# Sampling Program for Residential Wood Heating

Study Report: 1999 to 2002

Anne-Marie Carter André Germain Jacques Rousseau *Environment Canada* 

Michel Bisson Ministère de l'Environnement du Québec

> Claude Gagnon *City of Montreal*

September 2004



Environment Environnement Canada Canada





This sampling program for residential wood heating is a joint collaboration of the three following partners:

Environment Canada :

- Environmental Protection Branch, Québec Region
- Meteorological Service of Canada, Québec Region
- Laboratory of the Environmental Technology Centre, Ottawa

Ministère de l'Environnement du Québec :

- Direction du suivi de l'état de l'environnement
- Centre d'expertise et d'analyse environnementale du Québec

City of Montreal:

- Direction de l'environnement

This document is available in French under the title *Campagne d'échantillonnage* sur le chauffage résidentiel au bois, Rapport d'étude : 1999 à 2002

Published by authority of the Minister of the Environment © Public Works and Government Services Canada, 2004 Paper version: Catalogue number: EN154-27/2004E ISBN: 0-662-38369-9 PDF version: Catalogue number: EN154-27/2004E-PDF ISBN: 0-662-38370-2

#### Summary Sampling Program for Residential Wood Heating: 1999 to 2002

A study conducted in 1998 by the *Regroupement montréalais pour la qualité de l'air* (RMQA) identified residential wood heating as one of the main sources of air pollution in the Greater Montreal area. Several medical studies indicate that wood combustion may have a negative impact on human health.

During the winter of 1999, samples taken from a monitoring station located in Rivière-des-Prairies showed that the concentrations of several pollutants were greater in this residential area than in downtown Montreal. Furthermore, a survey conducted in 2000 confirmed that this residential district, located northeast of Montreal, is among the sectors of the island where most homes are heated by wood as a primary or secondary heating system.

The present study analyzes the results obtained between December 1998 and May 2002, by comparing values obtained in downtown Montreal with values measured in winter and summer in a residential area where residential wood combustion is popular. It also assesses the impact of residential wood combustion on the concentrations of various products found in the air, and includes an analysis of the influence of meteorological parameters. Polycyclic aromatic hydrocarbons (PAH), dioxins and furans (D/F), volatile organic compounds (VOC), fine particulate matter (PM<sub>2.5</sub>), and metals are among the pollutants measured in the course of the project.

## Meteorological parameters

Meteorological conditions may play a significant role in pollutant concentrations present in ambient air. For instance, the wind can disperse pollutants emitted by local sources such as wood combustion. During winter evenings, when wind speed is above 15 km/h in the residential area,  $PM_{2.5}$  concentrations are generally below 5 µg/m<sup>3</sup>. However, concentrations can increase to 60 µg/m<sup>3</sup> when wind speeds are below 2 km/h. Calm winds allow for the accumulation of pollutants near local emissions.

When weather conditions influence the variability of pollutant levels, this is a likely indication that the source of the pollutants is local. In a residential area characterized by residential wood combustion, meteorological conditions such as wind speed, relative humidity, temperature and air stability may explain up to 62% of the variability of particulate matter ( $PM_{2.5}$ ) concentrations measured in the evening. This suggests that in winter, the contribution of local sources to  $PM_{2.5}$  concentrations is important in the residential area.

## Particulate matter

In winter, daily concentrations of particulate matter ( $PM_{2.5}$ ) were 10% greater in the residential area (10.1 µg/m<sup>3</sup>) than in downtown Montreal, while no difference was noted in the summer. The mean seasonal concentrations of  $PM_{2.5}$  were the same downtown, irregardless of the season.

When only the evening levels of  $PM_{2.5}$  are taken into account (from 6 p.m. to midnight), the difference between concentrations measured in the residential area (13.9 µg/m<sup>3</sup>) and in downtown Montreal (11.0 µg/m<sup>3</sup>) reached 26% in winter. Lastly,  $PM_{2.5}$  concentrations measured

in the residential district in winter were 57% greater than the concentrations measured on summer evenings.

Another observation noted in the residential area is that  $PM_{2.5}$  concentrations are greater on winter weekend evenings. Hourly average concentrations reached 17.9 µg/m<sup>3</sup>, while they were only 14.6 µg/m<sup>3</sup> during weekdays- which represents a difference of about 20%. No such discrepancy was noted in summer, either during the day or at night.

## <u>Metals</u>

Among all the metals measured, potassium (K) measured in  $PM_{2.5}$  is recognized as a tracer for residential wood combustion. The concentrations of potassium measured in the residential sector in winter (0.13 µg/m<sup>3</sup>) were 150% greater than those measured at the same site in the summer, and 40% greater than those measured downtown in winter.

A few tracers were evaluated to identify the potential sources of pollutants in the ambient air. Only the potassium to iron ratio (K/Fe) provided an indication of the presence of residential wood combustion. In the residential sector, this ratio was 200% higher in winter (3.6) than in summer, and 80% higher than in the downtown area in winter.

## Polycyclic aromatic hydrocarbons

During the four winters, the mean daily concentration of polycyclic aromatic hydrocarbons (PAHs) measured in the area influenced by residential wood combustion was 74.6 ng/m<sup>3</sup>. This concentration is five times greater than the concentration measured in summer, and twice the concentration measured in the downtown area in winter. At the residential area, the highest monthly values occurred from November to February, reaching a peak in January.

The seasonal variations were much more pronounced in the residential area than in downtown Montreal. This means that the sources of PAHs were present throughout the year in the downtown area, while in the residential area, an important source of PAHs was present only in winter. Motor vehicle traffic explains the relatively constant concentrations found in the downtown area, while wood combustion may explain the important fluctuations noted between winter and summer in the residential area. Benzo(a)pyrene (BaP) followed the same distribution pattern as the entire family of PAHs.

PAHs were also measured using a continuous analyzer in the residential sector influenced by wood combustion. The hourly variation in PAH concentrations in winter show two peaks during the day: one around 8 to 9 a.m., and the second, which is three times higher, around 7 to 8 p.m. The highest mean hourly value (144 ng/m<sup>3</sup>) occurred during the evening on weekends in winter. This value was 30% higher than on weekday evenings in winter, and 10 times higher than during the evening in summer.

## Dioxins and furans

Among the dioxins and furans (D/F) emitted during wood combustion, 17 compounds are of particular concern as regards to their impact on human health. Their concentrations are expressed in terms of toxicity equivalent (TEQ) as compared to the most toxic product of the group, that is 2,3,7,8-TCDD. In the residential area, the mean concentration in toxicity equivalent was 2.5

times greater in winter (0.069 pg  $TEQ/m^3$ ) than in summer, and 1.7 times greater than in downtown Montreal in winter.

On an annual basis, the mean concentration in 2001 was 0.049 pg  $TEQ/m^3$  in the residential area, and 0.031 pg  $TEQ/m^3$  in the downtown area. In both cases, the concentrations stood below the annual criteria established at 0.060 pg  $TEQ/m^3$  by the Ministère de l'Environnement du Québec.

#### Volatile Organic Compounds

Contrary to the winter of 1999, we did not find any significant differences in the concentrations of volatile organic compounds (VOCs) measured in the residential area and in downtown Montreal. However, the presence of certain VOCs at levels similar to those measured downtown is probably caused by wood combustion in the residential area, since motor vehicle traffic, also known as a source of VOCs, is not important in this sector.

More specifically, nonpolar VOCs, such as alkanes, halogens and aromatics, do not follow seasonal trends, with the exception of the alkene/alkyne group. A few of the substances belonging to this family, such as 1,3-butadiene, ethylene and acetylene, were present in greater concentrations in winter than in summer.

Excluding formaldehyde, total polar VOCs followed a seasonal trend by which concentrations were greater in winter than in summer in the residential area. However, the concentrations remained lower than those recorded at the downtown site. The same trend was noted for certain individual substances such as methyl ethyl ketone/butyraldehyde, acetaldehyde, acrolein and benzaldehyde.

## List of abbreviations and acronyms

BaP	Benzo(a)pyrene
CEAEQ	Centre d'expertise et d'analyse environnementale du Québec
DL	Detection limit
DRU	Drummond Street monitoring station
EC	Environment Canada
EST	Eastern standard time
ETC	Environmental Technology Centre
HDD	Heating degree-day
Hivol	Modified high-volume sampler
HPLC	High pressure liquid chromatography
K/Fe	Potassium to iron ratio
kt	Kilotonne (1,000 tonnes)
n	Number of samples
N.A.	Information not available
NAPS	National Air Pollution Surveillance Network
ng	Nanogram (10 <sup>-9</sup> gram)
Ont.	Ontario Street monitoring station
РАН	Polycyclic aromatic hydrocarbons
PCDD	Polychlorodibenzodioxins
PCDF	Polychlorodibenzofurans
PM	Particulate matter
PM <sub>10</sub>	Particles with an aerodynamic diameter of less than 10 µm
PM <sub>2.5</sub>	Particles with an aerodynamic diameter of less than 2.5 µm
	(often referred to as <i>fine particles</i> )
PM <sub>2.5-10</sub>	Particles with an aerodynamic diameter of more than 2.5 µm and
	less than 10 μm
RDP	Rivière-des-Prairies monitoring station
RMQA	Regroupement montréalais pour la qualité de l'air
S1999	Summer season followed by the year. In this example, the data covers the period from May 1, 1999, to September 31, 1999.
SAB	Sainte-Anne-de-Bellevue monitoring station
TEOM	Tapered Element Oscillation Monitor (continuous sampler)
TEQ	Toxicity equivalence (toxicity equivalence factor in relation to
	2,3,7,8-tetrachlorodibenzodioxin)
2,3,7,8-TCDD	2,3,7,8-tetracholorodibenzodioxin
USEPA	U.S. Environmental Protection Agency
μg	microgram (10 <sup>-6</sup> gram)
μm	micrometer (10 <sup>-6</sup> meter)
VOC	Volatile organic compounds
W1999	Winter season followed by the year. In this example, the data covers the period from December 1, 1998, to March 31, 1999.

## Table of contents

Summary	i
List of abbreviations and acronyms	iv
Table of contents	V
List of tables	vi
List of figures	vii
1. Introduction	1
1.1 Issue	1
1.2 Objectives	2
2. Materials and methods	3
2.1 Sampling site	3
2.2 Pollutants and parameters studied	5
2.3 Sampling frequency	5
2.4 Statistical analysis	7
3. Analysis of data and results	8
3.1 Seasonal representativity of the sampling program at Rivière-des-Prairies	8
3.1.1 Temperature	8
3.1.2 Heating degree-days	10
3.1.3 Total precipitation	12
3.1.4 Compass wind rose	12
3.2 Continuous analysis of fine particulate matter (PM <sub>2.5</sub> )	14
3.2.1 Continuous analysis of PM <sub>2.5</sub>	14
3.2.2 Heating degree-days	19
3.2.3 Continuous measurement of PM <sub>2.5</sub> in relation to the wind	21
3.2.4 Dispersion index	25
3.3 Particulate matter measured with the dichotomous analyzer	28
3.3.1 Particulate matter (PM)	28
3.3.2 Comparison of methods: dichotomous sampler and TEOM	31
3.4 Elements measured with the dichotomous analyzer	32
3.4.1 Elements	32
3.4.2 Potassium to iron (K/Fe) ratio as an indicator	34
3.5 Polycyclic aromatic hydrocarbons (PAHs)	37
3.5.1 24-hour modified high-volume sampler	37
3.5.2 Benzo(a)pyrene and the Québec standard	39
3.5.3 Continuous PAH analyzer	41
3.5.4 Relationship between PAHs and wind direction	46
3.5.5 Indicators	47
3.5.6 Comparison of continuous measurements of PM <sub>2.5</sub> and PAHs	48
3.6 Dioxins and furans	52
3.6.1 Ambient air measurements	52
3.6.2 Toxicity equivalent	54
3.7 Volatile organic compounds (VOCs)	57
3.7.1 Nonpolar VOCs	57
3.7.2 Polar VOCs	60
4. Conclusion	64
5. Recommendations	64
6. Acknowledgments	65
7. References	66
Appendice 1: Continuous PM <sub>2.5</sub> and atmospheric dispersion variables	68
Appendice 2: Synthesis of statistical results of dioxins and furans at the RDP and Ontario Street stations.	71
Appendice 3: Synthesis of statistical results of nonpolar VOCs at the RDP and Ontario Street stations	80
Appendice 4: Contribution of nonpolar VOCs (%) at the RDP and Ontario Street stations	85
Appendice 5: Synthesis of statistical results of polar VOCs	87

## List of tables

Table 1.1.1	Comparison of the atmospheric emissions (kt) of the main sectors of emissions in Québec in 2002	. 2
Table 2.2.1	List of instruments used	
Table 2.3.1	Sampling frequency	. 6
Table 3.1.1	Deviations with respect to climatology (1970-1997)	. 1
<b>Table 3.1.2</b>	Total monthly and seasonal amounts of precipitation measured at Dorval Airport	
	in snow water equivalent	. 1
<b>Table 3.2.1</b>	Seasonal variation of PM <sub>2.5</sub> ( $\mu$ g/m <sup>3</sup> ) concentrations at different sampling stations	. 1
<b>Table 3.2.2</b>	Pearson's correlation coefficients between the heating degree-days and the PM <sub>2.5</sub>	
	concentrations ( $\mu g/m^3$ ) at RDP for two periods of the day	. 2
Table 3.2.3	Pearson's correlation coefficients between wind speed $(km/h)$ and $PM_{25}$	
1 1010 01210	concentrations ( $\mu g/m^3$ ) measured at RDP	2
Table 3.3.1	Synthesis of results for PM measured over 24 hours at the RDP and Ontario	• -
1 abic 0.0.1	Street stations ( $\mu g/m^3$ )	-
Table 3 4 1	Mean contribution (%) of elements measured in the fine and coarse particle	• •
1 abic 5.4.1	fractions	?
Table 3 / 3	Concentrations ratios and determination factors for notassium and iron	• •
1 able 5.4.2	measured in particulate matter at the DDD and Onterio Street stations	
Table 2.4.2	measured in particulate matter at the NDP and Ontario Street stations	• -
1 able 5.4.5	K /Fe ratios and determination coefficients calculated at the KDP and Ontario	,
T.L. 251	Street stations.	
1 able 3.5.1	Synthesis of results for total PAHs measured over 24 hours from the winter of	
	1999 to the winter of 2002 at the RDP and Ontario Street stations (ng/m <sup>2</sup> )	
<b>Table 3.5.2</b>	Seasonal variation of the contribution of different PAHs (%) to the total PAHs	
	measured at the RDP and Ontario Street stations	• -
<b>Table 3.5.3</b>	Seasonal synthesis of results for BaP measured over 24 hours, winter of 1999 to	
	winter of 2002, at the RDP and Ontario Street stations (ng/m <sup>3</sup> )	. 4
<b>Table 3.5.4</b>	Annual synthesis of results obtained for BaP concentrations measured over 24	
	hours at the RDP and Ontario Street stations (ng/m <sup>3</sup> )	. 4
Table 3.5.5	Comparison of relations between different PAHs measured at the RDP and	
	Ontario Street stations	. 4
Table 3.6.1	Synthesis of the statistics relative to dioxins and furans (pg/m <sup>3</sup> ) measured at the	
	RDP and Ontario Street stations (winters 2000 to 2002)	. 4
Table 3.6.2	Seasonal variation of the contribution of different homologous series (%) to the	
	whole of the dioxins and furans measured at the RDP and Ontario Street stations	. :
<b>Table 3.6.3</b>	Ratio of dioxin and furan concentrations between the RDP and Ontario Street	
	stations	
<b>Table 3.6.4</b>	Synthesis of statistics relative to the PCDD and PCDF ( $pg TEQ/m^3$ ) measured at	
	the RDP and Ontario Street stations	. 4
Table 3.6.5	Seasonal variation of the contribution of different congeners (%) to the toxicity	
	(TEO) of the whole of the 17 dioxins and furans with toxicity equivalents	
	measured at the RDP and Ontario Street stations	4
Table 3.6.6	Ratios of the concentrations in toxicity equivalents of dioxins and furans	•••
1 abic 5.0.0	hetween the RDP and the Ontario Street stations	4
Table 3 7 1	Synthesis of results obtained for nonnolar total VOCs measured over 24 hours	•••
1 abic 3./.1	from the winter of 2001 to the summer of 2002 at the DDD and Ontario Stroat	
	nom me while of 2001 to the summer of 2002, at the KDF and Ontallo Silect stations $(ug/m^3)$	•
Table 2 7 4	Stations (µg/m)	•
Table 3.7.2	Contribution of the families/substances	
1 able 5.7.3	Contribution of polar VOCs (%) at the KDP and Untario Street, in descending	
	order	. (

## List of figures

Figure 2.2.1	Location of sampling sites on the Island of Montreal	4
Figure 2.2.2	Location of the main sampling site at Rivière-des-Prairies	4
Figure 3.1.1	Mean monthly temperature from December to March at RDP	9
Figure 3.1.2	Mean monthly temperature from May to September at RDP	10
Figure 3.1.3	Heating degree-days per month from December to March at RDP	11
Figure 3.1.4	Rose wind observed in winter (1999 to 2002) at RDP (n=11469)	13
Figure 3.2.1	Daily means and evening means (from 6 p.m. to midnight) of PM <sub>2.5</sub> in	
	Montreal according to the season	15
Figure 3.2.2	Monthly means of PM <sub>2.5</sub> in Montreal	16
Figure 3.2.3	Daily means of PM <sub>2.5</sub> at different sampling stations according to weekday	17
Figure 3.2.4	Hourly variation of $PM_{2.5}$ at different sampling stations in winter (December to March) from 1999 to 2002 (n = 464)	18
Figure 3.2.5	Hourly variation of $PM_{2.5}$ at RDP according to season and weekday (n = 464)	10
Figure 2.2.(	Variation in DM concentrations (courses between ( n m and midnight)	19
Figure 3.2.6	variation in $PM_{2,5}$ concentrations (average between 6 p.m. and midnight)	21
	measured at KDP on the basis of the number of heating degree-days. Winter $2001 (n - 100)$	21
E	2001 (n = 109)	
Figure 5.2.7	dea Brainia (from December to Merch inclusively, Assistant)	22
E	des-Prairies (from December to March Inclusively, 4 winters)	22
Figure 5.2.8	Houris variation of Pivi <sub>2.5</sub> concentrations ( $\mu$ g/m) and wind speed (km/n) as	24
E:	We in as Person's correlation coefficient in winter $(n = 404)$	24
Figure 5.2.9	variation of $PM_{2,5}$ concentrations on the basis of mean wind speed in the	25
E	evening in winter at RDP $(n = 464)$ .	23
Figure 5.2.10	variation of $PM_{2.5}$ measured in the evening on the basis of the dispersion index	20
E' 2 2 1	(winter 1999 to winter 2002; n=464)	20
Figure 3.3.1	Seasonal variation of $PM_{2.5}$ and $PM_{2.5-10}$ (median)	28
Figure 5.5.2	Seasonal variation of $PM_{2,5}$ at the KDP and Ontario Street stations	29
Figure 5.5.5	Monthly variation of PM <sub>2.5</sub> (median)	29
Figure 5.5.4	2000 and 2002)	31
Figure 3.3.5	Relation between the PM2.5: TEOM vs dichotomous sampler (summers 1999	
8	and 2001)	32
Figure 3.4.1	Seasonal variation of total elements, of potassium (K), iron (Fe), lead (Pb),	
0	vanadium (V), nickel (Ni) and cadmium (Cd) present in PM <sub>2.5</sub> at the RDP and	
	Ontario Street stations (mean)	34
Figure 3.4.2	Seasonal variation of the potassium to iron (K/Fe) and K'/Fe ratios at the RDP	
0	and Ontario Street stations (mean)	36
Figure 3.5.1	Seasonal variation of PAH concentrations at the RDP and Ontario Street	
0	stations	37
Figure 3.5.2	Seasonal variation of BaP concentrations measured at the RDP and Ontario	
-	Street stations (median)	40
Figure 3.5.3	Variation of the annual mean of BaP measured at the RDP and Ontario Street	
	stations	41
Figure 3.5.4	Correlation between the results obtained with the continuous analyzer and the	
	MHVS at RDP	42
Figure 3.5.5	Seasonal variation of PAHs measured with the continuous analyzer at RDP	
	(24-hour mean)	43
Figure 3.5.6	Monthly variation of PAHs (week vs weekend) at RDP	43
Figure 3.5.7	Daily variation of PAH concentrations (summer vs winter) at RDP	44
Figure 3.5.8	Hourly variation of PAHs measured in winter (week vs weekend) at RDP	45
Figure 3.5.9	Hourly variation of PAHs measured in summer at RDP (1999 and 2000) and at	
	the Ontario Street station (2001) (week vs weekend)	45

## List of figures (cont'd)

<b>Figure 3.5.10</b>	Mean PAH concentrations according to wind direction at RDP (December to	
	March inclusively, 4 winters)	47
Figure 3.5.11	Relation between the hourly concentrations of PM <sub>2.5</sub> and PAHs measured at	
	RDP in winter $(n = 10,037)$	49
<b>Figure 3.5.12</b>	Variation of mean concentrations of PAHs and PM <sub>2.5</sub> at RDP in winter (PAH:	
C	$n = 434$ ; $PM_{2.5}$ : $n = 464$ )	50
<b>Figure 3.5.13</b>	Variation of the PAH/PM <sub>2.5</sub> ratio of mean concentrations measured at RDP in	
C	winter	50
<b>Figure 3.5.14</b>	Relation between the hourly mean concentrations of PAHs and PM <sub>2.5</sub> measured	
	at RDP in winter. The slant on the right represents the PAH/PM <sub>2.5</sub> ratio	51
Figure 3.6.1	Summary of winter and summer concentrations of dioxins and furans in	
C	Montréal (December 1999 to March 2002)	53
Figure 3.6.2	Summary of the winter concentrations of dioxins and furans in Montreal	
C	(December 1999 to March 2002)	55
Figure 3.7.1	Seasonal variation of the families of nonpolar VOCs	59
Figure 3.7.2	Seasonal variation of selected VOCs	60
Figure 3.7.3	Seasonal variation of total VOCs and of total VOCs without formaldehyde	61
Figure 3.7.4	Seasonal variation of individual polar VOCs	62
-	-	

## 1. Introduction

#### 1.1 Issue

The report *Sampling Program for Residential Wood Combustion: Winter of 1998-99*, published in March 2000, provided results of the air polluant measurement activities conducted in the residential area of Rivière-des-Prairies (RDP), located in northeast Montreal. The RDP district was singled out because it comprised an important number of homes using individual wood heating devices, as well as low levels of motor vehicle and industrial emissions. The data obtained at RDP had been compared to those obtained at a reference site located in downtown Montreal. The study report indicated that the area influenced by wood combustion showed higher levels of pollutants, namely polycyclic aromatic hydrocarbons (PAHs), volatile organic compounds (VOCs), particulate matter (PM) and certain metals, than those found at the downtown reference station. Residential wood combustion had been identified as a source contributing to the deterioration of ambient air quality in the RDP area.

A telephone survey on wood heating systems was then conducted in the region of Montreal (Labrèche *et al.*, 2000). This study revealed that 12.5% of Montreal households burn wood inside their homes, and confirmed that the RDP area presents a high density of fireplaces and wood stoves. Among the homes located in Montreal-East and equipped with a fireplace or a wood stove, 55.6% of the respondents use their wood combustion system for leisure, roughly 35% use it as a secondary heating device, while 7.4% use it as their main heating system (Bonvalot *et al.*, 2001). For purposes of comparison, for the whole of the Island of Montreal, 3.0% of households use wood combustion as their main source of heat.

A review of the documentation prepared by Brauer of the University of British Columbia in 1998 indicated that wood combustion has an impact on the health of populations. Residential wood combustion contributes to the emission of various pollutants. Environment Canada's Web site, the Criteria Air Contaminants Emission Summaries (Environment Canada, 2000), underlines that emissions from residential wood combustion represent an important source of pollutants in Québec (Table 1.1.1). When emissions from the industrial, transportation and residential heating sectors are combined, it is noted that wood heating is responsible for 49% of PM<sub>2.5</sub> emissions and for 23% of VOC emissions. The comparison of emissions from residential wood combustion with emissions from residential heating using other types of combustible materials, such as oil or natural gas, reveals a considerable difference: PM<sub>2.5</sub>, carbon monoxide (CO) and VOC emissions are respectively about 135, 200 and 350 times higher.

Several of the pollutants measured during this study are registered in the Toxic Substances List of the Canadian Environmental Protection Act (CEPA). In fact, the Canadian Council of Ministers of the Environment (CCME), deeming the situation rather disturbing, commissioned Environment Canada to develop measures aimed at reducing emissions from residential wood heating.

The initial study report (Bonvalot *et al.*, 2000) included several recommendations to obtain a better understanding of the wood combustion issue. It is on this basis that the City of Montreal,

Environment Canada and the Ministère de l'Environnement du Québec pursued the sampling program in order to better quantify the impact of residential wood heating.

Table 1.1.1	Comparison of the atmospheric emissions (kt) of the main sectors of emissions
	in Québec in 2002

Sector	<b>PM</b> <sub>10</sub>	PM <sub>2.5</sub>	VOCs	$\mathbf{CO}^2$	NOx <sup>3</sup>
Residential wood combustion	39.2	39.1	57.1	264.1	3.94
Residential heating: other	0.33	0.29	0.16	1.33	4.59
combustible materials					
Industry	46.4	26.8	40.9	334.5	41.2
Transport	16.1	14.1	149.9	1881.0	339.0
Contribution to residential	38.5%	48.9%	23.0%	10.7%	1.0%
wood combustion $(\%)^1$					

Note 1: Contribution of residential wood combustion with respect to to industry and transport.

Note 2: Carbon monoxide

Note 3: Nitrogen oxides

## **1.2 Objectives**

The primary objective of the present report is to assess the environmental impact of wood heating in a residential area where this type of heating is popular. It also aims at addressing the recommendations of the study report on the *Sampling Program for Residential Wood Combustion: Winter of 1998-99.* The recommendations put forward were the following:

- Pursue the collection of data on PAHs, PM<sub>2.5</sub>, PM<sub>10</sub>, polar and nonpolar VOCs and on elements such as metals, at the RDP station and the downtown reference site;
- Determine the dioxin and furan concentrations at the RDP station;
- Conduct an enhanced analysis of the meteorological parameters at the RDP station;
- Determine the links between the weather conditions and the PAH and PM concentrations measured using the continuous sampler;
- Clarify the impact of residential wood combustion by comparing ambient air values during the summer and winter seasons;
- Verify the use of tracers specific to wood combustion.

## 2. Materials and methods

## 2.1 Sampling site

The sampling program was conducted in the residential area of Rivière-des-Prairies (RDP), located in the northeast section of the City of Montreal. This site is mainly surrounded by single-family homes or duplex housing units built 15 to 20 years ago, and presents a high density of wood heating systems (Labrèche *et al.*, 2000). Furthermore, this site is only slightly influenced by motor vehicle traffic. Industrial emissions may influence this sector depending on the winds; however, the industrial facilities are relatively far from the sampling site and their emissions are present throughout the year, contrary to emissions from wood combustion which are present only during the winter.

Three other sampling stations constitute reference stations. The main reference station is located on Ontario Street, close to Montreal's downtown area, and is mostly influenced by motor vehicle traffic. The second, located on Drummond Street (DRU), is also influenced by motor vehicle traffic. The third reference station is located at Sainte-Anne-de-Bellevue (SAB), west of the Island of Montreal. This last station is representative of a semi-urban environment and is generally upstream of emissions from Montreal, since prevailing winds in the area blow mainly from the southwest and west.

Figure 2.2.1 displays the location of the four sampling stations on the Island of Montreal, and figure 2.2.2 shows the location of the main station in RDP. The study report by Bonvalot *et al.* (2000) presents further information on the RDP site as well as on the annual and seasonal compass wind roses.



**Figure 2.2.1** Location of sampling sites on the Island of Montreal.



**Figure 2.2.2** Location of the main monitoring site at Rivière-des-Prairies.

## 2.2 Pollutants and parameters studied

The pollutants measured in the framework of this sampling program are air pollutants linked to residential wood heating. These are polycyclic aromatic hydrocarbons (PAH), nonpolar volatile organic compounds (VOCs) such as alkanes, halogens and aromatics, polar VOCs such as aldehydes and ketones, and fine and coarse particles (PM<sub>2.5</sub> and PM<sub>10</sub>), to which dioxins and furans were added in the winter of 2000. The instrumentation, methods of analysis, quality control measures and detection limits are described in detail in the study report of Bonvalot *et al.* (2000). However, table 2.2.1 summarizes some information and includes an update.

Measured	Instruments used	Notes		
parameters				
Continuous PAH Analyzer (4 L/min)		Tracking of variations. Does not allow the analysis of		
PAHs		PAH particles with a diameter of $<1\mu$ m.		
PAHs	Hs High volume sampler and Analyses conducted at the laboratory of the ETC in			
(Hivol) foam (700 L/min)		Ottawa and at the CEAEQ at Laval. Analysis of 28 different PAHs.		
Dioxins and	High volume sampler and	Analyses conducted at the laboratory of the ETC in		
furans	foam (700 L/min)	Ottawa and at the CEAEQ at Laval. Ten homologous		
		series including 210 compounds (75 dioxins and 135		
		furans) of which 17 carcinogenic congeners were reported.		
Continuous	<i>TEOM</i> <sup>®</sup> with a Cyclone head	Tracking of variations. Only provides the total mass of PM		
PM <sub>2.5</sub>	(16.7 L/min)	with an aerodynamic diameter below 2.5 µm.		
PM <sub>2.5</sub> and	Dichotomous sampler (16.7	Analyses conducted at the laboratory of the ETC in		
PM <sub>2.5-10</sub>	L/min fine fraction and 1.67	Ottawa. Determines the total mass of particles (2.5 $\mu$ m and		
	L/min coarse fraction)	n) 10 µm) and their elements on filters.		
Nonpolar	6-liter stainless steel Summa <sup>®</sup>	Analyzed following the USEPA TO-17 method which can		
VOCs container with <i>Xontech</i> <sup>®</sup>		identify 155 alkanes, alkenes, alkynes, halogen and		
	sampler	aromatic substances.		
Polar VOCs	Aldehyde sampler (1L/min)	Absorption on a DNPH tube. Analyses conducted at the		
		laboratory of the City of Montreal following the USEPA		
		TO-11 method. Analysis 16 aldehydes and ketones.		
Temperature	HMP-35 sensor	Measured at 2 different heights: 2 and 10 metres from the		
and humidity		ground.		
Winds	RM-Young anemometer	Measures taken at an altitude of 10 metres.		

 Table 2.2.1
 List of instruments used

## 2.3 Sampling frequency

Table 2.3.1 presents the sampling periods for the various pollutants measured at the RDP and Ontario Street stations. Except for pollutants measured using a continuous sampler, the sampling dates generally coincide with those of the National Air Pollution Surveillance (NAPS) network in operation every six days. For PAHs and dioxins and furans, the sampling conducted in summer was less intensive. These substances were sampled every 12 days or every 24 days, except for the winter of 2000 during which they were measured more frequently.

Substances	Duration	RDP		Ontario Street		
		Sampling period Number of		Sampling period	Number of	
			samples		samples	
Continuous PAHs	Hourly mean	Dec. 5, 1998 to Feb. 24, 2002 (except Sept. 8 to Nov. 17, 1999, and May 4 to Nov. 30, 2001)	20,514	May 11, 2001 to Nov. 5, 2001	4,173	
28 to 30 PAHs (Hivol)	24 h (midnight to midnight)	Dec. 7, 1998 to May 8, 2002 <sup>1</sup>	118	Dec. 3, 1998 to May 20, 2002 <sup>2</sup>	101	
Fine and coarse PM and 47 elements	24 h every 6 days (midnight to midnight)	Dec. 7, 1998 to July 19, 2002 (except Oct. 3, 2000 to April 11, 2001)	161	Dec. 1, 1998 to Aug. 6, 2002	213	
155 nonpolar VOCs	24 h every 6 days (midnight to midnight)	Dec. 14, 2000 to Dec. 28, 2002	100	Dec. 14, 2000 to Dec. 28, 2002	115	
16 polar VOCs	24 h every 6 days (midnight to midnight)	Dec. 19, 1998 to Dec. 28, 2002	218	Dec. 19, 1998 to Dec. 10, 2002	212	
75 dioxins and 135 furans	24 h every 6 days (midnight to midnight)	Nov. 20, 1999 to May 21, 2002	57	Nov. 20, 1999 to May 21, 2002	52	
Continuous PM <sub>2.5</sub>	Hourly mean	December 4, 1998 to May 21, 1999 July 22, 1999 to September 6, 1999 October 14, 1999	21,229	Drummond Street station: <sup>3</sup> December 1, 1998 to June 15, 2001 August 30, 2001 to March 31, 2002 Sainte-Anne-de-	26,632	
		to May 9, 2000 December 13, 2000 to March 31, 2002		Bellevue station: December 1, 1998 to June 13, 2001 August 6, 2001 to March 31, 2002		

 Table 2.3.1
 Sampling frequency

1. The sampling frequency varied, depending on the seasons, as follows: W1999: every 6 days; S1999, S2000 and S2001: every 12 to 24 days; W2000: every 3 to 6 days; W2001 and W2002: every 12 days.

The sampling frequency varied, depending on the seasons, as follows: W1999: every 6 to 12 days; S1999: every 12 days; W2000: every 6 days; S2000 to W2002: every 12 days.
 Continuous PM<sub>2.5</sub> samplers were available at the DRU and SAB monitoring stations, and not on Ontario Street.

## 2.4 Statistical analysis

The contaminated samples and the results obtained when sampling and laboratory apparatus were defective have been eliminated from the databases for statistical processing. However, the extreme values have been retained in the databases. When the analyses based on wind direction are taken into account, extreme values may sometimes originate from local sources under nonprevailing winds, hence the importance of retaining them.

Certain data obtained during the sampling day on January 1, 2000, showed very high levels. It is likely that the fireworks that took place on that date to celebrate the new millennium contributed to an increase in air pollutant concentrations (Perry, 1999). Data for this date, which was not representative of the other days, was withdrawn from the database for the statistical analysis of 24-hour samples of PAHs and of PM and its elements.

For PAHs and dioxins/furans collected using the modified high-volume sampler, the values below the detection threshold were replaced by the detection limit over 2 ratio (DL/2).

One of the objectives of this project is to assess the impact of residential wood combustion which occurs most often in winter. The seasonal comparison of data was conducted by grouping the winter values, and grouping the summer values. The data used for the winter season were comprised between December 1 and March 31 of the following year, while the summer season included data from May 1 to September 30. For purposes of simplification, the abbreviation W1999 was used to refer to the winter, beginning, for example, on December 1, 1998, and ending on March 31, 1999, while the abbreviation S1999 was used to indicate the summer, beginning on May 1, 1999, and ending on September 31, 1999.

As a general rule, discussion on the results obtained was based on comparing the medians so as to minimize the impact of extreme values on the values indicative of the environment. The medians allow comparing data that are not normally distributed, and better reflect the state of the environment. It is important to note that the exposure of the population to pollutants is generally expressed by the comparison of arithmetic mean values. In order to allow interested parties to conduct these comparisons, we have added the arithmetic mean values and medians to the tables and figures.

The statistical comparison of the means was conducted using the F-Test (ANOVA) analysis when the data distribution was normal. When the data distribution was not normal, the variables were subjected to a logarithmic conversion. The Kruskal-Wallis test was also used to compare the medians when the data did not follow normal distribution patterns.

#### 3. Analysis of data and results

#### 3.1 Seasonal representativity of the sampling program at Rivière-des-Prairies

The sampling program for residential wood combustion in Rivière-des-Prairies (RDP) began in the winter of 1999 and ended in the winter of 2002, a period comprising four consecutive winters. The sampling program also covered the summers of 1999, 2000 and 2001. A climatological analysis was conducted to determine if the winters of 1999 to 2002 were representative of the winter conditions in this area during the period of the study. The RDP station being in operation only since December 1998, it can not be used as a climatological reference. The meteorological station located at the Dorval airport, where 28 years of data have been collected (1970 à 1997), was used as a reference. In order to validate this choice, hourly temperatures obtained at RDP and Dorval were compared. The study reveals a strong correlation (r = 0.98) of the temperatures at both stations with a mean deviation of -0.2°C.

#### 3.1.1 Temperature

One way of characterizing the climatology of the seasons consists in studying the variation of mean daily temperatures. The mean daily temperature is obtained by calculating the mean of the maximum and minimum temperatures in a day.

Daily average temperature = 
$$\frac{T_{\text{max}} + T_{\text{min}}}{2}$$
 (eq. 3.1.1)

Winter seasons

The winter of 1999 was rather mild with a mean seasonal temperature of -4.3°C, compared to -7.1°C for the years 1970 to 1997 (fig. 3.1.1), that is a mean temperature 2.8°C above the climatology. December 1998 and February 1999 were the months that differed the most from the normal climate values with mean temperatures that were higher by 4.9°C and 3.7°C respectively. The winter of 2000 was also mild with a deviation of +2.3°C for the season. The month of March 2000 was particularly mild with a variation of +4°C as compared to the climatology. However, it was the winter of 2002 that was the most remote from seasonal values with a variation of +4.2°C. The month of December 2001 was particularly mild with a mean temperature close to zero, representing a variation of 6.6 °C with normal climate values. Thus, the winters of the study period were warmer than the climatology, except for the winter of 2001 during which levels were close to the normal seasonal values.



Figure 3.1.1 Mean monthly temperature from December to March at RDP

#### Summer seasons

The sampling program also covered three summers (fig. 3.1.2). The summer of 1999 was the warmest with temperatures rising 2.4°C above normal climate values, a difference of 14%. All the months of the summer of 1999 registered mean monthly temperatures that were above normal climate values. The summer of 2001 was also warm, with a variation of 1.8°C or 10% above seasonal values, except for the month of July during which temperatures were slightly below normal seasonal values. Lastly, the summer of 2000 was close to seasonal values.



Figure 3.1.2 Mean monthly temperature from May to September at RDP

#### 3.1.2 Heating degree-days

Another way of characterizing the winter season is to use the concept of heating degree-days (HDD) which allows the assessment of residential heating needs. When the outdoor temperature is below 18°C, the inside of a building must be heated to maintain a pleasant temperature. A HDD is accrued for each degree below 18°C. HDDs are calculated by substracting the mean daily temperature from 18°C. When the mean daily temperature is above 18°C, no HDDs are taken into account.

*Heating* deg *ree* - *days* = 
$$\sum_{day} 18 {}^{0}C - \left(\frac{T_{max} + T_{min}}{2}\right)$$
 (*eq.* 3.1.2)

The heating degree-days (fig. 3.1.3) show results that are similar to those obtained through the analysis of daily temperatures. During the winters of 1999, 2000 and 2002, the heating degree-days were respectively 11%, 9% and 17% lower when compared to normal climate levels registered from 1970 to 1997. The most important differences in heating degree-days occurred in the months of December, with deviations attaining 25% for the year 2001. The winter of 2002 was without doubt the mildest winter of the sampling program period, both in terms of mean temperature and of heating degree-days.



Figure 3.1.3 Heating degree-days per month from December to March at RDP

Table 3.1.1 shows out for each winter the deviations from normal climatic daily temperatures, as well as the deviations from normal heating degree-days. The winters of 1999, 2000 and 2002 were warmer than normal, particularly the winter of 2002 with a mean temperature that was 4.2°C higher than normal. The same phenomenon was observed as regards to the heating degree-days. The winters of 1999, 2000 and 2002 showed deviations from normal levels ranging from -9 to -17%, which translated into an equivalent reduction in heating needs in comparison to normal levels. The winter of 2001 was more representative of a normal winter with a deviation of only 2% in heating degree-days.

	able 5.1.1 Deviations with respect to enhancelogy (1970-1997)				
	Deviations with respect to climatology				
Season	Daily temperature	Heating degree-days			
Winter 1999	2.8°C	-11%			
Winter 2000	2.3°C	-9%			
Winter 2001	-0.5°C	2%			
Winter 2002	4.2°C	-17%			

 Table 3.1.1
 Deviations with respect to climatology (1970-1997)

## 3.1.3 Total precipitation

The total amounts of precipitation, in liquid or solid form (expressed in millimetres), were investigated (table 3.1.2). As a general rule, the total amounts of precipitation were slightly higher (15%) than normal climatic levels during the winters of 1999, 2000 and 2001. However, strong variability was found in the amounts of precipitation from month to month. The winter of 2002 was drier than normal, particularly the month of January 2002. Amounts of precipitation registered during the summers of 1999 and 2000 were similar to seasonal values. Once again, strong variability was noted from month to month, particularly in the months of May and September, with variations attaining as much as 114% for the month of September 1999. The summer of 2001 was the driest of the three summers, with a very dry month of July presenting only 33mm of rain, compared to a normal level of 90mm, a variation of 63% below seasonal values.

<b>Table 3.1.2</b>	fotal monthly and seasonal	amounts of precipitation	measured at Dorval	Aırport
in snow water equivalent				

	Total amounts of precipitation in winter (mm)					
Season	December	January	February	March	Season (winter)	
Winter 1999	55	148	44	84	332	
Winter 2000	73	96	73	70	312	
Winter 2001	121	48	74	110	354	
Winter 2002	54	37	41	81	212	
Climatology						
(1970-1997)	82	70	60	72	285	

	Total amounts of precipitation in summer (mm)					
Season	May	June	July	August	September	Season
						(summer)
Summer 1999	44	89	74	67	195	468
Summer 2000	133	78	48	103	66	426
Summer 2001	70	76	33	63	67	309
Climatology						
(1970-1997)	75	84	90	94	91	435

## 3.1.4 Compass wind rose

Figure 3.1.4 represents the compass wind rose at RDP for the period from December to March inclusively, based on 16 compass points for four consecutive winters. Two prevailing wind directions were noted: the wind from the northeast which occurred 15.3% of the time at an average speed of 10.2 km/h; and the wind from the west-southwest which occurred 21.0% of the time at an average speed of 12.3 km/h. Calm winds (<1 km/h) occurred only 0.8% of the time, while wind speeds of 1 to 10 km/h were registered 58.2% of the time. Winds at speeds above 20

km/h occurred 5.7% of the time. The frequency of wind direction noted at RDP was compared to that in the region of Montreal. Though slightly different, the distribution of the frequency of wind direction at RDP is representative of the Montreal area.



Figure 3.1.4 Compass wind rose observed in winter (1999 to 2002) at RDP (n=11469)

#### Summary

Three out of the four winters had mean temperatures that were significantly higher, roughly 3 °C, than seasonal values. The analysis of the heating degree-days for these three winters shows a mean deviation approximately 12% below seasonal values. For the precipitations, three out of the four winters had total amounts of precipitation that were roughly 15% higher than the climatology.

Thus, the winter sampling program was conducted in relatively mild temperatures. Assuming that the heating degree-days are representative of the use of wood heating systems, it can be expected that wood heating activities were less important during the project. Among the four winters, the winter of 2001 is the most likely to reflect a normal usage of wood heating systems.

## 3.2 Continuous analysis of fine particulate matter (PM<sub>2.5</sub>)

According to the Criteria Air Contaminant Emissions Inventory (Environment Canada, 2000), residential wood combustion is an important source of particles measuring less than 2.5  $\mu$ m in diameter. We therefore paid particular attention to fine particulate matter. In order to emphasize the characteristics specific to a residential area influenced by wood heating systems, we will compare the concentrations of PM<sub>2.5</sub> measured at RDP with those of other types of environments. The Drummond Street station (DRU) is representative of an urban environment, while the Sainte-Anne-de-Bellevue station (SAB) is more representative of a semi-urban environment.

#### 3.2.1 Continuous analysis of PM<sub>2.5</sub>

Table 3.2.1 shows that the difference in concentrations was more important between stations during the winter. In winter, the mean daily concentration at the RDP station was considerably greater, exceeding the DRU station by 9.8% (p < 0.01) and the SAB station by 36.5%. When comparing winter to summer, the values were 1.1  $\mu$ g/m<sup>3</sup> (p < 0.06) higher in winter at RDP. On the other hand, there was no statistical difference between daily concentrations at the RDP and DRU stations in summer. The difference in concentrations measured in winter at the DRU and RDP stations may indicate the contribution of an additional source of PM<sub>2.5</sub> at RDP.

As to the SAB station, the opposite was noted since the mean daily concentration was greater in summer (p < 0.01). Given that the SAB station is located in a semi-urban environment, farming activities close to the station may have contributed in part to the PM<sub>2.5</sub> measured in summer.

Taking only the concentrations of  $PM_{2.5}$  measured between 6 p.m. and midnight into account (fig. 3.2.1), the concentration in winter at RDP (13.9 µg/m<sup>3</sup>) was 2.9 µg/m<sup>3</sup> or 26.4% (p<0.01) greater in comparison to the DRU station (11.0 µg/m<sup>3</sup>), and 5.9 µg/m<sup>3</sup> or 74.6% greater in comparison to the SAB station. In addition, the PM<sub>2.5</sub> concentrations measured at RDP in the winter were 5.0 µg/m<sup>3</sup> or 56.9% greater than those measured during the summer evenings. There were no seasonal deviations in PM<sub>2.5</sub> concentrations measured in the evening at the SAB or DRU stations.

	Riviè Pra	Rivière-des- Prairies		Drummond		Sainte-Anne-de- Bellevue	
	Winter	Summer	Winter	Summer	Winter	Summer	
Number of days	464	223	476	368	477	387	
Frequency of detection	96%	49%	98%	80%	98%	84%	
Arithmetic mean	10.1	9.1	9.2	9.1	7.3	8.4	
Geometric mean	7.9	6.5	7.9	7.1	5.6	6.4	
Standard deviation	7.4	6.9	5.2	6.4	5.5	6.4	
Minimum	0.6	0.1	1.1	0.2	0.2	0.1	
10 <sup>th</sup> percentile	3.0	1.9	4.1	2.9	2.0	2.1	
Median	8.0	6.9	7.8	7.5	5.8	7.1	
90 <sup>th</sup> percentile	20.0	19.6	16.6	18.3	14.8	15.8	
Maximum	52.2	32.9	39.5	36.3	33.2	41.2	

**Table 3.2.1** Seasonal variation of  $PM_{2.5}$  ( $\mu g/m^3$ ) concentrations at different sampling stations



**Figure 3.2.1** Daily and evening means (from 6 p.m. to midnight) of PM<sub>2.5</sub> in Montreal according to the season

Figure 3.2.2 presents the monthly variations of  $PM_{2.5}$  in winter, from December to March (4 months), and in summer, from May to September (5 months). January and February were the months with the greatest  $PM_{2.5}$  concentrations at the RDP station, with values of 12.0 µg/m<sup>3</sup> in January and 12.4 µg/m<sup>3</sup> in February. It was also during these two months that the differences in concentrations between the three stations were most evident. At the DRU station, the months of January (9.8 µg/m<sup>3</sup>) and February (11.1 µg/m<sup>3</sup>) showed high concentrations of PM<sub>2.5</sub>, as did the

months of August (10.8  $\mu$ g/m<sup>3</sup>) and September (10.1  $\mu$ g/m<sup>3</sup>). The DRU station, located downtown, is the station that registered the greatest concentrations of PM<sub>2.5</sub> for the months of August and September. Lastly, the SAB station was the station with the lowest concentrations of PM<sub>2.5</sub> irregardless of the month. In conclusion, the maximum levels occurred mainly in January and February, the two coldest months of the year, at the RDP station.



If part of the PM<sub>2.5</sub> measured in RDP was attributable to the use of wood heating systems, it was important then to verify any discrepancy between weekdays (Monday to Friday) and the weekends (Saturday and Sunday). Assuming that people are more available on the weekend, we could expect a more frequent usage of wood heating systems during this period. Figure 3.2.3 indicates that in winter, only the RDP station showed a significant difference (p < 0.05) between concentrations measured on weekdays (9.7 µg/m<sup>3</sup>) and weekends (11.3 µg/m<sup>3</sup>). An increase of 16.5% in PM<sub>2.5</sub> concentrations was found during the weekend in comparison to levels measured on weekdays. In summer, the PM<sub>2.5</sub> concentrations measured on weekdays were significantly greater than those registered during the weekends at the DRU and SAB stations. However, in summer at the RDP station, there was no significant difference (p > 0.05) between weekdays and

weekends. It is likely that the DRU station is more influenced by vehicle emissions, and that the SAB station is influenced by farming activities in summer.



**Figure 3.2.3** Daily means of PM<sub>2.5</sub> at different sampling stations according to weekday

An analysis of hourly behaviour of PM<sub>2.5</sub> allowed identifying the time of day when concentrations were highest. Figure 3.2.4 presents the hourly variation of the  $PM_{2.5}$ concentrations measured at three sampling stations during the winter. First, it was found that the PM<sub>2.5</sub> concentrations dropped in similar fashion at the three stations during the night to reach their lowest concentrations between 5 and 7 a.m. The concentrations then increased rapidly to attain a relative maximum level around 9 a.m. This maximum level may be linked to the break in nocturnal inversion caused by the sunrise, and to rush hour traffic. In the case of the SAB and RDP stations, the concentrations began to drop at 10 a.m. to rise once again around 4 p.m. This drop in concentrations may have been due to the increase in wind speeds during the day. For the DRU station, located downtown, motor vehicle traffic and urban activities were probably sufficiently important to maintain a relative consistency in PM<sub>2.5</sub> concentrations during the day. Beginning at 4 p.m., which corresponds to the beginning of sundown during the winter, the wind speeds diminished considerably with the stabilization of the atmosphere. PM<sub>2.5</sub> concentrations rose to attain a maximum around 9 p.m. (fig. 3.2.4). During the evening, the maximum difference between the SAB station and the DRU station was 3.7  $\mu$ g/m<sup>3</sup>, and 3.2  $\mu$ g/m<sup>3</sup> between the DRU and RDP stations. Using the SAB station as a reference, the maximum peak in RDP

represented a difference of 6.9  $\mu$ g/m<sup>3</sup> or an increase of 84% in comparison to the SAB station. The high concentrations of PM<sub>2.5</sub> found in RDP were due mainly to the high levels registered during the evening between 6 p.m. and midnight.



Figure 3.2.4 Hourly variation of  $PM_{2.5}$  concentrations at different sampling stations in winter (December to March), from 1999 to 2002 (n = 464)

The results of the preceding analyses show that the  $PM_{2.5}$  concentrations were greater in winter at RDP than at any other monitoring station in the Montreal area. The high concentrations of  $PM_{2.5}$  found at RDP were due mainly to increases in  $PM_{2.5}$  concentrations in the evening between 6 p.m. and midnight (figure 3.2.4). These evening increases were even more significant on weekends during the winter. Figure 3.2.5 shows that on weekends, the  $PM_{2.5}$  concentrations measured in the evening reached 17.9 µg/m<sup>3</sup>, while the concentrations were only 14.6 µg/m<sup>3</sup> on weekdays, which represents a difference of 3.3 µg/m<sup>3</sup> or 20%.

In summer, the maximum  $PM_{2.5}$  concentrations in RDP were measured on weekdays during the morning rush hour around 8 a.m. (EDT) (figure 3.2.5). The hourly difference in maximum morning levels measured in summer (7 a.m. EST) and in winter (9 a.m. EST) were due to the sun rising earlier in summer, and to the change to eastern daylight-saving time (EDT) in summer.

There was no significant difference in hourly behaviour between weekdays and weekends during the summer evenings.



**Figure 3.2.5** Hourly variation of  $PM_{2.5}$  concentrations at RDP according to season and weekday (n = 464)

#### 3.2.2 Heating degree-days

The heating degree-days represent an estimate of residential heating needs. These needs may be addressed in part through the use of wood combustion systems. Table 3.2.2 underlines the fact that the higher the number of heating degree-days required during a winter, the higher the correlation coefficient between the heating degree-days and the daily  $PM_{2.5}$  concentrations ( $\mu g/m^3$ ). The correlation coefficient was 0.24 for the winter of 2001 (the coldest), while it was insignificant for the winter of 2002. This relation suggests that the higher the number of heating degree-days required during a winter, the higher the PM<sub>2.5</sub> concentrations at RDP, and the greater the probability that wood combustion systems contribute to the PM<sub>2.5</sub> concentrations measured at RDP. Since the use of wood combustion systems requires human intervention, we will focus our analysis on the period during which people are most likely to be present to use wood combustion to heat their homes, more specifically during the evenings between 6 p.m. and midnight.

Winter	Heating	PM <sub>2.5</sub>	Pearson's correlation coefficients		
	degree-day (°C)	(µg/m³)	Day	Evening	
			(average over 24 hours)	(average from 6 p.m. to	
				midnight)	
1999	2698.7 HDD	9.7	0.14	0.15	
2000	2765.2 HDD	11.0	0.17	0.19	
2001	3089.5 HDD	11.5	0.24	0.25	
2002	2527.0 HDD	8.6	insignificant	insignificant	

**Table 3.2.2**Pearson's correlation coefficients between the heating degree-days and the<br/> $PM_{2.5}$  concentrations ( $\mu g/m^3$ ) at RDP for two periods of the day

Figure 3.2.6 shows the relation between the heating degree-days and the mean value of  $PM_{2.5}$  measured at RDP in the evening between 6 p.m. and midnight for the winter of 2001. Strong variability was noted in the range of data collected, with a variation coefficient of 21.3% for the heating degree-days and of 90.8% for the  $PM_{2.5}$ . This important variability indicates that the number of heating degree-days is not the main factor influencing the  $PM_{2.5}$  concentrations. However, the relation is significant (p<0.01) despite a low correlation coefficient of 0.25. According to figure 3.2.6, when the number of heating degree-days passed from 15 to 35°C, the mean concentrations of  $PM_{2.5}$  measured in the evening rose from 8.1 µg/m<sup>3</sup> to 20.1 µg/m<sup>3</sup>, which represents an increase of 148% in  $PM_{2.5}$  concentrations. Furthermore, figure 3.2.6 underlines that  $PM_{2.5}$  values above 50 µg/m<sup>3</sup> were measured only when the heating degree-days were above 23°C.

The existence of a positive relation between heating degree-days and  $PM_{2.5}$  concentrations implies that part of the variability of the  $PM_{2.5}$  concentrations may be explained ( $R^2 = 0.06$ ) by the use of wood combustion. Thus, for the winter of 2001, the variation in the number of heating degree-days explains 6.2% of the variation in  $PM_{2.5}$  concentrations. This percentage may at first seem very low, but we must remember that among the households equipped with residential wood combustion systems in Montreal-East, a mere 7.4% use wood combustion as the main source of heating, while 55.6% use it for leisure (Labrèche *et al.*, 2000).



Figure 3.2.6 Variation in PM2.5 concentrations (average between 6 p.m. and midnight) measured at RDP in relation to the number of heating degree-days. Winter 2001 (n = 109)

#### 3.2.3 Continuous measurement of PM<sub>2.5</sub> in relation to the wind

#### Wind direction

The wind allows air pollutants to travel far from their sources. When the distance between the sources and the sampling site is less than about 10 kilometres, the distance is considered on a local scale (mesoscale). The time scale taken into account is then a few hours. It is generally assumed that on a local scale, the pollutant plume is transported with moderate winds that remain relatively constant in terms of speed and direction. The wind noted at 10 metres above ground may then be used as a good estimator to determine the origin of pollutants on a mesoscale.



**Figure 3.2.7** Mean hourly concentrations of PM<sub>2.5</sub> according to wind direction at Rivière-des-Prairies (from December to March inclusively; four winters)

Figure 3.2.7 illustrates the mean concentrations of  $PM_{2.5}$  based on wind direction. The numerical value that appears at the end of every bar represents the number of data available used to calculate the mean hourly concentration. The highest concentrations of  $PM_{2.5}$  occurred when the winds were calm (less than 1 km/h) with a mean value of 29.2 µg/m<sup>3</sup>. However, calm winds occurred only 0.7% of the time, that is 74 hours during the four winters studied. The second highest concentration of  $PM_{2.5}$  occurred when the winds blew east-southeast with a value of 19.1 µg/m<sup>3</sup>. When the winds blew from the southeast, the concentration of  $PM_{2.5}$  was 17.7 µg/m<sup>3</sup>. The east-southeast and southeast winds stemmed from the residential area of RDP influenced by wood combustion. However, the winds blew from these directions less than 1.6% of the time. It was noted that when the wind blew from the south-southeast (from another residential area and from the Island of Montreal), the  $PM_{2.5}$  concentration reached 16.0 µg/m<sup>3</sup> (3.1% of the time).

The lowest mean concentrations occurred when the winds blew from the less densely populated northwest quadrant (5.5 to 7.4  $\mu$ g/m<sup>3</sup>).

#### Wind speed

Surface wind speed is one of the most important elements in the pollutant dispersion process occurring in the lower atmosphere. An increase in wind speed implies an increase in the volume of air in which the pollutants can disperse. Calm winds reduce ventilation in the boundary layer and allow the pollutants to accumulate. Furthermore, wind speed influences the vertical stability of the air mass. Strong winds promote vertical mix by mechanical turbulence. For most of the pollutants emitted on a local scale, a reduction in concentrations is noted with a rise in wind speed, since the pollutants emitted close to the ground are better dispersed.

In table 3.2.3., the relation between wind speed and  $PM_{2.5}$  concentrations measured at RDP is analysed on the basis of three time frames: hourly, daily (average over 24 hours) and mean values in the evening (between 6 p.m. and midnight).

	Pearson's correlation coefficients			
	Hourly Daily Evening		Evening	
		(average over 24	(average between 6 p.m. and	
		hours)	midnight)	
Winter 1999	-0.44	-0.49	-0.57	
Winter 2000	-0.53	-0.68	-0.69	
Winter 2001	-0.51	-0.68	-0.66	
Winter 2002	-0.48	-0.63	-0.67	
Winter season	-0.49	-0.61	-0.63	
Summer 1999	-0.35	-0.35	-0.32	
Summer 2000				
Summer 2001	0.13	0.13	insignificant	
Summer season	insignificant	insignificant	insignificant	

<b>Table 3.2.3</b>	Pearson's correlation coefficients between wind speed (km/h) and PM <sub>2.5</sub>
	concentrations ( $\mu g/m^3$ ) measured at RDP

In winter, the relationship between wind speed and  $PM_{2.5}$  concentrations is always negative. This means that  $PM_{2.5}$  concentrations increase when wind speed diminishes. Taking all winters into account, the winter hourly correlation coefficients varied between -0.44 and -0.53 for a coefficient of -0.49. The daily correlation coefficients (mean concentration over 24 hours) constantly exceeded hourly correlations by roughly 25%. This result is explained by the fact that  $PM_{2.5}$  concentrations rose markedly in the evening while the wind speed diminished rapidly. This result is shown in figure 3.2.8 which illustrates the hourly relation between wind speed and  $PM_{2.5}$  concentrations. The wind speed gradually increased as the sun rose around 6 a.m. to reach a maximum value during the afternoon. The wind speed then rapidly diminished as the sun set around 5 p.m. and reached its minimum value at the end of the night. Figure 3.2.8 also shows

that the hourly correlations between wind speed and  $PM_{2.5}$  concentrations were strongest in the evening between 6 p.m. and midnight. The correlation between the mean wind speed in the evening and the mean concentrations for the same period varied from -0.57 and -0.69 (table 3.2.5), for a coefficient of -0.63 for the four winters taken into account.

For the summer season (table 3.2.3), the relation between wind speed and  $PM_{2.5}$  concentrations is not as clear. During the summer of 1999, the hourly and daily correlation coefficient was -0.35. However, only 67 days of data are available for the summer of 1999, which represents 43.8% of the summer. As for the summer of 2000, only 8 days of sampling data are available. Only the summer of 2001 is complete with 149 days of data out of a total of 153 days. During the summer of 2001, the hourly and daily correlation coefficient was 0.13. In other words, the  $PM_{2.5}$ concentrations grew with the increase in wind speed. This result is explained by the fact that in summer, strong winds pick up dust particles from the ground. The correlation between the mean wind speed in the evening and the mean concentrations of  $PM_{2.5}$  for the same period was not significant. As a general rule, no significant correlation was found between wind speed and  $PM_{2.5}$  concentrations in summer.



**Figure 3.2.8** Hourly variation of  $PM_{2.5}$  concentrations ( $\mu g/m^3$ ) and wind speed (km/h) as well as Pearson's correlation coefficient in winter (n = 464)

Figure 3.2.9 shows the dependence of  $PM_{2.5}$  concentrations on mean wind speeds measured at RDP in winter between 6 p.m. and midnight. When the mean wind speed changed from 20 km/h to 2 km/h, the mean concentration of  $PM_{2.5}$  increased from 4 µg/m<sup>3</sup> to almost 50 µg/m<sup>3</sup>. As expected, the ventilation rate of the air mass above the sampling station influenced the  $PM_{2.5}$  concentrations. When the wind speed dropped below 4 km/h, the mean  $PM_{2.5}$  concentration

always exceeded 14  $\mu$ g/m<sup>3</sup>. Conversely, when the wind speed exceeded 18 km/h, the PM<sub>2.5</sub> concentration always dropped below 10  $\mu$ g/m<sup>3</sup>. The dependence between wind speed and PM<sub>2.5</sub> concentrations tends to demonstrate that local conditions as regards to air mass stagnation above the sampling site influence the PM<sub>2.5</sub> concentrations. Low wind speeds reduce the dispersion capacity of pollutants present in the ambient air. An increase in PM<sub>2.5</sub> concentrations when the winds are calm also indicates that the source of PM<sub>2.5</sub> may be local.



**Figure 3.2.9** Variation of  $PM_{2.5}$  concentrations on the basis of mean wind speed in the evening at RDP in winter (n = 464)

#### 3.2.4 Dispersion index

One of the factors that influence the concentrations of  $PM_{2.5}$  in the RDP district is atmospheric dispersion. Atmospheric dispersion represents the capacity of the atmosphere to dilute pollutants in a given air parcel. The greater the available air parcel, the more the pollutants will be dispersed throughout it. Conversely, the smaller the air parcel, the more the pollutants remain concentrated. The available air parcel is influenced by both wind speed and the height at which the pollutant can mix into the atmosphere. Furthermore, the concentration of pollutants in the lower atmosphere also depends on air mass stability, atmospheric turbulence and temperature.

All these meteorological factors were brought together to develop an atmospheric dispersion index that varies on a scale of zero to 10. A zero dispersion index indicates a nil atmospheric dispersion, while a dispersion index of 10 represents maximum dispersion. Figure 3.2.10

illustrates the variation of the dispersion index, developed on the basis of the above-mentioned meteorological factors, according to the  $PM_{2.5}$  concentrations measured in the evening at RDP in winter. In the case of concentrations exceeding 50 µg/m<sup>3</sup>, the dispersion index is always below 6. Conversely, when concentrations are below 10 µg/m<sup>3</sup>, the dispersion index is always above 6. Meteorological conditions favorable to atmospheric dispersion may in themselves explain up to 62% of the variability of  $PM_{2.5}$  concentrations measured in the evening at the RDP station in winter.



**Figure 3.2.10** Variation of PM<sub>2.5</sub> measured in the evening on the basis of the dispersion index (winter 1999 to winter 2002; n=464)

In Appendix 1, the  $PM_{2.5}$  concentrations are also compared with other meteorological parameters such as mixing height, vertical stability and precipitation.
#### Summary

The results of previous analyses underline that  $PM_{2.5}$  concentrations were greater in winter at RDP than at any other monitoring station in the Montreal area. The high concentrations of  $PM_{2.5}$  found at RDP were mainly due to increases in  $PM_{2.5}$  during the evening, between 6 p.m. and midnight. These increases measured in the evening were even more important on weekends during the winter. The  $PM_{2.5}$  concentrations measured in the evening reached 17.9 µg/m<sup>3</sup> during the weekends, while they stood at only 14.6 µg/m<sup>3</sup> on weekdays, which represents a difference of 20%.

Meteorological conditions influence pollutants present in the ambient air. For example, the wind disperses pollutants emitted by local sources such as wood combustion. In the evening, when the wind speed exceeded 15 km/h at RDP, the concentrations of  $PM_{2.5}$  were generally below 5  $\mu g/m^3$ . However, they could increase to over 60  $\mu g/m^3$  when the wind speed diminished to less than 2 km/h. Calm winds allow pollutants to accumulate around the sources of emissions.

Meteorological conditions favorable to atmospheric dispersion may in themselves explain up to 62% of the variability of PM<sub>2.5</sub> concentrations measured in the evening at the RDP station in winter.

## 3.3 Particulate matter measured with the dichotomous analyzer

## 3.3.1 Particulate matter (PM)

The dichotomous sampler separates the fine fraction, that is the particles measuring less than 2.5  $\mu$ m in diameter (PM<sub>2.5</sub>), from the coarse fraction, the particles with a diameter between 2.5 and 10  $\mu$ m (PM<sub>2.5-10</sub>).

Table 3.3.1 presents a synthesis of the statistics on particles sampled at the RDP and Ontario Street stations. The median levels of  $PM_{2.5}$  doubled from summer to winter at the RDP station, while the  $PM_{2.5-10}$  showed a slight drop. Figure 3.3.1 presents the median data of fine and coarse fractions by season at the two stations. Greater variability is noted in the  $PM_{2.5}$  concentrations measured at RDP where winter values were higher than summer concentrations, while concentrations of coarse particles remained relatively stable. Statistically, the median values of the coarse particle fraction at RDP were similar, except for the winter of 2002 when the median value was lower. At the Ontario Street station, no seasonal trend was apparent in the concentrations of the coarse particle fraction.



\* The sum of  $PM_{2.5}$  and  $PM_{2.5-10}$  represents  $PM_{10}$ .

Figure 3.3.1 Seasonal variation of PM<sub>2.5</sub> and PM<sub>2.5-10</sub> (median)

Figure 3.3.2 illustrates the seasonal variation of  $PM_{2.5}$ . At RDP, the median value in the winter of 2002 stood at 13.7 µg/m<sup>3</sup>, while the median was just below 11,9 µg/m<sup>3</sup> at the Ontario Street station. At RDP, the median values for the winters were statistically higher (p < 0.05) than those recorded for the summers, the exception being the summer of 2001, contrary to Ontario Street, where the median values were statistically similar, except for the last two seasons. With the exception of the summer of 2002, important seasonal variability was noted for the 90<sup>th</sup> percentiles at RDP where the winter values exceeded the summer values.



Figure 3.3.2 Seasonal variation of PM<sub>2.5</sub> at the RDP and Ontario Street stations

Figure 3.3.3 shows the variation of the monthly median values of fine particulate matter. In January, the median value was at its peak at both the RDP ( $18.2 \ \mu g/m^3$ ) and Ontario Street ( $14.4 \ \mu g/m^3$ ) stations. Until April at RDP, the medians diminished rapidly and stabilized until September to finally increase until December. A similar curve was noted at the Ontario Street station, but the values for December and January were approximately 25% lower, while summer values were slightly higher.



Figure 3.3.3 Monthly variation of PM<sub>2.5</sub> (median)

	Particle				Geometric	standard		10 <sup>th</sup>		90 <sup>th</sup>	
Station	size	Period <sup>1</sup>	n	Mean	mean	deviation	Min.	percent.	Median	percent.	Max.
		Total	163	12.59	9.40	10.16	0.14	3.65	9.33	25.74	57.77
	PM <sub>2.5</sub>	Winter	76	16.29	12.95	9.94	0.14	5.57	14.60	30.00	54.25
		Summer	62	8.90	6.75	8.96	0.32	3.27	7.09	14.04	57.77
		Total	163	7.49	5.77	5.24	0.07	2.40	6.31	14.30	29.54
RDP	PM <sub>2.5-10</sub>	Winter	76	7.48	45.33	6.09	0.07	2.00	5.61	16.65	29.54
		Summer	62	7.52	6.21	4.41	0.17	3.47	6.78	12.63	29.49
	PM <sub>10</sub>	Total	163	20.08	16.32	12.71	0.21	7.62	16.54	36.22	66.41
		Winter	76	23.77	19.64	13.12	0.21	9.71	21.99	44.04	64.67
		Summer	62	16.42	13.52	10.91	0.49	7.01	14.36	25.78	66.41
		Total	213	11.41	9.11	8.77	1.54	3.78	8.66	22.31	63.06
	PM <sub>2.5</sub>	Winter	77	14.03	11.56	9.39	2.69	5.02	11.41	25.06	60.54
		Summer	97	10.31	8.00	8.99	1.54	3.38	7.64	21.55	63.06
Ontario		Total	213	8.38	6.70	5.98	0.13	3.08	6.86	14.56	56.32
Street	PM <sub>2.5-10</sub>	Winter	77	8.78	6.48	8.24	0.56	2.83	6.05	16.80	56.32
		Summer	97	8.37	6.90	4.34	0.13	3.79	8.06	13.51	27.47
		Total	213	19.79	16.72	12.35	1.79	8.16	16.68	33.21	89.88
	$PM_{10}$	Winter	77	22.80	19.26	14.55	3.25	9.27	20.13	34.57	89.88
	••	Summer	97	18.68	15.65	11.49	1.79	7.57	16.07	33.60	73.00

**Table 3.3.1** Synthesis of results for PM measured over 24 hours at the RDP and Ontario Street stations ( $\mu g/m^3$ )

1 : "Total" refers to the entire sampling period from December 7, 1998, to July 19, 2002. "Winter" refers to all the winters between 1999 to 2002. "Summer" refers to all the summers between 1999 to 2002.

#### 3.3.2 Comparison of methods: dichotomous sampler and TEOM

Two devices were used to measure particulate matter. This section aims to compare the data obtained using these two sampling methods. The dichotomous sampler draws samples from the ambient air for 24 hours on a preweighed filter submitted to a given airflow. The filter is then withdrawn and weighed at the laboratory to measure the mass of particle deposits. The TEOM (*Tapered Element Oscillating Microbalance*) is a device that ensures the continuous measurement of particles. The device draws samples from the ambient air through a port that is heated to rid it of humidity, and is then directed into a filter cell leading to a tube with a tapered end. The tube naturally oscillates and as the particles accumulate on the cell, the tube's oscillation frequency diminishes. The quantity of particles is calculated using the corresponding changes in frequency.

The comparison of data was conducted on the basis of common sampling days (121 days). The 24-hour arithmetic mean (midnight to midnight) was calculated for the TEOM samples. The relation between the two sampling methods is linear and is expressed for the whole of the data as follows:

$$TEOM = 0.61 \text{ Dichot} + 0.55 \qquad (eq. 3.3.1)$$

The determination factor ( $\mathbb{R}^2$ ) is 0.77. The mean for the PM<sub>2.5</sub> fraction samples collected using the dichotomous sampler was 14.06 µg/m<sup>3</sup>, compared to 9.17 µg/m<sup>3</sup> for the TEOM, that is 65.2% of the value measured with the dichotomous sampler. As mentioned in the initial study report (Bonvalot *et al.*, 2000), this discrepancy between the two methods is documented in scientific literature by Moore and Barthelmie (1995) who suggest that part of the PM<sub>2.5</sub> fraction is lost due to volatilization when the TEOM heats the ambient air in the inlet port in winter. To illustrate this point, figures 3.3.4 and 3.3.5 compare the data obtained using the two sampling methods for the winter and summer seasons. Notice that the slopes of the regression lines obtained during the winters of 1999, 2000 and 2002 are less pronounced than those obtained in the summers of 1999 and 2001. This suggests that the TEOM device underestimates PM<sub>2.5</sub> concentrations in winter. The volatilization of particles at the entrance to the TEOM device may explain this reduction. On the other hand, the factors of determination are higher in winter than in summer. Since the values are lower in RDP in summer, the devices may be less accurate as the PM<sub>2.5</sub> concentrations approach the limit of detection.



**Figure 3.3.4** Relation between the PM<sub>2.5</sub>: TEOM vs dichotomous sampler (winters 1999, 2000 and 2002)





#### Summary

The  $PM_{2.5}$  concentrations measured with the dichotomous sampler at the RDP station were greater in winter than in summer, as well as in winter at the Ontario Street station. The highest monthly mean occurred at RDP in January. The comparison of the two sampling methods reveals that the TEOM sampler underestimates the concentrations obtained in winter.

#### 3.4 Elements measured with the dichotomous analyzer

## 3.4.1 Elements

Using the dichotomous sampler, 47 elements were analyzed in the fine and coarse particle fractions. The elements, as well as their contributions, are listed in table 3.4.1. The most important elements, in terms of their contribution, are, in descending order: sulphur, silicon, potassium, calcium, and iron. These five elements contribute for 76% of the elements measured at RDP.

	Pu				I			-	
Element	R	DP	Ontar	io Street	Element	R	DP	Ontar	io Street
	PM <sub>2.5</sub>	PM <sub>2.5-10</sub>	PM <sub>2.5</sub>	PM <sub>2.5-10</sub>	(cont'd)	PM <sub>2.5</sub>	PM <sub>2.5-10</sub>	PM <sub>2.5</sub>	PM <sub>2.5-10</sub>
S	45.54	4.74	52.56	2.80	Br	0.15	0.00	0.17	0.00
Si	11.12	18.24	7.04	17.14	Sn	0.14	0.05	0.24	0.06
K	7.46	4.16	6.46	4.15	Ni	0.12	0.04	0.23	0.06
Ca	6.66	34.36	6.84	34.85	Ga	0.11	0.05	0.23	0.09
Fe	4.91	9.17	5.57	10.96	As	0.10	0.01	0.08	0.01
Al	3.82	4.97	2.59	4.75	Ι	0.10	0.04	0.12	0.06
Na	3.48	7.37	4.12	7.16	Sb	0.09	0.05	0.12	0.08
Р	3.17	1.73	3.22	0.91	Cr	0.07	0.04	0.10	0.11
Cl	3.04	8.27	1.13	10.19	Se	0.04	0.01	0.09	0.01
Mg	2.03	1.61	0.94	1.06	Те	0.04	0.03	0.05	0.05
Zn	1.43	0.49	1.60	0.58	Cd	0.03	0.01	0.06	0.04
W	1.05	0.49	0.79	0.56	Hg	0.03	0.01	0.02	0.01
Ti	1.03	1.67	0.52	1.08	Sr	0.02	0.09	0.02	0.11
Cu	0.86	0.39	0.93	0.50	Mo	0.02	0.01	0.02	0.01
Mn	0.55	0.32	0.70	0.35	Ag	0.02	0.02	0.02	0.02
Pb	0.40	0.07	0.41	0.13	Zr	0.01	0.02	0.02	0.03
Nd	0.37	0.28	0.57	0.35	Pd	0.01	0.00	0.01	0.00
Ba	0.35	0.26	0.46	0.41	In	0.01	0.01	0.04	0.02
Pr	0.34	0.16	0.45	0.18	Со	0.01	0.02	0.01	0.01
Ce	0.32	0.17	0.35	0.41	Ge	0.01	0.00	0.00	0.00
La	0.32	0.17	0.39	0.29	Rb	0.01	0.00	0.00	0.00
V	0.23	0.13	0.40	0.13	Y	0.00	0.00	0.00	0.00
Sc	0.20	0.11	0.20	0.20	Nb	0.00	0.00	0.00	0.00
Cs	0.18	0.12	0.14	0.08	Total	100%	100%	100%	100%

**Table 3.4.1**Mean contribution (%) of elements measured in the fine and coarse<br/>particle fractions

Figure 3.4.1 illustrates the seasonal variation in total elements measured in the  $PM_{2.5}$  as well as a few selected individual elements for the RDP station and the reference station on Ontario Street. At RDP, for the years 1999 and 2000, the total elements were higher in the winter than in the summer. Inopportunely, the data is missing for the winter of 2001. The mean value for the winter of 2002 was lower than the preceding and subsequent summer values. Potassium (K) and cadmium (Cd) were the only elements whose winter means were higher that the summer means during the four years of sampling activity. At RDP, the winter values for potassium were statistically higher (p < 0.05) than the summer values, except for the winter of 2002 in relation to the summer of 2001. For cadmium, the summer values were close to the detection limit. The distribution patterns of the four other elements presented, namely iron (Fe), lead (Pb), vanadium (V) and nickel (Ni), were similar to the distribution patterns of the total elements.



**Figure 3.4.1** Seasonal variation of total elements, of potassium (K), iron (Fe), lead (Pb), vanadium (V), nickel (Ni) and cadmium (Cd) present in PM<sub>2.5</sub> at the RDP and Ontario Street stations (mean)

#### 3.4.2 Potassium to iron ratio (K/Fe) as an indicator

As mentioned by Bonvalot *et al.* (2000), the potassium measured in  $PM_{2.5}$  is known as a tracer indicating the presence of wood combustion. The mean concentration of potassium in winter at RDP was 0.132 µg/m<sup>3</sup>, which was roughly 150% greater than the mean summer concentration (table 3.4.2). In winter, it was also 40% greater than at the Ontario Street station. Lastly, this concentration was 80% greater than the mean concentration found in the coarse particle fraction (MP<sub>2.5-10</sub>) in winter.

Table 3.4.2 presents the concentrations of iron which were relatively constant as regards to both stations and both seasons. The presence of iron in the particles probably stems from the earth's crust. During the winter at RDP, the K/Fe ratio in fine particulate matter was 3.6, and was roughly 200% higher than in summer and 80% higher than at the Ontario Street station in winter. A higher ratio in particulate matter is characteristic of a possible source of wood combustion. In addition, a study of the determination coefficients ( $R^2$ ) between concentrations of potassium and iron underlines a lower correlation for fine particles than for coarse particles. This observation indicates that the sources of these two elements differ more strongly in winter at RDP.

	Station: BDP Ontario Street											
	Station:		KDP		, c	Intario Stre	et					
	Period <sup>1</sup> :	Total	Winter	Summer	Total	Winter	Summer					
PM 🔪	n:	133	55	54	162	58	73					
	$K (\mu g/m^3)$	0.091	0.132	0.054	0.072	0.093	0.055					
PM <sub>2.5</sub>	Fe ( $\mu g/m^3$ )	0.062	0.064	0.061	0.064	0.066	0.057					
	K/Fe	2.26	3.58	1.15	1.55	1.95	1.30					
	$R^{2}$	0.245	0.385	0.266	0.303	0.570	0.095					
	$K (\mu g/m^3)$	0.087	0.073	0.101	0.096	0.083	0.107					
PM <sub>2.5-10</sub>	Fe ( $\mu g/m^3$ )	0.203	0.203	0.201	0.254	0.246	0.263					
	K/Fe	0.46	0.39	0.55	0.38	0.33	0.42					
	$R^2$	0.726	0.780	0.745	0.885	0.922	0.848					

**Table 3.4.2**Concentrations, ratios and determination factors for potassium and iron<br/>measured in particulate matter at the RDP and Ontario Street stations

1: "Total" means the complete sampling period between December 7, 1998, and July 19, 2002.

2 :  $R^2$  = determination coefficient

We can also adjust the concentration of K to take into account the natural contribution of potassium in street dust. According to authors Lewis *et al.* (1988), this adjustment is possible by subtracting a proportion representative of city dust from the potassium found in the coarse particle fraction. The equation is as follows:

$$[K'] = [K_{PM2.5}] - ([K_{MP2.5-10}]/[Fe_{MP2.5-10}]) * [Fe_{MP2.5}] (eq. 3.4.1)$$

The element concentrations in the fine particle fraction were recorded for each sample, while the ratio of element concentrations in the coarse particle fraction was obtained for the period of the study and represents the mean ratio of street dust. Table 3.4.3 presents the K'/Fe ratios as well as the determination coefficients calculated for each season. It is noted that the K'/Fe ratios were higher at RDP in winter than in summer, and were also higher than at the Ontario Street station. In winter, the determination coefficient ( $R^2$ ) at the RDP station dropped to 0.21 and was lower than at the Ontario Street station. This could indicate that the origin of potassium and iron differ all the more at RDP than at the Ontario Street station.

Figure 3.4.2 presents the seasonal variations of the K/Fe and K'/Fe ratios. It is noted that the ratios were higher in winter than in summer, with significant differences (p < 0.05) between the winter and summer values recorded at the RDP station. Following the subtraction of the potassium fraction of street dust, the significant differences were emphasized between the K'/Fe ratios and the K/Fe ratios.

Station	RI	)P	Ontario	o Street							
Season	K'/Fe	$\mathbf{R}^2$	K'/Fe	$\mathbf{R}^2$							
W1999	4.42	0.20	1.82	0.13							
S1999	0.73	0.02	0.72	0.25							
W2000	2.56	0.15	2.05	0.11							
S2000	0.43	0.53	1.38	0.09							
W2001	N.D.	N.D.	1.68	0.40							
S2001	0.53	0.33	0.39	0.00							
W2002	2.72	0.29	1.08	0.56							
S2002	0.81	0.06	0.81	0.01							
Winter mean	3.23	0.21	1.66	0.30							
Summer mean	0.63	0.23	0.82	0.09							

 Table 3.4.3
 K'/Fe ratios and determination coefficients calculated at the RDP and Ontario Street stations



**Figure 3.4.2** Seasonal variation of the potassium to iron (K/Fe) and K'/Fe ratios at the RDP and Ontario Street stations (mean)

## Summary

The mean concentration of potassium (K) in winter at RDP was  $0.132 \ \mu g/m^3$ , and was roughly 150% greater than the mean concentration in summer. In winter, it was also 40% greater than at the Ontario Street station. During the winter at RDP, the K/Fe ratio in the fine particulate matter reached 3.6, and was roughly 200% higher than in summer and 80% higher than at the Ontario Street station in winter. A higher ratio in the fine particles is characteristic of a possible source of wood combustion.

#### 3.5 Polycyclic aromatic hydrocarbons (PAHs)

#### 3.5.1 24-hour modified high-volume sampler

Twenty-eight PAHs were analysed. Sampling was more frequent during the winters and less intense in the summers.

In the winter of 2002, the median concentration of PAHs measured at the RDP station reached  $37.0 \text{ ng/m}^3$ , while  $28.9 \text{ ng/m}^3$  was measured in the winter of 2001. The median values measured during the winters of 1999 and 2000 were higher, that is respectively 71.5 and 66.9 ng/m<sup>3</sup>. However, the 90<sup>th</sup> percentile values dropped by half beginning in the winter of 2000 and until the winter of 2002 (see figure 3.5.1 and table 3.5.1).



**Figure 3.5.1** Seasonal variation of PAH concentrations at the RDP and Ontario Street stations

At the RDP station, the median values in winter were clearly higher than the summer values. The seasonal discrepancies were statistically significant (p < 0.05), with the exception of the summer of 1999, when compared to the winters of 2001 and 2002.

At the Ontario Street station, the median values in winter were somewhat higher than the summer values, but the differences were not statistically significant. For the winter of 2002, an important increase in the median was noted as it rose to  $45.5 \text{ ng/m}^3$ .

	0117	<i>&gt;&gt;</i> <b>to t</b>	• •••••••••••••				••••••••••••	(iig/iii )
				Geometric	Standard			
Station	Season	n	Mean	mean	deviation	Minimum	Median	Maximum
	W1999	21	76.83	61.63	46.06	10.01	71.50	184.08
	S1999	7	15.70	14.03	7.32	5.27	14.97	27.53
	W2000	28	84.81	67.14	70.85	28.44	62.78	338.31
	S2000	11	17.45	14.86	10.63	5.20	12.14	39.16
RDP	W2001	10	58.43	37.98	65.32	11.70	28.85	211.42
	S2001	11	12.30	10.55	7.26	4.12	9.57	27.51
	W2002	8	53.43	41.61	46.36	20.04	37.02	159.01
Win	ter mean	67	74.62	56.70	60.38	10.01	56.35	338.31
Sumn	ner mean	29	15.07	12.87	8.72	4.12	12.14	39.16
	W1999	15	43.68	37.88	23.06	14.18	40.68	89.44
	S1999	10	32.16	29.74	11.05	9.42	34.09	45.61
	W2000	12	33.59	30.61	13.65	10.51	34.86	56.62
Ontario	S2000	10	22.05	20.09	10.18	11.38	19.01	42.00
Street	W2001	11	27.13	22.94	18.20	9.11	21.93	73.77
	S2001	12	21.22	18.52	11.63	8.08	20.71	49.20
	W2002	8	50.56	43.81	29.50	20.03	45.45	105.19
Win	ter mean	46	38.29	32.60	22.20	9.11	34.77	105.19
Sumn	ner mean	32	24.90	22.03	11.76	8.08	25.17	49.20

Table 3.5.1Synthesis of results for total PAHs measured over 24 hours from the winter<br/>of 1999 to the winter of 2002 at the RDP and Ontario Street stations (ng/m³)

The comparison of all the results show that except for the winter of 2002, the winter medians at RDP were higher than those recorded at the Ontario Street station, but only the values recorded during the winter of 2000 differ significantly (p < 0.05). The opposite was noted in the summer, as the medians at RDP were roughly half the medians recorded at the Ontario Street station. However, the differences were insignificant (except for the summer of 1999). Figure 3.5.1 clearly illustrates the discrepancies in the seasonal distribution of PAH concentrations between both stations [ $10^{\text{th}}$ ,  $50^{\text{th}}$  (median) and  $90^{\text{th}}$  percentile]. A study of the  $90^{\text{th}}$  percentiles at the RDP station in winter showed that the seasonal variation was much greater at the RDP station than on Ontario Street. This indicates that the source of PAHs were present all year in downtown Montreal, while an important source of PAHs was found only in winter at RDP. In summer, the importance of vehicle traffic explains the greater variability noted downtown in comparison to the residential area where few sources of PAHs are present.

On the whole, the mean of PAHs measured at RDP during the four winters is  $74.6 \text{ ng/m}^3$  (table 3.5.1). This concentration is five times higher than the mean measured at the site in summer, and twice as high as that measured at the Ontario Street station in winter.

Among all the substances measured in the winter, phenanthrene was the most present and constituted almost 30% of the total PAHs (table 3.5.2). Four other PAHs, namely fluoranthene, fluorene, pyrene and acenaphthylene, were found in important proportions at both stations. In summer, phenanthrene represented half of the PAHs measured in the air, thereby diminishing the importance of the majority of the other substances. A few substances such as fluoranthene and pyrene remained present in similar proportions throughout the year.

Station		RDP			<b>Ontario St.</b>	
Period	Total <sup>1</sup>	Winters	Summers	Total	Winters	Summers
Substance		1999 to 2002	1999 to		1999 to 2002	1999 to
			2001			2001
Acenaphtylene	7.8	10.3	1.6	5.8	8.0	1.6
Acenaphtene	2.8	2.8	2.4	3.3	3.7	2.1
Fluorene	10.1	10.2	8.7	10.4	11.4	7.7
2-Methyl-fluorene	3.2	2.4	4.5	3.3	3.3	3.2
Phenanthrene	34.9	29.8	48.5	38.6	30.5	52.2
Anthracene	2.9	3.2	2.0	2.6	2.3	2.8
Fluoranthene	10.8	10.6	12.1	10.7	10.6	11.7
Pyrene	7.7	8.0	7.2	4.4	3.8	4.8
Retene	0.6	0.3	1.1	3.5	4.5	2.6
Benzo(a)fluorene	0.8	0.9	0.5	0.6	0.7	0.4
Benzo(b)fluorene	0.4	0.5	0.2	0.3	0.4	0.2
1-Methyl-pyrene	0.5	0.6	0.4	0.4	0.4	0.3
Benzo(g,h,i)fluoranthene	1.3	1.6	0.6	1.0	1.3	0.6
Benz(a)anthracene	1.3	1.8	0.4	1.0	1.3	0.5
Chrysene	2.6	2.9	1.9	2.4	2.9	1.7
Triphenylene	0.7	0.7	0.7	0.7	0.8	0.5
7-Me-Benz(a)anthracene	0.03	0.02	0.04	0.02	0.02	0.02
Benzo(b)fluoranthene	3.9	4.4	2.8	3.6	4.6	2.5
Benzo(k)fluoranthene	1.0	1.1	0.6	0.9	1.2	0.5
Benzo(e)pyrene	1.9	2.1	1.4	1.9	2.5	1.4
Benzo(a)pyrene	1.2	1.5	0.3	0.9	1.2	0.4
Perylene	0.2	0.2	0.1	0.1	0.2	0.05
3-Methyl-cholanthrene	0.04	0.02	0.07	0.03	0.03	0.03
Indeno(1,2,3-cd)pyrene	1.5	1.7	0.8	1.3	1.6	0.8
Dibenz(a,c)&(a,h)anthracene	0.2	0.2	0.1	0.2	0.2	0.1
Benzo(b)chrysene	0.1	0.1	0.1	0.1	0.1	0.05
Benzo(g,h,i)perylene	1.6	1.8	1.0	1.7	2.1	1.1
Anthanthrene	0.2	0.2	0.1	0.1	0.2	0.1
Total contribution	100%	100%	100%	100%	100%	100%

**Table 3.5.2**Seasonal variation of the contribution of different PAHs (%) to the total<br/>PAHs measured at the RDP and Ontario Street stations

1. "Total" period represents the total sampling period from December 7, 1998, to May 8, 2002.

## 3.5.2 Benzo(a)pyrene and the Québec standard

For benzo(a)pyrene or BaP, the results obtained are presented in figure 3.5.2 and table 3.5.3. In winter, the medians were twice as high at RDP than at the Ontario Street station, except for the winter of 2002 when the values measured were close to  $0.33 \text{ ng/m}^3$  and  $0.26 \text{ ng/m}^3$  respectively. The values of BaP measured at both stations in the winters of 1999 and 2000 dropped by about half compared to the winters of 2001 and 2002.

At RDP, the median values of BaP were 10 to 30 times higher in winter than in summer, while they were 3 to 8 times higher at the Ontario Street station. The discrepancies were

statistically significant (p < 0.05) at RDP. However, in summer, the BaP concentrations measured at RDP were lower than those measured at the Ontario Street station. The heightened sensitivity of BaP to photodegradation in summer compared to winter (Germain *et al.*, 1993) may explain why the winter-summer discrepancy was greater in regards to BaP than for the other PAHs.

As mentioned in the report by Bonvalot *et al.* (2000), the deviation of PAHs and BaP from seasonal values varies more importantly in environments influenced by wood combustion than in those influenced by vehicle emissions.



**Figure 3.5.2** Seasonal variation of BaP concentrations measured at the RDP and Ontario Street stations (median)

Table 3.5.3	Seasonal synthesis of results for BaP measured over 24 hours, winter of
	1999 to winter of 2002, at the RDP and Ontario Street stations (ng/m <sup>3</sup> )

				Geometric	Stand.			` <b>`</b>
Station	Season	n	Mean	mean	deviat.	Minimum	Median	Maximum
	W1999	21	1.20	0.63	1.11	0.00	0.94	4.53
	S1999	7	0.04	0.03	0.03	0.01	0.04	0.11
	W2000	28	1.84	1.12	2.16	0.11	1.09	10.01
RDP	S2000	11	0.06	0.04	0.05	0.01	0.04	0.16
	W2001	10	1.15	0.49	1.75	0.04	0.43	5.54
	S2001	11	0.02	0.02	0.02	0.01	0.01	0.05
	W2002	8	0.75	0.41	1.06	0.08	0.33	3.31
	W1999	15	0.62	0.45	0.52	0.07	0.40	1.89
	S1999	10	0.09	0.07	0.05	0.01	0.09	0.18
Ontario	W2000	12	0.43	0.33	0.29	0.07	0.44	0.95
Street	S2000	10	0.08	0.06	0.08	0.02	0.05	0.29
	W2001	11	0.33	0.20	0.35	0.04	0.20	1.17
	S2001	12	0.10	0.07	0.10	0.01	0.07	0.38
	W2002	8	0.56	0.34	0.55	0.07	0.26	1.52

We also verified if the mean concentration of BaP respected the annual criteria of 0.9  $ng/m^3$  established by the Ministère de l'Environnement du Québec (see figure 3.5.3 and table 3.5.4). At RDP, the annual means reached 0.96  $ng/m^3$  in 1999 and 1.32  $ng/m^3$  in 2000. However, these values were not significantly higher (p < 0.05) than the criteria. In 2001, an important drop in the mean concentration of BaP was noted as it stood at 0.37  $ng/m^3$ . At the Ontario Street station, the annual mean values were between 0.20  $ng/m^3$  and 0.32  $ng/m^3$ , meeting the provincial criteria.



**Figure 3.5.3** Variation of the annual mean of BaP measured at the RDP and Ontario Street stations

Table 3.5.4	Annual synthesis of results obtained for BaP concentrations measured
	over 24 hours at the RDP and Ontario Street stations $(ng/m^3)$

Station		RDP		(	Ontario Stree	t
Year	1999	2000	2001	1999	2000	2001
n	35	42	28	29	27	27
Mean	0.96	1.32	0.37	0.32	0.27	0.20
Geom. mean	0.31	0.43	0.09	0.18	0.15	0.12
Stand. dev.	1.17	1.96	1.03	0.42	0.27	0.23
Minimum	0.00	0.01	0.01	0.01	0.02	0.01
10 <sup>th</sup> percentile	0.02	0.03	0.01	0.06	0.04	0.04
Median	0.51	0.54	0.06	0.17	0.17	0.14
90 <sup>th</sup> percentile	2.58	3.32	0.48	0.63	0.67	0.40
Maximum	4.53	10.01	5.54	1.89	0.95	1.17

# 3.5.3 Continuous PAH analyzer

The continuous PAH analyzer allows the verification of hourly, daily, weekly, monthly and seasonal variations in PAH concentrations at RDP. In summer, a low correlation was noted between the data from the continuous analyzer and the data obtained with the modified high-volume sampler (Hivol), as the concentrations stood at the limits of the measuring device's analytic method. The continuous analyzer was therefore moved to the Ontario Street station for the summer of 2001.

We calibrated the continuous analyzer by comparing the data obtained with the data provided by the modified high-volume sampler for the days covered by the National Air Pollution Surveillance (NAPS) network. We calculated the results by taking the daily means into account on one hand, and the hourly means on the other hand. For each season, the data obtained using the continuous analyzer were adjusted while taking into account the correlation calculated with the modified high-volume sampler. The process was applied for the whole of the data available for each individual season. Figure 3.5.4 presents the correlation of the data for three seasons.



**Figure 3.5.4** Correlation between the results obtained with the continuous analyzer and the Hivol sampler at RDP

We also verified if there were any discrepancies between the statistical values calculated for the sampling days of the NAPS network and the whole of the results obtained with the continuous analyzer. We did not find any significant discrepancies (p < 0.05) between the mean or median values calculated on the basis of the results or on the basis of the sole sampling days of the National Air Pollution Surveillance Network. However, the calculation based solely on the network's days caused a lack of certain minimum and maximum values. The seasonal variations recorded with the continuous analyzer (figure 3.5.5) were similar to those registered with the samples taken every six days using the high-volume sampler (figure 3.5.1). Only the winter and summer of 2000 differed statistically (p < 0.05) from the others, while the medians were lower than those recorded with the high-volume sampler.

The monthly variation is shown in figure 3.5.6 with the weekday/weekend discrepancies. The data originates from the monthly means of all the values available from December 1998 to February 2002. The winter monthly mean values were roughly 6 to 7 times higher than those obtained in summer. The figure also shows that the values measured

during the weekends were higher than those measured on weekdays in winter, while they were lower in summer. The highest values were measured in December, January and February.



**Figure 3.5.5** Seasonal variation of PAHs measured with the continuous analyzer at RDP (24-hour mean)



Figure 3.5.6 Monthly variation of PAHs (weekday vs weekend) at RDP

Figure 3.5.7 presents the daily variation of PAH concentrations in winter and summer. In winter, the weekend values were roughly 30% higher than the values recorded during the week. The maximum mean reached 78 ng/m<sup>3</sup> on Sundays. In summer, the weekend values were approximately 20% lower than the values obtained during the work week.



Figure 3.5.7 Daily variation of PAH concentrations (summer vs winter) at RDP

Figure 3.5.8 shows the hourly mean variation of the PAHs for the four winters sampled at the RDP station. In winter, the PAH concentrations measured during weekdays began to rise at 6 a.m., diminished starting at 8 a.m., stabilized between 11 a.m. and 4 p.m., and increased once again to reach a peak around 8 p.m. In the evening, we noticed that the means and medians were higher on Monday and Wednesday evenings, in comparison to the three other days of the work week (not included in figure 3.5.8). On Saturday mornings, the increase occurred two hours later than during the work week, and PAH concentrations remained relatively stable until 3 p.m. when they increased to reach a maximum of 158  $ng/m^3$  around 8 p.m. These behaviour patterns are similar to those observed in the winter of 1999 (Bonvalot et al., 2000). On Sunday, the PAH concentrations were high early in the morning and followed a distribution curve similar to that noted on Saturdays. As to the period of the day between 11 a.m. and 3 p.m., there were twice as many PAHs in the air during the weekend than during the week, and three times more during the evening than in the afternoon, both on weekdays and weekends. The highest hourly values occurred during the evening on weekends and these were roughly 30% higher than the evenings during the week.

Figure 3.5.9 presents the summer hourly variations measured at RDP in 1999 and 2000, as well as at the Ontario Street station in 2001. As in winter, two peaks were noted in the morning and the evening, with a few differences. At RDP in summer, the hourly variations resemble those noted in winter, but the PAH concentrations were approximately three to five times lower than in winter. The morning peak was stronger in summer (in terms of percentage) than in winter, while the evening peak was roughly 10 times lower and occurred later in summer than in winter.



**Figure 3.5.8** Hourly variation of PAHs measured in winter (weekday vs weekend) at RDP



**Figure 3.5.9** Hourly variation of PAHs measured in summer at RDP (1999 and 2000) and at the Ontario Street station (2001) (weekday vs weekend)

During the summer work week, the two distribution patterns at the RDP and Ontario Street stations were relatively similar, with a morning peak occurring between 5 a.m. and 11 a.m., and a second weaker peak beginning in the evening around 6 p.m. The PAH concentrations measured at RDP were half the concentrations measured at the Ontario Street station during the week, with a peak of 23 ng/m<sup>3</sup> in the morning at RDP. We can presume that the sources of PAHs are similar at both stations and stem from road transport. The distribution patterns are different during the weekends. At the Ontario Street station, the PAH concentrations remained stable during the day and reached a peak around 9 p.m. At RDP, on Saturdays, a slight peak was observed around 6 a.m. to 9 a.m., followed by a reduction in the afternoons and an important increase beginning around 6 p.m. to reach a maximum of 26 ng/m<sup>3</sup> at midnight. This increase may be explained by the use of BBQs, gas-powered lawnmowers or outdoor fires. On Sundays, the PAH concentration diminished throughout the day before increasing to attain a maximum around 10 p.m.

## 3.5.4 Relationship between PAHs and wind direction

Figure 3.5.10 shows the mean concentration of PAHs based on wind direction. The numerical value at the end of each bar represents the number of data available to calculate the mean concentration. The highest PAH concentrations were measured in calm winds with a mean value of 191 ng/m<sup>3</sup>. However, calm winds occurred only 0.7% of the time, that is 72 hours for the whole of the four winters studied. The east to southeast winds constituted the sector where the highest mean PAH concentrations were measured, with values ranging from 124 to 128 ng/m<sup>3</sup>. The winds blew from these directions only 3.1% of the time.

However, as shown in figure 3.1.4, the speed of winds from the east to south-east sector was below that of the wind from the northeast or the west to southwest sectors. For the north-northeast to east-northeast sectors, the wind speed of 11 to 20 km/h happened 21 to 36% of the time, while for the east to southeast sector, the frequency for this same wind speed category was always below 17% of the time. According to figure 3.1.4, the wind speed category comprised between 21 to 30 km/h never occurred when the wind blew from the east to southeast sector, while it was present for the northeast sector. Since there is a strong relation (r = -0.74) between wind speed and concentrations of PM<sub>2.5</sub> (see section 3.2.3) or of PAHs, it is not surprising that high PAH concentrations are linked to low wind speed. The relatively high wind speeds of the north-northeast to east-northeast sectors were responsible for the low PAH concentrations measured at RDP. Conversely, the higher PAH concentrations that stemmed from the east to southeast sector were caused in part by low wind speeds.



**Figure 3.5.10** Mean PAH concentrations according to wind direction at RDP (December to March inclusively, 4 winters). The number at the end of each segment indicates the number of data used to calculate the mean concentrations.

High concentrations from a second direction were also noted in south-southwest winds stemming from the residential area and the Island of Montreal with a value of  $126 \text{ ng/m}^3$  (3.3% of the time). The lowest mean concentrations occurred when the winds stemmed from the west to northwest quadrant.

## 3.5.5 Indicators

The usual method for identifying sources is to establish the relativity between the various PAHs. Thus, according to Aubin and Farant (2000), benzo(b)fluoranthene can serve as a basis for relativization between the different products to differentiate the sources. Furthermore, it had been noted in the initial report (Bonvalot *et al.*, 2000) that the chrysene/benzo(e)pyrene ratio (Chr/BeP) was greater at RDP than at the Ontario Street station. We conducted the same exercise while adding the pairs

phenanthrene/benzo(e)pyrene (Phe/BeP) and benzo(ghi)perylene/benzo(b)fluoranthene (BghiPer/BbFlt).

Table 3.5.5 presents the PAH ratios. At the RDP and Ontario Street stations, the Phe/BeP ratio did not reflect any significant difference (p < 0.05) between each of the winters or each of the summers. However, differences between winter and summer values were significant. The Phe/BeP ratio reflected no discrepancies between the two stations for each season taken one by one. It therefore appears that the Phe/BeP ratio allows the discrimination between the seasons but not between the sources "wood heating-transportation" on the Island of Montreal.

As for the Chr/BeP and BghiPer/BbFlt ratios, no trends were detected among the seasons or stations.

	and Ontario Street stations												
Ratio	Phen	anthrene/	Chi	rysene/	Benzo(ghi)perylene/								
	Benzo	o(e)pyrene	Benzo	(e)pyrene	Benzo(b)fluoranthene								
Season	RDP	<b>Ontario St.</b>	RDP	<b>Ontario St.</b>	RDP	<b>Ontario St.</b>							
W1999	17.4	14.2	1.46	1.24	0.39	0.47							
S1999	56.0	54.3	1.16	1.12	0.39	0.46							
W2000	15.3	18.9	1.29	1.16	0.43	0.62							
S2000	57.9	72.4	1.58	1.31	0.43	0.54							
W2001	16.5	16.9	1.46	1.29	0.42	0.48							
S2001	76.1	92.0	1.98	1.94	0.62	0.69							
W2002	20.5	27.9	1.73	1.55	0.47	0.59							

**Table 3.5.5**Comparison of relations between different PAHs measured at the RDP<br/>and Ontario Street stations

# 3.5.6 Comparison of continuous measurements of PM<sub>2.5</sub> and PAHs

Figure 3.5.11 illustrates the relationship between the hourly concentrations of PAHs and PM<sub>2.5</sub> measured during the winter. It is noted that the data did not follow a normal distribution curve. In fact, 83% of the data regarding PAHs have a value below 100 ng/m<sup>3</sup>, while 87% of the data regarding PM<sub>2.5</sub> have a value below 20  $\mu$ g/m<sup>3</sup>. However, there is a positive relation between PAHs and PM<sub>2.5</sub>; the PAH concentrations increased when the PM<sub>2.5</sub> concentrations increased. A trend line was superimposed on the graphic. The Spearman rank-order correlation coefficient between the hourly concentrations of PAHs and PM<sub>2.5</sub> was 0.73 (p < 0.01).

The relation between PAHs and  $PM_{2.5}$  may be better visualized using the hourly mean variation, as illustrated in figure 3.5.12. Though two orders of magnitude exist between the  $PM_{2.5}$  (µg/m<sup>3</sup>) and the PAHs (ng/m<sup>3</sup>), there was much similarity in the hourly behaviour of both pollutants, and the Spearman rank-order correlation coefficient was 0.93 (p < 0.01). This result suggests that the sources of PAHs and of  $PM_{2.5}$  were probably of the same nature, and that these two pollutants react in similar fashion to atmospheric conditions.



Figure 3.5.11 Relation between the hourly concentrations of  $PM_{2.5}$  and PAHs measured at RDP in winter (n = 10,037)



**Figure 3.5.12** Variation of mean concentrations of PAHs and  $PM_{2.5}$  at RDP in winter (PAH: n = 434;  $PM_{2.5}$ : n = 464)

#### PAH/PM<sub>2.5</sub> ratio

A study of the PAH/PM<sub>2.5</sub> ratio may contribute to some extent to the characterization of the source or sources of the pollutants. Figures 3.5.13 and 3.5.14 show the variation of the hourly PAH/PM<sub>2.5</sub> ratio during the day. The ratio ranges from 0.004 to 0.008 for a mean value of 0.006. As a general rule, the higher the hourly mean concentrations of PM<sub>2.5</sub>, the higher the PAH/PM<sub>2.5</sub> ratio. For example, it was found that between 6 p.m. and midnight, the PAH/PM<sub>2.5</sub> ratio was relatively constant with a mean value of 0.0077. During the day, between 7 a.m. and 3 p.m., the mean ratio was roughly 0.0044.

In the evening, the PAH/PM<sub>2.5</sub> ratio increased 75% above day levels, which means that during the evening, there were 75% more PAHs in comparison to  $PM_{2.5}$  than during the day. This result suggests that the sources present during the evening may have differed from those present during the day. A greater usage of wood heating systems in the evening be partly responsible for this result.



**Figure 3.5.13** Variation of the PAH/PM<sub>2.5</sub> ratio of mean concentrations measured at RDP in winter



**Figure 3.5.14** Relation between the hourly mean concentrations of PAHs and PM<sub>2.5</sub> measured at RDP in winter. The slopes represent the PAH/PM<sub>2.5</sub> ratio.

#### Summary

As a general rule, the graphics (figures 3.5.5 to 3.5.9) appear to indicate that the PAH concentrations in the ambient air at RDP were influenced by a winter source that may be linked to residential wood combustion. The concentrations measured were frequently greater in winter than in summer, during the weekend than during the week in winter, and in the evening than during the day in winter. Only the Phe/BeP ratio allows to discriminate between the winter and summer seasons, but not between the RDP and Ontario Street stations.

A positive relation between the PAHs and  $PM_{2.5}$  suggests that the sources of these two pollutants were probably of the same nature, and that these pollutants react in similar fashion to atmospheric conditions.

# 3.6 Dioxins and furans

According to the Canadian inventory, residential wood combustion emits an important quantity of dioxins and furans into the atmosphere (Environment Canada, 2000). Waste incineration, all types of combustion and iron and steel-mills also cause dioxin and furan emissions. Dioxins and furans, also called polychlorodibenzodioxins (PCDD) and polychlorodibenzofurans (PCDF), are two groups of substances comprised of 75 and 135 congeners respectively. Each of these two groups of congeners is divided into eight homologous series, of which only five were analyzed: tetra (T4), penta (P5), hexa (H6), hepta (H7) and octa (O).

Among all dioxins and furans, 17 congeners contribute the most to the toxicity of the mix and give rise to the most concerns (GC, 1990). These 17 products all contain chlorine atoms in the 2, 3, 7, and 8 positions on their molecule, and the World Health Organization (WHO) has attributed to these products a toxicity equivalent factor in relation to 2,3,7,8-tetrachlorodibenzodioxin (NATO, 1988). The factors used in this study originate from the update by authors Van den Berg *et al.*, 1998.

The analysis of this family of compounds began in the winter of 2000 at the RDP station and was pursued over the two following winters and through the summer of 2001. Data are also available at the Ontario Street station for the same periods, as well as for the summer of 2000. Other data are available for the period between 1992 and 1998 at the Ontario Street station.

# 3.6.1 Ambient air measurements

The results of table 3.6.1 show a reduction in the winter mean concentrations of PCDD/PCDF at the RDP station between the winter of 2000 (5.3 pg/m<sup>3</sup>) and the winter of 2002 (2.4 pg/m<sup>3</sup>), while these concentrations remained rather stable at the Ontario Street station. Furthermore, the summer concentrations were lower than winter concentrations, at both the RDP and Ontario Street stations. The drop in concentrations during the winter periods can be visualized in figure 3.6.1.

	Saasan	n	Moon	Ceometric	Standard	Minimum	Median	Maximum
Station	Season	п	witan	Geometric	deviation	wiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiii	wiculaii	
Station				mean	deviation			
	W2000	9	5.3	4.9	2.5	2.7	5.0	10.0
	S2000	-	-	-	-	-	-	-
RDP	W2001	21	3.5	2.5	3.0	0.6	2.1	11.0
	S2001	8	1.6	1.4	1.2	0.6	1.3	4.3
	W2002	8	2.4	2.3	0.9	1.4	2.3	4.1
	W2000	7	2.5	2.0	1.9	0.7	1.9	6.5
Ontario	S2000	5	1.7	1.2	1.4	0.5	1.7	3.8
Street	W2001	19	2.0	1.6	1.3	0.5	1.7	5.5
	S2001	9	0.9	0.8	0.6	0.4	0.8	1.8
	W2002	7	2.9	2.5	1.5	1.0	2.8	5.4

**Table 3.6.1**Synthesis of the statistics relative to dioxins and furans (pg/m³) measured<br/>at the RDP and Ontario Street stations (winters 2000 to 2002)



**Figure 3.6.1** Summary of winter and summer concentrations of dioxins and furans in Montreal (December 1999 to March 2002)

We studied the relative importance of the homologous series of PCDD and PCDF found in the residential area of RDP and at the Ontario Street station (table 3.6.2). At RDP, PCDD represented over 70% of the PCDD/PCDF mix in winter and approximately 52% in summer. The difference is a little less pronounced at the Ontario Street station. Table 3.6.2 shows that the concentrations of the homologous series of PCDD increased with the degree of chlorination, unlike those of PCDF that diminished when the number of chlorine atoms rose. This division of concentrations corresponds to data mentioned in literature (Lohmann *et al.*, 2000; Wagrowski and Hites, 2000). The division of the homologous series was similar at both measuring sites and varied very little between summer and winter.

	street stati	ons					
Station	R	kivière-des-Prairi	ies	<b>Ontario Street</b>			
Period Homologues	Total <sup>1</sup>	Winters 2000 to 2002	Summer 2001	Total	Winters 2000 to 2002	Summers 2000 and 2001	
T4CDD	1.6	1.6	2.0	1.6	1.7	1.2	
P5CDD	4.0	3.9	4.6	3.8	4.1	3.0	
H6CDD	11.7	11.9	10.0	9.5	10.5	7.1	
H7CDD	21.6	22.5	15.6	19.7	20.3	18.1	
OCDD	30.0	31.6	19.9	30.3	30.8	29.2	
Total PCDD	68.9	71.5	52.1	64.9	67.4	58.6	
T4CDF	8.6	7.8	13.3	11.9	10.8	14.5	
P5CDF	7.2	6.0	14.8	7.8	7.0	9.6	
H6CDF	6.6	5.8	11.9	7.1	6.6	8.4	
H7CDF	4.6	4.6	4.7	4.8	4.7	5.1	
OCDF	4.1	4.3	3.2	3.6	3.5	3.8	
Total PCDF	31.1	28.5	47.9	35.2	32.6	41.4	
Total PCDD/PCDF	100%	100%	100%	100%	100%	100%	

**Table 3.6.2**Seasonal variation of the contribution of different homologous series (%)<br/>to the whole of the dioxins and furans measured at the RDP and Ontario<br/>Street stations

1. "Total" represents the total sampling period from December 2, 1999, to March 21, 2002.

Table 3.6.3 shows that on average, during the winter of 2000, almost twice as many dioxins/furans were measured in the air at RDP than at the Ontario Street station; while the ratio was reduced to less than 1, that is 0.8, in the winter of 2002. In the summer of 2001, the ratios between statistical indicators at the RDP and Ontario Street stations varied from 1.4 to 1.9. **Table 3.6.3** 

Ratio of dioxin and furan concentrations between the RDP and Ontario Street stations

	Rivière-des-Prairies/Ontario Street							
	W2000	W2001	W2002	S2000	S2001			
Mean	2.1	1.8	0.8	_	1.8			
Geom. mean	2.4	1.6	0.9	-	1.8			
Median	2.6	1.3	0.8	-	1.6			
Minimum	3.6	1.3	1.4	-	1.6			
Maximum	1.5	2.0	0.8	-	2.4			

# 3.6.2 Toxicity equivalent

As was the case for the homologous series, the results for the 17 congeners causing the most concern showed a reduction in the mean winter concentrations expressed in terms of toxicity equivalent (TEQ) at the RDP station between the winter of 2000 (0.092 pg TEQ/m<sup>3</sup>) and the winter of 2002 (0.042 pg TEQ/m<sup>3</sup>), while for the same years, these remained rather stable at the Ontario Street station, standing at 0.046 pg TEQ/m<sup>3</sup> for the winter of 2000, and at 0.044 pg TEQ/m<sup>3</sup> for the winter of 2002 (table 3.6.4). As for the sum of the PCDD/PCDF, the summer concentrations expressed in terms of toxicity equivalent stood below the winter concentrations (< 0.030 pg TEQ/m<sup>3</sup>) at both stations. A study of the seasonal means revealed that the concentration in toxicity equivalent at RDP was 2.5 times greater in winter (0.069 pg TEQ/m<sup>3</sup>) than in summer (0.028 pg TEQ/m<sup>3</sup>),

and 1.7 times greater than at the Ontario Street station (0.041 pg  $TEQ/m^3$ ) in winter. The drop in winter indicators can be visualized in figure 3.6.2.

Station	Season	n	Mean	Geometric	Standard	Minimum	Median	Maximum
				mean	deviation			
	W2000	9	0.092	0.081	0.049	0.027	0.079	0.184
	S2000	-	-	-	-	-	-	-
	W2001	21	0.062	0.041	0.062	0.008	0.034	0.222
RDP	S2001	8	0.029	0.026	0.017	0.012	0.026	0.069
	W2002	8	0.042	0.039	0.017	0.021	0.044	0.072
Wi	nter mean	38	0.069	0.047	0.058	0.008	0.050	0.222
Sum	mer mean	8	0.028	0.026	0.017	0.012	0.026	0.069
	W2000	7	0.046	0.038	0.037	0.017	0.035	0.125
	S2000	5	0.026	0.022	0.016	0.009	0.024	0.051
Ontario	W2001	19	0.038	0.033	0.022	0.013	0.033	0.100
Street	S2001	9	0.020	0.018	0.010	0.012	0.015	0.041
	W2002	7	0.044	0.039	0.025	0.019	0.039	0.088
Wi	nter mean	33	0.041	0.035	0.026	0.013	0.034	0.125
Sum	mer mean	14	0.021	0.019	0.012	0.009	0.017	0.051

**Table 3.6.4**Synthesis of statistics relative to PCDD and PCDF (pg TEQ/m³)<br/>measured at the RDP and Ontario Street stations



**Figure 3.6.2** Summary of the winter concentrations of dioxins and furans in Montreal (December 1999 to March 2002)

We also studied, for the RDP and Ontario Street stations, the relative importance of each of the 17 congeners for which the toxicity equivalent factor was available. Octachlorodibenzodioxin (or OCDD) and 1,2,3,4,6,7,8-heptachlorodibenzodioxin (1,2,3,4,6,7,8-H7CDD) were the two most present congeners among the 17 causing the most concern measured at the RDP and Ontario Street stations (table 3.6.5). In addition, these two substances were the ones found in the largest proportions in the air sampled at the Ontario Street station, both in summer and in winter. 2,3,7,8-TCDD represented between 0.1% et 0.3% of the whole of the 17 congeners concerned.

Station	F	<b>Rivière-des-Prairies</b>			<b>Ontario</b> S	treet		
Period	Total <sup>1</sup>	Winters 2000	Summer	Total	Winters 2000	Summers 2000		
Congeners		to 2002	2001		to 2002	and 2001		
2378-T4CDD	0.1	0.1	0.2	0.2	0.2	0.3		
12378-P5CDD	1.0	0.7	2.1	1.1	0.9	1.4		
123478-H6CDD	1.0	1.0	1.1	0.8	0.9	0.7		
123678-H6CDD	1.7	1.6	2.2	1.5	1.5	1.4		
123789-H6CDD	2.5	2.5	2.3	2.1	2.4	1.6		
1234678-H7CDD	18.8	18.8	18.8	16.9	17.4	15.7		
OCDD	51.9	53.0	46.1	53.2	53.4	52.9		
Total PCDD	77.0	77.7	72.8	75.8	76.7	74.0		
2378-T4CDF	3.1	3.1	3.1	4.0	3.8	4.5		
12378-P5CDF	0.6	0.6	0.5	0.7	0.8	0.6		
23478-P5CDF	1.0	1.0	0.9	1.2	1.2	1.3		
123478-H6CDF	2.5	2.5	2.4	2.7	2.8	2.6		
123678-H6CDF	1.1	1.0	1.8	1.1	1.2	1.1		
234678-H6CDF	1.4	1.3	1.6	1.4	1.4	1.2		
123789-H6CDF	0.2	0.2	0.4	0.3	0.2	0.5		
1234678-H7CDF	5.2	4.7	8.1	5.7	5.2	6.7		
1234789-H7CDF	0.7	0.7	0.6	0.8	0.8	0.7		
OCDF	7.2	7.1	7.8	6.2	5.9	6.9		
Total PCDF	23.0	22.2	27.2	24.1	23.3	26.1		
Total PCDD/PCDF	100%	100%	100%	100%	100%	100%		

**Table 3.6.5**Seasonal variation of congener contribution (%) to the toxicity (TEQ)<br/>among the 17 dioxins and furans with toxicity equivalents measured at<br/>the RDP and Ontario Street stations

1. "Total" represents the total sampling period from December 2, 1999, to March 31, 2002.

Table 3.6.6 underlines that the mean concentration of the group of 17 congeners with a toxicity equivalent factor was twice as high at RDP than at the Ontario Street station in the winter of 2000. This proportion dropped to 1.6 in 2001, and finally dropped to 0.9 in 2002. In the summer of 2001, the ratios between the indicators at the RDP and Ontario Street stations varied from 1.4 to 1.7, with proportions almost identical to those of the homologous series.

				2111120-12				
	Rivière-des-Prairies/Ontario Street							
	W2000	W2001	W2002	S2000	S2001			
Mean	2.0	1.6	0.9	-	1.4			
Geometric mean	2.1	1.2	1.0	-	1.4			
Median	2.3	1.0	1.1	-	1.7			
Minimum	1.7	0.6	1.1	-	1.0			
Maximum	1.5	2.2	0.8	-	1.7			

Table 3.6.6	Ratios of the concentrations in toxicity equivalents of dioxins and furans
	between the RDP and the Ontario Street stations

The mean concentrations calculated for the period from January 2001 to December 2001 were 0.049 pg TEQ/m<sup>3</sup> at the RDP station and 0.031 pg TEQ/m<sup>3</sup> at the Ontario Street station. In both cases, these concentrations stood below the annual criteria established at 0.060 pg TEQ/m<sup>3</sup> by the Ministère de l'Environnement du Québec.

Appendix 2 presents a synthesis of the statistics relative to the RDP and Ontario Street stations according to the seasons.

# Summary

The 17 compounds which cause the most concern for human health are expressed in terms of toxicity equivalent (TEQ) in relation to the most toxic product of the group, 2,3,7,8 -TCDD. At RDP, the mean concentration in toxicity equivalent is 2.5 times greater in winter (0.069 pg TEQ/m<sup>3</sup>) than in summer (0.028 pg TEQ/m<sup>3</sup>), and 1.7 times greater than at the Ontario Street station (0.041 pg TEQ/m<sup>3</sup>) in winter.

On an annual basis, the mean concentrations in 2001 were 0.049 pg TEQ/m<sup>3</sup> at the RDP station and 0.031 pg TEQ/m<sup>3</sup> at the Ontario Street station. In both cases, these concentrations stood below the annual criteria established at 0.060 pg TEQ/m<sup>3</sup> by the Ministère de l'Environnement du Québec.

# 3.7 Volatile organic compounds (VOCs)

VOCs are grouped within two large families. The first is comprised of nonpolar VOCs, such as benzene, toluene and others, generally linked to mobile sources, namely gasoline. The second family is comprised of polar VOCs which are compounds that contain a carbonyl group, such as acroleine or formaldehyde, and that can be more representative of emissions linked to wood combustion.

# 3.7.1 Nonpolar VOCs

The 155 nonpolar VOCs to be analyzed were grouped into four families of chemicals: 46 alkanes, 43 alkenes et alkynes, 41 halogens and 25 aromatics. Total VOCs were also calculated. Following problems that occurred during the sampling procedures or the analyses, three substances were withdrawn from the database, namely Freon 22, 1,4-dichlorobenzene and naphthalene. Appendix 3 includes a list of the VOCs that were analyzed as well as the statistical results obtained.

At the RDP station, the highest seasonal median value of total VOCs was 60.8  $\mu$ g/m<sup>3</sup>, recorded during the winter of 2001. However, the median values measured in summer and winter were not statistically different (p < 0.05) (see table 3.7.1). At the Ontario Street station, the highest value was also measured during the winter of 2001 and stood at 114.2  $\mu$ g/m<sup>3</sup>. This value was the only median to statistically distinguish itself from the medians noted for the other seasons. Despite the fact that the median values at the RDP station were below those noted at the Ontario Street station, a greater variability of

concentrations was observed at RDP. In the winter of 2001 and the summer of 2002, the 90<sup>th</sup> percentiles were roughly 30% higher at RDP than at the Ontario Street station.

				Geometric	Standard			
Station	Season	n	Mean	mean	deviation	Minimum	Median	Maximum
	W2001	16	92.2	70.9	77.4	29.6	60.8	285.9
RDP	S2001	25	43.4	39.4	21.5	20.9	35.9	104.3
	W2002	18	52.4	47.4	28.1	27.7	43.5	144.9
	S2002	16	67.3	54.0	51.2	23.6	59.4	189.3
	W2001	18	108.8	101.8	39.1	46.0	114.2	191.7
Ontario	S2001	20	60.3	58.2	18.6	41.6	55.4	113.2
Street	W2002	19	78.6	73.3	32.6	37.6	64.8	152.8
	S2002	25	68.2	62.3	33.1	35.7	57.3	158.8

**Table 3.7.1** Synthesis of results obtained for nonpolar total VOCs measured over 24 hours, from the winter of 2001 to the summer of 2002, at the RDP and Ontario Street stations (ug/m<sup>3</sup>)

Seasonal variation of families such as total alkanes, alkenes/alkynes, halogens and aromatics are shown in f igure 3.7.1. For the alkanes, the highest median value at RDP was 30.7  $\mu$ g/m<sup>3</sup> in the summer of 2002. No seasonal trend could be distinguished for this family at RDP. As for the family of alkenes/alkynes, the highest median, a value of 12.9  $\mu$ g/m<sup>3</sup>, was noted during the winter of 2001. This value was statistically higher (p < 0.05) than the summer values. In contrast to the alkanes, this family displayed a seasonal pattern with higher values in winter than in summer. The concentrations of the family of halogens remained relatively constant at both the RDP and Ontario Street stations. Lastly, for the family of aromatics, the highest median value (11.9  $\mu$ g/m<sup>3</sup>) was noted in the winter of 2001 and no seasonal trend was apparent. However, for the alkanes, alkenes/alkynes and aromatics, a greater variability in concentrations was noted, as higher 90<sup>th</sup> percentile values were observed in the winter of 2001 and the summer of 2002 at RDP, in comparison to the Ontario Street station.



Figure 3.7.1 Seasonal variation of nonpolar VOC families

Table 3.7.2 illustrates the contribution (%) of the chemical families of nonpolar VOCs, and lists the 10 most important VOCs in descending order in terms of their contribution. These 10 VOCs contribute for 51.5% of the total VOCs measured at RDP. At the station on Ontario Street, the main substances are more or less the same, but in a different order: acetylene replaces freon 11. Appendix 3 presents the individual contribution of all the nonpolar VOCs.

A synthesis of the statistics obtained for the individual nonpolar VOCs is presented in Appendix 4. Certain substances are recognized as potential tracers for residential wood combustion. We therefore verified if it was possible to identify some of these by studying the seasonal variation of a few products (figure 3.7.2). The alkadienes were noted for their heightened presence in emissions linked to wood combustion (McDonald et al., 2000). At the RDP and Ontario Street stations, the winter concentrations of 1,3-butadiene were statistically higher (p < 0.05) than the summer concentrations, except for the winter and summer of 2002 at RDP. As for benzene, the statistical deviations were the same as for 1,3butadiene, but the 90<sup>th</sup> percentile value for the

<b>Table 3.7.2</b>	Contribution of VOC
	families/substances

Tammes/substances								
<b>Families/Substances</b>	RDP	Ont. St						
Alkanes	42.2	44.5						
Alkenes/alkynes	15.5	16.6						
Halogens	23.0	17.7						
Aromatics	19.3	21.2						
Total contribution	100%	100%						
Toluene	6.74	7.74						
Freon 12	6.44	4.79						
Propane	5.89	3.84						
Isopentane	5.72	6.83						
Ethane	5.49	4.22						
Butane	5.30	6.38						
Ethylene	4.43	4.28						
Freon11	4.06	2.84						
Isobutane	3.86	5.11						
m and p-xylene	3.51	4.15						
Total contribution	51.5%	50.2%						

winter of 2001 at RDP was twice as high as the value at the Ontario Street station. It was also noted that the summer medians for these two substances were lower at RDP than at the Ontario Street station.

For ethylene and acetylene, both graphics are similar: the concentrations measured in winter are statistically greater (p < 0.05) than those measured in summer at both stations, except for the winter and summer of 2002 at the Ontario Street station. Also, the summer medians noted for these two substances at RDP were below those calculated at the Ontario Street station. It was also noted that for the winter of 2001, the 90<sup>th</sup> percentile value was higher for ethylene at RDP than at the Ontario Street station.



Figure 3.7.2 Seasonal variation of selected VOCs

According to Khalil *et al.* (2003), methyl chloride is considered as a tracer for residential wood combustion. At the RDP and Ontario Street stations, very little variability in methyl chloride levels was noted throughout the two years of measurement activity (not illustrated). The winter and summer medians ranged between 1.14 and 1.20  $\mu$ g/m<sup>3</sup>, without any apparent seasonal trends.

# 3.7.2 Polar VOCs

A list of the 16 VOCs measured is included in Appendix 5, along with a synthesis of seasonal statistics. The seasonal variation of the total polar VOCs is presented in figure 3.7.3. Except for the summer of 2000, the winter medians were higher than the summer values at RDP, while on Ontario Street, the values were relatively constant. The contribution of formaldehyde was 44.9% at RDP in the summer, compared to 34.4% in the winter. Formaldehyde is known as a product of the decomposition of VOC oxidation, and this decomposition may explain the greater concentrations of formaldehyde at RDP

in the summer. The seasonal variation of total polar VOCs shown in figure 3.7.3 excludes the formaldehyde concentrations. It is noted that the winter medians are higher than the summer medians at RDP, with statistically significant (p < 0.05) results for the winters of 1999 and 2000. For the reference station on Ontario Street, except for the first year of sampling, the median values were constant at approximately 10 µg/m<sup>3</sup> and no seasonal trend was apparent.



COV polaires totaux







**Figure 3.7.3** Seasonal variation of total polar VOCs and of total polar VOCs without formaldehyde

The seasonal variation of a few individual polar VOCs is illustrated in figure 3.7.4. Methyl ethyl ketone, acetaldehyde and acroleine showed similar trends since their winter concentrations were greater than their summer concentrations at RDP, while no trend was apparent at the Ontario Street station. As to methyl ethyl ketone/butyraldehyde and acetaldehyde, the values noted for the winters of 1999 and 2000 were statistically higher (p < 0.05) than the summer values at RDP. Regarding acroleine, the concentrations measured in summer were almost nil at RDP, while they were slightly higher at the reference station on Ontario Street. The winter medians of these products were statistically higher than the summer medians at RDP. For benzaldehyde, the winter of 1999 distinguished itself statistically from the summers. Note that several winter 90<sup>th</sup> percentile values at RDP were higher than those at the Ontario Street station.



Figure 3.7.4 Seasonal variation of individual polar VOCs

Table 3.7.3 presents the contribution of polar VOCs at the two sampling stations. The most important polar VOCs in terms of presence were, in descending order: formaldehyde, acetone, acetaldehyde, methyl ethyl ketone/butyraldehyde and propionaldehyde. These five compounds contributed 90% of the polar VOCs at RDP. The short chain carbonyl molecules were the most abundant and could be the result of the combustion of cellulose (McDonald *et al.*, 2000). Certain compounds, such as formaldehyde, hexanal and valeraldehyde, were more abundant in summer than in winter at RDP.
		RDP			<b>Ontario Str</b>	eet
Period Substance	Total <sup>1</sup>	Winters 1999 to 2002	Summers 1999 to 2002	Total	Winters 1999 to 2002	Summers 1999 to 2002
Formaldehyde	37.52	34.38	44.86	24.17	25.96	23.99
Acetone	23.11	21.53	19.23	32.97	29.55	34.35
Acetaldehyde	18.43	20.30	16.56	17.98	19.63	16.63
MEK	6.57	8.62	4.39	10.55	11.16	9.60
+butyraldehyde						
Propionaldehyde	4.57	4.72	4.43	4.63	4.66	4.79
Hexanal	2.40	1.30	3.52	1.50	0.96	1.95
Benzaldehyde	1.89	1.99	1.77	1.57	1.41	1.77
Valeraldehyde	1.29	1.06	1.59	1.31	0.96	1.61
Acroleine	1.11	2.45	0.22	1.24	1.93	0.82
MIBK	1.05	1.18	1.00	1.47	1.34	1.51
Crotonaldehyde	0.76	0.92	0.91	1.06	0.97	1.34
m-Tolualdehyde	0.59	1.01	0.43	0.35	0.28	0.43
2.5-Dimethylben-	0.31	0.12	0.52	0.00	0.00	0.00
zaldehyde						
o-Tolualdehyde	0.23	0.17	0.36	0.02	0.02	0.03
Isovaleraldehyde/	0.13	0.24	0.09	0.94	0.97	0.97
2-Pentanone						
p-Tolualdehyde	0.06	0.02	0.13	0.22	0.20	0.20
Total	100%	100%	100%	100%	100%	100%

**Table 3.7.3**Contribution of polar VOCs (%) at the RDP and Ontario Street stations<br/>in descending order

1. "Total" represents the total sampling period from December 19, 1998, to December 28, 2002.

### Summary

As a general rule, the concentrations of polar and nonpolar VOCs measured at RDP, which belong to the family of alkenes/alkynes, are greater in winter than in summer, but they remain lower than the concentrations found at the reference station on Ontario Street. However, the 90<sup>th</sup> percentile values of certain compounds found at RDP in winter are sometimes greater than those noted at the Ontario Street station.

## 4. Conclusion

The objectives of the residential wood combustion sampling program, as described in section 1.2 of this report, have been attained. The concentrations of various pollutants measured in the Rivière-des-Prairies area have been linked to the use of residential wood heating systems. It was earlier mentioned that the air in this area is only slightly influenced by transport and industry emissions. Concentrations of fine particles, PAHs, dioxins and furans, and of certain metals measured at Rivière-des-Prairies are greater in winter than in summer, and are greater than concentrations measured at other sampling stations in Montreal.

In winter, at Rivières-des-Prairies, meteorological conditions alone can explain as much as 62% of the variability of the PM<sub>2.5</sub> concentrations measured in the evening, which suggests that the contribution of local sources is important.

Among the metals measured, potassium and iron may help to identify the sources of pollution. The high potassium to iron ratio (K/Fe) indicates the presence of wood combustion. This ratio is 200% higher at RDP in winter (3.6) than in summer (1.2), and 80% higher than downtown in winter (2.0).

## 5. Recommendations

Recommendations specific to statistical data analysis:

- More than 100 days of winter data on metals, PAHs and VOCs are available at RDP. It is therefore recommended to conduct a multivariate analysis such as Positive Matrix Factorisation (PMF) to help in identifying the sources of PM<sub>2.5</sub>, PAHs and VOCs at RDP.
- The local meteorological conditions greatly influence the concentrations of  $PM_{2.5}$ and PAHs measured at RDP in winter. It is recommended to carry out a statistical analysis where the variability of pollutant concentrations caused by local meteorological conditions is subtracted so as to highlight the behaviour of  $PM_{2.5}$  and PAHs attributable to wood combustion.
- Combined with the START model (*Suivi du transport atmosphérique régional et transfrontalier*), an additional analysis such as Potential Source Contribution Function (PSCF) would confirm the assumption that local sources are the main cause of the high concentrations of PAHs and PM<sub>2.5</sub> measured at RDP. These tools combine the air mass trajectories and back-trajectories with PM<sub>2.5</sub> concentrations to identify the source regions.

Recommendations specific to ambient air sampling activities:

- The RDP monitoring station is located in an urban environment where residential wood heating is popular. It is important to retain this station in order to track future trends and to compare results with those of a new station which will have the same purpose in Cap Rouge, near Québec City.
- The continuous measurement of carbon monoxide and of organic and elemental carbon would be relevant, since residential wood combustion is known as an important source of these pollutants.
- The measurement of various pollutants at the RDP station should be maintained according to the sampling frequency of the NAPS calendar, namely every 12 days for PAHs and every 24 days for D/F.
- It would be useful to install a sampling station in a resort area where wood combustion is an important source of heat during weekends in winter, and in an area close to camping grounds where campfires are popular in summer.

Recommendations specific to public awareness:

- Public awareness of the contribution of residential wood combustion to the degradation of air quality should be intensified.
- Public awareness of good practices of residential wood combustion should be intensified.
- The winter Info-Smog program should be broadened to include all south-western Québec once the fine particle monitoring stations are installed.

## 6. Acknowledgments

The authors wish to thank Christine Vincent, André Boisvert and Pierre Paquette of the City of Montreal, and Bruno Harvey of Environment Canada, for the installation and operation of the sampling instruments. They also wish to thank the lab staff at Environment Canada, the Ministère de l'Environnement du Québec and the City of Montreal. Their appreciation also goes to Pierre Walsh of the Ministère de l'Environnement du Québec, for having made available to this project a number of laboratory hours devoted to the analysis of dioxins and furans. The comments expressed by revisers Anne-Marie Labbé, François Granger, Mario Benjamin, Thérèse Lamartine, Domenic Mignacca, and Bruce Gillies were greatly appreciated.

#### 7. References

- Bonvalot Y., Gagnon C., Benjamin M., Germain A. and Dann T., March 2000, *Sampling Program for Residential Wood Combustion: Winter of 1998-99 Study Report*, Public Works and Government Services Canada, ISBN :0-662-29797-0.
- Bonvalot Y., Labrèche F., Carrier G., Farant J., Kosatsky T., June 2001, *Impact de la combustion du bois sur l'exposition de la population aux polluants émis*, Direction de la santé publique, Régie régionale de la santé et des services sociaux de Montréal-Centre, ISBN : 2-89494-308-3.
- Brauer M., 1998, *Health Impacts of Biomass Air Polution*, Report prepared for the Biregional Workshop on Health Impacts of Haze-Related Air Pollution, Kuala Lumpur, Malaysia, 1-4 June 1998, 62 p.
- Environment Canada, 1999, *Criteria Air Contaminants Emission Summaries*, available on the Web site: <u>http://www.ec.gc.ca/pdb/ape/cape\_home\_e.cfm</u>.
- Environment Canada, 2000, *Caractérisation des composés organiques provenant des poêles à bois résidentiels et de combustibles choisis*. Environmental Technology Centre, Ottawa (Ont.), 41p.
- Germain A., Perron F. and Van Coillie R., 1993, *Cheminements, écotoxicités et réglementations pour les HAP dans l'environnement*: Support document no. 3 for the evaluation report on the toxicity of PAHs for the *Canadian Environmental Protection Act*, Environment Canada, 102 p.
- Government of Canada, 1990, *Liste des substances d'intérêt prioritaire, rapport d'évaluation n° 1 : dibenzodioxines polychlorées et dibenzofurannes polychlorés,* Public Works and Government Services Canada, Ottawa (Ont.), 64 p.
- Khalil M.A.K. and Rasmussen R.A., 2003, *Tracers of wood smoke*; *Atmos. Environm.*, 37, 1211-1222.
- Labrèche F., Bonvalot Y. and Boivin M.-C., 2000, *Enquête téléphonique sur la possession et l'acquisition d'un système de chauffage au bois dans la région de Montréal*, Direction de la santé publique, Régie régionale de la santé et des services sociaux de Montréal-Centre, 54 p.
- Lewis C.W., Baumgardner R.E., Stevens R.K., 1988, Contribution of Woodsmoke and Motor Vehicle Emissions to Ambient Aerosol Mutagenicity, Environm. Sci. Technol. 22, 968-971.
- Lohmann R., Northcott G.L. and Jones K.C., 2000, Assessing the Contribution of Diffuse Domestic Burning as a Source of PCDD/Fs, PCBs, and PAHs to the U.K. Atmosphere. Environm. Sc. & Technol. 34 (14), 2892-2899.

- McDonald J.D., Zielinska B., Fugita E.M., Sagebiel J.C., Chow J.C., Watson J.G., 2000, *Fine Particle and Gaseous Emission Rates form Residential Wood Combustion*, *Environm. Sci. Technol.*, 34, 2080-2091.
- Moore C.T., Barthelmie R.J., 1995, *A review of comparative manual and automated PM*<sub>10</sub> *data*. Western States Air Resources Council (WESTAR), Portland, OR.
- NATO (North Atlantic Treaty Organization), 1988, International Toxicity Equivalency factor (I-TEF) Method of Risk Assessment for Complex Mixtures of Dioxins and Related Compounds. Pilot Study on International Information Exchange on Dioxins and Related Compounds. Comité sur les défis modernes. N° 186. 26 p. in GC (1990).
- Perry K.D., 1999, Effects of Outdoor Pyrotechnic Displays on the Regional Air Quality of Western Washington State, J. Air & Waste Manag. Assoc., 49, 146-155.
- Regroupement montréalais pour la qualité de l'air (RMQA), 1998, *Pollution atmosphérique et impacts sur la santé et l'environnement dans la grande région de Montréal*, ISBN : 2-89494-118-8, 356 pages.
- Van den Berg M., Birnbaum L., Bosveld B.T.C., Brunstrom B., Cook P., Feeley M., Giesy J.P., Hanberg A., Hasegawa R., Kennedy S.W., Kubiak T., Larsen J.C., van Leeuwen F.X.R., Liem A.K.D., Nolt C., Peterson R.E., Poellinger L., Safe S., Schrenck D., Tillitt D., Tysklind M., Younes M., Waern F., and Zacharewski T., 1998, Toxic Equivalency Factors (TEFs) for PCBs, PCDDs, PCDFs for Humans and for Wildlife, Environm. Health Perspecti., 106, 775.
- Wagrowski D.M. and Hites R.A., 2000, Insights into the Global Distribution of PolychlorinatedDibenzo-pdioxins and Dibenzofurans, Environm. Sc. & Technol. 34 (14) 2952-2958.

#### Appendix 1: Continuous PM<sub>2.5</sub> and atmospheric dispersion variables

#### Mixing height

The concentration of a pollutant at a given site depends on the degree to which it mixes with the immediate environment. The mixing height corresponds to the altitude up to which the pollutants are able to mix. The mixing height is not a variable measured directly using a measurement tool, but is calculated using the Global Environmental Multiscale (GEM) model of the Meteorological Service of Canada. For purposes of modelisation, the GEM meteorological model limits the mixing height to 1,000 metres. Figure A.1 shows the dependence between the mixing height and the PM<sub>2.5</sub> is -0.66 (p < 0.01). A trend curve was superimposed on figure A.1 solely to illustrate the behaviour of the PM<sub>2.5</sub> on the basis of mixing height.

The PM<sub>2.5</sub> concentrations increase with a drop in mixing height given the reduction of the volume of air available to disperse the pollutants. When the mixing height passes from 1,000 metres to 50 metres, the PM<sub>2.5</sub> concentration increases from 5.6  $\mu$ g/m<sup>3</sup> to 31.7  $\mu$ g/m<sup>3</sup>, which represents 5.7 times the initial value. The dependence between the mixing height and PM<sub>2.5</sub> concentrations at RDP tends to illustrate that the local conditions of vertical dispersion influence the PM<sub>2.5</sub> concentrations measured in a residential area influenced by wood combustion.



**Figure A.1.** Variation of  $PM_{2.5}$  concentrations in the evening at RDP on the basis of mixing height. Winter 1999 to winter 2002. (n=464)

#### Vertical stability

Vertical stability determines the capacity of a pollutant to disperse itself in the air column above it. The air column is determined by the above-mentioned mixing height. In a layer of the atmosphere characterized by great stability, pollutants are subject to very little vertical mix and remain very close to the ground. The more an air mass is unstable, the more the pollutants will rapidly occupy all the air column. The vertical stability of an air mass  $\Gamma$  can be estimated on the basis of the decrease rate of air temperature T (°C) as a function of altitude Z (m).

$$\Gamma = -\frac{dT}{dZ} \qquad (^{\circ}C/m)$$

The temperature values in altitude are obtained from observations at the Maniwaki aerological station located 200 kilometres northwest of Montreal. The pressure level of 925 mb was chosen as a height for temperature measurement so as to best reflect the atmospheric dispersion close to the ground. By definition, when the temperature decrease rate  $\Gamma$  is below 1°C/100 metres, the atmosphere is considered stable and pollutants can accumulate close to the ground. However, when  $\Gamma$  is greater than 1°C/100m, the atmosphere is considered unstable and the pollutants are rapidly diluted throughout the air column. In figure A.2, a vertical dotted line is included to distinguish between stable and unstable air masses. Note that in figure A.2, when the temperature decrease rate passes from 2°C/100m (unstable) to -1°C/100m (stable), the PM<sub>2.5</sub> concentrations increase from 2.6 µg/m<sup>3</sup> to 30.3 µg/m<sup>3</sup>, that is 11.6 times the initial value. When the air mass is unstable, the PM<sub>2.5</sub> concentrations at RDP are always below 25 µg/m<sup>3</sup>. However, great variability in PM<sub>2.5</sub> concentrations is noted when the air mass is stable, which suggests that other meteorological factors influence the PM<sub>2.5</sub> concentrations.



Figure A.2 Stability of the air mass at RDP. Winters 1999 to 2002. (n=464)

### Precipitation

Precipitation is among the meteorological processes that influence  $PM_{2.5}$  concentrations. Rain and snow have the capacity to capture and drag to the ground part of the  $PM_{2.5}$  in a process called "wet deposition". The  $PM_{2.5}$  is "washed" by precipitation, and the efficiency of this action depends heavily on the frequency, intensity and duration of the precipitation events, as well as on the type of precipitation (liquid or solid) involved.

Since there is no instrument to measure precipitations at RDP, we will use the daily precipitation values from the meteorological station at Dorval airport. The distance between the Dorval station and RDP is roughly 30 kilometres. Given this short distance, we can assume that the Dorval station is representative of precipitation events occurring at RDP.

Figure A.3 represents the mean PM2.5 concentrations noted in winter at RDP in the evening, according to 6 categories of precipitation amounts expressed in millimetres (water equivalent). The number in parenthesis represents the number of days available to calculate the mean  $PM_{2.5}$  for each category of precipitation amount. According to figure A.3, for precipitation amounts above 10mm (7.8% of the days), the mean  $PM_{2.5}$  concentration is 7.0 µg/m3. For days without precipitation (50% of the days), the  $PM_{2.5}$  concentration rose to 17.0 µg/m3, that is an increase of 142% in comparison to days with precipitation amounts above 10mm. We may conclude that the precipitations measured in the RDP area influence the  $PM_{2.5}$  concentrations.



**Figure A.3** Mean PM<sub>2.5</sub> concentrations measured in the evening, according to category of precipitation amount. Winter 1999 to winter 2002. (n=464)

# <u>Appendix 2 : Summary of Statistical Results for Dioxins and Furans at RDP and</u> <u>Ontario St Stations</u>

(n = 9; December 1, 1999 to March 31, 2000) Units : $ng/m^3$ except for concentrations in taxic equivalent (ng TEQ/m <sup>3</sup> )											
Units .	pg/m, exce	pt for cone		i toxic equiv	alent (pg 1						
	Detection Frequency	Mean	Geome- tric Mean	Standard Deviation	Median	Minimum	Maximum				
2378-T4CDD	44%	0.004	0.003	0.003	0.003	< LD	0.012				
12378-P5CDD	89%	0.028	0.021	0.018	0.024	< LD	0.061				
123478-H6CDD	100%	0.029	0.026	0.017	0.027	0.013	0.064				
123678-H6CDD	100%	0.053	0.044	0.035	0.043	0.021	0.114				
123789-H6CDD	100%	0.081	0.072	0.044	0.069	0.031	0.160				
1234678-H7CDD	100%	0.577	0.499	0.368	0.478	0.290	1.316				
OCDD	100%	1.551	1.422	0.737	1.354	0.767	3.035				
Total 7 PCDD		2.323	2.105	1.206	1.809	1.180	4.732				
2378-T4CDF	100%	0.076	0.066	0.045	0.061	0.024	0.175				
12378-P5CDF	100%	0.019	0.015	0.016	0.014	0.006	0.057				
23478-P5CDF	100%	0.030	0.025	0.021	0.021	0.010	0.075				
123478-H6CDF	100%	0.065	0.053	0.049	0.042	0.021	0.170				
123678-H6CDF	100%	0.029	0.024	0.024	0.021	0.010	0.088				
234678-H6CDF	100%	0.037	0.029	0.031	0.025	0.009	0.114				
123789-H6CDF	33%	0.004	0.003	0.005	0.003	< LD	0.018				
1234678-H7CDF	100%	0.125	0.102	0.098	0.091	0.053	0.355				
1234789-H7CDF	100%	0.020	0.016	0.020	0.014	0.007	0.072				
OCDF	100%	0.130	0.103	0.111	0.098	0.047	0.391				
Total 10 PCDF		0.535	0.446	0.396	0.374	0.246	1.439				
TOTAL 17		2.858	2.634	1.295	2.509	1.426	5.106				
PCDD/PCDF											
	1000/	0.002	0.062	0.091	0.082	0.010	0.272				
14CDD	100%	0.092	0.005	0.081	0.082	0.010	0.275				
	100%	0.230	0.187	0.193	0.202	0.024	0.038				
	100%	1.267	0.342	0.428	0.343	0.185	2.584				
	100%	1.207	1.092	0.784	1.040	0.394	2.364				
	100%	2 021	2.201	0.757	2.029	0.707	5.055 7.450				
	100%	3.621	3.364	2.130	5.028	1.927	7.430				
TACDE	1000/	0.480	0.412	0.270	0.462	0.104	0.027				
14CDF D5CDE	100%	0.469	0.412	0.270	0.402	0.104	0.927				
HCDE	100%	0.348	0.277	0.240	0.290	0.009	0.000				
H7CDF	100%	0.322	0.201	0.243	0.239	0.102	0.695				
OCDE	100%	0.232	0.194	0.178	0.174	0.103	0.003				
	100%	0.130	0.103	0.111	0.098	0.047	2.504				
TOTAL DCDD/DCDE		1.321 5 3 4 2	1.202	0.900	1.210	0.302	5.394 0.007				
		5.342	4.03/	2.312	4.773	2.00/	7.70/				
Concentration in toxic equivalent		0.092	0.081	0.049	0.079	0.027	0.184				

PCDD/PCDF: Statistics for Rivière-des-Prairies station for winter 2000 (n = 9; December 1, 1999 to March 31, 2000) Units :  $ng/m^3$  except for concentrations in toxic equivalent (i

Onits .	$p_{g/m}$ , exec			toxic equiv	arent (pg 1		1
	Detection Frequency	Mean	Geome- tric Mean	Standard Deviation	Median	Minimum	Maximum
2378-T4CDD	14%	0.002	0.001	0.001	0.001	< LD	0.004
12378-P5CDD	100%	0.011	0.010	0.006	0.010	0.005	0.022
123478-H6CDD	86%	0.012	0.009	0.008	0.011	< LD	0.028
123678-H6CDD	100%	0.021	0.017	0.015	0.018	0.005	0.053
123789-H6CDD	100%	0.031	0.023	0.021	0.029	0.003	0.071
1234678-H7CDD	100%	0.224	0.180	0.168	0.196	0.051	0.580
OCDD	100%	0.636	0.568	0.320	0.582	0.201	1.275
Total 7 PCDD		0.937	0.815	0.534	0.834	0.268	2.033
2378-T4CDF	100%	0.046	0.038	0.031	0.036	0.016	0.106
12378-P5CDF	100%	0.013	0.009	0.014	0.008	0.004	0.043
23478-P5CDF	100%	0.019	0.015	0.016	0.013	0.007	0.053
123478-H6CDF	100%	0.047	0.030	0.059	0.027	0.010	0.179
123678-H6CDF	100%	0.018	0.012	0.022	0.011	0.005	0.068
234678-H6CDF	100%	0.024	0.017	0.027	0.016	0.007	0.084
123789-H6CDF	14%	0.003	0.002	0.004	0.001	< LD	0.012
1234678-H7CDF	100%	0.092	0.058	0.117	0.048	0.020	0.350
1234789-H7CDF	86%	0.016	0.008	0.024	0.006	< LD	0.070
OCDF	100%	0.110	0.073	0.126	0.055	0.030	0.374
Total 10 PCDF		0.388	0.273	0.432	0.224	0.113	1.339
TOTAL 17		1.325	1.107	0.950	1.009	0.381	3.372
PCDD/PCDF							
T4CDD	100%	0.037	0.031	0.025	0.035	0.013	0.086
P5CDD	100%	0.101	0.073	0.084	0.078	0.012	0.273
H6CDD	100%	0.255	0.189	0.202	0.235	0.033	0.669
H7CDD	100%	0.486	0.389	0.361	0.421	0.098	1.244
OCDD	100%	0.636	0.568	0.320	0.582	0.201	1.275
Total PCDD		1.516	1.269	0.981	1.353	0.357	3.547
T4CDF	100%	0.276	0.233	0.185	0.228	0.094	0.642
P5CDF	100%	0.204	0.158	0.193	0.140	0.074	0.630
H6CDF	100%	0.194	0.136	0.219	0.123	0.055	0.680
H7CDF	100%	0.167	0.109	0.210	0.087	0.043	0.633
OCDF	100%	0.110	0.073	0.126	0.055	0.030	0.374
Total PCDF		0.951	0.735	0.908	0.642	0.363	2.959
TOTAL PCDD/PCDF		2.468	2.038	1.867	1.931	0.745	6.506
Concentration in toxic equivalent		0.046	0.038	0.037	0.035	0.017	0.125

PCDD/PCDF:

Statistics for Ontario station for winter 2000 (n = 7; December 1, 1999 to March 31, 2000) Units :  $pg/m^3$ , except for concentrations in toxic equivalent ( $pg TEQ/m^3$ )

Units :	pg/m, exce	pt for conce	entrations in	toxic equiv	alent (pg 1	EQ/III)	
	Detection Frequency	Mean	Geome- tric Mean	Standard Deviation	Median	Minimum	Maximum
2378-T4CDD	20%	0.002	0.002	0.001	0.002	< LD	0.003
12378-P5CDD	80%	0.007	0.005	0.004	0.007	< LD	0.010
123478-H6CDD	40%	0.007	0.004	0.007	0.003	< LD	0.017
123678-H6CDD	80%	0.014	0.009	0.010	0.013	< LD	0.028
123789-H6CDD	80%	0.018	0.010	0.020	0.011	< LD	0.052
1234678-H7CDD	100%	0.180	0.123	0.152	0.174	0.032	0.407
OCDD	100%	0.569	0.392	0.455	0.635	0.106	1.201
Total 7 PCDD		0.797	0.551	0.644	0.843	0.143	1.718
2378-T4CDF	100%	0.028	0.026	0.012	0.024	0.019	0.050
12378-P5CDF	60%	0.004	0.003	0.004	0.004	< LD	0.010
23478-P5CDF	100%	0.008	0.008	0.004	0.007	0.005	0.016
123478-H6CDF	100%	0.023	0.018	0.018	0.022	0.008	0.052
123678-H6CDF	80%	0.008	0.005	0.006	0.008	< LD	0.017
234678-H6CDF	80%	0.011	0.007	0.008	0.009	< LD	0.024
123789-H6CDF	0%	< LD	< LD	< LD	< LD	< LD	< LD
1234678-H7CDF	100%	0.059	0.049	0.039	0.051	0.024	0.115
1234789-H7CDF	20%	0.004	0.003	0.004	0.003	< LD	0.012
OCDF	100%	0.052	0.038	0.040	0.054	0.013	0.108
Total 10 PCDF		0.199	0.166	0.132	0.187	0.077	0.406
TOTAL 17		0.996	0.727	0.775	1.031	0.221	2.123
PCDD/PCDF							
T4CDD	40%	0.014	0.005	0.024	0.002	< LD	0.056
P5CDD	80%	0.027	0.013	0.029	0.015	< LD	0.072
H6CDD	100%	0.154	0.076	0.171	0.120	0.014	0.432
H7CDD	100%	0.396	0.264	0.357	0.380	0.074	0.954
OCDD	100%	0.569	0.392	0.455	0.635	0.106	1.201
Total PCDD		1.161	0.759	1.025	1.161	0.196	2.715
T4CDF	100%	0.152	0.127	0.104	0.112	0.059	0.317
P5CDF	100%	0.113	0.099	0.071	0.087	0.048	0.234
H6CDF	100%	0.112	0.097	0.067	0.109	0.045	0.221
H7CDF	100%	0.084	0.063	0.067	0.082	0.024	0.190
OCDF	100%	0.052	0.038	0.040	0.054	0.013	0.108
Total PCDF		0.513	0.438	0.338	0.452	0.219	1.070
TOTAL PCDD/PCDF		1.674	1.239	1.353	1.706	0.476	3.785
Concentration in toxic equivalent		0.026	0.022	0.016	0.024	0.009	0.051

Statistics for Ontario station for summer 2000 (n = 5; May 1st to September 30, 2000) Units : pg/m<sup>3</sup>, except for concentrations in toxic equivalent (pg TEQ/m<sup>3</sup>) PCDD/PCDF:

enne :	P8 ,	r		101111 11111	(r)	- ( )	1
	Detection Frequency	Mean	Geome- tric Mean	Standard Deviation	Median	Minimum	Maximum
2378-T4CDD	43%	0.002	0.001	0.002	0.001	< LD	0.012
12378-P5CDD	95%	0.013	0.009	0.012	0.007	< LD	0.049
123478-H6CDD	95%	0.020	0.014	0.018	0.013	< LD	0.066
123678-H6CDD	100%	0.033	0.024	0.028	0.016	0.006	0.104
123789-H6CDD	100%	0.051	0.035	0.050	0.026	0.006	0.194
1234678-H7CDD	100%	0.378	0.276	0.314	0.198	0.063	1.187
OCDD	100%	1.015	0.772	0.795	0.620	0.288	2.700
Total 7 PCDD		1.512	1.139	1.198	0.858	0.390	4.312
2378-T4CDF	100%	0.076	0.046	0.091	0.040	0.006	0.380
12378-P5CDF	90%	0.014	0.007	0.019	0.005	< LD	0.073
23478-P5CDF	95%	0.023	0.014	0.027	0.014	< LD	0.103
123478-H6CDF	100%	0.063	0.035	0.077	0.036	0.005	0.280
123678-H6CDF	100%	0.025	0.014	0.037	0.014	0.003	0.170
234678-H6CDF	100%	0.032	0.019	0.044	0.017	0.004	0.200
123789-H6CDF	62%	0.009	0.002	0.024	0.002	< LD	0.110
1234678-H7CDF	95%	0.083	0.056	0.084	0.062	< LD	0.380
1234789-H7CDF	90%	0.018	0.010	0.025	0.009	< LD	0.100
OCDF	100%	0.177	0.096	0.265	0.069	0.024	1.200
Total 10 PCDF		0.519	0.330	0.583	0.323	0.066	2.339
TOTAL 17		2.031	1.549	1.589	1.426	0.467	5.599
PCDD/PCDF							
TICDD	0.00/	0.075	0.025	0.007	0.022		0.222
14CDD	90%	0.065	0.025	0.096	0.023	< LD	0.322
PSCDD	100%	0.139	0.071	0.149	0.078	0.005	0.596
H6CDD	100%	0.423	0.276	0.407	0.197	0.036	1.500
H7CDD	100%	0.779	0.543	0.701	0.413	0.110	2.486
OCDD	100%	1.015	0.772	0.795	0.620	0.288	2.700
Total PCDD		2.422	1.749	2.069	1.573	0.468	7.604
TACDE	100%	0.277	0.163	0.205	0.180	0.017	1.015
PSCDF	100%	0.277	0.103	0.293	0.130	0.017	0.070
HCDE	100%	0.239	0.131	0.303	0.120	0.007	1 200
H7CDE	100%	0.244	0.144	0.153	0.100	0.029	0.640
OCDE	100%	0.101	0.110	0.155	0.129	0.019	1 200
Total PCDE	10070	1.118	0.090	1.205	0.009	0.024	1.200
		3 5 4 0	2 552	3.014	2 1 4 2	0.101	4.490
TOTAL FUDD/FUDF		3.340	2.332	3.014	2.143	0.030	10.043
Concentration in toxic equivalent		0.062	0.041	0.062	0.034	0.008	0.222

PCDD/PCDF:Statistics for Rivière-des-Prairies station for winter 2001<br/>(n = 21; December 1, 2000 to March 31, 2001)<br/>Units : pg/m³, except for concentrations in toxic equivalent (pg TEQ/m³)

Onto :	$p_{5}$ , $\mathbf{m}$ , exec			toxic equiv	utent (p5 1		1
	Detection	Mean	Geome-	Standard	Median	Minimum	Maximum
2378-T4CDD	26%	0.002	0 001	0.002	0.001	<ld< td=""><td>0.006</td></ld<>	0.006
12378-P5CDD	95%	0.002	0.001	0.002	0.007	<ld< td=""><td>0.000</td></ld<>	0.000
123478-H6CDD	79%	0.011	0.008	0.007	0.010	<ld< td=""><td>0.031</td></ld<>	0.031
123678-H6CDD	84%	0.019	0.000	0.007	0.017	<ld< td=""><td>0.031</td></ld<>	0.031
123789-H6CDD	89%	0.028	0.021	0.012	0.027	<ld< td=""><td>0.053</td></ld<>	0.053
1234678-H7CDD	100%	0.195	0.158	0.127	0.150	0.058	0.520
OCDD	100%	0.557	0.469	0.304	0.557	0.152	1 200
Total 7 PCDD	10070	0.820	0.690	0.459	0.770	0.240	1.864
2378-T4CDF	100%	0.046	0.037	0.032	0.045	0.013	0 140
12378-P5CDF	84%	0.008	0.006	0.007	0.008	<ld< td=""><td>0.032</td></ld<>	0.032
23478-P5CDF	95%	0.014	0.011	0.010	0.014	< LD	0.043
123478-H6CDF	100%	0.036	0.026	0.029	0.027	0.006	0.110
123678-H6CDF	95%	0.015	0.011	0.013	0.011	<ld< td=""><td>0.048</td></ld<>	0.048
234678-H6CDF	89%	0.018	0.013	0.016	0.015	< LD	0.067
123789-H6CDF	37%	0.003	0.002	0.003	0.002	<ld< td=""><td>0.010</td></ld<>	0.010
1234678-H7CDF	100%	0.064	0.051	0.077	0.036	0.000	0.290
1234789-H7CDF	63%	0.008	0.006	0.007	0.006	< LD	0.024
OCDF	95%	0.061	0.047	0.042	0.054	<ld< td=""><td>0.150</td></ld<>	0.150
Total 10 PCDF	,,,,	0.274	0.212	0.200	0.232	0.058	0.768
TOTAL 17	100%	1.094	0.917	0.630	0.964	0.298	2.631
PCDD/PCDF							
T4CDD	84%	0.037	0.019	0.040	0.022	< LD	0.160
P5CDD	100%	0.089	0.060	0.083	0.062	0.009	0.340
H6CDD	100%	0.231	0.159	0.178	0.170	0.023	0.720
H7CDD	100%	0.405	0.333	0.242	0.328	0.104	0.990
OCDD	100%	0.557	0.469	0.304	0.557	0.152	1.200
Total PCDD		1.319	1.064	0.824	1.074	0.330	3.410
T4CDF	100%	0.208	0.150	0.198	0.150	0.029	0.890
P5CDF	100%	0.143	0.101	0.105	0.158	0.008	0.440
H6CDF	100%	0.141	0.102	0.114	0.115	0.025	0.430
H7CDF	95%	0.088	0.050	0.080	0.075	< LD	0.320
OCDF	95%	0.062	0.048	0.042	0.054	< LD	0.150
Total PCDF		0.641	0.490	0.479	0.604	0.117	2.110
TOTAL PCDD/PCDF		1.960	1.580	1.275	1.677	0.508	5.520
Concentration in toxic equivalent		0.038	0.033	0.022	0.033	0.013	0.100

PCDD/PCDF: Statistics for Ontario station for winter 2001

(n = 19; December 1, 2000 to March 31, 2001)Units : pg/m<sup>3</sup>, except for concentrations in toxic equivalent (pg TEQ/m<sup>3</sup>)

0.1110 (	P8/ ,			tonie equit		L ( )	
	Detection Frequency	Mean	Geome- tric Mean	Standard Deviation	Median	Minimum	Maximum
2378-T4CDD	38%	0.001	0.001	0.0003	0.001	< LD	0.002
12378-P5CDD	100%	0.013	0.012	0.007	0.012	0.006	0.028
123478-H6CDD	75%	0.008	0.006	0.008	0.005	< LD	0.028
123678-H6CDD	100%	0.016	0.012	0.018	0.011	0.005	0.059
123789-H6CDD	100%	0.016	0.013	0.012	0.013	0.005	0.043
1234678-H7CDD	100%	0.134	0.106	0.121	0.081	0.059	0.418
OCDD	100%	0.308	0.262	0.210	0.224	0.129	0.750
Total 7 PCDD		0.496	0.416	0.370	0.342	0.213	1.327
2378-T4CDF	100%	0.017	0.016	0.007	0.018	0.009	0.030
12378-P5CDF	50%	0.003	0.002	0.004	0.002	< LD	0.012
23478-P5CDF	75%	0.006	0.004	0.004	0.006	< LD	0.011
123478-H6CDF	100%	0.016	0.014	0.011	0.013	0.005	0.037
123678-H6CDF	100%	0.013	0.010	0.011	0.010	0.004	0.040
234678-H6CDF	100%	0.012	0.009	0.011	0.008	0.004	0.037
123789-H6CDF	25%	0.003	0.002	0.003	0.002	< LD	0.010
1234678-H7CDF	100%	0.065	0.045	0.079	0.038	0.021	0.259
1234789-H7CDF	25%	0.005	0.003	0.008	0.002	< LD	0.026
OCDF	100%	0.055	0.038	0.055	0.034	0.014	0.178
Total 10 PCDF		0.194	0.151	0.181	0.147	0.067	0.628
TOTAL 17		0.691	0.573	0.544	0.497	0.280	1.955
PCDD/PCDF							
	1000/	0.024	0.021	0.012	0.022	0.010	0.052
I4CDD P5CDD	100%	0.024	0.021	0.013	0.022	0.010	0.033
	100%	0.070	0.002	0.042	0.004	0.050	0.104
	100%	0.100	0.134	0.122	0.120	0.033	0.448
	100%	0.232	0.203	0.210	0.139	0.113	0.739
Total PCDD	10070	0.308	0.202	0.210	0.224	0.129	0.730
		0.815	0.095	0.375	0.392	0.342	2.131
T4CDF	100%	0.179	0.167	0.070	0.180	0.097	0.284
P5CDF	100%	0.234	0.189	0.189	0.179	0.096	0.667
H6CDF	100%	0.212	0.158	0.221	0.141	0.064	0.747
H7CDF	100%	0.092	0.060	0.199	0.053	0.021	0.383
OCDF	100%	0.055	0.038	0.055	0.034	0.014	0.178
Total PCDF		0.772	0.637	0.612	0.590	0.296	2.211
TOTAL PCDD/PCDF		1.585	1.357	1.152	1.300	0.638	4.342
	1		I	I		1	1
Concentration in toxic equivalent		0.029	0.026	0.017	0.026	0.012	0.069

 

 PCDD/PCDF:
 Statistics for Rivière-des-Prairies station for summer 2000 (n = 8; May 1st to September 30, 2001) Units : pg/m³, except for concentrations in toxic equivalent (pg TEQ/m³)

Units .	pg/m, exce	pt for conce	entrations in	toxic equiv	alent (pg 1	EQ/III )	
	Detection Frequency	Mean	Geome- tric Mean	Standard Deviation	Median	Minimum	Maximum
2378-T4CDD	22%	0.001	0.001	0.001	0.001	< LD	0.003
12378-P5CDD	89%	0.008	0.007	0.004	0.007	< LD	0.016
123478-H6CDD	33%	0.003	0.003	0.002	0.003	< LD	0.007
123678-H6CDD	67%	0.006	0.005	0.004	0.005	< LD	0.013
123789-H6CDD	78%	0.008	0.006	0.005	0.005	< LD	0.016
1234678-H7CDD	100%	0.066	0.061	0.029	0.056	0.041	0.127
OCDD	100%	0.226	0.214	0.081	0.201	0.140	0.378
Total 7 PCDD		0.318	0.300	0.121	0.298	0.196	0.559
2378-T4CDF	100%	0.021	0.019	0.011	0.019	0.009	0.045
12378-P5CDF	56%	0.003	0.003	0.003	0.003	< LD	0.010
23478-P5CDF	89%	0.006	0.005	0.004	0.004	< LD	0.015
123478-H6CDF	100%	0.011	0.010	0.005	0.011	0.006	0.021
123678-H6CDF	78%	0.006	0.005	0.003	0.004	< LD	0.011
234678-H6CDF	56%	0.005	0.004	0.004	0.004	< LD	0.012
123789-H6CDF	22%	0.002	0.002	0.002	0.002	< LD	0.004
1234678-H7CDF	100%	0.030	0.026	0.015	0.021	0.014	0.056
1234789-H7CDF	33%	0.004	0.003	0.003	0.002	< LD	0.010
OCDF	100%	0.033	0.031	0.013	0.034	0.016	0.055
Total 10 PCDF		0.121	0.111	0.058	0.089	0.071	0.239
TOTAL 17		0.439	0.412	0.177	0.419	0.267	0.798
PCDD/PCDF							
TICDD	700/	0.015	0.000	0.010	0.015	. I D	0.020
14CDD	/8%	0.015	0.008	0.012	0.015	< LD	0.030
PSCDD	100%	0.034	0.028	0.018	0.033	0.009	0.058
H6CDD	100%	0.063	0.052	0.035	0.067	0.011	0.110
H7CDD	100%	0.138	0.125	0.071	0.111	0.079	0.298
OCDD	100%	0.226	0.214	0.081	0.201	0.140	0.378
Total PCDD		0.475	0.440	0.203	0.431	0.240	0.874
	1000/			0.110	0.110		0.404
T4CDF	100%	0.147	0.123	0.113	0.110	0.052	0.431
PSCDF	100%	0.088	0.077	0.054	0.081	0.031	0.221
H6CDF	100%	0.072	0.065	0.035	0.066	0.024	0.144
H7CDF	100%	0.045	0.039	0.027	0.035	0.017	0.099
OCDF	100%	0.033	0.031	0.013	0.034	0.016	0.055
Total PCDF		0.386	0.340	0.232	0.351	0.157	0.950
TOTAL PCDD/PCDF		0.861	0.782	0.428	0.782	0.397	1.824
	1						
Concentration in toxic equivalent		0.020	0.018	0.010	0.015	0.012	0.041

Statistics for Ontario station for summer 2001 (n = 9; May 1st to September 30, 2001) Units : pg/m<sup>3</sup>, except for concentrations in toxic equivalent (pg TEQ/m<sup>3</sup>) PCDD/PCDF:

	FØ , = = =	1		1	. U U		
	Detection	Mean	Geome-	Standard	Median	Minimum	Maximum
	Frequency		tric Mean	Deviation			
2378-T4CDD	88%	0.002	0.002	0.001	0.002	< LD	0.005
12378-P5CDD	100%	0.012	0.011	0.005	0.011	0.008	0.023
123478-H6CDD	100%	0.011	0.011	0.005	0.010	0.007	0.021
123678-H6CDD	100%	0.019	0.017	0.008	0.016	0.012	0.036
123789-H6CDD	100%	0.032	0.030	0.016	0.027	0.019	0.066
1234678-H7CDD	100%	0.249	0.231	0.119	0.209	0.168	0.514
OCDD	100%	0.750	0.703	0.295	0.618	0.478	1.173
Total 7 PCDD		1.076	1.011	0.421	0.889	0.698	1.839
2378-T4CDF	100%	0.038	0.034	0.019	0.042	0.014	0.073
12378-P5CDF	100%	0.008	0.007	0.004	0.007	0.002	0.014
23478-P5CDF	100%	0.015	0.012	0.008	0.016	0.004	0.024
123478-H6CDF	100%	0.032	0.026	0.019	0.036	0.006	0.063
123678-H6CDF	100%	0.013	0.012	0.006	0.013	0.004	0.024
234678-H6CDF	100%	0.017	0.015	0.008	0.017	0.004	0.028
123789-H6CDF	38%	0.001	0.001	0.0004	0.001	< LD	0.002
1234678-H7CDF	100%	0.065	0.059	0.027	0.064	0.019	0.115
1234789-H7CDF	100%	0.007	0.006	0.004	0.008	0.002	0.016
OCDF	100%	0.056	0.054	0.018	0.053	0.030	0.085
Total 10 PCDF		0.253	0.231	0.102	0.260	0.086	0.407
TOTAL 17	100%	1.329	1.267	0.445	1.265	0.857	2.140
PCDD/PCDF							
T4CDD	100%	0.056	0.050	0.030	0.051	0.025	0.112
P5CDD	100%	0.124	0.109	0.066	0.118	0.051	0.248
H6CDD	100%	0.293	0.265	0.154	0.252	0.153	0.615
H7CDD	100%	0.479	0.440	0.241	0.393	0.302	1.005
OCDD	100%	0.750	0.703	0.295	0.618	0.478	1.173
Total PCDD		1.702	1.595	0.707	1.517	1.063	3.154
T4CDF	100%	0.233	0.214	0.093	0.238	0.084	0.406
P5CDF	100%	0.167	0.153	0.066	0.176	0.053	0.254
H6CDF	100%	0.163	0.148	0.062	0.164	0.043	0.257
H7CDF	100%	0.109	0.101	0.039	0.112	0.039	0.176
OCDF	100%	0.056	0.054	0.018	0.053	0.030	0.085
Total PCDF		0.728	0.677	0.250	0.767	0.249	1.016
TOTAL PCDD/PCDF		2.431	2.307	0.864	2.306	1.365	4.150
Concentration in toxic equivalent		0.042	0.039	0.017	0.044	0.021	0.072

PCDD/PCDF:Statistics for Rivière-des-Prairies station for winter 2002<br/>(n = 8; December 1, 2001 to March 31, 2002)<br/>Units : pg/m³, except for concentrations in toxic equivalent (pg TEQ/m³)

01118 :	$p_{\mathbf{S}}$ , $\mathbf{m}$ , exce			i toxic equiv	arent (pg 1		1
	Detection	Mean	Geome-	Standard	Median	Minimum	Maximum
	Frequency		tric Mean	Deviation			
2378-T4CDD	100%	0.003	0.002	0.003	0.002	0.001	0.008
12378-P5CDD	100%	0.012	0.011	0.007	0.010	0.005	0.025
123478-H6CDD	100%	0.012	0.010	0.008	0.010	0.004	0.024
123678-H6CDD	100%	0.020	0.017	0.013	0.016	0.007	0.040
123789-H6CDD	100%	0.032	0.024	0.027	0.016	0.011	0.072
1234678-H7CDD	100%	0.276	0.238	0.163	0.245	0.109	0.534
OCDD	100%	0.997	0.866	0.526	1.043	0.304	1.886
Total 7 PCDD		1.353	1.184	0.712	1.369	0.451	2.589
2378-T4CDF	100%	0.047	0.041	0.030	0.038	0.020	0.109
12378-P5CDF	100%	0.010	0.008	0.006	0.008	0.004	0.018
23478-P5CDF	100%	0.015	0.013	0.008	0.014	0.006	0.026
123478-H6CDF	100%	0.034	0.029	0.016	0.039	0.010	0.054
123678-H6CDF	100%	0.014	0.012	0.007	0.013	0.005	0.022
234678-H6CDF	100%	0.017	0.014	0.008	0.019	0.004	0.027
123789-H6CDF	29%	0.001	0.001	0.001	0.001	< LD	0.003
1234678-H7CDF	100%	0.064	0.058	0.025	0.073	0.021	0.088
1234789-H7CDF	100%	0.010	0.008	0.006	0.008	0.003	0.020
OCDF	100%	0.073	0.067	0.032	0.065	0.028	0.119
Total 10 PCDF		0.285	0.257	0.119	0.337	0.101	0.412
TOTAL 17		1.637	1.446	0.819	1.706	0.552	3.001
PCDD/PCDF							
TICDD	1000/	0.070	0.0(0	0.040	0.056	0.020	0.1.40
14CDD	100%	0.072	0.062	0.042	0.056	0.029	0.142
PSCDD	100%	0.130	0.106	0.089	0.107	0.039	0.295
H6CDD	100%	0.330	0.262	0.238	0.261	0.090	0.740
H7CDD	100%	0.538	0.455	0.338	0.436	0.199	1.098
OCDD	100%	0.997	0.866	0.526	1.043	0.304	1.886
Total PCDD		2.068	1.793	1.168	1.991	0.709	4.161
T4CDF	100%	0.291	0.257	0.159	0.218	0.128	0.536
PSCDF	100%	0.291	0.257	0.139	0.218	0.128	0.330
H6CDF	100%	0.165	0.139	0.097	0.102	0.062	0.344
H7CDF	100%	0.105	0.145	0.000	0.133	0.040	0.202
OCDE	100%	0.117	0.100	0.040	0.134	0.042	0.100
Total DCDE	10070	0.073	0.007	0.032	0.005	0.020	1 107
		2 805	2 551	1 497	2 9 2 2	1.025	5 270
TOTAL FUDD/FUDF		2.093	2.331	1.40/	2.032	1.035	3.370
Concentration in toxic equivalent		0.044	0.039	0.025	0.039	0.019	0.088

PCDD/PCDF: Statistics for Ontario station for winter 2002

(n = 7; December 1, 2001 to March 31, 2002)Units : pg/m<sup>3</sup>, except for concentrations in toxic equivalent (pg TEQ/m<sup>3</sup>)

Station :	RDP				RDP				Ontario					Ontario						
Period :	W	inter 2	2001 a	nd 200	2	Su	mmer	2001 :	and 20	02	Wi	nter 2	001 ar	nd 200	2	Su	mmer	2001	and 2	002
<b>Substance</b> <sup>1</sup> ( $\mu$ g/m <sup>3</sup> )	n	$\mu^2$	δ	Min	Max	n	μ	δ	Min	Max	n	μ	δ	Min	Max	n	μ	δ	Min	Max
Ethane	34	3.85	1.51	2.26	8.78	41	1.69	0.61	0.83	3.13	37	3.89	1.00	2.57	7.10	45	2.04	0.62	0.93	3.64
Propane	34	3.99	2.71	1.32	12.7	41	3.95	6.05	0.44	27.3	37	4.27	2.37	1.53	11.4	45	2.05	1.16	0.74	5.72
Butane	34	4.78	4.98	1.08	23.4	41	2.76	3.25	0.40	15.6	37	7.79	4.54	1.84	18.0	45	2.80	1.58	0.88	7.63
Isobutane	34	3.92	4.42	0.80	20.0	41	1.90	2.08	0.23	8.39	37	7.05	4.50	1.36	17.1	45	1.90	1.15	0.70	5.87
Cyclopentane	34	0.23	0.26	0.05	1.31	41	0.23	0.24	0.05	1.19	37	0.34	0.17	0.11	0.84	45	0.29	0.15	0.14	0.79
Pentane	34	1.77	1.82	0.51	9.52	41	1.67	1.78	0.33	8.72	37	2.53	1.25	0.82	5.71	45	1.96	0.97	0.85	4.82
Isopentane	34	4.13	4.63	0.93	23.3	41	4.24	5.02	0.67	26.6	37	6.17	3.38	1.52	14.6	45	4.99	2.83	2.27	15.9
2,2-Dimethylpropane	34	0.05	0.02	0.02	0.12	41	0.04	0.02	0.02	0.10	37	0.06	0.02	0.03	0.11	45	0.04	0.01	0.02	0.07
Cyclohexane	34	0.24	0.23	0.06	1.19	41	0.17	0.17	0.04	0.79	37	0.38	0.23	0.12	1.06	45	0.24	0.14	0.10	0.84
Methylcyclopentane	34	0.66	0.88	0.14	4.42	41	0.45	0.46	0.10	2.31	37	0.91	0.47	0.29	2.15	45	0.59	0.30	0.28	1.65
2,2-Dimethylbutane	34	0.32	0.27	0.10	1.21	41	0.28	0.24	0.09	1.19	37	0.52	0.27	0.19	1.25	45	0.42	0.25	0.18	1.42
2,3-Dimethylbutane	34	0.31	0.35	0.05	1.61	41	0.30	0.29	0.07	1.46	37	0.49	0.27	0.16	1.27	45	0.41	0.19	0.22	1.08
3-Methylpentane	34	0.93	0.97	0.22	4.51	36	0.83	0.88	0.22	4.10	36	1.43	0.72	0.49	3.29	38	1.16	0.58	0.31	2.85
2-Methylpentane	30	1.49	1.48	0.34	6.56	40	1.32	1.28	0.33	6.36	34	2.10	1.04	0.73	5.14	45	1.77	0.82	0.91	4.39
Hexane	34	1.35	3.14	0.22	18.5	32	0.68	0.70	0.14	3.30	37	1.26	0.67	0.30	3.06	31	0.86	0.48	0.38	2.40
Methylcyclohexane	34	0.29	0.34	0.06	1.80	41	0.25	0.22	0.05	1.09	37	0.52	0.34	0.13	1.45	45	0.30	0.20	0.11	1.09
2,2,3-Trimethylbutane	34	0.01	0.01	0.00	0.05	41	0.01	0.01	0.00	0.03	37	0.01	0.01	0.00	0.04	45	0.01	0.01	0.00	0.03
3-Methylheptane	34	0.22	0.21	0.05	0.91	41	0.14	0.10	0.04	0.51	37	0.33	0.15	0.13	0.70	45	0.23	0.12	0.11	0.76
2-Methylheptane	34	0.22	0.22	0.05	0.98	41	0.15	0.10	0.05	0.53	37	0.32	0.14	0.12	0.67	45	0.23	0.12	0.10	0.71
4-Methylheptane	34	0.09	0.09	0.02	0.37	41	0.06	0.04	0.01	0.21	37	0.13	0.06	0.05	0.28	45	0.09	0.05	0.04	0.27
Heptane	34	0.49	0.47	0.12	2.25	41	0.35	0.26	0.10	1.34	37	0.72	0.37	0.29	1.83	45	0.42	0.21	0.19	1.21
3-Methylhexane	34	0.59	0.56	0.13	2.64	41	0.40	0.33	0.10	1.59	37	0.87	0.39	0.31	1.84	45	0.57	0.25	0.29	1.57
2,2-Dimethylpentane	34	0.05	0.04	0.02	0.16	41	0.03	0.02	0.01	0.09	37	0.07	0.03	0.04	0.15	45	0.04	0.01	0.02	0.10
2,4-Dimethylpentane	34	0.13	0.12	0.03	0.56	41	0.09	0.06	0.02	0.31	37	0.19	0.09	0.08	0.45	45	0.12	0.05	0.06	0.30
2,3-Dimethylpentane	34	0.23	0.20	0.05	0.92	41	0.15	0.11	0.05	0.52	37	0.32	0.14	0.13	0.71	45	0.21	0.08	0.11	0.49
2-Methylhexane	34	0.53	0.50	0.13	2.38	41	0.37	0.31	0.09	1.51	37	0.79	0.36	0.30	1.63	45	0.54	0.24	0.29	1.50
cis-1,4/t-1,3-																				
Dimethylcyclohexane	34	0.04	0.03	0.01	0.17	41	0.03	0.02	0.01	0.13	37	0.05	0.02	0.02	0.10	45	0.05	0.04	0.02	0.21
cis-1,3-Dimethylcyclohexane	34	0.08	0.08	0.02	0.43	41	0.09	0.07	0.02	0.38	37	0.11	0.05	0.04	0.26	45	0.12	0.09	0.04	0.55

Appendix 3 : Summary of Statistical Results of Non-polar VOCs at RDP and Ontario St Stations

<b>Substance</b> <sup>1</sup>	n	$\mu^2$	δ	Min	Max	n	μ	δ	Min	Max	n	μ	δ	Min	Max	n	μ	δ	Min	Max
cis-1,2-Dimethylcyclohexane	34	0.04	0.02	0.01	0.12	41	0.04	0.01	0.02	0.09	37	0.05	0.02	0.02	0.09	45	0.04	0.02	0.02	0.14
trans-1,4-DiMEcyclohexane	34	0.04	0.04	0.01	0.21	41	0.04	0.03	0.01	0.17	37	0.05	0.03	0.02	0.12	45	0.05	0.04	0.01	0.25
trans-1,2-DiMEcyclohexane	32	0.05	0.07	0.00	0.35	41	0.04	0.04	0.00	0.17	35	0.06	0.04	0.02	0.20	45	0.05	0.11	0.00	0.72
2,2,4-Trimethylpentane	34	0.37	0.40	0.07	1.75	41	0.26	0.17	0.07	0.85	37	0.48	0.24	0.16	1.27	45	0.32	0.16	0.11	0.77
2,2-Dimethylhexane	34	0.03	0.02	0.01	0.09	41	0.02	0.01	0.01	0.06	37	0.04	0.01	0.02	0.08	45	0.03	0.01	0.01	0.07
Octane	34	0.22	0.23	0.06	1.17	41	0.18	0.14	0.05	0.71	37	0.29	0.14	0.10	0.70	45	0.23	0.15	0.10	0.86
2,4-Dimethylhexane	34	0.13	0.12	0.03	0.53	41	0.08	0.05	0.03	0.24	37	0.17	0.07	0.07	0.36	45	0.11	0.05	0.04	0.27
2,5-Dimethylhexane	34	0.09	0.09	0.02	0.38	41	0.06	0.04	0.02	0.17	37	0.13	0.06	0.04	0.28	45	0.08	0.03	0.04	0.20
2,3,4-Trimethylpentane	34	0.14	0.14	0.03	0.62	41	0.12	0.07	0.03	0.39	37	0.19	0.13	0.07	0.83	45	0.12	0.05	0.05	0.26
2,2,5-Trimethylhexane	34	0.05	0.04	0.01	0.19	41	0.08	0.08	0.01	0.47	37	0.05	0.05	0.02	0.35	45	0.03	0.01	0.02	0.06
Nonane	34	0.20	0.23	0.04	1.22	41	0.18	0.14	0.03	0.65	37	0.27	0.14	0.08	0.71	45	0.25	0.16	0.10	0.77
3,6-Dimethyloctane	34	0.03	0.03	0.01	0.15	41	0.03	0.02	0.00	0.07	37	0.04	0.02	0.01	0.12	45	0.03	0.02	0.01	0.07
Decane	34	0.24	0.26	0.05	1.31	41	0.23	0.19	0.04	0.87	37	0.40	0.22	0.08	0.93	45	0.36	0.23	0.14	1.20
Undecane	34	0.19	0.20	0.04	1.01	41	0.17	0.13	0.03	0.59	37	0.38	0.22	0.05	0.92	45	0.26	0.15	0.10	0.78
Dodecane	34	0.13	0.10	0.03	0.47	41	0.12	0.06	0.03	0.30	37	0.26	0.14	0.03	0.62	45	0.19	0.10	0.07	0.50
Total Alkanes	34	32.7	30.8	10.6	144	41	24.0	22.7	5.83	106	37	46.2	22.5	15.0	107	45	26.2	12.13	13.2	67.2
Acetylene	34	3.04	2.41	0.83	11.1	41	0.79	0.45	0.29	2.36	37	3.99	2.23	1.41	10.3	45	1.38	0.58	0.62	2.87
Ethylene	34	4.44	5.48	1.20	32.5	41	1.93	3.59	0.54	23.6	37	4.31	1.92	1.81	9.73	45	2.54	0.89	1.30	4.82
1-Propyne	34	0.17	0.14	0.00	0.67	41	0.07	0.05	0.00	0.21	37	0.19	0.07	0.08	0.37	45	0.12	0.04	0.06	0.26
Propylene	34	1.31	1.07	0.39	5.15	41	0.61	0.43	0.21	2.28	37	1.54	0.78	0.53	3.54	45	1.00	0.44	0.43	2.25
1,3-Butadiene	34	0.26	0.20	0.08	1.02	41	0.11	0.06	0.03	0.31	37	0.32	0.12	0.15	0.61	45	0.23	0.09	0.10	0.55
1-Butyne	34	0.03	0.01	0.00	0.07	41	0.02	0.01	0.00	0.03	37	0.03	0.01	0.00	0.05	45	0.02	0.01	0.00	0.04
1-Butene/Isobutene	34	0.93	0.87	0.29	3.83	41	0.53	0.43	0.19	1.97	37	1.46	0.75	0.51	3.61	45	0.69	0.25	0.35	1.42
trans-2-Butene	34	0.34	0.43	0.07	2.11	41	0.22	0.29	0.05	1.35	37	0.67	0.39	0.16	1.65	45	0.31	0.16	0.16	0.96
cis-2-Butene	34	0.30	0.38	0.06	1.93	41	0.22	0.28	0.05	1.34	37	0.57	0.32	0.15	1.35	45	0.30	0.16	0.16	0.94
Cyclopentene	34	0.07	0.05	0.02	0.22	41	0.06	0.05	0.01	0.23	37	0.11	0.04	0.04	0.22	45	0.11	0.04	0.06	0.23
Isoprene	34	0.14	0.10	0.05	0.49	41	0.57	0.61	0.05	2.72	37	0.22	0.09	0.10	0.44	45	0.42	0.26	0.09	1.27
trans-2-Pentene	34	0.21	0.25	0.05	1.33	41	0.21	0.25	0.05	1.29	37	0.37	0.18	0.11	0.78	45	0.33	0.18	0.14	1.06
2-Methyl-1-butene	34	0.27	0.24	0.07	1.19	41	0.33	0.34	0.09	1.81	37	0.40	0.19	0.11	0.90	45	0.43	0.18	0.20	1.08
cis-2-Pentene	34	0.16	0.18	0.03	0.94	41	0.14	0.15	0.04	0.77	37	0.26	0.13	0.07	0.59	45	0.21	0.10	0.09	0.62
1-Pentene	34	0.19	0.17	0.06	0.90	41	0.20	0.16	0.07	0.83	37	0.27	0.11	0.12	0.53	45	0.25	0.10	0.13	0.64
2-Methyl-2-butene	34	0.31	0.43	0.06	2.23	41	0.22	0.26	0.04	1.32	37	0.53	0.35	0.11	1.38	45	0.39	0.21	0.16	1.29

<b>Substance</b> <sup>1</sup>	n	$\mu^2$	δ	Min	Max	n	μ	δ	Min	Max	n	μ	δ	Min	Max	n	μ	δ	Min	Max
3-Methyl-1-butene	18	0.05	0.04	0.02	0.18	41	0.07	0.07	0.01	0.36	21	0.09	0.04	0.04	0.18	45	0.10	0.05	0.04	0.29
Cyclohexene	34	0.04	0.02	0.00	0.09	41	0.03	0.01	0.00	0.07	37	0.06	0.02	0.03	0.10	45	0.04	0.01	0.03	0.07
1-Methylcyclopentene	34	0.08	0.06	0.03	0.27	41	0.05	0.03	0.01	0.14	37	0.13	0.05	0.04	0.29	45	0.09	0.04	0.04	0.23
2-Ethyl-1-Butene	34	0.06	0.05	0.00	0.26	41	0.08	0.08	0.00	0.40	37	0.13	0.08	0.02	0.36	45	0.17	0.08	0.07	0.44
cis-2-Hexene	34	0.05	0.05	0.00	0.22	41	0.04	0.02	0.01	0.11	37	0.08	0.04	0.03	0.19	45	0.05	0.02	0.03	0.12
1-Hexene	34	0.34	0.70	0.06	4.13	39	0.23	0.59	0.04	3.82	37	0.24	0.10	0.09	0.54	41	0.18	0.13	0.06	0.89
3-Methyl-1-pentene	34	0.03	0.03	0.01	0.14	41	0.03	0.02	0.00	0.10	37	0.05	0.02	0.02	0.10	45	0.04	0.01	0.02	0.09
trans-4-Methyl-2-pentene	34	0.01	0.01	0.00	0.05	41	0.01	0.01	0.00	0.05	37	0.01	0.01	0.00	0.04	45	0.02	0.01	0.00	0.05
cis-4-Methyl-2-pentene	34	0.02	0.04	0.00	0.19	41	0.02	0.04	0.00	0.15	36	0.03	0.04	0.00	0.13	45	0.04	0.04	0.00	0.16
4-Methyl-1-pentene	34	0.03	0.03	0.00	0.13	41	0.03	0.02	0.00	0.07	37	0.04	0.02	0.00	0.10	45	0.03	0.01	0.00	0.07
trans-3-Methyl-2-pentene	34	0.04	0.05	0.00	0.21	41	0.03	0.02	0.01	0.10	37	0.07	0.04	0.00	0.19	45	0.05	0.02	0.03	0.13
trans-2-Hexene	34	0.06	0.06	0.02	0.28	41	0.04	0.03	0.01	0.14	37	0.10	0.04	0.04	0.22	45	0.08	0.03	0.04	0.21
cis-3-Methyl-2-pentene	34	0.05	0.05	0.01	0.25	41	0.03	0.02	0.01	0.09	37	0.08	0.04	0.02	0.22	45	0.05	0.02	0.02	0.11
1-Methylcyclohexene	34	0.05	0.02	0.01	0.11	41	0.04	0.02	0.00	0.08	37	0.07	0.02	0.03	0.11	45	0.04	0.01	0.02	0.09
cis-2-Heptene	34	0.04	0.03	0.01	0.11	41	0.02	0.01	0.00	0.05	37	0.05	0.02	0.02	0.09	45	0.03	0.01	0.01	0.05
trans-3-Heptene	34	0.02	0.01	0.00	0.04	41	0.02	0.01	0.01	0.04	37	0.03	0.01	0.00	0.07	45	0.03	0.01	0.01	0.05
1-Heptene	34	0.11	0.13	0.00	0.54	41	0.05	0.05	0.00	0.17	37	0.14	0.13	0.00	0.47	45	0.06	0.07	0.00	0.25
cis-3-Heptene	12	0.07	0.06	0.02	0.26	16	0.08	0.07	0.02	0.25	13	0.16	0.13	0.04	0.43	25	0.12	0.07	0.04	0.34
trans-2-Heptene	34	0.03	0.03	0.01	0.11	41	0.01	0.01	0.00	0.04	37	0.04	0.02	0.02	0.09	45	0.02	0.01	0.01	0.05
1-Octene	34	0.04	0.03	0.01	0.14	41	0.03	0.03	0.00	0.20	37	0.04	0.01	0.02	0.07	45	0.02	0.01	0.00	0.07
trans-2-Octene	14	0.04	0.04	0.01	0.15	16	0.08	0.08	0.01	0.28	15	0.07	0.04	0.03	0.16	25	0.09	0.09	0.02	0.41
1-Nonene	34	0.03	0.03	0.00	0.10	41	0.03	0.03	0.00	0.11	37	0.03	0.03	0.00	0.09	45	0.02	0.03	0.00	0.13
1-Decene	34	0.04	0.04	0.00	0.19	41	0.02	0.03	0.00	0.09	37	0.05	0.04	0.00	0.17	45	0.02	0.02	0.00	0.08
1-Undecene	18	0.02	0.01	0.00	0.04	41	0.01	0.02	0.00	0.07	21	0.18	0.65	0.00	3.00	45	0.02	0.03	0.00	0.20
Total Alkenes & Alkynes	34	13.4	12.6	4.4	67.6	41	7.23	6.03	2.61	33.7	37	16.9	7.48	7.21	38.0	45	10.0	3.48	5.64	21.2
Freon11	34	1.71	0.16	1.35	1.97	41	1.84	0.23	1.43	2.49	37	1.79	0.29	1.35	3.08	45	1.86	0.21	1.50	2.27
Dibromomethane	34	0.09	0.03	0.02	0.14	41	0.09	0.03	0.02	0.13	37	0.10	0.02	0.06	0.13	45	0.08	0.02	0.05	0.12
Carbontetrachloride	34	0.66	0.06	0.53	0.75	41	0.64	0.06	0.53	0.88	37	0.68	0.06	0.59	0.79	45	0.64	0.05	0.51	0.73
Dibromochloromethane	34	0.06	0.02	0.00	0.08	41	0.05	0.02	0.01	0.09	37	0.06	0.01	0.02	0.08	45	0.05	0.01	0.03	0.08
Bromoform	34	0.06	0.02	0.02	0.11	41	0.05	0.01	0.01	0.07	37	0.06	0.01	0.03	0.10	44	0.05	0.01	0.03	0.08
Bromodichloromethane	34	0.09	0.03	0.03	0.15	41	0.08	0.03	0.02	0.15	37	0.11	0.03	0.07	0.19	45	0.10	0.03	0.05	0.18
Chloroform	34	0.13	0.03	0.08	0.19	41	0.20	0.08	0.09	0.49	37	0.15	0.03	0.08	0.21	45	0.15	0.05	0.07	0.28

<b>Substance</b> <sup>1</sup>	n	$\mu^2$	δ	Min	Max	n	μ	δ	Min	Max	n	μ	δ	Min	Max	n	μ	δ	Min	Max
Chloromethane	34	1.15	0.08	1.00	1.35	41	1.18	0.12	0.95	1.64	37	1.17	0.11	0.90	1.40	45	1.14	0.11	0.97	1.49
Dichloromethane	34	0.92	1.59	0.24	9.08	41	0.88	0.83	0.23	4.30	37	1.53	1.17	0.32	6.88	45	1.49	1.01	0.47	5.96
Bromomethane	34	0.13	0.03	0.05	0.16	41	0.14	0.03	0.07	0.19	37	0.14	0.02	0.08	0.20	45	0.22	0.57	0.09	3.96
Bromotrichloromethane	8	0.01	0.01	0.00	0.01	0			0.00	0.00	8	0.01	0.01	0.00	0.02	0			0.00	0.00
cis-1,2-Dichloroethylene	34	0.04	0.01	0.00	0.05	37	0.03	0.01	0.00	0.05	37	0.03	0.01	0.01	0.05	39	0.03	0.01	0.00	0.05
Ethylbromide	34	0.03	0.01	0.00	0.04	41	0.03	0.01	0.00	0.05	37	0.03	0.01	0.01	0.04	45	0.02	0.01	0.00	0.04
Tetrachloroethylene	34	0.43	0.53	0.10	3.03	41	0.38	0.32	0.08	1.74	37	0.60	0.30	0.19	1.46	45	0.52	0.31	0.14	1.81
Chloroethane	34	0.09	0.06	0.02	0.32	41	0.08	0.05	0.03	0.32	37	0.09	0.05	0.05	0.35	45	0.08	0.03	0.05	0.23
Trichloroethylene	34	0.18	0.17	0.05	0.94	41	0.19	0.18	0.04	1.09	37	0.23	0.11	0.08	0.49	45	0.17	0.12	0.05	0.71
EDB	34	0.05	0.02	0.00	0.08	41	0.05	0.02	0.00	0.08	37	0.06	0.02	0.03	0.08	45	0.04	0.01	0.01	0.07
trans-1,2-Dichloroethylene	34	0.03	0.01	0.00	0.04	41	0.03	0.01	0.00	0.05	37	0.03	0.01	0.01	0.05	45	0.03	0.01	0.01	0.05
1,2-Dichloroethane	34	0.08	0.01	0.04	0.10	41	0.06	0.01	0.03	0.07	37	0.08	0.01	0.07	0.11	45	0.06	0.01	0.05	0.09
1,1-Dichloroethane	34	0.03	0.01	0.00	0.05	41	0.03	0.01	0.00	0.05	37	0.04	0.01	0.01	0.05	45	0.03	0.01	0.01	0.05
1,1,2-Trichloroethane	34	0.04	0.01	0.00	0.05	41	0.04	0.01	0.00	0.06	37	0.04	0.01	0.02	0.06	45	0.03	0.01	0.00	0.06
Freon114	34	0.21	0.03	0.11	0.25	41	0.21	0.03	0.12	0.26	37	0.22	0.03	0.15	0.30	45	0.21	0.03	0.16	0.28
1,1-Dichloroethylene	34	0.06	0.02	0.00	0.09	41	0.05	0.02	0.00	0.09	37	0.06	0.02	0.02	0.10	45	0.05	0.01	0.02	0.09
Vinylchloride	34	0.02	0.01	0.00	0.04	41	0.02	0.01	0.00	0.03	37	0.02	0.01	0.01	0.03	45	0.02	0.01	0.00	0.03
1,1,1-Trichloroethane	34	0.44	0.17	0.27	1.20	41	0.43	0.38	0.30	2.77	37	0.30	0.05	0.24	0.53	45	0.26	0.04	0.19	0.47
1,1,2,2-Tetrachloroethane	34	0.05	0.02	0.00	0.07	41	0.05	0.02	0.00	0.08	37	0.06	0.01	0.03	0.08	45	0.04	0.01	0.02	0.07
trans-1,3-Dichloropropene	34	0.01	0.01	0.00	0.02	41	0.01	0.01	0.00	0.04	36	0.02	0.01	0.00	0.03	45	0.01	0.01	0.00	0.02
1,2-Dichloropropane	34	0.04	0.01	0.00	0.06	41	0.03	0.01	0.00	0.06	37	0.04	0.01	0.00	0.06	45	0.03	0.01	0.00	0.05
cis-1,3-Dichloropropene	34	0.00	0.00	0.00	0.01	41	0.00	0.00	0.00	0.01	37	0.00	0.00	0.00	0.01	45	0.00	0.00	0.00	0.01
Hexachlorobutadiene	34	0.01	0.02	0.00	0.06	41	0.02	0.03	0.00	0.07	37	0.01	0.02	0.00	0.06	45	0.01	0.02	0.00	0.06
1,4-Dichlorobutane	34	0.01	0.02	0.00	0.06	41	0.01	0.02	0.00	0.10	37	0.01	0.02	0.00	0.05	45	0.01	0.01	0.00	0.03
Chlorobenzene	34	0.04	0.01	0.01	0.06	41	0.04	0.01	0.01	0.06	37	0.00	0.01	0.00	0.04	45	0.01	0.02	0.00	0.06
1,3-Dichlorobenzene	34	0.04	0.02	0.00	0.07	41	0.03	0.02	0.00	0.07	37	0.05	0.02	0.00	0.09	45	0.04	0.02	0.00	0.06
1,2,4-Trichlorobenzene	34	0.07	0.10	0.00	0.34	41	0.07	0.04	0.00	0.15	37	0.08	0.09	0.00	0.34	45	0.07	0.04	0.00	0.14
1,2-Dichlorobenzene	34	0.04	0.03	0.00	0.08	41	0.04	0.02	0.00	0.07	37	0.06	0.02	0.00	0.10	45	0.04	0.02	0.00	0.07
Freon12	34	2.83	0.81	2.11	7.29	41	2.91	0.20	2.42	3.20	37	2.88	0.27	2.09	3.35	45	3.74	3.34	2.47	23.4
Benzylchloride	34	0.00	0.01	0.00	0.05	41	0.01	0.02	0.00	0.07	37	0.05	0.01	0.03	0.07	45	0.04	0.01	0.02	0.06
Freon113	34	0.68	0.06	0.54	0.80	41	0.72	0.06	0.54	0.80	37	0.83	0.18	0.63	1.79	45	1.18	0.33	0.63	2.12
Total Halogens	34	10.5	3.36	7.33	27.8	41	10.7	1.56	8.25	15.5	37	11.7	1.73	8.77	17.4	45	12.6	3.88	8.65	33.1

<b>Substance</b> <sup>1</sup>	n	$\mu^2$	δ	Min	Max	n	μ	δ	Min	Max	n	μ	δ	Min	Max	n	μ	δ	Min	Max
Benzene	34	2.02	1.75	0.68	7.77	41	0.84	0.64	0.25	2.80	37	1.98	0.76	0.92	3.99	45	1.28	0.65	0.64	3.81
Toluene	34	5.04	5.12	1.05	23.6	41	4.18	4.93	0.69	29.0	37	6.58	3.03	2.12	12.7	45	6.16	5.42	2.41	36.7
Styrene	34	0.23	0.28	0.02	1.37	41	0.14	0.12	0.03	0.50	37	0.20	0.11	0.02	0.45	45	0.14	0.06	0.05	0.30
Ethylbenzene	34	0.90	1.00	0.19	5.25	41	0.69	0.60	0.13	3.16	37	1.16	0.64	0.35	2.88	45	1.06	0.98	0.36	6.15
Indane	34	0.10	0.08	0.03	0.43	41	0.07	0.04	0.02	0.18	37	0.14	0.06	0.03	0.29	45	0.10	0.04	0.05	0.23
iso-Propylbenzene	34	0.07	0.05	0.02	0.28	41	0.06	0.04	0.02	0.29	37	0.08	0.03	0.04	0.16	45	0.06	0.02	0.03	0.14
n-Propylbenzene	34	0.16	0.16	0.04	0.86	41	0.12	0.07	0.04	0.38	37	0.21	0.10	0.08	0.51	45	0.16	0.07	0.08	0.39
sec-Butylbenzene	34	0.03	0.02	0.01	0.10	41	0.03	0.01	0.01	0.06	37	0.04	0.01	0.02	0.07	45	0.03	0.01	0.02	0.06
tert-Butylbenzene	34	0.02	0.01	0.00	0.04	41	0.02	0.01	0.00	0.05	37	0.03	0.01	0.00	0.04	45	0.02	0.01	0.00	0.04
iso-Butylbenzene	34	0.03	0.01	0.01	0.08	41	0.03	0.01	0.00	0.05	37	0.04	0.01	0.02	0.06	45	0.03	0.01	0.02	0.06
Hexylbenzene	34	0.20	0.13	0.03	0.59	40	0.12	0.06	0.03	0.24	37	0.19	0.13	0.06	0.58	45	0.12	0.07	0.03	0.36
m and p-Xylene	34	2.57	3.20	0.46	17.1	41	2.11	1.87	0.34	9.41	37	3.44	2.00	0.87	8.52	45	3.35	3.22	1.03	20.5
o-Xylene	34	0.85	0.94	0.17	4.87	41	0.65	0.57	0.13	2.83	37	1.14	0.63	0.33	2.94	45	0.98	0.85	0.36	5.47
3-Ethyltoluene	34	0.43	0.50	0.10	2.60	41	0.31	0.23	0.08	1.17	37	0.61	0.34	0.08	1.70	45	0.46	0.21	0.19	1.29
4-Ethyltoluene	34	0.24	0.24	0.06	1.33	41	0.18	0.12	0.05	0.61	37	0.32	0.16	0.08	0.80	45	0.25	0.11	0.11	0.63
1,3,5-Trimethylbenzene	34	0.21	0.24	0.02	1.29	41	0.15	0.11	0.04	0.54	37	0.30	0.16	0.02	0.81	45	0.23	0.10	0.10	0.59
2-Ethyltoluene	34	0.18	0.19	0.05	1.02	41	0.13	0.09	0.04	0.44	37	0.25	0.12	0.07	0.62	45	0.19	0.08	0.09	0.48
1,2,4-Trimethylbenzene	34	0.64	0.72	0.14	3.73	41	0.47	0.35	0.13	1.72	37	0.94	0.52	0.05	2.54	45	0.71	0.33	0.30	1.94
1,2,3-Trimethylbenzene	34	0.17	0.18	0.04	0.95	41	0.14	0.09	0.04	0.43	37	0.24	0.12	0.03	0.58	45	0.19	0.08	0.10	0.48
1,3-Diethylbenzene	34	0.06	0.04	0.01	0.19	41	0.04	0.02	0.01	0.10	37	0.07	0.03	0.02	0.15	45	0.06	0.02	0.03	0.12
p-Cymene	34	0.09	0.07	0.01	0.31	41	0.10	0.05	0.03	0.27	37	0.18	0.10	0.03	0.42	45	0.08	0.04	0.03	0.20
1,4-Diethylbenzene	34	0.13	0.10	0.03	0.51	41	0.11	0.06	0.03	0.27	37	0.18	0.08	0.04	0.41	45	0.14	0.06	0.06	0.31
n-Butylbenzene	34	0.05	0.03	0.02	0.15	41	0.04	0.02	0.01	0.09	37	0.06	0.02	0.02	0.13	45	0.05	0.02	0.02	0.10
1,2-Diethylbenzene	34	0.03	0.01	0.01	0.06	41	0.03	0.01	0.00	0.05	37	0.04	0.01	0.02	0.06	45	0.03	0.01	0.01	0.05
<b>Total Aromatics</b>	34	14.5	14.6	3.70	73.7	41	10.7	9.59	2.41	52.7	37	18.4	8.80	6.34	40.3	45	15.9	10.7	6.5	62.3
Total VOCs	34	71.2	59.5	27.7	286	41	52.7	37.4	20.9	189	37	93.3	38.5	37.6	192	45	64.7	27.6	35.7	159

n = number of samples;  $\mu$  = mean;  $\delta$  = standard deviation; Min = minimum value; Max = maximum value 1. The following substances were below the detection limit : 4-Methyloctane, 3-Methyloctane, 2.5-Dimethylheptane, 2-Methyl-1-Pentene. 2-Methyl-2-Pentene, cis-2-Octene, Bromochloromethane 2. Values can change due to rounding.

Substance	RDP	Ont.	Substance	RDP	Ont.
Alkanes	42.23	44.53	Alkenes/alkynes	15.47	16.55
Propane	5.89	3.84	Ethylene	4.43	4.28
Isopentane	5.72	6.83	Acetylene	2.83	3.01
Ethane	5.49	4.22	Propylene	1.48	1.60
Butane	5.30	6.38	1-Butene/Isobutene	1.13	1.32
Isobutane	3.86	5.11	Isoprene	0.70	0.43
Pentane	2.46	2.82	2-Methyl-1-butene	0.48	0.55
2-Methylpentane	1.85	2.37	1-Hexene	0.42	0.26
Hexane	1.18	1.13	trans-2-Butene	0.38	0.59
3-Methylpentane	1.17	1.42	cis-2-Butene	0.36	0.52
Methylcyclopentane	0.75	0.90	2-Methyl-2-butene	0.34	0.54
3-Methylhexane	0.72	0.86	1-Pentene	0.32	0.34
2-Methylhexane	0.66	0.82	1,3-Butadiene	0.31	0.35
Heptane	0.65	0.67	trans-2-Pentene	0.29	0.44
2,2,4-Trimethylpentane	0.47	0.50	cis-2-Pentene	0.21	0.29
2,2-Dimethylbutane	0.46	0.57	1-Propyne	0.18	0.19
2,3-Dimethylbutane	0.45	0.58	1-Heptene	0.13	0.12
Methylcyclohexane	0.39	0.45	2-Ethyl-1-Butene	0.12	0.21
Decane	0.37	0.47	1-Methylcyclopentene	0.11	0.14
Cyclopentane	0.34	0.41	Cyclopentene	0.11	0.15
Undecane	0.33	0.38	3-Methyl-1-butene	0.09	0.12
Octane	0.31	0.32	1-Methylcyclohexene	0.09	0.07
Cyclohexane	0.30	0.36	trans-2-Hexene	0.08	0.11
2,3-Dimethylpentane	0.29	0.33	Cyclohexene	0.07	0.07
Nonane	0.29	0.32	cis-2-Hexene	0.07	0.08
2-Methylheptane	0.29	0.33	1-Octene	0.06	0.04
2,3,4-Trimethylpentane	0.27	0.19	trans-3-Methyl-2-pentene	0.06	0.08
3-Methylheptane	0.27	0.33	cis-3-Methyl-2-pentene	0.06	0.08
Dodecane	0.24	0.31	1-Nonene	0.06	0.04
2,2,5-Trimethylhexane	0.21	0.05	cis-2-Heptene	0.06	0.05
2,4-Dimethylhexane	0.17	0.17	3-Methyl-1-pentene	0.05	0.06
2,4-Dimethylpentane	0.16	0.20	1-Decene	0.05	0.04
2,5-Dimethylhexane	0.14	0.12	4-Methyl-1-pentene	0.05	0.05
cis-1,3-Dimethylcyclohexane	0.13	0.14	1-Butyne	0.04	0.03
4-Methylheptane	0.11	0.13	cis-3-Heptene	0.04	0.08
2,2-Dimethylpropane	0.09	0.07	trans-3-Heptene	0.04	0.04
cis-1,2-Dimethylcyclohexane	0.07	0.06	trans-2-Heptene	0.03	0.04
2,2-Dimethylpentane	0.07	0.07	1-Undecene	0.03	0.05
trans-1,2-DiMEcyclohexane	0.06	0.06	cis-4-Methyl-2-pentene	0.03	0.05
trans-1,4-DiMEcyclohexane	0.06	0.06	trans-2-Octene	0.03	0.05
cis-1,4/t-1,3-	0.06	0.06	trans-4-Methyl-2-pentene	0.01	0.02
Dimethylcyclohexane			2-Methyl-1-Pentene	0.00	0.00
3,6-Dimethyloctane	0.05	0.05	2-Methyl-2-Pentene	0.00	0.00
2,2-Dimethylhexane	0.05	0.04	cis-2-Octene	0.00	0.00
2,2,3-Trimethylbutane	0.02	0.02			
4-Methyloctane	0.00	0.00			
3-Methyloctane	0.00	0.00			
2,5-Dimethylheptane	0.00	0.00			

Annexe 4 : Non-polar VOC Contribution (	%	) at RDP	and	Ontario	St Station
---	---	----------	-----	---------	------------

Substance	RDP	Ont.	Substance	RDP	Ont.
Halogens	22.99	17.72	Hexachlorobutadiene	0.04	0.02
Freon12	6.44	4.79	1,4-Dichlorobutane	0.03	0.02
Freon11	4.06	2.84	Benzylchloride	0.03	0.06
Chloromethane	2.71	1.80	trans-1,3-Dichloropropene	0.03	0.02
Freon113	1.63	1.59	cis-1,3-Dichloropropene	0.00	0.00
Carbontetrachloride	1.48	1.00	Bromotrichloromethane	0.00	0.00
Dichloromethane	1.47	1.95	Bromochloromethane	0.00	0.00
1,1,1-Trichloroethane	0.90	0.41			
Tetrachloroethylene	0.64	0.72	Aromatics	19.31	21.20
Freon114	0.47	0.33	Toluene	6.74	7.74
Chloroform	0.34	0.22	m and p-Xylene	3.51	4.15
Bromomethane	0.30	0.26	Benzene	2.16	2.05
Trichloroethylene	0.30	0.24	Ethylbenzene	1.20	1.34
Dibromomethane	0.20	0.14	o-Xylene	1.13	1.28
Bromodichloromethane	0.16	0.14	1,2,4-Trimethylbenzene	0.88	1.04
Chloroethane	0.16	0.12	3-Ethyltoluene	0.57	0.68
1,2,4-Trichlorobenzene	0.16	0.12	Styrene	0.35	0.22
1,2-Dichloroethane	0.15	0.11	4-Ethyltoluene	0.34	0.36
1,1-Dichloroethylene	0.12	0.08	Hexylbenzene	0.32	0.22
Dibromochloromethane	0.11	0.08	1,3,5-Trimethylbenzene	0.29	0.34
Bromoform	0.11	0.08	2-Ethyltoluene	0.26	0.28
1,1,2,2-Tetrachloroethane	0.11	0.07	1,2,3-Trimethylbenzene	0.25	0.28
EDB	0.11	0.07	n-Propylbenzene	0.23	0.24
Chlorobenzene	0.09	0.01	1,4-Diethylbenzene	0.22	0.22
1,2-Dichlorobenzene	0.09	0.07	p-Cymene	0.19	0.15
1,3-Dichlorobenzene	0.08	0.07	Indane	0.15	0.15
1,1,2-Trichloroethane	0.08	0.06	iso-Propylbenzene	0.11	0.10
1,2-Dichloropropane	0.07	0.05	1,3-Diethylbenzene	0.09	0.09
1,1-Dichloroethane	0.07	0.05	n-Butylbenzene	0.08	0.08
cis-1,2-Dichloroethylene	0.06	0.04	sec-Butylbenzene	0.06	0.05
Ethylbromide	0.06	0.04	1,2-Diethylbenzene	0.06	0.04
trans-1,2-Dichloroethylene	0.06	0.04	iso-Butylbenzene	0.06	0.05
Vinylchloride	0.04	0.03	tert-Butylbenzene	0.04	0.04

Period	Substance	n	μ	δ	Min	Med.	Max
	Formaldehvde	77	4.12	2.05	0.88	3.60	11.58
	Acetaldehyde	77	2.60	1.83	0.00	2.00	11.72
	Acrolein	77	0.38	0.66	0.00	0.17	3.50
	Acetone	77	2.59	1.83	0.00	2.26	11.26
	Propionaldehyde	77	0.59	0.45	0.00	0.51	2.26
	Crotonaldehyde	77	0.13	0.19	0.00	0.04	0.85
Winter	MEK	77	1.30	1.90	0.00	0.88	14.48
1999 to	Benzaldehyde	77	0.27	0.34	0.00	0.19	2.49
2002	2-Pentanone/Isovaleraldehyde	77	0.04	0.11	0.00	0.00	0.63
	Valeraldehyde	77	0.14	0.22	0.00	0.06	0.99
	o-Tolualdehyde	77	0.02	0.08	0.00	0.00	0.59
	m-Tolualdehyde	77	0.14	0.27	0.00	0.00	1.05
	p-Tolualdehyde	77	0.01	0.04	0.00	0.00	0.34
	MIBK	77	0.16	0.28	0.00	0.00	1.14
	Hexanal	77	0.13	0.17	0.00	0.07	0.71
	2,5-Dimethylbenzaldehyde	77	0.01	0.06	0.00	0.00	0.33
	Total Polar VOCs	77	12.60	7.24	2.25	10.74	45.38
	Formaldehyde	87	4.93	3.70	0.00	4.12	18.43
	Acetaldehyde	87	1.68	0.98	0.00	1.53	4.92
	Acrolein	87	0.02	0.08	0.00	0.00	0.68
	Acetone	87	1.94	1.82	0.00	1.52	11.07
	Propionaldehyde	87	0.46	0.31	0.00	0.43	1.57
	Crotonaldehyde	87	0.09	0.12	0.00	0.04	0.46
Summer	MEK	87	0.51	0.50	0.00	0.37	1.96
1999 to	Benzaldehyde	87	0.19	0.17	0.00	0.15	1.20
2002	2-Pentanone/Isovaleraldehyde	87	0.02	0.06	0.00	0.00	0.35
	Valeraldehyde	87	0.19	0.28	0.00	0.12	1.89
	o-Tolualdehyde	87	0.05	0.15	0.00	0.00	0.79
	m-Tolualdehyde	87	0.05	0.19	0.00	0.00	1.55
	p-Tolualdehyde	87	0.02	0.07	0.00	0.00	0.57
	MIBK	87	0.12	0.21	0.00	0.00	1.14
	Hexanal	87	0.41	0.59	0.00	0.24	3.66
	2,5-Dimethylbenzaldehyde	87	0.03	0.09	0.00	0.00	0.61
	Total Polar VOCs	87	10.74	5.71	1.24	9.20	31.00

Appendix 5 : Summary of Statistical Results for Polar VOCs

n = number of values;  $\mu$  = mean;  $\delta$  = standard deviation; Min = minimum; Med. = median; Max = maximum

Period	Substance	n	μ	δ	Min	Med.	Max
	Formaldehyde	70	3.06	1.18	1.14	3.05	7.30
	Acetaldehyde	70	2.55	1.79	0.79	1.99	10.45
	Acrolein	70	0.25	0.24	0.00	0.20	1.20
	Acetone	70	3.68	1.92	1.20	3.37	13.67
	Propionaldehyde	70	0.59	0.35	0.15	0.48	2.43
	Crotonaldehyde	70	0.13	0.13	0.00	0.10	0.81
Winter	MEK	70	1.47	1.17	0.24	1.19	8.77
1999 to	Benzaldehyde	70	0.19	0.12	0.00	0.15	0.78
2002	2-Pentanone/Isovaleraldehyde	54	0.15	0.11	0.00	0.15	0.51
	Valeraldehyde	70	0.12	0.08	0.00	0.12	0.45
	o-Tolualdehyde	70	0.00	0.01	0.00	0.00	0.05
	m-Tolualdehyde	70	0.04	0.04	0.00	0.04	0.25
	p-Tolualdehyde	70	0.03	0.04	0.00	0.00	0.20
	MIBK	70	0.18	0.22	0.00	0.12	1.13
	Hexanal	70	0.13	0.09	0.00	0.11	0.48
	2,5-Dimethylbenzaldehyde	54	0.00	0.00	0.00	0.00	0.00
	Total Polar VOCs	70	12.54	6.51	3.80	11.35	46.35
	Formaldehyde	89	3.33	1.61	0.93	2.98	9.62
	Acetaldehyde	89	2.36	1.33	0.76	2.04	7.74
	Acrolein	89	0.11	0.09	0.00	0.10	0.70
	Acetone	89	4.56	1.49	2.01	4.34	9.81
	Propionaldehyde	89	0.70	0.68	0.22	0.56	6.08
	Crotonaldehyde	89	0.18	0.13	0.02	0.16	0.73
Summer	MEK	89	1.36	0.74	0.36	1.22	4.01
1999 to	Benzaldehyde	89	0.24	0.12	0.08	0.22	0.83
2002	2-Pentanone/Isovaleraldehyde	65	0.19	0.11	0.00	0.17	0.55
	Valeraldehyde	89	0.22	0.14	0.06	0.19	0.86
	o-Tolualdehyde	89	0.00	0.01	0.00	0.00	0.03
	m-Tolualdehyde	89	0.06	0.05	0.00	0.05	0.34
	p-Tolualdehyde	89	0.03	0.05	0.00	0.02	0.40
	MIBK	89	0.21	0.14	0.00	0.17	0.73
	Hexanal	89	0.26	0.14	0.06	0.23	0.73
	2,5-Dimethylbenzaldehyde	70	0.00	0.00	0.00	0.00	0.00
	Total Polar VOCs	89	13.77	5.54	5.51	12.58	33.93

Summary of Statistical Results for Polar VOCs at Ontario St Station

n = number of values;  $\mu$  = mean;  $\delta$  = standard deviation; Min = minimum; Med. = median; Max = maximum