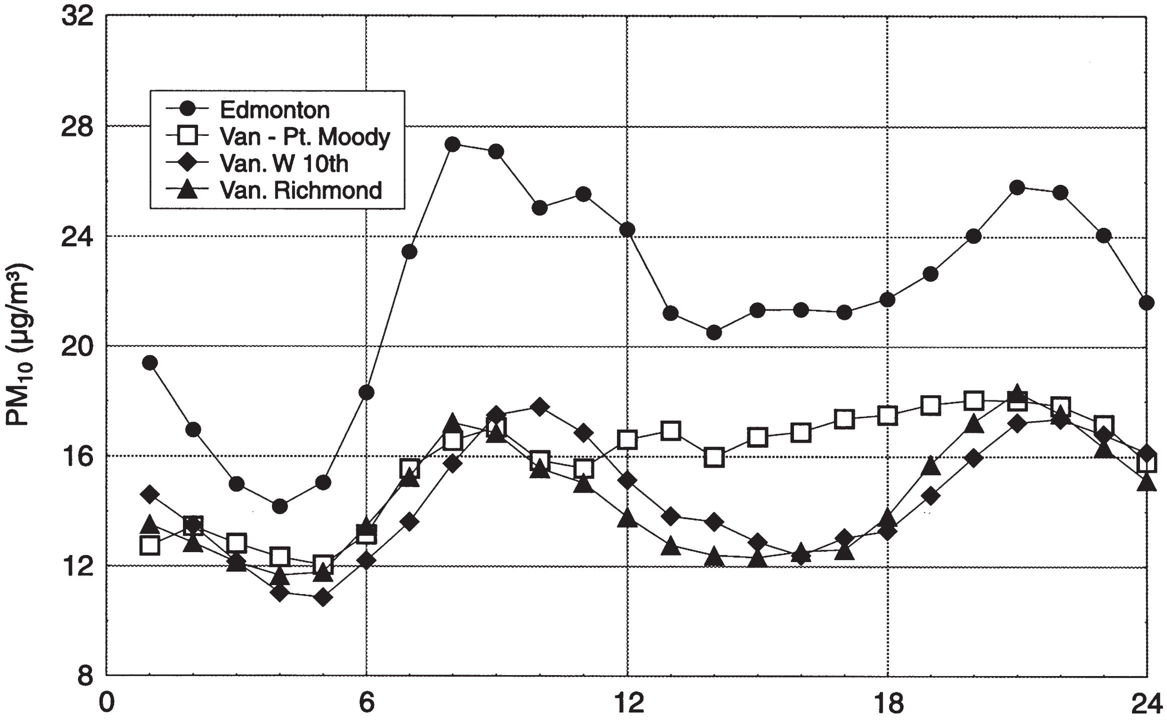
5.3.5 One-Hour Averaged Data PM_{10} Data

National Network (NAPS)

In 1994, ten sites (all but two in the Lower Fraser Valley) reported hourly PM_{10} concentrations using TEOM instruments. Summary statistics for these sites are shown in Table 5.19. The ratio of 1 h maxima to 24 h maxima ranged from 1.5 to 5. A maximum 1 h PM_{10} concentration of 255 µg/m³ was measured at the Abbotsford site and a maximum 1 h concentration of 204 µg/m³ at the Edmonton site. Diurnal variations in PM_{10} are provided for four of these sites in Figure 5.14. The Figure shows that a substantial increase in PM_{10} levels occurs during the morning rush hour with a minimum at most sites during the mid-afternoon and a secondary peak during the late evening. This is very similar to the diurnal profile measured in Cranbrook, BC as discussed below.

Figure 5.14 Diurnal Variation in PM_{10} Concentrations from Selected NAPS TEOM Monitoring Sites (1994).



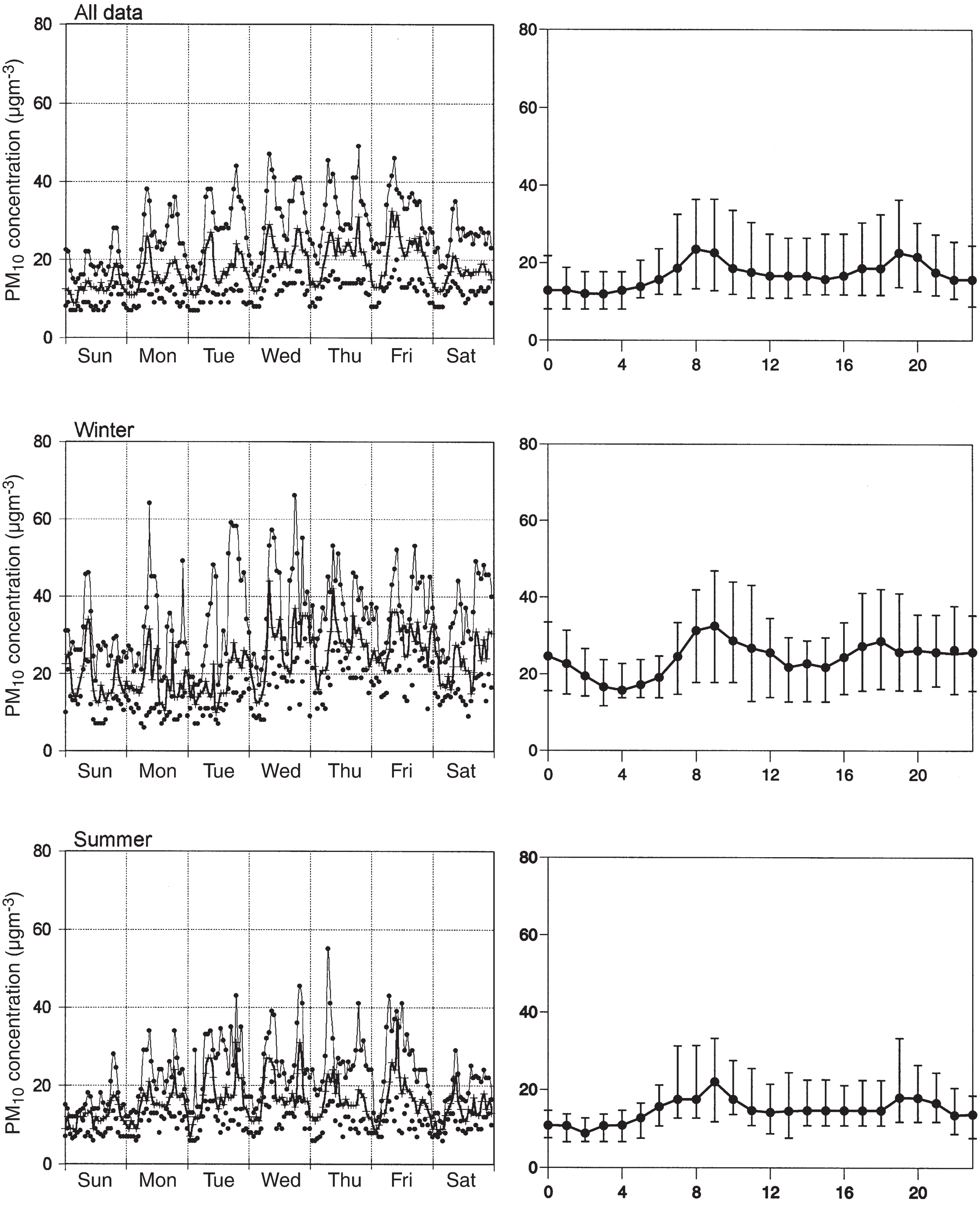
British Columbia

Only one site from the BC database made available hourly averaged PM_{10} data from a period of more than 24 months. This data record is from a site at Cranbrook (E206243), which commenced data acquisition in March 1992. Because of the short duration of this record, it was examined only with regard to diurnal and hebdomadal cycles and the seasonality of these cycles (Figure 5.15). It is clear from Figure 5.15 that in both the summer (July, August, September) and winter (December, January, February) months, the diurnal variability of PM_{10} concentrations is characterized by two periods of elevated concentrations: one during the early morning (8-10 a.m.) and one later in the day (from about 5 p.m. into the night). The former may be indicative of emissions during the morning rush-hour period. The latter may be related to wood burning in residential heating and late afternoon/early evening rush-hour traffic. In the absence of chemical speciation of the aerosols, these sources are speculative. However, the relative intensity of the nocturnal maximum during the winter supports wood burning and evening traffic. Interestingly, the weekday maximum of PM_{10} (especially during Wednesday to Friday/Saturday) is marked during the winter months but is much less evident in the summer data.

Table 5.19 Summary Statistics for Hourly PM_{10} Measurements (TEOM Instruments) – NAPS Network, 1994.

NAPS ID	City	Location		MIN	Percentiles							MAX	% Data	Annual Mean	Std. Dev.
					10	30	50	70	90	95	99				
070119	Winnipeg	65 Ellen Street	1 HR	0	7	14	20	28	45	55	76	99	56	–	–
			24 HR	3	12	17	21	27	38	43	54	61	56		
090122	Edmonton	127 St. & 133 Avenue	1 HR	0	6	11	17	25	45	55	80	204	88	22	17
			24 HR	4	9	14	20	26	37	44	60	75	88		
100110	Vancouver	6400 E. Hastings & Kensington	1 HR	0	5	9	12	16	25	30	41	126	63	–	–
			24 HR	3	7	10	13	16	23	26	31	40	63		
100111	Vancouver	Moody/ Esplanade, Port Moody	1 HR	0	6	11	15	20	30	35	47	89	96	17	10
			24 HR	4	8	12	16	20	28	31	36	40	96		
100118	Vancouver	2550 West 10th Avenue	1 HR	1	6	10	13	18	26	31	43	68	95	15	9
			24 HR	3	8	11	14	17	23	26	31	41	95		
100125	Vancouver	8544 116th Ave., Delta	1 HR	0	5	9	13	18	27	32	45	98	97	15	9
			24 HR	4	8	10	13	17	24	28	35	44	98		
100127	Vancouver	19000 & 72nd Ave., Surrey	1 HR	0	6	9	12	16	24	28	39	74	96	14	8
			24 HR	4	7	10	13	16	21	25	29	35	95		
100128	Vancouver	Williams & Aragon, Richmond	1 HR	1	6	9	12	17	26	32	45	89	98	14	9
			24 HR	4	8	11	14	17	22	25	31	43	99		
101002	Abbotsford	33660 South Fraser Highway	1 HR	0	6	11	17	24	38	47	77	255	44	–	–
			24 HR	3	9	14	20	25	34	40	49	53	44		
101301	Langley	23752 52nd Avenue	1 HR	0	5	9	12	16	24	29	39	65	97	14	8
			24 HR	3	7	10	13	16	21	25	30	35	97		

Figure 5.15 The Interquartile Range and Median PM_{10} Concentrations (µg/m³) at Cranbrook, BC by Day of Week and by Hour of Day for All Data, Winter (D,J,F) and Summer (J,J,A).



5.4 RELATIONSHIPS AMONG TSP, PM_{10} AND $PM_{2.5}$ AND INORGANIC CONSTITUENTS OF PARTICULATE MATTER IN CANADA

The following discussion is drawn largely from Brook et al., 1997.

5.4.1 TSP, PM_{10} and $PM_{2.5}$ and SO_4^{2-}

Fourteen urban sites in the NAPS dichotomous sampler network operating from 1986 to 1994 had simultaneous measurements of TSP, PM_{10}, $PM_{2.5}$ and SO_4^{2-} and combined summary statistics (only for days with all data available) are provided in Table 5.20. For this data set, daily TSP concentrations ranged from 10 to 575 µg/m³ with a majority of the concentrations between 10 and 100 µg/m^3. PM_{10} concentrations ranged from 5 to 175 µg/m^3; most of the concentrations were below 50 µg/m^3. Most of the 24 h $PM_{2.5}$ measurements were between 2 and 30 µg/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 mass distribution. As expected, a large majority of the SO_4^{2-} was found on the fine particles.

Summary statistics for the daily ratios of PM_{10}/TSP, $PM_{2.5}$/TSP, $PM_{2.5}/PM_{10}$, $PM_{2.5\text{-}10}/PM_{10}$ and Fine $SO_4^{2-}/PM_{2.5}$ are also provided in Table 5.20. On average, mean PM_{10} accounted for 50% of the TSP, while mean $PM_{2.5}$ accounted for 25% of TSP. The maximum PM_{10}/TSP and $PM_{2.5}$/TSP values were greater than one, which is not expected given that both $PM_{2.5}$ and PM_{10} are fractions of TSP. Errors of this nature are not surprising given the complications of operating an extensive monitoring program involving different agencies. The fact that the dichotomous sampler is a more precise instrument compared to the 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}. Sulphate was, on average across the urban sites, only responsible for 17% of the $PM_{2.5}$. The relationships between TSP, PM_{10}

Table 5.20: Combined Summary Statistics for 14 Urban NAPS Sites in Operation between 1986 and 1994. Sample size, n=2831, is based upon the number of 24 h Periods with Valid Measurements for TSP, PM_{10}, $PM_{2.5}$ and SO_4^{2-}. (FSO_4 and CSO_4 correspond to fine and coarse SO_4^{2-}, respectively)

	Percentiles					Statistics				
Measurement	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	0.6	1.9	3.1	6.0	8.8	39.0	2.9	3.3	1.9	2.4
CSO_4	0.1	0.3	0.4	0.6	0.9	4.6	0.4	0.3	0.3	2.2
Ratios										
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
$FSO_4/PM_{2.5}$	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.)

and $PM_{2.5}$ are dependent on concentration. Ratios of PM_{10} to TSP and $PM_{2.5}$ to TSP decrease with increasing TSP concentrations as a greater proportion of the TSP mass is represented by very coarse particles. As shown in Table 5.21, an exponential equation best fits the data sets.

Table 5.21: Relationships between TSP, PM_{10} and $PM_{2.5}$ (using data from 14 Urban sites)

Equation	r^2
Linear Relationship	
* $PM_{10} = 0.44 * TSP$	0.817
$PM_{2.5} = 0.73 + 0.49 * PM_{10}$	0.636
* $PM_{2.5} = 0.21 * TSP$	0.620
Exponential Relationship	
* $PM_{10} = 10{**}\ (0.826 * \log TSP)$	0.986
$PM_{2.5} = 10{**}\ (-0.25 + 0.949 * \log PM_{10})$	0.668
* $PM_{2.5} = 10{**}\ (0.636 * \log TSP)$	0.946

* Intercepts forced to zero

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 Figure 5.16. Only days with observations of all four parameters were used to allow a proper comparison between parameters at each site. Each of the sites 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. As discussed previously, much of the airborne PM observed in these areas is mechanically derived and likely consists of local crustal material.

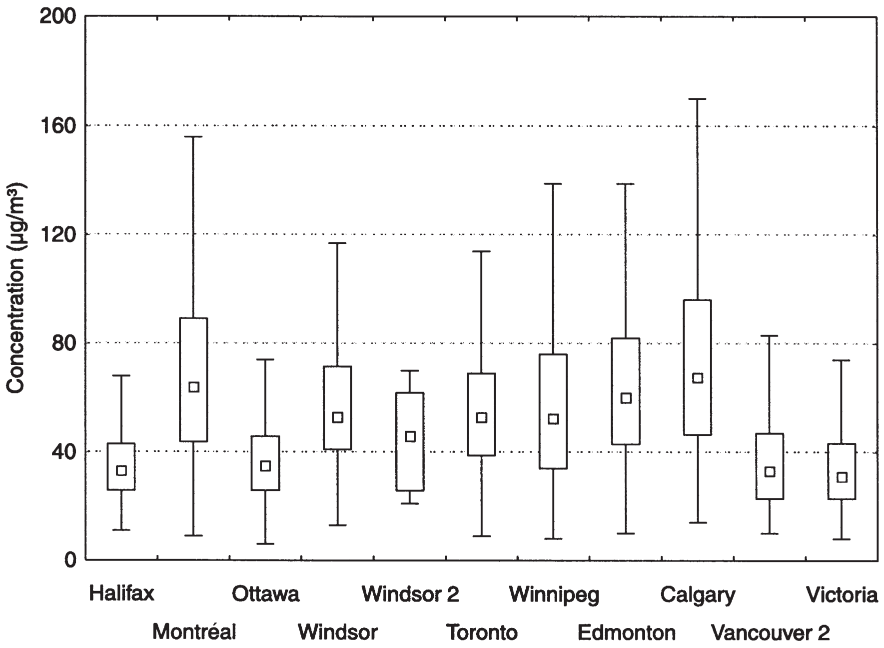
There is an obvious decrease in the SO_4^{2-} levels from the sites located east of the upper Great Lakes to those located west of the lakes. This is a direct reflection of the magnitude and spatial density of SO_2 emissions within and upwind of these two areas. SO_4^{2-} concentrations are highest in southern Ontario although the mean levels in µg/m³ are surprisingly similar from Ontario to Halifax, NS.

Mean $PM_{2.5\text{-}10}$, $PM_{2.5}$ and SO_4^{2-} concentrations were calculated separately for winter and summer periods and are displayed for selected sites in Figures 5.17. All available data for each site were used (i.e., sample size differs for parameters) and locations representing rural eastern Canada are included. As discussed in the preceding sections, summer mean $PM_{2.5}$ levels are higher over eastern Canada compared to the west. The reason for this difference is that in the summertime SO_4^{2-} increases dramatically at the eastern sites. East to west differences in mean $PM_{2.5}$ levels are less in the winter due to decreases in the eastern concentrations of SO_4^{2-} and to relatively large increases in $PM_{2.5}$ in Vancouver and Victoria. With the exception of Toronto and Windsor, all the sites shown have higher $PM_{2.5}$ 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 $PM_{2.5}$. Mixing heights are usually lower and energy consumption for heating is higher. Wood burning is also more prevalent.

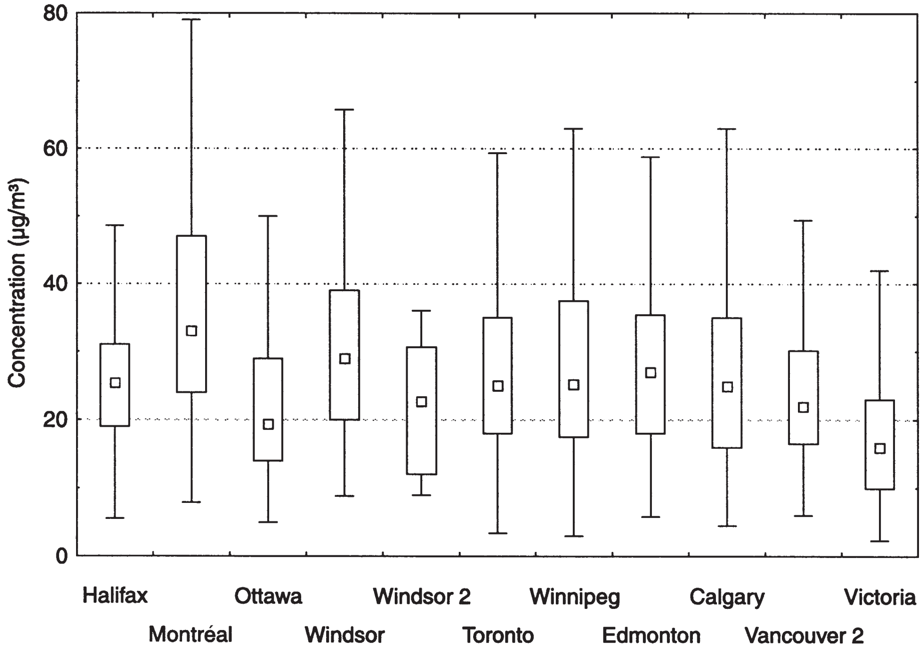
On average, increases in PM_{10} from summer to winter are generally equal to or less than the magnitude of the $PM_{2.5}$ increases. Therefore, the additional PM_{10} found in the winter is likely due to fine particles and not coarse particles. This suggests that combustion sources are an important contributor to wintertime particle pollution and shows that fine particles drive the seasonal PM_{10} variability. The Toronto, Windsor and Winnipeg sites are the only ones included in Figure 5.17 where PM_{10} 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. This may be due to snow cover and/or increases in precipitation, which would inhibit the suspension of crustal material. There are visible differences in the mean summer and winter $PM_{2.5}$ levels, but there is a large amount of overlap in the mass distributions with a similar amount of variability in both seasons. The sites with the largest differences in mean $PM_{2.5}$ between the summer and winter are Saint John, Kejimkujik, Windsor (both sites) and Walpole. These differences are probably a result of SO_4^{2-} seasonality since at each of these sites, a relatively large fraction of the $PM_{2.5}$ is comprised of SO_4^{2-}. Qualitatively, all sites west of Winnipeg have higher mean and median PM_{10} concentrations in the winter and all of those from Winnipeg east, excluding Ottawa, Montréal-Duncan/Décarie, Québec and Halifax, show the opposite tendency.

Figure 5.16 Comparison of the Distributions ofTSP, PM_{10}, $PM_{2.5}$ and SO_4^{2-} at 11 Urban Sites (1984-1993). The box plots indicate the median, 5th, 95th, 25th, and 75th percentiles.



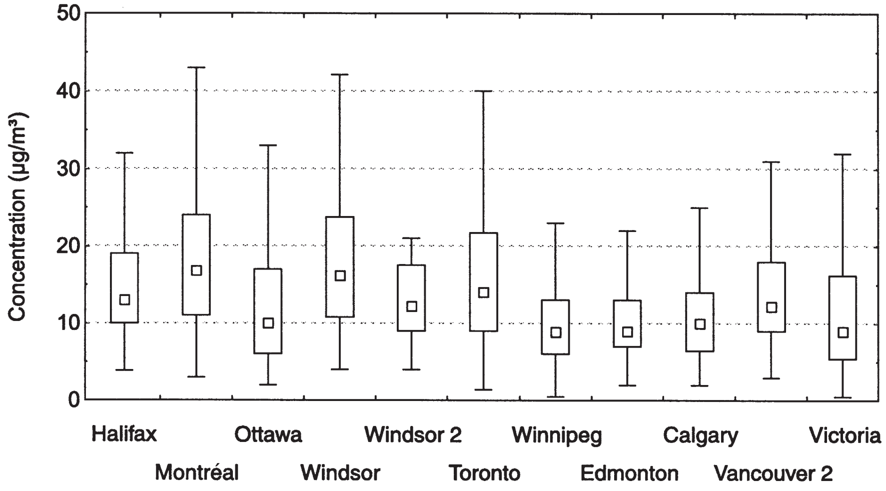
a) TSP



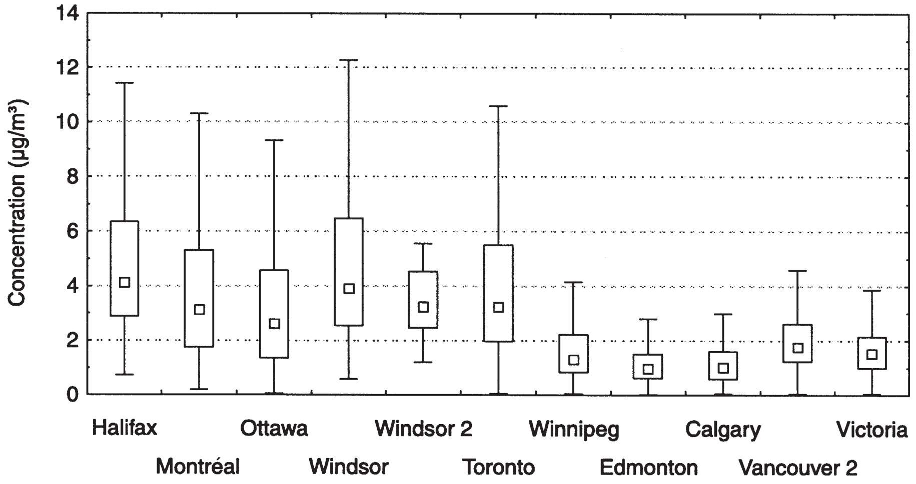
b) PM_{10}

Figure 5.16 Comparison of the Distributions of TSP, PM_{10}, $PM_{2.5}$ and SO_4^{2-} at 11 Urban Sites (1984-1993). The box plots indicate the median, 5th, 95th, 25th, and 75th percentiles. ***(continued)***

c) $PM_{2.5}$



d) SO_4^{2-}

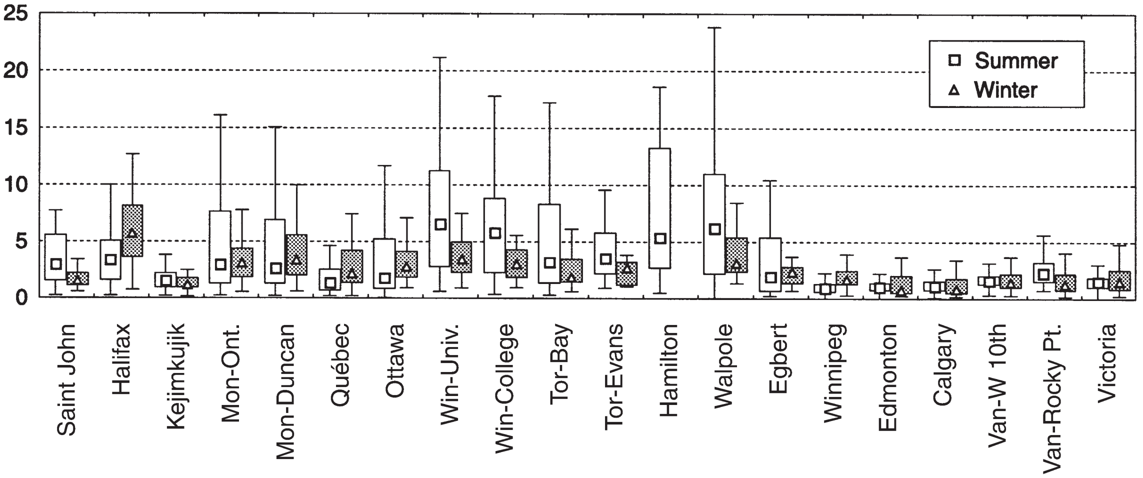


5.4.2 Site-Specific Relationship Between PM_{10} and $PM_{2.5}$

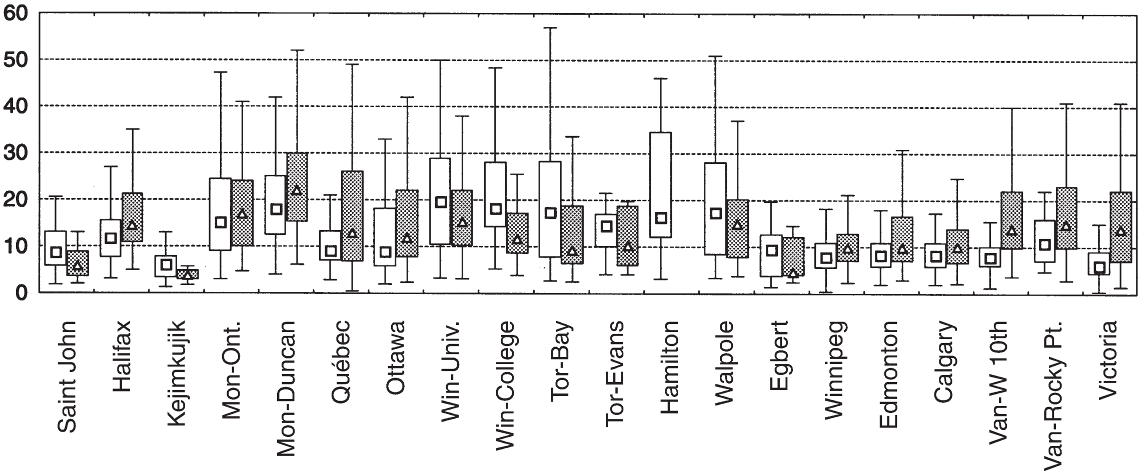
Site by site relationships between fine ($PM_{2.5}$), coarse and PM_{10} mass concentrations are shown for the NAPS Network dichotomous sampler sites in Table 5.22. On average across all sites, 53% of mean PM_{10} is made up of fine particles. However, there is a considerable amount of variability in their ratio among sites and between individual observations. Differences in the $PM_{2.5}$ to PM_{10} ratio across a variety of sites are displayed in Figure 5.18. At the urban locations, the mean ratio ranges from around 0.38 in the Prairies to 0.59 on the West Coast. The mean ratio ranges from 0.60-0.65 at the rural sites. From event to event, there is even more variability. For example, in Toronto the 5th and 95th percentiles of the ratio are about 0.15 and 0.90, respectively. The interquartile range (difference between the 25th and 75th 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 ±0.10 at a given site.

Figure 5.17 Comparison of $PM_{2.5-10}$, $PM_{2.5}$ Mass and SO_4 Concentrations Between Summer (J,J,A) and Winter (D,J,F) at NAPS Dichotomous Sampler Sites. The Box Plots Indicate the Median, 25th and 75th Percentiles and the Non-Outlier Minimum and Maximum Concentrations.

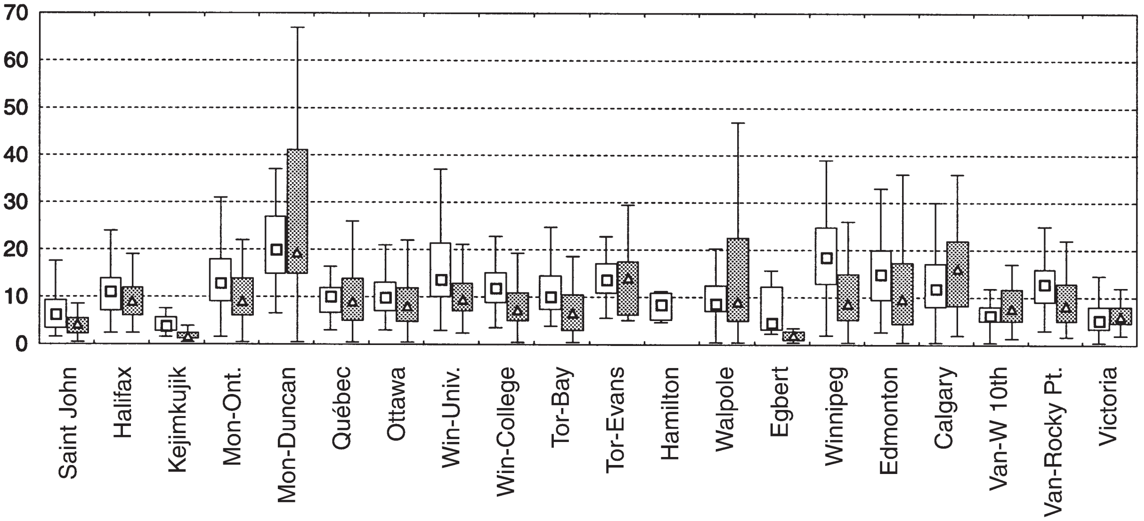
a) SO_4^{2-}



b) Fine



c) Coarse



There are relatively strong correlations (r^2) between PM_{10} and $PM_{2.5}$ at each site (see final column, Table 5.22). R^2 values 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. Accurate predictions of $PM_{2.5}$ from PM_{10} or vice versa are not likely even though day to day changes in PM_{10} or $PM_{2.5}$ are well correlated; there is considerable unexplained variability in their ratios. There are also relatively large standard errors for the regression coefficients.

The strength of the $PM_{2.5}$ to PM_{10} correlations listed in Table 5.22 is consistent with the belief that the temporal variations in $PM_{2.5}$ have a significant influence on the observed variability in PM_{10} (Kao and Friedlander, 1995; Wilson and Burton, 1995). Measures of variability reported in Table 5.22 and the r^2 values associated with the PM_{10} to coarse particle relationship also tend to support this notion. At a majority of the sites, the daily variations in PM_{10} 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-Duncan/Décarie. Coefficient of variations (standard deviations for both the fine and coarse mass divided by the mean PM_{10} concentration) were calculated to assess how much of the PM_{10} variability may be attributable to the variations in fine and coarse particles. These variability measures are larger for the fine than they are for the coarse at a majority of the sites. This does suggest that the fine mass has a greater influence on PM_{10} variability. However, the differences between the fine and coarse fractions are not overwhelming, which indicates that the coarse particles can also contribute substantially to the overall PM_{10} variability. In particular, the coarse mass dominates at the Prairie sites and has the potential to significantly influence the variability in PM_{10} at the Montréal-Duncan/Décarie 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, and construction).

The statistical results in Table 5.22 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 is in an area with agricultural activity.

Site by site relationships between $PM_{2.5}$ mass and fine SO_4^{2-} concentrations are shown for the NAPS Network dichotomous sampler sites in Table 5.23. Mean $SO_4^{2-}/PM_{2.5}$ ratios ranged from 0.24 to 0.34 at the eastern sites (excluding Montréal-Duncan/Décarie and Québec City) and from 0.12 to 0.16 at the sites west of Ontario. For sites with complete data, the correlation (r^2) between SO_4^{2-} and $PM_{2.5}$ was highest at the Atlantic and Ontario sites and smallest at the Winnipeg site.

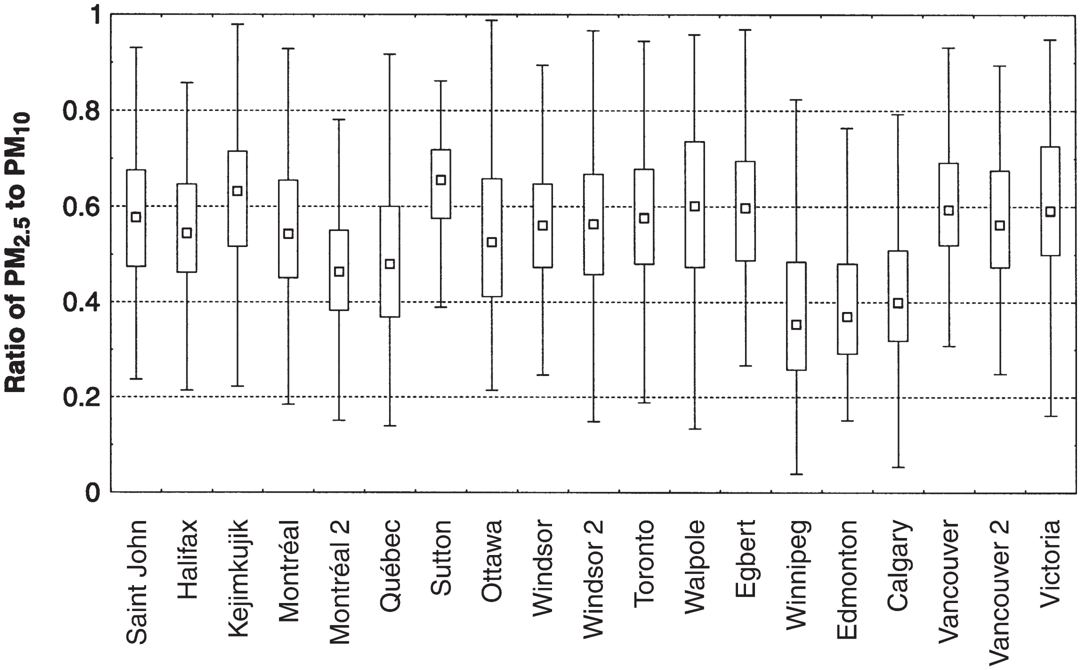
Mean concentrations and correlation coefficients were calculated separately for four pairs of urban-rural sites. Results are shown in Table 5.24. For each pair of sites, only the days when both sites provided valid measurements were used. With the exception of Walpole Island, particle mass concentrations are lower at the rural locations. Walpole Island is 55 km north of Windsor, and is influenced heavily by Detroit, Michigan. Egbert is 50 km north of Toronto, Sutton is 75 km southeast of Montréal and Kejimkujik is 120 km southeast of Saint John. 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 behaviour 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 influence sites in close proximity to one another similarly. 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, which are systematically higher for fine particles.

Table 5.22 Site by Site Relationships between Fine, Coarse and PM_{10} Mass (All samples 1984-1993).

Location	Number of Samples	Mean Fine Mass (μg/m^3)	Mean Coarse Mass (μg/m^3)	Mean $PM_{2.5}$ to Mean PM_{10} Ratio	C.V. for PM_{10}	C.V. for Fine Mass*	C.V. for Coarse Mass*	Coarse to Fine r^2	Coarse to PM_{10} r^2	Linear Equation $PM_{2.5} = a + b * PM_{10}$		
										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-Duncan/Décarie	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-College	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-W 10th	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 5.18 Distributions of the Ratio of $PM_{2.5}$ to PM_{10} Mass at the NAPS Dichotomous Sampler Sites. The Box Plots Indicate the Median, 5th and 95th and 25th and 75th Percentiles.



Although sample sizes decrease substantially for the SO_4^{2-} data 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 $PM_{2.5}$ suggests that some of the other fine mass constituents have more localized sources which do not impact evenly on their neighbouring 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. More unpaved roads, agricultural activity and open areas with large undisturbed fetches should enhance the suspension of crustal material (coarse particles) at the rural sites; these factors do not outweigh contributing to more coarse particles in urban areas.

Table 5.23 Site by Site Relationships between Fine SO_4^{2-} and Fine Mass ($PM_{2.5}$) – All samples 1984-1995.

NAPS ID	City	Address	N	Fine Mass ($PM_{2.5}$) $\mu g/m^3$	Fine SO_4^{2-} $\mu g/m^3$	Ratio of Mean SO_4^{2-} to Mean $PM_{2.5}$	Linear Equation $SO_4^{2-} = a + b * PM_{2.5}$		
							b	a	r^2
40203	Saint John	Forest Hills	172	8.4	2.8	0.33	0.37	-0.35	0.78
30101	Halifax	N. S. Technical College	310	13.8	4.7	0.34	0.40	-0.72	0.77
30118	Halifax	1657 Barrington St.	90	8.5	3.0	0.35	0.34	0.11	0.66
30119	Dartmouth	Harbor View School	83	6.9	2.3	0.34	0.36	-0.17	0.75
30501	Kejimkujik	National Park	107	6.5	2.2	0.34	0.42	-0.50	0.87
50104	Montréal	1125 Ontario Est	410	17.0	4.1	0.24	0.30	-0.97	0.62
50109	Montréal	Duncan/Décarie	316	20.9	4.0	0.19	0.21	-0.30	0.59
50307	Québec City	Parc Cartier Breboeuf	265	11.5	2.2	0.20	0.18	0.23	0.48
54101	Sutton		24	7.1	2.4	0.34	0.46	-0.87	0.92
60104	Ottawa	Rideau/Wurtemburg	392	12.5	3.4	0.28	0.32	-0.57	0.60
60204	Windsor	471 University Ave.	327	17.6	5.2	0.29	0.38	-1.43	0.76
60211	Windsor	College/Prince	184	15.5	4.5	0.29	0.42	-2.08	0.71
60417	Toronto	26 Breadalbane Street	272	16.7	4.6	0.28	0.36	-1.42	0.72
60424	Toronto	Bay & Grosvenor	187	14.6	3.7	0.25	0.31	-0.81	0.78
60403	Toronto	Evans & Arnold	72	12.6	3.1	0.25	0.33	-1.09	0.61
60512	Hamilton	Egin & Kelly	24	18.0	6.1	0.34	0.44	-1.76	0.92
61901	Walpole Island		236	17.0	5.5	0.32	0.29	0.45	0.64
64401	Egbert		55	8.8	2.7	0.31	0.33	-0.20	0.79
70119	Winnipeg	65 Ellen Street	455	10.3	1.6	0.16	0.06	1.03	0.15
90130	Edmonton	10255-104th Street	405	10.3	1.4	0.13	0.11	0.21	0.39
90204	Calgary	316-7th Ave.	143	14.5	1.8	0.12	0.13	-0.14	0.29
90227	Calgary	611-4th Street	380	10.0	1.3	0.13	0.10	0.34	0.31
100106	Vancouver	2294 West 10th Ave.	106	17.2	2.3	0.14	0.08	0.94	0.50
100111	Vancouver	Rocky Pt. Park	366	15.5	2.0	0.13	0.07	0.89	0.28
100118	Vancouver	2550 West 10th Ave.	295	12.9	1.8	0.14	0.08	0.76	0.41
100303	Victoria	1250 Quadra St.	391	11.6	1.7	0.15	0.10	0.59	0.53

Table 5.24 Direct Comparisons of Urban and Rural Site Measurements of Fine, Coarse and PM$_{10}$ Mass and Sulphate (r corresponds to the Pearson correlation coefficient).

			Coarse Fraction			Fine Fraction			Total (PM$_{10}$)		
Site 1	**Site 2**	**N**	**Site 1 Mean Mass (µg/m^3)**	**Site 2 Mean Mass (µg/m^3)**	**r**	**Site 1 Mean Mass (µg/m^3)**	**Site 2 Mean Mass (µg/m^3)**	**r**	**Site 1 Mean Mass (µg/m^3)**	**Site 2 Mean Mass (µg/m^3)**	**r**
Mass											
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
SO_4^{2-}											
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

5.4.3 Inorganic Composition of PM_{10} and $PM_{2.5}$

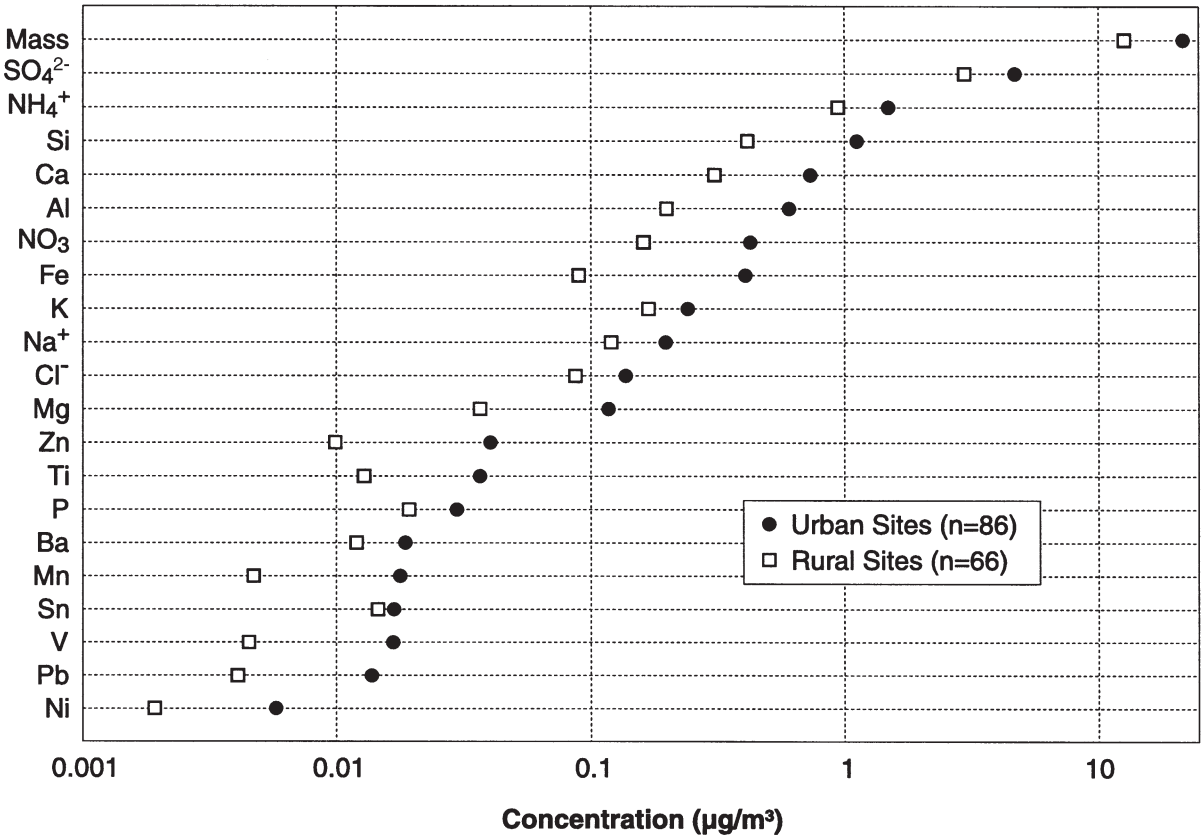
Forty elements and 25 anion and cation species are determined from the fine and coarse particles. Figure 5.19 is a comparison of the mean concentrations of the most abundant inorganic elements and ions measured during May-September 1993 at urban and rural sites (Saint John, Kejimkujik, Montréal, Sutton, Toronto and Egbert). For all components listed in Figure 5.19, the concentrations are higher at the urban sites. There are several elements/ions for which the urban-rural difference is disproportionately greater than the total mass difference, indicating that these constituents are enriched in urban areas. 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. Some of these species are common in crustal material (e.g., Si, Ca, Ti), indicating greater suspension of dust in urban areas. Industrial and combustion activities are likely responsible for the urban enrichment of some of the other species, such as NO_3^-, V and Pb. 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 Kejimkujik, both of which are situated near the ocean.

Median concentrations for some of the more abundant chemicals are listed in Table 5.25. Only selected cities, representing a range of geographical areas are included. Sulphate and sulphur 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. Concentrations of these elements are also high at Montréal-Duncan/Décarie. This is partially because this site has the highest median PM_{10} level. However, at Montréal-Duncan/Décarie, levels of Fe, Br, Mn, Cr are clearly enhanced, relative to PM_{10} and relative to the other Montréal site. The relatively high median Br 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 1984-86 to 1992. 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 concentration at Montréal-Duncan/Décarie 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 (Loranger and Zayed, 1994).

The effect of being located near the stack of an oil-burning boiler is evident in the median concentrations of V and Ni at Halifax, 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 than 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 US. The link between Se and coal combustion is evident in the concentrations shown in Table 5.25. Median Se concentrations are higher in Montréal and Toronto, which are closest to the US 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 a higher median NO_3^- concentration than their western counterpart of Vancouver. This could be a reflection of the temperature dependence of NH_4NO_3 formation since the eastern cities have colder climates (Section 2.7.5 describes how particle nitrate formation is favoured by low temperatures). However, the higher NO_3^- concentration could also be due to higher levels of HNO_3 in Toronto and Montréal. Brook (1994) found that in the summer of 1993 the HNO_3 concentrations were about a factor or two higher in southern Ontario compared to the Vancouver area.

Figure 5.19 Comparison of Urban and Rural Concentrations (µg/m³) of the Most Abundant Species (Summer 1993).



As described in Brook (1997) the fraction of fine and coarse mass accounted for by soil (crustal material), $SO_4^{2-}/NO_3^-/NH_4^+$, NaCl and other elements were determined using mass-reconstruction techniques and the inorganic species data. This methodology does not account for carbonaceous species (organic and elemental carbon) which are known to contribute significantly to the total mass of atmospheric particulate matter. It is assumed that the difference between reconstructed mass and total mass indicates an upper limit for particle mass associated with organic and elemental carbon. The results for summer and winter for the NAPS sites are illustrated in Figure 5.20. Consistent with other studies (Malm et al., 1994; Countess et al., 1980) soil is the largest identifiable component in the coarse fraction, while $SO_4^{2-}/NO_3^-/NH_4^+$ dominates the identifiable components within the fine fraction. Figure 5.20 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. On average, the $SO_4^{2-}/NO_3^-/NH_4^+$ component accounts for from about 20 to 45% of the fine fraction, depending upon site. The fraction of mass associated with the $SO_4^{2-}/NO_3^-/NH_4^+$ component is smallest at the three Prairie sites.

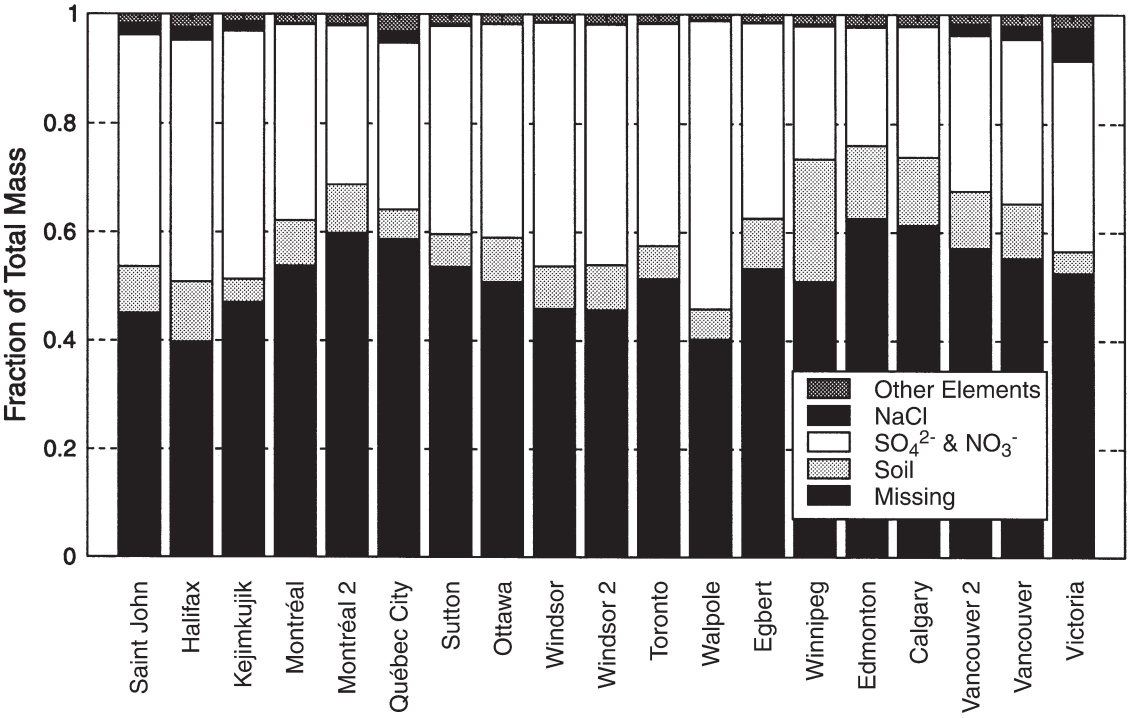
Soil-based inorganic compounds generally account for 5-15% of the fine mass, and are most significant to the overall mass in Winnipeg and least important in Toronto. There is very little seasonal difference in the percent of fine mass explained by soil. As expected, the NaCl component of the fine particles is larger at the sites near salt water. However, even at these locations it only accounts for a maximum of 5% of the $PM_{2.5}$. 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 Figure 5.20. 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 the mass reconstruction.

Table 5.25 Median Concentrations (µg/m³) of the Most Abundant PM_{10} Species for Selected Urban Sites (All Data 1986-1993).

Compound	Halifax	Montréal	Montréal Duncan	Ottawa	Toronto	Winnipeg	Calgary	Edmonton	Vancouver West 10th	Vancouver	Victoria
Sulphate	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
Sulphur	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**

Figure 5.20 Mean Fractional Contributions to the Total Fine and Coarse Mass from the Chemical Species Attributed to Soil, $SO_4^{2-}/NO_3^-/NH_4^+$, NaCl and other Elements.

a) Fine – Summer



b) Coarse – Summer

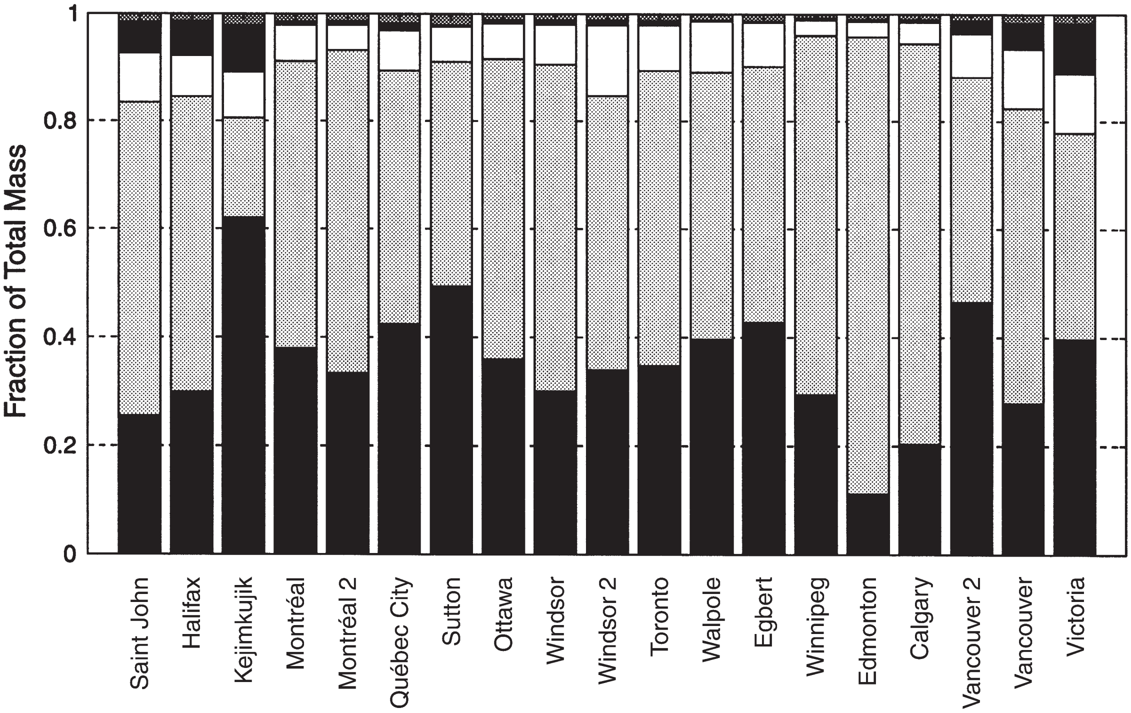
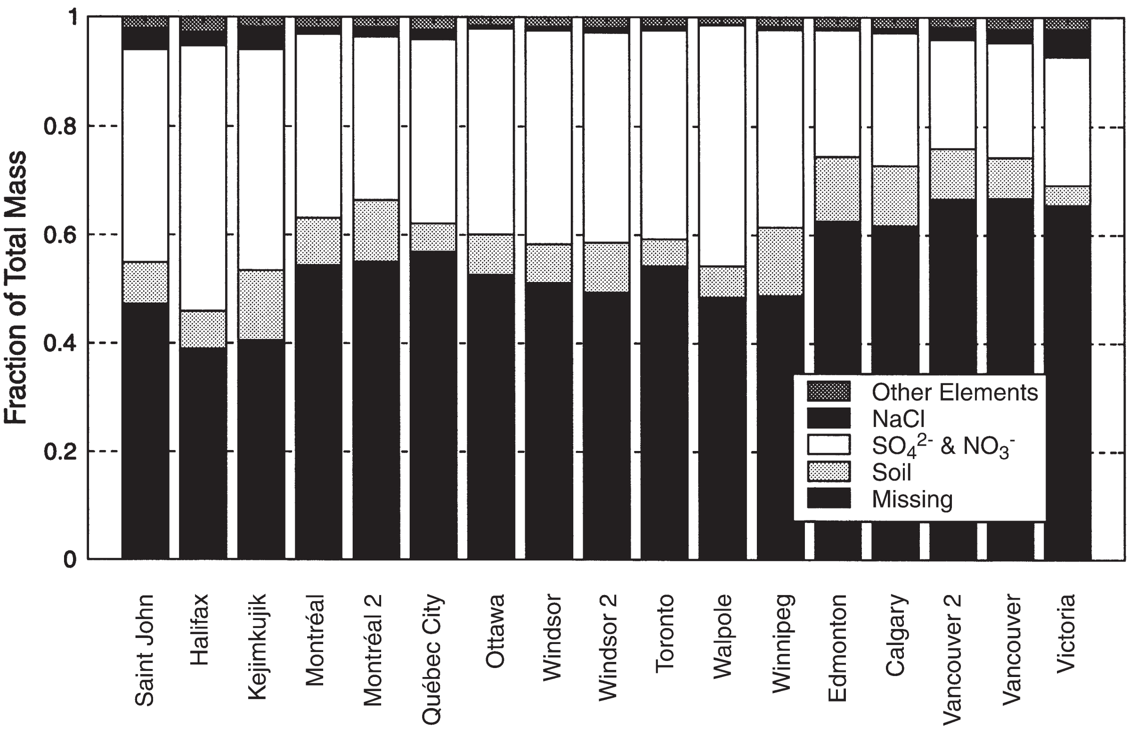
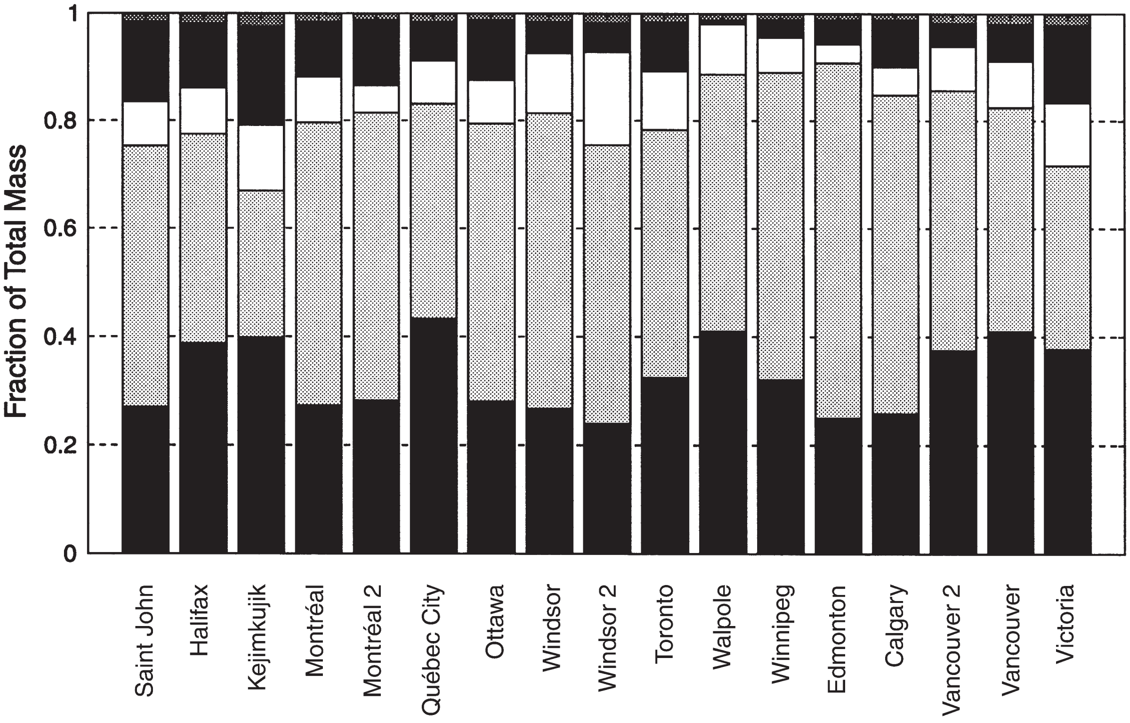


Figure 5.20 Mean Fractional Contributions to the Total Fine and Coarse Mass from the Chemical Species Attributed to Soil, $SO_4^{2-}/NO_3^-/NH_4^+$, NaCl and other Elements. ***(continued)***



c) Fine – Winter



d) Coarse – Winter

As expected, the amount of coarse mass associated with the soil component is much larger than with fine particles. On average across all sites, the soil fraction is about 50%. However, there is considerable variability with values ranging from 21% at Kejimkujik to 75% at Edmonton. From the fine to the coarse particles, the $SO_4^{2-}/NO_3^-/NH_4^+$ 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 use of road salt. At the coastal sites, this increase may also be due to increases in wind speed and hence, sea spray. The largest unexplained coarse fraction is observed at Kejimkujik. 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 Kejimkujik 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. Figure 5.20 shows that 20-40% of the coarse fraction also remains unexplained.

As discussed, 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 the site. There is apparently a greater percentage of carbon-related fine particles in the west (~62%) than there is on the east coast (40-46%). For 13 of the 19 sites, the estimated carbon percentage associated with the coarse particles is smaller than for the fine particles. Coarse particle carbonaceous species account for approximately 20-58% of total mass, depending on the site (excluding Kejimkujik and Edmonton). Slightly lower percentages occur in the wintertime, decreasing to about 40% of total mass.

5.4.4 Summary

On average across all sites, mean $PM_{2.5}$ accounted for 50% of mean PM_{10} and PM_{10} accounted for 50% 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 ±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 in relatively close proximity 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 is 46% higher in Toronto compared to Egbert, while the mean amount of fine particles is 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 neighbouring urban or rural sites.

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 percent 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 (40-45%). Due to the increased importance of crustal material, a greater portion of the coarse particle mass (~70%) was explained by the inorganic constituents.