

ASSESSING SOURCES OF PM_{2.5} IN CITIES INFLUENCED BY REGIONAL TRANSPORT

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ABSTRACT

The human health effects of fine particulate matter (PM_{2.5}) have provided impetus for the establishment of new air quality standards or guidelines in many countries. This has led to the need for information on the main sources responsible for PM_{2.5}. In urban locations being impacted by regional-scale transport, source-receptor relationships for PM_{2.5} are complex and require the application of multiple receptor-based analysis methods to gain a better understanding. This approach is being followed to study the sources of PM_{2.5} impacting southern Ontario, Canada, and its major city of Toronto. Existing monitoring data in the region around Toronto and within Toronto itself is utilized to estimate that 30-45% of the PM_{2.5} is from local sources, which implies that 55-70% are transported into the area. In addition, there are locations in the city that can be shown to experience a greater impact from local sources such as motor vehicle traffic. Detailed PM_{2.5} chemical characterization data were collected in Toronto in order to apply two different multivariate receptor models to determine the main sources of the PM_{2.5}. Both approaches produced similar results indicating that motor-vehicle-related emissions, most likely of local origin, are directly responsible for about 20% of the PM_{2.5}. Gasoline engine vehicles were found to be a greater overall contributor (13%) compared to diesel vehicles (8%). Secondary PM_{2.5} from coal-fired power plants continues to be a significant contributor (20-25%) and also played a role in enhancing production of secondary organic carbon mass (15%) on fine particles. Secondary fine particle nitrate was the single-most important source (35%) with a large fraction of this likely related to motor vehicle emissions. Independent use of different receptor models helps provide more confidence in the source apportionment as does comparison of results among complementary receptor-based data analysis approaches.

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INTRODUCTION

The long lifetime (>5 days) of ambient fine particles ($PM_{2.5}$) enhances their transport over large distances (≥ 1000 km) leading to relatively large areas with elevated concentrations (regional haze), including rural locations (NARSTO, 2003; Brook et al., 1999), and to complex source-receptor relationships. The importance of secondary formation from ambient gases such as sulphur dioxide, nitrogen oxides, ammonia, volatile organic compounds and semi-volatile organic compounds (MSC, 2001), further complicates these relationships. Consequently, identifying sources responsible for high concentrations of $PM_{2.5}$ over populated areas (i.e., cities) is difficult. Clearly, this makes development of specific control strategies aimed at reducing the human health risk challenging.

Southern Ontario and its largest city, Toronto, experience elevated $PM_{2.5}$ related to regional-scale transport. Development of control strategies is further complicated by the fact that some of the sources are in the U.S. and thus, cannot be managed through federal or provincial regulations. Southern Ontario is not unique in this respect. $PM_{2.5}$ moves across international boundaries throughout Europe and among states within the U.S. This paper describes the current situation in southern Ontario and presents results of receptor-based data analyses geared towards obtaining a better understanding of the regional and local sources of $PM_{2.5}$.

Receptor-Based Methods

Receptor methods for source apportionment or attribution include a variety of approaches for interpreting measurements of the physical and chemical properties of ambient particles to infer their possible or probable sources and to quantify the contributions from these sources (Brook et al., 2003). In areas with a $PM_{2.5}$ or PM_{10} problem, receptor methods help identify possible solutions and thus are an important tool for analysis and development of policy and/or specific PM management strategies. Receptor methods are often referred to as receptor models. However, receptor models are actually one type or class of receptor methods that provide the theoretical and mathematical framework for quantifying source contributions. Receptor models contrast with source-oriented chemical transport models in that receptor models start with observations at a given location and work backwards using as much information as is practical to determine the sources contributing to the observations and to quantify the contribution. Chemical transport models combine detailed emission rates with meteorological transport, chemical changes and deposition rates to estimate concentrations and their temporal variations at a receptor and/or at an array of grid points distributed geographically. Chemical transport models can be used to predict how atmospheric concentrations could change if emission rates are changed, while receptor models are not developed for predictive purposes.

Several reviews of receptor modeling methods and capabilities have been published in the past (e.g., Watson, 1984; Gordon, 1988; Hopke, 1985; Henry, 1997; Watson and Chow, 2002; Brook et al., 2003). Examples of semi-quantitative observationally-based data analyses that are considered receptor methods are: (1) Time series plots of single day, average or median hourly $PM_{2.5}$ or PM_{10} concentrations; (2) Averaging by wind speed; (3) Comparisons among source-oriented, neighborhood-scale, urban-scale and regional-scale PM mass and chemical concentrations; (4) Concentration directionality. A summary of the types of receptor models that have been used for source apportionment along with their data requirements, strengths, and weakness is given in Brook et al. (2003). Most of the models are statistically-based, but some physically-based or combined physical-statistical methods have been applied.

In this paper, southern Ontario $PM_{2.5}$ monitoring data (Ontario Ministry of the Environment Tapered Element Oscillating Microbalance – TEOM) are analyzed using several semi-quantitative receptor methods. In addition, results from quantitative source apportionment of detailed $PM_{2.5}$ composition data (Lee et al., 2003) from downtown Toronto, Ontario, are presented. Two relatively new approaches, which have become popular in the research community were used. These are Positive Matrix Factorization (PMF) (Paatero, 1997) and the UNMIX model (Kim and Henry, 2000; Henry, 2002). PMF and UNMIX provide a physical basis for estimating source contributions and profiles when fairly stringent assumptions are met. PMF and UNMIX have undergone a series of tests with a variety of simulated and real data sets to better understand their strengths, weaknesses and similarities (Willis, 2000) and have been applied for source apportionment in a variety of locations (e.g., Polissar et al., 2001; Poirot et al., 2001; Chen et al., 2002; Lee et al., 2002).

RESULTS

Background

The PM_{2.5} standard in Canada, referred to as the Canada-wide Standard (CWS), has been set at 30 µg m⁻³, 24 hour averaging time, with achievement based on the three-year average of the 98th percentile. Formal reporting on achievement of the CWS does not begin until 2010 and, as a minimum, provinces are to report on all communities with more than 100,000 population. Communities for which jurisdictions demonstrate (i) that continued exceedance of the CWS levels is primarily due to transboundary flow of PM and ozone or their precursor pollutants from the U.S. or from another province/territory, and (ii) that “best efforts” have been made to reduce contributions to the excess levels from pollution sources within the jurisdiction, will be identified in reporting as “transboundary influenced communities” that are unable to reach attainment of the CWS until further reduction in transboundary air pollution flow occurs. The CWS is clearly lower than the current U.S. daily standard of 65 µg m⁻³. It also tends to be lower than the U.S. annual standard of 15 µg m⁻³ (i.e., areas can be above the CWS and still have an annual mean less than 15 µg m⁻³).

An important issue with respect to a nationally consistent approach to achievement determination is the PM_{2.5} measurement methodology. It is well known that different technologies can lead to different concentration values and that PM_{2.5} is “defined” according to how it is measured. At present, Canada does not have a national standard for this method, which is in contrast to the U.S., where a Federal Reference Method (FRM) has been established. Many of the new PM_{2.5} monitors across Canada are “continuous” measurement instruments such as the Tapered Element Oscillating Microbalance (TEOM) or the Beta Attenuation Monitor (BAM). These have been installed for practical purposes and to enable near real time data reporting for air quality index reporting and forecasting. However, current information indicates that the operating conditions of the TEOMs across Canada lead to significant loss of nitrate and for the determination of 24 hour average PM_{2.5} concentrations this is most significant in the months from October to April (cold season) (Brook et al., 1999). Methods are being proposed to account for this low bias in cold season TEOM results, but at the present time these measurements are reported “as is” and often the warm season and cold season are investigated separately.

Figure 1 shows the current PM_{2.5} levels, expressed in terms of the CWS metric, for all stations across the country (from west to east). These measurements are from TEOMs and are assumed to be biased low, as discussed above. Almost all measurements west of Ontario, have 98th percentile PM_{2.5} concentrations of less than 30 µg m⁻³. Starting in extreme SW Ontario and extending eastward into Quebec a number of monitoring sites are above the 30 µg m⁻³ value. This area, referred to as the Windsor-Quebec Corridor (WQC), includes several large population centres such as Windsor, London, Hamilton, Toronto and Montréal. Mean PM_{2.5} levels are shown in Figure 2 on a map of the WQC. Some rural monitoring sites, such as Simcoe, Ontario, have relatively high PM_{2.5} levels, indicating regional-scale transport is occurring. Sources in the U.S. are also implicated since in some locations, such as Simcoe, high PM_{2.5} is observed under southerly flow conditions (see below) and there are no major sources between the site and the border. The highest concentrations shown in the figures are at Shawinigan, Quebec. This reflects the measurement site’s industrial setting, being located 3.5 km south of a large aluminum smelter.

Mean PM_{2.5} concentrations are higher in the urban areas since particles from local emissions are superimposed upon the regional background. In Hamilton and Toronto, the average PM_{2.5} levels are about 45% and 20% higher, respectively, than at Simcoe. Thus, while urban activities clearly contribute to the PM_{2.5} levels, a significant portion of the PM_{2.5} observed in the cities is from upwind sources. Regional-scale concentrations over the WQC and the contribution from both local and upwind sources are strongly dependent upon meteorological conditions. Precipitation, wind direction, local and large scale stagnation and vertical mixing are some of the most important factors and many of the high PM_{2.5} episodes leading to levels above the CWS are a result of specific weather patterns. Development of air quality management plans to reduce the risk to human health needs information on the relative impact of local versus upwind sources and on the main sources contributing to primary (i.e., directly emitted) and secondary (i.e., formed in the atmosphere from precursor gas emissions) PM_{2.5}. Although regional-scale air quality models are expected to be able to support development of management plans and to be able to address issues of local versus regional and primary versus secondary PM_{2.5}, validated models capable of operating on both regional

and urban scales are not yet available for widespread application. Fortunately, receptor-based methods utilizing observations can also be applied to provide policy-relevant information.

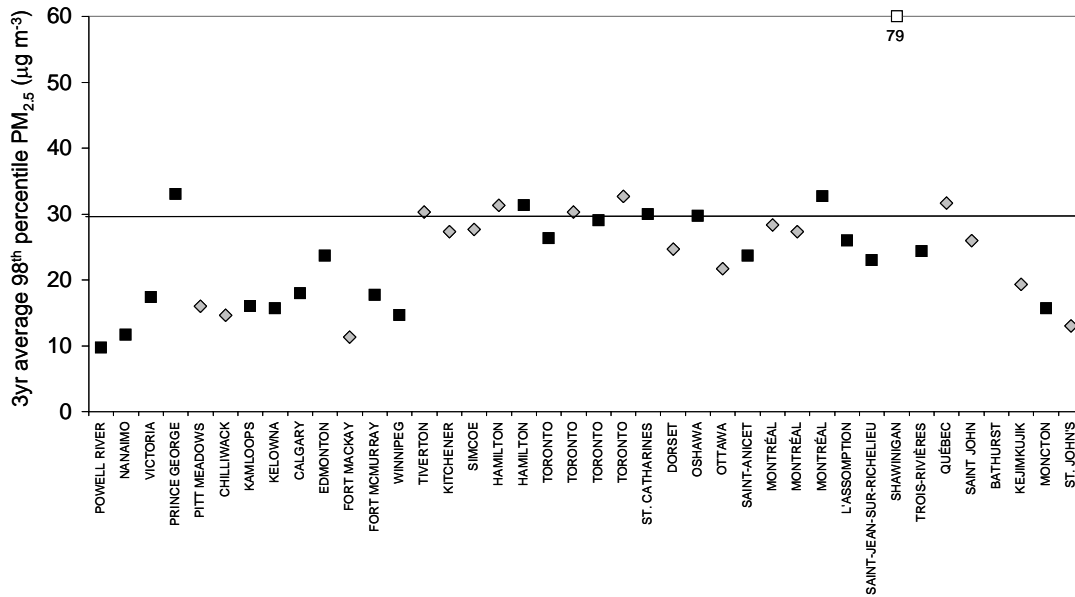


Figure 1. Canadian PM_{2.5} levels expressed as the three-year average 98th percentile concentration. Squares are for sites with data for the three most recent years (2000-2002). Diamonds are for sites with at least three-years of measurements, but not all of these years were during 2000-2002. The solid line shows the value of the Canada-wide Standard, which is to be achieved by 2010. PM_{2.5} was measured using a Tapered Element Oscillating Microbalance (TEOM).

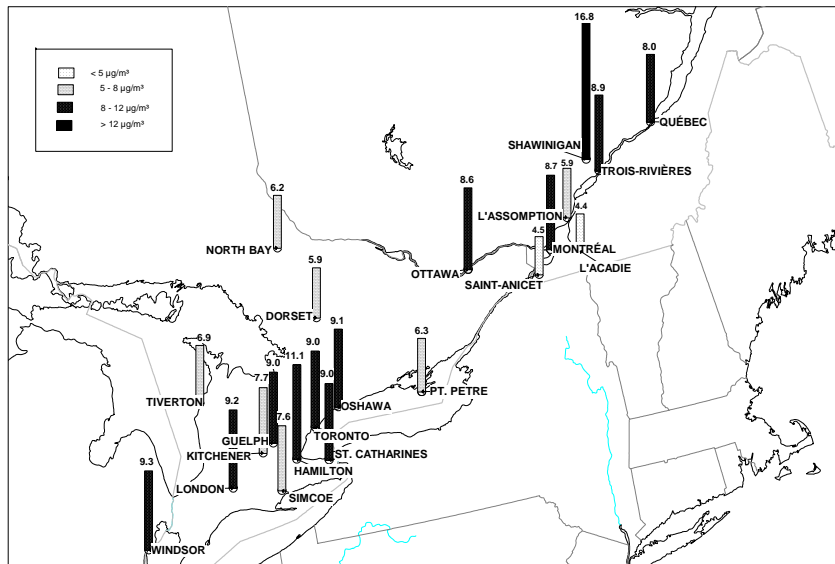


Figure 2. Annual average PM_{2.5} concentrations in the Windsor-Quebec corridor for 2001.

APPLICATION OF RECEPTOR METHODS IN SOUTHERN ONTARIO

Concentration Directionality and Analysis of Spatial Patterns

Comparison of concentrations occurring with different prevailing wind directions provides a clear indication of where the main PM_{2.5} sources are located. For example, in Brook et al. (2002) the median concentration at Simcoe under southerly flow was reported to be 20.3 $\mu\text{g m}^{-3}$ and the frequency of 6 h observations above 30 $\mu\text{g m}^{-3}$ was 18.5 %. In contrast, for northerly transport the median and frequency were 3.8 and 0.0, respectively. Clearly, reduction of regional PM_{2.5} in southern Ontario will need to consider sources located to the south. These results are expanded upon in this paper by including another year of data, different measurement sites and by excluding periods with precipitation. Figure 3 shows the median six-hour average PM_{2.5} for a southwest to northeast transect of sites running from Simcoe through the southern part of Hamilton (Hamilton Mtn.) and into south Toronto (Etobicoke) and north Toronto. The values shown are based upon the same observation periods at each site (i.e., equal sample size from the same 6 hr periods) and are based upon observations when there was no precipitation in the region. This approach provides a clearer picture of the differences between locations. Southerly and northerly flows were determined using three-day back-trajectories as described in Brook et al. (2002). It is important to note that the directionality of air masses is rarely straight and linear, and the actual trajectory often follows a more circuitous route between source and receptor. However, the trajectory sorting approach utilized here and in Brook et al. (2002) minimizes misclassification of transport direction. Median PM_{2.5} was around 4-6 times higher under southerly transport conditions compared to northerly flow, depending upon location. While some differences in meteorological conditions (e.g., wind speed) may have contributed to this directional dependence of PM_{2.5}, the major cause was the difference in emissions to north of the region compared to south of the region.

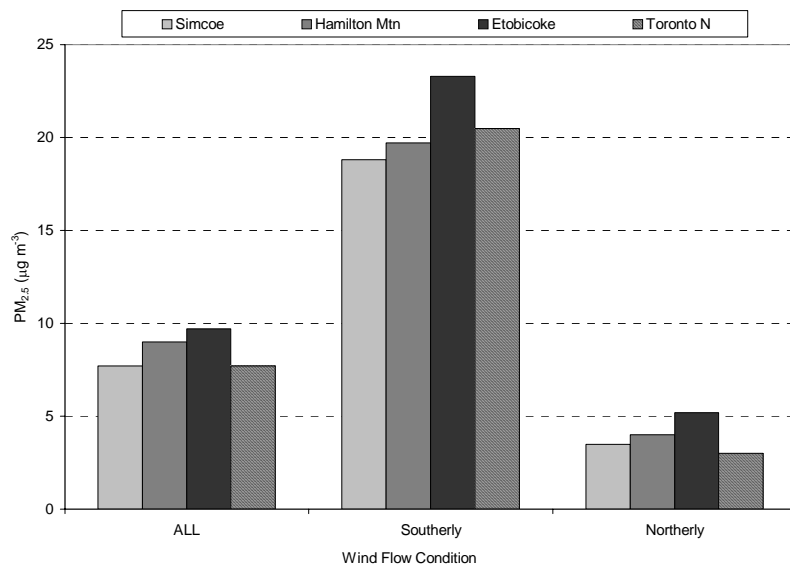


Figure 3. Median 6 hr PM_{2.5} concentrations for the warm seasons (May-September) of 1998-2001 (non-precipitating days). "All" represents all measurements in the period. The sites shown represent a southwest to northeast transect from a rural location (Simcoe) to the outskirts of Hamilton and two sites in Toronto. Etobicoke is in the southwestern part of Toronto and is impacted by traffic.

Among the sites shown in Figure 3, PM_{2.5} was highest at Etobicoke. This was due to the proximity of the site to traffic emissions and highlights the amount of intra-urban variability in Toronto. Site to site differences also varied by wind direction. Median PM_{2.5} was 12% higher at Etobicoke compared to Toronto North during high-concentration southerly flow periods. In contrast, it was 66% higher under northerly flow conditions. This is due to the amount of PM_{2.5} in the regional background. Not surprisingly, when the background levels are low, the within-city variation in PM_{2.5} is more pronounced.

Comparing concentrations between the sites during the same prevailing wind directions can provide an indication of the local contribution to $PM_{2.5}$, at the urban sites. Determination of the magnitude of this contribution is crucial for effective risk management. For example, a small local contribution relative to the regional background suggests that risk management options based upon local emission control policies will not likely be effective. To estimate the local contribution to urban $PM_{2.5}$ the location of the rural site(s) with respect to the urban centre of interest is important (e.g., the rural site should not be downwind of the city). Simcoe is too far to the southwest to directly compare with Toronto concentrations since regional $PM_{2.5}$ levels gradually decrease from south to north. Therefore, in Brook et al. (2002), $PM_{2.5}$ from Simcoe and a rural site northwest of Toronto (Egbert) were used to estimate the average spatial gradient in regional $PM_{2.5}$ and hence the likely regional concentration relevant for Toronto. The urban concentrations were then compared to this estimated regional background to estimate how much of the $PM_{2.5}$ in Toronto was due to local emissions. Furthermore, this comparison, which was only done for the warm season (May-Sept.), was done separately for different wind flow directions. This was because regional background concentrations vary depending upon direction (Figure 3). For high concentration, southerly-transport-periods 30-38 % of the $PM_{2.5}$, on a total mass basis, in Toronto was estimated to be due to local sources. During westerly flow conditions the local contribution was 30-45%. The city was responsible for a larger percentage, up to 52%, when the flow was northerly because $PM_{2.5}$ levels in the air mass entering the city were relatively low.

Multivariate Receptor Models

Analysis of the mass concentration data among sites and for different pollutant transport directions led to better quantification of the amount of $PM_{2.5}$ coming from outside the city. However, this analysis provided little information on the actual sources responsible for the local or the upwind fractions. Therefore, receptor modelling was undertaken using one year of daily $PM_{2.5}$ mass and chemical speciation measurements. Applying two techniques, PMF and UNMIX, was expected to provide more confidence in the results. Agreement between techniques, especially when applied independently, will enhance the international credibility of the results, which may provide scientific support to the development of new Canada/U.S. air quality agreements.

Successful application of all receptor-modelling approaches for $PM_{2.5}$ depends upon detailed chemical characterization. For the Toronto analysis, 15 trace metals (e.g., iron, nickel, zinc, vanadium, selenium), 7 inorganic ions (e.g., sulfate, nitrate, ammonium), 5 water-soluble organic acids (e.g., oxalic acid, malic acid), total black carbon (BC) and four separate fractions of total organic carbon (OC1-4), were quantified (Lee et al., 2003). Both PMF and UNMIX also require a relatively large number of samples, preferably >300, and a high frequency of above detection limit concentrations. The PMF results are reported in detail in Lee et al. (2003). In this paper we focus on some of the UNMIX results and on a comparison of the apportionment obtained by the two approaches. We also only present the annual average apportionment, while seasonal results are included in Lee et al. (2003).

Five major sources and three minor sources were found by PMF to be contributing to the Toronto $PM_{2.5}$ (Lee et al., 2003). The UNMIX analysis, which was undertaken in two stages, uncovered a possibility of nine different sources. Again, five major sources were found and the other four were relatively minor. Both sets of results are summarized in the pie charts in Figure 4. Secondary ammonium nitrate was found to be the most important source of $PM_{2.5}$ mass. This $PM_{2.5}$ constituent forms during relatively cool and humid conditions from the oxidation products of nitrogen oxides (NO_x). Gas phase ammonia (NH_3) is also required. On a province-wide basis, 55-60% of the NO_x is emitted from motor vehicles and industrial and power generation emissions are equally responsible for another 30% (Environment Canada, 2003). Thus, the NO_x emissions inventory suggests that motor vehicles are the major source of the secondary ammonium nitrate. Vehicles operating in Toronto and upwind are likely both responsible, but their relative importance cannot be determined solely from receptor-based methods.

Another secondary constituent, associated with sulphate forming from emissions from coal combustion, was found by both PMF and UNMIX to be the second most important source of $PM_{2.5}$ in Toronto. The Ontario inventory (Environment Canada, 2003) indicates that 70% of the SO_2 emissions are from power plants and metal smelters. Although there is a small power plant in Toronto, most of the emissions from these sources are not released locally (i.e., not from within Toronto). Thus, reducing the "secondary coal" fraction of $PM_{2.5}$ in Toronto will require emission reductions upwind of the city. Both PMF and UNMIX attributed another ~20% of the $PM_{2.5}$ to secondary

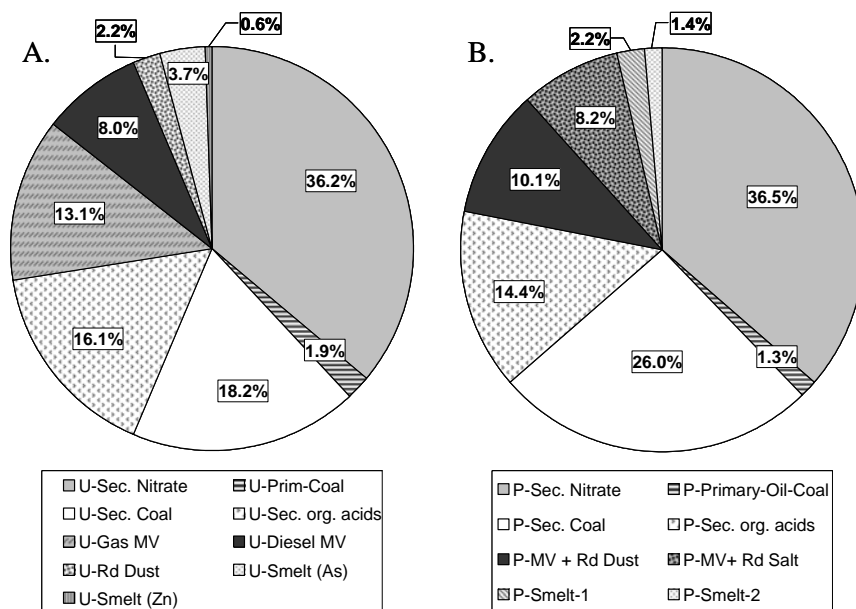


Figure 4. UNMIX (A) and PMF (B) receptor modelling results for 24 hr PM_{2.5} collected in downtown Toronto from Feb. 14, 2000 to Feb. 14, 2001. Percentages indicate the estimated contribution to the annual PM_{2.5} from the source indicated by the shading pattern.

organic carbon forming from gas phase volatile (VOC) and semi-volatile organic carbon (SVOC) emissions. Formation of this component of the PM_{2.5} appeared to be enhanced by the presence of inorganic acids, predominantly acidic sulphate (Lee et al., 2003). The acidic sulphate is likely from upwind power plant emissions, while the main sources of the SVOC and VOC gases, could be located upwind and/or within Toronto. Natural and anthropogenic emissions are both potentially involved. Thus, approaches for reducing this component of the Toronto PM_{2.5} are not clear based upon receptor method results.

The seasonal PMF results in Lee et al. (2003) revealed that secondary ammonium nitrate was responsible for 50% vs. 21% of the PM_{2.5} in the cold vs. the warm season. Conversely, secondary coal and secondary organic carbon were greater contributors in the warm season. These sources were two and four times more important in the warm compared to the cold season, respectively. These differences, which are due to seasonal differences in meteorological conditions including more intense sunlight (i.e., photochemical activity), are important to be aware of when considering strategies to reduce PM_{2.5} concentrations.

A number of local sources, linked to motor vehicle related emissions, were identified by PMF and UNMIX. In total, these sources were responsible for about 20% of the PM_{2.5} with reasonable agreement between the two separate analyses (18% from PMF and 22% from UNMIX). However, while both models identified a distinct influence from motor vehicles (MV), PMF split this influence into two components, interpreted as “MV exhaust + road dust” and “MV exhaust + road salt,” and the UNMIX analysis split the MV contribution into three components, interpreted as “gasoline MV exhaust,” “diesel MV exhaust” and “road dust.” These differences were due to differences in how the PMF and UNMIX analyses were conducted. All of the measured PM_{2.5} chemical constituents were used for PMF, while some were excluded in the UNMIX modelling in order to simplify interpretation. Most notably, sodium and chloride were not used and consequently, the influence of road salt was not identified. Instead, PM_{2.5} mass associated with road salt was likely included as part of the “road dust” source. Another difference was that the UNMIX modelling was undertaken in two steps. The first step focused on apportioning the PM_{2.5} mass using the inorganic ions, BC, total OC and selected trace elements. The second step focused on explaining the remaining mass based upon variations in OC1-4, BC, and inorganic and organic ions.

The two-step UNMIX modelling, with the second step emphasizing the OC fractions and BC, was advantageous because the gasoline and diesel emission sources were separated in step two. These sources were initially identified based upon the ratio of total OC (OC1 + OC2 + OC3 + OC4) to BC. The “Gasoline MV” source was found to be 80% carbon with an OC:BC ratio of 50:1. The “Diesel MV” source was 84% carbon with a ratio of 2.8:1 (i.e., much more BC). This identification was further supported by examining the day of week variation in the mass concentration of each of the UNMIX MV sources. Figure 5 shows that the diesel fraction of $PM_{2.5}$ declined substantially on weekends, which is consistent with urban traffic behaviour. In contrast, the gasoline MV fraction showed less day of week dependence, with maximum impact on Friday and Saturday. Both of these days typically have considerable automobile traffic spread throughout the day and into the night as opposed to typical workday rush hour patterns. Interestingly, the road dust contribution derived from UNMIX exhibited a day of week pattern representing a combination of the diesel and gasoline pattern. This characteristic is logical since road dust is presumably re-suspended by both types of vehicles. The strong day of week patterns exhibited by the MV-related sources implies that local traffic emissions were more important, as a day-of-week preference for emissions from more distant sources would be expected to be significantly attenuated by variable regional-scale transport times.

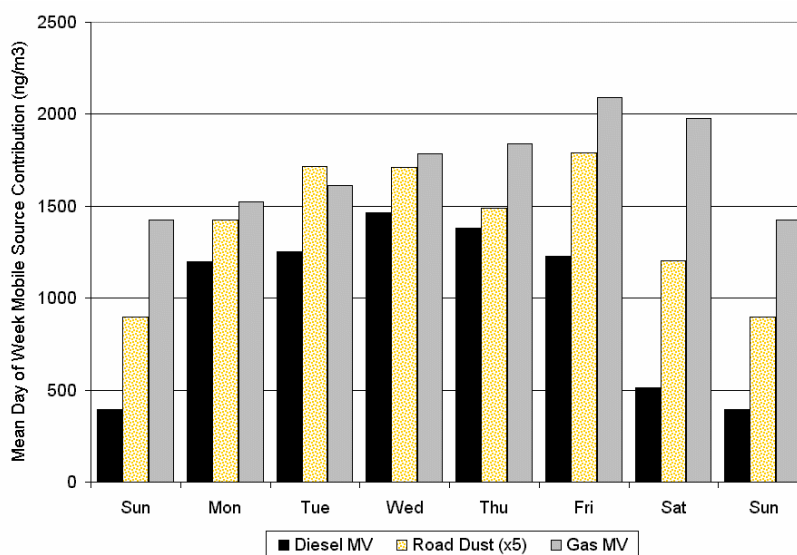


Figure 5. Mean day of week pattern in the $PM_{2.5}$ mass contribution ($ng\ m^{-3}$) from the three motor vehicle related sources determined by UNMIX for Toronto. Note: Sunday is shown twice.

In addition to the main sources described above, both PMF and UNMIX apportioned the remaining ~5% of the $PM_{2.5}$ among three primary sources. These were potentially linked to industrial emissions, including metal smelters, and primary coal and/or oil burning emissions. Some characteristics of these sources were similar between the two methods. For example, a high selenium (Se) to sulphate ratio was the main characteristic of the primary coal source and arsenic (As) was the main ‘marker’ for one of the sources labeled as being related to smelters. The main common feature between the two sets of results, however, was the minor mass contribution these sources were found to have on the observed $PM_{2.5}$ in Toronto.

In general, the independent application of different receptor models provided more confidence in the results. However, it is important to note that in both approaches, as with most other receptor models, deducing the number of sources is not straightforward. For example, Lee et al. (2003) reported that an eleven-source solution for Toronto also produced reasonable results. Similar model comparisons for Phoenix, AZ, $PM_{2.5}$ also demonstrated this fact (Willis, 2000). Thus, even when reasonable agreement is obtained, as reported above for Toronto, the results need to be interpreted in light of uncertainties in the measurement data, variations in environmental conditions and in actual emission characteristics and in light of the inherent subjectivity involved in determining the number of sources and uncertainty associated with the receptor method. PMF considers uncertainties in the measurements and error bars in

the source contributions are provided in Lee et al. (2003). However, accurate uncertainty estimates encompassing all of the issues are very difficult to quantify and will vary among different analyses and datasets. Nonetheless, some idea of uncertainty is important for decision-making. Applying multiple techniques, as presented here, provides a range of results, which can be viewed as an indication of overall uncertainty. Including analyses of different PM_{2.5} datasets in these comparisons would also be valuable. For Toronto, two additional years of measurements are currently being used for this purpose. Ultimately, the receptor method results also need to be reconciled with known 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 PM_{2.5}) and they need to be carefully examined to determine if the temporal (e.g., seasonal and day of week patterns) and meteorological (e.g., variation with wind direction) characteristics are realistic.

The results from the receptor models are not inconsistent with our earlier estimate of a 30-45% contribution from local PM_{2.5} sources. Simply assuming that the motor vehicle component (~20%) and about 50% of the secondary nitrate, which amounts to 10% of the PM_{2.5} in the warm season, are locally emitted/produced leads to consistency, although at the lower end of the range. In reality, the other sources found by the receptor models were also likely to have had a regional and local component. All proportions would likely have changed from sample to sample, as well. However, larger portions of the motor vehicle and secondary nitrate sources were clearly from local sources compared to the secondary coal and the secondary organic acid sources.

CONCLUSIONS

Application of receptor-based methods can provide information useful for managing the risk to human health attributed to poor air quality. In urban areas experiencing complex source-receptor relationships, due to a significant impact by regional-scale transport and/or due to a high population density in the surrounding area, these methods are essential for gaining a better understanding of the PM_{2.5} issue.

The type, quantity and spatial-temporal resolution of the PM_{2.5} data that are available governs the amount of information that can be obtained from receptor-based analyses. For assessing regional vs. local contributions, operating at least one site to measure the regional background PM_{2.5} along with the urban network is critical. For Toronto, Ontario, several measurement sites within the city and in the surrounding area were compared under specific wind flow patterns to estimate that 30-45% of the PM_{2.5} is locally generated. During periods of low regional background concentrations, which usually occur with northerly wind flow, the percent local contribution is largest. This percent can surpass 50% at urban sites significantly influenced by traffic emissions.

Detailed chemical characterization of PM_{2.5} is essential for application of receptor models. The more complete this characterization and the greater the amount of data available the more confident source apportionment results can be expected to be. Given the inherent uncertainty in measurement data, in actual source profile information and the subjective nature of the interpretation of receptor model results, applying more than one model can help increase confidence in results. Use of multiple models can be even more effective if they are run by independent groups of experienced investigators. This procedure was followed for Toronto PM_{2.5} source apportionment and the separate receptor model runs were found to be in good agreement. This apportionment indicated that motor vehicle related emissions (i.e., exhaust and road dust), most likely of local origin, were responsible for about 20% of the PM_{2.5}. Gasoline engine vehicles were found to be a greater overall contributor compared to diesel vehicles. Secondary PM_{2.5} from coal-fired power plant emissions was a significant contributor and also played a role in enhancing production of secondary organic carbon mass on fine particles. Secondary fine particle nitrate was found to be the single-most important source, particularly in the cooler months. Based upon the current Ontario emissions inventory, 55-60% of the observed fine particle nitrate in Toronto is estimated to be related to motor vehicle NO_x emissions.

The information provided through the receptor-based analyses presented in this paper can be used to target potential strategies for reducing ambient PM_{2.5} in Toronto. However, it is important to note that these results do not provide information on which of the identified PM_{2.5} sources produce the most toxic (acute or chronic) particles. Clearly, air quality improvement strategies should, if possible, attempt to consider the relative toxicity of the mix of emissions originating from the various sources, thereby leading to ambient PM_{2.5} reduction strategies providing the greatest

benefit to public health. Additional research is needed to gain a better understanding of which sources and or PM_{2.5} chemical constituents or precursors are more strongly linked to adverse human and environmental health impacts.

REFERENCES

- Brook, J.R., Vega, E., and Watson, J.G. 2003. *Receptor Methods*, Chapter 7 – North American Research Strategy on Tropospheric Ozone (NARSTO) Particulate Matter Assessment. Released March 2003 www.cgenv.com/Narsto/PMAssessment.html.
- Brook, J.R., Lillyman, C.D., Mamedov, A., Shepherd, M. 2002. Regional transport and urban contributions to fine particle (PM_{2.5}) concentrations in southeastern Canada. *J. Air Waste Manage. Assoc.* 52:174-185.
- Brook, J.R., Dann, T.F., and Bonvalot, Y., 1999. Observations and interpretations from the Canadian fine particle monitoring program. *J. Air Waste Manage. Assoc.* 49:35-44.
- Chen, L.W.A., Doddridge, B.G., Dickerson, R.R., Chow, J.C., and Henry, R.C. 2002. Origins of fine aerosol mass in the Baltimore–Washington corridor: implications from observation, factor analysis, and ensemble air parcel back trajectories. *Atmos. Environ.* 36:4541-4554.
- Environment Canada 2003. National Pollutant Release Inventory (NPRI), www.ec.gc.ca/pdb/npri/npri_home_e.cfm.
- Gordon, G.E. 1988. Receptor Models. *Environ. Sci. Technol.* 22:1132-1142.
- Henry, R.C. 2002. Multivariate receptor models - current practice and future trends. *Chemom. Intell. Lab. Sys.* 60:43-48.
- Henry, R.C. 1997. History and fundamentals of multivariate air quality receptor models. *Chemom. Intell. Lab. Sys.* 37:37-42.
- Hopke, P.K. 1985. *Receptor Modeling in Environmental Chemistry*. New York: John Wiley & Sons, Inc.
- Kim, B.-M., and Henry, R.C. 2000. Extension of self-modeling curve resolution to mixtures of more than three components. Part 3, *Chemom. Intell. Lab. Syst.* 52:145-154.
- Lee, P.K., Brook, J.R., Dabek-Zlotorzynska, E., and Mabury, S. 2003. Identification of the major sources contributing to PM_{2.5} observed in Toronto. *Environ. Sci. Technol.* 37:4831-4840.
- Lee, J.H., Hopke, P.K., Poirot, R.L., Liroy, P.J., and Oxley, J.C. 2002. Identification of sources contributing to mid-Atlantic regional aerosol. *J. Air Waste Manage. Assoc.* 52:1186-1205.
- MSC (Meteorological Service of Canada) 2001. Precursor Contributions to Ambient Fine Particulate Matter in Canada: A Report by the Meteorological Service of Canada (MSC). Ministry of Public Works and Government Services, 2001. En56-167/20001E, ISBN: 0-662-30650-3, May 2001.
- NARSTO 2003. North American Research Strategy on Tropospheric Ozone (NARSTO) Particulate Matter Assessment. Released March 2003 www.cgenv.com/Narsto/PMAssessment.html.
- Paatero, P. 1997. Least squares formulation of robust, non-negative factor analysis. *Chemom. Intell. Lab. Sys.* 37:23-35.
- Poirot, R.L., Wishinski, P.R., Hopke, P.K., and Polissar, A.V. 2001. Comparative application of multiple receptor methods to identify aerosol sources in northern Vermont. *Environ. Sci. Technol.* 35:4622-4636.
- Polissar, A.V., Hopke, P.K., and Poirot, R.L. 2001. Atmospheric aerosol over Vermont: chemical composition and sources. *Environ. Sci. Technol.* 35:4604-4621.
- Watson, J.G. 1984. Overview of receptor model principles. *J. Air Pollut Control Assoc.* 34:619-623.
- Watson, J.G., and Chow, J.C. 2002. Particulate pattern recognition. In *Introduction to Environmental Forensics*, eds. B.L. Murphy, and R. Morrison, pp. 429-460. New York: Academic Press.
- Willis R.D. 2000. Workshop on UNMIX and PMF as applied to PM_{2.5}. Final Report for USEPA under Contract No. 68-D5-0049. Office of Research and Development, National Exposure Research Laboratory, Human Exposure and Atmospheric Sciences Division, June 2000, EPA/600/A-00/048.