

# The Relationship Among TSP, PM<sub>10</sub>, PM<sub>2.5</sub>, and Inorganic Constituents of Atmospheric Particulate Matter at Multiple Canadian Locations

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## ABSTRACT

The Canadian NAPS (National Air Pollution Surveillance) network has produced one of the largest and more geographically diverse databases of high quality atmospheric particle measurements in the world. A maximum of ten and a minimum of two years of data are available for 19 Canadian locations. These data were used to investigate relationships between collocated measurements of TSP, PM<sub>10</sub>, PM<sub>2.5</sub>, SO<sub>4</sub><sup>2-</sup>, and other inorganic ions and elements at a variety of urban and rural locations. Amongst all locations and all 24-hour measurements, the 10th and 90th percentile TSP concentrations were 22 and 98 µg m<sup>-3</sup>, respectively. A majority of the PM<sub>10</sub> concentrations were below 47 µg m<sup>-3</sup> and most of the PM<sub>2.5</sub> concentrations across Canada were below 26 µg m<sup>-3</sup> (90th percentiles). On average across all sites, PM<sub>2.5</sub> accounted for 49% of the PM<sub>10</sub>, and PM<sub>10</sub> accounted for 44% of the TSP. However, there was considerable variability among sites, with the mean PM<sub>2.5</sub> to PM<sub>10</sub> ratio ranging from 0.36 to 0.65. This ratio also varied substantially from

measurement to measurement, but at most sites a majority (>50%) of the ratios were within ±10% of the median value. PM<sub>2.5</sub> concentrations tended to increase from summer to winter except at some of the eastern sites, particularly the rural locations, where sulfate was an important constituent. Coarse particles (2.5 µm < diameter < 10 µm) were found to exhibit the opposite seasonal pattern. Particle levels were highest at a high-density traffic site in Montréal, Québec. Excluding this site, which was influenced by local sources, the particle levels tended to be highest in southwestern Ontario. Depending upon site, only about 37% to 61% of the PM<sub>2.5</sub> could be explained given the measured concentrations of several inorganic ions and elements. Much of the unexplained portions are assumed to be carbonaceous and predominantly organic in nature. Due to the predominance of crustal material, a greater portion of the coarse particle mass (~70%) was explained by the inorganic constituents.

## IMPLICATIONS

The Canadian TSP Objective and the United States PM<sub>10</sub> Standard are currently under review. This is due, in part, to the increasing body of epidemiological evidence implicating airborne particles in human mortality and morbidity. It is not known what aspect of the particles—mass, size, composition, or all three—might be contributing to these effects. To help address this issue we present an analysis of the particle data collected by the Canadian National Air Pollution Surveillance (NAPS) network. The NAPS network has produced one of the largest and most geographically diverse databases of high quality measurements in the world. This database is unique in that a large number of simultaneous measurements of TSP, PM<sub>10</sub>, PM<sub>2.5</sub>, and sulfate were collected over a number of years and at a range of locations. This permits a robust analysis of the relationship among these different particle measures.

## INTRODUCTION

The debate over the scientific evidence for an underlying cause linking airborne particle levels to adverse health effects has intensified in recent years.<sup>1</sup> Particles have been associated with cardiorespiratory hospital admissions,<sup>2,4</sup> cardiorespiratory mortality,<sup>5,6</sup> and respiratory-related emergency department visits<sup>7,8</sup> in a range of epidemiological studies. Particle-associated effects have also been found for a variety of geographical areas.<sup>6</sup> However, the role of particles in contributing to these effects (either alone or in combination with other pollutants) is not clear.<sup>9</sup> There are studies presenting conflicting or inconclusive epidemiological evidence regarding particle effects.<sup>10,11</sup> A number of factors contribute to these uncertainties. It is not known what aspect(s) of mass, size, composition, or some combination of at least these three, might be contributing to the observed health effects. Attempts to identify a biological mechanism linking these effects to particle exposure have been inconclusive.

Epidemiological studies have relied upon different measures of the ambient particle levels (i.e., TSP, sulfate,  $PM_{10}$ , strong acidity), have used different statistical methods, and have accounted differently for the potential effects of other pollutants or weather. Consequently, it is difficult to verify and synthesize the findings of past health studies in order to assess the need for or appropriateness of modifying the current air quality standards or objectives for  $PM_{10}$  or TSP.

Epidemiological and physical evidence suggests that the fine fraction of the atmospheric particles (aerodynamic diameter  $<2.5 \mu\text{m}$ ) is likely to be responsible for the health effects. In simultaneous measurements of  $PM_{10}$  and  $PM_{2.5}$ , temporal variations in fine particles (i.e.,  $PM_{2.5}$  or sulfate) usually dominate or control the observed variability in  $PM_{10}$ .<sup>12,13</sup> Ambient concentrations of fine particles and sulfate ( $SO_4^{2-}$ ) tend to be more spatially homogeneous<sup>14</sup> and their levels have been found to be similar in both the outdoor and indoor environment,<sup>15,16</sup> although this depends upon the type of structure and/or ventilation system.<sup>17</sup> These factors reduce the potential for fine particle exposure misclassification. Fine particles contain a higher proportion of potentially harmful chemical species, such as acids, heavy metals, and PAHs, compared to particles greater than  $2.5 \mu\text{m}$  in diameter. They also dominate the particle number distribution of  $PM_{10}$  and are more directly related to anthropogenic emissions. Consequently, epidemiological findings relating daily variations in  $PM_{10}$  or TSP to mortality or morbidity may well be the result of exposure to fine particles, and resulting exposure misclassification probably weakened the reported relationships.<sup>13,18</sup> Some recent epidemiological results<sup>19-21</sup> support this conclusion. Dockery et al.<sup>19</sup> found similar adjusted rate ratios for  $PM_{10}$ ,  $PM_{2.5}$ , and  $SO_4^{2-}$ , while significant associations were not found for TSP or aerosol acidity. Thurston et al.<sup>20</sup> and Raizenne et al.<sup>21</sup> showed slight increases in statistical significance relating a health outcome to particulate matter as the size cut-off of the particle measurement decreased. In addition, in these two studies, fine particle sulfate ( $SO_4^{2-}$ ) and acidity measurements provided stronger statistical relationships than simple measures of particle mass. However, the role of particle chemistry (i.e., sulfate and acidity) is uncertain, since relatively similar particle-associated health effects have been observed in regions with differing particle chemistry.<sup>22</sup>

For the U.S., data on fine particle mass concentrations ( $PM_{2.5}$ ) are limited, particularly for urban areas and across multiple years and seasons. Up to ten years of measurements of the concentrations of TSP,  $PM_{10}$ ,  $PM_{2.5}$  and  $SO_4^{2-}$ , as well as other trace elements, are available for 19 Canadian locations.<sup>23</sup> These data provide an opportunity to examine the long-term relationship between these various measures of ambient particles. The purpose of this paper is to briefly describe the Canadian National Air Pollution Surveillance (NAPS) particle network and to present results of investigations into

the relationship between collocated measurements of TSP,  $PM_{10}$ ,  $PM_{2.5}$ ,  $SO_4^{2-}$ , and other inorganic ions and elements at a variety of urban and rural locations across Canada. These analyses provide information useful to air pollution health effect studies and to the regulatory assessment of the particle issue.

## METHODS

### Site Locations and Data Availability

A list of the dichotomous sampling sites (as of December 1993) is provided in Table 1. Dichotomous samplers (dichots) have operated at 19 different locations. All but five sites had a high volume sampler for total suspended particulates (TSP) collocated with the dichotomous sampler. Some of the 19 sites have been relocated and are no longer active. Since July 1992, 16 sites have been in operation, with three more sites added in the spring of 1993. With the exception of Kejimikujik, Sutton, Egbert, and Walpole Island, all the sites are located in urban areas. Windsor, Montréal, and Vancouver are the only cities where two different sites have operated simultaneously. Table 1 provides a summary of the start date of sampling and the number of valid sampling days by season (throughout this paper winter is defined as October through March and summer as April through September). The height above ground of the sampling inlets and a description of the site surroundings are also indicated in the table. All dichots were in pre-existing air quality monitoring locations operated by municipal or provincial agencies. Except for three sites (Halifax, Saint John, and Montreal-2), the dichot locations were selected because they were expected to be representative of the prevailing conditions in the region around the site (i.e., not influenced by local sources).

Normally, samples have been collected over a 24-hour sampling period on a six-day sampling schedule. The Vancouver sites at 2294 West 10th. Ave. and its successor at 2550 West 10th. Ave. operated on a three-day sampling schedule from January 1985 to December 1988. During this time period, a three-day sampling schedule was also followed at the Vancouver, Rocky Point Park site (Vancouver-2). Seven of the sites—Kejimikujik, Saint John, Montréal, Sutton, Egbert, Toronto (Bay St.), and Windsor-2—are also part of the Canadian Acid Aerosol Monitoring Program (CAAMP).<sup>24</sup> At all these sites, except Sutton and Egbert, samples were collected daily from June to September 1992, and all seven sites were operated daily from May to September 1993. For this analysis, the data from the two Toronto sites (Bay St. and Breadalbane St.), the two Calgary sites, and the two Vancouver sites on West 10th Ave. have been combined into one record. The distances between these sets of sites are relatively small, especially relative to the distances between cities.

Figure 1 is a map of Canada showing the locations of the urban and rural areas with dichotomous samplers. The network is sparse, but covers the main urban areas of Canada

**Table 1.** Dichotomous sampler monitoring locations and available data (1984-1993). Summer corresponds to the April through September time period and winter corresponds to the remaining months.

Location	Address	Height (m)	Site Type	Start Date	End Date	No. of Valid Sampling Days		Collocated TSP
						Summer	Winter	
Saint John	Forest Hills	5	Suburban - Industrial	23-Jun-92	21-Dec-93	230	62	
Halifax	N.S. Technical College	12	Urban	06-May-84	03-Dec-93	150	154	X
Kejimikujik	National Park	3	Rural	08-Jul-92	27-Dec-93	222	57	
Montréal	1125 Ontario Est	13	Urban	06-May-84	27-Dec-93	382	195	X
Montréal-2	Duncan/Decarie	4	Urban - Roadway	03-Sep-84	21-Dec-93	157	158	X
Québec City	Parc Cartier Breboeuf	4	Urban	13-Apr-85	27-Dec-93	113	108	X
Sutton		2	Rural	08-May-93	28-Sep-93	136	0	
Ottawa	Rideau/Wurtemberg	4	Urban	06-May-84	27-Dec-93	193	165	X
Windsor	471 University Ave.	12	Urban	20-Jul-87	27-Dec-93	176	176	X
Windsor-2	College/Prince	3	Urban	29-May-90	27-Dec-93	289	133	X
Toronto	26 Breadalbane Street	16	Urban	12-May-84	17-May-90	119	153	X
Toronto <sup>1</sup>	Bay & Grosvenor	2	Urban	12-Jun-92	27-Dec-93	250	64	X
Walpole Island		3	Rural	22-Jan-88	15-Dec-93	145	130	
Egbert		5	Rural	19-May-93	27-Dec-93	122	15	
Winnipeg	65 Ellen Street	4	Urban	06-May-84	27-Dec-93	241	206	X
Edmonton	10255-104th Street	6	Urban	30-May-84	15-Dec-93	209	171	X
Calgary	316-7th Ave.	9	Urban	28-Aug-84	27-Apr-87	61	83	X
Calgary <sup>2</sup>	611-4th Street	6	Urban	03-May-87	27-Dec-93	176	186	X
Vancouver	2294 West 10th Ave.	17	Urban	06-May-84	17-Jan-86	53	55	X
Vancouver-2	Rocky Pt. Park	4	Urban	28-Aug-84	27-Dec-93	142	218	X
Vancouver <sup>3</sup>	2550 West 10th Ave.	17	Urban	13-Dec-86	27-Nov-93	105	121	X
Victoria	1250 Quadra St.	12	Urban	13-Jan-85	27-Dec-93	195	200	X

<sup>1</sup> Relocated from 26 Breadalbane St.

<sup>2</sup> Relocated from 316-7th Ave.

<sup>3</sup> Relocated from 2294 West 10th Ave.

and provides measurements from coast to coast. These areas have widely different climates, geographical situations, terrain types (topography, soil, and vegetation), and different types of local and upwind (i.e., long-range transport) source regions. Figure 2 provides an indication of data capture over the 1984 to 1993 period. Gaps in the data series are due to operational problems with sampling equipment.

### Sampling Methods and Chemical Analysis

**Sampling Equipment.** All the samplers used in the program have received U.S. Environmental Protection Agency certification as reference sampling devices. The dichotomous samplers (dichots), which were manufactured by Graseby-Andersen, are equipped with an inlet with a 10- $\mu\text{m}$  cutpoint. The particles entering the sampler which are below 10  $\mu\text{m}$  in aerodynamic diameter ( $\text{PM}_{10}$ ) are divided into two size fractions using a virtual impactor with a 2.5- $\mu\text{m}$  cutpoint. These two fractions are referred to as the coarse fraction (2.5  $\mu\text{m}$  < diameter < 10  $\mu\text{m}$ ) and the fine fraction (diameter < 2.5  $\mu\text{m}$ ), respectively. The fine fraction is also referred to as  $\text{PM}_{2.5}$ . The dichots are operated at a total flow rate of 16.7 l  $\text{min}^{-1}$ . Particles are collected on 37-mm Teflon membrane filters (2  $\mu\text{m}$  pore size) supported by polyolefin rings (Gelman Sciences).

With the exception of Toronto and Windsor, where standard glass fiber filters were used, all high-volume samplers (hi-vol) employ low artifact filter media (Pallflex teflon-coated glass-fiber). The sampling effectiveness of the hi-vol depends on wind speed, with a cutpoint of about 50  $\mu\text{m}$  in 2  $\text{km h}^{-1}$  winds and about 22  $\mu\text{m}$  in 24  $\text{km h}^{-1}$  winds.<sup>25</sup> The hi-vols are operated at flow rates of 1.13 to 1.41  $\text{m}^3 \text{min}^{-1}$ .

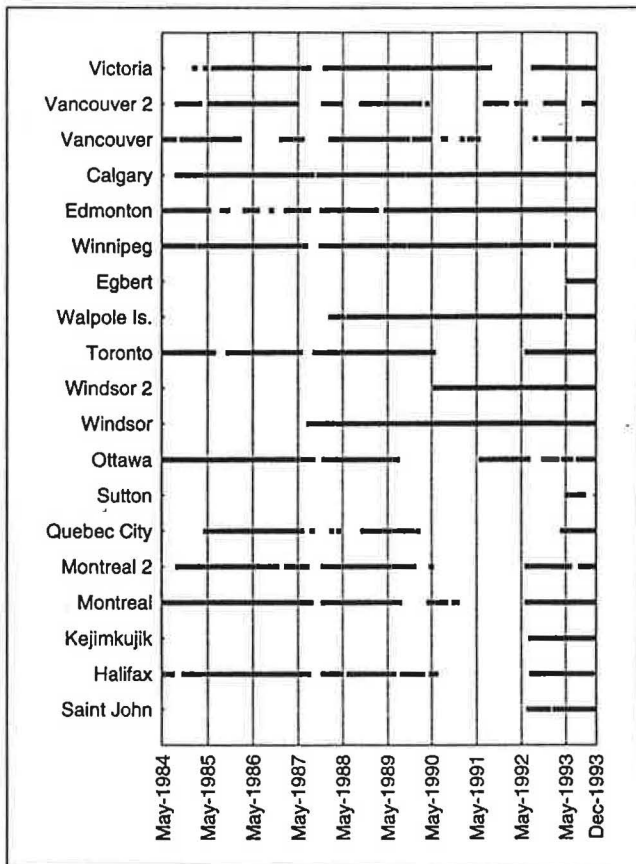
**Analytical Methods.** Mass determinations were performed by the Pollution Measurement Division, Environmental Technology Centre (ETC) in Ottawa. Dichotomous sampler filters are shipped to and from the field in plastic rings which are designed to fit directly into the dichotomous samplers. The filters, in their rings, are packaged in plastic petri dishes and shipped in a box designed to hold them in an upright position. Mass measurements are made using either a Mettler M3 or Mettler MT5 electronic microbalance. Most of the mass determinations on hi-vol filters are made by the operating agencies.

A polonium 210 radioactive source is used as a static charge control device when weighing dichotomous and hi-vol filters. A dedicated room, where relative humidity and temperature are controlled to 43%  $\pm$  5% and 23  $^{\circ}\text{C} \pm$  3  $^{\circ}\text{C}$ , is used to carry out mass determinations. Ten percent of all filters





**Figure 1.** Locations of the sites/cities in the NAPS dichotomous sampler network.



**Figure 2.** Data availability from the NAPS dichotomous sampler network (1984 to 1993).

(new and exposed) are randomly chosen for re-weighing. On average, new filters are within  $\pm 4 \mu\text{g}$  of original weight and exposed filters were within  $\pm 8 \mu\text{g}$  of original weight. The expected precision of ambient air  $\text{PM}_{10}$  concentrations equivalent to these values (assuming a sample volume of  $24 \text{ m}^3$  over 24 h) is  $1 \mu\text{g m}^{-3}$ .

After December 1986, all dichotomous filters were analyzed for the 40 chemical species shown in Table 2 (from

November 1985 to December 1986, only every fifth fine and coarse filter from each site was submitted for chemical analysis). In 1992, an additional ten chemical species were added. Nondestructive x-ray fluorescence (Kevex 770/8000 energy dispersive x-ray fluorescence [EDXRF] spectrometer) is used for elemental analysis and is carried out by the Analysis and Methods Division (AMD) of the ETC.<sup>26,27</sup> A 1,000-sec measurement time and three different excitation conditions are used. Direct filtered or unfiltered radiation from the Rh x-ray tube is used for the excitation of the x-ray fluorescence. The spectrometer is evacuated to improve the detection limits and to prevent oxidation of some aerosol components by ozone generated in the presence of air. Oxidation interferes with later ion chromatographic determinations of sulfate and nitrate. A sixteen-position sampler is used for automatic analysis of filter samples. Two National Institute of Standards and Technology (NIST) thin film x-ray standards (NBS 1832 and NBS 1833) are used with each set of 14 dichotomous filter samples. One set of samples per week is submitted for repeat analysis. The x-ray methods have been refined and improved over the course of this monitoring program.

In addition to internal quality assurance measures, the EDXRF results obtained by AMD have been compared directly to those from other laboratories. An intercomparison with U.S. EPA showed reasonable agreement for all elements considered (approximately 15), except for Cl, Al, and Si on coarse fraction filters and S on both fine and coarse filters. Some of the discrepancy may have been because AMD did not use an x-ray attenuation factor for coarse particles, as suggested by Dzubay and Nelson.<sup>29</sup> Coarse data have therefore been corrected using attenuation factors of 0.56 and 0.57 for Al and Si, respectively. Although the results were well correlated ( $r^2 = 0.94$ ), the AMD fine S concentrations were 25% smaller than the U.S. EPA values. The cause of this bias is not known. Nejedly et al.<sup>30</sup> reported on the results of an intercomparison of a variety of fine particle samplers and analytical methods. The EDXRF concentrations determined by AMD-ETC agreed reasonably well with the other methods. With the exception of K, the agreement among methods was better than 20%.

After EDXRF analysis, each filter is extracted in water (isopropanol wetting agent) and analyzed by ion chromatography (IC) (Dionex) using four methods: anion isocratic, anion gradient with and without concentrator column, and cation gradient.<sup>31,32</sup> Currently, 14 anion and 11 inorganic cation species are quantified. The list of ions discussed in this paper, the date when their analysis began, and their typical detection limits and air concentrations are shown in Table 2. Precision and accuracy are evaluated by repeat analyses of water samples provided by an independent agency. These samples are distributed to multiple laboratories across Canada and the median concentrations amongst all laboratories are assumed to represent the actual concentrations of the samples. As expected, the



**Table 2.** Summary of chemical species measured at the NAPS sites. Results for 14 urban areas (1984-1993). DL = detection limit.

Element or Ion	Start Date	No. of Samples	Typical	% of	Concentration ( $\mu\text{g m}^{-3}$ )		
			DL ( $\mu\text{g m}^{-3}$ )	>DL	Median	75th % <sup>90</sup>	95th % <sup>90</sup>
S	Nov-85	3435	0.0009	100%	0.850	1.452	3.191
Si	Nov-85	3435	0.0020	99%	0.929	1.736	4.221
Al	Nov-85	3435	0.0052	95%	0.720	1.779	7.714
Ca	Nov-85	3435	0.0050	100%	0.435	0.976	2.278
Fe	Nov-85	3435	0.0020	100%	0.284	0.477	0.901
K	Nov-85	3435	0.0048	100%	0.147	0.222	0.404
Cl	Nov-85	3435	0.0040	93%	0.146	0.483	2.085
Mg	May-92	710	0.0129	99%	0.111	0.201	0.544
Pb	May-84	4391	0.0007	99%	0.052	0.139	0.440
Ti	Nov-85	3435	0.0054	95%	0.026	0.045	0.097
Zn	Nov-85	3434	0.0008	99%	0.023	0.041	0.105
Mn	Nov-85	3435	0.0019	98%	0.020	0.032	0.064
P	Nov-85	3435	0.0015	88%	0.018	0.036	0.096
Br	May-84	4394	0.0003	99%	0.012	0.036	0.144
Sc	Nov-85	3435	0.0071	76%	0.010	0.021	0.045
Ba	Nov-85	3435	0.0051	34%	0.009	0.017	0.036
Cu	Nov-85	3435	0.0017	70%	0.009	0.022	0.045
Sn	Nov-85	3435	0.0039	60%	0.008	0.016	0.023
Sb	Nov-85	3435	0.0025	59%	0.007	0.017	0.032
W	May-92	710	0.0092	79%	0.006	0.011	0.019
V	Nov-85	3434	0.0039	53%	0.005	0.011	0.047
Te	Nov-85	3435	0.0025	45%	0.004	0.013	0.028
Ta	May-92	710	0.0020	53%	0.003	0.012	0.017
Pr	May-92	710	0.0040	38%	0.003	0.007	0.012
Cr	Nov-85	3435	0.0025	40%	0.002	0.006	0.015
Sr	Nov-85	3435	0.0003	96%	0.002	0.004	0.009
Ni	Nov-85	3435	0.0010	58%	0.002	0.004	0.014
Ce	May-92	710	0.0030	43%	0.002	0.006	0.013
Zr	Nov-85	3435	0.0003	64%	0.001	0.002	0.003
Co	Nov-85	3435	0.0016	45%	0.001	0.003	0.006
Hg	May-92	710	0.0007	51%	0.001	0.001	0.002
As	Nov-85	3435	0.0005	49%	0.000	0.001	0.003
Bi	May-92	710	0.0008	53%	0.000	0.001	0.002
Rb	Nov-85	3435	0.0003	37%	< DL	0.001	0.001
Se	Nov-85	3435	0.0008	36%	< DL	0.001	0.003
In	Nov-85	3435	0.0024	33%	< DL	0.006	0.011
Nd	May-92	710	0.0040	33%	< DL	0.005	0.010
Ga	Nov-85	3435	0.0007	31%	< DL	0.003	0.011
Mo	Nov-85	3435	0.0007	30%	< DL	0.001	0.004
Tl	May-92	710	0.0008	30%	< DL	0.000	0.001
Y	Nov-85	3435	0.0003	22%	< DL	0.000	0.001
Cd	Nov-85	3435	0.0021	18%	< DL	0.003	0.008
Nb	Nov-85	3435	0.0007	16%	< DL	< DL	0.002
Ge	Nov-85	3435	0.0005	15%	< DL	< DL	0.002
Ag	Nov-85	2734	0.0027	14%	< DL	0.002	0.004
La	Nov-85	3435	0.0060	10%	< DL	0.005	0.021
I	Nov-85	3435	0.0027	9%	< DL	< DL	0.007
Cs	Nov-85	3435	0.0040	3%	< DL	< DL	0.010
Pd	Nov-85	3435	0.0027	2%	< DL	< DL	0.002
SO <sub>4</sub> <sup>2-</sup>	May-84	4527	0.02	100%	2.171	3.710	8.790
NO <sub>3</sub> <sup>-</sup>	May-84	4525	0.03	98%	0.509	0.880	2.531
NH <sub>4</sub> <sup>+</sup>	May-92	549	0.02	99%	0.461	1.040	2.895
Na <sup>+</sup>	May-92	548	0.06	90%	0.200	0.575	2.106
Cl <sup>-</sup>	May-92	549	0.01	100%	0.114	0.452	3.020

precision and accuracy results obtained at AMD-ETC are a function of concentration. At concentrations common in the atmospheric samples (Table 2), mean accuracies for SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, Na<sup>+</sup>, and NH<sub>4</sub><sup>+</sup> are within 5% of the interlaboratory medians. Precision for these species is within 10%. For Cl<sup>-</sup>, precision and accuracy are within 20%. Complete details on calibration and quality control techniques for EDXRF and IC analyses are available from AMD, Ottawa.<sup>26</sup>

### Mass Reconstruction

The percentage of the total fine and coarse mass explained by the inorganic elements and ions is determined by comparing the sum of the concentrations of these chemical species to the total mass. Since EDXRF only quantifies the concentrations of individual elements, it is necessary to account for their molecular form. This is done using approaches described by Malm et al.<sup>33</sup> and Countess et al.<sup>34</sup> Reconstructed inorganic mass for both the fine and coarse particle samples is determined using:

$$\text{Mass}_{\text{rec}} = \text{SO}_4^{2-} + \text{NO}_3^- + \text{NH}_4^+ + 1.79\text{V} + 1.24\text{Zn} + 1.12\text{Ba} + \text{Pb} + \text{Br} + \text{Cl} + \text{Na} + \text{SOIL} + \text{Rem.} \quad (1)$$

where,

$$\text{SOIL} = 2.20\text{Al} + 2.49\text{Si} + 1.63\text{Ca} + 1.58\text{Fe} + 1.94\text{Ti} + 1.41\text{K} \quad (2)$$

$$\text{Rem.} = \sum(\text{all remaining elements}) \quad (3)$$

Prior to 1993, Na and NH<sub>4</sub><sup>+</sup> were not measured. Concentrations for samples collected prior to this time were estimated using:

$$\text{NH}_4^+_{\text{est}} = 0.375\text{SO}_4^{2-} + 0.290\text{NO}_3^- \quad (4)$$

$$\text{Na}_{\text{est}} = 0.649\text{Cl} \quad \text{Coarse particles} \quad (5)$$

$$\text{Na}_{\text{est}} = \beta_0 + \beta_1\text{S} \quad \text{Fine particles} \quad (6)$$

where  $\beta_0$  and  $\beta_1$  are site-specific regression coefficients determined from the 1993 S and Na measurements. For sites not located near salt water,  $\beta_0$  and  $\beta_1$  are assumed to equal zero (i.e., fine Na is negligible).

Eqs. 1-6 are based upon several assumptions listed below:

- Except where noted, these equations can be used to reconstruct both the fine and coarse mass.
- Both fine and coarse SO<sub>4</sub><sup>2-</sup> are fully neutralized (i.e., [NH<sub>4</sub>]<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>SO<sub>4</sub>) and there are no additional forms of S. Thus, crustal sources of S (e.g., gypsum), which contribute predominantly to the coarse mass, are neglected.
- Due to greater uncertainty in the EDXRF measurements of S, the SO<sub>4</sub><sup>2-</sup> values used in Mass<sub>rec</sub> are obtained from the IC analyses (SO<sub>4</sub><sup>2-</sup><sub>IC</sub>). The difference between S from EDXRF (S<sub>EDXRF</sub>) and (SO<sub>4</sub><sup>2-</sup><sub>IC</sub>)/3 provides an estimate of

the amount of mass associated with additional forms of S. Based upon this difference and a subset of the data for which there is greater confidence in the  $S_{XRF}$  values, we estimate that at the eastern sites, exclusion of additional forms of S (i.e., use of  $SO_4^{2-IC}$ ) leads to a 5% underestimate in potential S contribution to  $Mass_{rec}$  for fine mass. In contrast, in the Prairies, additional forms of S could potentially increase the fine S contribution by 10% to 15%. In Vancouver, additional S may be of greatest importance, leading to as much as a 30% increase in the  $Mass_{rec}$  associated with fine S. Additional forms of S are potentially much more important for coarse particles, leading to 50% to 300% more S by mass, depending upon site. However, coarse particle S tends to be about an order of magnitude smaller than fine particle S, and thus the overall impact on  $Mass_{rec}$  is small.

- All  $NO_3^-$  is in the form of  $NH_4NO_3$ .
- SOIL accounts for the predominant crustal elements in their most common oxidized form, plus a 14% scale-up to account for other soil compounds not included directly.<sup>33</sup>
- The only source for Al is soil in the form of  $Al_2O_3$ .
- V, Ba, and Zn, in the oxidized forms of  $VO_2$ , BaO, and ZnO, are only due to high-temperature combustion/industrial processes.<sup>34</sup>
- Pb (fine) is due to automotive emissions and is associated with fine Br and fine Cl.<sup>34</sup>
- All coarse Na is associated with Cl.
- Fine Na is only significant at sites near salt water (Vancouver, Victoria, Saint John, Halifax, Québec City, and Kejimikujik) and it is associated with fine S.<sup>35</sup> Eq. 6 is based upon the assumption that  $H_2SO_4$  will react with fine NaCl particles, driving off HCl (g) and leaving  $Na_2SO_4$ . Although this approach attributes both  $Na^+$  and  $NH_4^+$  to the same  $SO_4^{2-}$  molecules, the magnitudes and significance levels of  $\beta_0$  and  $\beta_1$  were found to be small.  $\beta_0$  and  $\beta_1$  ranged from 0.05 to 0.28 and 0.0 to 0.07, respectively. The strongest evidence for a Na-to-S relationship was found for Kejimikujik and Halifax.
- Soil- and smoke-derived K occurs as  $K_2O$ . Since K is included explicitly in Eq. 2, the K/Fe relationship used by Malm et al.<sup>33</sup> to scale-up Fe is not necessary.
- Due to some uncertainty in the quality of the Al determinations, separate SOIL terms were calculated by replacing  $2.20Al + 2.49Si$  with  $3.48Si$ . Whichever approach resulted in the larger SOIL estimate was used in Eq. 1.
- Elements that were found to be below detection limits were assumed to equal 0.5 times the detection limit.
- Potential molecular forms (e.g., oxides) are neglected for the remaining (Rem.) elements.
- The actual chemical makeup of each particle sample is complex and is not likely to conform to the characteristics

implied by Eqs. 1-6. However, the value of  $Mass_{rec}$  is not very sensitive to realistic changes in the assumptions highlighted above. The main portion of  $Mass_{rec}$ , particularly for fine particles, is due to the measured mass concentrations and not to the adjustments indicated in Eqs. 1-6.

Carbonaceous species (organic and inorganic [elemental]) contribute significantly to the total mass of atmospheric particulate matter. Malm et al.<sup>33</sup> report that on an annual basis, organic carbon species are responsible for 23% to 56% of the total fine mass, depending upon geographic location. Elemental carbon adds an additional 2% to 11% to the mass.<sup>33</sup> Countess et al.<sup>34</sup> observed similar percentages in the Denver aerosol. In contrast, in an area dominated by particulate sulfate, elemental and organic carbon were only found to account for 5% and 10% of the mass, respectively.<sup>36</sup>

Carbonaceous species are not quantified at the NAPS sites. In this paper, the difference between  $Mass_{rec}$  and the total mass is assumed to indicate an upper limit for the amount of the particle mass associated with organic and elemental carbon.

Formation of  $NH_4NO_3$  particles is dependent upon temperature and relative humidity and the concentrations of  $NH_3$  and  $HNO_3$ . Consequently, some of the atmospheric particles that are originally collected on the filters can evaporate during sampling, transport, storage, and analysis.<sup>37</sup> This will lead to an underestimate of what was actually present in the ambient air during sample collection. The importance of this bias is unknown, and it could vary seasonally and even among sites. Koutrakis et al.<sup>38</sup> showed that there was little loss of particle nitrate during sampling. Their study utilized data from sites located in small towns in eastern North America where particle nitrate levels generally tend to be low. In areas with higher  $NO_x$  levels (e.g., major urban areas and in the western U.S.), loss of particle  $NO_3^-$  can be much greater.<sup>39</sup>

$NH_4NO_3$  that evaporates after filter weighing but before IC will lead to an underestimate of  $Mass_{rec}$  and an overestimate of the mass of carbonaceous species. Evacuation of the sample during EDXRF, which precedes IC, could enhance this effect, and thus this factor will be assessed in future studies. Overall, it is important to note that mass and particle  $NO_3^-$  are underestimated and that the relative importance of other species may be overestimated; our results include these biases.

## RESULTS

Descriptive statistics for all valid observations of TSP,  $PM_{10}$ ,  $PM_{2.5}$ , and  $SO_4^{2-}$  concentrations from the 14 urban sites operating from 1986 to 1994 are included in Table 3. TSP ranged from about 10 to 575  $\mu g m^{-3}$  with a majority of the concentrations between 10 and 100  $\mu g m^{-3}$ .  $PM_{10}$  ranged from 5 to 175  $\mu g m^{-3}$ , but a majority of the concentrations were below 50  $\mu g m^{-3}$ . Most of the  $PM_{2.5}$  measurements were between 2 and 30  $\mu g m^{-3}$ . Overall, the mass distributions for the fine and coarse particles were very similar, suggesting that neither mode in the  $PM_{10}$  size range dominated the

**Table 3.** Combined summary statistics for the 14 urban sites in operation between 1986 and 1994. Sample size,  $n = 2831$ , is based upon the number of 24-hour periods with valid measurements for TSP,  $PM_{10}$ ,  $PM_{2.5}$ , and  $SO_4^{2-}$ .  $FSO_4^{2-}$  and  $CSO_4^{2-}$  correspond to fine and coarse  $SO_4^{2-}$ , respectively.

Measurement	Percentiles					Statistics				
	10	50	70	90	95	Max.	Mean*	S.D.*	Mean#	S.D.#
TSP	22.0	46.0	62.0	98.0	123.0	572.0	55.2	37.8	46.2	1.8
$PM_{10}$	11.3	24.0	32.0	47.4	58.0	175.0	27.6	16.3	23.6	1.8
$PM_{2.5}$	5.0	11.0	16.0	26.1	32.2	89.0	13.9	9.5	11.4	1.9
Coarse	4.4	11.0	15.4	25.4	33.0	87.0	13.7	10.4	10.7	2.0
$FSO_4^{2-}$	0.6	1.9	3.1	6.0	8.8	39.0	2.9	3.3	1.9	2.4
$CSO_4^{2-}$	0.1	0.3	0.4	0.6	0.9	4.6	0.4	0.3	0.3	2.2
<b>Ratios</b>										
$PM_{10}/TSP$	0.30	0.51	0.64	0.87	1.00	2.40	0.56	0.24	0.51	1.52
$PM_{2.5}/TSP$	0.10	0.26	0.37	0.54	0.64	1.41	0.30	0.19	0.25	1.91
$PM_{2.5}/PM_{10}$	0.29	0.50	0.60	0.74	0.80	1.00	0.51	0.17	0.48	1.45
Coarse/ $PM_{10}$	0.26	0.50	0.58	0.71	0.76	1.00	0.49	0.17	0.46	1.51
$FSO_4^{2-}/PM_{2.5}$	0.07	0.19	0.25	0.36	0.42	0.95	0.20	0.11	0.17	1.89

\* Arithmetic average and arithmetic standard deviation (S.D.).

# Geometric mean and geometric standard deviation (S.D.).

mass distribution. As expected, a large majority of the  $SO_4^{2-}$  was found on the fine particles.

Mass ratios of the various particle measures are also summarized in Table 3. On average,  $PM_{10}$  accounted for 56% of the TSP, while  $PM_{2.5}$  accounted for 30%. The maximum  $PM_{10}/TSP$  and  $PM_{2.5}/TSP$  values were greater than one, which is not an expected result. Difficulties of this nature are not surprising, given the complications of operating an extensive monitoring program involving different agencies (TSP measurements were provided by the Provincial Ministries). The fact that the dichotomous sampler is a more precise instrument compared to the standard high volume sampler, and that the maximum  $PM_{2.5}/PM_{10}$  value was 1.0, suggests that the outliers are likely due to invalid TSP measurements. However, these samples were not neglected because it could bias the statistics (i.e., there were likely to have been TSP measurements that were larger than the actual concentration, but they could not be identified). Consistent with the similarities in their distributions, fine and coarse particles accounted for equal portions (~50%) of the  $PM_{10}$ . On average across the urban sites, sulfate was responsible for only 20% of the  $PM_{2.5}$ .

#### Site-to-Site Differences in TSP, $PM_{10}$ , $PM_{2.5}$ , and $SO_4^{2-}$

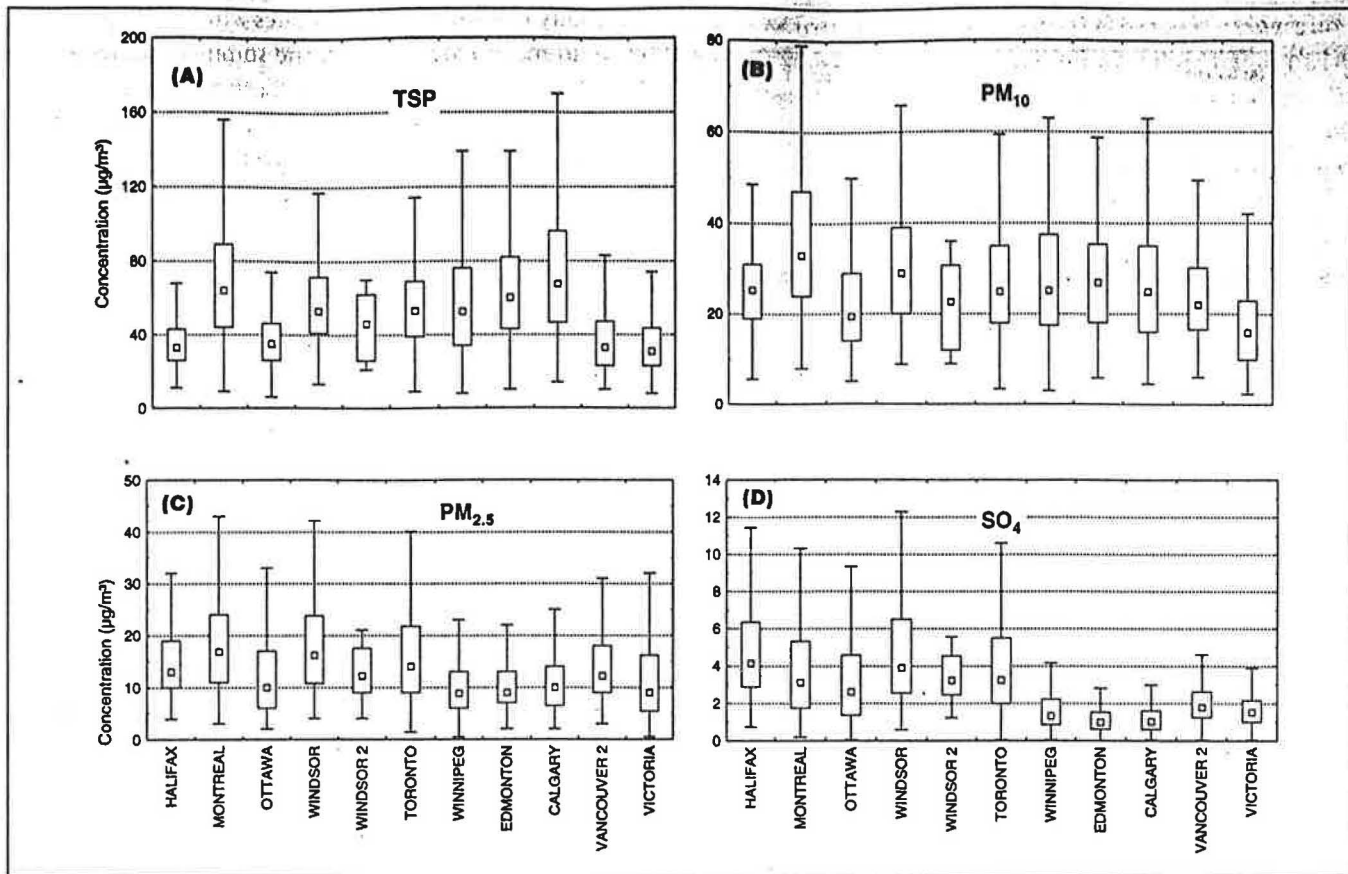
TSP,  $PM_{10}$ ,  $PM_{2.5}$ , and  $SO_4^{2-}$  mass distributions for a cross-section of Canadian cities are compared in the box plots in Figures 3A-D. Only days with observations for all four parameters were used to allow a proper comparison between parameters at each site. Each site has a relatively long data record ( $n > 220$  days; actual  $n$  depends upon site). Sites in the three Prairie cities of Winnipeg, Calgary, and Edmonton have large and variable TSP concentrations, but their  $PM_{2.5}$

concentrations are small relative to the other sites and exhibit less variability. This suggests that much of the airborne particulate matter observed in these areas is mechanically derived and likely consists of local crustal material. The levels of  $PM_{10}$  at these three Prairie sites are also consistent with this; i.e., compared to other locations,  $PM_{10}$  is not markedly lower at Winnipeg, Calgary, and Edmonton.

There is an obvious decrease in the  $SO_4^{2-}$  levels from the sites located east of the upper Great Lakes to those located west of the Lakes (Figure 3D). This is a direct reflection of the magnitude and spatial density of  $SO_2$  emissions within and upwind of these two areas.  $SO_4^{2-}$  concentrations are highest in southern Ontario, although the mean levels in  $\mu g m^{-3}$  are surprisingly similar from Ontario to Halifax, NS.

The effect of being located near a busy traffic area is exhibited by the Montréal-2 (Duncan St.) observations. TSP,  $PM_{10}$ , and  $PM_{2.5}$  concentrations at this site are higher and more variable than at any of the other sites. The additional  $PM_{2.5}$  mass is not due to  $SO_4^{2-}$  since there is very little difference in the  $SO_4^{2-}$  between the two Montréal sites (Figures 4A-B). This suggests that the vehicles in the vicinity of Duncan St. are contributing a substantial amount of primary and/or secondary fine particles, leading to a  $3 \mu g m^{-3}$  increase in mean annual  $PM_{2.5}$  from the Ontario St. to the Duncan St. site. The magnitude of this vehicular/roadway source is largest in the winter, with an increase in mean  $PM_{2.5}$  of  $4.6 \mu g m^{-3}$ . In summer the difference is only  $1.5 \mu g m^{-3}$ . Such within-city differences are not unique to Montréal. It is likely that if multiple sites were placed in a variety of settings within any city or region, systematic mass differences among sites would be observed, particularly if local particle sources were impacting any of the sites.





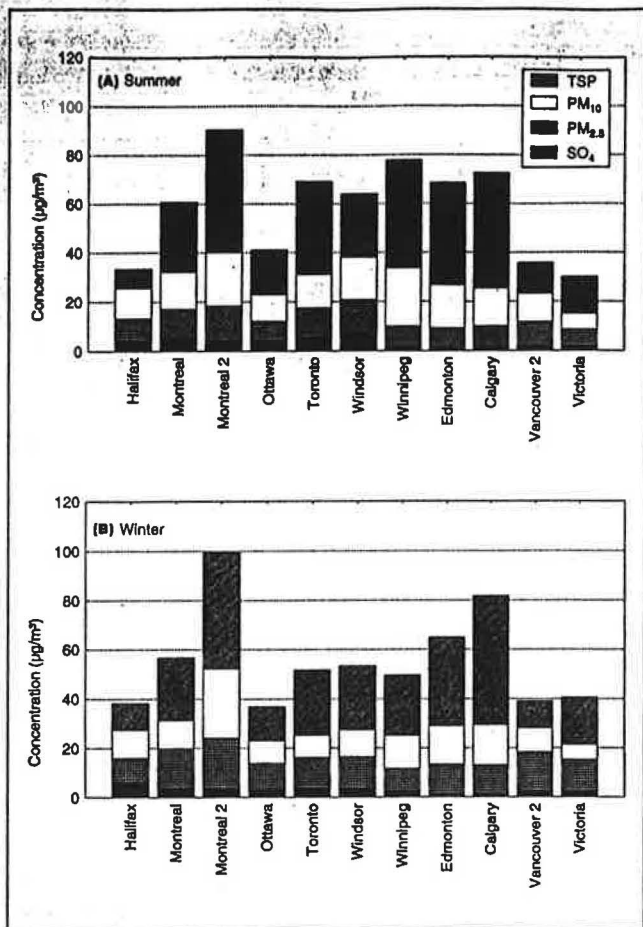
**Figure 3A-D.** Comparison of the distributions of TSP, PM<sub>10</sub>, PM<sub>2.5</sub>, and SO<sub>4</sub> at 11 urban sites (1984 to 1993). The box plots indicate the mean 24-hour concentration and the 5<sup>th</sup>, 25<sup>th</sup>, 75<sup>th</sup>, and 95<sup>th</sup> percentiles.

Mean TSP, PM<sub>10</sub>, PM<sub>2.5</sub>, and SO<sub>4</sub><sup>2-</sup> concentrations were calculated for winter and for summer periods separately and are displayed for selected sites in Figures 4A-B. During the summer, mean PM<sub>2.5</sub> levels are clearly higher over eastern Canada compared to the west. The reason for this difference is that in the summertime, SO<sub>4</sub><sup>2-</sup> increases dramatically at the eastern sites. East-to-west differences in mean PM<sub>2.5</sub> levels are less in the winter due to decreases in the eastern concentrations of SO<sub>4</sub><sup>2-</sup> and to relatively large increases in PM<sub>2.5</sub> in Vancouver and Victoria. With the exception of Toronto and Windsor, all the sites shown have higher PM<sub>2.5</sub> levels in the winter, but the differences are greatest at Vancouver and Victoria. A number of factors could be leading to this predominant wintertime increase in PM<sub>2.5</sub>. Mixing heights are usually lower and energy consumption for heating is higher. Wood burning is also more prevalent.

Increases in particle NO<sub>3</sub><sup>-</sup> due to lower temperatures in the winter do not appear to explain the increases in fine mass from summer to winter. There is no relationship across sites in the magnitudes of the mean seasonal changes in fine mass and NO<sub>3</sub><sup>-</sup>. On average, across the NAPS sites, the mean particle NO<sub>3</sub><sup>-</sup> concentration increases by a factor of two (100%) from summer to winter. However, there is considerable site-to-site variability in this seasonal change, ranging from 152% in Windsor (University Ave.) to -15% in Halifax.

On average, increases in PM<sub>10</sub> from summer to winter are generally equal to or less than the magnitude of the PM<sub>2.5</sub> increases. Therefore, the additional PM<sub>10</sub> found in the winter is likely due to fine particles and not coarse particles. This suggests that combustion sources are an important contributor to wintertime particle pollution and also shows that fine particles control the seasonal PM<sub>10</sub> variability. The Toronto, Windsor, and Winnipeg sites are the only ones included in Figure 4A-B where PM<sub>10</sub> clearly decreases from summer to winter. At Winnipeg, this is due to a decrease in coarse particles, while at Toronto and Windsor, both the coarse and fine particle levels drop slightly.

On average, coarse particles decrease from summer to winter at most of the sites shown. TSP also decreases from summer to winter. This may be due to snow cover and/or increases in precipitation, which would inhibit the suspension of crustal material. The only sites shown in the figures that do not follow this pattern are Calgary and Montréal-2. In Calgary, chinooks—strong and warm dry winds which blow down the mountains in winter—could lead to an increase in the suspension of coarse and larger particles. At the Montréal-2 site, the source of the coarse and larger particles may be the sand and salt applied to the nearby roads during the winter (NaCl increases in winter).



**Figure 4A-B.** Relationships between the mean TSP, PM<sub>10</sub>, PM<sub>2.5</sub>, and SO<sub>4</sub><sup>2-</sup> concentrations during the summer (April-Sept.) and winter (Oct.-March) at 11 urban sites (1984 to 1993). The top of each individual box indicates the mean concentration (e.g., during the winter in Halifax the mean TSP, PM<sub>10</sub>, PM<sub>2.5</sub>, and SO<sub>4</sub><sup>2-</sup> concentrations were 38, 28, 17 and 6 µg m<sup>-3</sup>, respectively).

Distributions of summer and winter particle mass concentrations are compared in Figures 5A-B for fine and coarse particles, respectively. In addition to showing distributions, these figures differ from the previous ones because all available data for each site are used (i.e., to assess site-specific seasonality, there is a different N for each site). Locations representing rural eastern Canada are also included. Most of these additional locations have higher mean PM<sub>2.5</sub> levels in the summer due to the importance of SO<sub>4</sub><sup>2-</sup> over eastern North America. Extremes in PM<sub>2.5</sub> concentration are also higher in the summer at these sites, as well as at the other sites in southern Ontario and rural eastern Canada. In addition to reasons discussed above, the wintertime increase in PM<sub>10</sub> at Halifax is due to the site being very close (<50 m) to the stacks of an oil-fired boiler, which supplies heat to the surrounding college during the winter. The site was moved away from this local source in the spring of 1994.

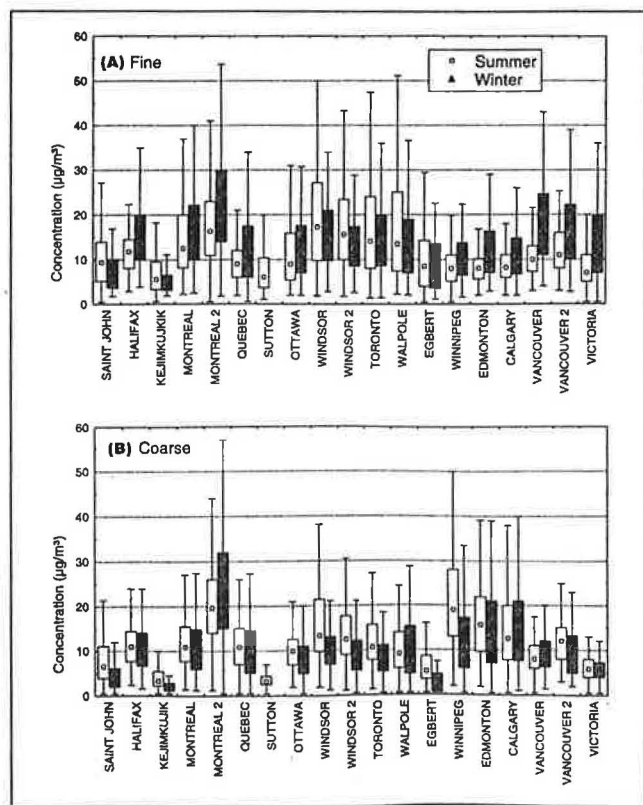
There are visible differences in the mean summer and winter PM<sub>2.5</sub> levels, but there is a large amount of overlap in the mass distributions (Figure 5A) with a similar amount of

variability in both seasons. The sites with the largest differences in mean PM<sub>2.5</sub> between the summer and winter are Saint John, Kejimikujik, Windsor (both sites), and Walpole. These differences are probably a result of SO<sub>4</sub><sup>2-</sup> seasonality, since at each of these sites, a relatively large fraction of the PM<sub>2.5</sub> is comprised of SO<sub>4</sub><sup>2-</sup> (Figures 4A-B).

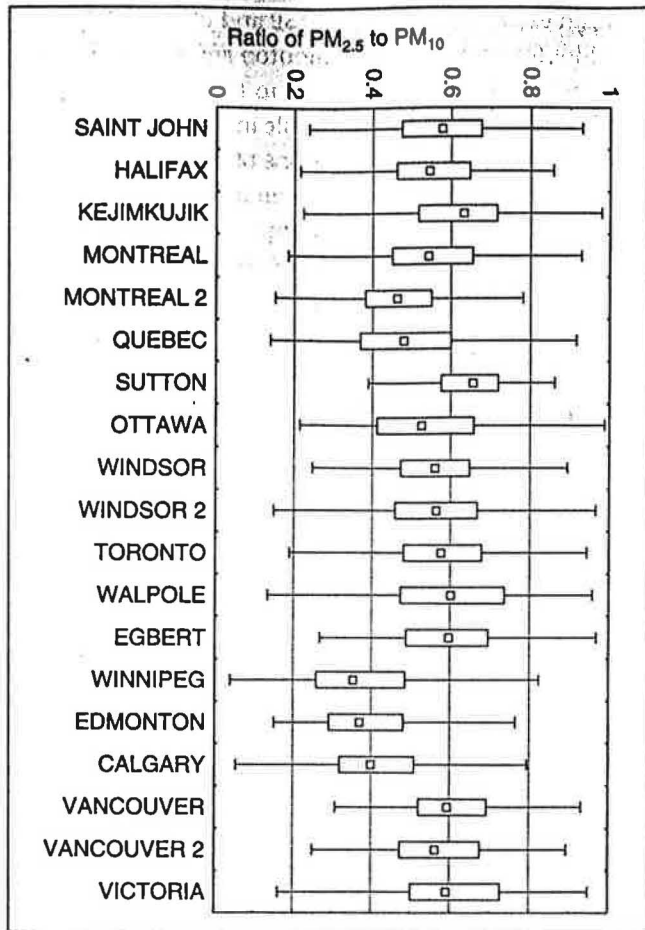
Figure 5B confirms what was inferred from Figure 4A-B; coarse particle concentrations tend to be smaller in the winter. When combined with the opposite seasonal pattern for fine mass, the seasonal differences in the mean PM<sub>10</sub> concentrations become quite small. Qualitatively, all sites west of Winnipeg have higher mean and median PM<sub>10</sub> concentrations in the winter, and all of those from Winnipeg east (excluding Ottawa, Montréal-2, Québec, and Halifax) show the opposite tendency (Figures 4A-B).

### Site-Specific Relationships between PM<sub>10</sub> and PM<sub>2.5</sub>

On average across all sites, 49% of the PM<sub>10</sub> is made up of fine particles. However, there is a considerable amount of variability in their ratio among sites and between individual observations. Differences in the PM<sub>2.5</sub> to PM<sub>10</sub> ratio across a variety of sites are displayed in Figure 6. At the urban locations, the mean ratio ranges from around 0.38 in the



**Figure 5A-B.** Comparisons of the particle mass (µg m<sup>-3</sup>) distributions between summer and winter at the NAPS dichot sites. All available data were used for each site. A. Fine mass. B. Coarse mass. The box plots indicate the mean 24-hour concentration and the 5<sup>th</sup>, 25<sup>th</sup>, 75<sup>th</sup>, and 95<sup>th</sup> percentiles.



**Figure 6.** Distributions of the mass ratio of  $PM_{2.5}$  to  $PM_{10}$  at the NAPS dichot sites. The box plots indicate the mean ratios and their 5<sup>th</sup>, 25<sup>th</sup>, 75<sup>th</sup>, and 95<sup>th</sup> percentiles.

Prairies to 0.59 on the west coast. The mean ratio ranges from 0.60 to 0.65 at the rural sites as well as at the Saint John, NB, site. From event to event, there is even more variability. For example, in Toronto the 5<sup>th</sup> and 95<sup>th</sup> percentiles of the ratio are about 0.15 and 0.90, respectively. The interquartile range (the difference between the 25<sup>th</sup> and 75<sup>th</sup> percentiles) for Toronto (combined sites) is close to 0.25. The interquartile range is between 0.15 and 0.25 for most of the sites. This indicates that about 50% of the time, the ratio of  $PM_{2.5}$  to  $PM_{10}$  does not vary by much more than  $\pm 0.10$  at a given site.

Linear regression results relating  $PM_{2.5}$  to  $PM_{10}$  are listed in Table 4. There are relatively strong correlations ( $r^2$ ) between  $PM_{10}$  and  $PM_{2.5}$  at each site. Values of  $r^2$  are greater than or equal to 0.70 at all but the three Prairie sites. As expected, correlations are larger at sites where  $PM_{2.5}$  comprises a larger fraction of  $PM_{10}$  and/or at sites with stronger fine-to-coarse correlations. Winnipeg, Calgary, and Edmonton have the smallest mean  $PM_{2.5}$  to  $PM_{10}$  ratios. Even though day-to-day changes in  $PM_{10}$  or  $PM_{2.5}$  are well correlated, accurate predictions of  $PM_{2.5}$  from  $PM_{10}$  or vice versa are not likely, since there is considerable unexplained variability in their ratio (there are also relatively large standard errors for the regression coefficients).

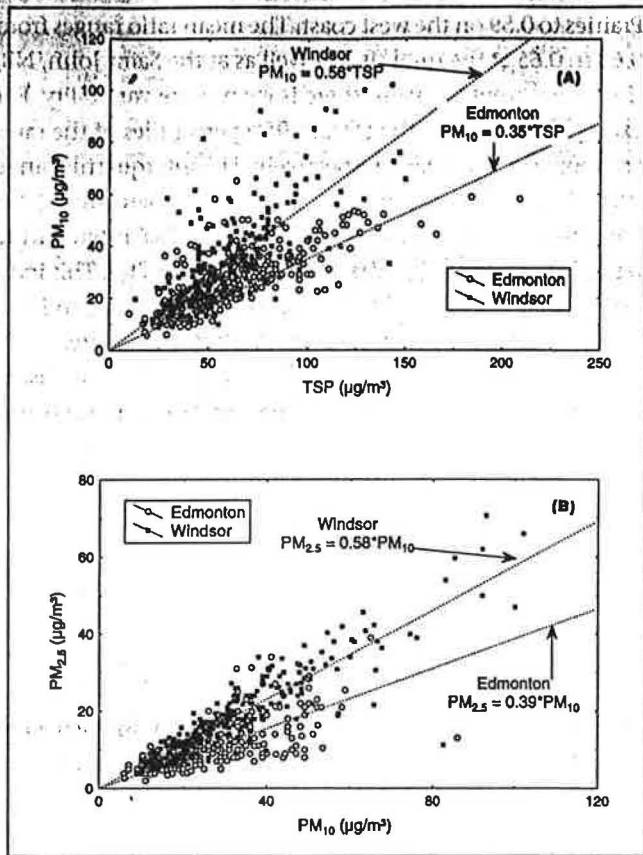
Given the relatively large amount of site-to-site variation in the  $PM_{2.5}$  to  $PM_{10}$  relationship, it would be difficult to justify an equivalent  $PM_{2.5}$  standard, objective, or guideline derived from an overall national relationship. Such an approach would have non-uniform impacts, depending upon location, and could have little relevance for health protection. There

**Table 4.** Site-by-site relationships between fine, coarse, and  $PM_{10}$  mass (all samples 1984-1993). C.V. = coefficient of variation.

Location	Number of Samples	Mean Fine	Mean Coarse	Mean $PM_{2.5}$ to Mean $PM_{10}$ Ratio	C.V. for $PM_{10}$	C.V. for Fine	C.V. for Coarse	Coarse to Fine $r^2$	Coarse to $PM_{10}$ $r^2$	Linear Equation $PM_{2.5} = a + b \cdot PM_{10}$		
		Mass ( $\mu g/m^3$ )	Mass ( $\mu g/m^3$ )			Mass*	Mass*			b	a	$r^2$
Saint John	292	10.1	7.3	0.58	0.74	0.37	0.29	0.37	0.77	0.58	0.09	0.86
Halifax	304	14.1	11.5	0.55	0.55	0.25	0.23	0.25	0.66	0.55	0.06	0.74
Kejimkujik	277	7.2	4.2	0.63	0.90	0.49	0.34	0.49	0.56	0.69	-0.62	0.86
Montréal	577	15.9	11.9	0.57	0.58	0.30	0.28	0.30	0.55	0.65	-2.12	0.81
Montréal-2	314	20.9	23.7	0.47	0.63	0.25	0.33	0.25	0.76	0.46	0.37	0.70
Québec City	221	11.9	11.6	0.50	0.65	0.28	0.35	0.28	0.63	0.54	-0.72	0.70
Sutton	136	7.7	3.5	0.68	0.40	0.40	0.22	0.40	0.66	0.83	-1.59	0.98
Ottawa	358	12.6	10.0	0.56	0.63	0.31	0.31	0.31	0.54	0.63	-1.66	0.77
Windsor	352	18.1	13.8	0.57	0.65	0.32	0.27	0.32	0.71	0.57	-0.16	0.81
Windsor-2	422	16.8	12.9	0.56	0.62	0.28	0.26	0.28	0.56	0.59	-0.76	0.73
Toronto	586	16.8	11.3	0.60	0.64	0.33	0.27	0.33	0.62	0.64	-1.14	0.84
Walpole	275	17.6	12.2	0.59	1.07	0.45	0.35	0.45	0.59	0.56	1.00	0.70
Egbert	137	10.4	6.6	0.61	0.80	0.45	0.31	0.45	0.71	0.64	-0.49	0.89
Winnipeg	447	10.3	18.4	0.36	0.75	0.22	0.48	0.22	0.82	0.29	2.02	0.42
Edmonton	380	10.5	16.4	0.39	0.61	0.19	0.41	0.19	0.76	0.34	1.32	0.46
Calgary	504	11.2	15.6	0.42	0.66	0.24	0.41	0.24	0.79	0.41	0.30	0.65
Vancouver	334	15.5	9.2	0.63	0.52	0.33	0.23	0.33	0.49	0.74	-2.71	0.88
Vancouver-2	360	15.6	11.3	0.58	0.57	0.29	0.25	0.29	0.56	0.65	-1.78	0.81
Victoria	393	11.5	6.3	0.65	0.51	0.37	0.27	0.37	0.36	0.81	-2.91	0.91
All sites	6669	13.8	12.1	0.53	0.63	0.38	0.37	0.13	0.66	0.52	0.32	0.70

\* Coefficient of variation is determined relative to the  $PM_{10}$  mean concentration (i.e., Standard Deviation for particle size of interest/mean  $PM_{10}$ ).





**Figure 7A-B.** Comparison of (A) PM<sub>10</sub> to TSP and (B) PM<sub>2.5</sub> to PM<sub>10</sub> relationships observed at the Windsor and Edmonton sites.

is even more site-to-site variability in the PM<sub>10</sub> to TSP relationship (not shown). Therefore, the same conclusion is true with respect to deriving an equivalent PM<sub>10</sub> objective or guideline using all the TSP and PM<sub>10</sub> data.

As an example, the PM<sub>10</sub> to TSP and PM<sub>10</sub> to PM<sub>2.5</sub> relationships for Windsor and Edmonton are shown in Figures 7A-B. In Windsor, the overall PM<sub>10</sub> to TSP ratio based upon a linear regression slope is 0.56, while in Edmonton it is 0.35. Using the Canada-wide mean slope of 0.44 (Table 3) to derive a PM<sub>10</sub> air quality objective from the existing TSP objective would have a much greater impact on Windsor, since a larger percentage of the TSP there consists of PM<sub>10</sub>. The differences between cities are not as great for the PM<sub>2.5</sub> to PM<sub>10</sub> ratios, but they are still visible. Ideally, new standards, objectives, or guidelines should be based upon linkages between the particle measure of concern and observed health effects.

The strength of the PM<sub>2.5</sub> to PM<sub>10</sub> correlations listed in Table 4 is consistent with the belief that the temporal variations in fine particles have a significant influence on the observed variability in PM<sub>10</sub>.<sup>12,13,18</sup> Measures of variability reported in Table 4 and the r<sup>2</sup> values associated with the PM<sub>10</sub> to coarse particle relationship also tend to support this notion. At most of the sites, the daily variations in PM<sub>10</sub> are correlated more with the fine particles than with the coarse particles. Again, the Prairie sites are an exception to this pattern. The coarse particle variations are also of greater potential importance at Montréal-2. To assess how much of the variation in PM<sub>10</sub> may be attributable to the variations in fine and coarse particles, the standard deviations for both the fine and coarse mass were divided by the mean PM<sub>10</sub> concentration. These variability measures are larger for the fine fraction than they are for the coarse fraction at a majority of the sites. This does suggest that the fine mass has a greater influence on the PM<sub>10</sub> variations. However, the differences between fine and coarse fractions are not overwhelming,

**Table 5.** Direct comparisons of urban and rural site measurements of fine fraction, coarse fraction, PM<sub>10</sub> mass, and sulfate. The Pearson correlation coefficient is represented by r.

Site 1	Site 2	N	Coarse Fraction			Fine Fraction			Total (PM <sub>10</sub> )		
			Mean Mass (µg/m <sup>3</sup> )	Mean Mass (µg/m <sup>3</sup> )	r	Mean Mass (µg/m <sup>3</sup> )	Mean Mass (µg/m <sup>3</sup> )	r	Mean Mass (µg/m <sup>3</sup> )	Mean Mass (µg/m <sup>3</sup> )	r
<b>MASS</b>											
Saint John	Kejimkujik	370	7.0	4.0	0.22	10.1	7.8	0.67	17.1	11.8	0.54
Montréal	Sutton	131	8.9	3.5	0.53	11.6	7.6	0.82	20.6	11.2	0.78
Toronto	Egbert	253	9.9	6.2	0.50	14.3	10.8	0.86	24.2	17.0	0.78
Windsor	Windsor 2	193	12.7	11.5	0.49	16.7	15.7	0.81	29.5	27.2	0.70
Windsor	Walpole	249	13.7	13.0	0.26	18.3	18.3	0.58	31.9	31.3	0.50
Windsor 2	Walpole	186	12.2	14.8	0.26	16.6	21.1	0.56	28.7	35.8	0.46
<b>SO<sub>4</sub><sup>-</sup></b>											
Saint John	Kejimkujik	44	0.36	0.17	0.36	3.1	2.3	0.84	3.5	2.5	0.83
Montréal	Sutton	15	0.22	0.15	0.64	3.1	2.8	0.92	3.4	2.9	0.91
Toronto	Egbert	9	0.26	0.30	0.53	5.1	4.7	0.90	5.4	5.0	0.90
Windsor	Windsor 2	111	0.49	0.94	0.49	4.8	4.1	0.90	5.3	5.1	0.92
Windsor	Walpole	161	0.52	0.40	0.51	5.8	5.8	0.71	6.3	6.1	0.73
Windsor 2	Walpole	74	0.89	0.39	0.34	4.2	7.2	0.69	5.2	7.4	0.78

**Table 6.** Median concentrations ( $\mu\text{g}/\text{m}^3$ ) of the most abundant  $\text{PM}_{10}$  species for selected urban sites (all data from 1986 to 1993).

Compound	Halifax	Montréal	Montréal-2	Ottawa	Toronto	Winnipeg	Calgary	Edmonton	Vancouver-2	Vancouver	Victoria
Sulfate	4.59	3.45	3.68	2.98	3.62	1.59	1.29	1.15	1.93	1.93	1.81
Nitrate	0.35	0.62	0.63	0.44	0.65	0.44	0.37	0.33	0.55	0.57	0.42
Sulfur	1.82	1.38	1.50	1.25	1.48	0.63	0.50	0.46	0.82	0.87	0.67
Aluminum	1.147	0.619	1.895	0.928	0.300	1.060	0.454	1.236	1.700	1.352	0.196
Calcium	0.113	0.856	1.079	0.618	0.800	1.013	0.986	0.441	0.167	0.204	0.125
Silicon	0.563	0.931	1.249	0.653	0.827	1.360	1.859	2.486	0.644	0.660	0.427
Chlorine	0.424	0.078	0.170	0.062	0.101	0.068	0.093	0.077	0.190	0.249	0.353
Iron	0.176	0.315	0.608	0.184	0.339	0.255	0.345	0.497	0.325	0.221	0.157
Potassium	0.094	0.179	0.232	0.138	0.147	0.164	0.170	0.172	0.118	0.139	0.091
Magnesium	0.064	0.071	0.122	0.089	0.109	0.350	0.140	0.100	0.110	0.198	0.084
Lead	0.015	0.042	0.070	0.018	0.046	0.019	0.041	0.057	0.058	0.055	0.054
Titanium	0.015	0.033	0.052	0.019	0.026	0.022	0.029	0.040	0.032	0.019	0.018
Zinc	0.019	0.046	0.068	0.020	0.042	0.017	0.018	0.018	0.024	0.029	0.015
Bromine	0.005	0.007	0.015	0.004	0.007	0.004	0.007	0.011	0.017	0.012	0.015
Phosphorus	0.027	0.034	0.036	0.022	0.026	0.012	0.013	0.012	0.015	0.019	0.010
Manganese	0.010	0.026	0.044	0.015	0.023	0.014	0.019	0.026	0.022	0.024	0.015
Barium	< DL	0.010	0.027	< DL	0.010	0.009	0.011	0.012	0.008	0.008	0.005
Scandium	0.005	0.015	0.018	0.011	0.014	0.015	0.014	0.009	0.008	0.005	0.004
Vanadium	0.098	0.008	0.013	< DL	< DL	< DL	0.002	0.004	0.005	0.006	0.006
Copper	0.008	0.010	0.015	0.011	0.011	0.006	0.004	0.006	0.014	0.014	0.002
Antimony	0.007	0.007	0.010	0.005	0.008	0.006	0.007	0.007	0.008	0.008	0.009
Tin	0.014	0.009	0.012	0.006	0.010	0.006	0.007	0.006	0.008	0.007	0.008
Nickel	0.020	0.003	0.004	0.001	0.002	< DL	< DL	< DL	0.003	0.002	0.003
Chromium	0.001	0.003	0.006	< DL	0.003	0.002	< DL	0.003	0.004	0.003	< DL
Selenium	< DL	0.001	0.001	< DL	0.001	< DL	< DL	< DL	< DL	< DL	< DL
Sampling Days	251	536	266	412	545	411	445	426	503	362	368

which indicates that the coarse particles can also contribute substantially to the overall  $\text{PM}_{10}$  variability. In particular, the coarse mass dominates at the Prairie sites and also has the potential to significantly influence the variability in  $\text{PM}_{10}$  at the Montréal-2 and Québec City sites. The greater influence by fine particles is most evident at the rural locations and at sites not heavily impacted upon by urbanization (i.e., traffic, industry, or construction).

The statistical results in Table 4 indicate that there is some common variability between the fine and coarse size fractions. In general, the correlation ( $r^2$ ) between the fine and coarse particles is smaller at the sites where the suspension of crustal material is thought to be a more important factor. This includes Winnipeg, Edmonton, and Walpole Island, which are in an area with agricultural activity.

#### Urban-Rural Differences

Mean concentrations and correlation coefficients were calculated separately for four pairs of urban-rural sites. Results are shown in Table 5. Walpole Island is 55 km north of Windsor, Egbert is 50 km north of Toronto, Sutton is 75 km southeast of Montréal, and Kejimikujik is 120 km southeast of Saint John. For each pair of sites, only the days when both sites provided valid measurements were used. With the exception of Walpole Island, particle mass concentrations were lower at the rural

locations. Although the distance between Walpole Island and Windsor is not much smaller than that separating the other pairs of sites, Walpole is influenced heavily by Detroit MI. This may explain why the mean  $\text{PM}_{10}$ ,  $\text{PM}_{2.5}$ , and coarse particle concentrations are higher at Walpole Island compared to Windsor-2, and why they are essentially the same as at Windsor.

For the other pairs of sites, the urban enhancement in concentration is greatest for the coarse particles. For example, the mean coarse particle concentration is 46% higher in Toronto compared to Egbert, while the mean amount of fine particles is only 28% higher in Toronto. This behavior stems from the slower rate of deposition of fine particles, which leads to more spatial homogeneity and greater importance of long-range transport, which is likely to similarly influence sites in close proximity to one another. Consequently, sites that are close together experience similar fine particle levels, while coarse particle levels differ more between sites. This is also reflected in the urban versus rural correlation coefficients (Table 6), which are systematically higher for fine particles. Similar differences in the inter-site correlations of fine and coarse particle concentrations have been observed around Philadelphia PA.<sup>40</sup> Although sample sizes decreased substantially for the  $\text{SO}_4^{2-}$  data (daily sampling was carried out for mass at these sites, but only one in six samples were analyzed

for  $SO_4^{2-}$ ), there appears to be a clear increase in correlation compared to the fine mass correlations. This is due to the strong influence of long-range transport on  $SO_4^{2-}$  levels in eastern Canada (i.e., the further the pollutants travel, the more they become homogeneously mixed over large areas). Some of the increased correspondence between sites in the fine mass compared to coarse mass is driven by similarity in  $SO_4^{2-}$  levels. Conversely, the apparent decrease in correlation from  $SO_4^{2-}$  to  $PM_{2.5}$  (N is different for PM and  $SO_4^{2-}$ ) suggests that some of the other fine mass constituents have more localized sources, which do not impact evenly on their neighboring urban or rural sites.

The higher particle concentrations at the urban sites are a reflection of the greater amounts of human activity (e.g., traffic and construction). The paved surfaces and smaller amounts of vegetation probably contribute to the elevated concentrations of coarse particles as well. Greater numbers of unpaved roads, agricultural activity, and more open areas with large undisturbed fetches should enhance the suspension of crustal material (coarse particles) at the rural sites, but these factors obviously do not outweigh those leading to more coarse particles in urban areas.

### Inorganic Composition of $PM_{10}$ and Fine and Coarse Particles

Figure 8 compares the mean concentrations of the inorganic elements and ions measured from May to September 1993 at the urban and rural CAAMP sites (i.e., the same sites as in Table 5, except that Walpole Island and Windsor are omitted, since Walpole Island does not appear to be a true rural site). The concentrations are higher at the urban sites for all the components listed. There are several elements/ions for which the urban-rural difference is greater than the total

mass difference. The relative amounts of Ca, Si,  $NO_3^-$ , Fe, Al, Mg, Zn, Ti, Mn, V, Pb, and Ni are larger in the urban particle samples compared to the rural samples. A number of these species are common in crustal material (e.g., Si, Ca, Ti), indicating greater suspension of dust in urban areas. This is consistent with the higher urban coarse particle concentrations shown in Table 5. Industrial activities and other combustion processes are likely responsible for the urban enrichment of some of the other species, such as  $NO_3^-$ , V, and Pb. There is generally very little urban enhancement in  $SO_4^{2-}$ ,  $NH_4^+$ , Na, Cl, Ba, and P, whereas the rural particles appear to contain a greater proportion of K and particularly Sn. In general, it appears that Ba, P, and K levels were affected by processes similar to those affecting  $SO_4^{2-}$  and  $NH_4^+$  (i.e., long-range transport and slow deposition velocities). In addition, the slightly higher proportion of K could be due to more vegetative sources or to more wood/biomass burning in the rural areas, while the higher proportion of Sn is difficult to explain. The similarity in the relative levels of Na and Cl between the urban and rural sites is likely driven by Saint John and Kejimikujik, both of which are situated near the ocean.

Median concentrations for some of the more abundant chemicals are listed in Table 6. Only selected cities representing a range of geographical areas are included. Sulfate and sulfur are the most abundant  $PM_{10}$  constituents at all of the sites shown. Al, Ca, and/or Si are the next most abundant elements. Some of the chemical differences among sites are consistent with their geographical locations and the sources in the vicinity and upwind of the sites. Median concentrations of Si, Ca, Mg, and Fe, which are typically associated with crustal material, tend to be high at the two Prairie sites. This is likely due to the intensive agriculture and the open, flat terrain surrounding these cities, which are conducive to the generation of soil-based particles.

Concentrations of these elements are also high at Montréal-2. This is partially due to the fact that this site has the highest median  $PM_{10}$  level. However, at Montréal-2, particle levels of Fe, Br, Mn, and Cr are clearly enhanced, relative to  $PM_{10}$  and relative to the other Montréal site. The relatively high median Ba and Pb concentrations are consistent with the influence of motor vehicles. Leaded fuel was in use during the early part of the monitoring program, and consequently Pb levels have dropped considerably from 1984-1986 to 1992.<sup>23</sup> The higher median concentrations of Br and Fe could also be due to the traffic near the site. Although Mn as MMT (methylcyclopentadienyl manganese tricarbonyl) is used in Canada as a gasoline additive, the relatively high

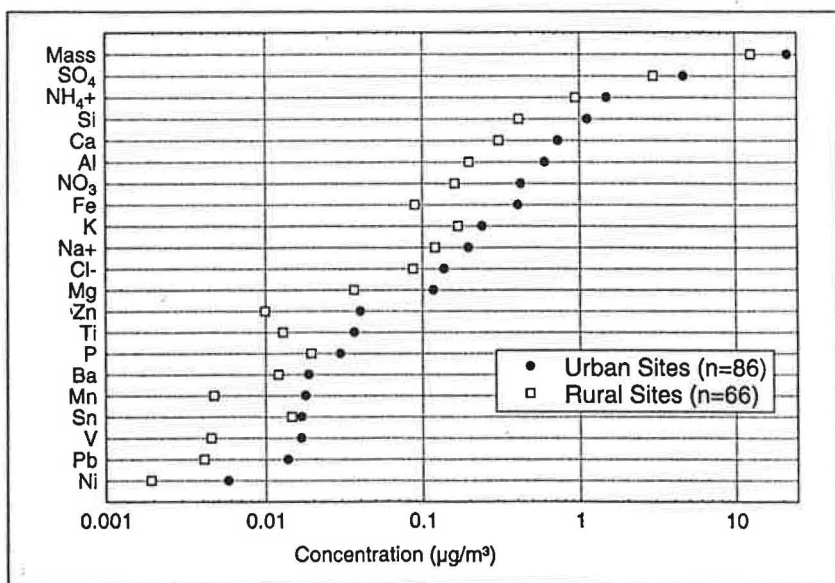
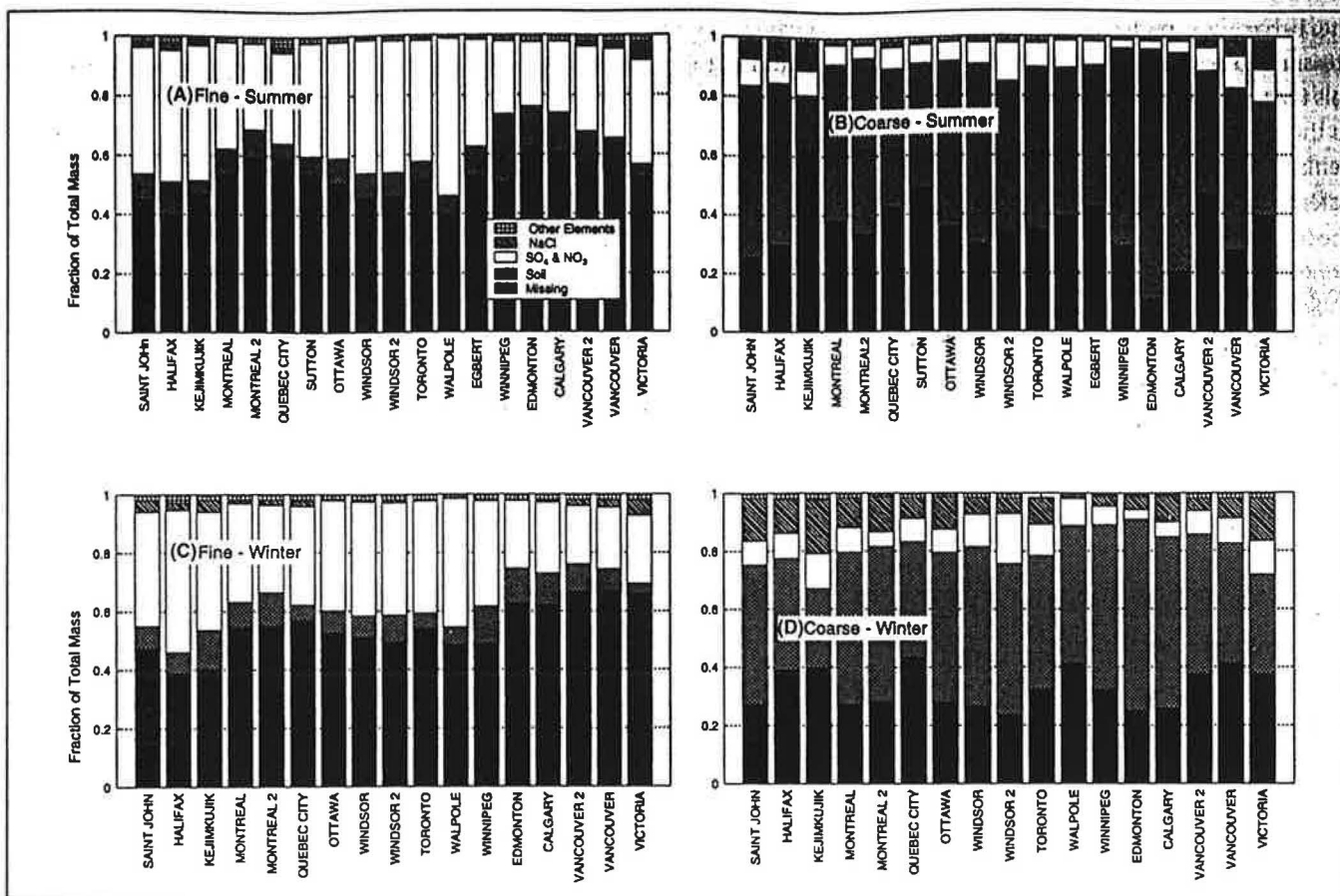


Figure 8. Comparison of the urban and rural concentrations ( $\mu g\ m^{-3}$ ) of the most abundant species (summer 1993).





**Figure 9.** Mean fractional contributions to the total fine and coarse mass from the chemical species attributed to soil (crustal material),  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  (includes  $\text{NH}_4^+$ ), NaCl, and other elements. See section on Mass Reconstruction in the text.

concentration at Montréal-2 is likely a result of a nearby ferro- and silico-manganese plant. This is also supported by the drop in Mn levels since the closure of this plant.<sup>41</sup>

The effect of being located near the stack of an oil-burning boiler is evident at Halifax in the median concentrations of V and Ni, which are higher than at any other site. The high mean annual concentrations are due to a dramatic wintertime increase in the levels of V and Ni, since Halifax concentrations are not much different from the other sites during the summer (not shown). However, some of the elevated Ni and V concentrations observed at Halifax are also likely due to use of oil for heating and electricity generation throughout the Maritime region and the east coast of the U.S. The link between Se and coal combustion is evident in the concentrations shown in Table 6. Median Se concentrations are higher in Montréal and Toronto, which are closest to the U.S. Midwest and southern Ontario, where coal consumption is high.

As expected, Cl concentrations are higher at the coastal sites. A marine source of Br may also be affecting Vancouver and Victoria, but this does not show up at Halifax. Toronto and Montréal, Canada's two major eastern cities, have higher median  $\text{NO}_3^-$  concentrations than their western

counterpart of Vancouver. This could be a reflection of the temperature-dependence of  $\text{NH}_4\text{NO}_3$  formation, since the eastern cities have colder climates. However, the higher  $\text{NO}_3^-$  concentration could also be due to higher levels of  $\text{HNO}_3$  in Toronto and Montréal. Brook<sup>24</sup> found that in the summer of 1993, the  $\text{HNO}_3$  concentrations were about a factor of two higher in southern Ontario compared to the Vancouver area.

All of the inorganic constituents were included in Eqs. 1-6 to calculate  $\text{Mass}_{\text{rec}}$  for each site. Consistent with other studies,<sup>33,34</sup> soil is the largest identifiable component in the coarse fraction, while  $\text{SO}_4^{2-}/\text{NO}_3^-/\text{NH}_4^+$  dominates the identifiable components within the fine fraction. Figures 9A-D show the percentage of mass accounted for by each of these components, as well as the percentages attributable to NaCl, other inorganic species, and the percent of mass that is unexplained. The general makeup of the fine particles is shown in Figures 9A and C for summer and winter, respectively. On average, the  $\text{SO}_4^{2-}/\text{NO}_3^-/\text{NH}_4^+$  component accounts for about 20% to 45% of the fine fraction, depending upon site. These values are within the range reported by Malm et al.<sup>33</sup> for the IMPROVE network and they are consistent with the result for Denver found by Countess and coworkers.<sup>34</sup> Most of the NAPS

sites behave as expected, with the  $\text{SO}_4^{2-}/\text{NO}_3^-/\text{NH}_4^+$  fraction increasing from winter to summer, but at Halifax and Winnipeg this fraction is larger in the winter. At Halifax this is likely due to the increase in the rate of oil combustion due to increased demand for heating. At Calgary and Edmonton there is no apparent seasonality to this component. Along with Winnipeg, the fraction of mass associated with the  $\text{SO}_4^{2-}/\text{NO}_3^-/\text{NH}_4^+$  component is smallest at these three Prairie sites.

Soil-based inorganic chemicals generally account for 5% to 15% of the fine mass. They are most important to the overall mass in Winnipeg and least important in Toronto. The range of percentages at the NAPS sites is within the ranges reported by Malm et al.<sup>33</sup> and Countess et al.<sup>34</sup> There is very little seasonal difference in the percent of fine mass explained by soil. The only sites where differences are clearly evident are located in Vancouver and in the Prairies. At these sites, there is an increase in the soil fraction from winter to summer. This is presumably due to agricultural activities in the summer, as well as to a greater frequency of precipitation and snow cover in the winter, which suppresses suspension of crustal material. As expected, the NaCl component of the fine particles is larger at the sites near salt water. However, even at these locations it only accounts for a maximum of 5% of the  $\text{PM}_{2.5}$ .

A large portion of the fine mass is not explained by the elements or compounds for which chemical analysis results are available. The average percent of unexplained mass is shown by the lower portion of the columns in Figures 9A-B. The unexplained mass ranges from 40% at Halifax during both seasons to 70% of the total at the Vancouver sites during the winter. On average, only about 45% of the total mass can be explained by  $\text{Mass}_{\text{rec}}$ . There is a slight increase in the percent unexplained from summer to winter, although at six sites the opposite pattern is observed.

Figures 9C-D show that a portion of the coarse fraction also remains unexplained.  $\text{Mass}_{\text{rec}}$  averages about 70% with a range of 60% to 80% at most sites. As expected, the amount of coarse mass associated with the soil component is much larger than for fine particles. On average across all sites the soil fraction is about 50%. However, there is considerable variability, with values ranging from 21% at Kejimikujik to 75% at Edmonton. This range encompasses the soil fraction reported by Countess et al.<sup>34</sup> for Denver, which is 64% (using their lower estimate). Malm et al.<sup>33</sup> did not break down the coarse particle components. From the fine to the coarse particles, the  $\text{SO}_4^{2-}/\text{NO}_3^-/\text{NH}_4^+$  component decreases substantially in importance and the NaCl fraction increases. During the winter, the coarse mass contribution by NaCl is larger at all sites. This is associated with the use of road salt. At the coastal sites, this increase may also be due to increases in wind speed and hence to sea spray.

The largest unexplained coarse fraction is observed at Kejimikujik. This could be associated with the forest environment throughout the region surrounding the site. This

environment, plus the lack of agriculture and the proximity to the ocean, may be the reason for the small percentage of soil-related elements. The forests around Kejimikujik could also be a source of organic material, leading to a relatively large unexplained mass fraction. The soil fractions are also relatively small at the other coastal sites, particularly Victoria. The inland sites with the smallest soil fractions are Québec City and Sutton, both of which are in regions with significant amounts of forested landscape.

Table 7 contains a site-by-site summary of the actual mean mass values ( $\mu\text{g m}^{-3}$ ) associated with the components included in  $\text{Mass}_{\text{rec}}$  and the mean percent of total mass explained. The mean mass concentrations and sample sizes are different from those in Table 4 because there were fewer samples with complete chemical analysis. As discussed in the section on Mass Reconstruction, the unexplained mass is assumed to be associated with carbonaceous species. Under this assumption, fine particle carbonaceous species account for from 65% to 40% of the total mass, depending upon site. There is apparently a greater percentage of carbon-related fine particles in the west (~62%) than there is on the east coast (40% to 46%). These values agree well with Malm et al.'s<sup>33</sup> results for the Cascades and Northern Rockies (65%) and for the Northeast (36%). Over the northeast states, Poirot et al.<sup>42</sup> reported that about 30% of the fine mass consists of carbon, which is 10% to 15% less than the east coast results indicated in Table 7. Malm et al.<sup>33</sup> did not have sites in the upper Midwest to compare with the NAPS sites in Ontario and Québec. However, their carbon fractions for Boundary Waters (44%) and Northern Great Plains (47%) are in reasonable agreement with the unexplained fraction in Winnipeg (50%). The percents of explained mass for Toronto are similar to findings reported by Sturges et al.<sup>43</sup> Using semi-quantitative x-ray diffraction, they found that in the spring-summer 43% of the  $\text{PM}_{2.0}$  and 46% of the  $\text{PM}_{15}$  could be accounted for. In the winter these percentages increased to 61% and 52%, respectively.

For 13 of the 19 sites, the estimated carbon percentage associated with the coarse particles is smaller than for the fine particles. This is expected given the typical dominance of the soil contribution, and has been seen elsewhere.<sup>33</sup> However, Countess et al.<sup>34</sup> found that only 10.7% of the coarse mass was due to organic and elemental carbon, which is at least a factor of two smaller than the results inferred from Table 7, depending upon site. In contrast to most of the sites, there is an increase in the amount of unexplained mass (from 43.8% to 56.5%) from the fine to the coarse particles at Kejimikujik. The cause of this increase is unknown, as is its representativeness relative to the long-term conditions at the site, since the calculations were based only upon 36 samples. As discussed above, the estimated carbon fraction (i.e., unexplained mass) for the fine particles agrees with nearby observations by Malm et al.,<sup>33</sup> and thus there is no reason to discount the coarse particle results.

**Table 7.** Fraction of mass accounted for by the various compositional groups described in the Mass Reconstruction section of text (all data from 1986 to 1993).

City/Location	N	Mean Mass Explained	Mean Total Mass ( $\mu\text{g m}^{-3}$ )	Mean Mass Fractions ( $\mu\text{g m}^{-3}$ )				
				Missing	Soil	SO <sub>4</sub> /NO <sub>3</sub>	NaCl	Other El.
<b>Coarse Fraction</b>								
Saint John	60	74.0%	8.3	2.2	4.5	0.7	0.7	0.1
Halifax	160	64.4%	11.7	4.2	5.2	1.0	1.2	0.2
Kejimikujik	36	43.5%	3.9	2.2	0.8	0.4	0.4	0.1
Montréal	225	67.5%	12.2	4.0	6.4	0.9	0.7	0.2
Montréal-2	209	69.7%	23.2	7.0	13.0	1.2	1.8	0.3
Québec City	113	56.9%	13.6	5.9	5.7	1.1	0.7	0.2
Sutton	11	50.6%	3.9	1.9	1.6	0.3	0.0	0.1
Ottawa	195	68.6%	11.3	3.5	6.0	0.8	0.7	0.1
Windsor	277	71.9%	14.0	3.9	8.0	1.4	0.6	0.2
Windsor-2	135	71.4%	11.4	3.3	5.8	1.8	0.4	0.2
Toronto	237	66.6%	12.0	4.0	5.9	1.2	0.7	0.2
Walpole Island	183	59.6%	13.0	5.3	6.3	1.2	0.1	0.2
Egbert	11	57.2%	9.3	4.0	4.4	0.8	0.0	0.1
Winnipeg	296	69.0%	19.5	6.1	11.9	1.0	0.4	0.2
Edmonton	278	81.3%	16.5	3.1	12.3	0.5	0.4	0.2
Calgary	353	76.2%	15.4	3.7	10.0	0.7	0.9	0.2
Vancouver-2	202	60.5%	10.0	3.9	4.7	0.8	0.4	0.2
Vancouver	204	63.3%	9.0	3.3	4.1	0.9	0.6	0.2
Victoria	258	61.6%	6.7	2.6	2.4	0.8	0.8	0.1
<b>Fine Fraction</b>								
Saint John	66	54.1%	10.9	5.0	0.9	4.5	0.3	0.2
Halifax	175	60.7%	13.4	5.3	1.1	6.3	0.3	0.4
Kejimikujik	59	56.2%	8.5	3.7	0.7	3.7	0.2	0.1
Montréal	254	45.9%	18.0	9.7	1.5	6.2	0.1	0.3
Montréal-2	208	43.2%	20.5	11.7	2.2	6.1	0.2	0.4
Québec City	117	42.6%	12.9	7.4	0.7	4.2	0.2	0.3
Sutton	15	46.4%	8.9	4.8	0.5	3.4	0.0	0.2
Ottawa	277	48.1%	12.9	6.7	1.0	5.0	0.0	0.2
Windsor	280	50.8%	18.3	9.0	1.4	7.6	0.1	0.3
Windsor-2	135	52.3%	16.3	7.8	1.4	6.7	0.1	0.3
Toronto	242	46.8%	16.7	8.9	0.9	6.5	0.1	0.3
Walpole Island	189	54.9%	17.0	7.6	1.0	8.1	0.0	0.2
Egbert	11	46.7%	12.0	6.4	1.1	4.3	0.0	0.2
Winnipeg	291	50.4%	9.7	4.8	1.6	3.1	0.0	0.2
Edmonton	301	37.4%	10.5	6.6	1.3	2.4	0.0	0.2
Calgary	321	38.4%	10.1	6.2	1.2	2.4	0.1	0.2
Vancouver-2	316	37.3%	13.1	8.2	1.3	3.1	0.3	0.2
Vancouver	239	36.0%	13.9	8.7	1.2	3.4	0.1	0.3
Victoria	246	38.9%	11.0	6.7	0.4	3.0	0.6	0.3

Soil: see Eq. 2.

NaCl: sum of the measured or estimated mass of Na<sup>+</sup> and Cl<sup>-</sup>.SO<sub>4</sub>/NO<sub>3</sub>: sum of the measured mass of SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup>; plus the measured or estimated mass of NH<sub>4</sub><sup>+</sup>.

Other El.: sum of the measured mass of all other available elements with multipliers as shown in Mass Reconstruction section (e.g., 1.79\*V).

The main factors that could reduce the estimated elemental and organic carbon fractions are the amount of water on the samples, the amount of carbon from crustal material, exclusion of additional forms of S, and the loss of particle NO<sub>3</sub> between gravimetric and IC analyses. It is not known how much water was present on the filters at the time of mass

determination. Countess et al.<sup>34</sup> estimated that at 45% relative humidity, water can account for 4.8% of the mass. This value is probably relevant for some of the Canadian samples, depending upon chemical composition, but further work is needed to adequately assess the importance of water. As discussed in the section on Mass Reconstruction, further work is also needed to determine how much NO<sub>3</sub> is lost during EDXRF. The potential contribution from additional forms of S is estimated to lead to no more than a 5% decrease in the estimated elemental and organic carbon fractions.

The contribution by crustal carbon (e.g., calcite) at the NAPS and CAAMP sites is unknown. Davis and Maughan<sup>44</sup> found that calcite (CaCO<sub>3</sub>) accounted for an average of 2.5% of the fine mass and 5.5% of the coarse mass in Helena MT. From samples collected in Toronto, Sturges et al.<sup>43</sup> found that calcite accounted for 1.2% and 2.4% of the PM<sub>15</sub> for the winter and spring/summer, respectively. Calcite was responsible for less of the Toronto fine mass (PM<sub>2.0</sub>), explaining only 0.9% to 1.5% for the winter and spring/summer. The soil multiplication factors in Eq. 2, which were derived by Malm et al.,<sup>33</sup> may already account for typical amounts of calcite and water. However, they do not discuss these factors in detail and only state that the mean stoichiometric factors are scaled up by 1.16 to account for other compounds. Nonetheless, with or without corrections for water and crustal carbon, the amount of unexplained mass is large at the NAPS and CAAMP sites.

## SUMMARY AND CONCLUSIONS

Twenty-four-hour measurements of TSP, PM<sub>10</sub>, PM<sub>2.5</sub>, SO<sub>4</sub><sup>2-</sup>, and other inorganic ions and elements collected from 19 urban and rural locations in Canada were examined. Up to ten years (1984-1993) of data for every sixth day were available. Daily summertime measurements were collected in 1992 and 1993 at up to six locations.

Amongst all locations, most of the 24-hour TSP concentrations were below 98  $\mu\text{g m}^{-3}$ , a majority of the PM<sub>10</sub> concentrations were below 47  $\mu\text{g m}^{-3}$ , and most of the PM<sub>2.5</sub> concentrations across Canada were below 26  $\mu\text{g m}^{-3}$  (based upon 90th percentiles). As expected, these three measures of ambient particle concentration were found to be correlated.

Overall/nationwide mean ratios or statistical relationships could be used to estimate equivalent PM<sub>10</sub> and PM<sub>2.5</sub>



air quality standards or objectives corresponding to existing  $PM_{10}$  or TSP standards. However, differences among sites would lead to non-uniform impacts, depending upon location, and could have little relevance for health protection.

On average across all sites,  $PM_{2.5}$  accounted for 49% of the  $PM_{10}$ , and  $PM_{10}$  accounted for 44% of the TSP. The strength and nature of the correlations between TSP,  $PM_{10}$ ,  $PM_{2.5}$ , and coarse particles varied depending upon site and particle size. For example, the mean  $PM_{2.5}$  to  $PM_{10}$  ratio ranged from 0.40 at three different urban sites in the Prairies to 0.60 at the rural and west coast sites. This ratio also varied substantially from measurement to measurement, but at most sites a majority (>50%) of the ratios were within  $\pm 10\%$  of the median value.

At a majority of the sites, the daily variability in fine particle mass had a stronger influence on the variations in  $PM_{10}$  than did the coarse particle mass. This was most evident at the rural locations and at sites not heavily impacted by urbanization (i.e., traffic and construction). While this is consistent with the idea that fine particles control the variability in  $PM_{10}$ , it was not true at all sites or over all geographical areas. For example, the coarse mass dominated the  $PM_{10}$  variability at the Prairie sites and at the site most heavily impacted by traffic.

Comparison of the urban and rural sites that were relatively close to one another indicated that particle mass concentrations were lower at the rural locations. This urban enhancement in concentration was greatest for the coarse particles. For example, the mean coarse particle concentration was 46% higher in Toronto compared to Egbert, while the mean amount of fine particles was only 28% higher in Toronto. This is also reflected in the urban versus rural correlation coefficients, which were systematically higher for fine particles and even higher for ambient  $SO_4^{2-}$ . The decrease in correlation from  $SO_4^{2-}$  to  $PM_{2.5}$  suggests that some of the other chemical species contributing to the fine particle mass had more localized sources, which did not impact evenly on their neighboring urban or rural sites.

Particle concentrations differed between the summer (May to September) and winter (October to April). Fine particle levels tended to be higher in the winter, except at a few sites where sulfate was an important constituent. The wintertime increase could not be explained by increases in particle nitrate concentrations or increases in any of the other inorganic constituents. Thus, the increase appears to have been due most likely to differences in the meteorological conditions (e.g., lower mixing layer heights). However, there was no data on elemental or organic carbon to determine if their concentrations increase from summer to winter. In contrast to the fine particles, the concentrations of coarse particles were higher in the summer.

Estimates of the amount of fine and coarse particle mass due to carbonaceous material were assumed using a mass

balance approach. Depending upon site, only about 37% to 61% of the  $PM_{2.5}$  could be explained given the measured concentrations of several inorganic ions and elements. Thus, carbonaceous material, which was likely to have been predominantly organic in nature, was responsible for about half of the overall fine particle mass. This fraction was higher in Alberta and British Columbia (~65%) than it was on the east coast (40% to 45%). Due to the increased importance of crustal material, a greater portion of the coarse particle mass (~70%) was explained by the inorganic constituents.

Measurements of elemental and organic carbon concentrations are needed across Canada to verify the estimates presented in this paper. These measurements, as well as a breakdown of the predominant organic chemical species, are also necessary in order to develop proper control strategies. In addition, more reliable measurements of the true amount of particulate nitrate are needed before control strategies can be developed.

#### ACKNOWLEDGMENTS

The authors would like to thank Dr. Joe Dlouhy, Dr. Eva Dabek-Zlotorzynska, Ms. Sandra Callaghan, and all others who contributed to the analyses of the mass and chemical composition of the particle samples. We also gratefully acknowledge the provincial, municipal, and federal regional agencies for their cooperation. In addition, the measurements would not have been possible without the dedication of the site operators, who reliably collected the samples throughout the program.

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