



Canadian Environmental Protection Act

Priority Substances List
Assessment Report

Chlorinated Wastewater Effluents



Government
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**PRIORITY SUBSTANCES LIST
ASSESSMENT REPORT**

CHLORINATED WASTEWATER EFFLUENTS

Government of Canada
Environment Canada
Health and Welfare Canada

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Synopsis

The priority substance "chlorinated wastewater effluents" (CWWE) is defined in this assessment to include only those effluents to which chlorine or chlorination agents are added for disinfection (e.g., effluents from municipal wastewater treatment plants) or biofouling control (e.g., effluents from thermal and nuclear power generating stations). In Canada, there are approximately 400 municipal wastewater treatment plants (MWTPs) discharging chlorinated wastewater effluents to aquatic systems. Total discharges of CWWE from MWTPs are estimated to be approximately 6.11×10^6 m³/day. Most of the 11 major power utilities in Canada use chlorination of cooling waters at some or all of their thermal power generating stations to control biofouling. Effluent flows from these power generating stations vary from an annual mean of 10 000 m³/day to an annual mean of 7.8×10^6 m³/day. Chlorination at power generating stations may take place on an irregular, daily, weekly, seasonal, or continuous basis. Little information is available on discharges of CWWE from industry. There is evidence that some industrial plants use chlorination for disinfection or control of biofouling and discharge their effluents directly to the Canadian environment.

In situ testing and biological surveys downstream from Canadian MWTPs demonstrated that CWWE have caused acute lethality to fish, and changes in community structure (e.g., reductions in diversity, shifts in species composition) in benthic invertebrate communities. These effects were evident up to 500 m from the outfalls of several MWTPs. In most cases where testing was conducted, the observed effects were reduced or eliminated by dechlorinating effluents before discharge or by switching to discharges of non-chlorinated effluents. *In situ* tests and biological surveys of receiving waters near MWTPs in Nova Scotia, Ontario, British Columbia, Alberta, and the eastern United States have shown that harmful effects to aquatic biota frequently occur when total residual chlorine levels exceed 0.02 mg/L.

Laboratory tests with whole effluent samples demonstrated that CWWE from MWTPs in Nova Scotia and Ontario were acutely lethal to fish and invertebrate species, particularly in effluents where total residual chlorine levels exceeded 0.1 mg/L. When the CWWE whole effluent samples were dechlorinated in a study involving eight Ontario MWTPs, the acute lethality to rainbow trout (*Oncorhynchus mykiss*) and the water flea, *Daphnia magna*, declined significantly.

Little information was available to compare the toxic effects of chlorinated and dechlorinated wastewater effluents discharged to marine ecosystems. However, for two MWTPs in Nova Scotia that discharge to marine waters, total residual chlorine levels in the effluent were slightly above 0.2 mg/L. This level is higher than the levels of total residual chlorine associated with effects to freshwater biota in *in situ* and whole effluents tests.

There is insufficient information to estimate the exposure of humans to chlorinated wastewater effluents or their products. In addition, information on the effects of CWWE to the environment on which human life depends was not identified. Therefore, detailed

consideration of whether CWWE is "toxic" as defined under Paragraphs 11(b) and 11(c) of the Act is not included in this assessment.

Therefore, on the basis of available data which demonstrate that chlorinated wastewater effluents discharged to the Canadian environment by municipal wastewater treatment plants have caused harmful effects to freshwater biota, the Minister of the Environment and the Minister of National Health and Welfare have concluded that chlorinated wastewater effluents are "toxic" as defined under Paragraph 11(a) of the *Canadian Environmental Protection Act*.

1.0 Introduction

The *Canadian Environmental Protection Act* (CEPA) requires the Minister of the Environment and the Minister of National Health and Welfare to prepare and publish a Priority Substances List that identifies substances, including chemicals, groups of chemicals, effluents, and wastes, that may be harmful to the environment or constitute a danger to human health. The Act also requires both Ministers to assess these substances and determine whether they are "toxic" as defined under Section 11 of the Act which states:

"...a substance is toxic if it is entering or may enter the environment in a quantity or concentration or under conditions

- (a) having or that may have an immediate or long-term harmful effect on the environment;
- (b) constituting or that may constitute a danger to the environment on which human life depends; or
- (c) constituting or that may constitute a danger in Canada to human life or health."

Substances that are assessed to be "toxic" as defined under Section 11 may be placed on Schedule I of the Act. Consideration can then be given to developing regulations, guidelines, or codes of practice to control any aspect of these substances' life cycle, from the research and development stage through manufacture, use, storage, transport, and ultimate disposal.

In this assessment, the priority substance "chlorinated wastewater effluents" (CWWE) is defined to include only those effluents to which chlorine or chlorination agents are added for disinfection or for biofouling control. This report will focus on:

- effluents from Canadian municipal wastewater treatment plants (MWTPs) that have been treated with chlorine for disinfection;
- industries that discharge wastewater effluents directly to the environment after chlorine disinfection (*e.g.*, tire manufacturers, food processing plants); and
- industries and power generating stations that discharge cooling waters treated with chlorine for biofouling control, including control of zebra mussels (*Dreissena polymorpha*).

Industries that produce wastewater effluents containing chlorinated compounds from processes not related to disinfection or biofouling control (*e.g.*, pulp and paper mills using chlorine for bleaching processes) are not considered in this assessment.

Over the past century, chlorination has become the most common method of disinfecting wastewater effluents in Canada and the United States. This use has come about because of chlorine's powerful disinfecting capabilities, ease of application, and low cost. Section 11 of CEPA does not consider the benefits of using a substance when determining if the substance is "toxic". The benefits of chlorinating wastewater effluents and the relative costs of alternative methods of disinfection, therefore, will not be considered in this assessment. If a substance is declared "toxic", then such benefits may be considered in developing appropriate control options.

The potential effects of CWWE on human health have not been widely studied, although information is available on the effects in experimental animals and humans exposed to disinfection by-products, such as the trihalomethanes. It is not possible, on the basis of the available data, to identify how much CWWE contributes to human exposure to disinfection by-products. However, since the general population has limited direct contact with CWWE, exposure is likely to be extremely low. Therefore, this assessment addresses only the environmental effects of CWWE. Similarly, information was not identified on the effects of CWWE on the environment upon which human life depends. Therefore, detailed consideration of whether chlorinated wastewater effluents are "toxic" as defined under Paragraphs 11(b) and 11(c) of CEPA are not included in this assessment.

Disinfection is defined as the process of destroying harmful viruses and micro-organisms by using agents such as chlorine, bromine, or ozone or by using other methods such as ultraviolet irradiation. In many areas of Canada, effluent wastewaters are disinfected to protect downstream municipal water supplies, recreational waters, and shellfish-growing areas from bacterial contamination and other agents causing waterborne disease. Disinfection is the final stage before the effluent is discharged to the receiving environment. However, chlorine may be added at other stages of the wastewater treatment process for purposes other than disinfection. These include odour control, destruction of cyanides and phenols, nitrogen removal, improved filter operation, control of foaming, and prevention of sludge bulking (White, 1972). In addition, many municipal wastewater treatment plants dechlorinate wastewater effluents by adding either sulphur dioxide, sodium metabisulphite, sodium bisulphite, sodium sulphite, sodium thiosulphate, hydrogen peroxide, or by using activated carbon before discharge to the receiving environment.

Chlorination is practiced at power generating stations primarily to control biofouling of cooling system condenser tubes, condenser water intake delivery systems, and to control algal growth in cooling towers. Some industrial sectors, including the pulp and paper, petroleum refining, and organic chemical manufacturing industries, also use once-through cooling waters for cooling of processes, turbines, and other equipment. In Ontario and Quebec, chlorine is used to prevent buildup of zebra mussels in pipes. Zebra mussels were introduced accidentally and have recently become established in the Great Lakes and St. Lawrence River. Rapid population growth has led to fouling of intake and outfall pipes at drinking water treatment plants, and at industrial and power generating stations using water on a once-through basis either as cooling or process water.

Much of the information available on CWWE is either unpublished or out of print. To access this information, staff were contacted from the provinces, federal departments, and academia who have been actively involved with this issue in Canada. These contacts provided much of the background information for this assessment. In addition, recent review papers were consulted and searched manually. For the section on Entry into the Environment (Subsection 2.2), contacts were made with officials at several municipal wastewater treatment plants to obtain information not routinely gathered by the provinces. A background report was prepared by Uwe Scheider under contract to Environment Canada. This report reviews the physical and chemical properties of chlorine, the reactions between chlorine and other substances during chlorination, and the substances produced as a result of chlorination. Another background report on the fate and levels of substances in CWWE released to the Canadian environment was prepared by Diane Koniecki under contract to Environment Canada.

Although much of the research on CWWE has been conducted outside Canada, available data on sources, fate, levels, and effects of CWWE on the Canadian environment were emphasized. All original studies that form the basis for determining whether chlorinated wastewater effluents are "toxic" under CEPA have been critically evaluated by the following Environment Canada staff:

R.L. Breton
S.A. Jones
D.R.J. Moore, Task Group leader
R. Scroggins

In this report, a synopsis is presented which will appear in the Canada Gazette. A summary of technical information that is critical to the assessment is presented in Section 2.0. A Supporting Document that discusses the technical information in greater detail has also been prepared and is available upon request. The assessment of whether chlorinated wastewater effluents are "toxic" as defined under CEPA is presented in Section 3.0.

As part of the review and approvals process established by Environment Canada for their contributions to Priority Substance Assessment Reports, this Assessment Report was reviewed by a number of experts from Environment Canada, representatives from the environmental departments of each of the Provinces that were nominated by the CEPA Federal-Provincial Advisory Committee, and Henryck Melcer of the Wastewater Technology Centre. The final Assessment Report was reviewed and approved by the Environment Canada/Health and Welfare Canada CEPA Management Committee. The Supporting Document was reviewed by staff at Environment Canada (Les Rutherford, Atlantic Region and Fred Zaal, Western and Northern Region).

Copies of this Assessment Report and the unpublished Supporting Document are available upon request from:

Commercial Chemicals Branch
Environment Canada
14th Floor, Place Vincent Massey
351 St. Joseph Boulevard
Hull, Quebec
K1A 0H3

Environmental Health Centre
Health and Welfare Canada
Room 104
Tunney's Pasture
Ottawa, Ontario
K1A 0L2

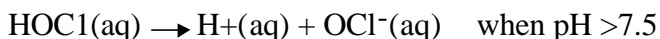
2.0 Summary of Information Critical to Assessment of "Toxic"

2.1 Identity, Properties, and Uses

The chlorine element is a member of the halogen family and is the second most reactive non-metallic substance, after fluorine. It is usually electronegative (-I), but can also exhibit an electropositive character [*e.g.*, chlorine monoxide (+I) and chlorine dioxide (+IV)]. The -I oxidation state (*e.g.*, hydrochloric acid, HCl) is the most stable form of the chlorine element, such that all substances in which the chlorine element has an oxidation state greater than -I are oxidizing agents (Neumüller, 1979; Chang, 1988). Because of this oxidizing ability, chlorine gas, chlorine oxoacids, and chlorine oxides are widely used as bleaching agents, disinfectants in water purification and treatment, and inhibitors of biofouling in cooling waters.

In Canada, addition of chlorine gas [Cl₂(g)], hypochlorite salts [NaOCl or Ca(OCl)₂], and chlorine dioxide (ClO₂) are the most common chemical control methods used for wastewater disinfection and biofouling control in cooling waters (Supply and Services Canada, 1987; Bunce, 1990; Jafvert and Valentine, 1992). Inorganic monochloramine (NH₂Cl) was widely used in the past but is rarely used today due to its slow oxidant reaction time compared to these other substances, and uncertainties about its risk to human health (Bunce, 1990).

Chlorine gas added to water will hydrolyze rapidly to form a 0.4 to 0.5% aqueous solution of hypochlorous acid as shown in the following equations (Neumüller, 1979; Petrucci, 1989; Jafvert and Valentine, 1992):



The species HOCl and OCl⁻ are referred to as free residual chlorine and are strong oxidizing agents that may react with organic substances by electrophilic substitution, addition, or oxidation reactions (Petrucci, 1989). As a neutral molecule, HOCl is approximately 100 times more effective as a disinfectant than OCl⁻ because it can penetrate cell membranes of microorganisms more easily and destroy intracellular, life-sustaining substances (Bunce, 1990). Hypochlorite salts added to water also produce an aqueous solution of hypochlorous acid.

A variety of substances in the influent can react with hypochlorous acid or, to a lesser extent, with chlorine dioxide to form chlorinated by-products (Johnson and Jensen, 1986). For example, phenols can be chlorinated by one of four reaction pathways:

- (i) electrophilic aromatic substitution to form chlorophenols;

- (ii) oxychlorination to form chlorobenzoquinones and chlorinated muconic acid derivatives;
- (iii) addition to form various chlorinated cyclohexene derivatives; and
- (iv) subsequent to one of the above reactions, intramolecular rearrangement to form chlorohydroxyacetones and chlorohydroxycyclopentenes (NRCC, 1978; Johnson and Jensen, 1986).

Oxychlorination of ammonia and electrophilic chlorine substitution of aromatic amines and other organic nitrogenous substances lead to the formation of inorganic and organic chloramines, respectively (NRCC, 1978). These chloramines are known as combined residual chlorine. The sum of free residual chlorine and combined residual chlorine is referred to as the total residual chlorine (TRC).

Trihalomethanes are generated as a result of the "haloform reaction" in which the methyl ketone groups in humic acids are first converted to trihalo ketone groups. The resulting trihalo ketones are then hydrolyzed to yield the trihalomethanes and carboxylic acids (Manahan, 1984; Bunce, 1980). Numerous other chlorinated by-products can be formed by a variety of reactions between hypochlorous acid or chlorine dioxide and influent substances.

Oxidation is the predominant reaction between hypochlorous acid or chlorine dioxide and organic substances. The production of chlorinated substances from oxidation reactions is relatively minor. Substances containing alcohol, aldehyde, and carbohydrate substituents, and substances with sulphhydryl or other reduced sulphur linkages are subject to oxidation, but are rarely subject to substitution or addition reactions (NRCC, 1978).

2.2 Entry Into the Environment

There are two major sources of CWWE in Canada: (i) effluents from municipal wastewater treatment plants (MWTPs) and from industrial plants treated with chlorine products for disinfection, and (ii) cooling waters from power plants and industrial plants treated with chlorine products to control biofouling.

2.2.1 *Municipal Wastewater Treatment Plants*

In Canada, approximately 2800 municipal wastewater treatment plants (MWTPs) discharged approximately 1×10^7 m³/day of wastewater effluents to the environment in 1992 (Supply and Services Canada, 1987; Tate and Lacelle 1992; additional data provided by the Provinces). Of this total, approximately 400 plants (14%) discharged a total of 6.11×10^6 m³/day (61%) of effluents that had been chlorinated before discharge (Supply and Services Canada, 1987; additional data provided by the Provinces and selected MWTPs).

Of the plants discharging CWWE, 302 (75%) were located in three provinces: Ontario (175 plants), Manitoba (80 plants), and British Columbia (47 plants, 22 of which dechlorinate their effluents before discharge). In terms of flow, 89% of chlorinated wastewater effluents from MWTPs produced in Canada were generated in Ontario (73%) and British Columbia (16%) (Supply and Services Canada, 1987; additional data supplied by the Provinces and selected MWTPs).

The quantities of chlorination agents used to treat wastewaters and the contact time between application and eventual release play a major role in the amount of total residual chlorine (TRC) and chlorinated by-products discharged to the environment. The TRC levels observed in final effluents vary from 0.2 to 0.8 mg/L (mean = 0.64 mg/L) in Newfoundland; 0.15 to 0.5 mg/L (mean = 0.25 mg/L) in Prince Edward Island; 0.1 to 2.1 mg/L (mean = 0.58 mg/L) in Nova Scotia; 0.05 to 1.0 mg/L (mean = 0.4 mg/L) in New Brunswick; 0.7 to 1.2 mg/L in Saskatchewan; and 0.6 to 3.2 mg/L in Alberta (Garron, 1992; additional data supplied by the Provinces and selected MWTPs). No information was available from the remaining provinces on TRC levels in MWTPs. Contact times also vary by province and range from 15 to 90 minutes in the Atlantic provinces and Alberta (Alberta Environment, 1988; Garron, 1992). The mean TRC level in effluents from provinces for which information was available was approximately 0.95 mg/L. Multiplying this level by the estimated total flow of CWWE in Canada ($6.11 \times 10^6 \text{ m}^3/\text{day}$) indicates that approximately 5800 kg/day ($2.1 \times 10^6 \text{ kg/year}$) of total residual chlorine are discharged to the Canadian environment from municipal wastewater treatment plants.

2.2.2 Cooling Waters from Power Generating Stations

An Environment Canada survey of each of the 11 major power utilities in Canada in 1992 (Environment Canada, 1992a) indicated that at power generating stations owned and operated by four of the utilities (New Brunswick Power, Manitoba Hydro, SaskPower, TransAlta Utilities Corp.), cooling waters are not chlorinated.

Chlorination of cooling waters at the thermal power generating station in Newfoundland (Newfoundland and Labrador Hydro) was conducted for a one-hour period daily from mid-July to the end of August in 1990 and 1991. The flow rate was approximately 280 000 m^3/day with a total residual chlorine (TRC) level of 0.4 mg/L and discharge was to the Atlantic Ocean at Conception Bay.

Nova Scotia Power employs intermittent chlorination of its cooling waters throughout the year at some thermal power generating stations and information for one station is available. This station generates 60 000 to 420 000 m^3/day of cooling waters with TRC levels of 0.2 to 0.4 mg/L.

Hydro Quebec employs intermittent chlorination (30 minutes, twice daily) of the cooling and service waters at one thermal power generating station. The flow rate varies from 300 000 to 600 000 m^3/day and TRC levels are negligible at the outfall to the St. Lawrence River.

Of the eight thermal power generating stations in Ontario (Ontario Hydro), several practice intermittent chlorination of their cooling waters (TRC = 0.002 mg/L). Cooling water flows range from 540 000 to 7.8×10^6 m³/day and discharge outfalls are located on the north shore of Lake Superior, Lake Erie, and Lake Ontario, and on the St. Clair River.

Two thermal power generating stations in Alberta use intermittent chlorination of cooling waters. The first (Alberta Power Limited) chlorinates weekly and discharges 1.6×10^6 m³/day of cooling water (TRC negligible) to the Battle River. The second (Edmonton Power) chlorinates nine times yearly (residual chlorine levels not specified) and discharges 250 000 to 590 000 m³/day of cooling water to the North Saskatchewan River.

The only thermal power generating station operated by B.C. Hydro continuously chlorinates its cooling and service waters with a total mean flow of 10 000 m³/day (860 to 59 000 m³/day) and a TRC concentration of <0.01 mg/L at the discharge outfalls located in Burrard Inlet.

As indicated by these examples, chlorination practices for cooling waters vary widely among the power utilities. The observed differences make it difficult to compare the amounts of TRC in wastewaters discharged by utilities with the amounts discharged by MWTPs.

Most nuclear power generating stations in Canada do not chlorinate their cooling waters. The only nuclear reactor operated by Hydro Quebec chlorinates twice daily (total chlorination duration is two hours per day) and discharges 2.6×10^6 m³/day of cooling water to the St. Lawrence River. The maximum TRC in the effluent is 0.1 mg/L.

2.2.3 Industrial Sources of Chlorinated Wastewater Effluents

Little information is available on industrial wastewater effluents chlorinated for control of biofouling or for disinfection. Residual chlorine has been detected in wastewaters from meat processing, and natural gas plants in Alberta (Alberta Environment, 1991). Chlorination for disinfection is practiced in fish and poultry processing plants in British Columbia and the effluents are discharged to the environment (David, 1992). The petroleum refining, pulp and paper, and petrochemical industries discharge cooling waters (OMOE, 1990a; 1991a; 1992a) that may use chlorine to control biofouling (Madé, 1992).

Most wastewaters and cooling waters generated by industry are not treated by municipal wastewater treatment plants and are discharged directly to the Canadian environment. In 1981, only 11% of the influents received at Canadian MWTPs were from industrial discharges to municipal sewer systems, with an additional 8% coming from commercial sources (Supply and Services Canada, 1987). Since 1981, industries that discharged effluents directly to the environment have been forced to improve their waste disposal methods, for economic and regulatory reasons. The response has been to recycle process waters, use less water, and connect with MWTPs (Hawley, 1984). As a result, approximately 30% of influents received at Ontario MWTPs in 1989 were from

industrial sources, an 18% increase since 1981 (OMOE, 1989). There is no information on whether this trend is evident in other Canadian provinces.

The amount of chlorinated wastewaters generated by the use of chlorinated products to control zebra mussels within pipes is unknown. However, the following factors suggest that the use of chlorinated products for this purpose will result in relatively minor discharges of CWWE to the Canadian environment:

- the systems modification (i.e., change in injection location) required to control zebra mussels within intake pipes falls within the existing requirements for treatment of potable water with chlorine;
- the levels of chlorination for potable water treatment and to control zebra mussels are similar;
- dechlorination of treated waters is mandatory; and
- the use of chlorine to control zebra mussels in both potable and industrial applications must meet existing Ontario and federal environmental and human health objectives.

Ontario and Quebec are the only provinces using chlorine to control zebra mussels, although other provinces may soon be forced to consider this option. In Ontario, chlorination within intake pipes takes place only when zebra mussels are a problem (June to October) and then only when intake pipes are operating. As a result, discharges of CWWE to the receiving environment from this use will be relatively minimal.

2.3 Exposure-related Information

2.3.1 Fate

A variety of halogenated substances are discharged to aquatic systems as a result of chlorination of wastewaters and cooling waters. The chlorination reaction products include the residual chlorine substances that possess an oxidative capacity, and the inorgano- and organochlorines formed by the reaction between residual chlorine substances and natural or anthropogenic organic substances. Due to the complexity of reactions and diversity of substances involved, the fates of selected substances are used to provide insight into the likely behaviour in the environment of related groups of substances.

Total Residual Chlorine (TRC) is the sum of free residual and combined residual chlorine. Free residual chlorine is the free available oxidant in solution and includes hypochlorous acid (HOCl), hypochlorite ion (OCl⁻), and chlorine gas [Cl₂(g)]. Combined residual chlorine refers to the organic and inorganic chloramines formed by reaction of free residual chlorine with ammonia or other nitrogenous substances (Morris, 1978; NRCC, 1978; Helz, 1981; Jolley and Carpenter, 1983). Chlorination of salt water leads to the formation of free and combined residual bromine. The term total residual

oxidants is used to refer to the sum of these oxidative products in salt water (Scott and Vernberg, 1979; Grove, 1983).

The fate of TRC in receiving waters is governed by the physical processes of mixing, dilution, and volatilization and several chemical processes, including oxidation, combination with organic substances, and photodegradation. Results from laboratory and field studies have suggested that the half-life of TRC in receiving waters is relatively short, ranging from less than one hour to several days (Brooks and Seegert, 1977; Wisz *et al.*, 1978; Heinemann *et al.*, 1983; Helz *et al.*, 1984). Factors, such as ice formation that prevents volatilization and dark conditions that prevent photodegradation, tend to increase the persistence of TRC (Brooks and Seegert, 1977; Hostgaard-Jensen *et al.*, 1977). Other factors, such as increased dilution during spring runoff and increased concentrations of easily oxidized substances (e.g., iron(II), sulphide, and some organic substances), tend to decrease the persistence of TRC in receiving waters (Johnson, 1978; Wisz *et al.*, 1978; Helz *et al.*, 1983).

Inorganic Chloramines. Monochloramine (NH_2Cl) is the principal inorganic chloramine in receiving waters because of its rapid formation and stability in effluents and natural waters (Kovacic *et al.*, 1970; Murphy *et al.*, 1975; Johnson, 1978; Margerum *et al.*, 1978). Monochloramine is a weaker oxidizing agent and is more resistant to degradation than is free residual chlorine (Snoeyink and Markus, 1974; Johnson, 1978). In water, monochloramine decomposes by hydrolysis to form ammonia (NH_3) and hypochlorous acid (HOCl). The half-life for the reaction was found to be 10 hours (Margerum *et al.*, 1978).

Low pH conditions and low concentrations of ammonia favour the formation of dichloramine (NHCl_2) (Wisz *et al.*, 1978; Helz, 1981; Jafvert and Valentine, 1992). Dichloramine is not formed above pH 7.5 since it is oxidized to nitrogen gas (N_2), nitrate (NO_3^-), and chloride (Cl^-) as rapidly as it is produced (Johnson, 1978). At lower pH levels, dichloramine hydrolyzes to form monochloramine (NH_2Cl) and hypochlorous acid (HOCl), although the half-life of approximately 9 days for the hydrolysis of dichloramine is much longer than the corresponding half-life (10 hours) for the hydrolysis of monochloramine (Margerum *et al.*, 1978).

Trichloramine (NCl_3) is rarely found in receiving waters because of its rapid conversion to dichloramine (NHCl_2) via hydrolysis (Helz, 1981).

Organic Chloramines. Several organic chloramines have been identified in chlorinated wastewater effluents from MWTPs and power generating station cooling waters, including chlorinated pyrimidines, purines, nucleosides, and several other related substances (Glaze and Henderson, 1975). Little information is available about the fate of these substances when released to aquatic systems. Stanbro and Smith (1979) reported that *N*-chloroaniline degrades by oxidative decarboxylation to form acetaldehyde, ammonia, carbon dioxide, and chloride ion between pH 5 to 9 (half-life = 46 minutes). 5-Chlorouracil in the monoanionic form was also found to be rapidly degraded (half-life < 2 days, pH 7.3 to 8.3) by photolysis, although this substance is much more resistant to

photolysis at higher pH levels (Southworth and Gehrs, 1976). No other information was found concerning the environmental fate of organic chloramines.

Chloralkyl and Chloralkene Substances*, such as chloroform, tri- and tetrachloroethylene, and 1,1,1-trichloroethane, have frequently been detected in chlorinated wastewater effluents and cooling waters (Glaze and Henderson, 1975; Grove *et al.*, 1985; OMOE, 1991c). In general, chloralkyl and chloralkene substances detected in wastewaters contain one to three carbon atoms with one to four chlorine atoms, although under saltwater conditions, the chlorine atoms may be replaced by bromine atoms (e.g., bromodichloromethane, dibromochloromethane, bromoform). These chloralkyl and chloralkene substances are volatile substances that do not partition to sediments or tissues in significant amounts (Helz and Hsu, 1978; CCREM, 1987). For example, the half-life of chloroform due to volatilization was estimated to be 1.2 days in the lower Rhine River, 2 to 9.8 days in a well mixed estuary, and 31 days in a lake in the Rhine River basin (Helz and Hsu, 1978; Zoeteman *et al.*, 1980). Biodegradation in water and river bottom biofilms may also be an important degradation process, particularly for less volatile substances such as bromoform (Tabak *et al.*, 1981). Measured half-lives for these substances due to biodegradation range from 7 to 28 days for chloroform (anaerobic conditions, unacclimated cultures) to 98 days to 4.5 years for the chlorinated ethanes and ethylenes under aerobic or anaerobic conditions (unacclimated cultures)(Howard *et al.*, 1991). Other chemical degradation processes, such as hydrolysis, oxidation, and photolysis, are not considered to be important removal mechanisms from water for CWWE chloralkyl and chloralkene substances (CCREM, 1987; Howard *et al.*, 1991).

The most important degradation process for CWWE chloralkyl and chloralkene substances that have volatilized to the atmosphere is reaction with hydroxyl radicals (U.S. EPA, 1978; Atkinson, 1985). The photo-oxidation half-life for chloroform in the atmosphere has been estimated to range from 26 days in polluted areas to 260 days in pristine areas (Howard *et al.*, 1991). The principal product of this reaction is phosgene (Spence *et al.*, 1976). 1,1,1-trichloroethane has a much longer half-life in the atmosphere (half-life = 0.6 to 6.2 years) and can cause ozone depletion after transport to the stratosphere (McConnell and Schiff, 1978; Howard *et al.*, 1991).

Chloraryl Substances*. The environmental fate of chloraryl substances, such as the chlorophenols and chlorobenzenes, is a function of the degree of chlorination and molecular weight of the substance under consideration. For example, sorption to organic matter and tissues increases with molecular weight and degree of chlorination (Convery *et al.*, 1980; Wegman and van den Broek, 1983; CCREM, 1987). Biodegradation is a rapid removal mechanism for the mono- and di- chloraryl substances (e.g., half-life = 1 to 26 days for monochlorophenol, aerobic conditions), but is slower for the penta- and hexa- chloraryl substances (e.g., half-life = 23 to 178 days for pentachlorophenol, aerobic conditions)(Tabak *et al.*, 1981; Howard *et al.*, 1991). Photolysis is the major removal

* Although the focus of these sections are chloralkyl, chloralkene, and chloraryl substances; alkyl, alkene and aryl derivatives with other functional groups (e.g., bromo, methoxy, hydroxyl) are also discussed.

mechanism for pentachlorophenol because of its resistance to biodegradation (half-life = 0.04 to 4.6 days)(Howard *et al.*, 1991). Volatilization and partitioning to sediments and tissues tend to be more important removal processes for the chlorobenzenes, particularly hexachlorobenzene, than for the chlorophenols because the former are less reactive (Carlson *et al.*, 1975; Bean, 1983). Oliver and Niimi (1983) observed that the bioconcentration factor in rainbow trout (*Oncorhynchus mykiss*) increased from 269 for 1,2-dichlorobenzene, to 1300 for 1,2,4-trichlorobenzene, to 12 000 for hexachlorobenzene.

In the atmosphere, chloraryl substances react with hydroxyl radicals with photo-oxidation half-lives in the range of <1 day to ~ 3 days for the chlorophenols and chlorobenzenes (Howard *et al.*, 1991). The only exception is hexachlorobenzene which has a much longer photo-oxidation half-life (half-life = 156.4 days to 4.2 years) and is therefore transported through the atmosphere to remote areas (Howard *et al.*, 1991).

Other Halogenated Substances. A number of surfactants used in domestic, industrial, and agricultural applications have the potential to be chlorinated during wastewater disinfection. For example, halogenated alkylphenol polyethoxycarboxylates (APECs) have been detected in wastewater effluents (Ball and Reinhard, 1985). These substances may be significant environmental contaminants because they are non-volatile, resistant to biodegradation, and large quantities of precursors [alkylphenol polyethoxylates (APEOs)] are produced commercially and eventually treated in wastewater treatment plants (Ball and Reinhard, 1985; Ball *et al.*, 1989).

2.3.2 Concentrations

Residual chlorine and halogenated organics have been identified in effluents and receiving waters from municipal wastewater treatment plants, power generating stations, and several industries in Canada. The presence of free and combined residual chlorine in effluents can be attributed to the disinfection process, since any residual chlorine in the influents would have reacted with other substances or volatilized before the disinfection stage. In contrast, some of the chloralkyl, chloralkene, and chloraryl substances detected in monitoring studies of effluents have also been detected in the influents, often at higher concentrations (OMOE, 1988). Since they are less reactive with other substances, their presence in the effluents may not be due solely to chlorination. The types and levels of substances found in CWWE and the receiving environment are briefly described in this subsection. The focus of the discussion is on substances found in effluents and receiving waters, since no information was found on levels in sediments, tissues, and in the atmosphere.

Total Residual Chlorine. A 1990 survey of disinfectant chemical use at municipal wastewater treatment plants in the Atlantic provinces found that mean total residual chlorine (TRC) levels ranged from 0.25 mg/L in effluents from MWTPs in Prince Edward Island to 0.64 mg/L in effluents from Newfoundland MWTPs (Garron, 1992). Downstream monitoring conducted in 1991 at two MWTPs located on Fales Brook and Nine Mile Brook in Nova Scotia indicated that TRC levels declined rapidly

after discharge. At Fales Brook, the mean TRC level was 0.06 mg/L near the outfall and below the detection limit (0.01 mg/L) 180 m downstream. Similarly, at Nine Mile Brook, the mean TRC level was 0.16 mg/L near the outfall and below the detection limit (0.01 mg/L) in 4 out of 5 samples 70 m downstream (Rutherford, 1992).

Beak Consultants Limited and CH2M HILL Engineering Limited conducted a study of the acute and chronic effects of effluents from ten Ontario MWTPs in the summer and winter of 1989/1990 (OMOE, 1991b). The study included measurements of TRC levels at the time of effluent sampling. Mean TRC levels in effluents ranged from below the detection limit (0.02 mg/L) to 1.0 mg/L in winter, and from 0.16 to 0.53 mg/L in summer for the eight plants that practiced seasonal or year-round chlorination for disinfection. Another study by CH2M HILL Engineering Limited (OMOE, 1991c) of three MWTPs in Ontario reported a similar range for TRC levels in effluents in the summer of 1986. Levels of TRC in effluent samples ranged from <0.05 to 1.1 mg/L at the Welland MWTP; 0.05 to 0.27 mg/L at the Waterloo MWTP; and 0.1 to 0.5 mg/L at the Galt MWTP. However, the results of the latter study are suspect because of lack of precision and accuracy of the analytical method used, and because some samples were aerated in open containers before analysis (OMOE, 1990b).

A September 1982 *in situ* monitoring study of the Avon River below the Stratford, Ontario MWTP indicated a gradual decline in TRC levels from 17 m downstream of the outfall (0.17 to 0.35 mg/L) to 209 m downstream of the outfall (0.003 to 0.1 mg/L) (Flood *et al.*, 1984a). Levels of TRC as high as 0.23 mg/L have been observed in Otter Creek, 53 m downstream of the Tillsonburg MWTP (Flood *et al.*, 1984b), and as high as 0.1 mg/L in the Grand River, 100 m downstream from the Waterloo MWTP (OMOE, 1992b). Earlier studies conducted on Ontario MWTP wastewater discharges between 1976 and 1977 indicated that TRC levels declined rapidly in some receiving waters (*e.g.*, Grand River, Brantford MWTP where levels declined from a mean of 1.4 mg/L at the outfall to a mean of 0.002 mg/L 41 m downstream), but not in others (*e.g.*, Aurora Creek, Aurora MWTP where levels declined from a mean of 0.82 mg/L 1.5 m downstream to 0.46 mg/L 2092 m downstream) (Wisiz *et al.*, 1978).

In a study of TRC levels in the south Saskatchewan River near the Saskatoon MWTP, TRC was detected up to 500 m downstream (mean = 0.08 mg/L) in July, 1987 and up to 140 m downstream (mean = 0.06 mg/L) in August, 1987 (SEPS, 1989). No other recent information was found for the Prairie and Pacific regions.

Limited data were available on TRC levels in cooling waters discharged by power generating stations that use chlorine to control biofouling. The recommended code of practice for steam electric power generating stations is a TRC level of ≤ 0.2 mg/L at the outlet of the cooling water system undergoing chlorination (Environment Canada, 1985; 1992b).

Inorganic Chloramines. No recent information on levels of inorganic chloramines in effluents or receiving waters was found for Canada. Based on studies conducted in 1976 and 1977 in Aurora Creek, Ontario downstream from the Aurora

MWTP, monochloramine levels were found to be much higher in winter than in summer. The mean monochloramine level in the effluent for both summer and winter was 1.2 mg/L. However, approximately 3000 m downstream, the mean level in winter was 0.32 mg/L, while in summer the mean at the same location was below the detection limit (0.002 mg/L)(Wisiz *et al.*, 1978). The pattern observed for dichloramine at the same location was similar except that dichloramine levels were lower.

Organic Chloramines. No recent information was available on levels of organic chloramines in CWWE in Canada. In a 1979 survey of MWTPs in southern Ontario, Craig *et al.* (1983) detected chloroaniline (<1 µg/L) and dichloroaniline (<1 to 10 µg/L) in effluent samples.

Several studies of chlorinated effluents from MWTPs and cooling waters from power generating stations discharging to the Mississippi River in the United States in the early 1970s identified the following organic chloramines: 5-chlorouracil, 8-chlorocaffeine, 6-chloro-2-aminopurine, 8-chloroxanthine, and 5-chlorouridine (Jolley, 1975; Jolley *et al.*, 1976). Concentrations of each of the organic chloramines ranged from 0.6 to 7 µg/L in effluent and cooling water samples.

Chloralkyl and Chloralkene Substances. The Ontario Ministry of the Environment conducted a pilot monitoring study of 37 MWTPs in Ontario, including one tertiary treatment plant, 28 secondary treatment plants, and seven primary plants that chlorinated their effluents for disinfection (OMOE, 1988). Of the 28 chloralkyl and chloralkene substances analyzed, 15 were detected (the detection limits ranged from 2 to 20 µg/L) in at least one effluent sample. Of these substances, only three (tetrachloroethylene, chloroform, 1,1,1 -trichloroethane) were detected in more than 25% of the samples from either primary, secondary, or tertiary treatment plants. The maximum levels observed ranged from just above the detection limit for most of the 15 chloralkyl and chloralkene substances detected to between 100 and 420 µg/L for di-, tri-, and tetra- chloroethylene and 1,1,1 -trichloroethane in primary treatment plants, and chloroform in secondary treatment plants.

Chloroform, 1,1,1 -trichloroethane, and tri- and tetra- chloroethylene were identified in a 1986 study of effluents from the Galt, Welland, and Waterloo MWTPs in Ontario (OMOE, 1991c). The observed effluent levels for each of these substances ranged from 0.5 to 2.64 µg/L. A 1979 study of CWWE from nine MWTPs in southern Ontario identified the above substances, as well as several other halomethanes, chloroethanes, and chloroethylenes (Craig *et al.*, 1983). Levels of these substances in effluent samples were in the low µg/L range.

Several studies of cooling waters from thermal and nuclear power generating stations, and chlorinated effluents from MWTPs in the United States also found a variety of halomethanes, chloroethanes, and chloroethylenes occurring in the low µg/L range in effluent samples (Roberts *et al.*, 1980; Bean *et al.*, 1983; Grove *et al.*, 1985).

Chloraryl Substances. A pilot monitoring study of 37 MWTPs in 1986 detected 8 of a possible 14 chloraryl substances in at least one effluent sample (detection limits ranged from 2 to 10 µg/L)(OMOE, 1988). These substances had a low detection frequency and were rarely detected at levels exceeding 10 µg/L.

The only chloraryl substance identified in a 1986 survey of effluents from the Gait, Welland, and Waterloo MWTPs was 1,4-dichlorobenzene, with levels ranging from 0.5 to 2.43 µg/L in effluent samples (OMOE, 1991c). A 1979 survey (Craig *et al.*, 1983) identified several chloraryl substances in effluent samples, including chloro-, dichloro-, and hexachloro- benzene, pentachlorophenol, chlorotoluene, tetrachloromethoxybenzene, and *p*-chloroanisole. Levels for each were in the low µg/L range.

At least 13 chloraryl substances have been identified in cooling waters from thermal and nuclear power generating stations in the United States. These include nine mono-, di-, and tri-halophenols and four di- and tri- chlorobenzenes (Bean *et al.*, 1983; Grove *et al.*, 1985). Levels in effluent samples of each of these substances were in the low ng/L to low µg/L range.

Other Halogenated Substances. No information was available on levels of chlorinated surfactants and other substances in CWWE in Canada. Several studies have qualitatively identified chlorinated surfactants in effluents from MWTPs in the United States (Ball and Reinhard 1985; Ball *et al.*, 1989).

2.4 Effects-related Information

Several studies on fish have shown that free or combined chlorine can adversely affect both the structure of the gill (Servizi and Martens, 1974; Bass and Heath, 1975a;b; Wiley, 1983) and the ability of hemoglobin in the blood to transport oxygen (Buckley, 1976; Grothe and Eaton, 1975). The resulting damage to gill membranes and oxidation of hemoglobin to methemoglobin suggests that the ultimate cause of mortality from exposure to free or combined chlorine is asphyxiation (Rosenberger, 1971; Dandy, 1972; Bass and Heath, 1975a;b; Cairns *et al.*, 1975). In addition, several studies have also suggested that free and combined chlorine may have other sites of toxicity, including the nervous system (Fobes, 1971; Wolf *et al.*, 1975).

A study by Katz (1979) indicated that exposure to residual chlorine increased gill permeability which in turn may lead to increased accumulation and hence toxicity of other chemical substances found in CWWE.

There are three categories of studies on the effects of CWWE on the environment:

- (i) *in situ* studies of community structure, population survival, or other biological endpoints;
- (ii) whole effluent tests; and

- (iii) chemical tests for chlorinated substances known to occur in CWWE (e.g., total residual chlorine, monochloramine).

This section will focus on the first two categories, since they provide the most direct evidence of effects to the Canadian environment.

Much of the available information on *in situ* and effluent testing was generated in the 1970s and earlier. Only those studies applicable to current practices in Canada are discussed in the following subsections.

2.4.1 In situ Surveys and Field Tests

In situ studies using caged sockeye salmon (*Oncorhynchus nerka*) and pink salmon (*O. gorbuscha*) were conducted in 1972 and 1973 in three tributaries of the Fraser River in British Columbia downstream from MWTPs (Servizi and Martens, 1974). In one tributary, during February and March 1972, 100% mortality of caged sockeye salmon fingerlings was observed at each of five stations located between 9 and 92 m downstream (control mortality = 0%). The total residual chlorine (TRC) level at the 92 m station was 0.07 mg/L. Twenty percent mortality occurred at the sixth station, 185 m downstream, where the TRC concentration was 0.02 mg/L. Higher levels of TRC occurred in October and November, 1972 and 100% mortality of sockeye salmon fingerlings was observed at the furthest station, 277 m downstream from the effluent outfall (TRC = 0.24 mg/L). When the chlorinator was not operating at the MWTPs on tributaries I and III, mortality of sockeye and pink salmon fingerlings and alevins either did not occur or declined significantly. Undiluted effluent from the MWTP on tributary II, which had been dechlorinated by storage in a lagoon (TRC was below the detection limit of 0.02 mg/L), caused no mortality to juvenile salmon.

The Ontario Ministry of the Environment has conducted *in situ* toxicity testing downstream from several MWTPs using chlorination for disinfection. Mortality of caged juvenile rainbow trout (*Oncorhynchus mykiss*) after acute exposures was observed in the Grand River downstream from the Waterloo MWTP (100% mortality at the 100 m station)(OMOE, 1992b), the Avon River downstream from the Stratford MWTP (66% mortality at the 475 m station)(Flood *et al.*, 1984a), and Otter Creek downstream from the Tillsonburg MWTP (100% mortality at the 53 m station) (Flood *et al.*, 1984b). No mortality was observed at the control stations located above the MWTP outfall at each of these sites. Chemical characterization of the receiving waters at each site indicated that TRC levels above approximately 0.04 mg/L were associated with 100% mortality during acute exposures (Figure 1). The available data on levels of ammonia, metals, and other substances discharged by the MWTPs indicated that these were below the levels normally associated with toxic effects to rainbow trout. Disinfection of the effluents from the Tillsonburg MWTP using ultraviolet light instead of chlorination led to a reduction in observed mortality of rainbow trout (100% to $\leq 6\%$ at the 53 m station).

In a recent study, Szal *et al.* (1991) examined the effects of CWWE from three sites near MWTPs discharging effluents to streams in Massachusetts. At each site, caged fathead minnows (*Pimephales promelas*) experienced 100% mortality after a 24-h

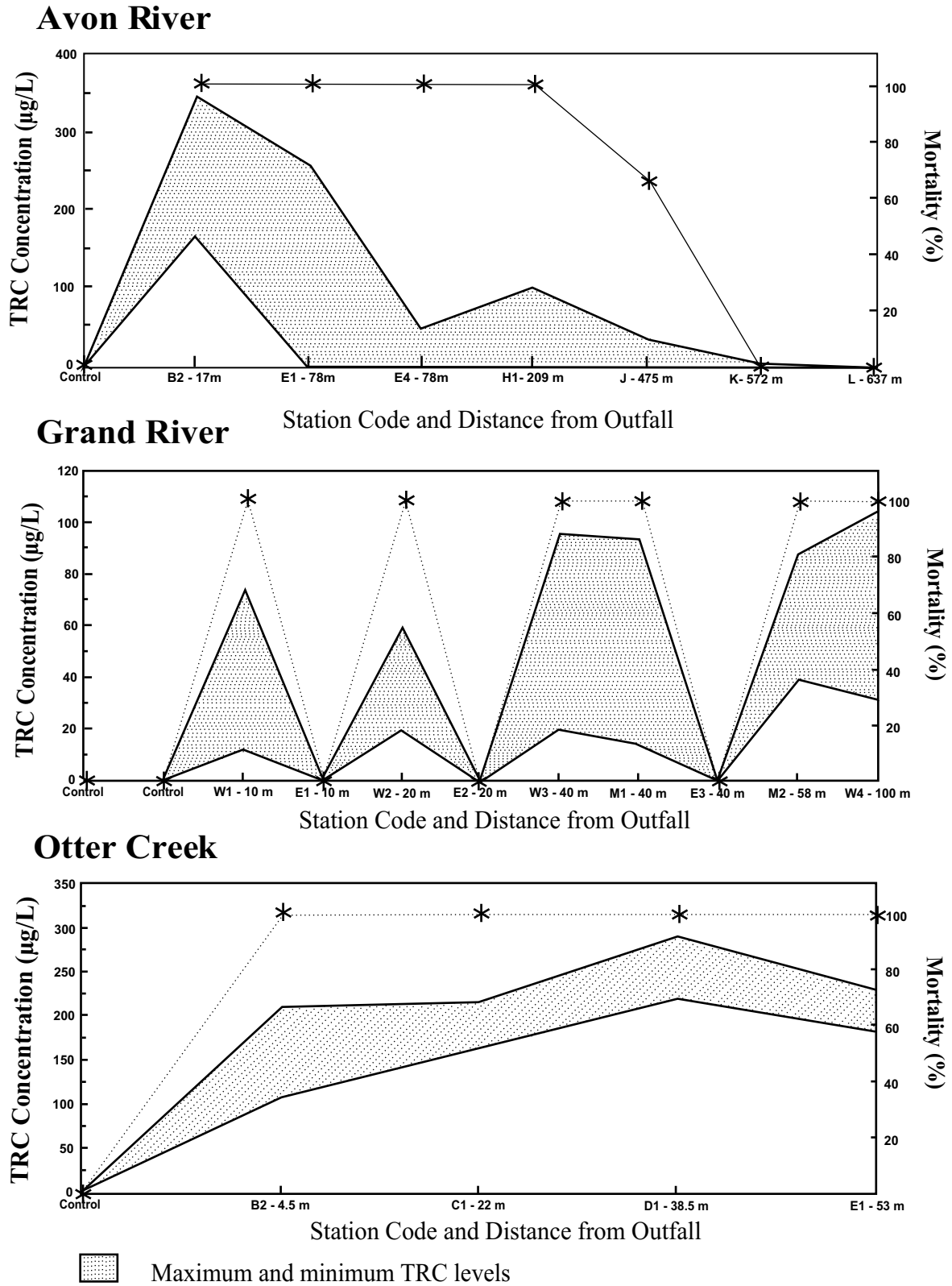


Figure 1 Total Residual Chlorine Versus Mortality of Rainbow Trout Downstream from Three Municipal Wastewater Treatment Plants in Ontario (Periods for the studies ranged from 48 h to 120 h.)

exposure at distances ranging from 21 to 91 m downstream and 25 to 85% mortality at distances ranging from 183 to 427 m downstream. Chlorination of wastewater effluents was determined to be a major cause of mortality because: (i) survival at control stations was $\geq 85\%$; and (ii) survival in whole effluents that had not been chlorinated was $\geq 90\%$ in laboratory tests. The relationship between TRC levels and minnow mortality varied among sites. Minnows exposed to between 0.05 and 0.35 mg/L of TRC experienced no mortality at one site, while at another site where TRC levels ranged from ≤ 0.03 to 0.14 mg/L, minnows experienced 100% mortality. Variations in apparent TRC toxicity levels at different sites may have been associated with interactive effects among TRC, ammonia, and oxygen saturation (Szal *et al.*, 1991).

In a study by Osborne *et al.* (1981), 40% mortality of caged rainbow trout (*Oncorhynchus mykiss*) was observed 100 m downstream from a MWTP on the Sheep River in Alberta (mean TRC = 0.35 mg/L). No mortality occurred when caged fish were exposed to non-chlorinated whole effluent for 24 hours. A biological survey conducted downstream from the Sheep River MWTP demonstrated a shift in structure from a community dominated by mayflies, chironomids, caddisflies, and stoneflies, to one dominated by oligochaete worms, after chlorine disinfection was begun in 1977 (Osborne, 1985). This shift in structure was apparent up to 500 m downstream in 1979. Osborne (1985) hypothesized that the shift in community structure occurred because oligochaete taxa are more tolerant of exposure to TRC than are other aquatic insect taxa (Arthur *et al.*, 1975; Brooks and Seegert, 1977).

In Nova Scotia, biological surveys conducted near three MWTPs discharging CWWE revealed that benthic community structure was significantly altered at the furthest station sampled for each MWTP (Figure 2) (Rutherford, 1992). For example, in Fales Brook, taxa evenness was significantly depressed 180 m from the Greenwood MWTP effluent outfall. This was due to an increase in the number of chironomids found below the effluent outfall and a corresponding decrease in the number of invertebrates belonging to other taxa. In Halifax Harbour, the total number of invertebrates was significantly reduced 100 m from the effluent outfall when compared to a control station 2.5 km from the outfall. This resulted from decreases in the abundance of several annelid, crustacea, and mollusc species. It is not possible to determine whether residual chlorine or other substances produced by effluent chlorination contributed to the observed effects on benthic community structure at these three sites. For example, the Eastern Passage MWTP is a primary treatment facility that discharges effluent with ammonia levels in the range of 19 to 20 mg/L. Ammonia may be a greater factor than TRC in causing the observed changes in community structure at this facility (OMOE, 1990b).

Tsai (1970, 1971) examined species diversity and abundance changes of fish downstream from over 150 MWTPs in the eastern United States. Fish species, particularly salmonids, were adversely affected (e.g., reductions in diversity, shifts in community structure) downstream from MWTPs in which chlorination was the final process before discharge. Brook trout (*Salvelinus fontinalis*) and brown trout (*Salmo trutta*) were absent from receiving waters in which mean TRC concentrations

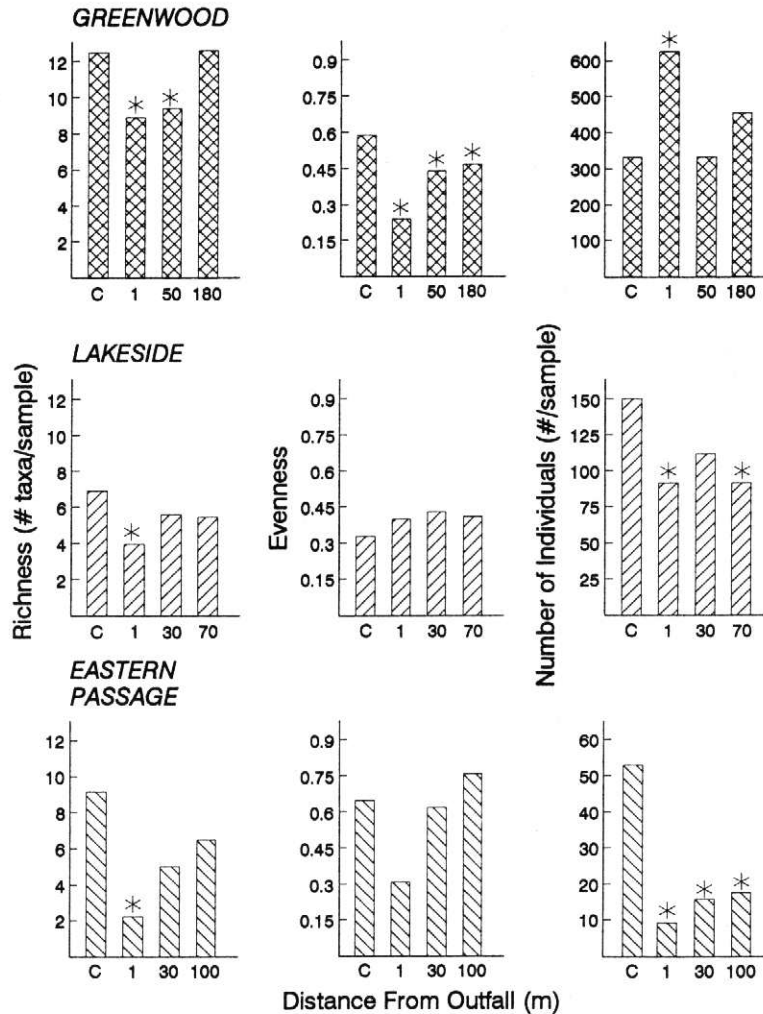


Figure 2 Effects on Benthic Communities of Chlorinated Wastewater Effluents Discharged by Three Municipal Wastewater Treatment Plants in Nova Scotia

Taxa richness, taxa evenness, and the number of individuals on artificial substrates after a four-week colonization period near three MWTPs in Nova Scotia that discharge CWWE (Rutherford, 1992). Sampling was conducted at an upstream control station (control = C) and at three stations downstream from each of the two MWTPs discharging to freshwater rivers (Greenwood and Lakeside). The control station was located 2.5 km from the MWTP discharging to the marine environment (Eastern Passage). Evenness was calculated using the formula:

$$R = H/H_{\max} = -\sum_{i=1}^n (p_i \log p_i) / \log n,$$

where: p_i is the relative frequency of taxon "i", and n is the number of taxa in the sample.

The symbol * is used to denote treatment effects that were significantly different from the control ($p < 0.05$) as determined by one-way ANOVAs and Duncan's multiple range tests conducted for each endpoint at each MWTP.

exceeded 0.02 mg/L. No effects on species diversity or community structure were observed downstream from MWTPs that dechlorinated effluents by storage in open lagoons.

2.4.2 Whole Effluents

A study of ten Ontario MWTPs was conducted in the summer and winter of 1989/1990 by Beak Consultants Limited (OMOE, 1991b). Eight of these plants practiced seasonal or year-round chlorination for disinfection. Of a total of 123 grab and composite samples of effluent collected (both chlorinated and non-chlorinated), 43 contained 0.1 mg/L of TRC or greater. Of these, 33 (77%) were acutely lethal to rainbow trout (*Oncorhynchus mykiss*) before dechlorination, while 18 (42%) were lethal after dechlorination (TRC levels were less than the detection limit of 0.01 mg/L following dechlorination of the samples by addition of sodium sulphite). When *Daphnia magna* was used as the test species, 28 (65%) of the 43 samples with TRC levels at or greater than 0.1 mg/L were acutely lethal, while 8 (19%) were lethal following dechlorination. Furthermore, the LC₅₀s for samples tested as received were distributed toward lower effluent concentrations (greater toxicity) than were dechlorinated samples for both rainbow trout and *Daphnia magna*. These results occurred despite declines in TRC levels between time of collection and time of testing and the rapid dissipation of TRC during testing.

A 1991 study of four MWTPs in Nova Scotia (CFB Cornwallis, Eastern Passage, Greenwood, and Lakeside) indicated that CWWE effluents from all four plants were not toxic to the algal species, *Selenastrum capricornutum* (Rutherford, 1992). For the remaining species tested in laboratory bioassays (rainbow trout, threespine stickleback, and oyster) acute lethal effects were more pronounced with effluents from the CFB Cornwallis and Eastern Passage treatment plants, which had mean TRC levels slightly above 0.2 mg/L. Mean TRC levels in effluents from the Greenwood and Lakeside treatment plants were \leq 0.005 mg/L and 0.12 mg/L, respectively. For example, the 96-h LC₅₀ (expressed as percent of whole effluent) for rainbow trout was 32.9% when exposed to effluents from the Eastern Passage treatment plant, 35.4% from the CFB Cornwallis treatment plant, >100% for the Lakeside treatment plant, and 70.7% for the Greenwood treatment plant. Threespine stickleback (*Gasterosteus aculeatus*) and a luminescent bacterium (*Photobacterium phosphoreum*) were found to be less tolerant of exposure to effluents from the Eastern Passage plant with an observed mean 96-h LC₅₀ of 8.8 to 11.4% and a 15-minute inhibition concentration (IC₅₀) of 8.0 to 9.7%, respectively. Abnormal shell development in larval oysters (*Crassostrea gigas*) was observed at levels as low as 0.2% after a 48-h exposure to effluents from the CFB Cornwallis plant. Dechlorination using sodium thiosulphate was found to detoxify one sample from CFB Cornwallis, but only partially detoxified other samples in the study, indicating that TRC was responsible for some but not all of the observed effluent toxicity.

2.4.3 *Effects of Substances Found in Chlorinated Wastewater Effluents*

The evidence presented in the preceding subsections indicates that total residual chlorine and other chlorinated compounds produced by chlorination are important contributors to the observed toxicity of treated wastewaters from some of the MWTPs tested. Toxicity may also be caused or enhanced by a number of other factors, including high concentrations of ammonia, metals, surfactants and other compounds, high biological oxygen demand, or extremes of pH and temperature (for a review, see OMOE, 1990b).

Toxicity studies are available for substances produced by chlorination of wastewater effluents and are briefly reviewed in the Supporting Document for CWWE. For in-depth reviews, the reader is referred to documents such as the *Canadian Water Quality Guidelines* (CCREM, 1987; and updates). For this report, the toxicity data on single substances found in CWWE were not deemed critical to the assessment because of the availability of *in situ* studies and whole effluent test results.

3.0 Assessment of "Toxic" Under CEPA

In Canada, there are approximately 400 municipal wastewater treatment plants (MWTPs) discharging chlorinated wastewater effluents (CWWE) to aquatic systems. Total discharges of CWWE effluents are estimated to be approximately 6.11×10^6 m³/day. Based on an estimated total residual chlorine (TRC) concentration of 0.95 mg/L in final effluents, it is estimated that approximately 5800 kg of TRC are discharged to the Canadian environment from MWTPs daily.

Most of the 11 major power utilities in Canada employ chlorination of cooling waters at some or all of their thermal power generating stations to control biofouling. Effluent flows from these power stations vary from a mean of 10 000 m³/day to a mean of 7.8×10^6 m³/day. Levels of TRC in cooling waters generally vary from 0.002 to 0.4 mg/L and chlorination may take place on an irregular, daily, weekly, seasonal, or continuous basis.

Little information is available on discharges of CWWE effluents from industry. There is evidence that some industrial plants employ chlorination for disinfection or control of biofouling and discharge their effluents directly to the Canadian environment.

Insufficient information was available to determine if the practice of chlorinating cooling waters in power generating stations and other industries causes harmful effects to aquatic biota in Canada. Therefore, the remainder of this assessment will focus on the available evidence for MWTPs that chlorinate for disinfection.

3.1 CEPA 11(a) Environment

A variety of substances are discharged to aquatic systems in Canada as a result of wastewater chlorination. These substances can be broadly classified as total residual chlorine, which includes free chlorine (HOCl, OCl⁻, Cl₂) and the organic and inorganic chloramines (NH_xCl_{3-x}), chloralkyl and chloralkene substances, chloraryl substances, and other halogenated substances.

Levels of free chlorine and the organic and inorganic chloramines are rapidly reduced in most aquatic systems due to dilution, volatilization, chemical degradation, and reaction with other substances. Chloralkyl, chloralkene substances, and the lower chlorinated chloraryl substances discharged in CWWE effluents are generally non-persistent in aquatic systems.

It is important to note that substances not produced by chlorination (*e.g.*, ammonia, metals) and other characteristics of wastewater effluents (*e.g.*, temperature, pH, biological oxygen demand) may cause harmful effects to aquatic biota. The evidence presented in this subsection addresses only the issue of whether chlorination of wastewater effluents produces compounds that at least partially contribute to the observed toxicity of these effluents following discharge to Canadian aquatic ecosystems.

In situ testing and biological surveys downstream from Canadian MWTPs demonstrated that CWWE effluents have caused acute lethality to fish (Servizi and Martens, 1974; Osborne *et al.*, 1981; Flood *et al.*, 1984a; b; OMOE, 1992b), and changes in community structure (*e.g.*, reductions in diversity, shifts in species composition) to benthic invertebrate communities (Osborne, 1985; Rutherford, 1992). These effects were evident up to 500 m from the outfalls of several MWTPs. In most cases where testing was conducted, the observed effects were reduced or eliminated by dechlorinating effluents before discharge or by switching to discharges of non-chlorinated effluents (Servizi and Martens, 1974; Osborne *et al.*, 1981; Flood *et al.*, 1984b; Osborne, 1985). For example, caged rainbow trout (*Oncorhynchus mykiss*) experienced 40% mortality 100 m downstream from an MWTP located on the Sheep River, Alberta. No mortality occurred when fish were exposed to whole effluents that had not been chlorinated (Osborne *et al.*, 1981). *In situ* tests and biological surveys of receiving waters near MWTPs in Nova Scotia, Ontario, British Columbia, Alberta, and the eastern United States have shown that harmful effects to aquatic biota frequently occur when TRC levels exceed 0.02 mg/L.

Laboratory tests with whole effluent samples demonstrated that CWWE effluents from MWTPs in Nova Scotia and Ontario were acutely lethal to fish and invertebrate species, particularly in effluents where TRC levels exceeded 0.1 mg/L (OMOE, 1991b; Rutherford, 1992). When the CWWE whole effluent samples were dechlorinated in the study involving eight Ontario MWTPs, the acute lethality to rainbow trout (*Oncorhynchus mykiss*) declined from 77% to 42% of the samples tested, and for *Daphnia magna*, acute lethality declined from 64% to 18% of the samples tested. The results from two MWTPs discharging to marine waters in Nova Scotia indicated that CWWE effluents may be acutely lethal at levels of $\leq 10\%$ effluent. Marine bivalve larvae were found to be particularly sensitive, with effects observed at 0.2% CWWE.

Little information was available to compare the toxic effects of chlorinated and dechlorinated or non-chlorinated wastewater effluents discharged to marine ecosystems. For two of the MWTPs in Nova Scotia that discharge to marine waters, however, TRC levels in the effluent were slightly above 0.2 mg/L (Rutherford, 1992). This level is higher than the levels of TRC associated with effects to freshwater biota in *in situ* and whole effluent tests.

Therefore, on the basis of available data, which demonstrate that chlorinated wastewater effluents discharged to the Canadian environment by municipal wastewater treatment plants have caused harmful effects to freshwater aquatic biota, chlorinated wastewater effluents are considered to be "toxic" as defined under Paragraph 11(a) of CEPA. There is insufficient information to make an assessment of "toxic" as defined under Paragraphs 11(b) and 11(c) of CEPA.

4.0 Recommendations for Research and Evaluation

The available information was sufficient to conduct an environmental assessment for CWWE. The available information indicated that power generating stations and some industrial sectors in Canada discharge chlorinated wastewater effluents. Little information was available, however, to assess the potential for harmful effects from these sources. *In situ* testing and biological surveys near power generating stations and industrial outfalls are required before these sources can be assessed. This research is considered to be of medium priority.

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