

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/9005594>

Identification of the Major Sources Contributing to PM_{2.5} Observed in Toronto

ARTICLE *in* ENVIRONMENTAL SCIENCE AND TECHNOLOGY · DECEMBER 2003

Impact Factor: 5.33 · DOI: 10.1021/es026473i · Source: PubMed

CITATIONS

117

READS

100

4 AUTHORS, INCLUDING:



Patrick K H Lee

Environment Canada

12 PUBLICATIONS 213 CITATIONS

SEE PROFILE



Ewa Dabek

Analysis and Air Quality, Air Quality Research...

101 PUBLICATIONS 2,015 CITATIONS

SEE PROFILE

Identification of the Major Sources Contributing to PM_{2.5} Observed in Toronto

PATRICK K. H. LEE,[†]
JEFFREY R. BROOK,^{*,‡}
EWA DABEK-ZLOTORZYSKA,[§] AND
SCOTT A. MABURY[†]

*Department of Chemistry, University of Toronto,
80 St. George Street, Toronto, Ontario, M5S 3H6, Canada,
Air Quality Research Branch, Meteorological Service of
Canada, Environment Canada, 4905 Dufferin Street, Toronto,
Ontario, M3H 5T4, Canada, and Environmental Technology
Centre, Environmental Protection Service, Environment
Canada, 335 River Road, Ottawa, Ontario, K1A 0H3, Canada*

The chemical composition of Toronto PM_{2.5} was measured daily from Feb 2000 to Feb 2001, and source apportionment was undertaken using positive matrix factorization (PMF). In Toronto, PM_{2.5} levels were influenced both by local urban activities and also by regional-scale transport. Although several PMF solutions were possible, an eight-source model for explaining the observed Toronto PM_{2.5} was found to provide realistic results and interesting insights into sources. The four main sources were coal combustion related to regional transport and secondary sulfate (26%), secondary nitrate related to both local and upwind sources of NO_x and NH₃ (36%), secondary organic aerosols (SOA) formed from a variety of precursor organic emissions (15%), and motor vehicle traffic (10%). The other detectable sources were road salt (winter) and three types of primary PM_{2.5} hypothesized to be associated with smelters, coal and oil combustion, industry, and local construction. Overall, motor vehicle-related emissions (including road salt and nitrate) were estimated to be responsible for about 40% of the PM_{2.5}. In the summer, the SOA mass was estimated to contribute ~20% to the PM_{2.5}. Inclusion of water-soluble, low-molecular-weight organic acids led to identification of this component, thus providing a significant improvement in PMF's ability to resolve sources. Without organic acid measurements the SOA portion of the observed PM_{2.5} was assigned to the secondary coal component, increasing its contribution and resulting in a source profile with an unrealistic amount of organic mass. This suggests that in the northeastern part of North America, there are physical and/or chemical processes that lead to close interaction between secondary organic and inorganic aerosols.

1. Introduction

Ambient fine particles, or PM_{2.5}, are believed to represent a significant health concern (1–3). This has led to new air

quality standards in Canada and the United States. Fine particles reduce visibility, directly and indirectly affect the Earth's radiative balance, and influence the fate of hazardous pollutants in the environment. Therefore, it is important to understand the physical and chemical processes influencing the concentrations of particles in the atmosphere, including the role of human activities, and to determine their origin. A fine particle speciation measurement site was established in downtown Toronto, Ontario, Canada, in Feb 2000, to provide the data necessary to better understand these processes in an urban setting, to support future health studies, and for source-receptor analyses.

Receptor models can provide quantitative information on the source contributions to observed ambient PM_{2.5}. A range of methodologies based upon abstract factor analysis (AFA) have been studied extensively, including the classic chemical mass balance (CMB) and principal component (PCA) analyses (4). CMB requires a priori knowledge of the specific sources influencing the observations and the chemical characteristics of the particle emitted from these sources, which in practice is difficult to ascertain. PCA may suffer from the presence of negative regression coefficients, and it is also difficult to obtain unbiased quantitative source contributions. In this investigation, we applied another algorithm of AFA known as Positive Matrix Factorization (PMF).

Application of the PMF model in air quality studies has become increasingly popular for source apportionment of PM (5–7). There have been a number of recently published studies focusing on PM_{2.5} source apportionment in eastern North America (8). This recent work has utilized twice per week measurements collected for the IMPROVE program (9). Rural measurements of trace metals and a limited number of inorganic ions were available. Total organic carbon (OC) and elemental or "black" carbon (EC) were either measured or inferred. Polissar et al. (10) examined the 1988–1995 measurements from northern Vermont and reported that 11 sources contributed the PM_{2.5}. Similarly, Lee et al. (11) identified nine factors contributing to the mid-Atlantic regional aerosol from 1991 to 1999. In both studies, coal combustion was identified as the major contributor to the observed PM_{2.5}.

In this paper, we present results from a PMF analysis using 1 complete year of daily 24 h PM_{2.5} measurements from an urban location, Toronto, Ontario, starting in Feb 2000. This data set includes PM_{2.5} speciation for a larger suite of compounds and elements than has been used previously: 15 trace metals, 7 inorganic ions, 5 water-soluble organic acids, and EC and OC separated into four fractions. Eight clearly identifiable source types contributing to PM_{2.5} in downtown Toronto were found.

2. Experimental and Methodology Section

2.1. Sampling Methods. Samples were collected for daily 24-h periods from Feb 14, 2000 to Feb 14, 2001. The measurement site was located on the roof of the Gage building (223 College Street, ~17 m above ground, 43.66N, 79.39W) 1.5 km west of the center of downtown Toronto. Filters (47 mm Gelman Teflo, 2 μm pore size) for gravimetric determination of PM_{2.5} and for measurement of heavy metals were collected using a low volume air sampler (Partisol-FRM 2000, R&P Co., NY) operating at 16.7 L/min flow rate. Another low volume sampler, the Versatile Air Pollution Sampler – VAPS (12), with the two PM_{2.5} channels each having flow rates of 15.0 L/min, was used to collect samples for determination of organic and elemental carbon (OC and EC) and water-

* Corresponding author phone: (416)739-4916; fax: (416)739-5708; e-mail: jeff.brook@ec.gc.ca. Corresponding author address: MSC of Environment Canada, 4905 Dufferin St., Toronto, ON, M3H 5T4, Canada.

[†] University of Toronto.

[‡] Meteorological Service of Canada, Environment Canada.

[§] Environmental Protection Service, Environment Canada.

soluble ions. These samples were collected on 47 mm quartz (prefired at 850 °C for 2 h) and Teflon filters (Gelman Teflo, 2 µm pore size), respectively. The Teflon filter in the VAPS was preceded by sodium carbonate and citric acid denuders and followed by a nylon filter, which enabled more accurate measurement of fine particle nitrate and ammonium.

A weekly field blank filter, which was exposed to the environment for the length of time typically required to assemble the VAPS and perform leak tests, was collected throughout the study. Other than this simulated loading and unloading of the VAPS, the blanks were handled identical to the samples. All filters were stored at 4 °C prior to chemical analysis except for the time (≤7 days) the filter packs remained at the monitoring site before shipment to laboratory. During this time, the filter packs were stored at room temperature and sealed in plastic bags.

2.2. Analytical Methodology. After gravimetric analysis, the Teflon filter used for determination of PM_{2.5} mass was used for trace metal analysis. Heavy metals were digested in 40% HNO₃ using a closed microwave digester (Perkin-Elmer Multiwave). The solutions were then analyzed by inductively coupled plasma (ICP) – atomic emission spectroscopy (Perkin-Elmer Optima 3000DV, AS90) for Al, Ca, Cu, Fe, Mg, Mn, and Zn. A separate aliquot was analyzed by ICP – mass spectroscopy for As, Ba, Cd, Cr, Ni, Pb, Se, and V since they were below detection limit too often using ICP-AES. An intensive quality control program was implemented to maintain the accuracy and precision throughout this project. This included periodically using standard reference materials of urban particulate matter (SRM 1648, NIST Gaithersburg, MD 20899), field-blank filters, digesting acid-blanks, standard reference solutions, and standard addition. The results for SRM and standard reference solutions were within ±10%, and all blank samples were close to or below the detection limits.

Teflon filters in the annular denuder portion of the VAPS were extracted in water and analyzed for water-soluble ions of K⁺, Na⁺, Cl⁻, PO₄³⁻, NH₄⁺, SO₄²⁻, NO₃⁻, and oxalate (OA) by ion chromatography (IC – Dionex DX-300). Water-soluble formate (FA), malic acid (ML), malonate (MA), and succinate (SA) were analyzed by capillary electrophoresis (CE – Beckman P/ACE System 2100) (13). The nylon filter was extracted in carbonate/bicarbonate and analyzed by IC for determination of nitrate.

A punch (1.45 cm²) from the quartz filter was analyzed by thermal optical transmission (TOT – Sunset Laboratory, Inc., Forest Grove, OR) to determine the OC and EC concentrations. The temperature program used was a combination of the NIOSH 5040 (14) and TOR (15) approaches. The filter piece was heated in pure He stepwise to 250 °C for 150 s (OC1), 450 °C for 150 s (OC2), 550 °C for 180 s (OC3), and 900 °C for 90 s (OC4) and cooled to 550 °C for 50 s. Then 2% O₂ was added to the He, and the filter was combusted at 550, 700, and 800 °C for 240, 210, and 150 s, respectively. The laser transmittance signal was used to separate the carbon evolving in these final combustion steps into EC and pyrolyzed carbon (PC). The PC was added back to the four OC fractions: 11.5%, 33.6%, 24.6%, and 30.3% to OC1, 2, 3, and 4, respectively. These percentages were determined by examining the typical amount (300 samples) of charring that takes place during each temperature step, as indicated by the reduction in laser transmittance. The final result is five reported numbers for total carbon, OC1-4 and EC.

2.3. Experimental Result and Data Handling. Summary statistics for the 32 chemical species available for PMF receptor modeling study are given in Table 1. For nitrate, the Teflon and nylon filter results were added to correct for the negative artifact during sampling. The only measurements requiring blank correction were OC1-4. The blanks for all other species were small compared to the samples, and thus

TABLE 1. Summary Statistics of the Chemical Composition and Overall Mass for the Downtown Toronto PM_{2.5} Samples Collected from Feb 14, 2000 to Feb 14, 2001

species ^a	concentration (ng/m ³)			detection limit (ng/m ³)	missing + BDL ^b (%)
	median	min.	max.		
PM2.5	12700	1040	42200	590	2.7
Al	35	5.3	3000	2.1	2.5
Ca	83	14	570	8.5	15
Cu	2.5	BDL	27	0.9	13
Fe	55	4.8	450	0.9	2.5
Mg	14	2.1	123	1.3	2.5
Mn	3.8	BDL	30	0.9	7.4
Zn	16	BDL	228	2.1	4.9
As	0.4	BDL	6.0	0.042	13
Ba	3.0	0.73	127	0.004	3.8
Cd	0.3	0.03	50	0.004	3.8
Cr	1.2	BDL	189	0.021	4.7
Ni	0.8	0.09	38	0.021	3.8
Pb	3.4	0.33	36	0.002	3.8
Se	1.0	BDL	9.3	0.2	24
V	0.5	BDL	3.5	0.021	6.3
K	73	BDL	1840	2.4	1.6
Na	51	BDL	390	3.4	1.9
Cl	29	BDL	590	2.9	1.4
PO ₄ ³⁻	16	BDL	171	3.8	30
NH ₄ ⁺	1190	BDL	7550	2.9	1.4
SO ₄ ²⁻	2270	19	21500	2.9	1.1
NO ₃ ⁻	1840	37	18000	2.9	1.1
FA	9.4	BDL	98	1.4	3.3
ML	10	BDL	138	1.4	23
MA	14	BDL	116	1.0	7.4
OA	90	BDL	670	1.0	4.1
SA	6.7	BDL	60	1.4	23
OC1	1260	201	3510	137	1.1
OC2	880	BDL	2560	137	1.1
OC3	610	BDL	4180	137	1.1
OC4	910	192	2480	137	1.1
EC	460	BDL	1710	137	1.6

^a OC1-4: organic carbon, EC: elemental carbon, FA: formate, ML: malic acid, MA: malonate, OA: oxalate, SA: succinate. ^b BDL: below detection limit.

blank correction was not necessary. For the PMF analysis all missing values were replaced by the median value, and below detection limit (BDL) results were replaced with half the analytical detection limit. Less than 5% of the samples (*N* = 367) were BDL or missing for most of the species. Phosphate, Se, ML, and SA had the greatest frequency of BDL but were available for at least 70% of the days.

2.4. Receptor Modeling – Positive Matrix Factorization (PMF). The fundamental principle of receptor modeling is to identify the source to receptor relationship by mass balance and conservation. Multivariate receptor models are based on the analysis of the correlation between measured concentrations and source emission of chemical species. The assumption is that highly correlated compounds come from the same source and the chemical characteristics of the sources are constant throughout the measurement period. The PMF proposed by Paatero and Tapper (16, 17) is an advanced receptor modeling technique that apportions the measured aerosol concentrations to their sources. The model utilizes nonnegative factor elements and is a weighted least-squares fit. Each individual measurement is weighted by the standard deviation of its error. Any matrix **X** can be factorized into two matrices as

$$\mathbf{X}_{ij} = \sum_{p=1}^n \mathbf{G}_{ip} \cdot \mathbf{F}_{pj} + \mathbf{E}_{ij} \quad (1)$$

where **X** is the measured matrix, **G** and **F** is the calculated factor matrix, and **E** is the residual matrix for the unexplained

part of **X**. Thus, **GF** represents almost all the primary variation of **X** and leaves **E** as secondary noise.

The objective of PMF is to minimize the sum of squares, Q

$$Q = \sum_{i=1}^r \sum_{j=1}^c \left[\frac{e_{ij}}{s_{ij}} \right]^2 \quad \text{where } e_{ij} = x_{ij} - \sum_{p=1}^n g_{ip} \cdot f_{pj} \quad (2)$$

where e_{ij} , x_{ij} , g_{ip} , and f_{pj} are the elements of **E**, **X**, **G**, and **F** matrix, respectively. s_{ij} is the standard deviation of x_{ij} and n is the number of factors. Equation 2 is solved iteratively, proceeding until the difference in the Q value from one iteration to the next is less than 0.003. This process is repeated more than once using different initial values for g_{ip} and f_{pj} in order to obtain the optimum solution. Minimization of the sum of squares on residual error, weighted inversely with the standard deviation, allows flexibility in treating outliers, missing and BDL data. Standard deviations for each data point, x_{ij} , are recomputed at each iteration step according to the following formula

$$s_{ij} = c_1 + c_2 \max(|x_{ij}|, |g_{ip} f_{pj}|) \quad (3)$$

where c_1 is the measured detection limit of the data, and c_2 is 0.1 times the maximum of the measured or fitted data. The second term on the right-hand side is to ensure larger errors apply to the larger values, preventing the high concentration data or outliers from unduly influencing the factor solution. This recalculation of the standard deviation at each iteration helps prevent errors from getting too small, which could lead to erroneous results. We also increase the c_1 value for the missing and BDL data so that they have a negligible effect on the model results. To ensure that BDL or missing measurements did not significantly influence our PMF results, a factor of 100 times the standard deviation (i.e., c_1 times 100) was applied to their weights.

To view the importance of each analyte between the sources, each column of the **F** matrix is normalized to yield the explained variation (EV), which quantifies the contribution each analyte makes to the variation in a given source identified by the PMF analysis (17, 18). The value of EV ranges from zero, indicating no explanation, to 1, which indicates that the analyte explains all the variation in the source profile. The weakness in EV is that a good estimate of s_{ij} is required. The EV profile provides an initial identification of the sources pending careful examination of the results (e.g., comparison with known source profiles, trajectory analysis, etc.) to determine if they are reasonable based upon initial knowledge of the potential sources influencing the measurements site.

2.5. Determination of the Number of Sources. In most AFA approaches, including PMF, deducing the number of sources contributing to urban $\text{PM}_{2.5}$ is not straightforward. In applying these approaches more than one valid solution can usually be obtained, and no definitive, objective/statistical output is derived indicating which of these solutions (i.e., number of components or sources the original data can be reduced to) best represents reality. Furthermore, any such objective output regarding an optimum solution must be interpreted in light of uncertainties in the measurement data and variations in environmental conditions, such as meteorology and chemical processing in the atmosphere and variations in actual emission characteristics. Therefore, determining the number of sources that explain the observed $\text{PM}_{2.5}$ inherently involves subjectivity and requires experience with respect to application and interpretation of the AFA and the characteristics of the airshed of interest (e.g., general knowledge or inventory-based information of the types of local and regional sources expected to contribute to $\text{PM}_{2.5}$).

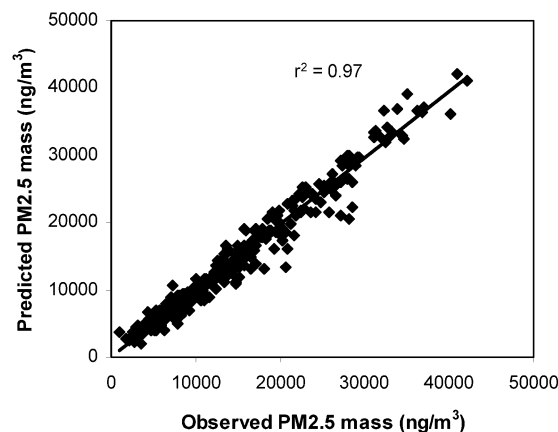


FIGURE 1. Correlation between predicted and observed mass by multiple linear regression. (eight-source PMF model for Toronto, Ontario from Feb 2000 to Feb 2001.)

In this study, we carried out a detailed examination of the features of PMF solutions (robust mode) for models with from 6 to 11 sources. We also varied the rotation strength (FPEAK values from -1 to $+0.9$) and generally considered model fit and interpretability of the results in selecting a final solution to report. Limiting our detailed analysis to 6–11 source solutions was based upon an initial assessment of what we expected to be a reasonable and interpretable number and consideration of previously reported PMF results (e.g., refs 8, 10, 11, and 19). In addition, quantitative information derived from the residual matrix **E** (20, 21) and the AFA eigenvalues, which are known to produce good results in the analysis of chemistry data sets (22–24), was used as initial guidance. These approaches are described in Malinowski (23–26) and Lee (27). This information suggested that a model with eight factors might be optimal for explaining the Toronto observations, although there was also evidence indicating 11 factors or sources could be reasonable. After examining 6–11 source solutions, as indicated above, we selected an eight-source model with no rotation (FPEAK = 0) since most of the major features were similar among the different solutions considered. The main differences were related to the number and characteristics of the minor sources (i.e., those responsible for considerably less than 10% of the $\text{PM}_{2.5}$).

3. Results and Discussion

The sum of the mass concentrations of all the species in Table 1 (excluding FA, ML, MA, OA, and SA, but multiplying OC by 1.4) was, on average, $3 \pm 2\%$ higher than the observed total mass concentration (i.e. $\text{PM}_{2.5}$). This supports the hypothesis that the selected 32 species are enough to constitute total mass. Multiple factors would have contributed to this overestimation, but the largest effect was likely due to a positive artifact in the OC measurement (28). The OC values were blank-corrected but not corrected for this potential artifact. We estimate this high bias in OC to be $1\text{--}2 \mu\text{g m}^{-3}$ based upon a limited number of parallel Teflon-quartz filter samples and OC measurements from the final stage of parallel MOUDI measurements.

Given that the measurements adequately explained the observed mass, the eight-source contribution profile (**G** matrix) predicted by PMF was applied to the multiple linear regression (MLR) against the observed $\text{PM}_{2.5}$ (29, 30). The resulting predicted mass from the PMF-MLR correlated well with the observed mass ($r^2 = 0.97$, slope = 0.99), as shown in Figure 1. This agreement indicates that it is appropriate to determine the percent contribution of each source to the total mass for the full data set and separately for the summer

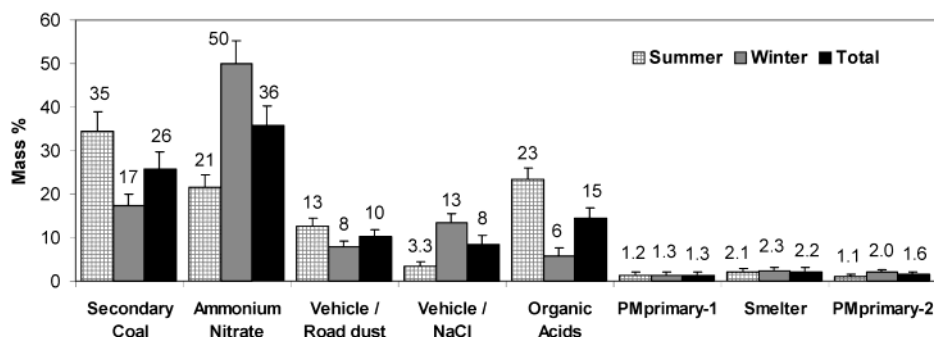


FIGURE 2. Percent contribution, by source, to the $PM_{2.5}$ observed in Toronto, as determined using PMF-MLR (summer corresponds to May–Oct and winter is Nov–April).

(May–Oct) and winter (Nov–Apr) time periods. These results are shown in Figure 2.

Figure 3 displays the EV and mass concentration associated with each chemical species for each of the eight sources (derived from the **F** matrix). These results provide the rationale for the names assigned to the sources in Figure 2. EV provides a relative indication of how much of the temporal variation of the chemical species measured can be explained by a given source. This is useful for identifying the likely origin of a source. For example the source labeled NaCl in Figure 3 has large EV values for Na and Cl, which are markers for sea salt or, more likely, road salt. The mass concentration provides information on how much of the chemical species is associated with a given source. Due to large differences in the magnitude of the concentrations among the chemical species, mass concentrations in Figure 3 are plotted on a log scale.

3.1. Description of the Sources. The first source in Figure 3 has large EV values for SO_4^{2-} , NH_4^+ , Se, and PO_4^{3-} . This is likely associated with SO_2 emissions from coal-fired power plants forming secondary sulfate and reacting with NH_3 from a variety of sources (e.g., agriculture) during regional-scale transport to Toronto. Thus, much of the mass associated with this apparent source (“secondary coal”) results from oxidation of SO_2 in the atmosphere as opposed to primary emissions. Se provides the best indication that the SO_2 and subsequent sulfate were associated with coal combustion (31). Phosphate is also known to be emitted during coal combustion (32). There are two power plants in the vicinity of Toronto. Lakeview generating station is about 20 km west of the measurement site, and Nanticoke is ~110 km to the southwest on the shore of Lake Erie. Nanticoke is the largest emitting power plant in Canada (33). Further upwind, there are also many coal-fired power plants located in the U.S. Midwest and southeast.

Figure 4(a) is a plot of the 3-day back trajectories for days with a large contribution from the secondary coal source as predicted by PMF. The majority of trajectories associated with this source exhibited a similar tendency in terms of transport direction, and thus, for the purpose of clarity, only the top 6 days are shown. Consistent with the locations of the known SO_2 sources, these trajectories originated south of Toronto. There also appears to be a tendency for the flow, particularly for the high events shown, to move across the Nanticoke area suggesting that, in addition to the U.S. power plants, this Ontario source may have contributed to the sulfate observed in Toronto. Figure 2 shows that the percent contribution to $PM_{2.5}$ from the secondary coal source is estimated to be two times larger in the summer compared to the winter. This is due to greater photochemical activity in the summer, which increases the formation of sulfate, and partially due to meteorological conditions (e.g., more transport from the south in summer). Separate summer and winter PMF analyses (not shown) revealed that the ratio of

sulfate to Se (a primary emission product of coal combustion) was about 6 times higher in the summer compared to the winter. Thus, while in each of these analyses a sulfate-rich source with high Se EV values was identified, much more sulfate was produced between the source areas and Toronto during the summer.

Separation of OC into four fractions was intended to provide some additional power in separating different sources. For example, Watson et al. (34) showed that there is relatively more high-temperature OC (i.e., OC3 or OC4) in diesel emissions compared to gasoline vehicle emissions. Although, our analysis was not successful in separating these two sources, differences in the mass concentration and EV for OC1-4 were observed among the source profiles. The secondary coal source has an OC4 with a noticeably higher mass concentration and EV than OC1-3. None of the other sources exhibited this pattern suggesting something unique about the OC associated with coal combustion. The cause of this tendency toward OC4 requires further research. It may reflect a chemical aging process since the carbon associated with the secondary coal source would have traveled farther than locally emitted OC (e.g., from vehicles). It could also reflect the result of interactions between inorganic acids and organic carbon on the particles or indicate that the OC on particles generated from coal combustion is more tightly bound to the particles (i.e., not simply on the surface).

To gain more insight into the value of resolving the OC into four temperature fractions, the PMF analysis was repeated with total OC (i.e., using OC and EC instead of OC1-4 and EC). The results (not shown) were generally the same indicating that the percent contributions and source profiles shown in Figures 2 and 3 were not sensitive to the additional resolution of the OC. However, as mentioned above, there are differences among sources in the distribution for OC1-4 shown in Figure 3. This provides some unique insight, which can be followed-up by future, more detailed analysis.

The second source in Figure 3 is dominated by NO_3^- and NH_4^+ . Clearly, this is associated with ammonium nitrate aerosol originating from the oxidation products of NO_x and subsequent reaction with NH_3 . The main sources of NO_x in the region are motor vehicles (~60% of NO_x in Toronto is from vehicles) and power plants, which are predominantly outside of the local area. A plot of the 3-day back trajectories on the 6 highest loading days in Figure 4(b) shows that the origin was from the west. These trajectories crossed over the agricultural areas of southern Ontario and into similar regions in the United States. This indicates that NH_3 availability played a significant role in the particle nitrate episodes and that NH_3 emissions within the city (e.g., three-way catalytic converters (35)) were not, by themselves, responsible for ammonium nitrate episodes. There are also significant NO_x sources, point sources and major cities, west of Toronto. Presumably, this NO_x would have more time to oxidize and

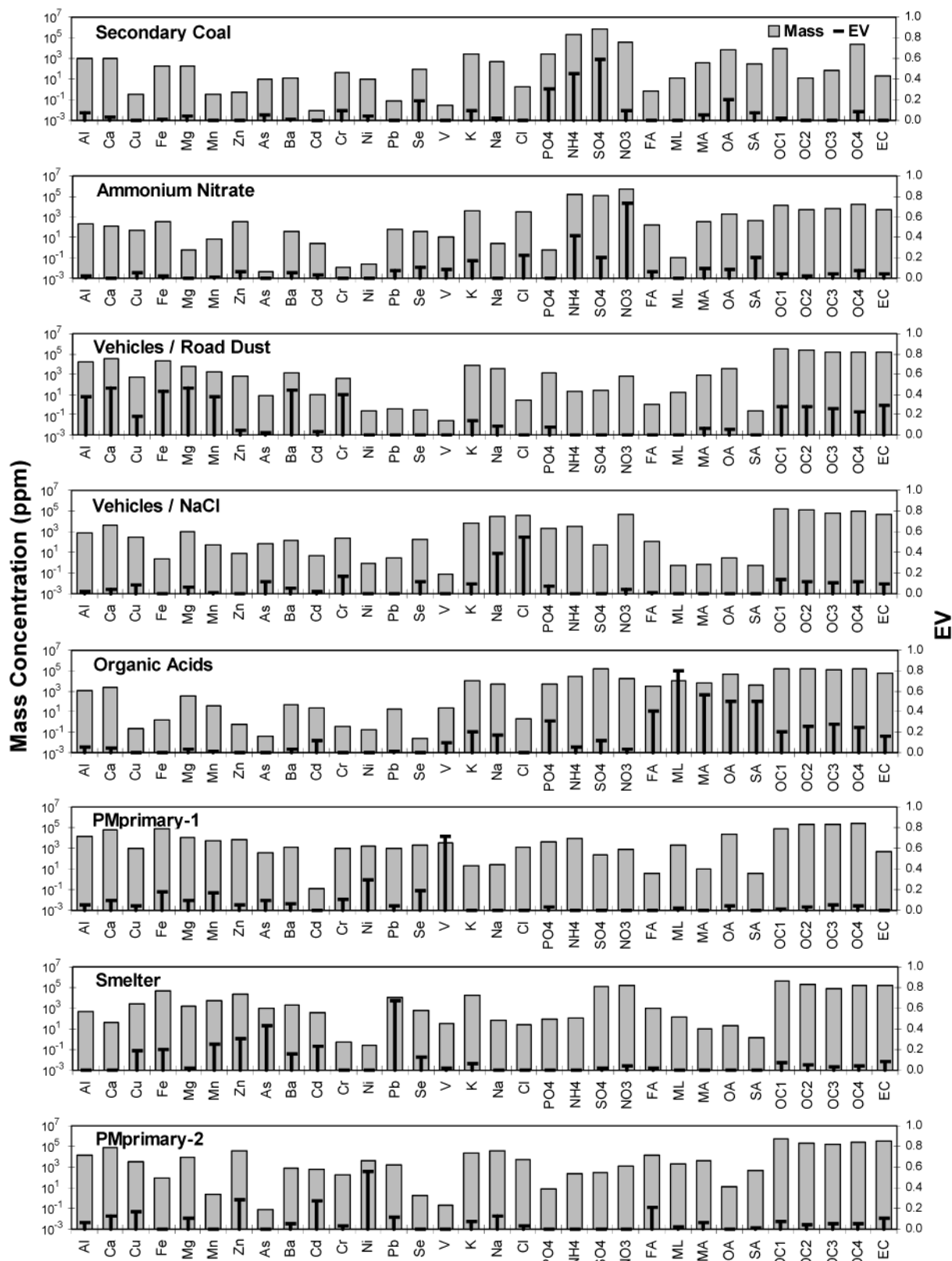


FIGURE 3. Toronto source profiles plotted as mass concentration and EV versus chemical species or carbon fraction.

then react with NH_3 compared to the local traffic-related NO_x . It is interesting to note that the transport path for the high loading days was westward, away from the sources of sulfate, suggesting that, in addition to NH_3 availability, particle nitrate is more significant when there is less competition with acidic sulfate for NH_3 .

Figure 2 shows that the contribution from the secondary ammonium nitrate component was twice as large in the winter (50.1%) compared to the summer (21.5%). The source contribution plot (not shown) also indicated that the magnitude and percent contribution of this source was greatest from Feb to April 2000 and from November to Feb

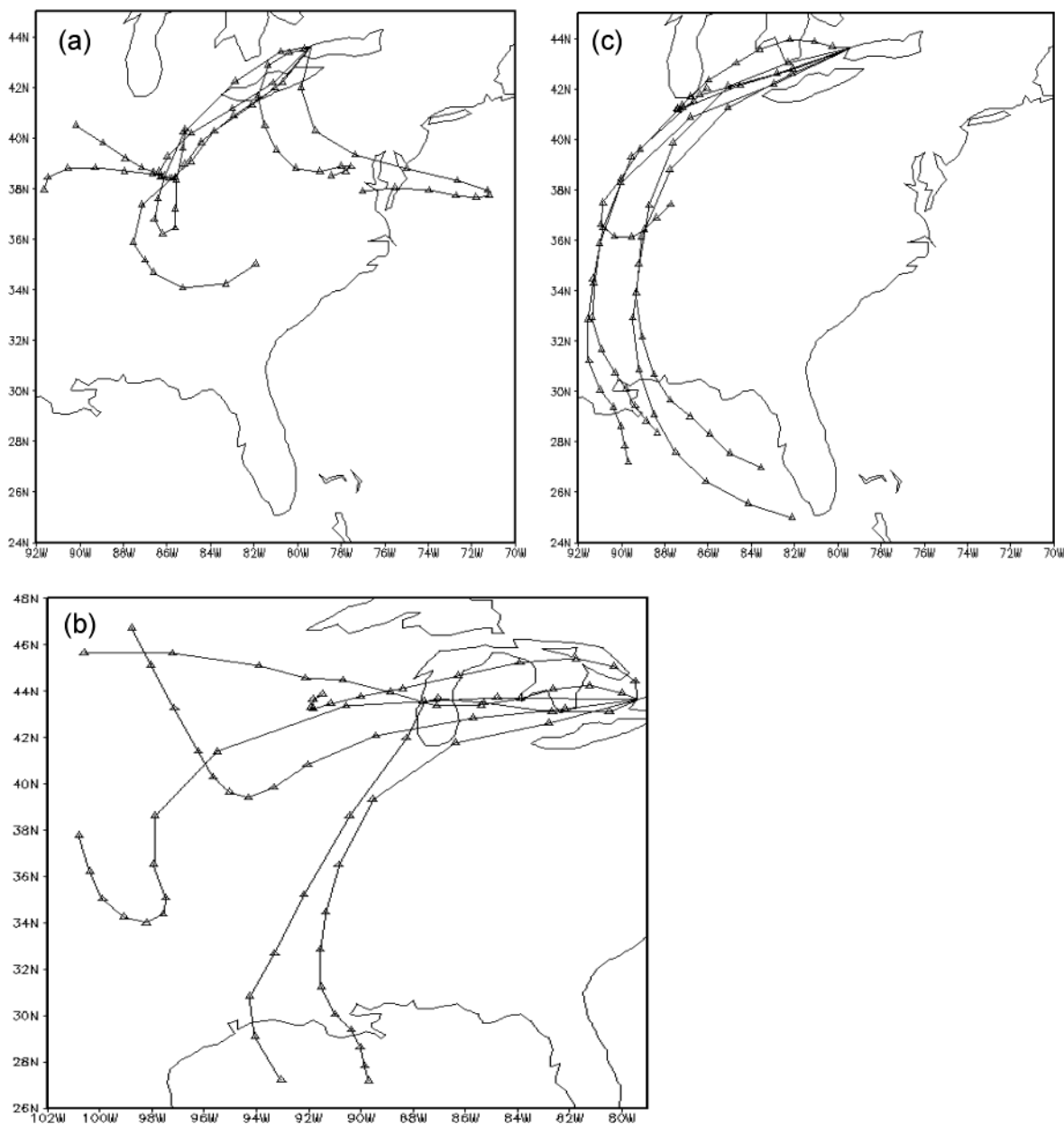


FIGURE 4. Three-day back trajectories (925 mb arrival height) associated with the six highest loading days for (a) secondary coal, (b) ammonium nitrate, and (c) organic acid source. Triangles indicate 6-h intervals. The top six trajectories were found to be sufficient for exhibiting the general transport direction bias associated with these sources.

2001. It was much less important in the summer, and most of the cases leading to the 21.5% summer average in Figure 2 occurred in May and October. This wintertime haze phenomenon frequently appears in southern Ontario during the cooler months reflecting the fact that the formation and stability of ammonium nitrate is temperature dependent (36). Similar results were reported for Phoenix and Denver (30, 37).

The third source in Figure 3 explains the majority of the OC1-4 and EC variation as well as Al, Ca, Fe, Mg, Mn, Ba, and Cr. The Mn and EC suggest that it is related to local motor vehicle traffic. The association of Mn with traffic is a result of the use of MMT (methylcyclopentadienyl manganese tricarbonyl) as a fuel additive in Canada. The relatively high EV values for Al, Ca, and Mg suggest that this source also includes $PM_{2.5}$ from road dust. Fe, Cu, and Zn likely reflect a variety of vehicle-related influences such as engine, tire and brake wear, and lubricating oils. The 3-day back trajectories for days with large contribution from this vehicle

component (not shown) did not indicate a clear directional preference, which is not surprising given the traffic density is high for several kilometers in all directions from the site.

The fourth source has high EV on Na and Cl indicating it is a sodium chloride salt. Given that Toronto is not close to the ocean and that this source is much more important in the winter compared to the summer indicates that the likely source is sodium chloride released as deicing salt on roads. Other constituents associated with road dust, including the sand spread on the roads during icy conditions, were also likely to have contributed to the total mass assigned to this source.

The water-soluble low-molecular-weight organic acids (LMW acids) led to the determination of a unique source that exhibited a strong seasonal dependence (fifth source). In the summer it contributed 23.4% to the $PM_{2.5}$ and only 5.9% in the winter. Thus, summertime meteorological conditions and more active photochemistry influenced the strength of this source, implying that secondary formation

played a role. The LMW mono- and dicarboxylic acids included in the PMF are known to be the photochemical products of hydrocarbons in the atmosphere. This is also implied by their water-solubility since atmospheric processing of organics is believed to increase their solubility or hygroscopicity (38, 39). Incomplete combustion of fossil fuels and biomass burning (e.g., wildfires) are major sources of their precursors (40, 41), and there are also some relatively minor primary sources for some of the dicarboxylic acids (42, 43). The potential link with biomass burning is suggested by the relatively large EV for the water-soluble K on this source profile. For secondary formation, the oxidant most likely responsible for the photochemically related production of the acids is ozone (44).

The 3-day back trajectories associated with high contributions from this organic-acid-related source (Figure 4c) indicate similar directions and anticyclonic type curvature as found for the coal combustion source. However, the transport distances appear to have been longer, originating further south, although still crossing over high SO₂ emission regions. The role this longer distance plays in accentuating the magnitude of the organic acid contribution is unclear. It may be reflecting certain precursor sources further south, which could include biogenic sources or wildfires. It could also be related to greater time spent over forested areas south of the Midwest or higher humidity in air masses originating further south (i.e., closer to the Gulf of Mexico).

The secondary organic characteristics and possible link with biomass burning lead to there being a considerable amount of OC associated with the organic-acid-related source (Figure 3). The EV values for OC1-4 are also high, second only to the motor-vehicle related source. To gain a clearer picture regarding which OC fractions may be more related to the secondary organics the ratios of OC1-4 to total OC were calculated. The ratio for OC1_{acid}/OC1_{total} is 0.18. Similarly the ratios for OC2, OC3, and OC4 to the total are 0.24, 0.26, and 0.22, respectively. This suggests a slight preference toward OC2 and OC3 for secondary dicarboxylic acids or other secondary organic compounds, which may help interpret measurements when only OC1-4 are available (i.e., when LMW organic acids are not measured).

LMW acids have not been used in past PMF studies (20, 30). Thus, identification of an organic-acid-related source, likely related, at least partially, to secondary organic aerosols, has not previously been quantified using PMF. This suggests measurement of these acids, which is relatively simple, is advantageous. To more clearly demonstrate what additional information they provide we excluded them and repeated the PMF analysis. Eight sources resulted from this run with the organic acid source being replaced by a minor Al-related crustal source. A large majority of the OC1-4 and EC, and thus mass, that was attributed to the organic acid source was then linked with the secondary coal source. This led to unrealistically high OC concentrations with the secondary coal source (32). Consequently, on an annual basis, 38% of the PM_{2.5} was apportioned to coal combustion, which is 12% higher than shown in Figure 2. This higher result is closer to, but still less than, the coal contributions estimated by Chen et al. (19), Polissar et al. (10), and Lee et al. (11). Inclusion of the LMW acids reduces this inferred contribution and leads to a more realistic coal combustion source profile (32), thus offering the next level of refinement in multivariate source apportionment.

Many of the previous eastern North American studies recognized that the high OC content of the "secondary coal" source was inconsistent with emissions profiles and offered a variety of possible explanations (10, 11, 19). The LMW acids included in this study have helped show that indeed this OC is not directly associated with the emissions from the coal combustion sources. Indirectly, the acidic sulfates forming

from the coal combustion emissions could be enhancing the amount of SOA mass based upon the mechanisms proposed by Jang et al. (45). Recent evidence suggests that heterogeneous processes, particularly in cloudwater, may also be involved in the formation of this SOA mass given its apparent link to oxalate (46). If this is the case, then our results may be some of the first observational evidence of the importance of these mechanisms. Alternatively, the particles associated with the secondary coal source could simply be providing a surface for condensation/partitioning of gaseous OC (from secondary and perhaps primary sources) as opposed to reactions on the particle surface. However, additional research is needed to determine which processes are most responsible for the organic acid source and its link to the secondary coal source.

As Figure 2 shows, the overall contribution to PM_{2.5} from the organic acid source was 23% in the summer and 6% in the winter. In terms of absolute mass, the organic acid source contribution in winter was one-quarter of the amount in the summer (an average of 3.2 µg/m³ in the summer vs 0.8 µg/m³ in the winter). Assuming that the primary OC associated with the water-soluble LMW organic acid sources does not vary seasonally and that SOA formation is at a minimum in the winter suggests that the average SOA contribution to PM_{2.5} in the summer is at least 18% (i.e., three-quarters of the summer mass of the organic acid source/total summertime PM_{2.5}). This is likely a low estimate because SOA formation is not zero in the winter months (47). In addition, secondary organic mass may also form locally from VOC and SVOC emissions in the Toronto area. This source may have been partially attributed to the motor vehicle component. Thus, given the present information as an initial estimate, we suggest that on average about 20% of the summer PM_{2.5} in Toronto is secondary OC. The peak absolute values determined for the organic acid source indicate that this percentage could be higher, in the range of 35–40%, during strong summertime, photochemical episodes. Clearly this issue is of great importance and should be examined in more detail than we have here. Our results suggest that PMF or other factor analysis approaches may provide an alternate means for estimating SOA contribution to total OC or PM_{2.5}. However, further research is needed to refine our estimates and to determine how much of this SOA mass forms from biogenic versus anthropogenic precursors.

The remaining sources were identified based upon relatively clear trace element signatures. They were found to be relatively minor contributors to total mass and, as indicated earlier, and as we will describe below, the number and characteristics of these sources changed when different PMF solutions were considered. The sixth source was associated with variations in V and Ni suggesting an oil combustion source (10). However, the relative amounts of V and Se are not consistent with pure oil combustion emissions suggesting that we may have identified a mixed source picking up a variety of primary PM_{2.5} sources whose contributions appear to vary coincidentally in Toronto. Many of the back-trajectories (not shown) associated with the highest contributions passed near eastern Lake Erie. This region includes the largest local coal-fired power plant in Ontario (Nanticoke) and a considerable amount of other activities (e.g., refineries (31), steel production, a high density of Great Lakes ship traffic). The total OC and EC concentrations in this source were low because it is associated with primary emissions and the carbon-based fuels would have been efficiency combusted. Although identification of the specific sources or processes responsible for this primary PM_{2.5} source ("PM_{primary-1}") is currently not possible, Figure 2 shows that in Toronto they were responsible for <2% of the mass, on average.

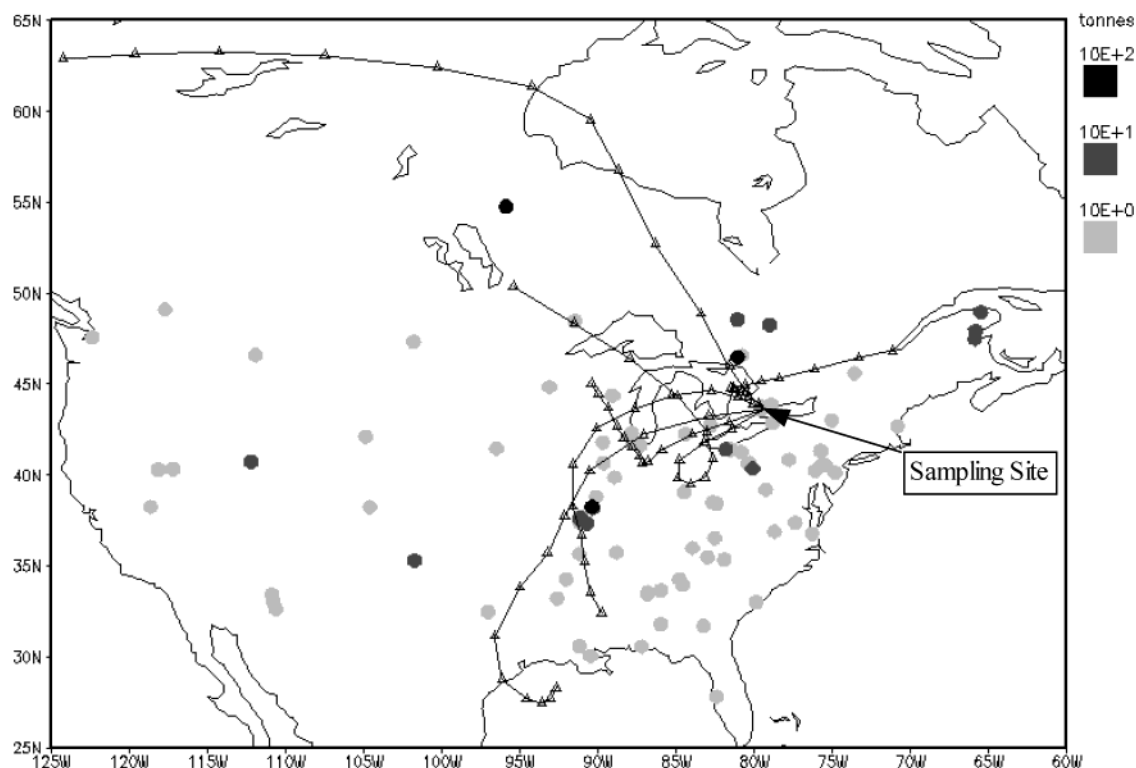


FIGURE 5. Three-day back trajectories for the six highest contribution days for the smelter source compared to the locations of the top 100 Pb emitters in the year 2000 (unit: tonnes/year).

The seventh and eighth sources contributed to only 2.2% and 1.6% of the mass, respectively. Figure 3 shows that one of them was associated with variations in Pb, As, Zn, Mn, Cd, and Ba, while the other is linked to emissions of Ni, Cd, and Zn. As with the sixth source, specific identification is difficult. These metals are released by a variety of industries such as steel production, mining, metal works, mineral smelters, and incinerators. Coal combustion also produces most, if not all, of these elements. Trajectories for the highest loading days of the seventh source are shown in Figure 5 along with year 2000 annual Pb emissions (48, 49). The individual trajectories, although uncertain, suggest that in most cases the air mass flowed across some known large Pb emitters. These include areas with smelter and mining industries such as Missouri and Central Ontario. Consequently, we labeled this source as “smelter”, but in reality it could also represent another ambiguous primary $PM_{2.5}$ source (i.e., like the sixth source). Polissar et al. (10) also concluded that they could detect a smelter source influencing northern Vermont, but it was characterized by As, S, and Mn as opposed to As and Pb in our result. However, such discrepancies are not unexpected given the different locations and time periods involved. In addition, since the early to mid 1990s (the period studied by Polissar et al.) there have been significant changes in the Canadian smelter emissions due to SO_2 controls aimed at reducing acid deposition.

The eighth source is also labeled as a “primary $PM_{2.5}$ ” source (PMprimary-2), and the top six back-trajectories are shown in Figure 6. Some may have passed near smelter and other industries that reported large Ni and Cd releases (48, 49), such as in northern Manitoba, central Ontario, and the U.S. Midwest. However, the locations of these sources are scattered and not necessarily coincident making it difficult to identify which types of sources may have emitted Ni and Cd in the proportions identified by the PMF analysis. Clearly, the PMprimary-2 trajectories do not appear to agree as well with the source locations compared to smelter the source. Instead, the main unique feature of this last source is the

greater travel distance of the trajectories associated with the high days. This implies stronger wind speeds and, coupled with the fact that the influence from the PMprimary-2 source was much stronger from Feb to April, 2000, suggests a local source and a systematic change in emissions. A large building was being constructed just north of the sampling site during the study and higher wind speeds may have generated more dust (note the relatively large Ca concentration and EV in Figure 3). There may have been a change in activities coinciding with the drop in this source’s contribution in April, but we have been unable to obtain information to determine the feasibility of this explanation.

As indicated earlier, PMF solutions with fewer and more than the eight sources and a range of rotation strengths were considered. The main results discussed above, in terms of source profiles and average percent contributions, did not change significantly with these different analyses. Only the last three sources were affected, but even they were found to be relatively common among the different solutions. The most interesting alternate model indicated 11 potential sources. Most of these were the same as reported above, and the three additional sources could be interpreted as (a) a source characterized by a high aluminum EV value and low EVs for all other compounds, which could be a crustal source (note Si was not measured) or local wear of aluminum materials; (b) a source related to Ni and Cr, which may be associated with steel production or metal processing; and (c) a biomass burning or wood smoke source as indicated by large EV values for OC, EC, FA, K, and a few other trace elements.

Wood combustion is thought to be a significant emitter of $PM_{2.5}$, but the third source above did not show a seasonal preference consistent with wintertime residential wood combustion or summertime wildfires. Thus, even though the current Toronto emissions inventory (50) as well as a recent paper on the 1995 data for Pittsburgh, PA (47) indicate that wood combustion is one of the major sources of primary OC emissions, our PMF analyses could not resolve such a

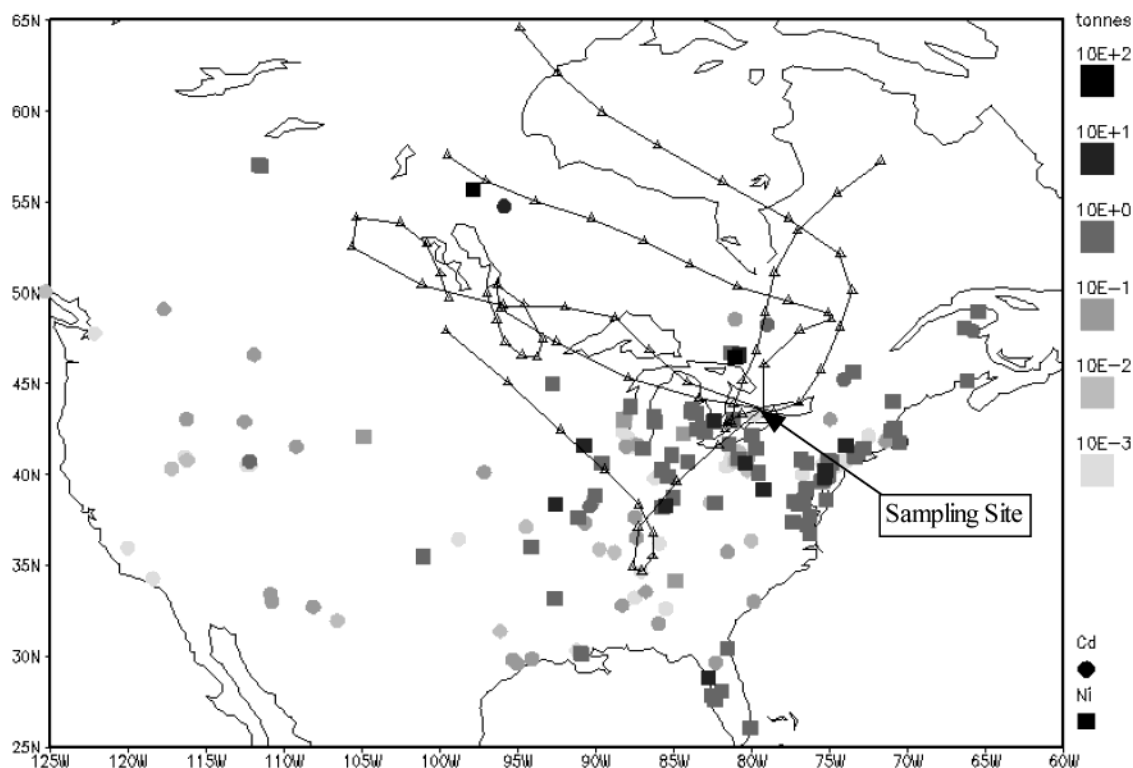


FIGURE 6. Three-day back trajectories for the six highest contribution days for the PM_{primary-2} source compared to the locations of the top 100 Cd and Ni emitters in the year 2000 (circles are Cd and squares are Ni, unit: tonnes/year).

source. Wood combustion may have been one of the contributors to the “organic acid” source, and, also based upon the variance in potassium, it may have contributed to the organic mass ascribed to the “secondary nitrate” source. This latter source seems reasonable given that residential wood combustion is more prevalent in the winter months when the levels of particle nitrate are also higher. However, the lack of a specific and significant wood smoke source suggests that the inventory requires modification. This supports a growing consensus among the federal, provincial, and municipal authorities responsible for air quality modeling, reporting, and inventory development. With respect to the third source identified in the 11 sources model, cooking emissions from the large number of restaurants in downtown Toronto, some located within 50 m of the measurement site, could have also been responsible. This is consistent with the relatively small temporal variability in this source and its lack of seasonal pattern. Furthermore, with the exception of highly specialized organic tracers, meat-cooking emissions are known to be very similar to emissions from wood combustion (51).

In summary, there were eight main source categories contributing to the PM_{2.5} during the year-long period of study. These were as follows: secondary ammonium nitrate; secondary products and primary emissions from coal combustion; secondary organic aerosols + biomass burning; motor vehicle emissions plus road dust and wintertime road salting (two separate sources); and primary PM_{2.5} emissions from coal and/or oil combustion, smelters, and industry (three separate sources). Overall, motor vehicle-related emissions are estimated to be responsible for about 40% of the PM_{2.5}. This is based upon the assumption that 60% of the annual contribution from ammonium nitrate is related to motor vehicles, which is based upon the NO_x emissions inventory for Toronto, and that the road salt source is entirely due to motor vehicles. Thus, among all the sources identified, motor vehicles were either directly or indirectly associated with the single largest fraction of the PM_{2.5}. This is not

surprising given the urban location of the measurement site. This estimate of vehicle contribution is without considering that motor vehicle related VOC emissions, upwind and in Toronto, were likely one of the precursors for the SOAs (organic acid source). Inclusion of the water-soluble organic acids was found to be very useful in properly apportioning the contribution from coal combustion (i.e., secondary sulfate) and in identifying an independent contribution from secondary organic aerosol mass.

Acknowledgments

We would like to acknowledge Richard L. Poirot (Vermont Department of Environment Conservation) for his many helpful comments, Pentti Paatero (University of Helsinki) for PMF program support, and Philip K. Hopke (Clarkson University) for initial assistance in learning PMF. We thank ANALEST (University of Toronto) for access to the ICP-AES instrument and NLET from National Water Research Institute for ICP-MS (Henry Wong). We also acknowledge Jacinthe Racine (CMC) for providing the back-trajectories. This research was supported by financial contribution from the Toxic Substances Research Initiative, Government of Canada.

Literature Cited

- (1) Brook, R. D.; Brook, J. R.; Urch, B.; Vincent, R.; Silverman, F. S. *Circulation* **2002**, *105*, 1534–1536.
- (2) Pope, C. A. I.; Burnett, R. T.; Thun, M. J.; Calle, E. E.; Krewski, D.; Ito, K.; Thurston, G. D. *JAMA, J. Am. Med. Assoc.* **2002**, *287*, 1132–1141.
- (3) Samet, J. M.; Dominici, F.; Currier, F. C.; Coursac, I.; Zeger, S. L. *N. Engl. J. Med.* **2000**, *343*, 1742–1749.
- (4) Hopke, P. K. *Receptor modeling for air quality management*; Elsevier: New York, 1991.
- (5) Paterson, K. G.; Sagady, J. L.; Hooper, D. L.; Bertman, S. B.; Carroll, M. A.; Shepson, P. B. *Environ. Sci. Technol.* **1999**, *33*, 635–641.
- (6) Prendes, P.; Andrade, J. M.; Lopez-Mahia, P.; Prada, D. *Talanta* **1999**, *49*, 164–178.

- (7) Yakovleva, E.; Hopke, P. K.; Wallace, L. *Environ. Sci. Technol.* **1999**, *33*, 3645–3652.
- (8) Poirot, R. L.; Wishinski, P. R.; Hopke, P. K.; Polissar, A. V. *Environ. Sci. Technol.* **2001**, *35*, 4622–4636.
- (9) Eldred, R. A. *J. Air Waste Manage. Assoc.* **1997**, *47*, 194–203.
- (10) Polissar, A. V.; Hopke, P. K.; Poirot, R. L. *Environ. Sci. Technol.* **2001**, *35*, 4604–4621.
- (11) Lee, J. H.; Hopke, P. K.; Poirot, R. L.; Lioy, P. J.; Oxley, J. C. *J. Air Waste Manage. Assoc.* **2002**, *52*, 1186–1205.
- (12) Stevens, R. K. *Water Sci. Technol.* **1993**, *27*, 223–233.
- (13) Dabek-Zlotorzynska E.; Piechowski M.; McGrath M.; Lai E. P. C. *J. Chromatogr.* **2001**, *910*, 331–345.
- (14) Birch, M. E.; Cary, R. A. *Aer. Sci. Technol.* **1996**, *25*, 221–241.
- (15) Chow, J. C.; Watson, J. G.; Pritchett, L. C.; Pierson, W. R.; Frazier, C. A.; Purcell, R. G. *Atmos. Environ.* **1993**, *27A*, 1185–1201.
- (16) Paatero, P. *Chemom. Intell. Lab. Syst.* **1997**, *37*, 23–35.
- (17) Paatero, P.; Tapper, U. *Environmetrics* **1994**, *5*, 111–126.
- (18) Juntto, S.; Paatero, P. *Environmetrics* **1994**, *5*, 127–144.
- (19) Chen, L. W. A.; Doddridge, B. G.; Dickerson, R. R.; Chow, J. C.; Henry, R. C. *Atmos. Environ.* **2002**, *36*, 4541–4554.
- (20) Chueinta, W.; Hopke, P. K.; Paatero, P. *Atmos. Environ.* **2000**, *34*, 3319–3329.
- (21) Lee, E.; Chan, C. K.; Paatero, P. *Atmos. Environ.* **1999**, *33*, 3201–3212.
- (22) Brereton, R. G.; Gurden, S. P.; Groves, J. A. *Chemometrics and Intelligent Laboratory Systems* **1995**, *27*, 73–87.
- (23) Malinowski, E. R. *Anal. Chem.* **1977**, *49*, 612–617.
- (24) Malinowski, E. R. *Journal of Chemometrics* **1999**, *13*, 69–81.
- (25) Malinowski, E. R. *Factor Analysis in Chemistry*, 2nd ed.; John Wiley & Sons Inc.: New York, 1991.
- (26) Malinowski, E. R. *J. Chemom.* **1988**, *3*, 49–60.
- (27) Lee, P. K. H. Masters Thesis, Receptor Modeling on Canadian Atmospheric Fine Particulate Matter (PM_{2.5}) by PMF, University of Toronto, 2002.
- (28) Turpin, B. J.; Saxena, P.; Andrews, E. *Atmos. Environ.* **2000**, *34*, 2983–3013.
- (29) Kumar, A. V.; Patil, R. S.; Nambi, K. S. V. *Atmos. Environ.* **2001**, *35*, 4245–4251.
- (30) Ramadan, Z.; Song, X. H.; Hopke, P. K. *J. Air Waste Manage. Assoc.* **2000**, *50*, 1308–1320.
- (31) Keeler, G. J.; Samson, P. J. *Environ. Sci. Technol.* **1989**, *23*, 1358–1364.
- (32) Lee, S. W. *J. Air Waste Manage. Assoc.* **2001**, *51*, 1568–1578.
- (33) Commission for Environmental Cooperation “Taking Stock 1998”. Communications and Public Outreach Department of the Commission for Environmental Cooperation, 1998.
- (34) Watson, J. G.; Chow, J. C.; Lowenthal, D. H.; Pritchett, L. C.; Frazier, C. A.; Neuroth, G. R.; Robbins, R. *Atmos. Environ.* **1994**, *28*, 2493–2505.
- (35) Fraser, M. P.; Cass, G. R. *Environ. Sci. Technol.* **1998**, *32*, 1053–1057.
- (36) Brook, J. R.; Dann, T. F.; Bonvalot, Y. *J. Air Waste Manage. Assoc.* **1999**, *49*, 1096–2247.
- (37) Solomon, P. A.; Moyers, J. L. *Atmos. Environ.* **1986**, *20*, 207–213.
- (38) Saxena, P.; Hildemann, L. M.; McMurry, P. H.; Seinfeld, J. H. *J. Geophys. Res.* **1995**, *100*, 18755–18770.
- (39) Crocker, I. D. R.; N. E., W.; Flagan, R. C.; Seinfeld, J. H. *Aer. Sci. Technol.* **2001**, *35*, 637–647.
- (40) Rohrl, A.; Lammel, G. *Environ. Sci. Technol.* **2001**, *35*, 95–101.
- (41) Suzuki, Y.; Kawakami, M.; Akasaka, K. *Environ. Sci. Technol.* **2001**, *35*, 2656–2664.
- (42) Narukawa, M.; Kawamura, K.; Takeuchi, N.; Nakajima, T. *Geophys. Res. Lett.* **1999**, *26*, 3101–3104.
- (43) Kawamura, K.; Laplan, I. R. *Environ. Sci. Technol.* **1987**, *21*, 105–110.
- (44) Kawamura, K.; Ikushima, K. *Environ. Sci. Technol.* **1993**, *27*, 2227–2235.
- (45) Jang, M.; Czoschke, N. M.; Lee, S.; Kamens, R. M. *Science* **2002**, *298*, 814–817.
- (46) Warneck, P. *Atmos. Environ.* **2003**, *37*, 2423–2427.
- (47) Cabada, J. C.; Pandis, S. N.; Robinson, A. L. *J. Air Waste Manage. Assoc.* **2002**, *52*, 732–741.
- (48) U.S. Environmental Protection Agency, Toxic Release Inventory Program, NC, 2000.
- (49) Environment Canada, National Pollutant Release Inventory, Canada, 2000.
- (50) Environment Canada, Pollution Data Branch, Canada, 2002.
- (51) McDonald, J. D.; Zielinska, B.; Fujita, E. M.; Sagebiel, J. C.; Chow, J. C.; Watson, J. G. *J. Air Waste Manage. Assoc.* **2003**, *53*, 185–194.

Received for review December 27, 2002. Revised manuscript received August 11, 2003. Accepted August 27, 2003.

ES026473I