

# Concentration and Source Origin of Trace Metals in PM<sub>2.5</sub> Collected at Selected Canadian Sites within the Canadian National Air Pollution Surveillance Program

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## 1 Introduction

Airborne particulate matter (PM) is a complex mixture of thousands of organic and inorganic species that emerge from a wide range of natural and anthropogenic sources. Numerous epidemiological studies have confirmed that PM and especially the respirable fraction of PM, the PM<sub>2.5</sub> (for particles <2.5 µm diameter), has adverse effects on human health. Although there is no evidence to pinpoint any single feature or component of PM as the cause for the observed epidemiological effects, it is apparent that metals contribute, at least in part, to the toxic and carcinogenic effects associated with exposure to airborne PM and for this reason have been the object of several epidemiological studies (Goldoni et al. 2006; Kawata et al. 2007; Lippmann et al. 2006). In addition, trace metals are proven to be useful tracers and are extensively used to identify sources of emissions to be targeted by the emission reduction policies (Querol et al. 2001; Lee et al. 2003; Gotschi et al. 2005; Querol et al. 2006; Querol et al. 2007b; Viana et al. 2007; Jeong et al. 2008). Therefore, monitoring of elemental composition of PM has become a crucial part of air quality programs in many countries around the world.

The Canadian National Air Pollution Surveillance (NAPS) network is one of the major air quality monitoring initiatives in the country. It was established in 1969 as a joint program of the federal and provincial governments to monitor and assess the quality of the ambient air in Canada's urban centers. Air quality data are measured at 319 sites, located in 216 communities in all provinces and territories with the aim of providing the information needed to evaluate air pollution control

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strategies, identify air quality trends and warn of emerging air pollution issues (NAPS 2008).

The objectives of this study were to quantify the trace metals in  $PM_{2.5}$  of Eastern and Western Canada, to analyze their annual and seasonal trends and identify their source origin, by evaluating a database of trace metal concentrations obtained over a 2-year period (May 2004–December 2006) from the NAPS network. Over 1000  $PM_{2.5}$  samples collected at seven selected sites were analyzed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) after microwave assisted acid digestion. This technique offers low detection limits, wide linear dynamic range, multielement capability, ability to measure isotope ratios and high sample throughput. Principal Components Analysis (PCA) was used to identify sources of trace metals at each sampling site.

## 2 Materials and Methods

### 2.1 Sample Collection

The sampling sites were selected to represent different urban and rural settings, and were located from East to West of Canada as shown in Fig. 1 and described in Table 1. NAPS network sampling sites are equipped with R&P Partisol-Plus



**Fig. 1** Locations of the seven NAPS sampling sites included in this study

**Table 1** The sampling sites geographical location, site classification and major local emission sources

Location	Latitude and longitude	Site classification	Local PM sources		
			Traffic related	Industrial pollution	Other sources
Abbotsford, BC	49°01' N, 122°20' W	Urban-residential	Airport traffic	Building materials, mining and quarrying	–
Vancouver, BC	49°12' N, 122°59' W	Urban-commercial	Urban traffic	Building materials, oil and gas refining, storage and distribution, sand mills and wood products	–
Simcoe, ON	42°51' N, 80° 16' W	Rural-agricultural	Farming related traffic	–	Farming processes
Toronto, ON	43°39' N, 79°23' W	Urban-commercial	Urban traffic	Building materials	–
Windsor, ON	42°17' N, 83°04' W	Urban-residential	Urban traffic	Primary metal manufacturing, building materials, waste treatment, electricity generation, auto industry	–
Montréal, QC	45°31' N, 73°33' W	Urban-commercial	Urban traffic	Building materials, oil and gas refining, storage and distribution, chemical products manufacturing	–
Canterbury, NB	45°57' N, 67°28' W	Rural-undeveloped	–	–	Local heating

Model 2025-D sequential dichotomous sampler that simultaneously collects coarse (PM<sub>2.5-10</sub>) and fine PM (PM<sub>2.5</sub>) particles, with flow rates of 1.7 and 15 L/min, respectively. Samples were collected over 24 h using a one-in-three day schedule, on Teflon filters (PTFE, 47-mm diameter) with a polyethylene support ring (PALL Corporation, NY, USA). Compared to other materials used for sampling of airborne PM, such as quartz, glass, cellulose or polycarbonate, Teflon filters had the lowest blanks for metals and were used throughout this study. The Teflon filters were weighed before and after sample collection using a Mettler Microbalance (MT-5, Mettler-Toledo Inc., Highstown, NJ), under controlled relative humidity ( $45 \pm 5\%$ ) and temperature ( $23 \pm 3$  °C).

## 2.2 Sample Digestion and Analysis

A closed vessel microwave assisted reaction system (MARS 5, CEM Corporation, Matthews, NC) was used for acid digestion of samples. All digestions were performed in 7-mL Teflon digestion microvessels (Micro Vessel<sup>TM</sup>, CEM Corporation, Matthews, NC) accommodated inside the standard 100-mL Teflon liners (HP-500 Plus, CEM Corporation, Matthews, NC). The pressure inside the liners and the internal temperature of the microvessels were monitored in a control vessel assembly, which is equipped with pressure and temperature sensor units. The PM<sub>2.5</sub> laden Teflon filters were digested at 175 °C with 2 mL of 40% (v/v) HNO<sub>3</sub>, following a two-step digestion program (Celo et al. 2005a, b). Reagent blanks, filter blanks and other QA/QC samples were prepared in the same manner.

The ICP-MS measurements were performed using an Agilent Technologies 7500c ICP-MS system (Agilent Technologies, Wilmington, DE, USA), equipped with an octopole collision/reaction system (ORS), a Babington nebulizer, a Peltier cooled (2 °C) quartz Scott-type double pass spray chamber and an Agilent I-AS integrated autosampler. Spectral interferences were minimized or eliminated either by choosing a non-interfered isotope or by using the ORS with H<sub>2</sub> as the reaction gas. The instrument conditions for ICP-MS measurement were summarized by Chen et al. (2008). The precision and accuracy of the ICP-MS measurements were checked by analyzing Certified Reference Materials (CRMs) prepared in the same matrix as the digested samples, spikes and duplicates. The 95% expanded relative uncertainties above quantitation limit (3 times limits of detection) (CAEAL January 2006) ranged from 10 to 25%. Results were accepted when measured concentrations of CRMs and spiked samples were within 10–20% of target values and the relative percent deviation (RPD %) of duplicates was less than the reported uncertainty.

The limits of detection (LOD) were established from at least seven replicate analysis of reagent blanks fortified at a concentration no greater than 5–10 times the instrument detection limit and treated the same way as samples. The standard deviation value was then multiplied by the one-tailed Student's test value for 99%

confidence level. LOD of most of the elements of interest were below 1 ng/m<sup>3</sup>. The only exceptions were Zn and Fe with LOD of 4 and 3 ng/m<sup>3</sup>, respectively.

### ***2.3 Treatment of Data Less Than Limits of Detection***

Chemical data resulting from trace and ultratrace analysis are usually characterized by a certain percentage of observations that are below LOD. These data are generally reported as “less than the detection limit” and data sets with “less-than” observations are termed “censored data” in statistical terminology. Censored data may not present a problem in monitoring studies when most of the concentrations of analytes of interest are well above detection limits. However, for most of environmental studies this is not the case. Analyses of trace metals in PM are one example of data sets with a considerable amount of observations being below the respective LOD.

During the recent years several studies have been focused on the statistical methodologies that should be used for estimation of summary statistics (mean, standard deviation, median and interquartile range) or for performing other statistical analysis of censored data sets (Gilliom and Helsel 1986; Helsel and Gilliom 1986; Helsel 1990; Kuttatharmmakul et al. 2000; Finkelstein and Verma 2001; Jain et al. 2008; Jain and Wang 2008). In many monitoring studies, the censored data are substituted by LOD/2 or LOD/ $\sqrt{2}$  (Helsel 1990; Finkelstein and Verma 2001). Also the Maximum Likelihood Estimation (MLE) method has been used in many environmental disciplines, such as air quality studies (Owen and DeRouen 1980) and traces level water quality (Helsel and Gilliom 1986) and was shown to provide an accurate estimate of summary statistics for highly censored data sets (Helsel 1990; Kuttatharmmakul et al. 2000; Finkelstein and Verma 2001). Nevertheless, MLE and other robust statistical methods require computations using statistical software which are not practical or available for routine analysis of monitoring programs. Thus, these are recommended only for compounds which have a significant impact in the risk assessment and for which the data sets are adequate (Smith 1991).

The percentages of censored observations (less than LOD) of data sets included in this study are summarized in Table 2. The number of observations was above 200 at all sites except for Simcoe and Windsor which had 149 and 89 observations, respectively. Although the sample size was quite large, the percentage of censored data for some elements was quite significant. For example, concentration of Be was below LOD in all samples whereas Co, Ag and Tl were more than 50% censored at all sites. Other elements such as Cr, Mo and Se were censored at 40% or more at several sampling sites. For this reason, choosing the best way of treating the data sets for estimation of summary statistics becomes an important issue in this study.

With the goal of choosing a method that provides the best estimations of summary statistics without the need of extensive statistical calculations, we

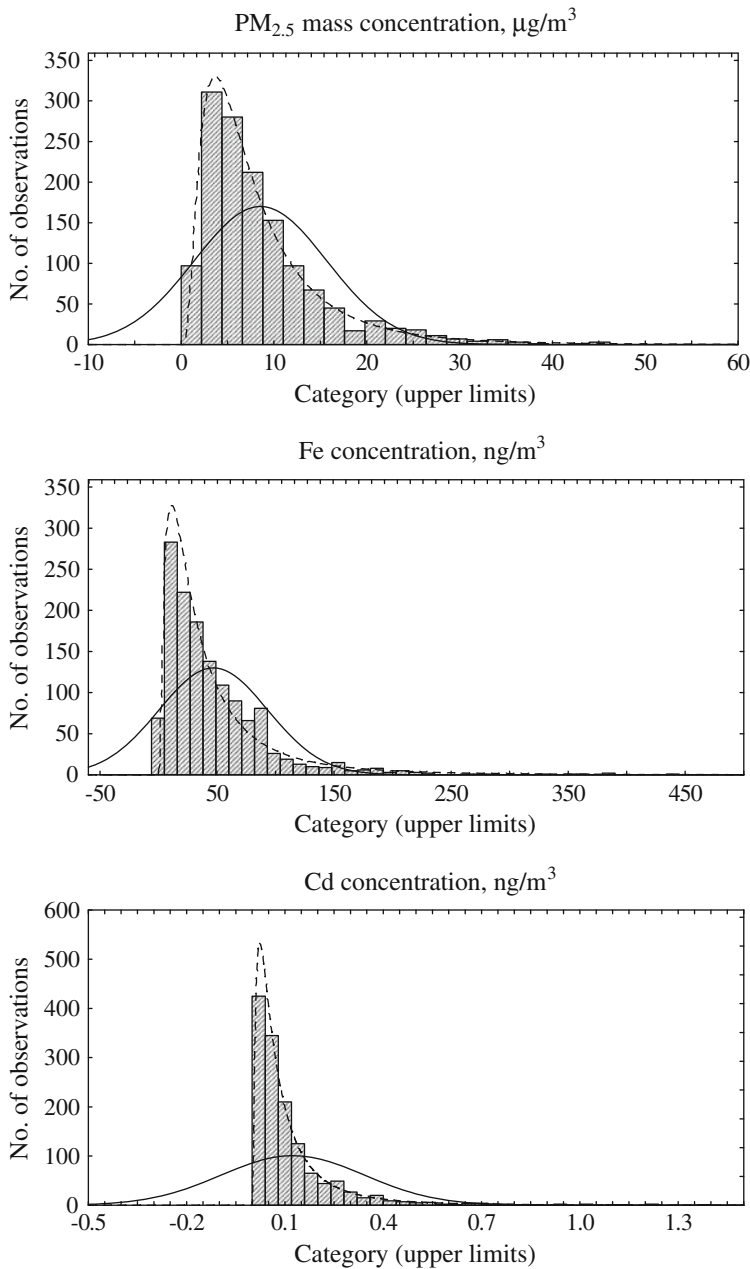
**Table 2** Percentages of censored observations (less than LOD) for each site included in this study (2004–2006)

	LOD (ng/m <sup>3</sup> )	Abbotsford N = 217	Vancouver N = 224	Simcoe N = 150	Toronto N = 226	Windsor N = 91	Montréal N = 209	Canterbury N = 261
Be	0.03	100	100	100	100	100	99	100
V	0.1	12	0	6	12	1	6	8
Cr	0.4	67	31	46	37	13	29	93
Mn	0.1	0	0	1	0	1	1	3
Fe	3	1	0	1	1	1	0	9
Co	0.03	94	76	97	89	59	63	94
Ni	0.3	36	5	17	36	8	11	39
Cu	0.3	5	0	1	0	1	0	5
Zn	4	18	5	3	5	1	2	37
As	0.1	3	4	3	2	1	2	27
Se	0.2	64	59	7	15	8	29	73
Sr	0.1	20	3	7	8	1	3	56
Mo	0.06	45	5	40	18	1	13	84
Ag	0.07	93	86	98	95	84	73	94
Cd	0.02	17	13	3	3	1	1	31
Sn	0.1	13	1	21	8	1	13	45
Sb	0.1	16	0	18	6	2	6	55
Ba	0.1	1	0	3	0	1	1	15
Tl	0.03	94	91	88	83	68	75	95
Pb	0.1	1	0	1	1	0	0	11

N is number of samples analyzed at each site

compared the simple substitution of “less than” data with  $\text{LOD}/2$  and  $\text{LOD}/\sqrt{2}$  against the MLE method as described by Finkelstein and Verma (2001). We found out that using substitution with  $\text{LOD}/\sqrt{2}$ , summary statistics for highly censored elements such as Cr, Co, Ag and Tl, were closer to MLE than substitution with  $\text{LOD}/2$ , whereas for the other elements both substitution methods yielded values that were within  $\pm 15\%$  of MLE results. Thus the simple substitution with  $\text{LOD}/\sqrt{2}$  was used as the best approach for the calculations of summary statistics in this study.

Methods of hypothesis testing based on data sets with censored observations have also been discussed in several publications (Helsel 1990 and references therein). The widely used parametric statistical tests are based on the assumption that the observations follow a known distribution which is usually assumed to be of normal shape. Alternatively, the non-parametric or robust tests do not require any assumption of the distributional shape and the results are less depended on the “less than LOD” observations (Helsel and Gilliom 1986; Helsel 1990). As illustrated in Fig. 2, the distributions of  $\text{PM}_{2.5}$  mass and metal concentrations in our study are lognormal rather than normal. Therefore, using average and standard deviation to estimate summary statistics and parametric tests for testing of hypothesis may result in erroneous conclusions. Consequently, our further discussions and conclusions are based on the median and interquartile range (IQR) values and the non-parametric methods for testing of various hypotheses.



**Fig. 2** Distributional plots of PM<sub>2.5</sub> mass, Fe and Cd concentration; normal distribution fitting and lognormal distribution fitting

STATISTICA ver. 8 software (StatSoft Inc., Tulsa, OK, USA) was used for all statistical analyses.

### 3 Results and Discussion

#### 3.1 Particle Mass Concentrations

The presence of particulate matter in the atmosphere is a consequence of both natural and anthropogenic sources. Background PM is generally defined as the distribution of PM concentrations that would be observed in the absence of primary and secondary anthropogenic emissions (Health Canada and Environment Canada 1998). The range of expected background concentrations on an annual basis is from 4–11  $\mu\text{g}/\text{m}^3$  for  $\text{PM}_{10}$ , and 1–5  $\mu\text{g}/\text{m}^3$  for  $\text{PM}_{2.5}$  for remote sites in North America (Health Canada and Environment Canada 1998). Summary statistics for mass concentrations of  $\text{PM}_{2.5}$  collected at selected NAPS sites during May 2004–December 2006 sampling period are presented in Table 3. The IQR of mean 24-h  $\text{PM}_{2.5}$  concentrations at all sites was 5–11  $\mu\text{g}/\text{m}^3$ . These levels were substantially above background concentrations indicating that anthropogenic activities make a significant contribution to ambient  $\text{PM}_{2.5}$  loadings. The sampling site with the highest median concentration of  $\text{PM}_{2.5}$  was Windsor (9.9  $\mu\text{g}/\text{m}^3$ ) followed by Simcoe site with a concentration of 8.7  $\mu\text{g}/\text{m}^3$ . Canterbury had levels of  $\text{PM}_{2.5}$  comparable with the background level for remote sites in North America. The medians of average 24-h concentration of  $\text{PM}_{2.5}$  at all sampling sites were below 15  $\mu\text{g}/\text{m}^3$  that is recommended by the Canadian National Ambient Air Quality Objective (NAAQO) as the level of  $\text{PM}_{2.5}$  (24 h averages) above which there are demonstrated effects on human health and/or environment (Health Canada and Environment Canada 1998). The  $\text{PM}_{2.5}$  standard in Canada, referred to as the Canada-Wide Standard (CWS) has been set at 30  $\mu\text{g}/\text{m}^3$  (24-h average), based on 98th percentile ambient measurement annually, averaged over 3 consecutive years (<http://www.ccme.ca>). The standard is to be achieved by 2010. With

**Table 3** Summary statistics of  $\text{PM}_{2.5}$  mass concentrations ( $\mu\text{g}/\text{m}^3$ ) (2004–2006)

	Abbotsford	Vancouver	Simcoe	Toronto	Windsor	Montreal	Canterbury
Arithmetic mean	7.1	6.7	10.5	9.9	11.8	9.9	4.5
Geometric mean	6.0	6.0	8.0	7.5	10.0	8.1	3.5
Median	6.4	6.2	8.7	7.5	9.9	8.0	3.43
Minimum	0.5	0.8	0.9	0.3	2.6	1.1	0.4
Maximum	20.5	18.9	35.6	36.2	32.4	36.0	29.5
Lower quartile	4.1	4.4	4.9	4.4	6.3	5.2	2.4
Upper quartile	9.4	8.5	13.5	12.8	15.5	12.7	5.2
98th percentile <sup>a</sup>	18.0	15.7	26.1	35.8	34.0	29.9	16.6

<sup>a</sup> Calculated as the average of the 98th percentile of each year from 2004 to 2006



**Table 4** Mean levels and range of PM<sub>2.5</sub> (µg/m<sup>3</sup>) reported at different regions of the world

Country	Years	Mean	Range	Source
Oxford, Ohio	2005	15.6	3.3 to 38	Wojas and Almquist (2007)
Spain	NR	NR	20 to 30	Moreno et al. (2006b)
Toronto, Canada	2000–2001	12.7*	NR	Lee et al. (2003)
Korea	2002	29	7.5 to 246	Kim et al. (2005)
Europe	2000–2001	19.1	3.7 to 45	Gotschi et al. (2005)
Taichung, Taiwan	2005	38.1	22 to 46	Fang et al. (2007)
Beirut, Lebanon	2004	38.5	20 to 67	Saliba et al. (2007)
Cartagena, Spain	2004–2005	22	7 to 47	Negral et al. (2008)
Hong Kong	2002–2003	42.3	29 to 71	Hagler et al. (2007)
Singapore	2000	22.2*	12.2 to 48.1	Balasubramanian and Qian (2004)
Guangzhou, China	2004	97.5	52 to 187	Wang et al. (2006)
South Brazil	2001–2002	15	1 to 44	Braga et al. (2005)
Edinburg, UK	1999–2000	7.1*	3.6 to 18.3	Heal et al. (2005)
Hong Kong	2000–2001	79.6	28 to 117	Ho et al. (2003)
Barcelona, Spain	2005–2006	29		Perez et al. (2008)

The asterisk (\*) indicates median concentrations

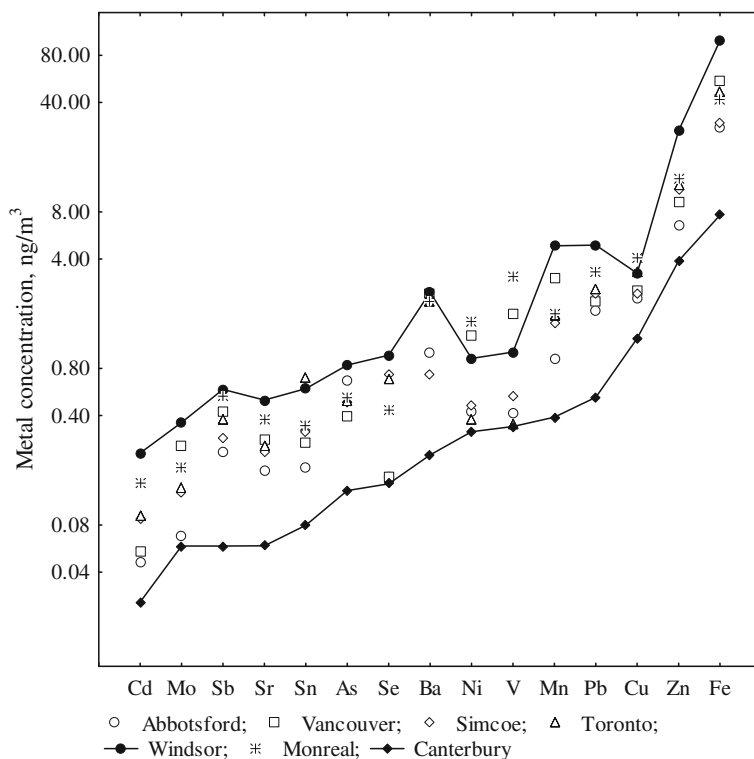
NR non-reported values

the exception of Canterbury, PM<sub>2.5</sub> levels at Eastern sites were close to or exceeded the CWS whereas Western sites had PM<sub>2.5</sub> concentrations well below this standard. On the other hand, the PM<sub>2.5</sub> mass concentrations found at all Canadian sites were generally lower than values reported for other regions of the world (Table 4).

## 3.2 Trace Metals Concentrations

### 3.2.1 Spatial Variations

The median concentrations of most of the trace metals ranged from 0.1 to 1 ng/m<sup>3</sup> (Fig. 3). Be, Tl, Co and Ag were detected at the level of the respective LOD (less than 0.1 ng/m<sup>3</sup>) at all sites. Ba, Mn, Pb, Cu, Zn and Fe had concentrations that exceeded 1 ng/m<sup>3</sup> at most of the sampling sites. The most abundant metals at each site were Fe and Zn with overall median concentrations of 35 and 9 ng/m<sup>3</sup>, respectively. The least polluted site was Canterbury where the average sum of metal concentration was 20 ng/m<sup>3</sup>. The metal concentrations increased with the anthropogenic inputs and reached the maximum at Windsor site (average sum of metal concentration was 189 ng/m<sup>3</sup>), which is characterized by intensive industrial activities in the vicinity of the city. Metal concentrations at this site were up to 10 times higher than at Canterbury. Similar trace metal concentrations were observed at Toronto, Montreal and Vancouver sampling sites, which agrees with the similar human activities at these highly dense commercial urban areas. The highest level

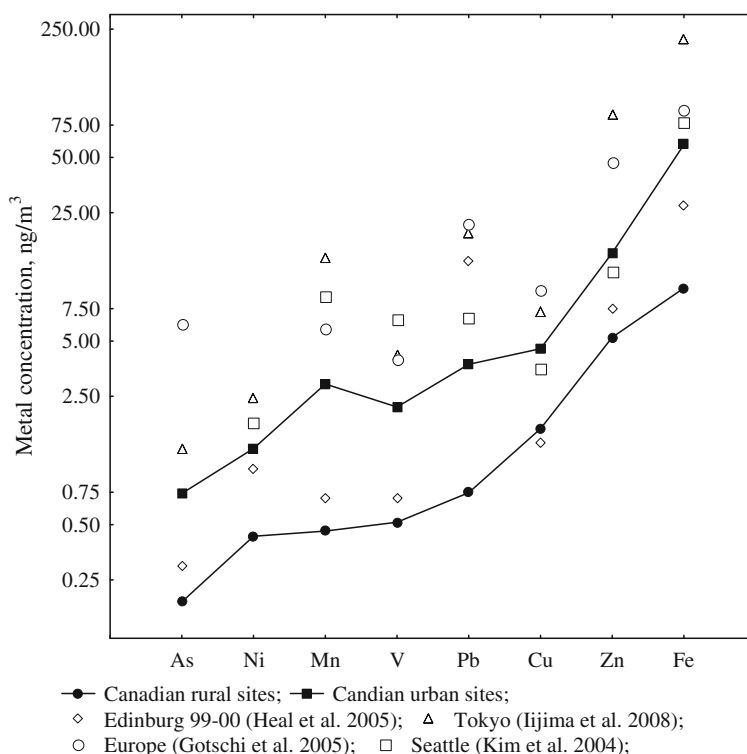


**Fig. 3** Median metal concentrations sorted by the concentration values at Canterbury site (2004–2006 data)

of Ni and V, tracers of oil-burning and/or oil-refining industries, were recorded at Vancouver and Montreal, both sites located close to oil refining facilities. Compared to the elemental composition of  $\text{PM}_{2.5}$  samples collected in urban areas of Europe, Japan, and the USA, the Canadian urban aerosols were equally or less loaded with trace metals (Fig. 4). Although Windsor samples had the highest levels for almost all metals, these were lower than concentrations found in Tokyo and in many European cities. Also, the metal concentrations at all sites were much lower than the guidelines published by WHO (2000).

### 3.2.2 Seasonal and Annual Variations

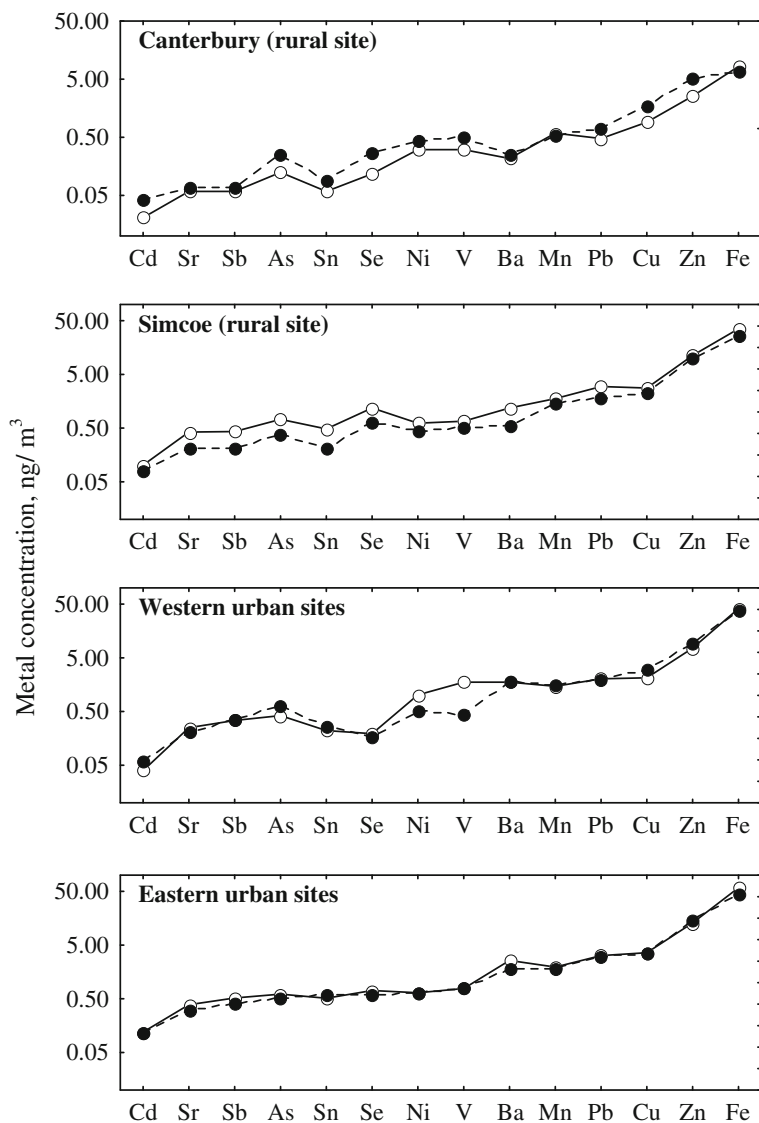
The seasonal variations of trace metal composition of atmospheric aerosols are controlled by several meteorological factors such as temperature, humidity and wind velocity and direction. Cold seasons are usually characterized by persistent thermal inversions, high precipitation and low wind velocities which favor the accumulation of anthropogenic exhaust emissions and reduce the presence of road



**Fig. 4** Median trace metal concentrations at Canadian urban and rural sites, together with values reported for urban sites at different regions in the world

dust in the PM<sub>2.5</sub> fraction of atmospheric aerosols. Dry climate conditions during the warm seasons favor the formation and lift-up of dust particles, which is often the reason for elevated concentrations of crustal elements in the atmospheric aerosols during that time of the year (Gotschi et al. 2005; Qureshi et al. 2006; Querol et al. 2007b; Teixeira et al. 2009).

In this study, the seasons were defined as cold (October to April) and warm (May to September). With this definition all sites had similar distribution of data between seasons (about 50:50), which avoids any seasonal bias due to coverage period at each site. Also, this classification generally coincided with overall temperature profiles in Canada. Seasonal median concentrations of trace metals are presented in Fig. 5. The concentrations of Fe and Mn were higher during the warm season at all sites, suggesting a link of these elements with crustal component of PM<sub>2.5</sub>. At the Simcoe site the concentrations of all elements were up to 70% higher during the warm seasons (Fig. 5). The highly intensive agricultural activities during this period of the year may enhance the metal concentrations in aerosols by both dust re-suspension and increased human made emissions. Also, the wet washout of metals from the atmosphere is generally less significant during this



**Fig. 5** Median concentrations of trace metals for samples collected during warm (filled circle) and cold (open circle) seasons of the sampling period

time of the year. The opposite trend was typical at Canterbury site where most of the metals had elevated concentrations during the cold months of the year. Considering that there is no industrial activity in the vicinity of this sampling site, the main pathways of metals in this region are long-range transport and local activities such as house heating, which are generally favored by winter conditions

(Bottenheim et al. 2004). The Abbotsford and Vancouver sampling sites, both located in Western Canada and in the vicinity (20 km or less) of petrochemical facilities, were characterized by a 3- and 6-fold increase in concentrations of Ni and V, respectively, during the warm periods of the year. Similar trends were reported for other regions close to petrochemical and oil fired power plants (Querol et al. 2007a). The seasonal variations of metals at other sites were generally not significant and typically had a slight upward trend in the cold season, especially for elements that are indicators of anthropogenic activities such as As, Se, Cu, Zn and Cd.

The annual variations of trace metal concentrations in urban PM<sub>2.5</sub> were not statistically significant (Kruskal–Wallis ANOVA,  $p > 0.05$ ), whereas at the rural sites (Canterbury and Simcoe) the sum of metal concentrations dropped significantly (by 19 and 15%, respectively) from 2004 to 2006. Samples from the Toronto site were also collected and analyzed during 2000–2001 sampling campaign from Lee et al. (2003). Compared to the results of this study, the trace metal composition of PM<sub>2.5</sub> in Toronto has not changed significantly during this period of time.

### 3.3 Source Apportionment

The principal intention of many monitoring studies related to atmospheric aerosols is the identification and apportionment of pollutants to their sources. This information is crucial for the development and implementation of policies protecting human health and the environment. Receptor modeling, which provides information regarding source characteristics from the measurements of particle chemical composition at a sampling site, is the most commonly used source apportionment technique (Paatero et al. 2005). The most widespread receptor methodologies used in source apportionment studies to date are the Principal Components Analysis (PCA), Positive Matrix Factorization (PMF) and Chemical Mass Balance (CMB). The theoretical basis and applications of these methods have been previously described in many publications (Paatero et al. 2005; Rizzo and Scheff 2007; Viana et al. 2008; Junninen et al. 2009). Viana et al. (2008) summarized the theoretical limitations and advantages of these models and confirmed their agreement in the identification and interpretation of the major PM sources. However, the authors recommended that using a combination of the three models would probably yield a more robust solution. Shi and co-authors (Shi et al. 2009) applied a combination of PCA-CMB and PMF-CMB to identify the major PM sources and their average contributions to particulate pollutants. The authors concluded that the combined models are superior only for some relatively complicated receptors.

In the present study, the source apportionment of the trace metals in PM<sub>2.5</sub> was carried out using the PCA with normalized varimax rotation of the original variables. The number of factors that were retained in each case was determined by the

**Table 5** Factor analysis pattern after normalized varimax rotation for trace metal concentration in PM<sub>2.5</sub> at all sampling sites (factors loadings >0.7 are highlighted and loadings <0.3 are omitted from this table)

Factor 1		Factor 2		Factor 3		Factor 4		Factor 5	
%		%		%		%		%	
variance = 41.2		variance = 11.2		variance = 10.9		variance = 8.7		variance = 6.8	
Mn	0.876	Se	0.862	V	0.905	Sr	0.923	As	0.923
Fe	0.880	Sn	0.659	Ni	0.906	Ba	0.866	Cu	0.866
Zn	0.803	Cd	0.651	Cu	0.319	Sb	0.375	Sb	0.473
Mo	0.628	Pb	0.465					Cd	0.470
Sb	0.389	Sb	0.330					Zn	0.421
Pb	0.331							Mo	0.358
								Pb	0.375

scree test (Cattell 1996). The metals which were below LOD in more than 50% of the observations, such as Be, Cr, Co and Tl, were not included. The outliers were identified using Grubb's test and were not included in the principal components and correlation analysis.

Applied to the trace metal concentrations in PM<sub>2.5</sub> at all sites, the PCA revealed 5 factors that accounted for 80% of the variance (Table 5).

*Factor 1* accounted for 41% of the variance and had significant loadings on Fe and Mn that are typical mineral elements and consequently, associate this factor with the crustal fraction of PM<sub>2.5</sub> (Heal et al. 2005; Moreno et al. 2006a; Salvador et al. 2007). Fe and Mn were also loaded at same principal component and were strongly correlated (Spearman Rank Order Correlations more than 0.85) at each sampling site. The presence of these elements in PM<sub>2.5</sub> is mainly a result of local and regional dust resuspension by wind, convection and other natural processes. The less significant loading of Zn and Mo, at this component suggests some effect of road traffic induced resuspension dust (Heal et al. 2005; Querol et al. 2007b). A similar composition of the crustal component was observed at each sampling site, except for Canterbury where Fe and Mn were grouped together with Ba and Sr, which in low-traffic areas, are also indicators of natural crustal sources (Moreno et al. 2006a, b).

*Factor 2* had the highest loading on Se which is considered a tracer of coal combustion processes. The moderate loadings of Sn, Cd, Sb and Pb suggest that this factor may present a mixture of several industrial emissions, including fly ash from high efficiency coal burning industrial facilities (Salvador et al. 2007; Junninen et al. 2009).

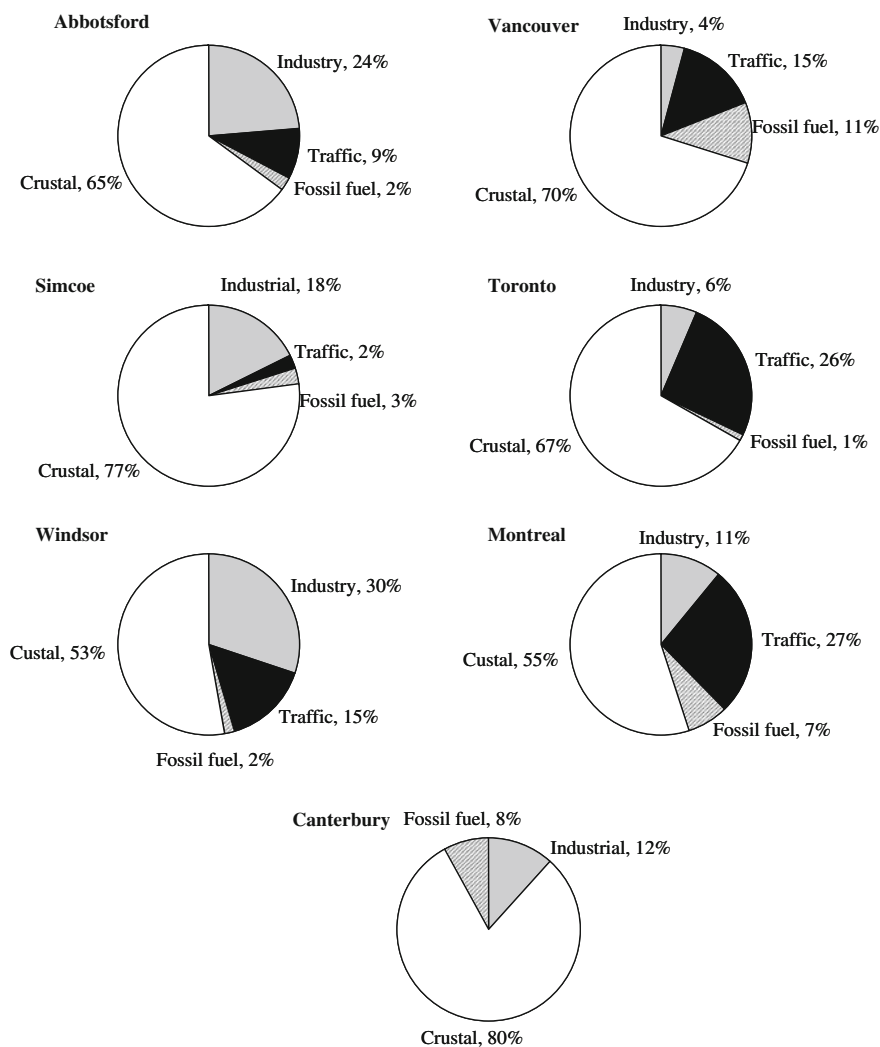
*Factor 3* had the highest loadings on Ni and V which have been reported as tracers of petrochemical industry and oil combustion (Moreno et al. 2006a; Meza-Figueroa et al. 2007; Salvador et al. 2007; Viana et al. 2007). The same link was identified by PCA at each sampling site with the exception of Simcoe and Toronto where, unlike the other sites, there was no correlation between these elements (Spearman Rank Order Correlations less than 0.5). The Abbotsford,

Vancouver, Montreal and Windsor sites have known industrial facilities of oil refining or transportation which explain the strong correlations (Spearman Rank Order Correlations above 0.80) and high concentrations of Ni and V at these sites. At the Canterbury site, these elements were also significantly correlated (Spearman Rank Order Correlations is 0.75), they were loaded at the same factor together with Se and were found at higher concentrations during the cold season, which suggests that domestic fossil fuel burning (oil and/or coal) used for heating during the winter is the main source of these elements in this region.

*Factor 4* linked Sr and Ba which were also loaded at the same factor at each sampling site, regardless of the land use and anthropogenic emissions. Sr which is a tracer of crustal source (Moreno et al. 2006b), showed very small variations of concentration between sampling sites (medians ranged from 0.2 to 0.5 ng/m<sup>3</sup>) whereas Ba was 3 to 4 times higher at sampling sites located close to high traffic areas. Also, the Ba-Sr factor at each site (except for Canterbury) had moderate loadings on Sb and Cu which are tracers of traffic related sources of emission, due to brake lining and tire wear. Such a chemical composition indicated that this factor represents traffic-related resuspended road dust.

*Factor 5* had significant loadings on Cu and As, followed by less significant Pb, Sb, Cd, Zn, which are all identified as tracers of multiple industrial pollution sources (Moreno et al. 2006a; Minguillon et al. 2007; and references therein). When PCA was applied to elemental composition of PM<sub>2.5</sub> at each sampling site, these elements were grouped together in different combinations and usually accounted for most of the variance. At the Western urban sites, Zn, As Cd and Pb were loaded at the same factor and accounted for 42% of the variance. The concentration of As at Abbotsford site (0.7 ng/m<sup>3</sup>) was higher than the overall Canadian median (0.4 ng/m<sup>3</sup>). The most likely sources of these elements are the emissions from a building material manufacturing facility and a mine located nearby. Pb, Cu and Mo were also associated with this group which implies some effect of air traffic in the composition of PM<sub>2.5</sub> in this area. At the Vancouver site Cd, Pb and Zn were grouped together implying that industrial emissions from a nearby metal manufacturing facility may be the major source of these elements in this area. Sn and Sb were also moderately loaded on the same factor (loading factors ca. 0.5) suggesting some effect of traffic related emissions at this component. Cd, Pb, Cu, Mo and As were also loaded at the same principal component at each Eastern urban site and accounted for 40–50% of the total variance. The chemical composition of this factor indicated that the emissions from industrial facilities located close to the sampling sites are the most likely source of these elements in this area.

Based on this analysis, the major sources of trace metals in PM<sub>2.5</sub> at the urban sites included in this study are, natural dust resuspension processes (indicated by the presence of mineral elements such as Fe and Mn), industrial emissions (Cu, As, Cd, Pb, Mo and Sn), fossil fuel refining and/or burning processes (Ni, V, Se) and traffic related emissions (Ba, Sr Sb, Zn). The mineral component comprises 55–65% of the trace metal concentrations in PM<sub>2.5</sub> in urban areas and above 70% at rural sites. The contribution of the anthropogenic sources depends on the human



**Fig. 6** Contribution of emission sources to the trace metal concentrations

emissions at each sampling site (Fig. 6). The industrial component accounts for 30 and 24% of the total inputs of metals at Windsor and Abbotsford sites, respectively, whereas traffic related sources have a major input at the Vancouver, Toronto and Montreal sampling sites. The principal components of trace metals at the Simcoe and Canterbury sites have a different structure. At the Simcoe site, the “industrial” component is a mixture of transported industrial pollutants and emissions from local farming, whereas at the Canterbury site the “industrial” component signifies the contribution of the long range transport in the region and



accounts for 12% of the trace metals concentrations in PM<sub>2.5</sub>. The crustal component which at this site is significantly loaded on Fe, Mn, and Sr is linked to the local dust resuspension. The fossil fuels component indicates the contribution of local domestic emissions.

## 4 Conclusions

This chapter presents a summary of composition and source origin of trace metals in PM<sub>2.5</sub> collected at selected urban and rural sites across Canada, within the National Air Pollution Network Surveillance program, during the May 2004 to December 2006 sampling period. The PM<sub>2.5</sub> mass concentrations found at all Canadian sites ranged from 5 to 11  $\mu\text{g}/\text{m}^3$  (IQR). The overall median was 7.2  $\mu\text{g}/\text{m}^3$  and was lower than most of the values reported for other regions of the world. The least contaminated site was Canterbury NB (rural), whereas Windsor ON (urban) was the site with the highest concentration of PM<sub>2.5</sub>.

The trace metals were analyzed by ICP-MS after microwave assisted acid digestion. Our results showed that metal concentrations were significantly higher at sites closer to industrial manufacturing facilities and high traffic areas. Sites located in areas with similar land use had a comparable elemental composition of PM<sub>2.5</sub>. The Windsor site, located close to several industrial facilities, had the highest concentrations of almost all metals. Ni and V concentrations were higher at the Vancouver and Montreal sites which are located close to oil and gas refining, storage and distribution facilities. Compared to the elemental composition of PM<sub>2.5</sub> samples collected in urban areas in Europe, Japan, and the USA, the Canadian aerosols were equally or less loaded with trace metals. The seasonal trends were more prominent at rural sites which showed elevated concentrations of all elements during warm seasons in Simcoe and during cold seasons in Canterbury. There was no significant annual trend of metal concentrations at urban sites, whereas there was a downward trend at rural sites during the 2004–2006 sampling period.

The source origin of trace metals in PM<sub>2.5</sub> was analyzed by PCA. The major component at all sites were crustal elements (Fe, Mn) which accounted for up to 70% of trace metals concentration. Industrial component accounted for 30 and 24% of the total inputs of metals at the Windsor and Abbotsford sites, respectively whereas traffic related sources had a major input at the Montreal, Toronto and Vancouver sampling sites, which are located in typical urban areas, close to major traffic routes throughout the cities.

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