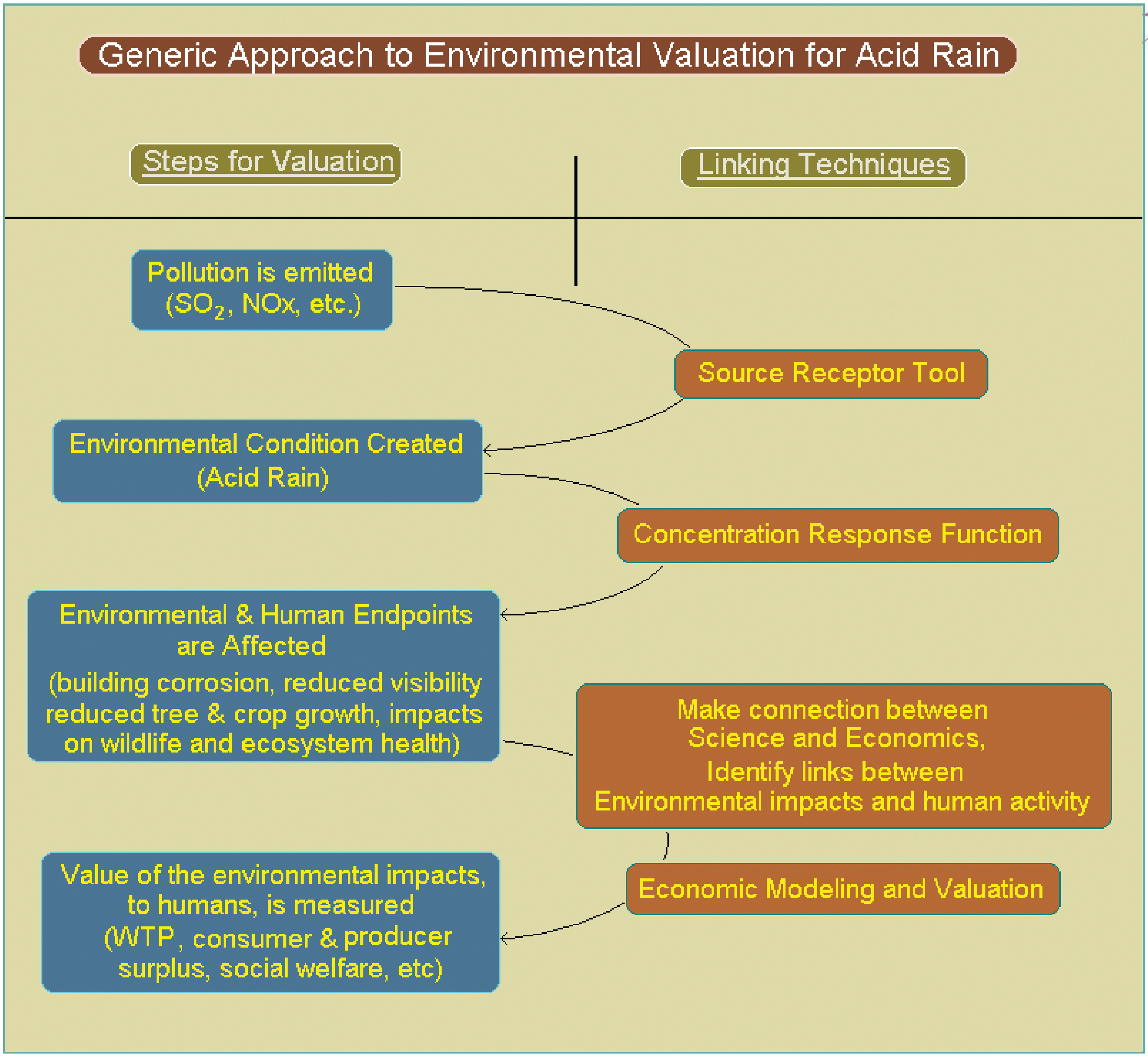

Figure 10.1: Illustration of the steps in the valuation process.

of the affected population. Many other studies have treated this step as being implicitly part of the valuation process. We consider this step directly because, in many cases, failure to consider it explicitly results in an inability to make an effective connection between the science and the economics of pollution impact valuation. For human health effects, the link between pollution effects and human activity is direct but for environmental effects this link must be established in order to evaluate the economic impact.

10.3.1.2 *Sustainability and sources of marginal and total value*

In the context of sustainable decision-making, it is useful for policy makers to be able to compare the present value of resources to potential future values of these resources in the context of future costs of reducing acid deposition. For many natural resources, the benefits of protection will be felt primarily by future generations while the costs of protecting these resources will be borne by present generations. Thus, it is necessary to compare future benefits with present costs. This has led to a great deal of debate over the notion of discounting. On one hand, standard economics teaches that a dollar today is worth 1+r dollars a year from now (where r is the real interest rate); hence, future benefits should be discounted. On the other hand, the present value of a stream of benefits that stretches out indefinitely could be extremely large, or even infinite. Whatever technique and discount rate is used, there is bound to be controversy as some people may argue that technological change makes it unreasonable to value benefits several hundred years into the future, while others have a moral objection to any notion that a human life in the future is worth less than a human life today. This debate has not been settled and there is currently no government-wide discount rate being used in Canada.

Although there is no agreement about an appropriate discount rate, there is general agreement that sustainable policies require consideration of the full social, economic and environmental value of Canadian resources both today and in the future.

The concept of total economic value (TEV) is essential to full-cost accounting. TEV acknowledges that environmental resources have value beyond their direct consumption. In order for the impacts of acid deposition to be assessed fully, the TEV of the affected environmental resources must be considered. Failure to consider all sources of value results in underestimates of the benefits of pollution abatement and inhibits sustainable development planning.

As described in recent work conducted for Environment Canada's Natural Capital project (Gardner Pinfold Consulting et al., 2002), the breakdown of TEV is as follows: The total economic value of a resource is made up of use value and non-use value (or passive use value). Use value includes direct use, indirect use, and option value. Direct use involves the consumption of a resource such as logging or mining. Indirect use is the non-consumptive use of a resource, such as tourism. Option value is when people do not currently use the resource but wish to be able to use it in the future either directly or indirectly. Non-use value is subdivided into vicarious consumption, bequest value, and pure existence value. Vicarious consumption means people enjoy the knowledge that the environment is available to people in other parts of the world. Bequest value means people want to leave the environment for the enjoyment of future generations. Pure existence value occurs when individuals value the environment for its own sake, irrespective of any present or future use by human beings. Figure 10.2 provides a visual representation of TEV.

Total economic value has become more common in economic and political discussions. Many people place a real and personal value on goods or services that they will never themselves experience. In order to account fully for the benefits to society of a policy, policy makers must include estimates of changes in the TEV of environmental endpoints in their cost-benefit analysis.

It should be noted that although TEV is a useful tool for illustrating the many sources of value for environmental goods and services, it is not used directly in cost-benefit analysis (CBA) calculations. For CBA, it is not total value that must be measured but changes in total value. For instance, to compute the benefits of reducing acid deposition, policy makers need to understand the change in environmental conditions resulting from the reduction in acid deposition and the value of that change. It is not TEV *per se* that is of use for policy oriented CBA; it is changes in TEV.

In the following section we discuss some of the valuation techniques that are used by economists. These techniques, for the most part, are designed to capture the value of marginal changes in environmental conditions.

10.3.1.3 Valuation approaches/techniques

A variety of techniques can be used to value pollution effects on environmental endpoints.

When acid deposition, or other pollution, results in damages to a marketed product or services, an estimate of the economic significance of these damages can be based on market prices. The acid deposition impacts would ideally be measured by a loss in producer and consumer surplus. That is, damages are equal to losses in producer profits plus the lost benefit to consumers

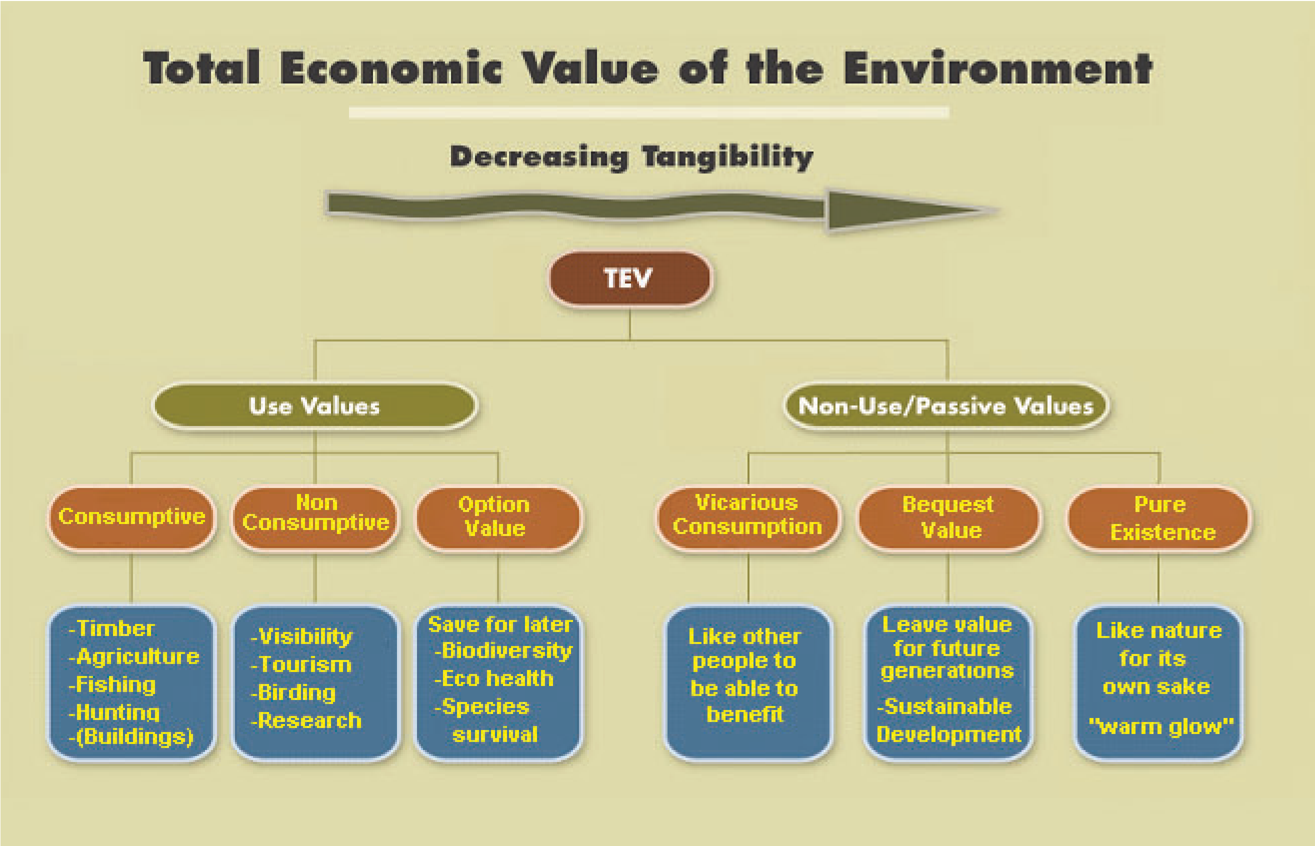

Figure 10.2: Illustration of the factors considered in the determination of Total Economic Value of the environment.

from having to pay higher prices (if any). Typical approaches used to value acid deposition impacts on market goods include measuring changes in productivity, in net income of an industry, or of preventative expenditures, as well as estimating replacement costs. All of these techniques rely on observations of the marketed environmental good or service.

When pollution affects non-traded environmental endpoints, economic valuation is more challenging. Economists use two main approaches to determine the value of endpoints that are not marketed: revealed preference and stated preference. The revealed preference approach looks at people's market choices and infers from these choices the value that the consumer places on some other non-marketed attribute. For instance, the choice to pay more money for an equivalent house in an area where there is better air clarity can be used as an indication of the value one places on visibility. Similarly, time and money spent traveling to a location can provide an indication of the value people place on recreation in a given wilderness area. These are examples of hedonic pricing and the travel cost approach. While the revealed preference approach has drawbacks, its main advantage is that it is based on actual behaviour and expenditures rather than hypothetical activities or scenarios. On the other hand, it can be challenging to isolate a particular variable of interest, such as visibility, using revealed preference approaches. Revealed preference approaches are also largely ineffective at indicating the non-use value that people have for certain environmental goods.

The difficulties of using the revealed preference approach to estimate non-use value are one of the main reasons that the stated preference approach has become the most common technique for estimating the value of non-market environmental endpoints.

At the most basic level, the stated preference approach to valuation involves asking people how much they value a particular environmental good or service. In most cases, surveys are used to collect this information. Contingent valuation (CV) surveys and contingent choice (CC) surveys are among the most popular survey techniques and they have been widely used in the environmental valuation literature. CV surveys estimate environmental values by asking participants questions such as "how much would you be willing to pay for 'X'". CC surveys ask respondents to choose which of several hypothetical scenarios they prefer. By analyzing preference choices of many individuals between various scenarios, researchers can estimate the average value that respondents place on marginal changes in a particular environmental good or service.

Because conclusions are based on hypothetical responses, some economists have argued against the use of CV and other stated preference techniques. Overcoming this limitation is essential to creating an effective stated preference study. Survey questions must be designed in such a way that respondents carefully consider the questions and provide answers that are honest and accurate. Caution must also be used in aggregating willingness-to-pay (WTP) responses from stated preferences surveys since an individual's WTP to protect small areas does not increase proportionally with the size of the area being protected.

Another consideration when valuing acid deposition damages is the potential for double counting damages or calculating damages based on inaccurate behaviour predictions. For example, in the case of agricultural damages, a DRF could indicate the total crop loss for a given acid deposition level. However, a farmer might decide to take a compensatory action, at a cost, and thereby partially negate some of the effects. When estimating the acid deposition damages to this farmer, it would be incorrect to assume damages are equal to predicted crop losses, to increased production costs, or to the sum of the two. It is the net change in farmer profits that measure actual damages. Similarly, liming of streams and small lakes may negate some of the negative impacts of acid deposition on fish; in which case, damages caused by acid deposition should be measured according to either the value of the loss in fish or the cost of liming. Estimated damage values should not be used in cost-benefit analysis if damages do not actually occur because of preventative measures. In such cases, it is the preventative expenditures that should be included in cost-benefit analysis. To accurately estimate the impacts of a change in acid deposition levels, one needs to know both the change in the physical effects and the change in human behaviour resulting from those effects. It is the change in human behaviour (or perception), not the physical effect itself, which is to be valued.

10.3.2 Benefits valuation efforts for selected endpoints

In the following sections we examine, in turn, the valuation work that has been conducted on material corrosion, agriculture, the timber industry, visibility, non-marketed environmental resources, and health. For each endpoint, we will examine the recent and ongoing valuation work and assess the current ability to value these endpoints as they relate to acid deposition in Canada.

10.3.2.1 *Material corrosion*

There has been considerable research, in both the scientific and economic areas, into the effects of acid deposition on building and material corrosion. It is generally believed that by accelerating the rate of corrosion of materials such as wall cladding, roofing, bridges and transmission lines, acid deposition accelerates the frequency that these materials must be repaired or replaced. On the science side, there has been substantial research into the impacts of acid deposition on corrosion rates. From the economics side, research is being conducted on repair costs and whether, in fact, repair frequency is wholly, partially, or at all affected by accelerated corrosion rates. Until recently, most research in this area has come from outside Canada. Economists in Europe completed some of the first cost-benefit analyses of acid deposition and corrosion (e.g. EternE Project; AEA Technology report Cost-Benefit Analysis for the Protocol to Abate Acidification, Eutrophication and Ground Level Ozone in Europe (Holland et al., 1999)). These analyses laid the foundation for cost-benefit analyses of acid deposition and corrosion in the Canadian context.

Five key elements are required to determine the economic implications of corrosion of buildings caused by acid deposition: 1) ambient levels of relevant pollutants by region, 2) corrosion DRFs for different materials, 3) repair/replacement scenarios, 4) an inventory of material type and usage by region, and 5) repair/replacement costs.

The most comprehensive set of corrosion DRFs is from the United Nations/Economic Commission for Europe (UNECE)'s International Co-operative Program (ICP) materials study (Swedish Corrosion Institute, online). This study spanned over eight years, from 1987 to 1995, during which corrosion data was monitored at 39 different observation stations.

Recent work by Environment Canada has made significant progress towards valuing the damages caused by acid deposition to Canadian buildings and materials. Efforts have focused on using the ICP corrosion-response functions to come up with valuation figures for Canada. Jean-Jacques Hechler, in collaboration with scientists from Meteorological Services of Canada (MSC), has completed work that supports the use of ICP DRFs to accurately predict corrosion rates in Canada. The main tasks for the purpose of economic valuation are to identify the materials at risk and identify the standard replacement procedures and costs for those materials in Canada.

LECG Economics (2003) has developed an inventory of the materials at risk of damages from acid deposition in Canada by census district and by type of use. MSC is in the process of completing corrosion maps for affected areas in Canada. The Environmental Economics Branch (EEB), Environment Canada, is currently coordinating work to determine the repair and replacement costs of key materials affected by acid deposition and to determine when and why these repairs and replacements are undertaken. Once this work is complete, all the necessary information to develop thorough estimates of most of the damages caused by corrosion due to acid deposition in Canada will be available.

In Canada, little work has been done to estimate the damages of acid deposition to culturally or historically significant buildings and monuments or outdoor works of art. This is not because the value of these damages is thought to be insignificant, for indeed, the destruction of cultural heritage monuments is seen by the public as one of the main problems caused by acid deposition. However, there is a lack of information on the monetary value placed on these buildings. "In the public arena most concern about pollutant damage to materials has focused on historic monuments. . . Given the relative abundance of modern buildings compared to older ones, it may be anticipated that damages to the former will outweigh those to the latter. However, without data on the way that people value historic monuments the relative importance of damage to the two types of structure is a matter of speculation." (AEA Technology, 1999).

The primary tool currently being used by Environment Canada for the valuation of air pollution is the Air Quality Valuation Model (AQVM) developed by Health Canada and Environment Canada. The environmental component of AQVM (AQVM-E) has a limited capacity to estimate corrosion damages in Canada. Relying on several American studies by Mathtech Inc. (Horst et al., 1986), AQVM-E estimates the central value of materials damaged by SO_2 to be \$2.50 per household per $\mu g/m^3$ per year (Chestnut et al., 1999). These figures are based on American data. Furthermore, the DRFs and range of materials considered in the AQVM-E are extremely limited compared to the ICP study. Thus, the current corrosion estimates included in the AQVM-E are very rough estimates only.

In summary, despite the lack of information on the value of corrosion damage to culturally and historically significant buildings, monuments, and works of art, recent economic work has contributed to a much better understanding of the damages caused by acid deposition.

10.3.2.2 *Agriculture*

Economic valuation of acid deposition impacts on agriculture requires the definition of a clear relationship between acid deposition and changes on crop yield and quality. The main impediment to valuation of these impacts is the lack of a consensus about the dose-response relationship relating acid deposition to crop growth. While acid deposition is not believed to have a large negative impact on crop growth, there is no agreement about whether the damages are positive, negative, or insignificant.

Some scientists have suggested that acid deposition may actually be beneficial for crops because nitrogen deposition acts as a crop fertilizer (Holland et al., 1999). In the UK, "SO_2 has been shown to damage crops directly at high pollutant concentrations. However, at the ambient levels currently present in the UK, these impacts are likely to be very low and may in fact be beneficial." (DETR, 1999). Other research has observed direct and indirect negative impacts of acid deposition on crops (Velikova et al., 2000). Although the science community is not in complete agreement about the direction of the effects of acid deposition on agriculture, it is generally agreed that any effects of acid deposition alone on agriculture are very small compared to the effects of other pollutants on agriculture.

Some economic studies have tried to take into account the negative effects of acid deposition on crop yields. Since the value of agriculture is primarily a market value, the value of acid deposition impacts on agriculture would be fully measured by changes in producer and consumer surplus. Consumer surplus is often hard to estimate but many studies have examined the economics of acid deposition impacts on crops from the producer side. In Canada, the Victor and Burell (V&B) model estimated the effects of acid deposition on crops in southern Ontario in the early 1980s. The model takes into account both crop losses and preventative expenditures but not consumer surplus effects through price changes. In Europe, the ExternE model also values damages to crops from acid deposition although it does not look at preventative expenditures. Various other models, such as Regional Air Pollution Information and Simulation (RAINS), also try to account for acid deposition damages to crops. The valuation results of the European studies are not transferable to Canada because the value of agriculture differs significantly between Europe and Canada. On the other hand, the approaches used in these models, and in the V&B model, could be applied in Canada once the science community develops more robust DRFs.

Kulshreshtha et al. recently completed an inventory of Canadian crops and their market values (Kulshreshtha et al., 2003). While the Kulshreshtha study and the AQVM-E approach focus on ozone, the valuation methodology could be applied to crop damages or benefits due to acid deposition once appropriate DRFs become available. The lack of DRFs linking acid deposition with crop effects is the primary unknown in valuing the effects of this issue. This may represent an area for future work.

10.3.2.3 *Timber industry*

The determination of damages caused to Canadian trees by acid deposition appears to be particularly challenging and requires a better understanding of dose-response relationships. It is known that acid deposition damages the leaves of trees and affects the concentration of soil nutrients required for tree growth but the dose-response relationships for these phenomena are not clearly defined. Once the effects of acid deposition on trees are fully understood, the links between acid deposition, tree health and quality and quantity of timber can be established.

Some of the first work to establish ERFs (exposure-response functions) in Canada was done in the early 1980s by Victor and Burell (V&B) (1982). V&B studied the effects of acid deposition on a range of endpoints in southern Ontario, including timber. Until recently, much of the work on timber impacts of acid deposition followed the V&B approach and used the same ERFs. The ExternE project in the EU, for instance, uses the ERFs from V&B. As of 2000, "No new or improved E/RFs have been developed since the ERFs developed for policy analysis in the early 1980s." (DSS, 2000).

More recently, a number of projects in Canada and elsewhere have been undertaken to improve the scientific understanding of the link between acid deposition and tree growth/health. Dr. Paul Arp (2004), at the University of New Brunswick, is working on a project that will contribute to Canadian valuation work from the science side. This project attempts to establish a functional relationship between the exceedance of critical loads for acid deposition, nutrient availability and tree growth. The critical load approach is not universally accepted for policy application purposes in the economic community (Krupnick, 2004). However, as few DRFs have been established, Arp's work could represent an important step towards valuing acid deposition impacts on forests.

On the economic side, a great deal of valuation work has been conducted in Canada and the U.S.. Significant valuation research in Canada has been spurred by the importance of the forestry industry to the Canadian economy. In 2003, the Canadian forestry sector contributed roughly 3% of Canada's GDP. The value of forest product exports was $39.6 billion and the balance of trade was $29.7 billion. Forest products made up about 12% of total Canadian exports and accounted for roughly half of Canada's positive balance of trade (NRCan, 2004). In Europe, where forestry makes up a smaller part of the economy, the effects of acid deposition on timber are negligible compared to health and agricultural effects (Holland et al., 1999). As a result, European interest in acid deposition impacts on forests has focused on recreational and aesthetic impacts.

Recent Canadian effort has focussed on improving the economic valuation of forest impacts. Forestry valuation work done by V&B is out of date and some of the underlying assumptions in the model are no longer valid. For example, it is assumed that if forests are damaged, companies will have to go farther to get more lumber. This assumption is not reasonable today because firms are currently harvesting at or above the maximum allowable limit (Vertinsky et al., 2003). Current work accounts more accurately for operating practices of Canadian forestry companies. Based on Statistics Canada's input/output model, Vertinsky et al. (2003) assessed the economic impacts on the forestry sector of a change in annual allowable cut (AAC) due to a broad change in air quality conditions. The model estimates that for each 1% net increase in AAC in eastern Canada, the value of exports of timber products will increase by about $335 million. The outcome of the model is broken down by product, such as pulp and paper, lumber, particle board, and other materials. Vertinsky and Nelson (2003) have developed a similar model for western Canada.

There are potential limitations to the Vertinsky model. Certain underlying assumptions are questionable. For example, Vertinsky assumes that additional timber made available and harvested will be exported entirely to the U.S. with no price change. Because the model assumes that excess wood is exported and prices remain constant, the result is that there is no effect on Canadian consumer surplus. Like agriculture, timber is a marketed commodity so the value of acid deposition impacts would be measured by a change in producer and consumer surplus. It is also important to note that changes in economic activity in the timber industry are not necessarily equivalent to changes in social welfare, as they not only fail to account for potential consumer surplus but they also do not fully capture producer surplus (firm profits). Nonetheless, the model represents a valuable development in acid deposition analysis and provides a useful basis for further Canadian forestry valuation work.

In summary, economic valuation of the benefits and damages of acid deposition to timber is currently impeded by our limited capacity to relate acid deposition to forest growth/health and by our incomplete understanding of the links between tree growth and social value. However, work by Dr. Arp and others is improving our knowledge of the science and Vertinsky and others are rapidly improving our understanding of the value of changes in tree growth to the Canadian economy.

10.3.2.4 *Visibility*

Changes in visibility are one of the most noticeable effects of acid deposition. Smog and haze resulting from acid deposition are easy for people to observe. Particularly in major cities, smog is considered a serious problem by a large number of Canadians. Economic analysis indicates that the visibility benefits of pollution control can be substantial (Chestnut et al., 1999).

In order to assess the economic impacts of changes in visibility, a scientific relationship between acid deposition and visibility needs to be established. Some studies, particularly in the U.S., have attempted to develop a quantitative relationship between air pollution and visibility. The metrics used in visibility studies have often been controversial as "visibility" itself is hard to quantify. Some studies have tried to use measures such as the number of days of "good" visibility, the average visual range, or a measure called the "deciview" level, in order to quantify visibility levels.

The economic value of visibility is derived largely from the enjoyment that people get from the view they have at home, at work, and in recreational areas. Another source of value for visibility derives from the fact that many individuals link air clarity with overall air quality. There is a common perception that if the air is clear, the air is clean. Therefore, people who value physical health are also likely to value improved air clarity. This link between good visibility and perceived health benefits presents a challenge for valuation. It can be hard to isolate the value that individuals place on visibility for its own sake from the value they place on what they perceive to be health benefits.

The primary cause of poor visibility is particulate matter (PM) in the air. As a result, most visibility work in the past has focused on PM rather than acid deposition. It is possible to apply much of the PM focused valuation work to acid deposition once DRFs linking acid deposition with visibility are available. The scientific links between acid deposition, PM and visibility are discussed elsewhere in this report.

Visibility represents a challenge for monetary valuation because the value of visibility is dependent on people's perception rather than on market value. Valuation of visibility must be based on approaches such as revealed preferences or stated preferences. Although it is sometimes possible to estimate visibility values based on market observation (revealed preferences), particularly when it comes to tourism, stated preference approaches tend to be better at capturing the full range of visibility values. Most recent estimates of the value of visibility have been based on stated preference approaches such as contingent valuation (CV) and contingent choice (CC). These studies have been controversial due to poorly defined visibility metrics or a failure to accurately represent natural variability in visibility (e.g. snowy or rainy days). Despite the controversy, in the absence of a market for visibility, stated preference surveys are often seen as the best way to value changes in visibility.

Before 2000, most of the visibility valuation work in Canada was based upon studies and surveys conducted in the U.S. (DSS, 2000). In 1999, the U.S. EPA released results of a study to measure the benefits of the U.S.'s 1990 Clean Air Act (EPA, 1999). The report estimated the benefits of visibility improvements attributable to the Act to be between $40 to $137 U.S. per household, depending on location, with higher values in residential areas compared to recreational areas. It should be noted that the Science Advisory Board overseeing the U.S. EPA cost-benefit analysis decided not to include the visibility figures in formal assessments due to concerns about validity. Nonetheless, the methodology and approach of recent U.S. studies are useful to Canadian researchers and policy makers although the results themselves are not transferable.

The environmental component of the air quality valuation model (AQVM-E) uses a logarithmic valuation function, similar to the EPA's, for valuation of visibility in Canada. The availability of Canadian data to support this kind of analysis is extremely limited. To date, visibility studies used to support the AQVM-E are all from the U.S.. The AQVM-E calculates the expected value of a 5% improvement in visibility (visual range) to be $10 per household per year for an area of typical visibility (Chestnut et al., 1999). These valuations must be treated as rough estimates only because they are based on valuation studies that are not current and not Canadian.

Recently, more research into valuation of visibility has been conducted in Canada. Of particular note is the study by Haider et al. (2002), which used a CC survey to estimate economic value of improved summer visibility in the lower mainland of British Columbia. The Haider et al. model isolated the health and non-health component of respondents' valuations. The final estimates for the welfare benefits for a 5% improvement in visual range were $29.38 CAN per household per year, and $48.55 CAN per household per year for a 20% increase in visual range (Haider et al., 2002). These values are at the low end of the most recent visibility value estimates from the U.S.. This, the authors argue, can be attributed to the superior air clarity in lower mainland BC compared to many American cities. Further research is currently ongoing, and attempts are being made to transfer the results of the Haider et al. study to other parts of Canada.

10.3.2.5 Non-market environmental goods and services

The emphasis of this section is on environmental goods and services that are not directly bought and sold in markets. This group generally includes items like biodiversity, ecosystem health, wildlife health, plant life health, the abundance of wildlife, soil erosion, and the preservation of natural functions. For many of these endpoints there is an incomplete understanding of the dose-response relationships for acid deposition which prevents valuation analyses that would be relevant for policy development.

The economic value of non-market environmental endpoints depends on the relationship of these endpoints to human beings (Figure 10.2). Environmental resources have value (in the economic sense) only in so far as they have value to humans. Hence, the establishment of a link between environmental effects and humans is critical to estimate value.

Even when environmental effects are relatively well understood, valuing these end points is complicated because they are not traded in markets. Therefore, the value of these goods and services must be based on either stated preference or revealed preference approaches. From a qualitative perspective, there is a lot that can be said about the value of these environmental goods and services. It appears Canadians place substantial value on things like biodiversity, species survival and the recreational value of wilderness areas. Quantitatively, however, there are enormous gaps in the knowledge necessary to value most non-market environmental resources.

In broad terms, the value that people have for nature is made up of the value that they place on it due to their own personal use (use value) and the value that they place on it irrespective of their own use (passive use value). Use value is easier to measure than non-use value because it is more likely to be represented by actual consumer spending. Of course, the environmental goods and services themselves are not bought or sold, but there are observable market transactions related to these goods and services that give an indication of their economic value. Using valuation techniques like the travel cost method, economists can estimate the value of environmental resources based on observed expenditures.

According to the 1996 Canadian Nature Survey, Canadians spend over $7.2 billion on outdoor activities in natural areas in Canada (Federal-Provincial Task Force on the Importance of Nature to Canadians, 2000). This figure does not include expenditures on wildlife viewing (e.g. bird watching), fishing or hunting, which accounted for an additional $4 billion in expenditures. These expenditures are not direct expenditures in order to purchase the environmental good or service, but expenditures in order to appreciate the good or service, such as binoculars, plane tickets, hotel accommodations, camping equipment, canoe rentals, etc.

Nature related expenditures contribute meaningfully to the Canadian economy as a whole. In 2000, the use of nature-related activities contributed $12.1 billion to Canada's GDP (more than 1% of total GDP), $5.9 billion to personal income, and $5.4 billion to government revenue (Federal-Provincial-Territorial Task Force on the Importance of Nature to Canadians, 2000).

We must keep in mind that expenditures alone underestimate the total value of these resources to users. Use value is the amount that people would be *willing* to pay rather than the amount they actually do pay. The expenditures needed to visit a national park, for instance, would include the costs of park admission, lunch and money for gasoline. However, the value of the park to users is likely higher. In 1993, daytime park users in British Columbia spent 19.7 million days in parks and received an estimated benefit of $30.90 per person per day (Stanley, 1997). In the Nature Survey, Canadians indicated that they would be willing to spend an additional $2 billion, beyond their current expenditures, in order to continue using the natural environment in its current condition (Federal-Provincial-Territorial Task Force on the Importance of Nature to Canadians, 2000).

In considering the value of natural environments to users, one must consider the opportunity costs involved in addition to expenditures and willingness to pay. In 1996, Canadians spent 1.5 billion days engaged in nature-related activities (Federal-Provincial-Territorial Task Force on the Importance of Nature to Canadians, 2000). Individuals could have used this time to pursue other sources of entertainment, vacations, or work. Part of the cost of enjoying nature is the absence of time to pursue other activities. This opportunity cost contributes to the use value that people have for the natural environment. Travel cost methods permit us to measure values based on travel expenses and the opportunity cost of recreation rather than simply the direct financial costs.

The above figures are indicative of values that people place on environmental resources in their current state. These values do not indicate the relative change in value that people would assign to the site if the site were to change as a result of acid deposition. As stated in Section 10.3.1.2, cost-benefit analysis requires the value of marginal changes in a resource rather than the total value of the resource. The above figures indicate little about the potential changes in value due to marginal resource damages or improvements. None the less, they do provide some indication of the type and magnitude of the use values that people have for certain environmental amenities.

There are also substantial non-market use values attached to Canada's natural water resources. There has been some work to estimate these values. The project "Monitoring the Value of Natural Capital: Water" (Gardner Pinfold Consulting et al., 2002), developed jointly by Environment Canada and Statistics Canada, aims to develop a methodology to value water and to set-up a framework for a national water resource account. The project addresses the challenge of linking human uses to a monetary valuation for water. While not directly addressing the changes in values of water associated with acid deposition, the report provides a useful framework for non-market benefits analysis of various environmental impacts. In the future, a similar framework could be applied to a forest inventory identifying the value of our forests and linking the value to damages from acid deposition and other pollutants.

In general, we have very little information available on the change in the value of non-market environmental goods and services resulting from changes in the environment. For instance, we know that bird watching is a very large industry and that people spend substantial amounts of money on binoculars and on trips into the woods. However, we have no idea how much these expenditures would decline if, for example, the blue heron became extinct.

Recreational fishing is one area where there is some capacity to quantifiably value the link between acid deposition and an environmental effect. The acidification of lakes and rivers are well documented in eastern Canada and atmospheric models can link acid deposition levels with acidification of lakes. Wildlife models can determine probabilities of fish type and quantity occurring in a lake with a given acidity level. Hence, the probability of a fisherman catching certain types of fish can be calculated. Through surveys of fishermen in the U.S. and observations of spending patterns, economists have gained an understanding of how much an increased or decreased probability of fishing success is worth to fishermen. Models like the AQVM-E have been able to include this information to estimate the benefits of acid deposition reductions. Based on a number of different studies, including Talhelm et al. (1987) in Ontario and Quebec and Englin et al. (1991) in the north eastern U.S., the AQVM-E estimates that the value to fishermen of a 1% change in acid deposition levels ranges from $0.003 to $0.07 per fisherman per day, with an expected value of $0.03 (Chestnut et al., 1999). These numbers may seem small given that, in 1996, average expenditure on fishing for those who participated in fishing was $27 per day (or $40 per day for those whose primary purpose was fishing) (Federal-Provincial-Territorial Task Force on the Importance of Nature to Canadians, 2000). The relationship between acid deposition levels and the willingness of fishermen to pay to avoid its impacts may be nonlinear, or non-continuous. This highlights the need for further work to clarify the relationship between fish habitat and availability and its value to fishermen.

Except for recreational fishing, economists have a limited understanding of how the use value that Canadians have for unmarketed ecosystems changes in response to changes in acid deposition levels. Since "sixty-one percent of the forest lands in the Canada land inventory having high recreational potential are exposed and sensitive to the effects of acidification" (Smith, 1995), it is possible that acid deposition could significantly reduce the use value that Canadians have for wilderness areas. Because acid deposition is not highly localised at a regional level, it is unlikely that acid deposition impacts could be avoided easily by the use of alternate (substitute) locations for recreation. Further research is needed to value the link between environmental effects and human activity.

The non-use, or passive use, value that Canadians have for non-market environmental endpoints is even less well quantified than the use value. We know that non-use values exist and are significant. Canadians routinely indicate an interest in protecting and preserving environmental resources that they have no contact with and from which they derive no direct benefit. For example, there has been substantial support for protecting Canada's caribou herds and northern wilderness areas from damaging oil exploration even though most Canadians do not eat caribou meat or travel to northern areas to view caribou. The desire to protect these animals and their environment must be motivated by a desire to preserve them for the inhabitants of the region (vicarious consumption), for future generations (bequest value), or simply for their own sake (pure existence value). These desires indicate a passive use value which is generally not captured by any market.

This is not to say that there are no market indicators of consumers' passive use values. There are some forms of market choices that can give economists an indication of the non-use value that Canadians have for environmental goods and services. For instance, the fact that people purchase dolphin safe tuna, even though they do not personally benefit directly from the existence of dolphins, indicates a willingness to pay for something that is of little or no direct personal use.

Similarly, contributions to environmental charities can be an indication of non-use value. Canadians are often willing to contribute to environmental groups not because they receive a direct benefit, but because they feel that protecting animals or the environment is the right thing to do. This indicates an interest in protecting the environment for future generations, for people in other parts of the world, or simply for its own sake. According to the National Survey on Giving, Volunteering and Participating, Canadians donated $98.9 million to environmental charities in 2000 (Hall et al., 2001).

Although they provide some indication of people's passive use value of the environment, contributions to environmental charities and purchases of green products are underestimates of the non-use value that people place on the environment. There has been some research conducted that attempts to link donations to environmental charities with willingness to pay for non-marketed environmental goods. However, there is no widely accepted model that allows this connection to be made nor is there an accepted method for estimating total economic value based on the purchase of green products.

Since market observations do not fully capture non-use value, stated preference approaches have been used in most attempts to estimate the total economic value of certain non-market environmental goods and services. Contingent valuation (CV) has been the tool of choice for most of this work and numerous CV surveys have been conducted in the past decades to examine the non-use value of non-marketed environmental goods. As an example, Adamowicz et al. (1998) used both CV and choice experiment (CE) approaches to measure passive use values associated with preserving the woodland caribou, a threatened species in west central Alberta. Although results differed depending on which survey and what model was used, the results indicated that the non-use value for an increase in caribou from 400 to 600 was between $75.42 and $142.82 per household. There are many other surveys and models similar to this one that estimates the value of a given change in some endpoint (e.g. a particular species; the clarity of a particular lake).

The major challenge in quantifying the non-use value impacts of acid deposition arises from the vast number of endpoints affected. Depending on the level of detail desired, there could be more environmental endpoints to quantify than there are species of plant and animal life in the Canadian wilderness. The development of surveys is both time consuming and costly. It is not feasible to value each endpoint affected by acid deposition. Efforts have therefore focussed on main environmental indicators.

A University of Alberta (UofA) research team is developing a survey instrument that will estimate willingness-to-pay for improvements in freshwater ecosystem health due to a reduction in acid deposition. Because "improved ecosystem health" is something that most respondents will not identify with in a quantified manner, this instrument will attempt to translate the concept into terms that are more concrete to the respondents. In this case, these more concrete terms are the number of loons on a lake or the number of young birds born. By using the loon as a "champion species", it will be possible to estimate the value of the ecosystem as a whole based on survey responses related to loons. The loon is also a keystone species that is both vital to and representative of overall ecosystem health. This will be highlighted in the survey. Without needing to know the precise biological interactions that take place in the ecosystem, it is enough that people know that loons are a keystone species in the valuation experiment.

Further research into the non-use value of unmarketed Canadian resources is needed to improve our understanding of the total impacts of acid deposition in Canada. Canada is the second largest country in the world but most of the land mass is generally unused by humans. Since most of Canada's land is unused, the value of this land is highly dependent on its non-use value. The land is valuable for two reasons: It supports the larger Canadian ecosystem and thus, indirectly provides use values; and for many people the existence of this land and the life it supports is valuable. These values can be substantial and are wholly non-use values. Estimates of the loss in passive use value associated with large scale environmental effects can reach the billions of dollars. For instance, CV surveys estimated the damages, in terms of lost passive use value, caused by the Exxon Valdez oil spill to be approximately $3 billion (U.S.) (Carson et al., 1992). To fully account for the social damages caused by acid deposition, it is imperative that we consider not only those areas close to urban centers but also the largely uninhabited and unused Canadian expanses that are also being damaged by acid deposition.

In conclusion, the total economic value of non-marketed environmental goods and services in Canada is largely unknown. We have some indications of the use value of some of these goods and services but very little information on passive use values. The main scientific gaps are the identification of DRFs linking acid levels to quantifiable changes in environmental endpoints. The main economic gaps are our ability to determine how use values will change in response to changes in the quantity/quality of environmental endpoints. We also need more research into passive use values. Since the total economic value of non-market resources in Canada is potentially quite large, further research in this area could contribute substantially to an understanding of the full benefits of acid deposition abatement. The omission of most of these benefits from current cost-benefit analysis implies that current policy analyses may significantly underestimate the benefits of acid deposition abatement.

10.3.2.6 *Health effects*

The effects of acid deposition on human health are dealt with in Chapter 9. This section briefly reviews the main focuses of the economic valuation of health benefits and attempts to put them in the context of the environmental benefits of acid deposition abatement. It does not provide details on the full range of health effects and their monetization.

Health effects are among the best understood and most thoroughly valued impacts of acid deposition. The monetized health benefits of reducing acid deposition and its precursors are substantial.

> *"The expected health benefits to Canada of a 50% SO_2 reduction in both eastern Canada and the U.S. (i.e., reductions above and beyond the current commitments in the Eastern Canada Acid Deposition Program and U.S. Acid Rain Program) are the following: 550 premature deaths per year would be avoided; 1,520 emergency room visits per year would be unnecessary; and 210,070 asthma symptom days per year would be avoided. Economists estimate that society values these health benefits in a range from just under $500 million per year up to $5 billion per year."*
> **(http://www.ec.gc.ca/acidrain/acidhealth.html)**

In most studies, the value of the effects of pollution on human health dwarfs all other impacts. Generally, the monetized value of improvements in human health make up between 30 and 95% of the total monetized value of pollution abatement (Pearce, 2001).

Health effects tend to dominate benefit valuations due to the high damage value usually attributed to human mortality. The valuation of human life is controversial and there is some disagreement among both economists and policy makers about the appropriate figure(s) to use. The figure currently being used in the health component of the AQVM (AQVM-H) to value the damages of one human death is $4.1 million (Chestnut et al., 1999). This figure is about 20 times the value of the second most serious health outcome and 500 times the value of the third most serious health outcome in the AQVM. Other pollution valuation models contain similar figures to the AQVM-H. As indicated by Pearce (2001), in most valuation exercises, mortality effects account for 50% or more of the total human health benefits of pollution abatement.

10.3.2.7 *Summary*

In Canada and abroad, scientists have been working on establishing DRFs that link acid deposition to various environmental effects. Economists have been working on estimating the monetary value of a variety of these environmental effects. Currently, however, the capacity of models like Canada's AQVM to estimate the benefits of acid deposition abatement is limited in most areas.

10.4 COSTS OF ACID DEPOSITION ABATEMENT

10.4.1 Approach to cost estimation

Three broad approaches can be used to estimate the costs associated with the implementation of an environmental policy: direct costs approach, partial equilibrium analysis, and general equilibrium analysis. The direct costs approach seeks to capture the costs incurred from a private perspective and does not capture other changes in the economy. To overcome this limitation, a partial equilibrium analysis can be used to consider one sector or economic group at a time. This approach allows the analysis to capture some elements of social costs associated with a policy but fails to consider the impacts arising because of one sector's forward and backward linkages to the rest of the economy. In order to avoid these limitations, Environment Canada uses a general equilibrium analysis approach which provides a complete accounting of costs and takes into account linkages within the economy.

10.4.2 Current cost assessment work

As discussed in the benefits section of this chapter, the majority of clean air valuation work completed in Canada in the past decade has focused on particulate matter (PM) and ozone. The Canada Wide Standards (CWS) for PM and Ozone have been one of the major drivers behind the quantification of the costs and benefits of reducing these pollutants and their precursor emissions. In recent years, Environment Canada has made significant efforts to develop its capacity to estimate the costs of meeting the CWS for PM and Ozone. In response to a 2001 report by an expert panel for the Royal Society of Canada (RSC), Environment Canada has expanded its focus on costs to include economy wide cost effects and the possibility of multi-pollution targets and non-technologically oriented cost solutions. As a result, Environment Canada's ability to estimate the economic costs of meeting the CWS for PM and Ozone has greatly increased in the past three years. There has been comparatively less effort spent directly on the quantification of acid deposition abatement costs. There is considerable overlap between ozone, PM and acid deposition. This is particularly true on the cost side, as the primary pollutants responsible for acid deposition, NO_x and SO_2, also contribute significantly to the formation of PM and ozone (see Chapter 11). Though not focused on acid deposition, a great deal of the research into the costs of emission abatement can be applied to analyze the costs of acid deposition reduction. Although Environment Canada does not currently have the capacity to fully estimate all the costs associated with reducing acid deposition, there are a number of models and approaches in place to facilitate cost analysis.

One of the primary cost assessment tools used by Environment Canada is the Energy 2020 model. Energy 2020 is a multi-sector energy-environment analysis system that simulates the supply, price and demand for fuels. This model includes supply and demand information for energy and relates changes in the electricity market to changes in the rest of the economy (Backus et al., 1995). The model can compute not only the direct costs of acid deposition abatement in the energy sector but also many of the resulting indirect costs.

The Energy 2020 model is currently being adapted for the Canadian context by the Canadian Energy Research Institute to include macroeconomic forecasts for Canada and to conduct criteria air contaminant and climate change policy analysis. Work is also planned to update the Energy 2020 model with new information on costs, energy use and multi-pollutant emission coefficients.

Other tools used for estimating pollution abatement costs include AERCo$t, RDIS, AERdat, and the MERAF reports. AERCo$t is a software database that is useful for determining the range of costs associated with proposed emission reductions (REAB, 2000). It can provide information on a wide range of air pollutants at the national, provincial, regional, and sectoral or plant level. Area, mobile and point sources for all sectors in Canada are included in the program. AERCo$t includes a variety of pollutants, including NO_x and SO_2.

The AERdat database and accompanying reports provide provincial, national and sectoral cost estimates of reducing Criteria Air Contaminant (CAC) emissions by 25, 50 and 75%. The database covers 95% of emissions and 39 source sectors. The cost estimates are intended to reflect the order of magnitude and relative costs of applying a wide range of emission reduction technologies. Estimates are based on the U.S. Environmental Protection Agency's inventory of costs of air pollution technology. The AERdat was developed only as a tool for preliminary analysis of the CWS for PM and Ozone, so caution must be used in applying these numbers to Canadian policy analysis.

The reports from the Multi-pollutant Emission Reduction Analysis Foundation (MERAF) can also be used in emission reduction cost analysis. These reports, developed in consultation with industry and other stakeholders, are intended to inform and support the development of emission reduction actions for the six multi-pollutant emission reduction strategy (MERS) sectors (pulp and paper; lumber and allied wood products; electric power; iron and steel; base metal smelting; and concrete and asphalt plants).

Environment Canada is also working with Informetrica on the development and application of Informetrica's macroeconomic model to examine scenarios and implications of clean air initiatives for several industrial sectors, including the MERS sectors. The Informetrica model will be linked to Energy 2020 to create an integrated energy, emissions and economy model. This model will be able to estimate the direct, indirect and induced effects of various existing and proposed climate change and clean air policy initiatives. Impacts will include GDP, industry gross output, employment, personal disposable income, tax interaction, and sector-specific competitiveness effects.

Environment Canada is in the process of improving and preparing data on emissions, efficiencies, and abatement costs associated with various process technologies in the six MERS sectors. These datasets are being improved to reflect proper aggregation levels and to make them suitable for use in Energy 2020.

In summary, there is considerable ongoing work to develop and refine various modeling tools that could be expanded for use to estimate the costs of acid deposition abatement.

10.5 CONCLUSIONS

Currently, we are not able to quantify and monetize all of the costs and benefits associated with acid deposition abatement. Further advancements in the models for cost and benefit valuation should improve our socio-economic assessment of acid deposition policy. Ongoing work in Canada and elsewhere, including the work reviewed in this chapter, indicates that we are making significant improvements in our ability to value in monetary terms the numerous potential benefits and costs of acid deposition abatement.

In recent years, our ability to quantify and estimate human health damages caused by acid deposition has evolved considerably. Although environmental economic research has improved our understanding of environmental damages, there are still large gaps in our understanding of the nature and value of acid deposition impacts. Despite the fact that some modeling capacity currently exists (e.g. the Air Quality Valuation Model), acid deposition models do not adequately account for environmental benefits resulting from abatement. With respect to the determination of costs associated with acid deposition, models such as Energy 2020 and Informetrica represent substantial progress in the estimation of economic costs of SO_x and NO_x reductions.

Ongoing improvements in modeling and valuation will improve Canadians' understanding of the socio-economic impacts of acid deposition policies. This will support more effective and efficient management strategies. In particular, this work will enable us to continue to identify linkages with other air issues, leading to efficient, coordinated action on multiple fronts, such as electricity generation, transportation, PM, ground level ozone and climate change.

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CHAPTER 11

Co-Benefits and Linkages to Other Air Issues

M. Little and H.A. Morrison

11.1 KEY MESSAGES

- Acid deposition is linked to many other environmental issues by common precursor pollutants, common sources of pollutants and the interrelationship between broad-scale phenomena such as climate, weather, and chemistry.
- The interrelationship between environmental issues implies that policy measures to address one issue can benefit (or harm) the others.

11.2 INTRODUCTION

Acid deposition is the end product of reactions between sulphur oxides (SO_x), nitrogen oxides (NO_x) and water in the atmosphere. In addition to the formation of acid deposition, SO_2 and NO_x contribute to other environmental issues such as particulate matter (PM) and tropospheric ozone (Seinfeld and Pandis, 1998), climate change (Pentcheva, 2002), reductions in visibility (McDonald and Shepherd, 2004), eutrophication (Smol and Hall, 1996), and mercury bioaccumulation (Frost et al., 1999). The interrelationship between these issues implies that policy measures to address one issue can benefit (or harm) the others. This chapter describes the linkages between acid deposition and other environmental issues and the potential impacts of emission abatement measures for SO_x and NO_x on these issues.

11.3 PARTICULATE MATTER

Particulate matter (PM) shares precursor emissions (SO_x and NO_x) with acid deposition. PM is a dynamic pollutant with a composition that varies depending on the source of emissions, pathway of formation and prevailing meteorology. Consequently, PM is a suite of pollutants that spans a range of sizes and is comprised of a variety of chemical constituents. PM can be primary or secondary in origin. Primary PM describes PM that is emitted into the air directly in particle form. This type of PM can be "fine" (i.e. $PM_{2.5}$) or "coarse" (i.e. $PM_{2.5\text{-}10}$) and is primarily comprised of black carbon, organic carbon and soil dust. Secondary PM refers to PM that is formed in the ambient air when "precursor gases" react to form particles. The most common gases involved in the formation of secondary PM in Canada are sulphur dioxide (SO_2), nitrogen oxides (NO_x), volatile organic compounds (VOCs) and ammonia (NH_3) (Brook and Dann, 1999). Secondary $PM_{2.5}$ comprises more than half of the total $PM_{2.5}$ mass in eastern Canada and a substantial portion in the rest of the country (EC, 2001).

Figure 11.1 illustrates some of the pathways that link precursor gases with formation of secondary PM. This figure also illustrates the relationship between PM precursor gases and ground-level ozone and acid deposition.

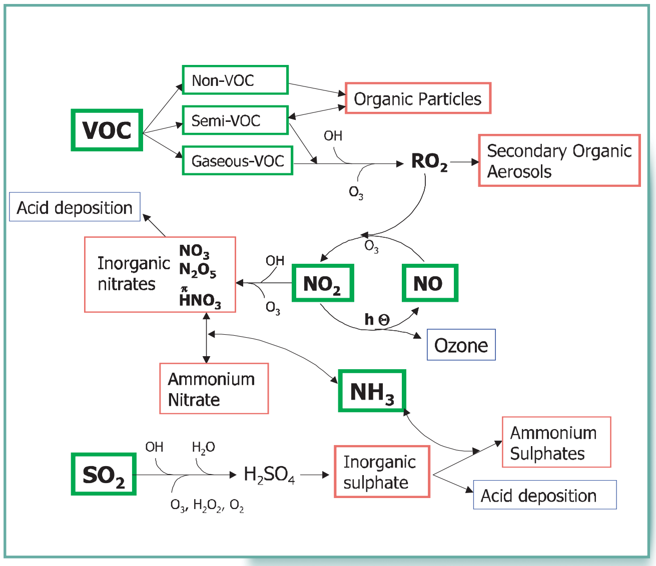

Figure 11.1: Common reaction pathways for the formation of secondary PM. Green boxes are precursor gases, orange boxes are particles ($PM_{2.5}$ or $PM_{2.5\text{-}10}$) and blue boxes are other air quality outcomes. Reproduced from EC, 2001 with permission.

The relationship between ambient levels of precursor gases and $PM_{2.5}$ is complicated. As a result of declining SO_2 emissions in the 1990s, ambient levels of SO_2 and particle sulphate decreased significantly during the early to mid-1990s. For SO_2, the long-term trends in ambient levels of $PM_{2.5}$, particle sulphate and SO_2 track each other closely - the rate of change in particle sulphate mass being slower at many sites in Eastern Canada than that for SO_2 (SC2-AQC, 2004). This suggests that reductions in emissions of SO_2 will lead to reductions in concentrations of $PM_{2.5}$ (NARSTO, 2003).

The relationship between ambient levels of NO_x and $PM_{2.5}$ has not been described. The relationship between gaseous HNO_3 and particle nitrate (NO_3^-) has been described however, and exhibits an inverse relationship in the presence of sulphur dioxide and ammonia (i.e. particle nitrate levels increase as gaseous HNO_3 levels decrease due to conversion of HNO_3 to NO_3^-). This relationship suggests that, in general, increases in ambient levels of NO_x will increase the probability that NO_x will be converted into particulate nitrate and hence, potentially increase levels of $PM_{2.5}$ (NARSTO, 2003).

Seasonal differences in particle sulphate and particle nitrate levels may also impact acid deposition. In Eastern Canada, particle nitrate levels are higher during the winter season, while particle sulphate levels are significantly higher during the summer season. Precipitation levels are generally higher in the summertime, which may translate to seasonal patterns in wet deposition. These patterns have not yet been described in detail.

The relationship between emissions of SO_2, NO_x and ammonia (NH_3) is very important when determining the impact of changes in SO_2 and NO_x emissions on PM levels. For example, if SO_2 emissions are reduced but emissions of ammonia (NH_3) increase and emissions of NO_x remain relatively constant, there exists the potential for a significant increase in the formation of ammonium nitrate aerosol. This increase in nitrate aerosol formation may confound potential reductions in PM from the reduction in SO_2 emissions. This outcome stresses the importance of considering the complex chemistry of PM when addressing abatement options to improve air quality.

11.3.1 Visibility

PM increases the extinction of light travelling through the atmosphere, hence reducing visibility. In most regions of Canada, the sulphate and nitrate components of PM contribute most greatly to reductions in visibility (McDonald and Shepherd, 2004). Light extinction of particles is influenced by the size of particles and relative humidity. Under humid conditions, the light extinction properties of sulphates generally dominate those of other fine particle constituents (on a per unit mass basis) due to the fact that this ion is associated with more water (McDonald and Shepherd, 2004). Due to the relationship between acid deposition precursors, PM and visibility, reductions in PM will improve visibility and benefit acid deposition.

11.4 TROPOSPHERIC OZONE

Tropospheric ozone (O_3) primarily shares the precursor emission of NO_x with acid deposition. The formation of tropospheric ozone can occur via a series of chemical reactions; the most common of which involves nitrogen oxides, volatile organic compounds (e.g. solvents), and sunlight (Figure 11.1). In general, increases in the emissions of NO_x result in increases in concentrations of tropospheric ozone on the regional scale; however, in urban areas, ozone levels seem to be more influenced by VOC emissions (i.e. VOC emission controls are more effective for reducing ozone than NO_x emission controls) and increases in NO_x emissions lead to decreases in ozone levels, the so-called “NO_x disbenefit” (NARSTO, 2003). The non-linear relationship between concentrations of NO_x and VOCs and ozone production complicates the forecasting of NO_x emission reductions on ozone levels.

11.5 CLIMATE CHANGE

Carbon dioxide (CO_2) is the most important gas contributing to climate change. The primary anthropogenic source of CO_2 is combustion of fossil fuels. Fossil fuel combustion is also an important source of SO_2 and NO_x (see Chapter 2). Hence, reductions in the use of fossil fuels will benefit both issues.

Both particulate matter and ground-level ozone play a role in climate change. Ground-level ozone is a radiatively active gas which exerts a warming effect on the climate. Ozone is the third most important greenhouse gas in terms of global impact on radiative forcing (carbon dioxide and methane are the most important). For the most part, increasing concentrations of tropospheric ozone are understood to exert a warming effect on climate at seasonal scales.

Sulphur plays a role in climate change via the formation of PM (e.g., ammonium sulphate). This role is complex but in simplistic terms can be broken down into two main effects. The first is a direct cooling effect resulting from the scattering of light away from the Earth's surface. The second is an indirect cooling effect from interfering in cloud processes and becoming cloud condensation nuclei. This latter process results in changes to cloud microphysical properties and longer lived clouds which, in turn, result in greater amounts of light being reflected away from the Earth's surface.

Another way in which acid deposition is linked to climate change stems from the relationship between climate and the quantities and patterns of deposition. Climate change is expected to change precipitation patterns within the next century (IPCC, 2001). It is generally accepted that precipitation is likely to increase globally (due to increases in near surface evaporation resulting from higher temperatures). Regionally, the changes in precipitation patterns are much less clear. It is speculated that summer dryness will occur in some regions and increases in precipitation will occur in other regions. Changes in precipitation patterns could significantly alter the location and severity of acid deposition. Regional changes in precipitation patterns, specifically drought followed by rain, can cause the release of stored sulphur from wetlands into surface waters.

Another potential impact of climate change is a perturbation of synoptic weather patterns (IPCC, 2001). Changes to synoptic weather patterns would affect the transport and dispersion of pollutants. If climate change produces more frequent southerly air flows, deposition levels of sulphate and nitrate in Canada could increase relative to levels prior to climate change.

The fourth mechanism by which acid deposition is linked to climate change stems from the relationship between a warming climate and biogenic emissions of NO_x. To date, effects of a changing climate on temperatures are speculative; however, the IPCC's third assessment report states that without a reduction in anthropogenic emissions of greenhouse gases, surface temperatures could increase by 5°C globally over the next century (IPCC, 2001). Emissions of NO_x from soils (a process that involves soil bacteria) represent an important and non-trivial source of NO_x accounting for up to 20% of NO_x emissions on a globally averaged basis (Yienger and Levy, 1995). Quantities of NO_x emitted from soils by bacteria are governed by land use/land cover, fertilizer application, temperature, and precipitation conditions. In temperate non-parched soils, NO_x emissions increase with increasing temperatures up to about 35°C. Hence, a warming climate could lead to changes in composition, abundance and productivity of soil bacteria which, in turn, could alter emissions of NO_x.

Climate change is also expected to change patterns of precipitation. Biogenic NO_x emitted from soils is highly dependent on soil moisture. In addition, NO_x emissions from soils depend on the cycling of precipitation events. For instance, NO_x emissions from soils tend to be highest directly after a significant rainfall following a period of drought. This type of climate event is likely to occur more frequently in the coming century and would likely increase the contribution of soils to global NO_x emissions.

Although it is understood that climate change and acid deposition are linked, the effects of changes in SO_2 and NO_x emissions on climate are still speculative. Further development of global climate models is required to fully understand the influence of anthropogenic emissions on climate.

The co-benefits of controlling SO_2 and NO_x emissions are dependent on the control methods and technologies utilized. Emission reductions can be achieved either through a decrease in combustion and/or use of a substance in production or technological and engineering solutions (e.g., scrubber design). Since much of the anthropogenic SO_2 and NO_x is produced through combustion, strategies geared toward the reduction of these emissions would also likely result in a reduction of CO_2 emissions. This would, over the long term, decrease climate warming trends. The co-benefits of end of pipe solutions for the control of SO_2 and NO_x emissions on climate change are much less clear and highly dependent on the control technology chosen.

11.6 EUTROPHICATION

Acid deposition has been linked to eutrophication via two primary mechanisms; the first involving phosphorus (P) and the second involving nitrogen (N).

The first mechanism has been observed in some mesotrophic freshwater lakes in southcentral Ontario (Smol and Hall, 1996). In these lakes, analysis of diatoms in the lake sediments suggested that pre-industrial total P concentrations were significantly higher than at present. One explanation for this 'de-eutrophication' is that lake and/or watershed acidification processes have reduced P loading, or increased the rate of P loss from lakes.

De-eutrophication with regard to P is consistent with the observed effects of soil acidification. Phosphate ions become less soluble with increasing soil acidification due to the formation of aluminium phosphate and iron phosphate. Another possible explanation for this decrease in the release of P from soils is a decline in nutrient loading from the watershed as a result of logging. For instance, early succession forests (50-100 years following forest clearance) may retain nutrients more strongly than mature, old-growth forests (Smol and Hall, 1996).

The second mechanism by which acid deposition has been linked to eutrophication involves nitrogen (N) cycling (Anderson et al., 2002). In many estuarine and coastal waters, N is the most important nutrient that limits primary production of photosynthetic organisms (Dugdale and Goering, 1967; Glibert, 1988). Increased loadings of N to these environments have been linked to algal blooms. Of special concern to resource managers is the relationship between eutrophication and harmful algal blooms. On local to global scales, one of the most rapidly increasing sources of nutrients to the coastal zone is the atmosphere. In estuarine and coastal waters, it has been estimated that 20-40% of nitrogen inputs can be of atmospheric origin, from industrial, agricultural and urban sources (Duce 1986; Fisher and Oppenheimer, 1991; Paerl, 1995, 1997; Driscoll et al., 2001). Atmospheric inputs are important not only because of their magnitude, but because the mix of atmospheric nutrients, like other nutrient sources, can stimulate productivity of some phytoplankton species disproportionately over others. Experimental manipulations have shown that rainwater can enhance productivity more than the addition of a single N source (Paerl, 1997). The high proportion of dissolved organic N in rainwater, representing up to 40% of its total N, is thought to be significant in this enhancement (Timperley et al., 1985; Paerl, 1997).

11.7 MERCURY BIOACCUMULATION

Emissions of mercury and other hazardous pollutants work in synergy with SO_2 and NO_x to enhance the deleterious effects of acid deposition on fish and wildlife. As levels of acidity in surface waters increase, the rate of conversion of mercury (Hg) into toxic and bioavailable methyl mercury (MeHg) increases (Frost el al., 1999). Recent studies have shown that significant declines in atmospheric deposition of sulphate and Hg are associated with declines in Hg levels in fish and fish-consuming wildlife such as the Common Loon (see Chapter 6). Thus, reductions in acid-causing emissions would benefit the mercury issue.

11.8 SUMMARY AND CONCLUSIONS

Many co-linkages exist between acid deposition and other environmental issues. This chapter describes many of these linkages and highlights the necessity of considering the consequences on many different issues of changes in emissions of acid-causing pollutants. Overall, it is becoming clear that programs targeting SO_2 emissions will reduce the potential for acid deposition and as a co-benefit improve air quality, visibility, and also the severity of mercury contamination within the food chain. It is also apparent that reducing NO_x emissions will also improve eutrophication of estuarine environments. Less clear are the impacts of SO_2 and NO_x emission changes on climate change.

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CHAPTER 12

CONCLUSIONS: Answers to Objective Questions including Scientific Gaps and Future Work

12.1 IS ACID DEPOSITION STILL AFFECTING THE CANADIAN ENVIRONMENT AND THE HEALTH OF CANADIANS? IF SO, WHERE, HOW, AND TO WHAT EXTENT IS IT AFFECTING THESE ENDPOINTS?

Acid deposition is still affecting the Canadian environment and the health of Canadians.

12.1.1 Canadian Environment

In Canada, the primary indicator of whether or not acid deposition is still affecting the environment is the occurrence of exceedances of critical loads. In this assessment, critical loads are defined as "a quantitative estimate of an exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge"[1]. For the first time in North America, combined maps of the critical load values for both aquatic[2] (i.e. lake) and terrestrial (i.e. upland forest soils) ecosystems have been produced for those regions where lake chemistry and/or soil chemistry and acid deposition data were available. The combined critical load maps take into account the acidity of wet and dry deposition derived from both sulphur and nitrogen pollutants and express critical loads as acid equivalents[3] per hectare per year (eq/ha/yr). To produce these combined critical load maps, the most sensitive element of the environment - either the aquatic or terrestrial ecosystem - determines the critical load of a particular area (i.e. mapped grid square). Two methods were used to calculate critical load exceedances for aquatic and terrestrial ecosystems. The first method, N-leaching, accounts for the acidity of wet and dry deposition of sulphur and only the component of nitrogen deposition that is estimated to be acidifying (i.e. not retained in the watershed). The second method, Steady-state, assumes that all sulphur and nitrogen deposition is acidifying.

N-leaching critical load exceedances best estimate the immediate impact on the environment of current levels of acid deposition. This method is considered an "optimistic" indicator of impacts because ecosystems have yet to reach equilibrium with acid deposition. Steady-state critical load exceedances are considered a more accurate measure of the sustainable (long-term) impacts of current levels of acid deposition and may be considered a more "pessimist" measure of the short-term current impact. Exceedances of critical loads occur when levels of acid deposition exceed the level that the ecosystem can assimilate without significant harmful effects.

The results of this assessment confirm that although levels of acid deposition have declined in eastern Canada over the last several decades (e.g., Figures 12.1 and 12.2), approximately 21-75% of eastern Canada, corresponding to approximately 0.5-1.8

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[1] Definition employed by the UN ECE (Nilsson, J. and Grennfelt, P.. 1988. Critical loads for sulphur and nitrogen. Report from a workshop held at Skokloster, Sweden. Miljørapport 1988:15, Nordic Council of Ministers, Copenhagen, Denmark. 31pp.).

[2] Water chemistry data were compiled for 3130 lakes from all the Canadian provinces and territories (except PEI) to assess their current status. In the eastern provinces (defined as ON and eastwards), where lake chemistry is changing due to reductions in acidic deposition, the sampling period for these "current status" lakes was 1997 or later. This restriction was relaxed for the western provinces and territories. The compiled databases provide a sample population that is not a representative subset of the overall lake resource. Geographically, the lakes are irregularly distributed, often occur in clusters, and there are numerous areas where sample data are unavailable or too out-of-date. Lake samples in the eastern provinces tend to be located in acid sensitive terrain, and in both sensitive and insensitive terrain in the west and north. The available sample populations were skewed to larger lakes, and it is likely that many aquatic effects occur in the small lakes.

[3] Since S and N have different atomic weights, it is impossible to report combined critical load values on a mass basis (e.g., kg/ha/yr). Instead, combined critical loads must be reported on a charge equivalency basis, referred to as acid equivalents (e.g., eq/ha/yr).

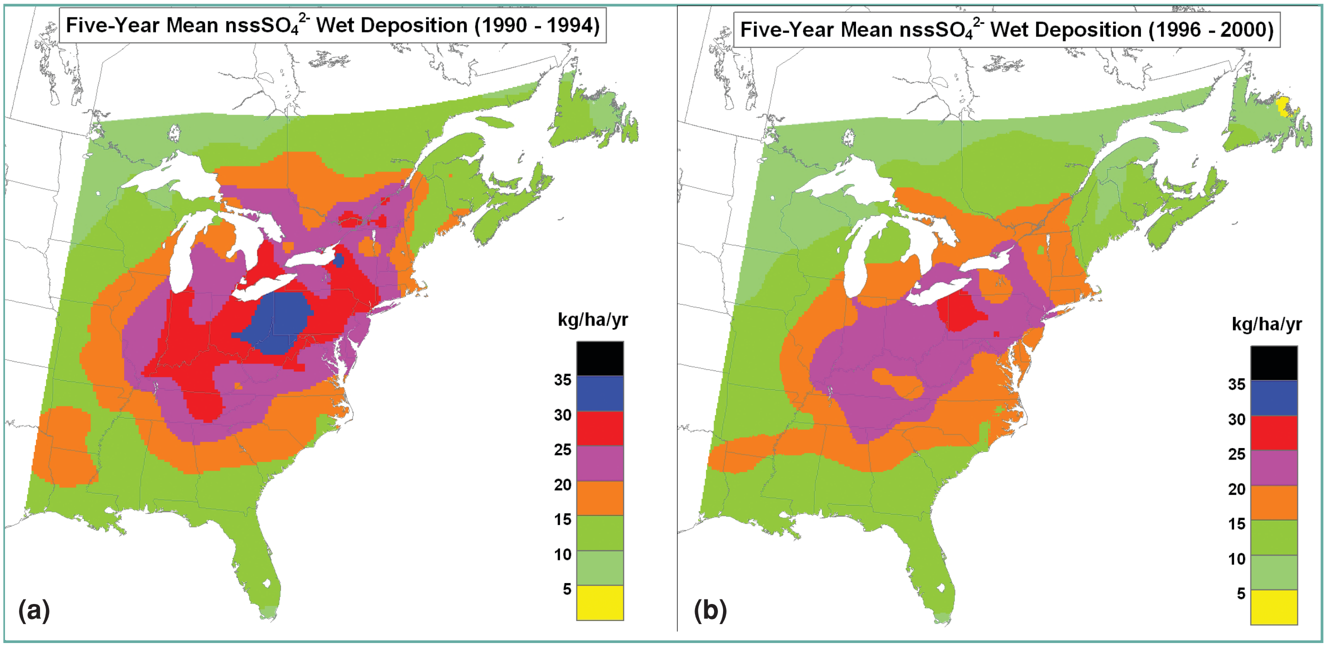

Figure 12.1: Changes to the spatial patterns of non-sea-salt-sulphate (SO_4^{2-}) wet deposition (in kg/ha/yr) in eastern North America from the early to late 1990s. The map on the left shows the 5-year-mean wet deposition pattern for the period 1990-1994 and the map on the right shows the 5-year-mean pattern for the period 1996-2000. A significant decrease in the area receiving deposition in excess of 20 kg/ha/yr has occurred in response to decreases in SO_2 emissions. (Note: 1 kg SO_4^{2-}/ha/yr is equal to 20.8 eq/ha/yr).

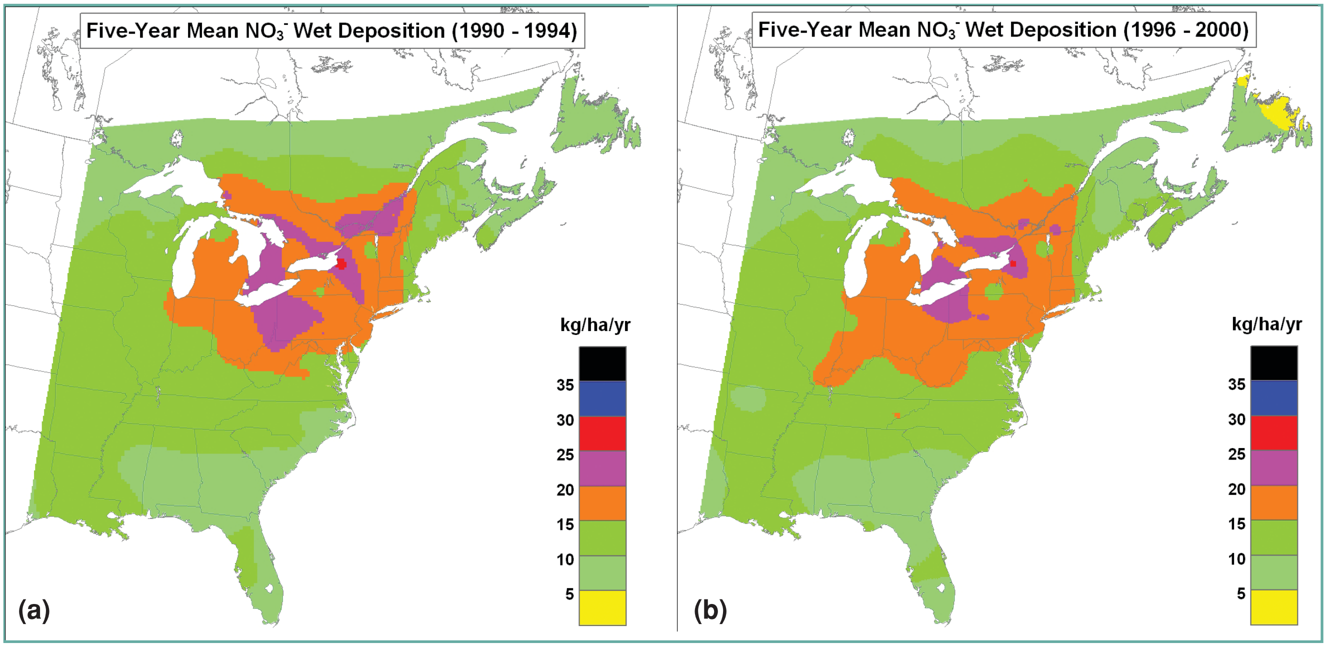

Figure 12.2: Spatial patterns of NO_3^- wet deposition over eastern North America in the early and late 1990s. The map on the left shows the 5-year-mean wet deposition pattern for the period 1990-1994 and the map on the right shows the 5-year-mean pattern for the period 1996-2000. In comparison to Figure 12.1, no major changes between the two sets of patterns are apparent; an observation that concurs with the relative constancy of NO_x emissions in this region over the same period. (Note: 1 kg NO_3^-/ha/yr is equal to 16.1 eq/ha/yr).

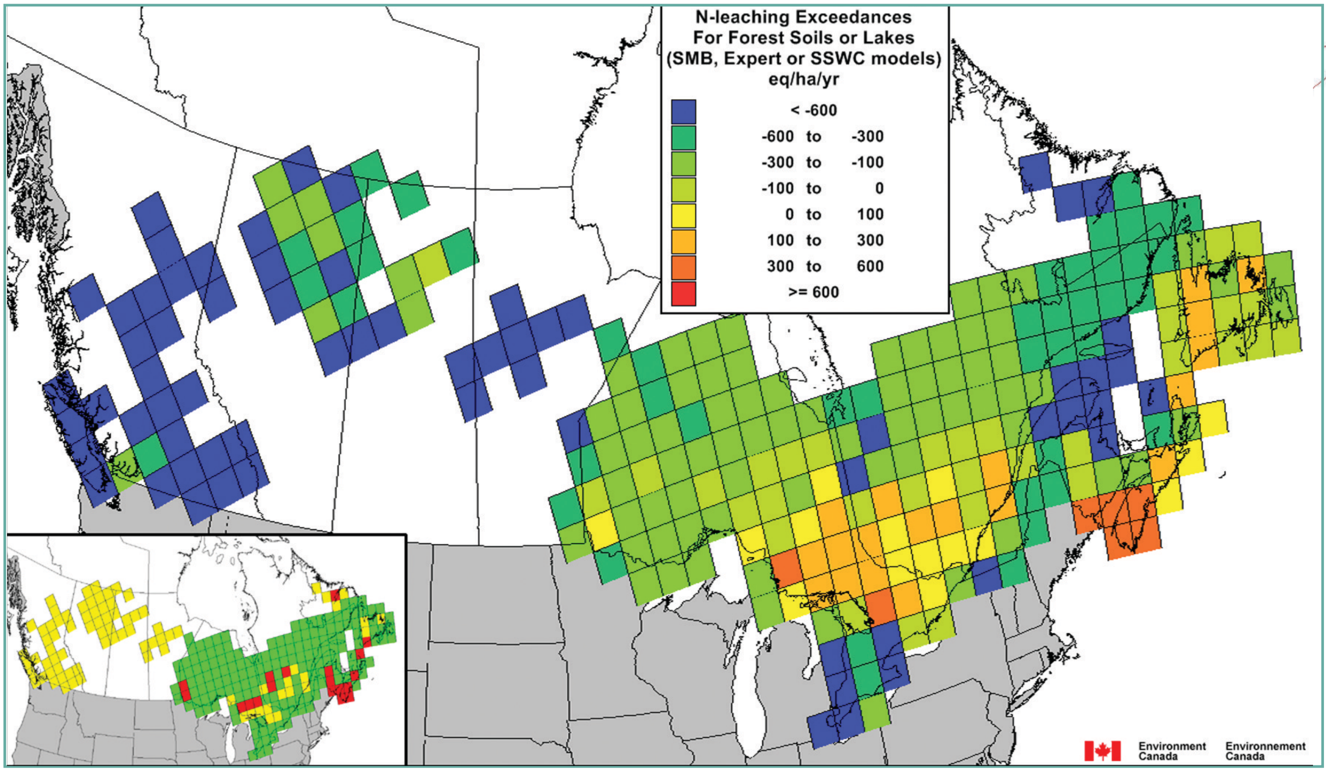

Figure 12.3: Aquatic or upland forest soil **N-leaching** critical load exceedances (wet + dry deposition in eq/ha/yr) for acidity (S+N) based on average deposition data from 1994-1998. Critical loads were calculated using either water chemistry models (i.e., "Expert" or "SSWC") or a forest soil model (i.e., "SMB"). The critical load value for a given square is either the 5th percentile lake value or the 5th percentile soil polygon value. The index map (lower left) indicates the model selected for each grid square: red = Expert (aquatic), yellow = SSWC (aquatic), green = SMB (upland forest soils). The forest soil component was obtained by laying the grid over the soil polygon exceedance map. The forest critical load map was produced by the Forest Mapping Working Group of the New England Governors/ Eastern Canadian Premiers (NEG/ECP) Secretariat in cooperation with Ontario, Environment Canada and Natural Resources Canada – Canadian Forest Service.

million km^2, continues to receive levels of acid deposition in excess of critical loads (Figures 12.3 and 12.4) according to best and worst case scenarios, respectively.

It should be noted that lake chemistry data are not available for sensitive terrain in some provinces, most notably northern and southeastern Manitoba, northern Saskatchewan, Nunavut, the Northwest Territories and the coastal mountain ranges of British Columbia. Hence, for these regions, the results presented in Figure 12.3 are unlikely to accurately represent the regional situation; however, there are no other independent critical load analyses to support (or refute) these values. In the other provinces, specifically Newfoundland and Labrador, Nova Scotia, New Brunswick, Quebec and Ontario, the spatial coverage of lake chemistry data and, in some cases, the amounts of data are not adequate to represent the regional situation. It should also be noted that the critical loads for upland forest soils assume no forest harvesting and no forest fires. Since both harvesting and fires make forests more sensitive to acid deposition, the critical load values for forests reported in this assessment are if anything, too high. Furthermore, not all components of nitrogen in dry deposition are taken into account in the critical load exceedance calculations, hence, reported exceedance values are underestimates.

In regions where the critical loads are being or have been exceeded, the following effects are being observed:

12.1.1.1 *Forest Effects*

Acid deposition is removing essential nutrients such as the base cations, calcium (Ca^{2+}), magnesium (Mg^{2+}) and potassium (K^{+}), from soils via leaching. This loss of nutrients is negatively affecting the health and growth of

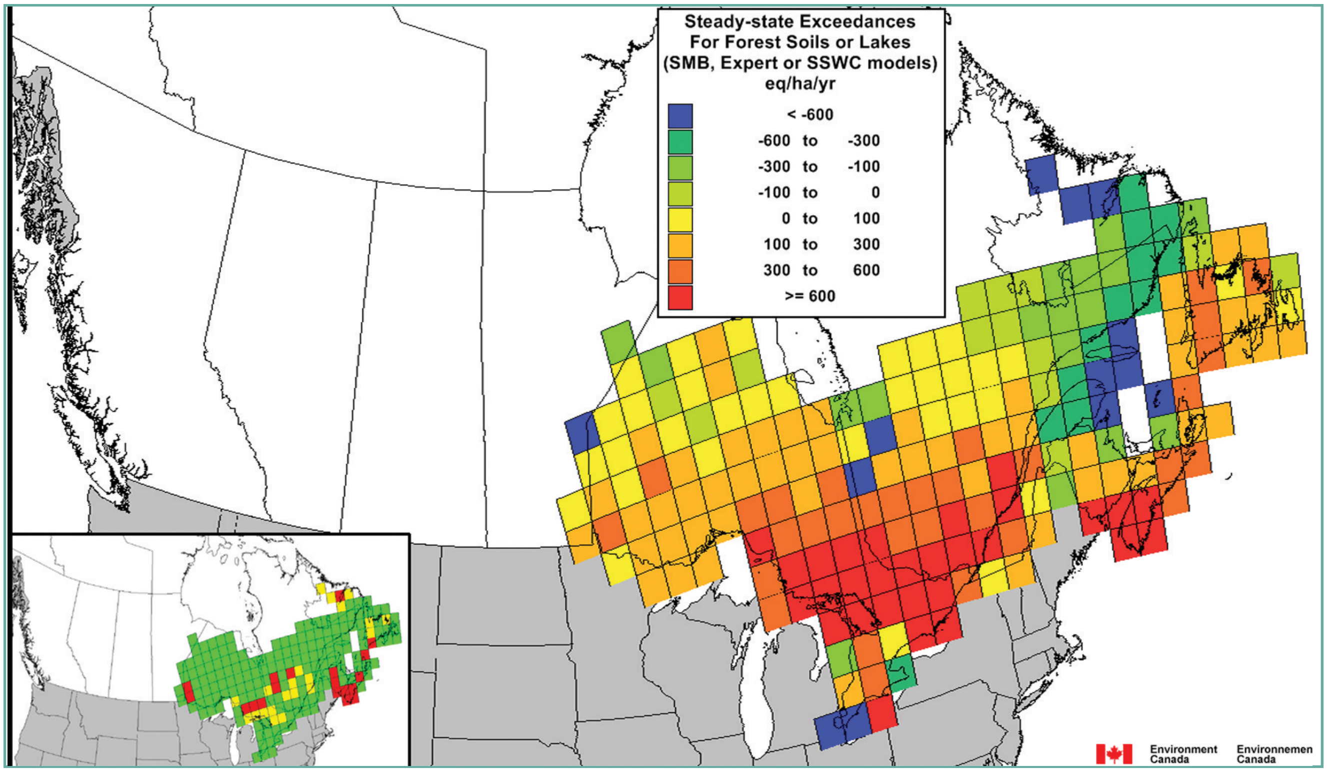

Figure 12.4: Aquatic or upland forest soil **Steady-state** critical load exceedances (wet + dry deposition in eq/ha/yr) for acidity (S+N) based on average deposition data from 1994-1998. Critical loads were calculated using either water chemistry models (i.e., "Expert" or "SSWC") or a forest soil model (i.e., "SMB"). The critical load value for a given square is either the 5th percentile lake value or the 5th percentile soil polygon value. The index map (lower left) indicates the model selected for each grid square: red = Expert (aquatic), yellow = SSWC (aquatic), green = SMB (upland forest soils). The forest soil component was obtained by laying the grid over the soil polygon exceedance map. The forest critical load map was produced by the Forest Mapping Working Group of the New England Governors/ Eastern Canadian Premiers (NEG/ECP) Secretariat in cooperation with Ontario, Environment Canada and Natural Resources Canada – Canadian Forest Service.

trees and depleting the capacity of soils to neutralize future loadings of acid deposition over much of eastern Canada. Net losses of base cations from forested watersheds in eastern Canada are widespread, particularly for Ca^{2+}. At a site in south-central Ontario, soil Ca^{2+} pools were reported to have declined by up to 30% since the early 1980s[4]. Recent declines in sulphate deposition have resulted in lower net losses of Ca^{2+} and, in turn, this has slowed down the rate of soil acidification; however, widespread net losses of Ca^{2+} (and in some cases Mg^{2+}) are still occurring in eastern Canada.

Although the rate of soil acidification has slowed down, further reductions in acid deposition are needed to meet critical loads for upland forest soils and prevent base cation levels in soils from falling below levels considered unsuitable for forest health and productivity. Currently, many areas in eastern Canada receive levels of acid deposition that exceed critical loads. In Ontario, sugar maple growth has been observed to be lower in areas where the critical load for soils is exceeded[5]. Analyses from the Research and Monitoring of Forest Ecosystems network in Québec show that, between the 1970s and the 1990s, hardwood and the coniferous stands located in areas where the critical loads were exceeded had a

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[4] Watmough, S.A., Dillon, P.J.. 2004. Major element fluxes from a coniferous watershed in central Ontario, 1983-1999. Biogeochemistry 67, 369-398.

[5] Watmough, S.A.. 2002. A dendrochemical survey of sugar maple in south-central Ontario. Water, Air and Soil Pollution 136, 165-187.

growth rate 30% lower than forest sites located in areas with no exceedances[6]. Even in the event of large reductions in acidifying emissions, recovery of soils from acidification (i.e. replacement of base cations) is likely to be extremely slow because the most important process for replacing base cations – primary weathering – is slow.

12.1.1.2 *Aquatic and Soil Chemistry*

Many lakes in southeastern Canada are still acidified (i.e. have lost some or all of their capacity to neutralize acids) and many do not meet the critical load pH condition of ≥ 6; a key threshold for the sustenance of fish and other aquatic biota. In eastern Canada, between approximately 25% (New Brunswick) and 40% (Ontario) of sampled lakes had pH levels less than 6. These percentages include those lakes that have been naturally acidified by organic acids associated with dissolved organic carbon (DOC). These types of lakes occur widely in Nova Scotia and to a lesser extent in Newfoundland but are not common in the other provinces. In Nova Scotia, 80% of sampled lakes had pH levels less than 6 and it is estimated that natural organic acids would leave approximately 40% of these lakes incapable of attaining a pH of 6 with significant reductions in acidifying emissions. In most provinces, however, the percentage of lakes with pH <6 is a reasonable indicator of the effect of acidic deposition. Results from lake chemistry models suggest that approximately 500,000 - 600,000, or ~15%, of sensitive lakes in southeastern Canada (south of 52°N latitude) that were historically capable of having pH >6 will have pH <6 under levels of acid deposition similar to present conditions.

In many lakes, chemistry is responding to reductions in acidifying emissions (i.e. lakes are becoming less acidic) but several factors are acting to delay or diminish the response. For example, there is mounting evidence that the size of acid-neutralizing base cation reservoirs in watershed soils determines the extent to which acid deposition acidifies surface waters. Net losses of base cations from forested watersheds in eastern Canada are widespread, particularly for calcium (Ca^{2+}). Hence, the capacity of watersheds to neutralize acid deposition is declining concomitant with the decline in the acidity of deposition.

In addition, the release of sulphate into surface waters exceeds the amount of sulphate received via acid deposition in most eastern Canadian forested watersheds. Likely sources of this “extra” sulphate are desorption of sulphate bound to soil, release of sulphate during the decomposition of organic matter, and drought-induced mobilization of reduced sulphur stored in wetlands or similar landscape features. All of these processes generate acids. The original source of much of this soil-bound sulphur is past inputs from acid deposition. Surface water critical load models, which are based solely on current SO_4^{2-} inputs from deposition, underestimate critical load exceedances in those watersheds that exhibit substantial net losses of sulphate.

12.1.1.3 *Aquatic Biology*

Algae, invertebrates and waterbird food chains continue to show acidification effects, particularly in lakes and rivers where fish communities have been impacted. Acidification effects often extend across trophic levels, altering the composition of biological communities and impacting ecosystem function. Impacts include direct acidity effects, metal toxicity, loss of prey, and reduced nutritional value of remaining prey. For example, most acid-sensitive invertebrate species are absent from lakes acidified below pH 6. Minnows and other small fish can be extirpated from small, acidified lakes and wetlands, causing important changes to the invertebrate food source of breeding waterbirds and other top predators. A general increase in the number of breeding fish-eating waterbirds (e.g. Common Loon, Common Merganser) was observed in much of southeastern Canada (i.e. Ontario, Quebec and Newfoundland). Recent observations from the Sudbury, Ontario region suggest that these increases may be related to improved habitat conditions in previously damaged lakes.

Elevated levels of mercury (Hg) in Common Loons, loon chicks and the fish they consume remain a cause for

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[6] Ouimet, R., Duschesne, D., Houle, D., Arp, P.A.. 2001. Critical load and exceedances of acid deposition and associated forest growth in the northern hardwood and boreal coniferous forests in Quebec, Canada. Water, Air and Soil Pollution: Focus 1, 119-134.

concern. Acidification of aquatic systems leads to increases in toxic methylmercury concentrations in water, sediment, and biota, and often results in elevated levels in the prey of fish-eating wildlife. Mercury concentrations in Common Loon adults, eggs, young and their fish prey tend to be higher in low pH lakes. Mercury concentrations in loons increase along a trajectory from west to east across southeastern Canada. High Hg levels in loons are associated with impacts to breeding productivity including reduced breeding success, reduced chick growth rates and modified chick behaviours which may increase mortality.

Atlantic salmon populations in rivers of the Southern Upland region of Nova Scotia continue to be severely impacted by acidification. Salmon in rivers with pH in the borderline toxicity range of pH 5.0 to 5.4 are at high risk of death due to sub-lethal effects which reduce feeding and growth, increase gill damage, and cause endocrine and osmoregulatory disruption. It is predicted that salmon from most Southern Upland Rivers will become extinct if adult survival rates remain at current low levels and pH recovery continues to be delayed.

12.1.2 Human Health

Recent epidemiological studies generally found small but significant associations between ambient aerosol acidity and the following outcomes: respiratory symptoms, impaired lung function, hospital admissions and emergency room visits, and premature mortality. Susceptible human sub-populations were identified for the different health outcomes. The toxicity of aerosol acidity might contribute to the associations between particulate matter (PM) and health effects. However, it is difficult to separate the effects of PM from that of aerosol acidity, because the measured components of PM were generally highly correlated with one another.

New clinical studies indicate that humans with asthma or allergies may be particularly sensitive to short-term exposure to acid aerosols alone, or to sequential exposure to sulphuric acid and ozone, compared with normal subjects. However, exposure levels in clinical studies were generally higher than levels measured in Canadian cities.

Results from recent animal toxicological studies suggest that exposure to acid aerosols can produce effects on immune defense mechanisms at concentrations close to those observed in eastern Canada. The effects of pollutant mixtures on human health endpoints can either increase or decrease compared with the effects of exposure to individual pollutants depending on the pollutants studied, the relative concentrations of individual pollutants in mixtures, and the endpoints measured.

12.2 WHAT ARE THE CURRENT AND FORECASTED TRENDS IN ACID-CAUSING EMISSIONS?

12.2.1 Sulphur Dioxide

In Canada, total emissions of sulphur dioxide (SO_2) declined by approximately 50% between 1980 and 2000 and are projected to decline by an additional 4% between 2000 and 2020 (Figure 12.5). These emission forecasts assume that no emission reductions are taken beyond those agreed to in Canada as of 2003. In eastern Canada, emissions of SO_2 declined by 53% between 1985 and 2000, while in western Canada emissions of SO_2 declined by 6% during this period. Between 2000 and 2020, emissions of SO_2 are predicted to decline by 21%

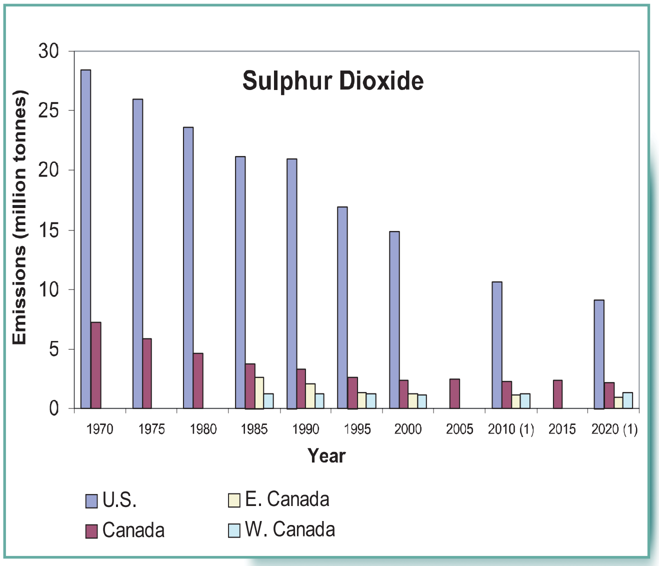

Figure 12.5: Estimated emissions of sulphur dioxide (SO_2) in the U.S. and Canada, including eastern (east of Manitoba) and western (west of Ontario) Canada. 1 - U.S. emissions forecasts are based on REMSAD emissions summaries.

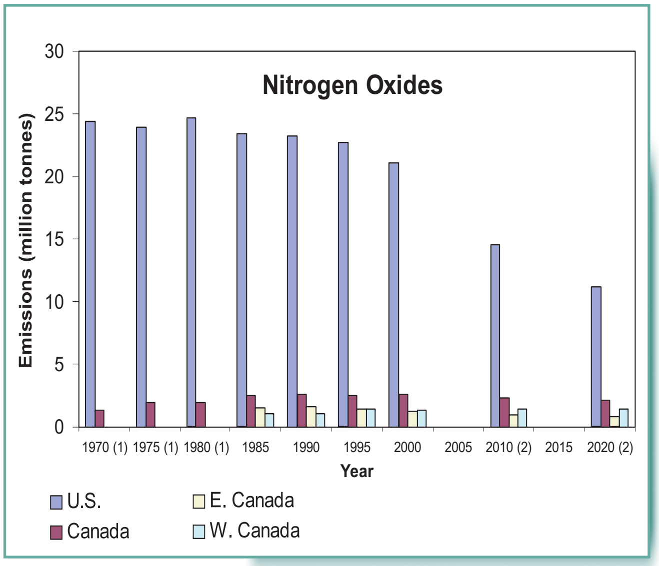

Figure 12.6: Estimated emissions of nitrogen oxides (NO_X) in the U.S. and Canada, including eastern (east of Manitoba) and western (west of Ontario) Canada. 1 - Canadian NO_X emissions for 1970 through 1980 are based on older methodologies and are not comparable to 1985 and beyond. 2 - U.S. emissions forecasts are based on REMSAD emissions summaries.

in eastern Canada and increase by 15% in western Canada. SO_2 emissions in western Canada are predicted to exceed emissions in eastern Canada by 2010.

In the U.S., total emissions of SO_2 declined by approximately 40% between 1980 and 2000 and are predicted to decline by approximately 38% from 2000 levels in 2020 (Figure 12.5). These emission forecasts assume that no emission reductions are taken beyond those described in the Canada-U.S. Air Quality Agreement and agreed to as of 2003.

12.2.2 Nitrogen Oxides

In Canada, nitrogen oxides (NO_X) emissions were approximately constant between 1985 and 2000 but are predicted to decline by approximately 17% between 2000 and 2020 (Figure 12.6). These emission forecasts assume that no emission reductions are taken beyond those agreed to in Canada as of 2003. In eastern Canada, emissions of NO_X decreased by 17% between 1985 and 2000 and are predicted to decrease by approximately 39% between 2000 and 2020. In western Canada, NO_X emissions increased by 29% between 1985 and 2000 and are predicted to increase by approximately 5% between 2000 and 2020. As of 2000, emissions of NO_X in western Canada surpassed emissions in eastern Canada. Western Canadian emissions of NO_X are predicted to continue to exceed emissions from eastern Canada to 2020.

In the U.S., NO_X emissions declined slightly between 1985 and 2000 and are predicted to decline by approximately 47% from 2000 levels in 2020 (Figure 12.6). These emission forecasts assume that no emission reductions are taken beyond those described in the Canada-U.S. Air Quality Agreement and agreed to as of 2003.

12.3 WHERE ARE THE MAJOR INDUSTRIAL SOURCES OF ACID-CAUSING EMISSIONS THAT AFFECT CANADIAN ECOSYSTEMS?

12.3.1 What are the major industrial source sectors of acid-causing emissions in Canada and the U.S.?

In Canada, major source sectors of acid-causing emissions are non-ferrous mining and smelting, electric power generation, upstream oil and gas and transportation.

Sulphur dioxide and nitrogen oxides emission source sectors in eastern Canada are concentrated along the Windsor–Quebec City corridor with hotspots also found in central Ontario, central Quebec, south-central New Brunswick, east-central Nova Scotia and Newfoundland (Figures 12.7 and 12.8). The Windsor-Quebec City corridor is highly urbanized and has emissions source sectors that include thermal electric power generation and on-road transportation. The hotspots in central Ontario and central Quebec are associated with non-ferrous mining and smelting operations. The hotspots in south-central New Brunswick, east-central Nova Scotia and Newfoundland are associated with electrical power generation and other industrial emissions (e.g. mining and pulp and paper).

In western Canada, large SO_2 and NO_X emission source sectors are observed in Alberta and in defined hotspots in Manitoba and Saskatchewan. Emissions from Alberta are primarily from thermal electric power generation, upstream oil and gas and petroleum refining. High emission areas in Saskatchewan are sites of thermal electric power generation. High emission areas in Manitoba are associated with non-ferrous mining and smelting operations.

In the U.S., major source sectors of acid-causing emissions are electric power generation and on-road vehicles. Major sources of sulphur dioxide and nitrogen oxides emissions in the eastern U.S. are located in a highly industrialized and urbanized area from southeast Ohio to the western part of Virginia and western Kentucky to central Tennessee[7].

12.3.2 What are the major emission source regions that affect Canadian ecosystems?

Analyses of wet and dry deposition data, source attribution techniques and atmospheric models have enabled researchers to identify source regions of acid-causing emissions that affect Canadian ecosystems.

Within the area of eastern Canada bounded by the Manitoba-Ontario border, Newfoundland, the Canada-U.S. border and 51° north latitude, Canadian sources emit less than 10% of total SO_2 and NO_x emissions in eastern North America; however, that same area of eastern Canada receives roughly 30% of total sulphate

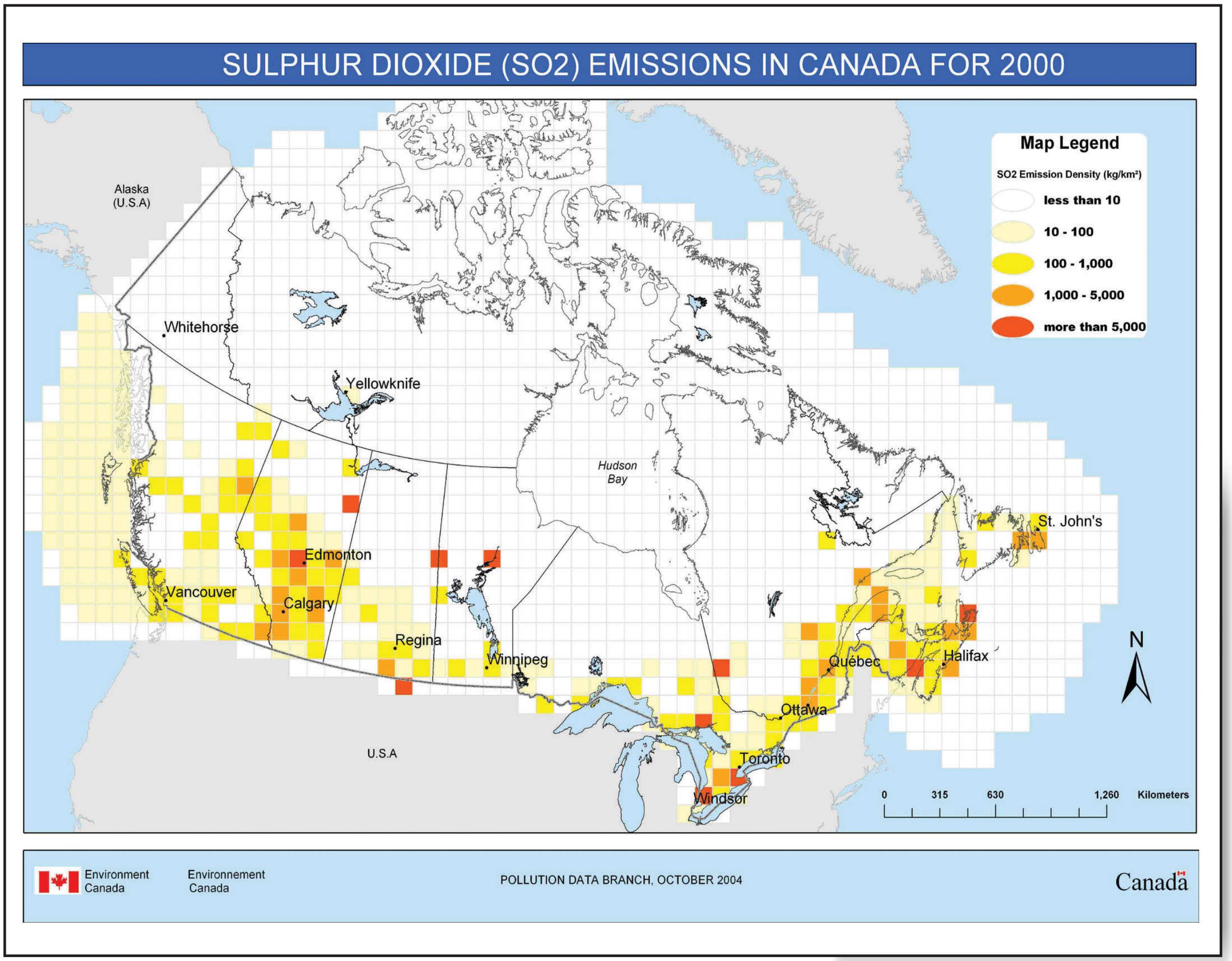

Figure 12.7: Distribution of sulphur dioxides (SO_2) emissions in Canada for 2000 (kg/km^2).

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[7] Subcommittee on Scientific Co-operation (SC2) – Air Quality Committee (2004) Canada-United States Transboundary PM Assessment. Catalogue No: En56-203/2004E. 129pp.

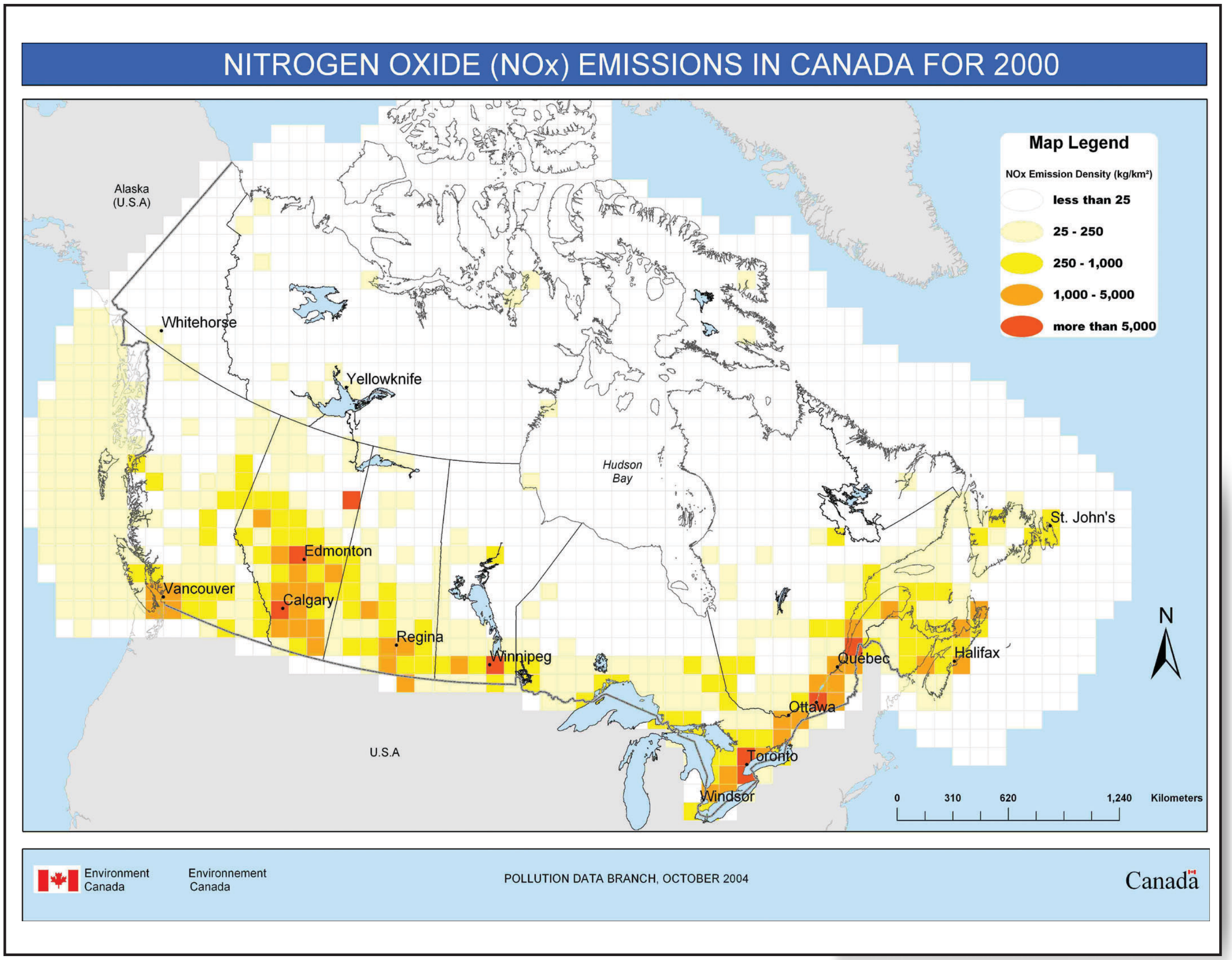

Figure 12.8: Distribution of nitrogen oxides (NO_x) emissions in Canada for 2000 (kg NO_2/km^2).

and nitrate wet deposition in eastern North American (Figure 12.9). This large imbalance is due to long range transport and subsequent wet deposition of Midwestern and eastern U.S. emissions on eastern Canada. It is estimated that between 45 and 70% of sulphate and nitrate wet deposition in eastern Canada is attributable to emission sources in the eastern U.S[8].

Wet and dry deposition data collected by the Canadian Air and Precipitation Monitoring Network (CAPMoN), combined with air mass trajectories, have been used to estimate the contribution of different emission source areas in North America to sulphur and nitrogen deposition at specific locations in Canada. In Ontario, Quebec and Nova Scotia, all CAPMoN measurement sites located within 200 km of the U.S. border are estimated to receive 50-70% of their sulphur and nitrogen deposition from emissions in the U.S. and from southern Ontario and southern Quebec (Figure 12.10). The remaining 30 to 50% of the sulphate and nitrate at CAPMoN sites is attributable to Canadian sources to the north, west and east of the measurement locations; areas to the east of each measurement site make the lowest contribution to acid deposition at any given site. U.S. emission sources in the Great Lakes, Ohio River Valley and U.S. Midwest states appear to have the largest impact on wet and dry deposition in eastern Canada (Figure 12.10).

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[8] Based on mass balance calculations.

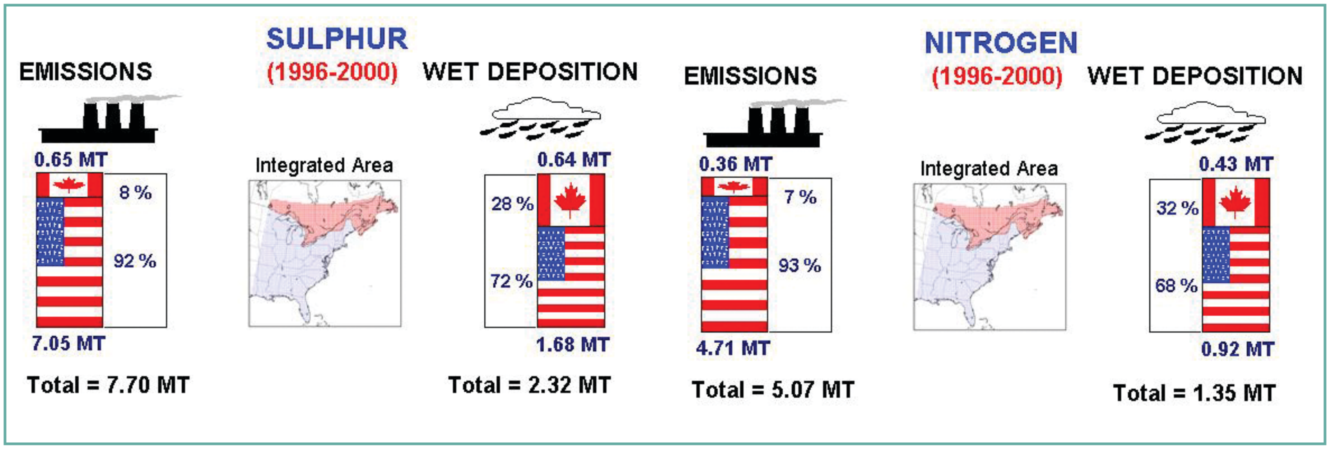

Figure 12.9: Five-year average (1996-2000) total emissions (megatonnes; MT) and wet deposition (MT) of sulphur and nitrogen over eastern Canada and the eastern U.S. (areas shown in map inset). The percentage values indicate the fraction of total eastern North American emissions and wet deposition in each country.

In western Canada, little measured data are available for estimating source attribution. At one measurement site in the prairies near the Alberta-Saskatchewan border, approximately 45-55% of wet and dry deposition is attributed to emission sources in central and northern Alberta/British Columbia (Figure 12.10). Sources in southern Alberta, southern BC and the northwest U.S. account for approximately 30% of the wet and dry deposition while sources east of the site account for approximately 30% of the remaining wet and dry deposition.

Atmospheric chemistry models have been used to determine emission sources that affect Canadian ecosystems. For eastern Canada, results from the ADOM (Acid Deposition and Oxidant Model) suggest that SO_2 and NO_x emissions from both Canada and the U.S. contribute to acid deposition in eastern Canada. This conclusion is derived from comparisons of different emission scenarios for Canada and the U.S. For example, Figure 12.11 illustrates the change in sulphate wet deposition resulting from a further 5% decrease in U.S. SO_2 emissions from those projected for 2010 under the Canada-U.S. Air Quality Agreement (AQA) (reductions equal to 611 Ktonnes/yr) and no change in emissions from Canada beyond those described in the AQA. Annual sulphate wet deposition in eastern Canada is predicted to be reduced from over 0.8 kg SO_4^{2-}/ha/yr in southwestern Ontario to 0.1-0.4 kg SO_4^{2-}/ha/yr in the Atlantic provinces, central Quebec and Ontario. In percentage terms (Figure 12.11b), this corresponds to a 1-4% reduction in sulphate wet deposition in eastern Canada relative to the 2010 AQA scenario, with the largest percent decreases occurring in southern Ontario, southern Quebec, New Brunswick, and Nova Scotia.

Figure 12.12, on the other hand, illustrates the change in sulphate wet deposition resulting from a 32% decrease in SO_2 emissions from Canada from projected 2010 levels (equal to 619 Ktonnes/yr) and no change in emissions from the U.S. For this scenario, annual sulphate wet deposition in eastern Canada is predicted to be reduced by 0.1-3.0 kg SO_4^{2-}/ha/yr or by up to 15% in percentage terms, with the largest percentage decreases occurring along the Sudbury, Ont.-Rouyn, Quebec corridor and near Prince Edward Island. Decreases as large as 5% also occur in the northeastern U.S. as a result of the reduction in Canadian emissions. Since the actual total decrease in SO_2 emissions is nearly identical for these two scenarios, comparison of the corresponding responses suggests that a one tonne reduction of Canadian SO_2 emissions has a greater impact *in Canada* than a one tonne reduction in the U.S.

For western Canada, results of the REgional Lagrangian Acid Deposition (RELAD) and AES Lagrangian Sulphur Model (ALSM) models suggest that Canadian SO_2 and NO_x emission sources are the primary contributors to acid deposition. This conclusion is based on examination of continental emission maps and comparisons of model outputs to measured data. For example, Figure 12.13 shows the 30-year mean annual

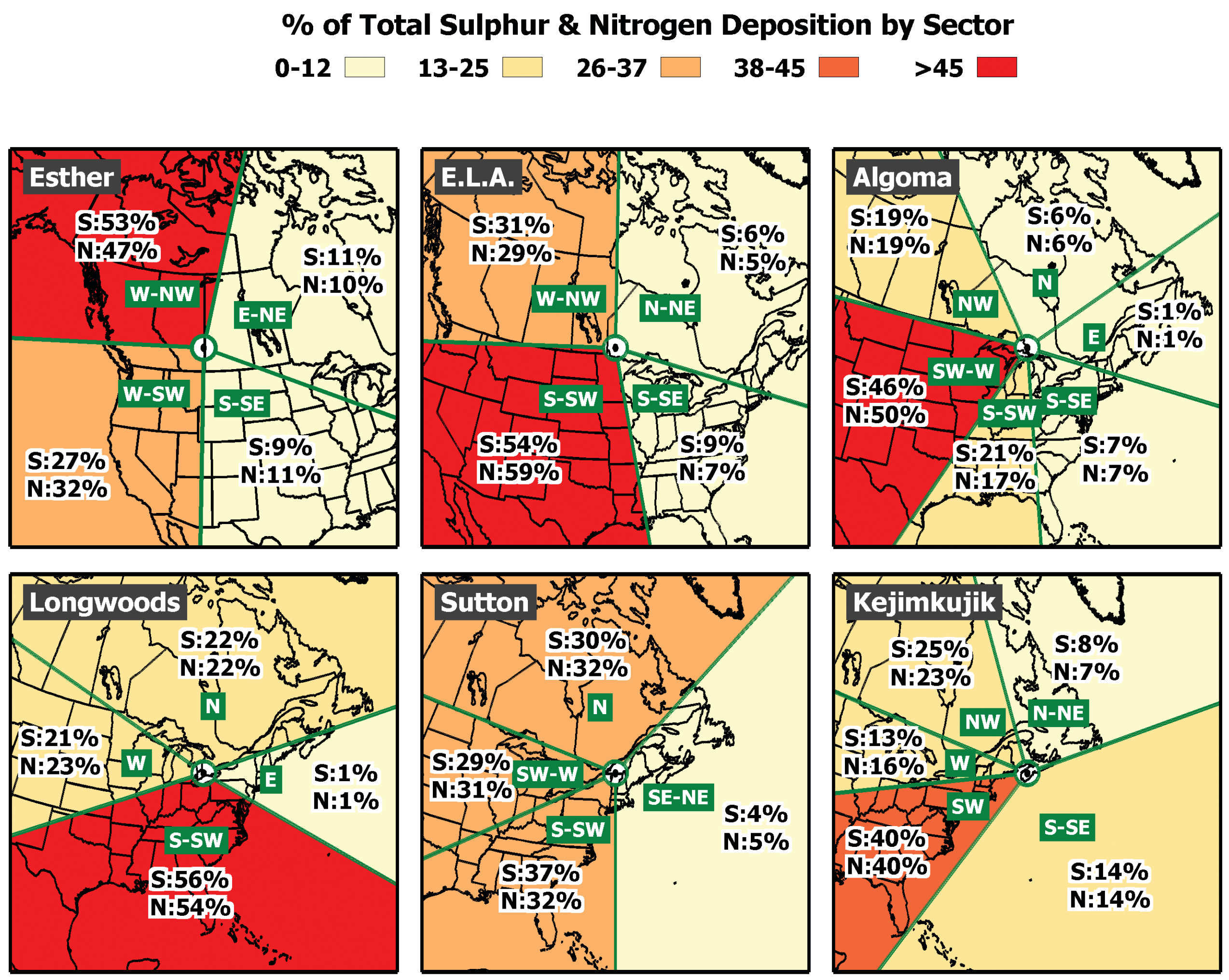

Figure 12.10: The percentage contribution of different source regions to total sulphur and nitrogen deposition at selected CAPMoN sites across Canada.

sulphate and nitrate wet deposition fields predicted by RELAD based on 1995 emissions. From west to east, the local peaks in sulphate wet deposition, evident in Figure 12.13a, are associated with the Calgary-Edmonton corridor, the Fort McMurray area of Alberta, Flin Flon, Manitoba and Thompson, Manitoba. In contrast, peaks in nitrate wet deposition (Figure 12.13b) are predicted to occur in Alberta, along and to the east of the Calgary-Edmonton corridor, consistent with the different source types contributing to SO_2 and NO_x emissions in western Canada.

12.4 ARE FURTHER EMISSIONS REDUCTIONS NECESSARY IN CANADA AND THE U.S.? IF SO, BY HOW MUCH, AND FROM WHERE, DO EMISSIONS NEED TO BE REDUCED?

Since levels of sulphur and nitrogen deposition currently exceed critical loads for aquatic and upland forests over a vast area of eastern Canada, there is a clear need to further reduce SO_2 and NO_x emissions that impact this region. In western Canada, data on critical loads are

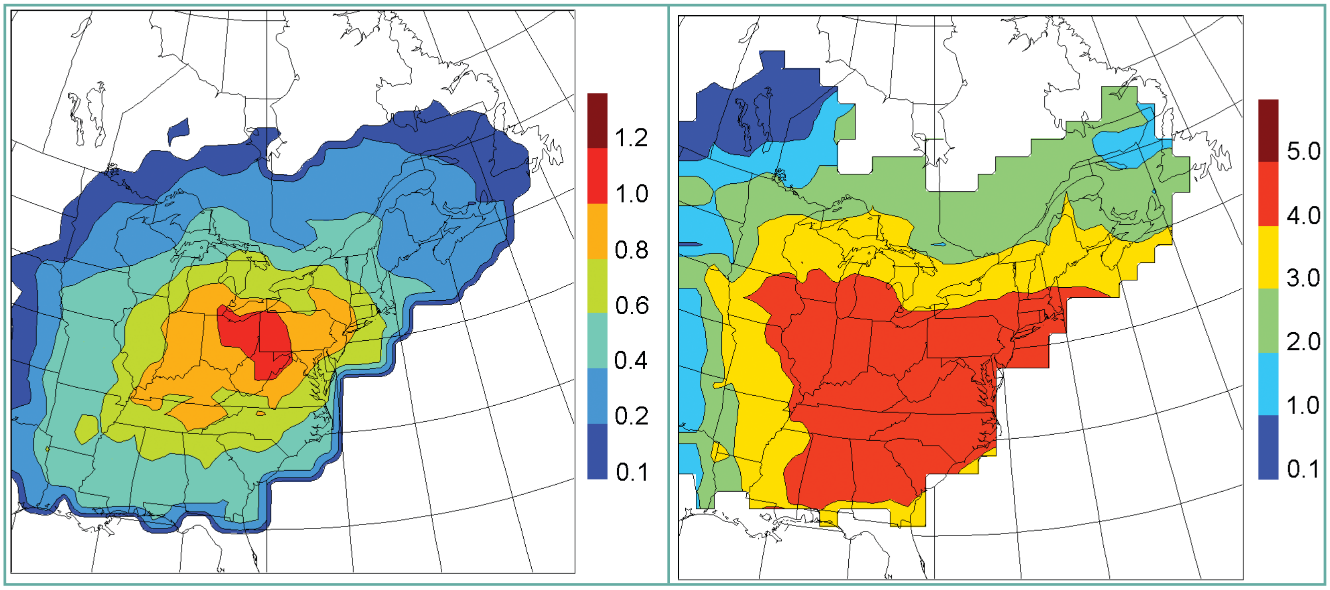

Figure 12.11: Plots of (a) actual difference and (b) percent difference in predicted annual sulphate wet deposition (units of kg SO_4^{2-}/ha/yr) between ADOM SO_2 emission control scenarios "PST2010A"[9] and "PST2010B"[10]. Panel (b) was calculated as (PST2010A - PST2010B) / CCUSA2. The corresponding difference in U.S. SO_2 annual emissions between the two scenarios is 611 Ktonnes/yr, or 5% of U.S. emissions from "CCUSA2"[11] scenario levels. (Note: 1 kg SO_4^{2-}/ha/yr is equal to 20.8 eq/ha/yr)

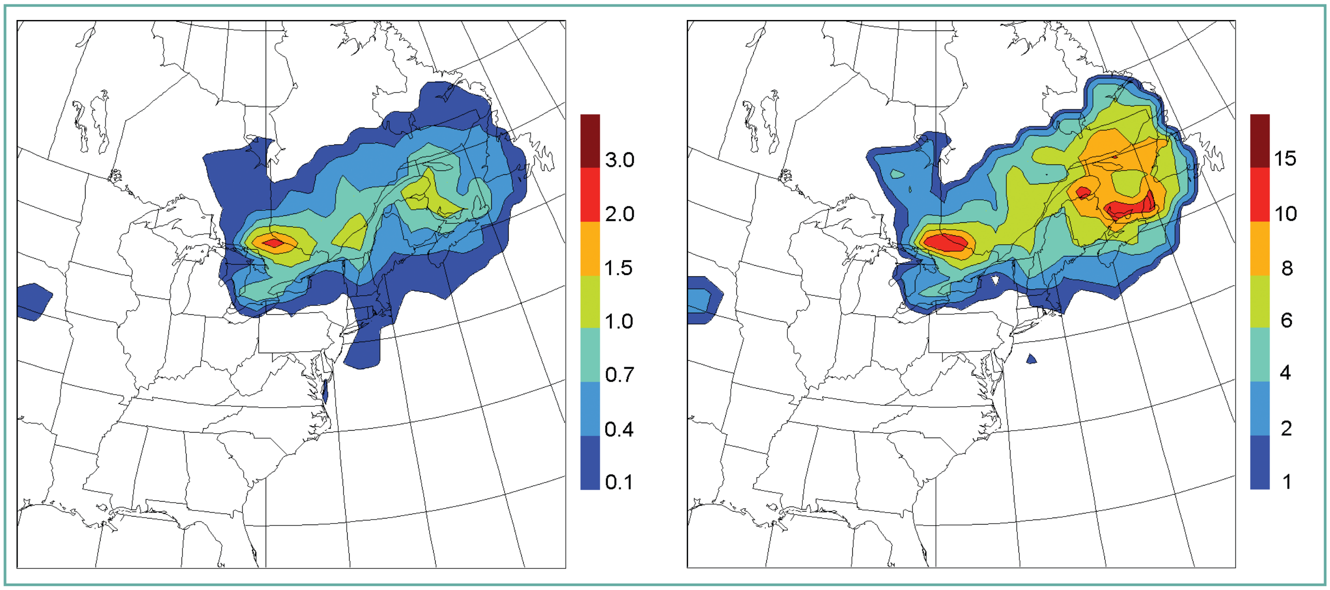

Figure 12.12: Plots of (a) actual difference and (b) percent difference in predicted annual sulphate wet deposition (units of kg SO_4^{2-}/ha/yr) between ADOM SO_2 emission control scenarios "CCUSA2" (see footnote 16) and "5CONLY"[12]. Panel (b) was calculated as (CCUSA2 - 5CONLY) / CCUSA2. The corresponding difference in Canadian SO_2 annual emissions between the two scenarios is 619 Ktonnes/yr, or 32% from "CCUSA2" scenario levels. (Note: 1 kg SO_4^{2-}/ha/yr is equal to 20.8 eq/ha/yr).

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[9] In scenario "PST2010A" the province of Ontario is assumed to reduce annual SO_2 emissions by a further 50% from the 1985 ECARP cap (885 to 443 Ktonnes SO_2/yr), the province of Quebec by a further 45% (500 to 275 Ktonnes/yr), and New Brunswick and Nova Scotia/PEI each by a further 25% (175 to 131 and 194 to 146 Ktonnes/yr, respectively). The United States is assumed to reduce its annual SO_2 emissions by a further 55% from 2010 levels described in the Canada-U.S. Air Quality Agreement (12,446 to 5,578 Ktonnes/yr).

[10] This scenario is very similar to the "PST2010A" scenario. The only difference is that U.S. SO_2 emissions are reduced to 40% of 2010 levels, that is, a 60% reduction, as compared to the 55% reduction considered in scenario "PST2010A".

[11] Scenario "CCUSA2" predicts levels of deposition in 2010 using SO_2 emission levels that would occur when the 1985 Eastern Canada Acid Rain Program (ECARP) and Title IV, Phases 1 and 2 of the 1990 U.S. Clean Air Act Amendments are fully implemented.

[12] This simple scenario is very similar to the "CCUSA2" scenario; the only difference is that Canadian SO2 emissions in the eastern-Canada Sulphur Oxide Management Area (or SOMA) are rolled back by 50% from the provincial caps mandated under the 1985 ECARP. The ADOM domain approximates the SOMA for southeastern Canada.

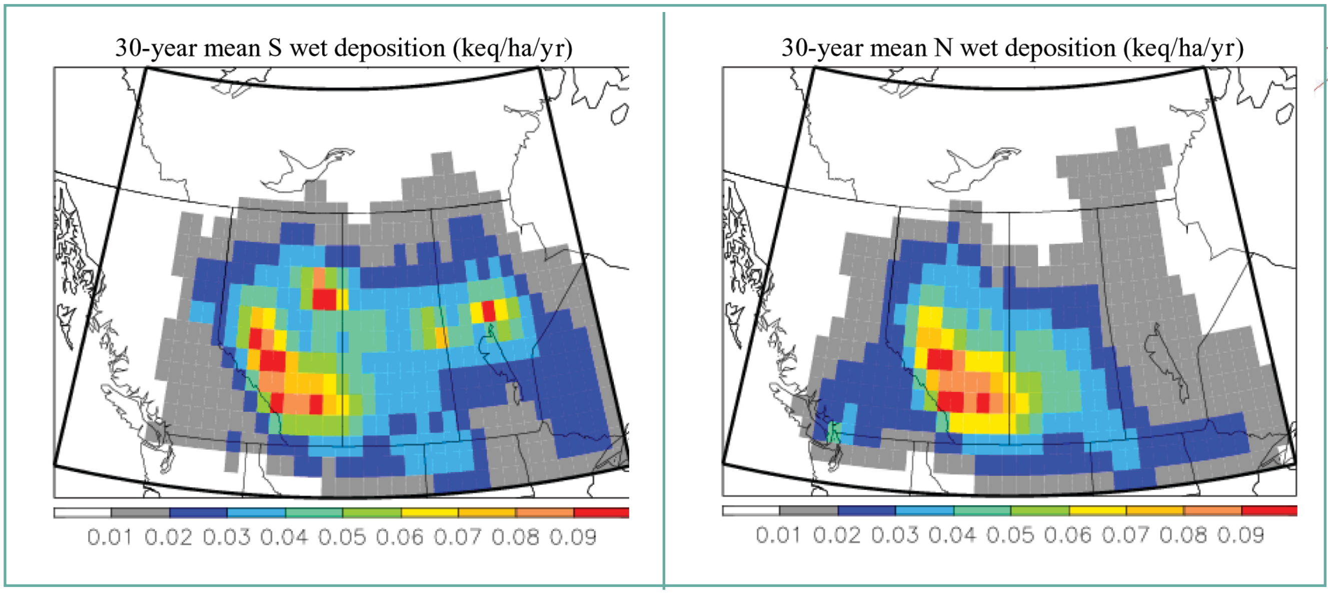

Figure 12.13: Wet deposition of sulphur (keq/ha/yr) and nitrogen (keq/ha/yr) predicted by RELAD based on the average meteorological conditions from 1971 to 2000 and Canadian emissions data from 1995. The RELAD domain is indicated by the dark black outline. Each grid cell is 1° of latitude by 1° of longitude in size. (Note: 1 keq/ha/yr of wet sulphur deposition is equal to 48.1 kg/ha/yr and 1 keq/ha/yr of wet nitrogen deposition is equal to 62.1 kg/ha/yr)

insufficient to make specific conclusions about the need to reduce emissions that impact this region.

Using the most realistic future-year SO_2 emission scenarios data available to date, the ADOM model predicts that sulphate critical loads for aquatic ecosystems[13] will still be exceeded in central Ontario and Quebec, even if SO_2 emissions from both Canada and the U.S. are reduced by a further 50% beyond what they have agreed to achieve in Canada-U.S. Air Quality Agreement (AQA) in 2010. This result is consistent with the predictions of a similar ADOM modelling scenario published in the 1997 assessment[1]. Only for an SO_2 emission control scenario that constitutes a further 75% reduction in SO_2 emissions from those currently agreed to by Canada and the U.S. for 2010 in the AQA, are the 1997 aquatic critical load exceedances predicted to be completely eliminated in eastern Canada. It is important to note that the 1997 aquatic critical loads have been revised in this assessment and new critical loads have been estimated for both aquatic and upland forest ecosystems. These new critical loads are lower than those published in the 1997 assessment in many areas and higher in a few areas; hence, reductions in SO_2 emissions greater than 50% or 75% could be required to meet new, lower critical loads.

Finally, it is important to note that a 75% reduction in SO_2 emissions in eastern Canada and the eastern U.S. (needed to meet 1997 aquatic critical loads) translates into a greater reduction in SO_2 in terms of megatonnes (MT) from the U.S. than from Canada. This is because emissions of SO_2 from eastern Canada constitute only 9% of eastern North American emissions (based on 2000 emission estimates; see Figure 12.9).

The ADOM model results suggest however, that on a tonne-by-tonne basis, a reduction of one MT in emissions from eastern Canada would produce a larger reduction in deposition in eastern Canada than would a one MT reduction in emissions from the eastern U.S. This is because a larger proportion of each MT emitted by Canadian sources is deposited in Canada compared to a MT emitted by U.S. sources. Thus, although emissions from the eastern U.S. need to be reduced for critical loads to be met in eastern Canada (since 45% or more of sulphur deposition in eastern Canada is attributable to U.S. emissions), on a tonne-by-tonne

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[13] Using critical loads published in the 1997 Canadian Acid Rain Assessment.

basis, it is more efficient to reduce a tonne of emissions in Ontario and Quebec than a tonne in the Ohio River Valley or northeastern states. However, a very large percentage reduction in both countries is required to reach the goal of entirely eliminating aquatic critical load exceedances in eastern Canada.

The deposition data analyses, although not able to estimate the level of SO_2 and NO_x emissions reductions needed to meet critical loads, are consistent with the ADOM modelling results. The analyses suggest that emission reductions are needed in eastern Canada, the Midwestern and eastern U.S. and western Canada to reduce acid deposition in eastern Canada. Within eastern Canada, the largest emission reductions appear to be needed in Ontario, and Quebec. In the U.S., the largest reductions are needed in the Midwest states in order to reduce deposition in northwestern Ontario, in the Great Lakes states and the Ohio River Valley in order to reduce deposition in the remainder of Ontario and Quebec, and in the states of the Ohio River Valley, and the East Coast in order to reduce deposition in Atlantic Canada. Complementary modelling results suggest that the most efficient place to reduce emissions that affect Canada would be in the northern tier of the Midwest, Great Lakes, Ohio River Valley, and East Coast states. In fact, emission reductions in the southern tier of the American states would have very little benefit to acid deposition levels in Canada.

12.5 WILL NO_X REDUCTIONS COMPENSATE FOR THE NEED TO REDUCE SO_2? IS NITROGEN SATURATION A PROBLEM AND HOW WILL CHANGING NO_X EMISSIONS IMPACT ON CANADIAN ECOSYSTEMS?

For watersheds in eastern Canada, sulphur deposition is still clearly the predominant acidifying agent; only a small number of watersheds demonstrate acidification that can be ascribed to nitrogen and recent trend information suggests that acidification at these sites may be declining. Critical load analyses, that separate the two acidifying components, show that there are some cases where reductions in sulphate deposition alone can be effective in decreasing exceedances, but in other cases, reductions in both sulphate and nitrogen deposition will be necessary (e.g. Muskoka River watershed in Ontario). Hence, according to our current understanding of the role of nitrogen in acidification, reductions in NO_x emissions will not compensate for the need to reduce SO_2.

Although nitrogen saturation is not a problem in most of eastern Canada, the capacity for terrestrial watersheds to retain nitrogen deposition is finite. It is reasonable to hypothesize that a dramatic decrease in nitrogen deposition may protect many sites from ever becoming nitrogen saturated. At this point in time, however, it is not possible to establish a particular threshold of nitrogen deposition that would prevent future nitrogen saturation in Canada.

12.6 ARE THERE OTHER FACTORS THAT MIGHT DECREASE THE EFFICACY OF EMISSION REDUCTIONS?

There are several factors that might decrease the efficacy of emission reductions. These factors include the following:

- Leaching of base cations decreases the capacity of soils to neutralize future acid loadings – i.e. increases the susceptibility of soils to acid deposition.
- Under the oxygen-limited conditions that characterize wetland sediments, sulphate from deposition is converted to sulphides, which are stable storage products for sulphur. When the water level goes down during dry periods, oxygen penetrates into formerly anaerobic wetland soils resulting in sulphur oxidation and release of sulphate. Hence, climatic changes can cause temporal variability in sulphate fluxes from wetland-dominated watersheds and confound the expected relationship between decreased sulphate deposition and sulphate concentrations in lakes and rivers.
- Declines in inputs of sulphate to soils, as a result of reductions in acid deposition, are expected to cause the release (desorption) of sulphate previously stored in soils. The release of stored sulphate into lakes and rivers confounds the effects of SO_2

emission reductions. The amount of sulphate stored in soils and available for release is dependent on the characteristics of the soil and the concentration of sulphate in deposition. In watersheds, such as Plastic Lake in the Muskoka-Haliburton region of Ontario, stored sulphate is predicted to be released into surface waters for up to several decades[14].

- Mineralization (the transformation of organic sulphur into inorganic sulphate) and immobilization (the transformation of inorganic sulphate into organic sulphur) are microbial processes that occur concurrently within the soil. Mineralization may be a source of sulphate to drainage waters if sulphate release from organic sulphur compounds exceeds the rate of sulphate immobilization. A number of studies have suggested that mineralization is responsible for net sulphate export from watershed soils in Canada.
- When terrestrial ecosystems become nitrogen saturated (i.e. receive more nitrogen than they can use), nitrogen forms acid which can leach from the soil and acidify surface waters.

12.7 ARE AFFECTED ECOSYSTEMS RECOVERING IN RESPONSE TO PAST REDUCTIONS IN SO_2 EMISSIONS? IF SO, HOW IS RECOVERY PROCEEDING? IF NOT, WHY, WHEN, AND UNDER WHAT CONDITIONS, CAN WE EXPECT RECOVERY TO ACCEPTABLE ENVIRONMENTAL OBJECTIVES? WHAT ROLE DO NO_X EMISSIONS PLAY?

At present, full scale chemical and biological recovery has not been observed in any ecosystem but there are encouraging signs of improvement.

Lakes in eastern Canada located near smelters, that have dramatically reduced their emissions for a significant period of time (e.g. at Sudbury and to a lesser extent at Rouyn-Noranda), provide the most definitive evidence of chemical recovery (increasing pH and/or alkalinity). Lakes in southeastern Canada that are predominantly affected by long-range sources of acid deposition show a general decline in sulphate but a relatively smaller compensating increase in pH and/or alkalinity. Factors such as declining base cations in precipitation and watershed soils, drought-induced mobilization of stored sulphur, and damaged in-lake alkalinity generating mechanisms are constraining (most likely delaying) chemical recovery; biological recovery will necessarily lag behind chemical recovery. In the end, lakes will probably recover to a state that is more dilute (lower ion concentrations and therefore more sensitive) than their pre-acidification state.

It is likely that many lakes will recover to a different state than their original one. Algae and zooplankton communities in some highly damaged lakes (e.g. Sudbury area) are responding to acidity reductions but recovery is constrained by metal toxicity and re-acidification events.

Experimental acidification research shows that aquatic ecosystems can be resilient to acid-stress but that recovery will often be complex and slow and may result in permanently altered biological communities. The increases in numbers of loons and some other waterbirds breeding in southeastern Canada are encouraging signs of recovery but observations of declining loon breeding success will be cause for concern if trends continue and are widespread. Habitat suitability for waterbirds breeding in small lakes and wetlands of southeastern Canada is predicted to improve for fish-eating birds (e.g. Common Loon, Common Merganser) and small fish (e.g. minnows) and decline for some insectivorous diving ducks (e.g. Common Goldeneye), with the degree of change related to the prevalence and magnitude of chemical change.

With respect to soil chemistry, evidence of lake recovery in some regions supports the notion that soil chemistry may also be recovering because soil chemistry (i.e. base cation concentrations) largely controls the acidity of lake water. However, empirical and modelling evidence

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[14] Eimers, M.C., Dillon, P.J., Schiff, S.L.. 2004. Sulphate flux from an upland forested watershed in south-central Ontario, Canada. Water Air and Soil Pollution 152, 3-22.

suggests that base cation reservoirs in soils throughout southeastern Canada continue to decline; a phenomenon which threatens the long-term sustainability of forests and impedes the recovery of lakes and rivers. In order to achieve recovery of terrestrial ecosystems, the level of acid deposition would need to decline to the point where inputs of base cations to soils from weathering of bedrock and deposition equals or exceeds the loss of base cations by acid leaching.

In terms of the role played by NO_x emissions, as mentioned previously, for watersheds in eastern Canada, sulphur deposition is still clearly the predominant acidifying agent (usually accounting for >90 % of acid leaching from soils). However, nitrate does contribute to soil acidification at a few sites such as the Muskoka River Watershed in Ontario.

12.8 WHAT ARE SOME OF THE SOCIO-ECONOMIC BENEFITS OF ACID DEPOSITION MITIGATION?

Acid deposition has negative impacts on lakes, rivers, soils, forests, wildlife, biodiversity, buildings, and human health. The socio-economic benefits of decreasing or avoiding these negative impacts could be significant. Furthermore, reductions in PM and ozone that accompany reductions in acidifying emissions would have a wide range of environmental, economic and human health benefits.

At current levels of acid deposition, it is estimated that over half a million cubic meters of wood is being lost from forests in Atlantic Canada each year due to soil nutrient loss. At market prices, the value of this lost wood is in the hundreds of millions of dollars per year.

The decline of fish in lakes and rivers of eastern Canada has significant impacts on the fishing industry, particularly for Atlantic salmon. The effects of declining fish populations will also have non trivial effects for recreational fishermen who spent $1.9 billion on fishing in 1996.

The corrosive impacts of acid deposition can be significant, particularly for electrical transmission towers. Acid deposition can reduce the life expectancy of transmission towers by 50% and greatly increase repair frequency with an annual cost of thousands of dollars per tower.

There is some indication that damages to the overall integrity of the environment and ecosystem could be amongst the most economically significant impacts of acid deposition. In 1996, Canadians spent over $12 billion on nature related activities. This $12 billion in expenditures likely represents only the tip of the iceberg of the full value Canadians place on the environment.

Acid aerosols, PM and ozone can lead to a variety of adverse human health effects ranging from subtle changes and mild symptoms to hospital admissions and premature mortality. The elderly, children and people suffering from cardio-respiratory conditions such as asthma appear to be the most susceptible groups to the effects of outdoor air pollution. These impacts place a high cost on the medical system.

Reductions in emissions of SO_2 and NO_x will also have considerable benefits beyond acid deposition reductions (see below).

12.9 WHAT ARE THE LINKAGES AND IMPLICATIONS OF OTHER ENVIRONMENTAL PROBLEMS WITH ACID DEPOSITION, IN PARTICULAR, OZONE AND PARTICULATE MATTER FORMATION, CLIMATE CHANGE AND MERCURY?

12.9.1 Particulate Matter

Particulate matter (PM) shares precursor emissions (SO_2 and NO_x) with acid deposition. The relationship between ambient levels of precursor gases and $PM_{2.5}$ is complicated. For SO_2, long-term trends in ambient levels of $PM_{2.5}$, particle sulphate and SO_2 track each other closely. This suggests that reductions in emissions of SO_2 will lead to reductions in concentrations of $PM_{2.5}$.

The relationship between ambient levels of NO_x and $PM_{2.5}$ is also complicated; however, there is evidence that under NH_3^- limited conditions, reductions in SO_2 emissions with no concomitant change in NO_x and NH_3 emissions can result in an increase in PM levels due to the enhanced formation of ammonium nitrate particles. Thus, SO_2 and NO_x emission reductions should occur at the same time in order to reduce PM.

12.9.2 Ozone

Tropospheric ozone (O_3) primarily shares the precursor emission of NO_x with acid deposition. The formation of tropospheric ozone occurs via a series of chemical reactions the most common of which involves nitrogen oxides, volatile organic compounds (e.g. solvents), and sunlight. In general, increases in the emissions of NO_x result in increases in concentrations of tropospheric ozone on the regional scale; however, in urban areas, ozone levels seem to be more influenced by VOC emissions (i.e. VOC emission controls are more effective for reducing ozone than NO_x emission controls) and increases in NO_x emissions lead to decreases in ozone levels, the so-called "NO_x disbenefit". The non-linear relationship between concentrations of NO_x, VOCs and ozone production complicates the forecasting of NO_x emission reductions on ozone levels.

12.9.3 Climate Change

Acid deposition and climate change are linked in several ways: 1) Fossil fuel combustion is the primary anthropogenic source of carbon dioxide (CO_2), an important greenhouse gas, as well as SO_2 and NOx which are precursors of acid deposition. Consequently, reductions in the use of fossil fuels will benefit both issues. 2) SO_2 and NO_x contribute to the formation of particulate matter and ground-level ozone which directly and indirectly impact on the radiation balance of the atmosphere (i.e. the amount of heat and light that are reflected into space or towards earth). For the most part, ground-level ozone is understood to exert a warming effect on climate and sulphate is understood to exert a cooling effect on climate at seasonal scales; 3) A changing climate may change the quantities and patterns of precipitation which could then affect the transport, dispersion, deposition and release of acid-causing pollutants; and, 4) a warmer climate may also increase biogenic emissions of NO_x, SO_x and VOCs. For example, increases in surface temperatures can stimulate increases in emissions of NO_x from soil bacteria. Despite the fact that acid deposition and climate change are linked, our capacity to predict the effects of increases or decreases in emissions of SO_2 and NO_x on climate is limited.

12.9.4 Mercury

Emissions of mercury and other hazardous pollutants work in synergy with SO_2 and NO_x to enhance the deleterious effects of acid deposition on fish and wildlife. As levels of acidity in surface waters increase, the rate of conversion of mercury (Hg) into toxic and bioavailable methyl mercury (MeHg) increases. Recent studies have shown that significant declines in atmospheric deposition of sulphate and Hg are associated with declines in Hg levels in fish and fish-consuming wildlife such as the Common Loon. Thus, reductions in emissions of acid-causing emissions would benefit the mercury issue.

12.10 WHERE DO WE NEED TO CONTINUE ATMOSPHERIC AND EFFECTS MONITORING?

Atmospheric monitoring needs to be continued at all current measurement locations and increased in both western and eastern Canada to continue to track the effectiveness of emission controls, provide data for the assessment of exceedances of critical loads and to support human health studies. The highest priority for new deposition monitoring sites is in Ontario and Newfoundland since there are insufficient numbers of monitoring sites currently operating in these provinces. A high priority also needs to be given to the placement of sites in western Canada, where acid-causing emissions are projected to increase in the future but where very little deposition monitoring is taking place.

Aquatic and soil chemistry monitoring needs to continue and increase at sites that have exceeded, continue to exceed, or have the potential to exceed critical loads for acid deposition. Monitoring of surface waters (e.g. large and small lakes, rivers, wetlands) is necessary to determine trends in surface water chemistry such as pH, sulphate, nitrate and base cation concentrations. Data on these variables are essential for determining the extent to which ecosystems are being acidified, recovering from acidification, or are susceptible to damage from acidification in the future. Data on these variables also indicate the extent to which acid deposition is impacting or could impact biodiversity.

Monitoring of aquatic biota, wildlife and forests must continue in areas where critical loads are exceeded or have been exceeded. Integrated chemical and biological monitoring in these areas is necessary to determine how changes in surface water and soil chemistry are affecting biodiversity and ecosystem productivity and, if necessary, to support the development of management actions for ecosystem recovery.

12.11 WHERE SHOULD WE FOCUS FUTURE RESEARCH EFFORTS FOR ACID DEPOSITION?

12.11.1 Emissions

Research needs to focus on the development of improved statistics, methodologies and emission factors to determine emissions from the on-road transportation, agriculture, and residential wood combustion sectors.

Currently, a large percentage of the emission rates used to estimate emissions from industrial and non-industrial sources are based on measurements performed in the U.S. a number of years ago. There is a need to update these emission rates to reflect Canadian weather, fuels characteristics, operations, industrial processes, and emission control equipment and practices.

There is also a need to improve emission inventories for elements that govern total acidity of deposition. For some effects modelling, the controlling atmospheric input is not a particular acidifying species such as sulphate or nitrate but rather total acidity. Unfortunately, prediction of pH is particularly difficult because it requires the concentrations or depositions of *all* acidifying species to be estimated correctly, including total ammonia and base cations. Base cations pose a particular problem because they are present in crustal material (i.e. fugitive dust) in varying proportions and emissions of bulk crustal material are still not well characterized.

12.11.2 Atmospheric Deposition Monitoring and Analysis

Future efforts in the area of atmospheric and precipitation monitoring should focus on improving the capacity to characterize total sulphur and nitrogen deposition. Improvements are especially necessary for nitrogen because current dry deposition estimates are biased low in the absence of several unmeasured species. Although current acid deposition models predict both dry and wet deposition, it has not been possible until very recently to make measurement-based estimates of dry deposition on a routine basis at multiple sites. As a consequence it has not been possible to accurately assess the role of dry deposition in acid deposition, accurately determine the contribution of sulphur and nitrogen to total acidity, nor evaluate model predictions of dry deposition directly. The increased accuracy in the improved total deposition measurements will also enhance Canada's ability to determine when and where critical loads are being exceeded.

Future efforts should also focus on increasing the number of sites at which wet and dry deposition are measured in eastern and western Canada to permit accurate characterization of atmospheric deposition across the country. The increased number of sites would enable the determination of the spatial distribution of wet and dry deposition across all of Canada and, in combination with U.S. data, across all of North America. It will also allow us to fill large gaps in knowledge as to where critical loads are being exceeded and increase the capacity to assess human exposure to acid aerosols. It will also provide a stronger basis for determining whether emission reduction programs in Canada and the U.S. are being effective at reducing acid deposition where needed. This is particularly important in western Canada where, due to the paucity of measurements, such questions cannot be answered.

In addition, future research efforts should be focused on developing more sophisticated data analysis techniques to determine source-receptor relationships. This will improve our capacity to assess the efficacy of new emission reductions in Canada and the U.S.

12.11.3 Forests and Soils

The negative effects of decreasing soil fertility on forest health are becoming increasingly supported by recent studies. These observations are raising concerns about the effects of acid deposition on the productivity of Canadian forests located on poorly buffered soils. Quantification of the relationship between acid deposition and forest health remains difficult, however. Further research is necessary to elucidate this relationship.

One of the major uncertainties, with respect to quantifying the time it will take for forest soils and surface waters to recover, is the rate of primary weathering and the size of the exchangeable pool of base cations. For this reason, determination and validation of these variables should be a focus of future research.

The release of excess sulphur from soils may be partly responsible for the lack of recovery observed in lakes and rivers in eastern Canada and is an additional source of acid that is not accounted for in critical load models. Consequently, future research should focus on elucidating the processes governing transformation and export of sulphur from terrestrial watersheds to surface waters in the context of decreasing sulphur deposition.

Finally, although nitrogen saturation does not appear to be a problem in eastern Canada, the capacity of forests to accumulate atmospherically deposited nitrogen is finite. Detection of nitrogen saturation in surface waters must be the subject of monitoring efforts in existing research sites in both eastern and western Canada.

12.11.4 Aquatic Chemistry

With respect to aquatic chemistry, future research should focus on implementing a robust survey framework across Canada and supporting research on soils.

Currently, our capacity to assess the status of lake chemistry in Canada is severely limited by the necessity of compiling existing monitoring data without regard to site selection. Ideally, a statistically-based regional survey of lakes such as the stratified random sampling designs that have been employed in the U.S. and Nordic Europe would be preferable to assess current status.

Such a lake survey, if occasionally repeated (approximately once per decade – a rotating schedule of lake sampling would be instituted so that a tenth of the lakes were sampled every year) and integrated with an organized hierarchy of temporal monitoring and site-specific research, would provide all the information needed to accurately estimate resource-level status and change, identify the causes of change, and predict future conditions.

12.11.5 Aquatic and Terrestrial Biota

Ecosystem recovery is a primary objective of emission reductions. Understanding and predicting biological responses to emission reductions and consequent habitat recovery is necessary for evaluating the adequacy of controls and to direct conservation and management efforts. Identifying the nature and rate of biological recovery requires multi-disciplinary research, integrated habitat and biological monitoring, and robust predictive models. Information derived from these studies is essential for understanding how persistent biodiversity losses influence ecosystem function and for determining the emission reductions needed to meet ecosystem objectives.

The pace and nature of ecosystem recovery are influenced by many other environmental stressors. Future research efforts should include a focus on the interactions of acidification with other ecosystem stressors and those interactions should be integrated into model refinements. Relevant stressors include those related to atmospheric or climatic issues, metals and other toxics, land use/forest management practices and invasive species. Understanding the interactions between acidification and other stressors will provide more realistic predictions of ecosystem recovery.

A biomonitoring framework compatible with the lake chemistry survey described above would be the ideal foundation for estimating resource-level status and change and for predicting future biological conditions. With such a framework, efforts to understand biological recovery mechanisms could be specifically focused to investigate particular mechanisms and ecosystem stressors. The results of these more intensive investigations would be required to properly interpret observed trends and refine predictive models.

Acidification effects on terrestrial wildlife have received relatively little attention to date. Losses of available calcium sources have the potential to impact terrestrial invertebrates and the wildlife on which they depend (e.g. songbirds). Data-based investigations of potential effects should continue but should be supplemented by targeted field investigations.

Options for managing or actively rehabilitating acidified lakes, wetlands and rivers should be identified and explored with regard to their effectiveness, costs and overall efficiency.

The Integrated Assessment Model (IAM) is used to predict chemical and biological responses to various scenarios of SO_2 emission reductions. This model is an important integrative assessment tool and needs to be maintained and improved to reflect the new knowledge developed above.

12.11.6 Atmospheric Chemistry Models

For Canada, there are a number of areas in acid deposition modelling where further research is needed. Firstly, it has not been possible until very recently to evaluate directly the predictions of dry deposition by models. Efforts are needed to acquire appropriate data sets of sulphur and nitrogen dry deposition and use these to evaluate model predictions.

Some of the key properties of ammonia and nitric acid, needed to accurately predict wet and dry deposition and smog formation, require further investigation. The need for this information is becoming increasingly important as policy-makers seek scientifically defensible predictions of the consequences of changes in emissions of multiple pollutants (e.g., SO_2, NO_x, and ammonia) on air quality and acid deposition.

As emission control scenarios become more realistic, the level of effort required to prepare emissions data for acid deposition models becomes increasingly large. Consequently, there is a need for ready access to sophisticated and flexible emissions processing systems and, data on emissions of primary particulate matter including crustal material (i.e. dust).

To evaluate acid deposition model performance against newer sets of air chemistry and precipitation chemistry measurements, it is also necessary to compile year-long files of meteorological data for input to the acid deposition models.

All of the acid deposition models discussed in this assessment calculate deposition for grid widths ranging from 91 to 127 km. In some situations (e.g. near major sources of emissions), the use of smaller grid spacing and improved spatial resolution of emissions data would improve the accuracy of model predictions.

12.11.7 Socio-economics

Although environmental economic research is evolving, there are still large gaps in our understanding of the nature and value of acid deposition impacts. Despite the fact that some economic-evaluation modelling capacity currently exists (e.g. the Environment Canada's Air Quality Valuation Model), economic-evaluation models for acid deposition do not adequately account for environmental benefits resulting from abatement. Hence, future research efforts should focus on quantifying the benefits and costs associated with acid deposition effects on forest growth and productivity, recreational fishing, wildlife consumption and biodiversity.

12.12 CONCLUSIONS

While Canada has been very successful at reducing acid-causing emissions, acid deposition is still affecting the Canadian environment and the health of Canadians. The results of this assessment confirm that although levels of acid deposition have declined in eastern Canada over the last several decades, approximately 21-75% of eastern Canada, corresponding to approximately 0.5-1.8 million km^2, continues to receive levels of acid deposition in excess of critical loads according to best and worst cases, respectively.

It is estimated that on the order of a further 75% reduction in SO_2 emissions will be required from Canada and the U.S., beyond those agreed to for 2010, in order to protect eastern Canadian ecosystems from damage by acid deposition. At present, there is insufficient data on the capacity of western Canadian ecosystems to assimilate acid deposition without being harmed, hence; it is not possible to accurately assess the extent to which acid deposition is affecting ecosystems in the west.

Future research and monitoring will be required to verify the effectiveness of emission reductions and better understand the complex and long-term impacts of, in some cases, irreversible damage caused by acid deposition. The presence of acid-sensitive geology and increasing emissions of SO_2 and NO_x suggests that new monitoring efforts should expand into the western provinces to ensure that acid deposition does not damage ecosystems in this region.

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2004 Canadian Acid Deposition Science Assessment: Summary of Key Results

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