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Receptor model based identification of $PM_{2.5}$ sources in Canadian cities

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ABSTRACT

Source apportionment of 24–hour integrated $PM_{2.5}$ chemical speciation data, collected at five Canadian urban sites, Windsor, Toronto, Montreal, Halifax, and Edmonton was performed using the receptor model, Positive Matrix Factorization (PMF). In order to determine the influences of local and regional sources, in–depth wind direction and back trajectory analyses were performed using the conditional probability function (CPF) and the potential source contribution function (PSCF). The highest $PM_{2.5}$ levels were observed in Windsor followed by Toronto and Montreal. Secondary sulfate and nitrate were the major factors contributing to the $PM_{2.5}$ mass, accounting for 41% – 61% in the five sites. These secondary factors were associated with trans–boundary emissions from Ohio, Pennsylvania, and New York. An elemental carbon (EC)–rich factor was identified in Windsor, Toronto, and Montreal, characterized by distinct EC and organic carbon (OC) profiles. The EC–rich factor accounted for 6% – 19% of the total $PM_{2.5}$ mass in summer and also appeared to be related to trans-boundary pollutants. The combined contributions of traffic and road dust ranged from 14% to 19%, with a portion of the nitrate factor also coming from vehicles. In Halifax, sea salt was the second strongest source, contributing 18% of the $PM_{2.5}$. In Edmonton, strong correlation of volatile organic compounds with the major $PM_{2.5}$ factors suggested that local industrial sources were significant sources of secondary aerosol. Further, biomass burning contributed 12% of the $PM_{2.5}$ mass in Edmonton.

Both local and regional sources were found to contribute at all sites. Thus, $PM_{2.5}$ can be reduced at all the sites through local controls. However given the significant contribution of trans–boundary contributions to the $PM_{2.5}$ mass, a substantial reduction of $PM_{2.5}$ in four of the cities will also require agreements to limit the production and transport of trans–boundary pollutants.

Keywords:
Source apportionment
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1. Introduction

Fine particulate matter ($PM_{2.5}$, particles smaller than 2.5 µm in aerodynamic diameter) has been associated with a variety of adverse health effects, visibility reduction, as well as changes in the Earth's radiation balance (e.g., Dockery et al., 1993; Burnett et al., 1995; Hinds, 1999). Fine PM may be formed directly from a primary source, such as, motor vehicles, industrial facilities, biomass burning, or indirectly through the conversion of gaseous emissions to the atmosphere from anthropogenic or natural sources. As a result, atmospheric fine particles are complex mixtures of primary (e.g., soot, sea salt, and dust) and secondary components (i.e., sulfate, nitrate, ammonium, and organic matter). This complexity in composition presents both challenges and opportunities in regards to understanding aerosol physical–chemical processes and elucidating sources of ambient particles.

A number of urban sites across Canada are known to experience elevated levels of particulate matter. Research into the sources and causes of high $PM_{2.5}$ levels is needed to understand and regulate the factors that contribute to reduced air quality. Source–receptor relationships for particulate matter can be quantified using a number of techniques. Receptor modeling, in contrast to emissions modeling, provides a method to distinguish the relative contributions of different sources based upon measurements at receptor sites. Airborne particle sources for most locations are unknown and data on the chemical composition of particles emitted from the sources are either unknown or are often ascribed similar, but likely not exact, profiles which can lead to errors in the modeling results.

Positive Matrix Factorization (PMF) avoids these limitations and can identify $PM_{2.5}$ sources and estimate their contributions in the absence of a priori information on sources (Paatero, 1996). Specifically, PMF functions by examining the correlation structure in the PM speciation temporal variability using a weighted multi-variate statistical approach; associations between components are found, allowing the composition of potential "factors" to be estimated.

Applying a mass balance in relation to these "source profiles" allows the mass contribution of each "factor" to be estimated. The presence of marker elements that are associated with particular "factors", along with seasonal or weekday/weekend trends, or diurnal trends for high time resolution data, can allow the identity of these "factors" to be resolved and thereby named as sources. Regional and local source contributions to $PM_{2.5}$ have been

apportioned using PMF in many ambient aerosol studies (e.g., Xie et al., 1999; Lee et al., 2003; Buset et al., 2006; Jeong et al., 2008).

Source apportionment of $PM_{2.5}$ was performed using the receptor model, PMF, to identify possible sources of $PM_{2.5}$ and determine their influence at five urban National Air Pollution Surveillance (NAPS) sites: Windsor, Toronto, Montreal, Halifax, and Edmonton. Use of meteorological data such as wind direction and back–trajectory analyses allowed insight into the geographic location of the sources. In addition, a correlation study was conducted to evaluate relationships between the resolved source contributions and gaseous pollutants including volatile organic compounds (VOC) and meteorological variables; this analysis helped to improve the interpretation of identified sources. This analysis was performed in support of the development of strategies to achieve compliance with a new Canada–Wide Standard for $PM_{2.5}$.

2. Experimental

2.1. Site description

$PM_{2.5}$ samples were collected on every third day at the five NAPS sites located in Toronto, Windsor, Montreal, Quebec, Halifax, and Edmonton as shown in Figure 1. The sampling periods for the five sites are summarized in Table 1.

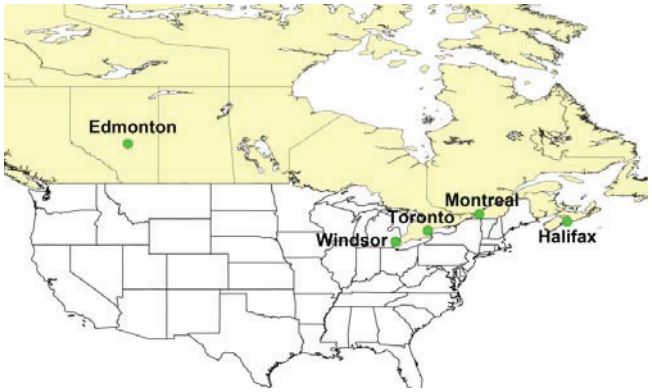


Figure 1. *Locations of the five NAPS monitoring sites in Canada.*

Table 1. *Summary of measurement periods at the five sites*

Site	Sampling Period (every 3 days)	Number of Samples	Number of Species
Windsor	June 2, 2004 – Mar 4, 2008	190	34
Toronto	Mar 1, 2004 – Sep 3, 2007	341	31
Montreal	Jan 21, 2003 – Nov 17, 2007	403	31
Halifax	Apr 14, 2006 – Jan 19, 2008	114	33
Edmonton	May 11, 2006 – Jan 19, 2008	154	33

The Toronto monitoring site (latitude 43.658, longitude –79.397) was located in the Toronto metropolitan area, Ontario and situated by busy local roads. High traffic expressways were situated to the east and south of the monitoring site. There was no major point source within 15 km of the site. During the measurement period, prevailing winds were from the west and the southwest.

The Windsor site (latitude 42.293, longitude –83.073) was surrounded by many local stationary sources and mobile sources in the U.S. and Canada. The Ambassador Bridge, the busiest international border crossing between Canada and the US, was located within 1 km of the measurement site. The dominant wind direction in Windsor was from the southwest, meaning the possible influence of direct emissions from several coal–fired power plants located along the Lake Erie. Samples were collected at the Windsor site from 2004 to 2008, with a year–long gap between March 2005 and March 2006.

The monitoring site (latitude 45.521, longitude –73.563) in Montreal was located in downtown Montreal, Quebec. Two major oil refinery facilities were situated ~15 km north of the site and a rail yard was located ~3 km southwest of the site. Prevailing south–west and northeast winds existed during the monitoring period, promoting PM transport from these local oil–related stationary sources to the receptor site.

The sampling site (latitude 44.647, longitude –63.574) in Halifax, Nova Scotia was located in the Halifax downtown area. This site was located ~1 km northwest of oil refinery facilities and ~2 km southeast of an oil–fired power plant. Several marine ports were situated nearby the Halifax site, contributing possible marine vessel emissions. The prevailing winds in Halifax were from the west and northwest.

Lastly, the sampling site (latitude 53.486, longitude –113.465) in Edmonton was located south of downtown Edmonton, Alberta. Two major highways run ~0.5 km and ~5 km to its south. Oil refinery and related industries were located ~7 km northeast of the Edmonton site. A major cement kiln and mixed industrial facilities were located ~14 km northwest of the site. The prevailing winds were from the northwest and southeast.

2.2. Sampling and chemical analysis

Integrated twenty–four hour ambient aerosol samples were collected by a Partisol–Plus 2025D sequential dichotomous particulate sampler (Rupprecht & Patashnick Co., Inc.) along with a Partisol 2300 speciation sampler (Rupprecht & Patashnick Co., Inc.) using a one–in–three day schedule. All collected samples were analyzed by the Analysis and Air Quality Section (AAQS) of Environment Canada in Ottawa. Details of the analytical methods and laboratory quality control checks are described elsewhere (Hassan et al., 2007; Celo et al., 2010; Dabek-Zlotorzynska et al., 2011; www.epa.gov/ttnamti1/files/ambient/pm25/spec/specfinl.pdf).

In brief, Teflon filter samples obtained by the Partisol–plus 2025D sequential dichotomous sampler were analyzed for trace metals (Al, Sb, Ba, Br, Ca, Cd, Cr, Co, Fe, Pb, K, Mn, Ni, Rb, S, Se, Sr, Si, Sn, Ti, V, and Zn) by energy dispersive X–Ray Fluorescence (XRF) analysis. The Partisol 2 300 speciation sampler was equipped with honeycomb–type annular denuders and three cartridges consisting of two Teflon– nylon filter packs and a quartz filter pack. The first Teflon–nylon filter pack was extracted and analyzed by Ion Chromatography (IC) to quantify water–extractable anions, cations, and organic acids: sulfate, nitrate, ammonium, calcium, chloride, potassium, magnesium, sodium, acetic acid, formic acid, oxalic acid. The aqueous extract of $PM_{2.5}$ from the second Teflon filter was analyzed by Inductively–Coupled Plasma Mass Spectrometry (ICPMS) to quantify water–soluble species (Al, Sb, As, Ba, Be, Cd, Cr, Co, Cu, Fe, Pb, Mn, Mo, Ni, Se, Ag, Sr, Tl, Sn, Ti, V, Zn). Field blank filters were taken most months and the average of all these values was used for blank corrections. Concentrations of organic carbon (OC) and elemental carbon (EC) were determined, based on particulate matter collected on the quartz filters of the Partisol 2 300 speciation sampler, using a DRI Model 2001 thermal/dual-optical carbon analyzer. The eight fractions, OC1, OC2, OC3, OC4, EC1, EC2, EC3, and (pyrolyzed OC) OP obtained by the reflectance method were applied for the PMF modeling in this study to provide further separation of carbonaceous sources. Positive artifacts of OC were estimated by measuring OC–fraction concentrations on a backup quartz filter positioned behind a Teflon filter. These positive OC artifacts were subtracted from the concentrations of each OC fraction measured on the directly exposed quartz filters. Continuous concentrations of $PM_{2.5}$, measured by using a Tapered Element Oscillating Microbalance (TEOM), and ambient gaseous

pollutants (CO, NO_x, SO_2, O_3, and VOCs) were obtained from measurements at collocated or nearby NAPS sites. The 24–hour samples of VOCs were collected every sixth day and analyzed using gas chromatography with a quadrupole mass–selective detector.

2.3. PMF analysis

Prior to applying PMF, the data was screened so as to eliminate values that could detract from the quality of the analysis. Chemical species containing more than 90% of data below the minimum detection limit were excluded from the PMF analysis. Duplicate PM chemical species measured by both XRF and ICPMS (or IC) were carefully selected for PMF analysis by comparing data completeness and the signal–to–noise ratio of each species. Data validation tests to identify values that appeared abnormal as compared to the overall data were carefully performed using scatter plot and time series analysis. All species measured on a few unique days were thereby excluded from the analysis. Distinct impacts of fireworks observed on Holidays were also excluded from the PMF analysis to minimize the influence of single episodic occurrences exhibiting a unique profile. Subsequently, all data were exported to the statistical software (STATISTICA 8, StatSoft Inc.) and analyzed to compile statistical summaries (see Tables S1–S5 in the Supporting Material, SM). Average concentrations of $PM_{2.5}$ species measured at the five monitoring sites are presented for comparison in Table 2.

Table 2. *Average concentrations of $PM_{2.5}$ chemical species at the five sites*

	Windsor	Toronto	Montreal	Halifax	Edmonton
	(μg m^{-3})	(μg m^{-3})	(μg m^{-3})	(μg m^{-3})	(μg m^{-3})
Al	2.60x10^{-2}	3.11x10^{-2}	4.50x10^{-2}	n/a	n/a
As	1.00x10^{-3}	n/a	n/a	1.81x10^{-4}	2.30x10^{-4}
Ba	2.20x10^{-3}	4.66x10^{-3}	1.36x10^{-2}	1.03x10^{-3}	2.12x10^{-3}
Br	n/a	1.32x10^{-3}	2.59x10^{-3}	n/a	n/a
Ca	7.20x10^{-2}	5.80x10^{-2}	6.84x10^{-2}	1.47x10^{-2}	4.09x10^{-2}
Cd	2.30x10^{-4}	n/a	n/a	3.14x10^{-5}	8.20x10^{-5}
Cl	1.00x10^{-1}	3.99x10^{-2}	1.01x10^{-1}	1.72x10^{-1}	6.92x10^{-2}
Co	n/a	n/a	n/a	2.01x10^{-4}	8.77x10^{-5}
Cr	3.50x10^{-4}	n/a	n/a	1.65x10^{-4}	4.84x10^{-4}
Cu	3.60x10^{-3}	n/a	n/a	9.15x10^{-4}	1.94x10^{-3}
Fe	1.20x10^{-1}	6.61x10^{-2}	5.69x10^{-2}	8.10x10^{-3}	1.62x10^{-2}
K	6.50x10^{-2}	4.42x10^{-2}	4.20x10^{-2}	2.99x10^{-2}	4.10x10^{-2}
Mg	1.80x10^{-2}	1.14x10^{-2}	9.08x10^{-3}	1.57x10^{-2}	6.31x10^{-3}
Mn	4.20x10^{-3}	6.25x10^{-3}	4.70x10^{-3}	7.96x10^{-4}	3.37x10^{-3}
Na	5.50x10^{-2}	4.97x10^{-2}	8.27x10^{-2}	1.45x10^{-1}	5.41x10^{-2}
Ni	5.30x10^{-4}	2.32x10^{-3}	3.82x10^{-3}	3.33x10^{-3}	6.59x10^{-4}
Pb	3.80x10^{-3}	2.86x10^{-3}	3.99x10^{-3}	1.85x10^{-3}	6.22x10^{-4}
Sb	n/a	n/a	n/a	1.82x10^{-4}	2.09x10^{-4}
Se	7.90x10^{-4}	9.17x10^{-4}	1.46x10^{-3}	n/a	n/a
Si	7.60x10^{-2}	8.32x10^{-2}	1.01x10^{-1}	n/a	n/a
Sr	5.60x10^{-4}	5.68x10^{-4}	3.42x10^{-3}	2.05x10^{-4}	1.92x10^{-4}
Ti	3.70x10^{-4}	1.25x10^{-2}	1.05x10^{-2}	1.74x10^{-4}	2.54x10^{-4}
V	1.30x10^{-3}	7.91x10^{-3}	8.56x10^{-3}	8.64x10^{-3}	2.81x10^{-4}
Zn	3.60x10^{-2}	1.09x10^{-2}	1.20x10^{-2}	7.78x10^{-3}	1.05x10^{-2}
Formate	3.10x10^{-2}	2.47x10^{-2}	1.87x10^{-2}	1.67x10^{-2}	1.24x10^{-2}
Oxalate	1.20x10^{-1}	1.05x10^{-1}	8.98x10^{-2}	7.58x10^{-2}	4.98x10^{-2}
Ammonium	1.70	1.36	8.98x10^{-1}	5.93x10^{-1}	6.05x10^{-1}
Nitrate	2.70	2.31	1.20	2.63x10^{-1}	1.47
Sulfate	3.60	2.88	2.23	2.27	8.88x10^{-1}
OC1	1.30x10^{-1}	1.12x10^{-1}	1.05x10^{-1}	9.31x10^{-2}	8.94x10^{-2}
OC2	4.70x10^{-1}	3.42x10^{-1}	2.97x10^{-1}	1.96x10^{-1}	1.99x10^{-1}
OC3	4.60x10^{-1}	2.64x10^{-1}	2.37x10^{-1}	1.99x10^{-1}	2.22x10^{-1}
OC4	5.10x10^{-1}	4.17x10^{-1}	3.89x10^{-1}	3.31x10^{-1}	3.60x10^{-1}
OP	6.60x10^{-1}	6.69x10^{-1}	6.96x10^{-1}	3.67x10^{-1}	3.93x10^{-1}
EC1	1.20	1.02	1.03	6.61x10^{-1}	6.69x10^{-1}
EC2	6.50x10^{-1}	5.53x10^{-1}	5.05x10^{-1}	3.43x10^{-1}	5.00x10^{-1}
EC3	6.40x10^{-2}	4.81x10^{-2}	4.37x10^{-2}	4.43x10^{-2}	3.87x10^{-2}

n/a: not available

Data below the detection limit were replaced by one–half of the detection limit for each species

Multivariate methods are based on the assumption that each aerosol source type has a unique chemical signature and hence that highly correlated chemical compounds originate from the same source. A large number of chemical species are measured at a receptor site over time and species of similar variability are grouped into a set of factors. Where PMF differs from other multivariate statistical methods is that it takes an explicit least–squares approach in which the method minimizes the object function (Q) by using a unique algorithm (Paatero, 1997). Details of PMF are described elsewhere (e.g., Xie et al., 1999). Briefly, any matrix X ($n \times m$), where n is the number of chemical species and m is the number of samples, can be factored into two matrices G ($n \times p$) and F ($p \times m$) as well as residual matrix E, where p is the number of sources and E is the unexplained part of X. The goal of multivariate receptor modeling is to determine the number of sources, the source contributions over time (g_{ik}), and the chemical profiles (f_{kj}) of identified sources. The task of PMF is to minimize the object function (Q), defined as follows:

$$Q = \sum_{i=1}^{n}\sum_{j=1}^{m}\left(\frac{e_{ij}}{s_{ij}}\right)^2 \quad (1)$$

where s_{ij} is the uncertainty in the j^{th} element for the i^{th} sample. This factor analysis ensures that all of the species profiles (matrix F) should be non–negative and each sample must have a non-negative source contribution (matrix G). PMF is able to simultaneously change the elements of G and F in each iterative step so that Q is minimized.

PMF uses point–by–point uncertainties, s_{ij}, to weight each value, x_{ij}. There are a number of models available to estimate the uncertainties (s_{ij}) in the PMF analysis. For this project, the uncertainties (s_{ij}) were heuristically calculated by the error model:

$$S = C_1 + C_3 \max\left(\left|x_{ij}\right|, \left|\sum_{k=1}^{p} g_{ik} f_{kj}\right|\right) \quad (2)$$

where C_1 is the analytical error derived from the individual measurement or estimated if no datum–specific error was available (σ_{ij}). C_3 is a dimensionless error constant used as the estimation of the relative uncertainties of large values and can be chosen by trial and error (Paatero, 1996). The analytical errors for the measured data were estimated by Environment Canada. In order to treat incomplete data (e.g., data below the detection limit and missing data) and to estimate their uncertainties (s_{ij}) for PMF in this report, the approach developed by Polissar et al. (2001) was used. The concentration values for data below the detection limit were replaced by half of the detection limit for the given element, and their corresponding errors were set at 5/6 times the detection limit values. For the missing data, the median of all the concentrations measured for the given species was used as its species concentration, and its accompanying error was set at four times the median value so that it had minimal effect on the PMF results. In addition, the final uncertainties (s_{ij}) were revised by iterating the PMF analysis so as to obtain physically meaningful factors. In order to reduce the influence of weak and poor variables on the PMF analysis, chemical components with high noise were down–weighted based on their signal–to–noise ratios (S/N) ratio (Paatero and Hopke, 2003). In this work, the species were classified into three groups; good (S/N ≥ 2), weak (1< S/N <2), and poor (S/N < 1). While there was no down–weighting of good species, species with weak or poor signal–to–noise were down–weighted by multiplying their C_1 values in Equation (2) by two and three, respectively.

2.4. Application of supporting analysis

A linear regression analysis was carried out to investigate the relationship between identified sources and gaseous pollutants as

well as atmospheric parameters. In addition, an independent *t*–test was conducted to evaluate significance between $PM_{2.5}$ speciation data at the monitoring sites. A *p*–value of < 0.05 was considered statistically significant in both tests. Temporal variations of gaseous pollutants (CO, NO_x, SO_2, O_3) during the measurement period were examined and compared with mass contributions of resolved sources to support the identification of the sources. Pearson correlation coefficients (*r*) between the variations of PMF source contributions and VOCs as well as meteorological parameters provided further useful information for the identification of sources.

In order to ascertain the most probable source locations of resolved sources, analyses of the conditional probability function (CPF) (Ashbaugh et al., 1985; Kim and Hopke, 2004) and the potential source contribution function (PSCF) were conducted for PMF–resolved sources at all sites. The back trajectory analysis, PSCF, is useful for identifying the possible geographic origin of long–range transported sources, while CPF provides a conditional probability that high values are related to specific wind direction and thus is better suited for associating pollutants with local sources. CPF is defined as follows:

$$CPF = \frac{m_{\Delta\theta}}{n_{\Delta\theta}} \quad (3)$$

where $m_{\Delta\theta}$ is the number of times that the source contribution exceeded a certain threshold criterion while wind came from a direction sector ($\Delta\theta$) and $n_{\Delta\theta}$ is the total number of times the wind came from the same wind direction. In this study, the direction sector ($\Delta\theta$) was set to be 30 degrees dividing the wind into 12 discrete bins. All time periods of wind speed less than 1 m sec^{-1} were removed from the analysis. The threshold was set as the highest 25% of the source contribution concentrations.

PSCF was calculated using 3–day back trajectories for PMF–modeled source contributions based on the HYbrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model with EDAS 40 km gridded meteorological data (Draxler and Rolph, 2003). The PSCF has been applied to identify pollutant sources in a number of studies (e. g., Cheng and Lin, 2001). Seventy–two–hour back trajectories starting at noon local time at a height of 500 m above the ground level were calculated for every sample day at each site. The region covered by the trajectories was divided by 8 660 grid cells of 0.5° latitude by 0.5° longitude. PSCF is defined as follows:

$$PSCF_{ij} = \frac{m_{ij}}{n_{ij}} \quad (4)$$

where n_{ij} is the total number of times that trajectory passed through cell (*i,j*) and m_{ij} is the number of times that source contribution exceeded the threshold criterion while trajectory passed through cell (*i,j*). In this work, the criterion value was set at the 75th percentile of each factor at all sites. In addition, an arbitrary weight function [$W(n_{ij})$] of PSCF was applied to account for the positive PSCF artifact of cells that contained less than 3 times the average number of points per grid cell (*PPC*).

$$W(n_{ij}) = \begin{cases} 0.7 & \text{if } PPC < n_{ij} \le (3 \times PPC) \\ 0.4 & \text{if } (0.5 \times PPC) < n_{ij} \le PPC \\ 0.2 & \text{if } (0.5 \times PPC) \ge n_{ij} \end{cases} \quad (5)$$

In this study, *PPC* values were 11 in Windsor, 34 in Toronto, 40 in Montreal, 11 in Halifax, and 15 in Edmonton, reflecting the different durations of the sampling periods at the different sites.

The spatial distribution of $PM_{2.5}$ mass concentrations and its chemical compositions between sampling sites were determined using correlations and coefficients of divergence (COD, Wongphatarakul et al., 1998). COD provides information on the degree of uniformity between sampling, where small values (close to 0) imply homogeneity between sites, and higher COD values (close to 1) indicate more heterogeneity. The COD is defined as follows:

$$COD_{jk} = \sqrt{\frac{1}{p}\sum_{i=1}^{p}\left[(N_{ij} - N_{ik})/(N_{ij} + N_{ik})\right]^2} \quad (6)$$

where N_{ij} is the i^{th} concentration measured at the *j* site. Both *j* and *k* represent monitoring sites, and *p* is the number of samples.

3. Results and Discussion

3.1. Temporal characteristics of species concentrations

As shown in Figure 2, the highest $PM_{2.5}$ mass concentrations, on average, were observed in Windsor followed by Toronto and Montreal. The $PM_{2.5}$ concentrations in Windsor and Toronto were statistically higher than the concentrations at the remaining sites ($p < 0.05$). In addition, no significant seasonal patterns of the $PM_{2.5}$ concentrations were observed in Windsor, Toronto, Montreal, and Halifax with high *p*–values, whereas a statistically significant winter–high trend was found in Edmonton ($p < 0.05$), indicating distinct seasonality in $PM_{2.5}$ chemical compositions in Edmonton.

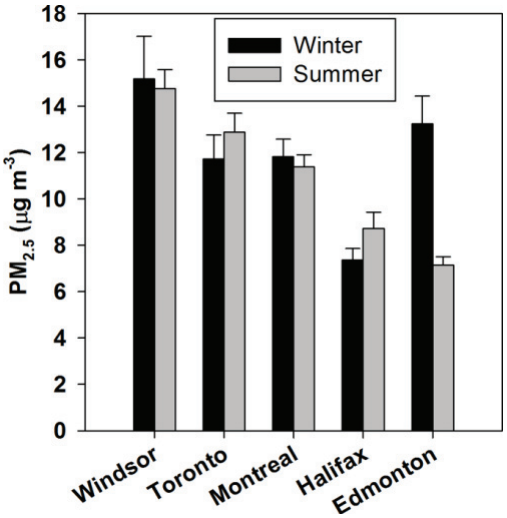


Figure 2. *Variations of $PM_{2.5}$ mass concentrations in winter (December–February) and summer (June–August) at the five sites. Error bars represent standard errors.*

Sulfate was the dominant component of $PM_{2.5}$ mass at the urban sites (see the SM, Tables S1–S5), except for the Halifax site where the major chemical species comprised mostly of nitrate. The concentrations of sulfate and nitrate in Windsor were, respectively, higher than the average sulfate in Edmonton by a factor of 4 and average nitrate in Halifax by a factor of 9. The carbon profiles at the five sites showed a similar profile with EC1 being the major form of EC or OC. On average, total OC and EC levels in Windsor were higher than in the other cities, whereas the lowest average concentrations of OC and EC were observed in Halifax. In terms of the minor chemical components of $PM_{2.5}$, significant contributions of Na and Cl species were found in Halifax, presumably due to the influence of sea salt at this sea–side city. The concentrations of Ni and V in Halifax were significantly higher than the concentrations in Windsor and Edmonton indicating a higher impact of residual fuel–oil combustion or ship emissions. The concentration of Zn was clearly higher in Windsor suggesting possible impact of metal industries.

Seasonal differences in the major $PM_{2.5}$ chemical species at the five sites are presented in Figures 3. In the Toronto area, strong seasonality in the nitrate and sulfate concentrations was observed and the lowest concentrations of these secondary pollutants were found in spring (Figure 3b). Higher concentrations of Na, Cl, and K were observed in the winter season, while formate and oxalate levels were higher in summer. Crustal elements, Ca, Fe, and Si, were more significant in spring months, suggesting contributions of fugitive dusts under certain meteorological conditions. Similar to trends in Toronto, sulfate and nitrate measured in Windsor were strongly dependent on season (Figure 3a). The winter–high patterns in Na and Cl concentrations and summer–high trends in organic acids were consistent with Toronto. Concentrations of crustal materials were also higher in spring. In Montreal, the seasonal variability of major $PM_{2.5}$ chemical species was similar to Toronto and Windsor including the lower concentrations of most species in spring, as shown in Figure 3c. The concentrations of salt in Montreal were higher in winter than in summer by a factor of ~4.7. As presented in Figure 3d, the winter–high trend in nitrate was not observed in Halifax. Higher sulfate concentrations were found in winter and spring, suggesting the influence of local primary sources of sulfur and sulfate in winter. The concentrations of salt were distinctly higher among the minor chemical species, especially in colder months. Figure 3e illustrates the interesting seasonal difference of the $PM_{2.5}$ speciation in Edmonton underlying the higher winter time $PM_{2.5}$ concentrations.

The concentrations of ammonium, nitrate, Cl, K, EC1 were higher in the colder months by factors of approximately 5, 10, 5, 2, and 2, suggesting impacts of local combustion sources such as wood burning and industrial emissions on winter air quality in Edmonton. The low summertime $PM_{2.5}$ in Edmonton was likely due to the low contribution of sulfate in summer months as compared to strong nitrate formation in winter. This seasonal pattern for Edmonton was the opposite of the pattern in Halifax; in Halifax, $PM_{2.5}$ was lower in the winter due to the low concentrations of nitrate in winter and high sulfate concentrations in summer.

The spatial homogeneity between Toronto and Montreal, in the $PM_{2.5}$ mass and chemical composition, was evaluated using coefficients of divergence (COD) and Pearson correlations (Figure 4). Interestingly, relatively low COD values (< 0.26) and high correlations ($r > 0.6$) for EC1 and EC2, implied that these components are relatively homogeneously distributed throughout Eastern Canada. Previously, EC1 and EC2 have been used as markers of local diesel emissions. However, the spatial uniformity suggested that much of the EC in Toronto and Montreal might be due to long–range transported combustion sources. The higher correlation between ammonium and nitrate concentrations for Toronto and Montreal with the higher COD values was likely due to a similar seasonality in the formation of these species and the different contributions of local sources at the sites. In contrast, the higher correlation with the slightly lower COD values for oxalate and sulfate might suggest that the two sites were commonly impacted by strong photochemical production of oxalate and sulfate in warmer months, more likely contributed by regional sources of oxalate and sulfate.

3.2. PMF results

The PMF model was run in the default robust mode to decrease the influence of extreme values on the PMF solution at each site. To ensure that the appropriate number of factors was chosen, the scaled residuals, the ratio of the PMF–modeled residual (e_{ij}) to the input uncertainty (s_{ij}) were also examined at all sites. For the final analysis, PMF was applied to the data using 4 to 15 factors and the resultant change in the Q values was examined. The final solution at each site had an adequately small range of Q values from random runs to confirm the achievement of a similar global minimum. PMF analysis was conducted by varying the rotational parameter, FPEAK (Paatero et al., 2002). Rotational ambiguity was also examined using the G–space plots for PMF–resolved factors as suggested by Paatero et al. (2005).

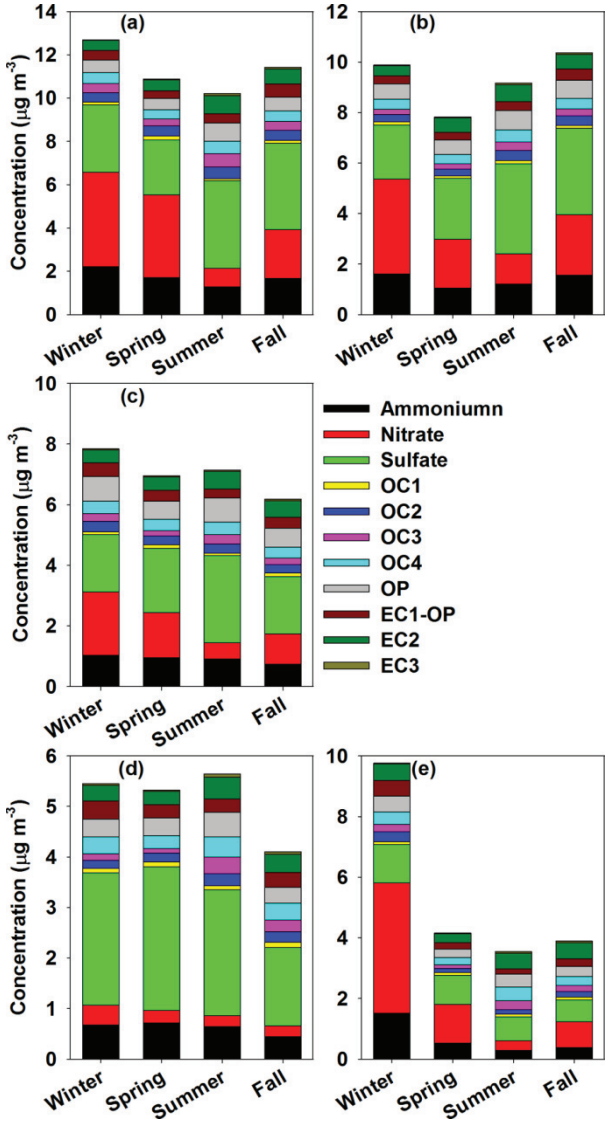


Figure 3. *Seasonal variation of major chemical species of $PM_{2.5}$ in* ***(a)*** *Windsor,* ***(b)*** *Toronto,* ***(c)*** *Montreal,* ***(d)*** *Halifax, and* ***(e)*** *Edmonton. Winter (December–February), Spring (March–May), Summer (June–August), and Fall (September–November). Data below the detection limit were replaced by one-half of each species' detection limit.*

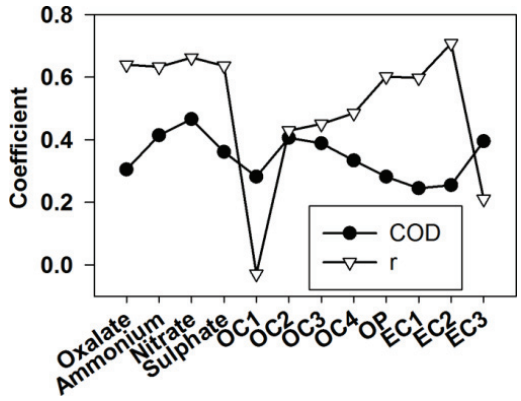


Figure 4. *Coefficients of divergence and Pearson correlation coefficients of major $PM_{2.5}$ chemical components between Toronto and Montreal.*

To quantitatively estimate the mass contribution of resolved factors, multiple linear regression was performed. Because of uncertainties introduced by the measurement matrix, a fraction of the measured variation is not captured by PMF. The unexplained portion was addressed by regressing the obtained factor values against the measured $PM_{2.5}$ mass concentrations. In order to confirm that PMF–resolved sources effectively reproduced the measured total mass, the reconstructed $PM_{2.5}$ contributions from all sources were compared with the measured $PM_{2.5}$ concentrations. The temporal characteristics of the PMF–resolved factors were assessed by examining time series plots, weekday/weekend, and seasonal differences, which assisted in their interpretation. The types and locations of local stationary sources near the sampling sites were identified by examining the national pollutant release inventory (NPRI) data. Local meteorological trends as well as important episodic events due to meteorology over the period were investigated to obtain a better understanding of the measurement sites.

Source profiles and contributions of PMF–resolved factors at the five sites are provided in the Supporting Material (Figures S1–S10). The average source contributions and seasonal variations of PMF–resolved sources to the total $PM_{2.5}$ concentrations at the five sites are summarized in Table 3 and Figure 5, respectively. These factors are discussed in general in this paper along with their contributions at the five sites. Detailed discussion of each of the PMF–resolved factors at each of the five sites is provided in the Supporting Material.

Windsor. The most reasonable result was found with eight factors including secondary sulfate, secondary nitrate, traffic emissions, an EC–rich factor, road salt, soil/road dust, steel making, and oil combustion. On average, 95% of the scaled residuals estimated using PMF was distributed between +2 and –2. Due to the high residuals found in preliminary runs, some species required down–weighting beyond the policy used for the other sites, described previously. Uncertainties were multiplied by 2 for Mg, Ba, Mn, Sr and Zn and uncertainties were multiplied by 3 for Ca, Cd, Cu, Se, Al and Si. This policy provided a better solution in terms of more physically meaningful factor profiles and was likely required due to the complexity of the Windsor site, caused by the larger number of local industrial sources as compared to the other sites. The reconstruction of the $PM_{2.5}$ mass concentration explained by the PMF–resolved factors was compared to the measured Partisol 2 300 $PM_{2.5}$ mass concentration [slope = 0.96 ± 0.02 (standard error), intercept = 0.47 ± 0.42, and r^2 = 0.91]. The source profiles (value ± standard deviation) and time series of the PMF–resolved factors are shown in Figures S1 and S2 (see the SM).

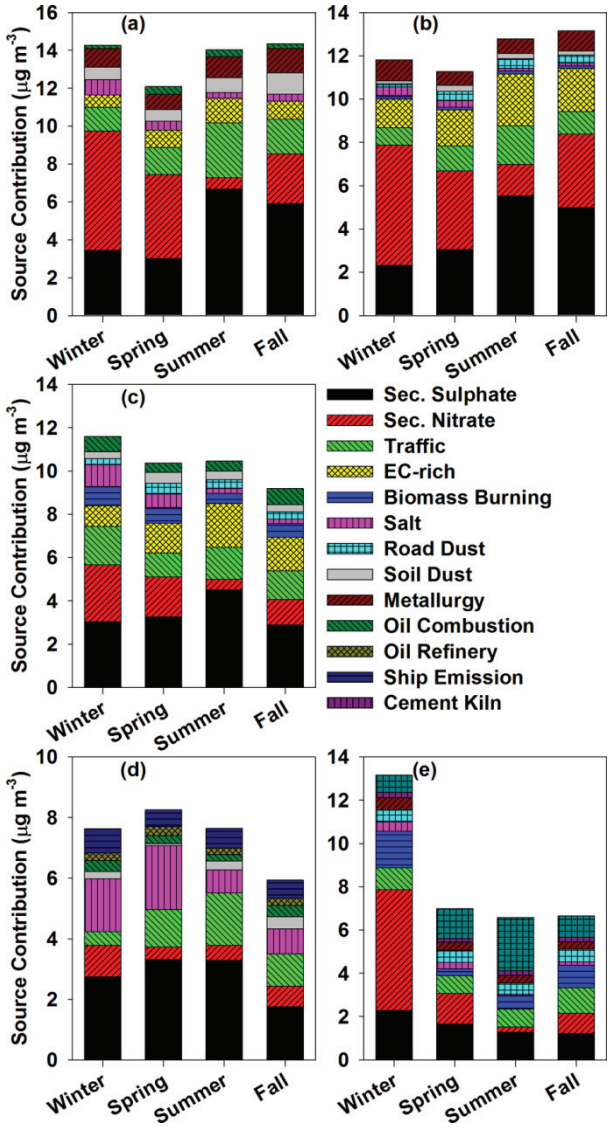


Figure 5. *Seasonal contribution of PMF–resolved sources in* ***(a)*** *Windsor,* ***(b)*** *Toronto,* ***(c)*** *Montreal,* ***(d)*** *Halifax, and* ***(e)*** *Edmonton. Winter (December–February), Spring (March–May), Summer (June–August), and Fall (September–November).*

Table 3. *Average contributions of PMF–resolved sources at the five sites*

	Windsor	Toronto	Montreal	Halifax	Edmonton
	% (μg m^{-3})	% (μg m^{-3})	% (μg m^{-3})	% (μg m^{-3})	% (μg m^{-3})[a]
Sec. sulfate	37.1 (5.2 ± 0.6)	33.4 (4.1 ± 5.7)	33.7 (3.5 ± 3.8)	37.3 (2.6 ± 2.6)	19.0 (1.5 ± 1.7)
Sec. nitrate	24.0 (3.4 ± 5.7)	26.4 (3.2 ± 4.6)	13.5 (1.4 ± 2.2)	9.3 (0.7 ± 0.6)	21.9 (1.8 ± 3.3)
Traffic	13.9 (2.0 ± 1.7)	10.4 (1.2 ± 1.3)	13.9 (1.4 ± 2.8)	14.2 (1.0 ± 1.1)	12.4 (1.0 ± 0.8)
EC–rich	6.1 (0.9 ± 0.5)	15.6 (1.9 ± 1.6)	14.9 (1.5 ± 1.1)		
Biomass burning		1.1 (0.1 ± 0.1)	6.4 (0.7 ± 0.6)		12.0 (1.0 ± 1.0)
Salt	2.3 (0.3 ± 0.3)	1.8 (0.2 ± 0.3)	4.4 (0.5 ± 0.6)	18.3 (1.3 ± 1.4)	2.5 (0.2 ± 0.3)
Road dust		3.2 (0.4 ± 0.3)	3.9 (0.4 ± 0.3)		7.0 (0.6 ± 0.5)
Soil dust	5.3 (0.7 ± 0.6)	1.9 (0.2 ± 0.2)	3.8 (0.4 ± 0.3)	3.8 (0.3 ± 0.5)	
Metallurgy	7.6 (1.1 ± 1.0)	6.2 (0.7 ± 0.6)			4.9 (0.4 ± 0.5)
Oil combustion	3.7 (0.5 ± 0.6)		5.5 (0.6 ± 0.5)	4.5 (0.3 ± 0.4)	
Oil refinery				3.5 (0.3 ± 0.3)	
Ship emission				9.1 (0.6 ± 0.7)	
Cement kiln					2.6 (0.2 ± 0.2)
Biogenic SOA					17.7 (1.4 ± 1.1)

[a] *(mean ± standard deviation)*

Toronto. On average, approximately 95% of the scaled residuals for nine factors estimated by PMF were distributed within ±2. Since a change in FPEAK was not found to improve the results, FPEAK was finally set equal to zero in Toronto. As a result, a good fit of the nine–factor modeled results was identified. A comparison of the reconstructed $PM_{2.5}$ contributions from all sources with measured $PM_{2.5}$ concentrations gave a slope of 0.97 ± 0.01 and an intercept of 0.38 ± 0.16 with a high linear correlation coefficient (r^2 = 0.96). Figure S3 presents the profiles of the nine sources identified in Toronto; secondary sulfate, secondary nitrate, traffic, EC–rich, biomass burning, road salt, road dust, soil dust, and smelter. The temporal source contributions of these sources are shown in Figure S4 (see the SM).

Montreal. PMF resolved a nine–factor solution with the FPEAK value of zero. On average, approximately 97% of the scaled residuals were distributed between –2 and +2. The reconstructed $PM_{2.5}$ contributions compared well with measured values at the Montreal site (slope = 0.96 ± 0.01, intercept = 0.16 ± 0.18, and r^2 = 0.91). Nine factors including secondary sulfate, secondary nitrate, traffic emissions, EC–rich, biomass burning, road salt, road dust, soil dust, and oil combustion were identified and compared. Figures S5 and S6 (see the SM) present the profiles and contributions of the nine sources identified in Montreal.

Halifax. PMF effectively resolved an 8–factor model including secondary sulfate, secondary nitrate, traffic, sea salt, soil dust, oil combustion, oil refinery, and ship emission factors with an FPEAK value of zero. Approximately 95% of the scaled residuals were distributed between –2 and +2. A comparison of the daily reconstructed $PM_{2.5}$ contributions with measured $PM_{2.5}$ concentrations showed that the PMF–resolved factor effectively reproduced the measured concentrations (slope = 1.04 ± 0.04, intercept = –0.66 ± 0.32, r^2 = 0.87). The identified source profiles and contributions in Halifax are depicted in Figures S7 and S8 (see the SM).

Edmonton. A nine–factor PMF solution with an FPEAK value of zero was selected as it yielded the minimum rotational ambiguity and mostly symmetric distributions of scaled residuals for all species within ± 2 standard deviations. Good correlation and agreement between the reconstructed $PM_{2.5}$ contributions and measured $PM_{2.5}$ concentrations were found (slope = 0.92 ± 0.03, intercept = 0.53 ± 0.27, r^2 = 0.87). Profiles and contributions for the factors including secondary sulfate, secondary nitrate, traffic, biomass burning, salt, road dust, steel mill, cement kiln and biogenic secondary organic aerosol sources resolved from the Halifax data are presented in Figures S9 and S10 (see the SM).

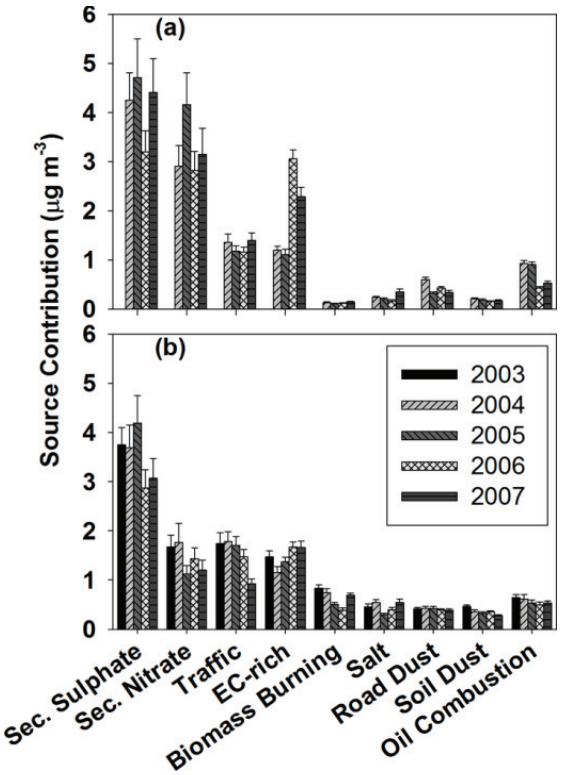


Figure 6. *Annual source contribution of PMF–resolved factors in* ***(a)*** *Toronto and* ***(b)*** *Montreal. Error bars represent standard errors.*

Table 4. *Correlation between PMF–resolved sources and VOCs in Edmonton*

	Correlated VOC[a] (r > 0.7)
Secondary sulfate	2,2,3–Trimethylbutane, 2,2–Dimethylpropane, cis–1,3–Dimethylcyclohexane, Cyclohexane, Methylcyclohexane, trans–1,4–Dimethylcyclohexane, trans–2–Octene
Secondary nitrate	1,2,3–Trimethylbenzene, 1,2,4–Trimethylbenzene, 1,2–Diethylbenzene, 1,3,5–Trimethylbenzene, 1,3–Butadiene, 1,3–Diethylbenzene, Isobutene, 1–Butyne, 1–Hexene, 1–Methylcyclohexene, 1–Methylcyclopentene, 1–Propyne, 2,2,3–Trimethylbutane, 2,2,5–Trimethylhexane, 2,2–Dimethylpentane, 2,2–Dimethylpropane, 2,3,4–Trimethylpentane, 2,3–Dimethylbutane, 2,4–Dimethylhexane, 2,5–Dimethylhexane, 2–Ethyltoluene, 2–Methylheptane, 2–Methylhexane, **2–Methylpentane**, 3,6–Dimethyloctane, 3–Ethyltoluene, 3–Methylheptane, 3–Methylhexane, 3–Methylpentane, 4–Ethyltoluene, 4–Methylheptane, Acetylene, Benzene, Bromodichloromethane, Bromoform, Bromomethane, cis–1,2–Dimethylcyclohexane, **cis–1,3–Dimethylcyclohexane, cis–1,4/t–1,3–Dimethylcyclohexane**, cis–2–Hexene, cis–3–Methyl–2–pentene, **Cyclohexane**, Cyclopentane, Decane, Dibromochloromethane, Dodecane, Ethane, Ethylbenzene, Ethylbromide, Ethylene, Heptane, **Hexane**, Indane, Isobutane, iso–Butylbenzene, iso–Propylbenzene, m and p–Xylene, **Methylcyclohexane, Methylcyclopentane**, Naphthalene, n–Butylbenzene, **Nonane**, n–Propylbenzene, **Octane**, o–Xylene, p–Cymene, Pentane, **Propane**, Propylene, sec–Butylbenzene, Toluene, **trans–1,4–Dimethylcyclohexane, trans–2–Octene**, Undecane
Traffic	None
Biomass burning	1,2–Dichloropropane, 1–Propyne, 2,2–Dimethylpentane, 2,3–Dimethylpentane, 2,4–Dimethylhexane, 2,5–Dimethylhexane, 2–Methylheptane, 2–Methylhexane, 3–Methylheptane, 3–Methylhexane, 4–Methylheptane, Acetylene, Benzene, cis–1,4/t–1,3–Dimethylcyclohexane, Cyclohexane, Ethane, Isobutane, Methylcyclopentane, Propane, Vinylchloride
Salt	None
Road dust	1,2–Dichloropropane
Steel mill	3–Methyl–1–butene
Cement kiln	None
SOA	Isoprene

[a] *VOC data in 2006, n=31, higher correlations (r > 0.8) were shown in bold.*

3.3. PMF factors

Secondary sulfate. The secondary sulfate factor was the most significant factor contributing to the $PM_{2.5}$ mass in all the cities except Edmonton. It was characterized by high loadings of sulfate, ammonium, oxalate and in some cities formate, OP and OC. This factor showed strong seasonality in that its summer mean was higher than its winter mean, except in Edmonton (Figure 5). The annual variation of this factor revealed a summer maximum in 2005 (Figure 6), consistent with the hottest summer present in this data. The PSCF plots for Windsor, Toronto and Montreal (Figure 8) identified possible sources in Ohio, Michigan, Pennsylvania, Kentucky, Tennessee, and Indiana, consistent with the known locations of many large coal–fired electric utilities. The PSCF plot for Halifax (Figure 8d) indicated potential source regions in central Pennsylvania, New York, and port areas in Maryland.

The contribution of the sulfate factor in Edmonton was lower than at the other sites, with a maximum in the winter rather than in the summer (Figure 5e). This winter–high trend might have been due to increased consumption of fossil fuels for winter heating under stagnation conditions and low inversions during the winter. Strong correlations with VOCs suggested that the sulfate factor in Edmonton was more related to local contributions (Table 4). However, further analysis is needed to clarify the winter formation of sulfate and determine contributions from local and regional sources.

Secondary nitrate. The secondary nitrate was represented by high contributions of nitrate, ammonium, and chloride. There was a strong winter–high pattern in the contribution of this factor (Figure 5). The secondary nitrate formation was strongly dependent on ambient temperature, consistent with the partitioning of HNO_3 to the particle phase being higher at lower temperature. As shown in Tables S6 – S10 (see the SM), the temporal variation of this factor was well correlated with NO_2, suggesting the influence of local vehicular exhaust on nitrate formation in this urban area. The PSCF plot (Figure 9) for Windsor, Toronto, and Montreal implied that it was also associated with sources broadly located in the American mid–west. These regions were previously identified as sources for nitrate observed in upper Midwestern US and New York State (Zhao and Hopke, 2006; Raman and Hopke, 2007). In particular, strong influences from the northeastern parts of Ohio along Lake Erie, Kentucky, and Tennessee might cause the higher nitrate concentration for Toronto, as compared to the concentration for Montreal.

The nitrate factor was the largest contributor to $PM_{2.5}$ mass in Edmonton. The strong correlation with VOCs, temperature, and relative humidity (RH) (Table 4 and Table S10) implied influences from local oil refinery sources and meteorological conditions. However, PSCF analysis for the factor also indicated that high nitrate concentrations were influenced by regional sources located in western Washington, southern Alberta, and southern Saskatchewan. In order to separate the influence of local and regional sources on nitrate formation, further source apportionment studies at both this urban site and a nearby background site are essential.

Traffic emissions. The traffic emission factor was characterized by high concentrations of OCs, ECs, and oxalate. The presence of oxalate in this factor profile and summer–high patterns suggested the incorporation of some SOA. The traffic factor was highly correlated with many VOCs associated with fresh gasoline and diesel fuel combustion emissions (Tables S11 – S14, see the SM) except in Edmonton. As shown in Tables S6 – S10 (see the SM), the correlations of the traffic factor with traffic markers, such as NO, NO_2, and CO were statically significant ($p < 0.05$). The contributions of the traffic factor for Toronto, Halifax and Edmonton tended to be higher on weekdays than on weekends. Although the traffic source in Montreal did not show a clear weekday–weekend difference, relatively high contributions of this factor were more frequently observed on weekdays, yielding a higher mean. Impacts of weekend border crossing traffic in Windsor could be one explanation of the slightly higher contribution of the traffic factor at this site on weekends. Gasoline emissions are indicated by OC2 and OC3 abundances, whereas high EC2 and OC2 fractions tend to be observed in diesel emissions (Liu et al., 2006). Based on the distribution of carbon species within the source profile, this factor at Toronto and Montreal sites appeared to be closer to gasoline vehicle exhaust, whereas this traffic factor for Windsor, Halifax and Edmonton likely had strong contributions from diesel combustion.

Elemental carbon–rich: The EC–rich factor was observed in Windsor, Toronto, and Montreal with the highest contribution observed in Toronto. This factor mainly exhibited high mass fractions of EC2 and EC3 as well as sulfate with a clear summer–high pattern. The annual temporal trend of the EC factor increased during 2006 and remained elevated (Figure 6). A high EC factor might normally be identified as a diesel vehicle emission source due to the high EC/OC ratio. However, a strong temporal variability and its lack of correlation with traffic–related pollutants suggested that this factor was not directly related to primary local combustion processes. Some sulfate in this factor profile suggested that it was associated with regional transport of primary and secondary pollutants from coal combustion processes. The PSCF analyses (Figure 10) for the EC–rich factor also supported the hypothesis that this factor was related to regional transports of primary and secondary emissions from coal combustion electric utilities, likely located in Ohio, western Pennsylvania, and western Indiana.

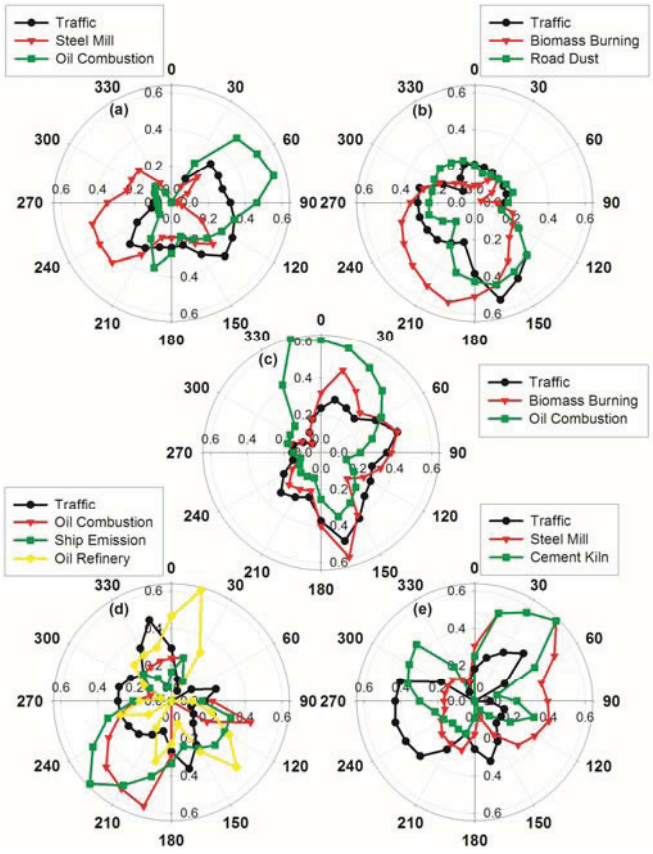


Figure 7. *CPF plots for PMF–resolved factors at the five sites.* ***(a)*** *Windsor,* ***(b)*** *Toronto,* ***(c)*** *Montreal,* ***(d)*** *Halifax,* ***(e)*** *Edmonton.*

Biomass burning. The biomass burning factor was characterized by high concentrations of K and EC with a winter–high trend. Recreational wood combustion for residential heating may account for higher wintertime contributions. This factor showed good correlations with most gaseous pollutants as well as VOCs,

especially for Edmonton (Table 4). The high correlation of biomass burning with VOCs is consistent with the result at a rural site in British Columbia (Jeong et al., 2008). In winter months the average $PM_{2.5}$ mass concentration at night (7 pm – 3 am) on weekends in Edmonton was much higher than the average on weekday. The difference is suggestive of higher recreational wood burning on weekend nights. The CPF plot for Montreal and Toronto was consistent with the direction of residential areas nearby these sites (Figure 7).

Salt. The road/sea salt factor was commonly observed at the five sites with the highest contribution in Halifax among the sampling sites. Almost all of the measured Na and Cl were contained in this factor. This factor showed a strong seasonality with winter and spring–high patterns. These results suggest that resuspension of road salt may occur as a result of vehicles driving through salt-laden puddles created from melting snow in winter or due to vehicle or wind induced resuspension of dust on dried roads in spring. The salt factor was the second largest source in Halifax. A winter/spring–high pattern may be related to the seasonal impact of sea salt aerosols from ocean breaking waves. The intensity of wave energy fluctuates seasonally, with the highest energy density occurring during the winter, when there are more storms and winds (Dunnett and Wallace, 2009). The molar ratio of Na to Cl for Halifax was closer to 1.0 than in the other cites, indicating much fresher salt. The above unity Na to Cl molar ratio may be indicative of some aged road salt or sea salt since lower Cl can be caused by reactions of NaCl with strong acids. The PSCF plot (Figure S16, see the SM) for Halifax indicated the North Atlantic Ocean as a dominant potential source region. The PSCF plot for Edmonton identified parts of Saskatchewan, and the northwest of Alberta as potential source regions (Figure S15, see the SM). Large salt deposits extend from the Northwest Territories down through Alberta, Saskatchewan, and into Manitoba.

Road dust. The source profile of the road dust factor was high in elements typically associated with road dust such as Ca, Mg and Fe. The temporal variation of this source showed a strong weekday high pattern (Figure S12, see the SM) and positive correlations with traffic–related gases (Tables S7, S8, and S10; see the SM). A mixture of dust emission from paved roads and diesel vehicle exhaust contributed to this factor. The CPF plot for Toronto suggested that higher contributions were associated with the direction of local busy roads (Figure 7b).

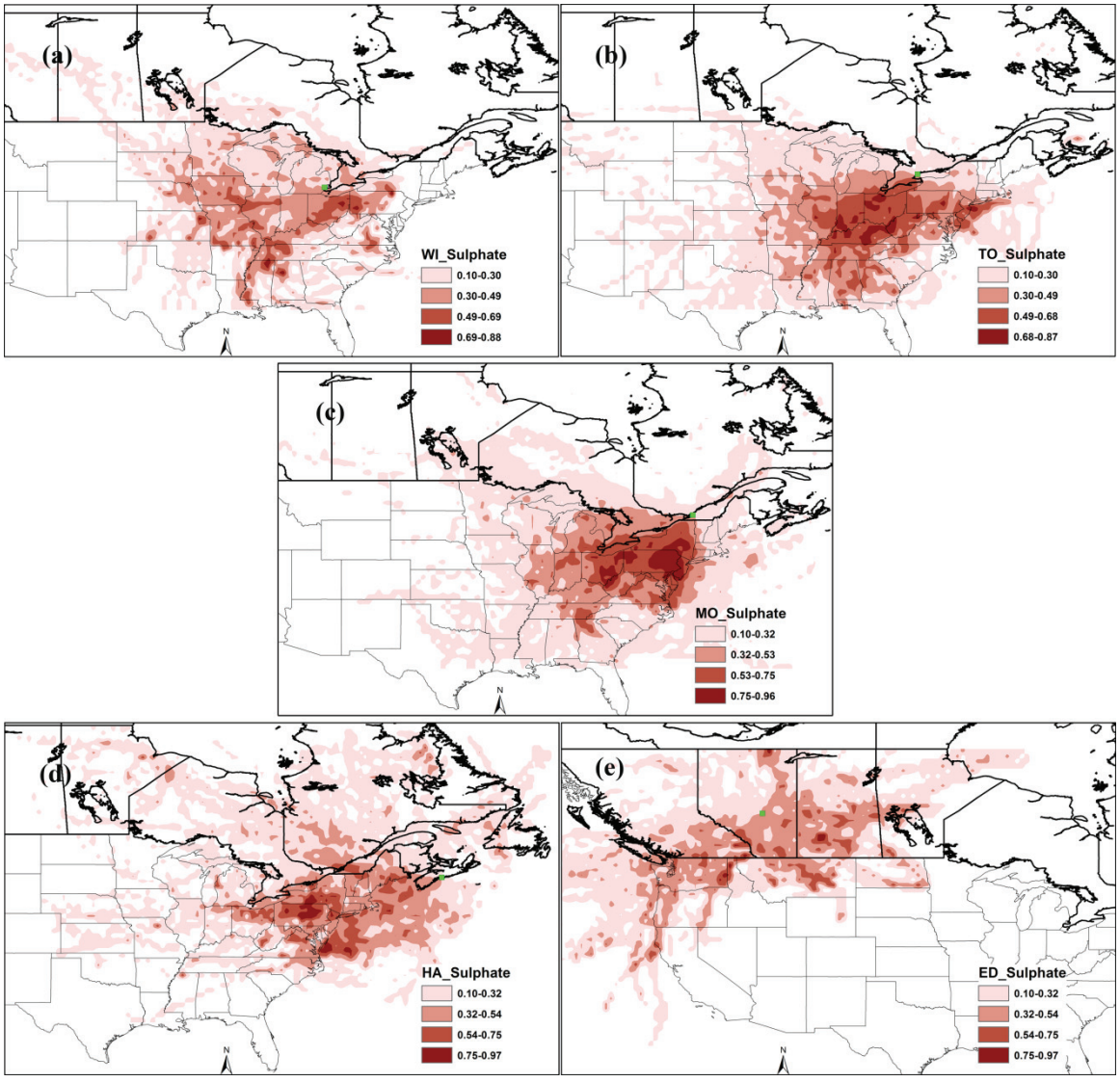


Figure 8. *PSCF plots for the highest 25% of secondary sulfate factors at the five sites.* ***(a)*** *Windsor,* ***(b)*** *Toronto,* ***(c)*** *Montreal,* ***(d)*** *Halifax,* ***(e)*** *Edmonton.*

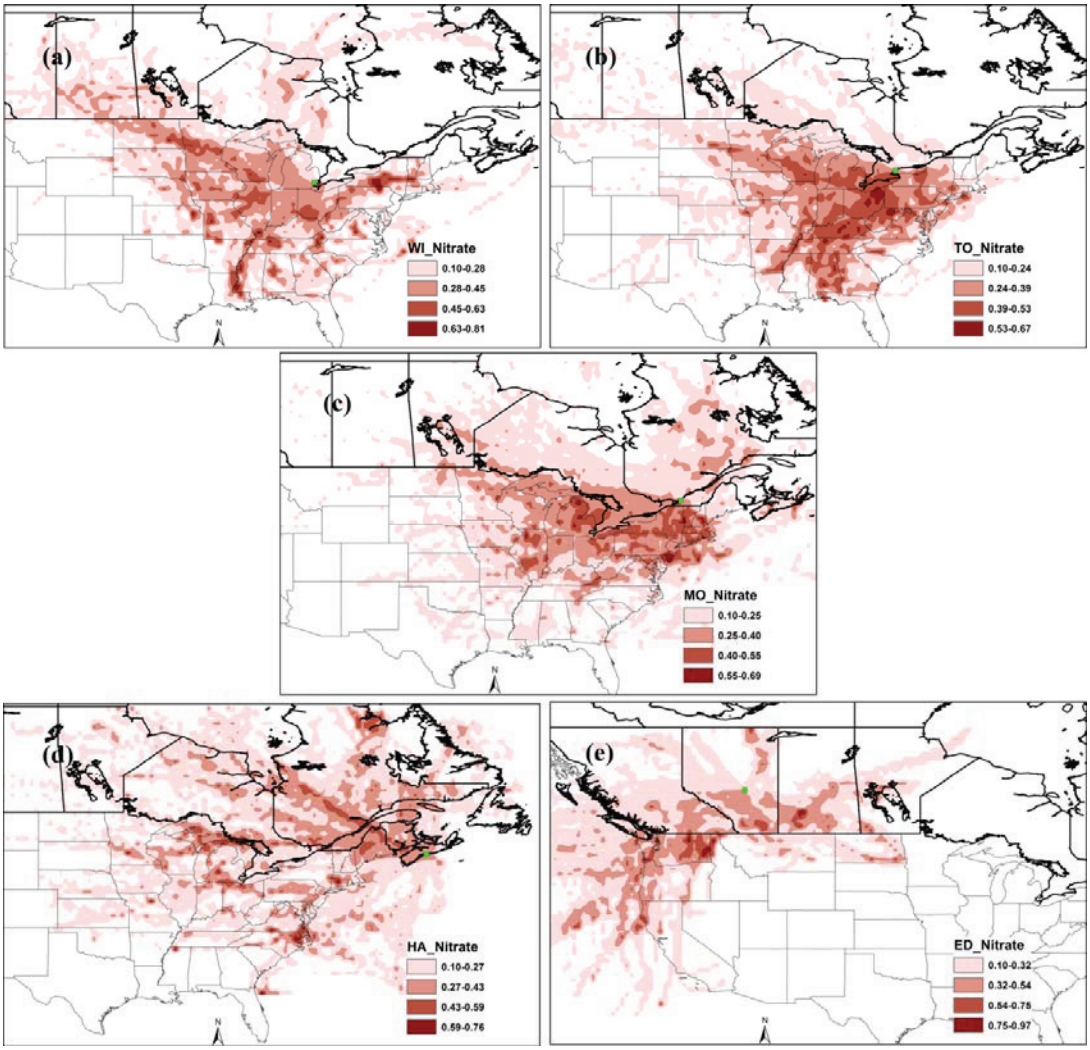


Figure 9. *PSCF plots for the highest 25% of the secondary nitrate contributions at the five sites.*
(a) *Windsor,* ***(b)*** *Toronto,* ***(c)*** *Montreal,* ***(d)*** *Halifax,* ***(e)*** *Edmonton.*

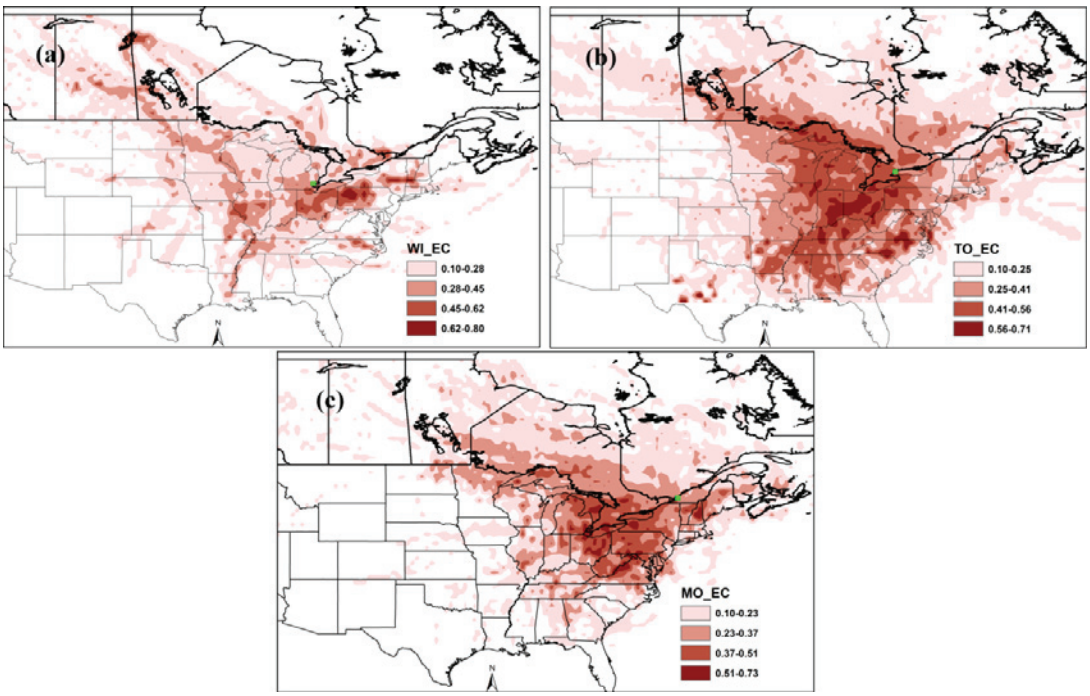


Figure 10. *PSCF plots for the highest 25% of the EC–rich contribution at* ***(a)*** *Windsor,* ***(b)*** *Toronto, and* ***(c)*** *Montreal sites.*

Soil dust. The soil dust was mainly represented by Al, K and Si. A negative correlation of the soil dust factor with RH and a positive correlation with ambient temperature were observed. Local and regional wind–blown soil dust are believed to have contributed to this crustal factor. The soil factor for Halifax was more likely affected by fugitive dust migration from building demolition or construction sites. The PSCF plot (Figure S13, see the SM) for Toronto identified parts of Ohio, southern Indiana, and northern Kentucky, mostly consistent with other PSCF studies with soil dust factors in northeastern US sites (Polissar et al., 2001; Liu et al., 2003).

Primary metallurgy. The ferrous/non–ferrous metallurgical emission factor as a local point source was identified by a mixture of several industrial species influenced by steel mills and nonferrous smelting emissions. The CPF plot for Windsor showed a strong directionality towards the southwest, consistent with the direction of steel manufacturing from the sampling site (Figure 7a). The PSCF plot for Toronto identified a strong influence from central Ontario and western Quebec, Canada (Figure S16, see the SM). The region, Rouyn–Noranda, Quebec, is the location of a large non–ferrous smelting plant. This result is comparable to a PSCF analysis of Cu/Ni smelter sources detected in New York State (Raman and Hopke, 2007). The CPF plot for Edmonton showed a contribution from the northeast, where a steel mill, the largest source of Zn in Alberta, was located (Figure 7d).

Oil combustion and refining. The oil combustion factor was dominated by the presence of Ni and V, suggesting that the source originates from residual fuel–oil combustion. The CPF plot for Windsor indicated possible sources to the northeast, the same direction as oil refining facilities in Sarnia (Figure 7a). The CPF plot for Montreal showed strong contributions from the northeast also suggesting impacts from oil refinery plants (Figure 7c). The higher contribution of this factor in fall and winter for Montreal suggested oil–based home–heating during the winter was a potential source. For Halifax, the CPF plot indicated contributions from the southwest directions, consistent with the direction of a significant source of Ni and V from the sampling site (Figure 7d, NPRI, 2006). A clear increase in the contribution during the cold months and a weekday–high pattern suggested crude oil combustion for heating was the source associated with this factor.

A separate oil refinery factor was also identified in Halifax, and was characterized by the presence of Pb, Zn, Cu, and Cr. Temporal variations of this factor were correlated with NO_2 and many VOCs (Tables S9 and S14, see the SM). The CPF plot points to the northeast and southeast regions suggesting influences of oil refinery facilities located ~1 km southeast of the monitoring site (Figure 7e).

Ship emissions. This factor was identified as a local source for Halifax, characterized by a large fraction of V, Ni, Zn, OC2, OC4 and sulfate. Ship engines commonly use low cost residual oil containing high concentrations of sulfate, Ni, and V. $PM_{2.5}$ emitted from ships mainly contains organic species with trace metals in fuel and lubricating oil, i.e., Ni, V, Zn, Pb (Hobbs et al., 2000; Isakson et al., 2001). In the source profiles of this ship emission factor the ratio of V to Ni was approximately 3.7, suggesting residual oil combustion characteristic of marine vessels (Querol et al., 2007). In addition, a statistically strong correlation was observed between SO_2 and the factor ($r = 0.65$). The CPF plot for this factor points to the southwest and the southeast sectors indicating the port areas.

Cement kiln. This industrial factor was characterized by a mixture of metal industry–related species for Edmonton. A strong weekday–high pattern and positive correlations with NO, NO_2, and CO suggested that this factor was associated with local anthropogenic sources (Table S10, see the SM). The NPRI indicated that a cement kiln, located 14 km northwest of the site, was a major source of Zn, Ni, Cu, Mn, Cr, and Pb in the area (NPRI, 2006; 2007). The CPF plot (Figure 7e) for this factor indicated the northwest and the northeast as the most influential directions.

Secondary organic aerosol. The SOA factor was identified as the third largest contributor for Edmonton with high concentrations of oxalate, formate, OP, OCs, ECs, sulfate and Fe. The presence of dicarboxylic acids with a strong summer–high trend was indicative of the production of secondary photochemical products. The high OP fraction in the SOA factor was likely secondary OC formed by photochemical oxidation of volatile organic precursors. The PSCF plot for the factor indentified high potential areas in the boreal forest regions of western and eastern Saskatchewan indicating contributions from biogenic sources (Figure S16, see the SM). In addition, the concentration of isoprene was highly correlated with this SOA factor ($r = 0.75$) supporting biogenic and secondary organic aerosol precursor emissions.

Secondary organic aerosol could be separated in Toronto and Montreal so as to isolate a factor containing most of the oxalate and formate. However, the resolution of the SOA required the inclusion of an additional factor in the PMF solution that was not clearly distinguishable from the traffic factor.

3.4. Contributions to $PM_{2.5}$ mass in each city

Windsor. Windsor was found to have the highest average $PM_{2.5}$ contributions (13.1 μg m^{-3}) as compared to the other sites included in this analysis. The secondary sulfate (37%) and nitrate (24%) factors contributed the most $PM_{2.5}$ mass, and their seasonal variability was consistent with secondary particle formation. The EC rich factor (6%), presumably a regional source from coal combustion, showed higher contributions in 2006 as compared to the other years, consistent with observations in Toronto and Montreal. The traffic factor accounted for 14% of the yearly $PM_{2.5}$ and up to 25% of the $PM_{2.5}$ in summer. The smelter factor and the oil combustion factor considered to be local point sources represented 8% and 4% of Windsor's $PM_{2.5}$ mass concentration, respectively. Less significant factors contributing to Windsor's air quality were salt (2%) and road/soil dust (5%). This salt factor was consistent with road salt used for de–icing operations in Windsor as it had high winter contributions. We may assume that the nitrate factor was fully contributed by local sources or regional sources. Based on the assumption, only 33% to 57% of the $PM_{2.5}$ mass in Windsor appeared to come from local sources.

Toronto. The sulfate (33%) and nitrate (26%) factors were the most significant sources at the downtown Toronto site. The EC–rich factor was also a major contributor (16%) to $PM_{2.5}$ mass. This factor is more likely related to regional scale sources due to the common increase in the source contributions in 2006 and 2007 and the spatial uniformity of EC2 concentrations among Toronto, Windsor, and Montreal. The traffic emissions factor was an important local source, accounting for 10% of the $PM_{2.5}$. The road dust factor accounted for 3% of the $PM_{2.5}$ mass and exhibited a strong weekend/weekday variation and seasonal variability with higher contributions in spring and summer. The road dust factor highly was correlated with traffic–related VOCs and as such can be classified as a local traffic–related source. The smelter factor (6%) was associated with emissions from northern Ontario industrial regions. The road salt (2%), soil dust (2%), and biomass burning (1%) were minor contributors to the $PM_{2.5}$ mass in Toronto. Overall, only 25% to 51% of the $PM_{2.5}$ mass in Toronto appeared to come from local sources.

Montreal. The sulfate factor was the largest contributor (34%) in Montreal. A strong winter–high seasonal pattern was observed in the contribution of the nitrate factor (14%). Similar to the EC–rich factor for Toronto and Windsor, significant contributions (14%) of this factor were identified in Montreal with a summer–high

pattern. The traffic factor and the road dust factor contributed 14% and 4% to the $PM_{2.5}$, respectively. A winter–high pattern suggests that the biomass burning factor (6%) was associated with emissions from fireplaces and woodstoves for winter heating. The oil combustion factor, influenced by local oil refinery plants, accounted for 6% of the $PM_{2.5}$ mass in Montreal. The road salt factor contributed 4% to the $PM_{2.5}$ mass. Overall, only 38% to 51% of the $PM_{2.5}$ mass in Montreal appeared to come from local sources.

Halifax. The sulfate factor was the largest fraction (37%) of the $PM_{2.5}$ mass with a typical summer–high pattern. Relatively lower contributions (9%) of the secondary nitrate were found in Halifax. In contrast to other sites, the salt factor was a dominant $PM_{2.5}$ contributor in Halifax, accounting for 18% of the $PM_{2.5}$ mass due to the influence of fresh sea salt. The traffic factor and the ship emissions accounted for 14% and 9% of the $PM_{2.5}$ mass, respectively. The oil combustion factor (5%) showed maximum values in winter, suggesting the influence of local winter heating emissions. The oil refinery factor as a local point source contributed 4% to the $PM_{2.5}$ mass concentration. The strong contribution of the crustal material factor, accounting for 4% of the $PM_{2.5}$ mass, was observed during the summer and fall of 2007 in Halifax probably due to impacts from construction sites near to the Halifax monitoring site. Overall, only 35% to 44% of the $PM_{2.5}$ mass in Halifax appeared to come from local sources.

Edmonton. A relatively low average $PM_{2.5}$ mass concentration (8 μg m^{-3}) was observed in Edmonton as compared to the levels at other major urban sites. The largest factor in Edmonton was secondary nitrate accounting for 22% of the total $PM_{2.5}$ mass. This factor consisted of both local oil refinery sources under certain meteorological conditions and regional sources. Interestingly, the maximum concentrations of the sulfate factor, the second largest source (19%), were observed in winter due to primary emissions from winter–coal combustion. Further analysis is needed to clarify the winter formation of sulfate and determine contributions from local and regional sources. The SOA factor accounted for 18% of the $PM_{2.5}$ mass with a strong summer–high pattern. Biogenic sources might be linked to contributions of this factor. The biomass burning factor (12%) was more likely related to wood burning for winter residential heating. The traffic factor and the road dust factor, as local sources, contributed 12% and 7% to the $PM_{2.5}$. The local industrial point sources identified were the steel mill source (5%) and the cement/industrial source (3%). The salt factor, accounting for 3% of the $PM_{2.5}$ mass, was linked to long range transported salt from salt mining sites and the eastern Pacific Ocean. Overall, more than half (60% – 82%) of the $PM_{2.5}$ mass in Edmonton appeared to come from local sources.

3.5. Comparison of the factors between the five cities

Figure 11 presents comparisons of the $PM_{2.5}$ source contribu–tions at the five sites. In order to base this comparison on the same measurement period, source contributions in 2006 and 2007 at the five sites were used. The contribution of the secondary sulfate factor was highest in Windsor, while the lowest contribution was found in Edmonton. The sulfate contributions at the sites also decreased with distance from the major mid–Atlantic source region, including the Ohio River Valley. This implies that these regional upwind sources make a substantial contribution to the secondary sulfate factor.

Although Montreal and Toronto are both metropolitan areas with strong local traffic emissions, the contribution of the nitrate factor was much higher in Toronto. This suggests a mixture of local and regional sources may impact the nitrate factor in Toronto. As shown previously, the PSCF plot for the nitrate factor in Toronto identified northwest Ohio as a possible source area. Secondary nitrate was the largest contributor to $PM_{2.5}$ mass in Edmonton, whereas the sulfate factor was dominant at the other sites.

Figure 11 also shows the comparison of the traffic sources resolved at the five sites. While the traffic factor contributions in Toronto and Montreal were similar, the contribution of the traffic factor at the Windsor site was higher than the levels in these two cities, possibly due to the proximity of the Windsor site to the Ambassador Bridge.

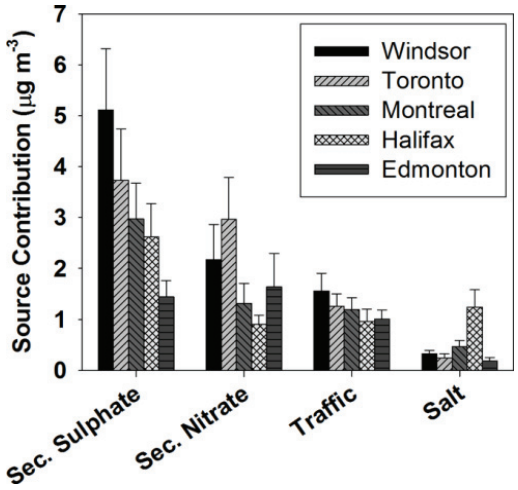


Figure 11. *Comparison of average source contributions at the five sites over the period of 2006–2007. Error bars represent 99% confidence.*

A molar Na/Cl ratio of 2 was observed in the salt factor at the Halifax site, indicating the strong influence of fresh sea salt, while the ratios at the other sites were higher: Montreal (5.3), Edmonton (5.8), Windsor (6.1), and Toronto (33.1). The high ratio in Toronto might be due to local depletion of Cl resulting from reactions of salt with NO_3^-, consistent with the high contribution of nitrate in Toronto. The temporal variations of the salt factor are also indicated a strong winter and spring–high seasonality. The salt contribution in Halifax was higher by a factor of approximately 6 than that in Edmonton.

Inter–site correlation of the time series of the contributions for the major $PM_{2.5}$ factors is presented in Table 5. Commonly observed factors were compared against the resolved factor at the Toronto site. The secondary nitrate and sulfate factors were highly correlated among three sites; Toronto, Montreal, and Windsor. The high correlations might be due to strong seasonal patterns and influences of regional source areas identified by the PSCF analysis for these long–range transported pollutants. It is worth noting that the concentrations analyzed were 24–hr averages and the synoptic weather patterns typically transport pollutants from Windsor to Montreal on this timescale. In contrast, the nitrate and sulfate factors in Halifax and Edmonton had weak correlations with the sources in Toronto, indicating impacts from local scale sources, unique meteorological conditions, and that these cities are likely not impacted by the same regional emissions. As described previously based on the PSCF analyses, the temporal trends of the EC–rich factors in Toronto and Montreal as well as Windsor showed good correlation (p = 0.005), supporting the presence of regional scale sources for the high EC peaks. Indeed, as a trans–boundary pollutant, this EC–rich factor was strongly associated with photo–chemical reactions. Further work has been undertaken to investigate which emission sources are responsible for the increase in the EC–rich factor.

4. Conclusions

Aerosol chemical composition data for $PM_{2.5}$ collected in Toronto, Montreal, Windsor, Halifax, and Edmonton were analyzed using PMF to identify major sources and estimate their contributions to the $PM_{2.5}$ mass. CPF and PSCF analyses identified possible local and regional source locations.

Table 5. *Inter–site correlation coefficients between $PM_{2.5}$ sources*

	n	Secondary Sulfate	Secondary Nitrate	EC–Rich
Toronto–Windsor	64	0.63	0.80	0.38
Toronto–Montreal	73	0.63	0.69	0.54
Toronto–Halifax	73	0.33	0.21	n/a
Toronto–Edmonton	97	–0.13	0.27	n/a

n/a: not available

Secondary sulfate was the major factor contributing to the $PM_{2.5}$ mass, except for Edmonton, where secondary nitrate was the dominant factor. Secondary sulfate plus nitrate factors provided the highest contributions to the $PM_{2.5}$ mass in Windsor (61%), Toronto (60%), Montreal (47%), Halifax (47%), and Edmonton (41%). The PSCF analysis indicated contributions of the large Ohio industrial regions from Illinois to New York, USA, were the main source areas for secondary sulfate in Windsor, Toronto, Montreal, and Halifax.

An elemental carbon (EC)–rich factor was identified in Windsor, Toronto, and Montreal, characterized by distinct EC and organic carbon (OC) profiles and associated with photochemical processing. The EC–rich factor accounted for a significant percentage of the total $PM_{2.5}$ mass in summer (18% in Toronto, 19% in Montreal) and also appeared to be related to trans-boundary pollutants.

Local sources also such as vehicular emissions, road/sea salt, crustal materials, biomass burning and industrial emissions were also commonly identified in the five cities. The combined contributions of traffic and road dust ranged from 14% to 19%, with a further portion of the nitrate factor also coming from vehicles. The Halifax site showed a strong salt factor contribution among the five sites, while biomass burning emissions strongly impacted the Edmonton site. In Halifax and Montreal oil–burning related factors were identified while smelter related factors were found in Windsor, Toronto and Edmonton. In Edmonton many VOCs were strongly correlated with the nitrate, sulfate, and biomass burning factors, indicating the importance of local contributions.

Both local and regional sources were found to contribute at all sites. Thus, $PM_{2.5}$ can be reduced at all the sites through local controls, particularly Edmonton. However, given the significant contribution of trans–boundary contributions to the $PM_{2.5}$ mass in Windsor, Toronto and Montreal, a substantial reduction of $PM_{2.5}$ in these cities will also require agreements to limit the impact of trans–boundary pollutants.

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Supporting Material Available

Descriptive statistics of $PM_{2.5}$ chemical composition data modeled by PMF in Windsor (Table S1), Descriptive statistics of $PM_{2.5}$ chemical composition data modeled by PMF in Toronto (Table S2), Descriptive statistics of $PM_{2.5}$ chemical composition data modeled by PMF in Montreal (Table S3), Descriptive statistics of $PM_{2.5}$ chemical composition data modeled by PMF in Halifax (Table S4), Descriptive statistics of $PM_{2.5}$ chemical composition data modeled by PMF in Edmonton (Table S5), Correlation coefficients (Pearson r) for PMF–resolved sources at Windsor site (Table S6), Correlation coefficients (Pearson r) for PMF–resolved sources at Toronto site (Table S7), Correlation coefficients (Pearson r) for PMF–resolved sources at Montreal site (Table S8), Correlation coefficients (Pearson r) for PMF–resolved sources at Halifax site (Table S9), Correlation coefficients (Pearson r) for PMF–resolved sources at Edmonton site (Table S10), Correlation analysis between PMF–resolved sources and VOCs in Windsor (Table S11), Correlation analysis between PMF–resolved sources and VOCs in Toronto (Table S12), Correlation analysis between PMF–resolved sources and VOCs in Montreal (Table S13), Correlation analysis between PMF–resolved sources and VOCs in Halifax (Table S14), Source profiles of the eight factors in Windsor (Figure S1), Source contributions of the eight factors in Windsor (Figure S2), Source profiles of the nine factors in Toronto (Figure S3), Source contributions of the nine factors in Toronto (Figure S4), Source profiles of the nine factors in Montreal (Figure S5), Source contributions of the nine factors in Montreal (Figure S6), Source profiles of the eight factors in Halifax (Figure S7), Source contributions of the eight factors in Halifax (Figure S8), Source profiles of the nine factors in Edmonton (Figure S9), Source contributions of the nine factors in Edmonton (Figure S10), Comparison of the traffic sources at the five sites between weekends and weekdays (Figure S11), Comparison of the road dust factors between weekends and weekdays (Figure S12), PSCF plots for the highest 25% of the salt and the soil dust factor in Toronto (Figure S13), PSCF plots for the salt and the soil dust factor in Montreal (Figure S14), PSCF plots for the salt and the soil dust factor in Edmonton (Figure S15), PSCF plots for the highest 25% for other factor (Figure S16). This information is available free of charge via the Internet at http://www.atmospolres.com.

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