

Responses to Reviewers

Title: Source Apportionment of Urban Particulate Matter using Hourly Resolved Trace Metals, Organics, and Inorganic Aerosol Components

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We thank all the referee for providing insightful comments and suggestions. All comments have been carefully considered and addressed. We believe we have improved the manuscript. The detailed responses to specific points are listed below (text in italics shows the reviewer's comments and corresponding responses are shown in blue).

Reviewer #2

General comments

The paper is focused on source apportionment by Positive Matrix Factorization of hourly resolved particulate matter sampled in Toronto (Canada). The topic is interesting, the data set is large. Obviously the joint use of metal, BC and ACSM data should give better results respect to the use of data from a single instrument; however, the joint use of data coming from different instruments in the PMF analysis it is not trivial and there are many inconsistencies in the reported factor profiles and in the interpretation of the results; furthermore, many important information are missing and the results of the PMF analysis for the identification of the sources is less clear respect to a traditional 24 h based study. Therefore, I cannot suggest the article for publication.

PMF enables the deconvolution of temporal patterns within time series data, hence the findings resolved are inherently related to the temporal characteristics of the input data. Certainly, 24-hr integrated filter data has traditionally been used for PMF analysis, and these data typically have better accuracy due to larger sample loadings and more sensitive analytical instruments. However, use of other data types is becoming more common. For example, PMF is routinely applied to deconvolve high time resolution aerosol mass spectrometry data, as was done in this study. Use of higher time resolution data also enables application of PMF to short-term intensive campaigns (a month or less) where using traditional methods would have resulted in too few filter samples collected; typically, at least 100 samples are required to obtain a reliable PMF solution.

To the best of our knowledge, this is the first study to use organic aerosol (OA), inorganic species (sulphate, nitrate, ammonium), black carbon, and trace metals data measured at high time resolution for source apportionment. One of the advantages of this approach was the resolution that provided more accurate results in terms of the identification, contributions, and locations of sources that last for short time periods (i.e., industrial plume event) and contain strong diurnal trends (i.e., traffic-related emissions). The combined approach was to compare and contrast PMF solutions using OA mass spectra or metals only as these have commonly been used in source apportionment studies. Since no other study has used this combination of high time resolution data, there is no direct point of comparison for the PMF solutions in this study.

We fully agree care must be taken when using data from different instruments. This often arises even with traditional filter-based data where different methods are used to measure different types of analytes (e.g. metals, ions, organic fractions etc.). PMF allows for incorporation of uncertainties so that data from different instruments receives appropriate weighting. Due to the unique combination of data types used in our study, the solution was very carefully investigated to evaluate the uncertainty in the PMF solution and the stability of the PMF solution upon perturbations to its uncertainty matrix. Detailed descriptions for the evaluation of the PMF solution has been discussed in our response and added in the revised manuscript.

Specific comments

1) The uncertainty of each metal is normally related to the square root of the number of counts in the peak; it depends on the number of counts in the peak, therefore it is not fixed for each element, it varies from spectra to spectra and it cannot be obtained from the measurements on a standard (formula (1) S.I. pag.1); this method clearly underestimate the uncertainty (which is a crucial parameter for PMF analysis)

We agree that the uncertainty estimation is one of the most important steps in positive factorization matrix (PMF) analysis and a comprehensive set of uncertainties is required.

The analytical uncertainty (global or overall uncertainty) of X-ray fluorescence (XRF) analysis is a combination of all sources of random errors and systematic errors introduced by fluctuations of peak and background intensities (i.e., statistical counting errors in the spectra), calibration procedures, matrix effects, and attenuation (e.g., Gutknecht et al., 2010). However, the statistical counting uncertainties based on Poisson statistics were only available for and relevant to the metals measured by the Xact metals monitor. Further, these tended to be small compared to the other sources of error. Alternatively, the overall uncertainty of analytical instruments can be estimated by comparing the replicated results from reference materials (Rousseau 2001). The repeated measurements take into account the errors introduced by the instrument and counting statistics. Thus, the analytical uncertainty in the PMF analysis was empirically estimated through the use of experimental data. Additional uncertainty (i.e., 5%) introduced by the fluctuation of flow rates was also propagated into the overall relative analytical uncertainty in the PMF modeling.

The comparison of the measured statistical counting uncertainties and estimated analytical uncertainty used in the study are depicted in Fig. R1. The statistical counting uncertainties were proportional to the measured concentrations, but were much lower than the analytical uncertainty used in the PMF analysis. By using our approach, the analytical uncertainty used in the PMF analysis encompassed the uncertainty variations from spectra to spectra.

In the Supplement of the revised manuscript, the explanation for the analytical uncertainty of the Xact data has been added.

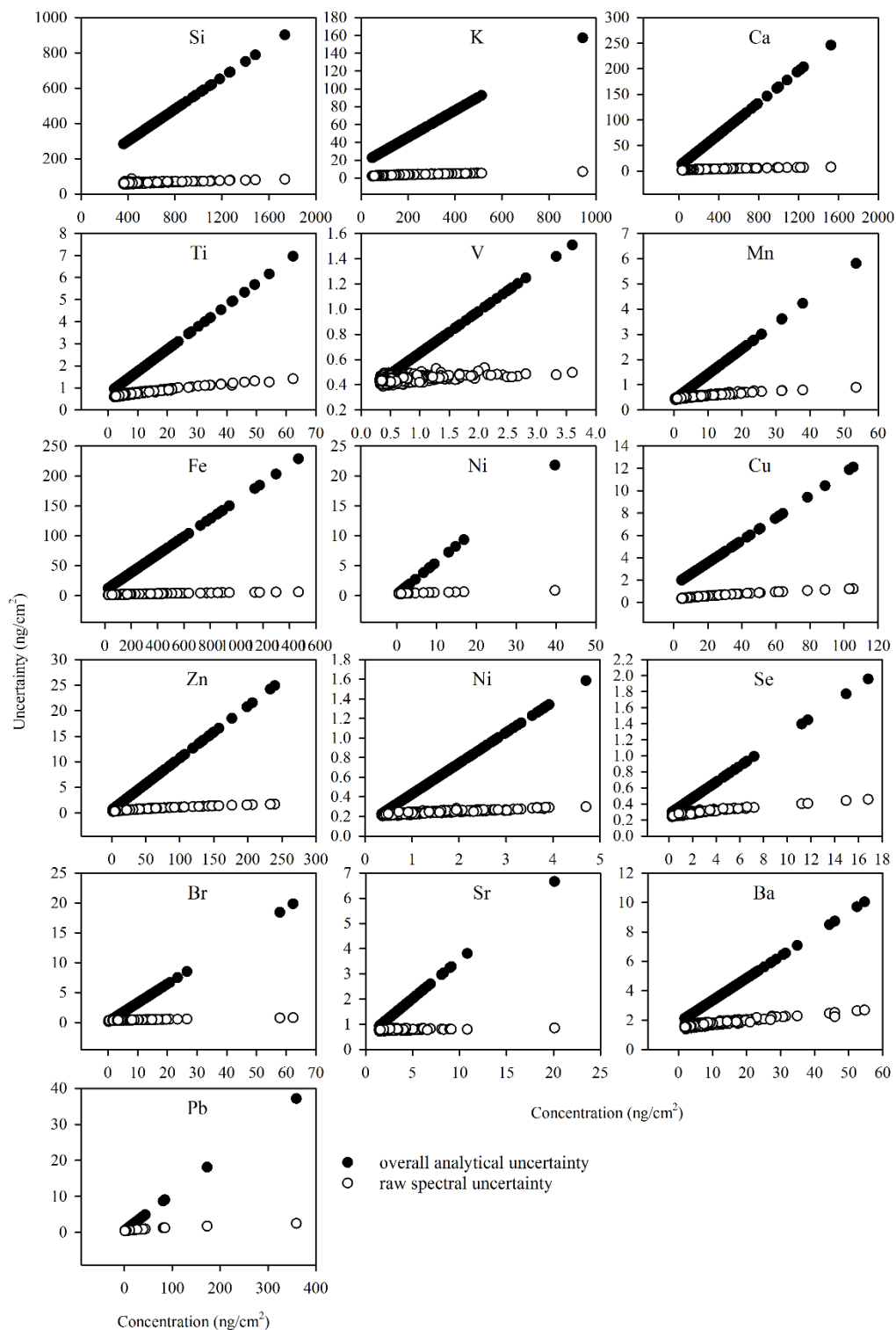


Figure R1. Comparison between measured concentrations (ng/cm² filter) and associated analytical uncertainties. The close circles represent the overall analytical uncertainties used for the PMF analysis, while the open circles represent individual spectral uncertainties introduced by the measurement process of X-ray peak intensities. Data below the detection limit were excluded for the comparison.

2) *PM_{2.5} Mass concentrations were measured at the 4th floor rooftop. Nothing is said about the positioning of the other instruments except they are 15 m apart from a main road. At which height? This is a crucial information. If the PM_{2.5} monitor and the other instruments are not positioned at the same height, the bias in the quantitative PMF results is relevant.*

All measurements were conducted at the sampling inlet of the SOCAAR lab, located 3 m above the ground level, except for meteorology and PM_{2.5} mass measurements sampled at the 4th floor (~20 m above the ground level). The sampling height have been described in Section 2.1 in the revised manuscript.

Unlike reactive and short lifespan ambient pollutants (i.e., NO_x, ultrafine particles), the vertical variations of PM_{2.5} mass within 17 m (roof vs. ground) has been found to be typically negligible based on coincident measurements at both heights. Fig. R2 shows the vertical variations in PM_{2.5} mass estimated by two optical particle sizers (OPS, TSI 3330) from May 1 to June 3, 2013, indicating minor vertical differences within 10%.

Further, as shown in Fig. S2 (b, d), good correlations were found between the PM_{2.5} mass measured at the roof level and the reconstructed mass measured at the ground level. Multiple linear regression was additionally used to estimate factor contributions in the PMF analysis as described in section 2.5. Given the small differences between the roof and ground levels, any potential biases due to any vertical variability in PM_{2.5} mass within 17 m was negligible with respect to the other uncertainties already accounted for in the analysis as shown in Fig. R2.

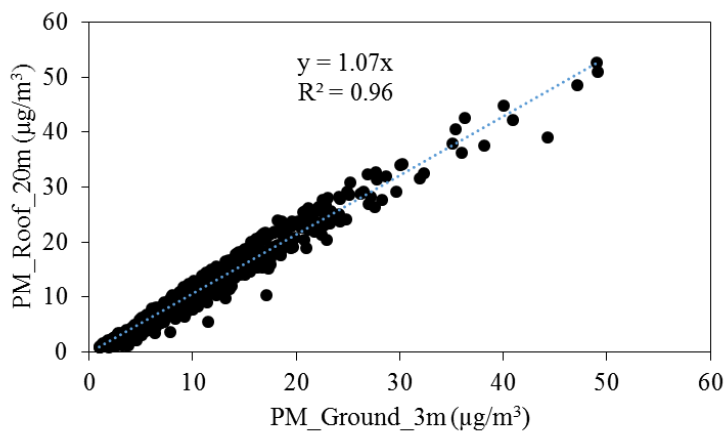


Figure R2. Comparison of hourly PM_{2.5} mass estimated by two optical particles sizers (TSI 3330) simultaneously measured at the ground level at 3 m and the roof level at 20 m from May 1 to June 3, 2013.

3) *In my opinion, the combination of PM₁ data for ACSM and PM_{2.5} data may introduce artefacts in PMF analysis. The reduction of the CE down to 0.5 may be arbitrary. The PM_{2.5} to PM₁ may be compound or day dependent. The authors present the regression for the winter period, but the results could be different in the summer period.*

Fig. S2 depicted the regression of ACSM mass to PM2.5 mass for both warm (a,b) and cold months (c,d). Good agreement was found between measured PM2.5 and reconstructed PM2.5 using the CE of 0.5 for the ACSM data in the both seasons. Further, the strong correlation coefficients indicate that the variability, even at the hourly level, was low. Typically, we need to assume the CE based on literature suggestions (i.e., CE=0.4~0.5). However in this study, we quantified an effective CE to take account of scaling of PM1 to PM2.5 for ACSM data (Page 2 Lines 3-12 in the Supplement).

Furthermore, Fig. S1 shows comparisons between the ACSM data and filter-based PM2.5 chemical speciation data, indicating good agreement with slopes and intercepts of 0.91 ± 0.10 and -0.08 ± 0.18 for sulphate ($r^2=0.84$) and 0.90 ± 0.07 and 0.17 ± 0.10 for ammonium ($r^2=0.93$). These results are comparable to those of other studies for size segregated PM mass and composition at urban sites (Theodosi et al., 2011; Pateraki et al., 2012). There was no significant difference in the concentrations of major chemical species (i.e., sulphate, nitrate, and ammonium) between PM1 and PM2.5. For instance, Pateraki et al. (2012) reported that the PM2.5/PM1 ratio for organic carbon, sulphate, nitrate, and ammonium ranged from 1.01 to 1.21 with a mean ratio of 1.11. In this study, as described in Page 2, Lines 8-9, the ratio of PM2.5 to PM1 was estimated based on particle size distributions measured by a collocated TSI Fast Mobility Particle Sizer (FMPS, TSI 3091) and Aerodynamic Particle Sizer (APS, TSI 3321) during the measurement period to evaluate the PM1/PM2.5 ratio. The mean and standard deviation of the ratio was 1.13 ± 0.16 , implying the difference between PM1 and PM2.5 and the day to day variation of the ratio was insignificant at this urban site. However, as this may not be the case at other sites that may exhibit significantly different aerosol chemical compositions, this type of empirical determination would be suggested for future studies in other locations.

4) The combination of stable markers like the metals and the organics (that maybe unstable at higher temperature) is an open problem in the PMF analysis; this may produce artefacts like the presence of factors which are simply related to the difference in the ratio between some markers in different seasons. The authors do not discuss such a problem that can be the origin of some of the problems in their results

Volatilisation and condensation can certainly create seasonal variability in the particle-phase concentrations of some species. This is often apparent in traditional filter-based PMF analysis involving metals and ions, in terms of nitrate. PMF accounts for this in terms on seasonality in nitrate related factor contributions. In this study, volatility of organic aerosols (OA) measured by the ACSM widely varies due to the complex mixture of compounds originating from a large variety of natural and anthropogenic sources, hydrocarbon-like OA (HOA) from traffic emissions and biomass burning like OA (BBOA), and low-volatile oxygenated OA (LV-OOA), and semi-volatile oxygenated OA (SV-OOA).

The resulting seasonality in the related factor contributions was discussed in the paper (Fig. 3). As with traditional filter based PMF, the strongest seasonality arose with nitrate related factors in winter and oxidised organic factors on summer.

5) Some important information are missing to have an idea of the quality of the PMF results. The graph of the measured PM_{2.5} mass vs the reconstructed PMF mass must be inserted at least in the SI.

We have added the correlation analysis between the measured PM_{2.5} (by a SHARP) and modelled PM_{2.5} mass predicted by using multiple linear regression (MLR) in the Supplement of the revised manuscript, indicating that the PMF-resolved sources effectively reproduced the measured mass and accounted for most of the variation in the measured PM_{2.5} mass.

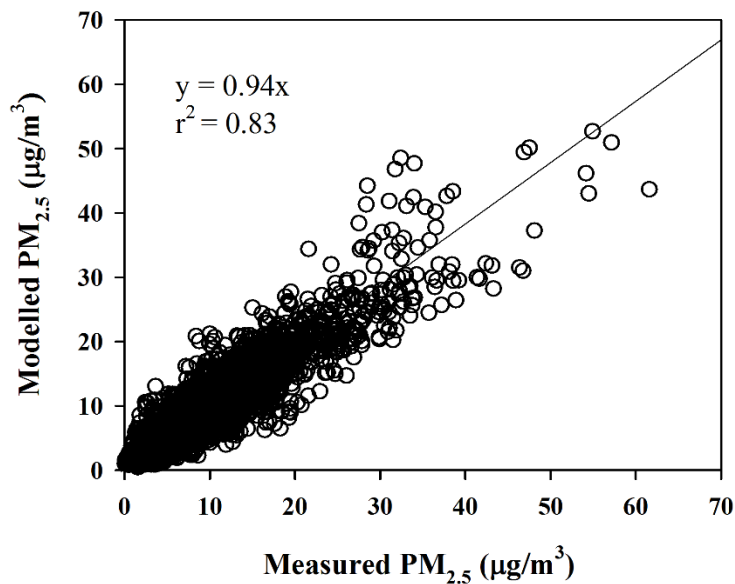


Figure R3. Comparison of hourly PMF-predicted PM_{2.5} mass by multi linear regression with the total PM_{2.5} mass measured by a PM_{2.5} monitor (SHARP 5030) for the 9-factor PMF_{Full} solution (4234 samples and 121 species).

Another necessary information is a table with the percentage of the mass of each element or compound explained by the PMF (by all the identified sources) respect to the measured element/compound mass (which is something different from what is reported in table 2).

The contribution of each species by factor (explained variation) in the 9-factor PMF_{Full} solution were shown in Fig. 1 in the original manuscript. We have added an additional summary table exhibiting the explained variations of key marker species for each factor in the Supplement of the revised manuscript.

Table R1. Contribution of key species to factor (explained variation) of the 9-factor PMF_{Full} solution.

9 Factor Solution	Key species (Explained Variation, %)
Road Dust	Ca (62%), Si (48%), Ti (4%), m/z 44 (9%)
Primary Vehicle Emissions	Ba (82%), Cu (67%), BC (36%), m/z 57 (13%)
Tire Wear	Zn (74%), Mn (40%)
Industrial Sector	Pb (74%), As (40%), BC (20%)
Cooking	m/z 55 (48%), m/z 57 (43%)
Biomass Burning	m/z 60 (53%), m/z 73 (35%), BC (10%)
Oxidised Organics	m/z 43 (48%), m/z 44 (46%)
Sulphate and Oxidised Organics	Se (80%), SO ₄ ²⁻ (68%), NH ₄ ⁺ (40%), m/z 44 (17%)
Nitrate and Oxidised Organics	NO ₃ ⁻ (88%), NH ₄ ⁺ (46%), m/z 44 (20%)

Furthermore, which is the percentage of the mass of each of the identified sources explained by the measured elements/compounds? If all the elements/compounds present in the source are measured this percentage must be 100%, otherwise less (e.g. for the road dust the oxygen from the oxides of Si, Ca, Fe, Ti is not measured) but sometimes PMF overestimates the mass of the source with a percentage above 100%. The sum of the percentage due to all the sources reported in tables 2 and 3. is 100%. Which is the percentage of the unexplained mass? It is quite strange if PMF reconstruct 100% of the mass. Without all these information, it is impossible to understand how good the PMF results are. PMF is a powerful instrument but it must be used with caution and many checks must be made before giving the results. All these information are missing.

The values in Fig. 1 (right y axis in red dots) show the explained variation of species in the PMF_{Full} solution. The contribution of each factor to the total PM2.5 are shown in Tables 1 and 3. As stated in Line 27-28, Page 5, the modelled concentrations of PMF-resolved factors were regressed against the measured PM2.5 mass (or total metal mass for PMF_{metal}, total organic mass for PMF_{org}) using multi linear regression (MLR). The MLR accounts for most of the variation in element oxides, water contents, and unexplained mass in the PMF analysis. Thus, the total percentage of source contributions in Tables 1, 3, and 4 should be 100%.

Finally, looking at fig. 1 I can see that the error bars for the contribution of all the typical markers are very high; this is unusual; I suppose therefore that the error on the contribution of each source, too, is very high, but it is not reported in any of the tables.

The bootstrap (BS) analysis was conducted to evaluate the uncertainties of the source profiles and the reproducibility of factors in every bootstrap (Paatero et al., 2014; Brown et al., 2015). The error bars of factor profiles in Fig. 1 were standard deviations of 100 BS runs for each species in each factor in the PMF results, where multiple PMF solutions are generated by using randomly resampled data sets. Since marker concentrations can often span a wide range of magnitude, it can be difficult to compare the uncertainties among species or solutions. As suggested by Paatero et al. (2014) and Brown et al. (2015), the interval ratio defined as the length of the 5th and 95th BS percentiles divided by the interval midpoint can be used to determine the reliability of identified factor. As shown in Table R2, higher uncertainty interval ratios were found for the key species of Primary Vehicle Emissions and Sulphate and Oxidised Organics factors. However, the interval ratios for key elements of each factor were still smaller than median ratios calculated for each factor.

In order to compare the relative uncertainty of PMF solutions, the interval ratios among 8-factor, 9-factor, and 10-factor solution was also compared. The overall uncertainty for the 9-factor solution was lower than the other solutions (Table R3). As noted in Line 15-25, Page 6, it was found to be likely stable for both 8-and 9-factor solution, but the split of Road Dust and Primary Vehicle Emissions factors was achieved in the 9-factor solution. Between the 8-and 9-factor solutions, all factors had smaller uncertainties in the 9-factor solution, except for two factors, suggesting the 9-factor solution was more stable with the lower uncertainties of the Road Dust and Primary Vehicle Emissions Factors.

The uncertainties for source contributions in Tables 1, 3, 4 in the original manuscript represent standard deviations of hourly contributions of each factor over the entire modelling period. Thus, the magnitude of errors in the factor profiles and contributions shouldn't be comparable. In fact, there is no straightforward way to estimate the modeling uncertainty of factor contributions as stated in Paatero et al. (2014).

The uncertainty interval ratio has been added in the revised manuscript as parts of PMF modelling validation.

Table R2. Uncertainty interval ratios of key elements by the error estimation of 100 bootstrap (BS) runs. The 5th and 95th percentiles were used as the BS uncertainty range for each factor profiles. The uncertainty interval ratios were determined by dividing the interval range by the midpoint of the interval.

9-Factor Solution	Marker Species	Interval Ratio*	Median Interval Ratio
Road Dust	Ca	0.97	2.74
Primary Vehicle Emissions	Ba	1.46	2.96
Tire Wear	Zn	0.38	2.46
Industrial Sector	Pb	0.41	1.62
Cooking	mz55	0.42	0.55
Biomass Burning	mz60	0.90	0.96
Oxidised Organics	mz44	0.78	1.39
Sulphate and Oxidised Organics	SO4	1.47	1.81
Nitrate and Oxidised Organics	NO3	0.14	1.55

*Interval ratio = (95th percentile - 5th Percentile)/Median

Table R3. Comparison of uncertainty interval ratios for each factor among three PMF solutions.

Factor	Marker Species	8-Factor	9-Factor	10-Factor
Road Dust	Ca	1.44 (Ca)/	0.97	1.30
Primary Vehicle Emissions	Ba	1.74 (Ba)	1.46	1.53
Tire Wear	Zn	0.34	0.38	1.00
Industrial Sector	Pb	0.47	0.41	0.41
Cooking	mz55	1.05	0.42	0.51
Biomass Burning	mz60	0.93	0.90	1.00
Oxidised Organics	mz44	1.35	0.78	0.71
Sulphate and Oxidised Organics	SO4	1.26	1.47	1.05
Nitrate and Oxidised Organics	NO3	0.13	0.14	0.13
Se-rich	Se	n/a	n/a	0.23

The lowest error intervals among the solutions are shown in bold. n/a: not applicable

Another investigation for the evaluation (i.e. random error in data values) of the PMF solutions is to examine the reproducibility of all factors in every bootstrap. Briefly, the BS factors are compared with the base run factors and then mapped to the base factor if the correlation is higher than a threshold ($r=0.8$ in this study). Table R4 summarizes the diagnostics of the BS analysis for three PMF_{Full} solutions (i.e., 8-, 9-, 10- factor solution) to compare the effect of random errors in the solutions. In the 9-factor solution, we found most bootstrap factors were well assigned to base factors in 82-100% of every bootstrap, except for Biomass Burning (i.e., 68%). This lower reproducibility of Biomass Burning is not surprising since the sporadic episodic event like a forest fire could be excluded in BS resamples and incorporated into other factors. The separation of Road Dust and Primary Vehicle Emissions from the 8- to 9-factor solution resulted in the presence of lower BS mapping for Road Dust in the 9-factor solution. However, the mapping percentage of Road Dust was still higher than a criteria suggested by EPA_{PMF} guide and overall reproducibility (i.e., average BS mapping percentages) for each factor in the 9-factor solution was higher than other solutions, suggesting the 9-factor solution was very reproducible and the optimal solution.

In addition to the BS analysis, displacement (DISP) analysis was conducted to evaluate rotational ambiguity in the PMF solution (Paatero et al., 2014; Brown et al., 2015). Multiple solutions may be generated with the same value of the object function Q due to rotational ambiguity. In DISP, each fitted element (only good species) in a source profile is displaced in turn from its fitted value until Q increases by a predetermined maximum change in Q. An uncertainty estimate for each element in each factor profile is thereby yielded and factor swaps may occur if factors change too much. Overall, there was no significant change in Q (dQ , $\%dQ < 0.1\%$) and no swapped factor in DISP in the solutions, indicating this nine-factor solution was a global minimum and well-defined PMF solution. A summary of diagnostic results of BS and DISP has been added in Supplement of the revised manuscript.

Table R4. Comparison of error estimation diagnostics for PMF_{Full} analysis.

	8-Factor Solution	9-Factor Solution	10-Factor Solution
Robust Mode	Yes	Yes	Yes
Seed Value	Random	Random	Random
# of Bootstraps in BS	100	100	100
R2 in BS	0.8	0.8	0.8
BS block size	579	579	579
DISP active species	All non-weak species	All non-weak species	All non-weak species
BS mapping	Biomass Burning 54%, Oxidised Organics: 91%, Cooking: 95%, Others: 99-100%	Biomass Burning 68%, Road Dust 82%, Others 99-100%	Se-rich: 61%, Biomass Burning 75%, Road Dust: 86%, Primary Vehicle Emissions: 96%, Others: 99-100%
Average BS mapping	92%	94%	91%
DISP %dQ	<0.1%	<0.1%	<0.1%
DISP swaps	None	none	None

In addition to the BS and DISP analyses of EPAPMF, the sensitivity of the PMF solution was examined using perturbations in uncertainty estimates. A detailed description of the perturbation approach can be found elsewhere (Christensen and Schauer, 2008). In this study, a perturbed uncertainty matrix was created by multiplying each original uncertainty by a random draw generated from a log-normal distribution with a mean of 1 and a standard deviation of 0.75. PMF solutions were obtained using the 50 perturbed uncertainty matrices and compared to the original PMF solution in terms of the similarity of source contributions and profiles. Box plots of the average contribution using the 50 perturbed uncertainty matrices are shown in Fig. R4. Overall, the average source contribution obtained from the perturbed uncertainty remained relatively stable. The absolute deviation between the original source contributions ranged from 2% (i.e., Nitrate and Oxidised Organics) to 25% (i.e., Industrial Sector) with an average of 10%, which is much smaller than the errors reported by Christensen and Schauer (2008). Fig. R5 depicts the similarity of different source profiles obtained using the original uncertainty and the perturbed uncertainty matrices. The correlation of the explained mass matrix represented by the percentage of species sum was estimated to illustrate the similarity in factor profiles. As shown in Fig. R5, the correlations ranged from 0.92 to 0.94 with an overall mean of 0.94, indicating a very strong stability of source profiles in the PMF solution. The variations of the correlation remained between 0.8 and 1.0, with Primary Vehicle Emission and Biomass Burning profiles having the lowest stability and the Secondary and Oxidised Organics or Nitrate and Oxidised Organics the highest. As discussed earlier in the BS and DISP error estimation of the PMF solution, Road Dust might be a less stable factor since the isolation of Road Dust and Primary Vehicle Emissions occurred in the 9-factor solution and there were confounding

elements between two factors. Overall, the PMF solution selected in our study was based on and supported by rigorous analyses to ensure that this solution was stable and well-defined. The details and outcomes of these analyses were originally omitted for the sake of brevity but have been added to the Supplement of the revised version.

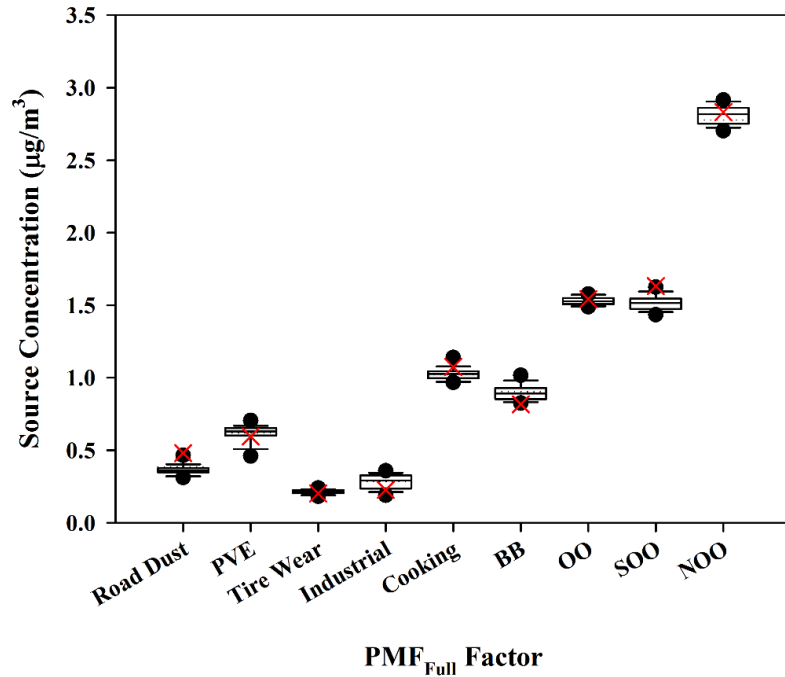


Figure R4. Average source contributions associated with 50 perturbed uncertainty matrices generated by multiplying the original uncertainty by random values from a log-normal distribution with a mean of 1 and a standard deviation of 0.75. The average contribution obtained using the original uncertainty is denoted with an X. Median concentrations are represented by the line inside each box; the top and bottom of each box represents the 75th and 25th percentile values, and the top and bottom of each whisker represent the 95th and 5th percentile values, respectively. PVE: Primary Vehicle Emission, Industrial: Industrial Sector, BB: Biomass Burning, OO: Oxidised Organics, SOO: Sulphate and Oxidised Organics, NOO: Nitrate and Oxidised Organics.

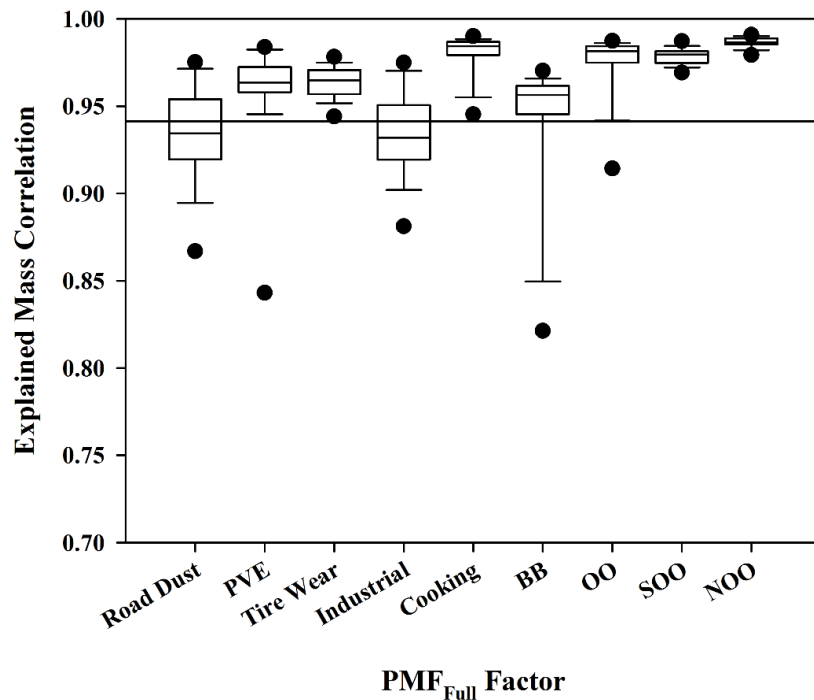


Figure R5. Average explained mass correlation between the original source profile and the perturbed source profiles obtained using 50 perturbed uncertainty matrices generated by multiplying original uncertainty by random log-normal distribution with a mean of 1 and a standard deviation of 0.75. Median concentrations are represented by the line inside each box; the top and bottom of each box represents the 75th and 25th percentile values, and the top and bottom of each whisker represent the 95th and 5th percentile values, respectively. The horizontal black line represents the mean of the correlation. PVE: Primary Vehicle Emission, Industrial: Industrial Sector, BB: Biomass Burning, OO: Oxidised Organics, SOO: Sulphate and Oxidised Organics, NOO: Nitrate and Oxidised Organics.

6) *The identification of the road dust source is questionable. The error bars for all the characteristic markers are very high.*

We agree that the uncertainty in the Road Dust factor profile was higher than that of the other eight factors however, its identification was still very robust. As discussed in the previous comment, the error bars in the source profiles represent the standard deviations of the BS analysis not the confidence interval. In the BS analysis Road Dust was mapped 82% of 100 BS runs, which was lower than other factors but remained in an acceptable range. As stated in Line 15-25, Page 6, the Road Dust and Primary Vehicle Emissions (PVE) factors were not separated in the eight-factor solution. Although the BS reproducibility for Road Dust was relatively lower than other factors in the nine-factor solution, this was still above the BS mapping criteria (80%) suggested by EPAPMF and the overall stability of the nine-factor solution was better with a very small decrease in Q and no swapped factors in DISP as compared to 8- and 10-factor solution as discussed in the previous comment. More importantly, the interpretation for the Road Dust and Primary Vehicle Emissions factors were more physically meaningful since diurnal and seasonal

variabilities of two factors appeared to be distinct and the fraction of $m/z/57$ in the PVE profile was higher in the nine-factor solution.

In the revised manuscript we have added detailed descriptions for the evaluation of the PMF solution.

The presence of V (50% of its mass in this source is unusual).

Agreed. As stated in line 16-19, Page 12, in the nine-factor solution some of Ni and V ended up mixed into the Road Dust factor. A Ni-V factor was resolved in an 11 factor solution, but the stability of the solution was very poor. Thus, we explained as a possible limitation of the PMF_{Full} analysis in the original manuscript (Line 16-19, Page 12).

The percentage of OA is very high compared to what is normally found in many articles (and higher respect to the primary vehicle emission source).

In most previous studies, thermal analysis of bulk organic carbon rather than OA mass spectra have been used for the source apportionment of road dust/mineral dust factors. In this study, different types of OA were associated with the Road Dust and Primary Vehicle Emissions factor. The OA associated with the Road Dust was found to be low volatility oxygenated organic aerosol (LV-OOA), which is highly aged OA, whereas the Primary Vehicle Emissions factor was distinguished by high loading of hydrocarbon-like organic aerosol (HOA). As stated Line 26-32, Page 7, the Primary Vehicle Emissions factor could be a mixture of tailpipe and non-tailpipe emissions with the co-presence of metals, black carbon, and HOA in the profile.

Amato et al. (2011; 2014; 2016) have consistently reported that organic carbon (OC) is abundant in road dust samples, accounting for 11 to 21 % of total PM₁₀ mass. OC was also one of major components in road/mineral dust and non-tailpipe emissions factors (Amato et al., 2011, 2014, 2016). Further, the contribution of OA (i.e., $1.8 \times \text{OC}$) will be larger than the OC fraction. Moreover, the fraction of OA in PM_{2.5} should be higher than the OA fraction in PM₁₀ since crustal elements are typically less abundant in PM_{2.5}. In most PMF studies, OC, one of the largest PM_{2.5} components, is used for source apportionment as a marker element for traffic-related sources. However, as reported in numerous PMF studies using OA measured by the aerosol mass spectrometry (AMS) or aerosol chemical speciation monitor (ACSM), much of this OC can be secondary and the contribution of primary OA in traffic emissions (i.e., HOA) is typically lower than other sources (e.g. 19% vs. 81% in this PMF_{org} result). One of the main features of this study was the apportionment of detailed organic fractions rather than bulk OC mass (or estimated Organic Matter). No previous studies have used mass spectrometry based analyses to examine the contribution of OA fractions (e.g. LV-OOA) in road/mineral dust and non-tailpipe emissions sources, thus supporting evidence based on other studies is not yet available. Thus, our study will provide needed data for comparison of the many future PMF studies that we anticipate will use a similar mix of high time resolution mass spectral and metals data.

No BC is present in this source at variance with the articles reported as references.

The BC was mostly apportioned to the primary vehicle emissions rather than the road dust. This is at variance with past studies as these factors have typically not been separated based on 24h filter data. This separation was made possible by the higher time resolution data that allowed the diurnal patterns of the primary vehicle emissions and road dust factors to be resolved (see Fig. 2). As shown in Figs. F4 and F12, the diurnal pattern of BC shows a dominant peak in the morning rush hours and strong correlations with the diurnal patterns of the Cu-Ba and Mn factors ($r=0.81$ and 0.92 , respectively) in the PMF_{metal} analysis, which were key markers for the Primary Vehicle Emissions factor in the PMF_{Full} analysis.

The time trend is not similar to that of traffic or of the typical traffic related gases. There is a similarity just at the beginning of the morning, but no decrease after the rush hour and it starts decreasing at 3 pm while traffic start decreasing at 6 pm.

Resuspension of road dust can be induced by vehicles but meteorology also plays a role. The diurnal peak in the morning was consistent with the traffic count in the morning rush hour while the persistence into the afternoon was related to atmospheric conditions. As stated in line 4-6, Page 7, meteorological parameters (i.e., dry road surface, low relative humidity and high temperature) contributed to the diurnal pattern of the Road Dust factor. The resuspension of road dust increased as temperature increased and the relative humidity dropped, implying a more favorable conditions in the midday rather than in the evening rush hours. Consequently, the diurnal pattern for the Road Dust factor did differ from that of traffic-related gases (e.g. NO_x and CO in Fig. S5) which had patterns similar to that of the Primary Vehicle Emissions factor. Both emission rates (e.g. traffic density) and removal rates (e.g. wind speed and chemistry) govern the temporal patterns of each pollutant. Thus even pollutants primarily emitted by vehicles (e.g. NO_x) do not exhibit diurnal patterns that exactly match traffic patterns.

Finally, it is known that the contribution of the road dust is mainly in the coarse fraction while the exhaust component is mainly in the PM_{2.5} fraction. It seems quite unreliable that the road dust contributes similar to the exhaust in the PM_{2.5} fraction or less if we consider also the tire wear source (see below for the problems in the identification of that source). This is probably due to the weakness of the profiles of the identified sources or to the fact that this source is not a traffic related source. In the reference Amato et al (2016) a similar source was identified but it was attributed to a local soil source related to anthropogenic activities, among which construction works. The weekend/weekday ratio would be the same as that of the traffic source. Which are the Enrichment Factors respect to Si of the crustal elements?

We acknowledge the reviewers point that the composition of the Road Dust factor is similar to that of soil particles. As described on page 6 and 7 of the original manuscript, the road dust certainly contained components often associated with soil (e.g. Si and Ca) and we described this factor as a mix of soil and vehicle abrasion related particles. However, the chemical profile and temporal patterns of this factor were much more consistent with road dust

In regards to this factor's profile, it agreed well with that of local road dust samples collected throughout Toronto. Specifically, road dust and soil dust samples were directly collected at 17 roadside locations (i.e., road dust) and 4 urban parks (i.e., urban soil dust) across Toronto area. PM_{2.5} re-entrained from these samples was analyzed by the Xact monitor for metal composition. A distinct difference was observed in the metal profiles of the road dust and urban soil dust. As shown in Fig. R7, the profile of the average road dust sample was characterised by a high Ca loading and relatively lower Si, which was consistent with the chemical profile of the Road Dust factor. Expressing this difference in terms of ratios, as suggested by the reviewer, the ratios of Si to Ca for road dust and urban soil dust samples were 0.78 ± 0.13 and 4.16 ± 0.19 , respectively. In the PMF_{Full} analysis, the Si/Ca ratio of the Road Dust factor was 1.02, which is much closer to the ratio of the road dust sample. Thus the Road Dust Factor was much closer in composition to Toronto road dust than Toronto soil dust.

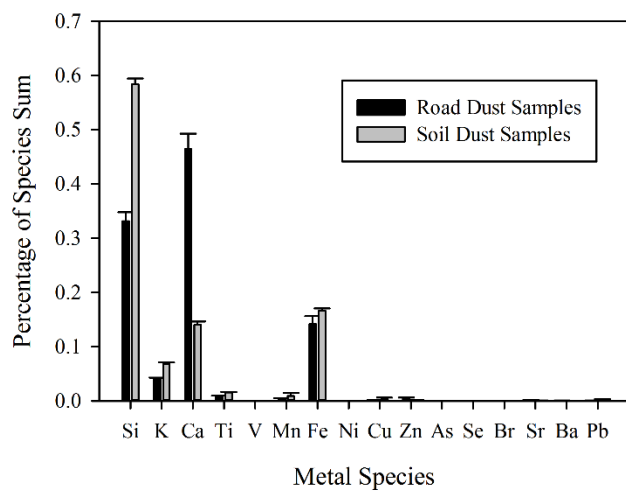


Figure R6. Average metal profiles of road dust and soul dust samples collected at 17 road sides (Road Dust) and 4 urban parks (Soil Dust) in Toronto. Error bars represent the 95% confidence interval.

In regards to the temporal pattern of this profile, we agree with the reviewer that the weekday/weekend pattern demonstrated that its emission was predominantly anthropogenic rather than natural and thus we stated that its origin was not predominantly due to natural wind entrainment of soil dust. We certainly considered this but rejected the possibility that these emissions were mainly due to emission of soils from construction sites. Firstly, the early 6:00 am rise in emissions (Fig. 2) indicated that the dominant mechanism underlying these emissions was not likely construction sites; heavy digging at construction sites does not start at 6:00 am in the city (It's not even allowed to start before 7 am). Secondly, the seasonality of the Road Dust factor was also inconsistent with construction being the dominant source; construction is typically more intense in summer months in Toronto while the Road Dust factor was higher (Fig. 3) in spring (April and May) than in summer (June and July) and the morning rush hour peak was observed during the both the winter and summer campaigns.

In regards to the relative magnitudes of the Road Dust and Vehicle Emission factors, Amato et al. (2016 ACP 16, 3289-3309) also reported the contributions of the non-exhaust emissions on PM_{2.5} ranged from 1% to 8% at multiple European cities. Moreover, the ratio of vehicle exhausts to non-exhaust emissions in PM_{2.5} fractions highly varied by locations, from 14.5 to 0.7, indicating that a higher contribution of non-

exhaust emissions as compared to direct traffic emissions is quite plausible. It is again emphasised that Primary Vehicle Emissions factor encompassed only primary emissions of PM_{2.5} and it did not account for secondary formations of PM_{2.5} (i.e., formation of secondary organic aerosol and nitrate from traffic induced NO_x). In the revised manuscript we have added a statement to highlight the contribution of the Primary Vehicle Emissions factor as primary emissions.

7) The identification of the Primary vehicle Emission source is more sounded, looking at its time trend in comparison with that of the traffic related gases or of the traffic counts; however also in this case the profiles shows some problems. Again the errors for the main markers are very high; a comparable contribution (micrograms/m³) from Si, Ca, Fe and BC is unreasonable in this source, where OC and BC are the main components (see many articles on PMF identification of traffic sources, e.g. the references reported in the article like Amato et al., 2016). This could be due to the combined use of data coming from different instruments, to the quality of the data or to the error estimate. The percentage of OC in this source is also too low (27%).

Ca, Fe, and BC are often associated with traffic-related sources. BC typically originates from incomplete combustion in diesel, and more recently, gasoline direct injection engines. In fact, the BC contribution in the factor profile was an order of magnitude higher, rather than comparable to, Ca and Fe (Fig 1). This is reasonable as Ca and Fe originate from lubricating oil degradation and engine wear in gasoline and/or diesel engines. Again, this study is different from other past PMF studies using OC and EC as key markers for vehicle emissions. As reported in many AMS/ACSM based PMF studies covering many locations, secondary LVOOA defined by regional scale aged organics constitutes the majority of OA, whereas the contribution of primary traffic-related OA, HOA is typically smaller than other OA sources. In this study, PMF_{org} results showed that HOA accounted for 19% of total OA fractions as shown in Table 4. This very reasonable as it describes only the primary vehicle emissions.

We agree that the level of Si may be inflated in the factor profile. Due to the high instrument background for Si, higher analytical uncertainty with downweighting was assigned to Si in the PMF analysis. As a result, Si became susceptible to cross-apportionment. Due to similar confounding metals between the Road Dust and the Primary Vehicle Emissions factor in the 9-factor solution, as stated in Line 15-17, Page 6, Si became spread between these factors and could not be fully resolved in the solution. In this study, we did not use any constraint to pull down specific species in the PMF_{Full} profile in order to enable comparison with the results from the PMF_{metal} and PMF_{org} analyses. The error estimation in the solution for random error in data values and rotational ambiguity and the uncertainty perturbation analysis support that the Primary Vehicle Emission factor was a reasonably good and well-defined factor. We have added a note regarding this uncertainty regarding the level of Si in this factor in the revised manuscript.

8) The identification of the Tire Wear source is not clear at all. In fig. 2 there is a maximum common with that of NO_x or CO but the time pattern is completely different and the weekday/weekend ratio may be typical also of industrial activities. I would not say that $r^2 = 0.32, 0.43, 0.17$ means "a strong correlation between the Tire Wear factor and traffic related pollutants" (p. 8 l.8). Furthermore, as reported in literature, most of the mass from the tire wear is due to the carbon component, Zn is a typical marker but it is a trace, not a main constituent (and Fe gives even a higher contribution).

We agree that ambiguity remains in the identification of the Tire Wear factor. We did discuss in Line 17-21, Page 8 in the original manuscript, the possibility that this was a mixed factor with that may have included contributions of an unknown industrial source:

“However, one contradiction was evident. The Tire Wear factor’s higher correlation ($r=0.37$, $p < 0.01$) with SO_2 was not consistent with traffic given the low sulphur fuel used in Canada. Closer investigation indicated that the measurement site was also being affected by occasional short term spikes with high Zn and SO_2 suggesting that mixed into this factor were plumes from an unknown local industrial source. No plausible source could be identified and the origin of these plumes is still under investigation.”

The issue here is that there are no known local industrial sources of Zn emissions in the downtown Toronto. Further, the contribution was higher in the winter (Jan-Feb) and there was a minor peak in the early morning, 3-4 am, which is not typical industrial activities. The factor also had a high loading of BC, suggesting vehicle emissions. In a long-term PMF study using 24-hr integrated filter data over 10 years, a similar factor characterized by Zn and Mn was also observed in Toronto (paper in preparation). Thus we have considerable evidence pointing to the presence of a distinct source of zinc emissions in Toronto. Tire Wear appears to be the most reasonable explanation based on the available information. However, we acknowledge the need to better reflect the remaining ambiguity. Thus, the statements in Lines 7-9 and 21-23, Page 8 have been revised as follows:

“It is interesting to note that despite the correlation between the Tire Wear factor and traffic-related pollutants, (i.e. UFP, NO_x), a weaker correlation was observed with vehicle count.” ... “In summary, the PMF_{Full} analysis allowed identification of a factor that was believed to originate mostly from tire wear. However, ambiguity remained in regards to this identification; mixed in with this were plumes from another source that could be recognised with the hourly time resolution data but not separated into a distinct stable factor.”

In regards to the factor profile it should be noted that Zn and Fe were in fact only minor components present at about 1% and that loading of BC in this factor profile (Fig. 1) was much higher than those of Zn and Fe. These loadings are given by the bars in Fig. 1 which are plotted on the log scale on the left hand side.

9) From what I have reported above, the conclusion (p. 14 l. 7) “the traffic related sources accounting for 17% of $\text{PM}_{2.5}$ ” is not justified.

As discussed in the previous comments, it is sufficient to consider the three factors, Road Dust, Primary Vehicle Emissions, and Tire Wear as traffic-related sources. We have reworded this statement to “Primary emissions from traffic related sources, accounting for 17% of $\text{PM}_{2.5}$,”

10) The Industrial sector source is identified by Pb and As, but the time trend of those two elements shown in fig. S4 is completely different.

The diurnal plots represented by the average concentrations for the entire measurement period are useful for identifying sources related to routine anthropogenic activities and/or photochemistry. The concentration of As was typically very low and the average hourly As concentration in the diurnal plot were mostly below the detection limit. However, the time series plot of Pb and As (Fig. R8) shows that there were sporadic increased Pb and As, presumably associated with the impact of sporadic industrial plume events mostly lasting for a couple of hours. In terms of their overall time series data, the concentrations of Pb and As were highly correlated (Spearman $r = 0.52$, $p < 0.00$).

The time series plot of Pb and As has been added in the Supplement of the revised manuscript.

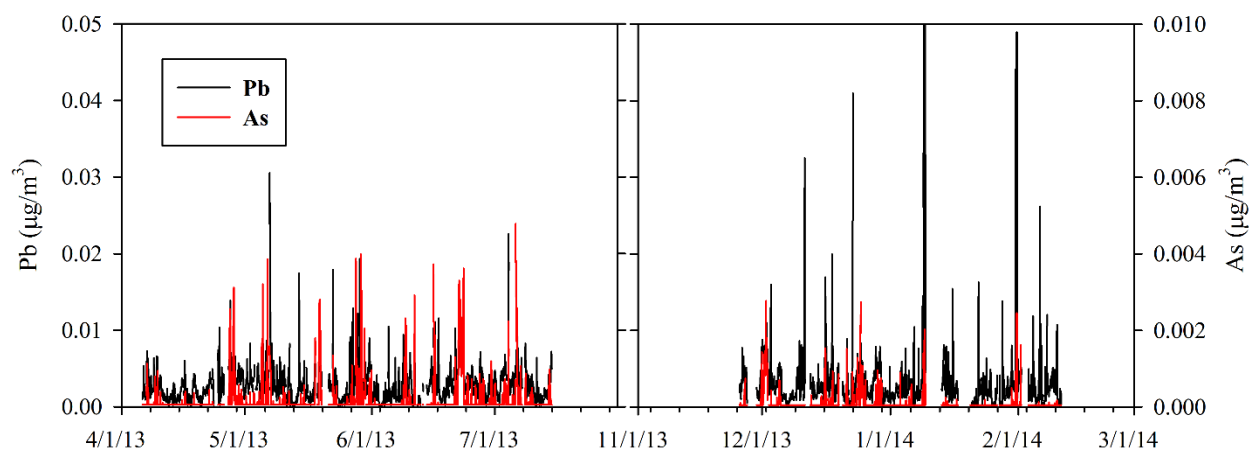


Figure R7. Time series plots of hourly Pb and As concentrations. The maximum concentration of Pb on January 9, 2014 was excluded from the chart.

11) Which are the metals that help in the identification of the cooking source as reported at p. 9 l. 3? There are plenty of articles that identify the cooking source with only organics.

We report that the inclusion of metal species in the PMF analysis enhanced the isolation of COA and HOA, which are typically hard to separate due to similar organic fragments. Specifically, including metals such as Cu and Ba helped to pull HOA into the Primary Vehicle Emissions instead of the Cooking factor. As shown in Fig. S15, PMF analysis with only the organics data yielded peaks at noon and in the evening for both HOA and COA. In the PMF_{Full} analysis, the Primary Vehicle Emissions factor associated with HOA showed a clear diurnal trend with a strong morning rush hour peak, whereas the Cooking factor related to COA displayed clear noon and evening peaks (Fig. 2).

12) In the Biomass Burning source the absolute contribution of K (a tracer) is higher than that of BC, which is quite strange looking at the literature

In the PMF_{Full} analysis, the contribution of K (0.015 $\mu\text{g}/\text{m}^3$) in the Biomass Burning factor was actually lower than that of BC (0.056 $\mu\text{g}/\text{m}^3$). These absolute contribution is shown by the bars in Fig. 1 and the log scale on the left hand side.

13) Why the nitrates source has such a correlation with SO₂, which is far higher than that of the sulphate source?

The reviewer has noted an interesting paradox and their question points to the need for greater explanation in our manuscript. As shown in Table S3, the monthly average concentrations of SO₂ in warmer months were below the detection limit, <0.1 ppb and higher concentrations were found in colder months. The sulphate factor shows the opposite seasonality reducing the strength of the correlation. Further, due to the closure of local large SO₂ sources (i.e., coal-fired power plants), SO₂ concentration in Toronto have substantially decreased over the last decade (Ontario Air Quality Report, 2014). As a result, minor industrial sources of SO₂ now dominate. These tend not to produce much secondary sulphate in Toronto, and most of the sulphate is long range, mainly originating from coal-fired power plants located several hundred kilometers southwest of the monitoring site (Jeong et al., 2013). Due to more abundant photochemical reactions in summer, little SO₂ remains in these long range air masses. Thus in summer the SO₂ and sulphate originate from different sources that are not associated. In contrast, the residence time of SO₂ can longer in the colder months due to the less oxidation of SO₂ to sulphate. The formation of nitrate from NO_x produced by industrial sources also can be enhanced in the winter months due to more favorable conditions of the formation of ammonium nitrate (i.e., low temperature), indicating SO₂ and nitrate exhibited the same seasonal patterns.

Conditional probability function analyses for SO₂, NO_x, CO and UFP have been added in the revised manuscript. As shown in Fig. R9, the strong and same directionality (i.e., southwest) of CPF were observed for both SO₂ and the Nitrate and Oxidised Organics factor (Fig. S9). In the revised manuscript the interpretation of high SO₂ correlation with the Nitrate and Oxidised Organics factor has also been described.

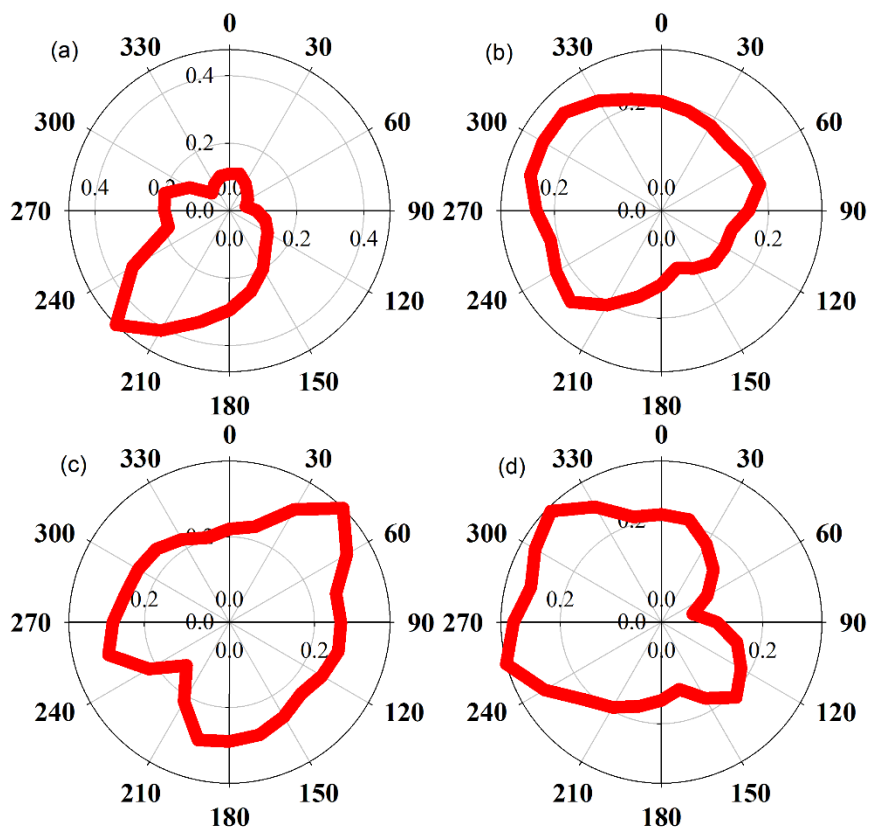


Figure R8. Conditional probability function (CPF) plots for SO₂ (a), NO_x (b), CO (c), and UFP (d) during the entire measurement period. The CPF threshold was set to the top 25th percentile.

14) All the discussion on the PMF with only metals and ACSM data is not very useful. The quality of the metal data is not very good. Si has background problems with a high noise (and Al is not measured, like Na and Cl), V, Ni, As, Sr are present only in very few cases and also Se is present in less than 30% of the cases. I am not sure they can be considered as good variables (no information on good or weak variables is reported). With only 11 “good” elements, they found 8 factors! In the discussion about the identification of the different sources, there are problems similar to the ones reported for the “full” analysis. The identification of 4 traffic sources is arbitrary. I understand that S was not used in the PMF_{full} analysis because there is the ACSM sulphate, but there is no reason for not using it in the PMF_{metals} analysis. Finally, the authors contradict themselves saying “PMF_{full} analysis did not always enable better resolution of factors”.

Many past source apportionment studies have used metal only or organic fragment only (e.g., Ulbrich et al., 2009; Richard et al., 2011). One of the main objectives of this study is to evaluate the PMF solution using the combination of these data. The PMF solutions with metals only or ACSM organics only are thus presented to compare and contrast the PMF solutions.

In terms of metal data, we initially screened 16 key elements (as tracers) among the 25 metal species measured by the Xact metals monitor, based on previous source apportionment studies using 24-hr integrated filter data in Toronto. The calculation of signal-to-noise ratios (S/N) and the determination of good ($S/N \geq 1$) and weak ($S/N < 1$) species in the PMF modeling were explained in the Supplement (Line 11-18, Page 3). Among 16 metal elements, 5 elements (Si, V, Ni, As, and Sr) were considered as poor species based on their S/N ratios and their analytical uncertainties were increased by 3. Although these poor metal species had high percentage of data below the detection limit (BDL), in the PMF modeling BDL is still valuable to identify episodic sources lasting for a couple of hours or less in a busy urban area. For this reason, these minor elements were used as variables in the PMF modeling with higher analytical uncertainties. Again, unlike 24-hr integrated filter data, the high temporal variability of hourly metal concentrations provided additional correlational structure to resolve sources more effectively. Detailed description of the determination of the 8-factor solutions for PMF_{metal} was provided in Line 15-22, Page 11. The 8-factor solution was chosen due to the high solution stability evaluated by EPAPMF BS and DISP analyses although the 6-factor solution was also examined as a physically reasonable solution.

The BS and DISP analyses the PMF_{metal} and PMF_{org} solutions were conducted and summarized in Table R5 and have been added in the revised manuscript.

One of the main objectives is to evaluate the PMF_{Full} solution by comparing the PMF_{metal} and PMF_{org} solutions under the same variables in the PMF analyses. In fact, we have examined the PMF_{metal} analysis with S and found that the majority of S was apportioned to the Se-rich and Ni-V factors related to fossil-fuel combustion, indicating that there was no change in the number of factors and the stability of the solution.

As compared to the 8-factor PMF_{metal} solution, the factor characterized by high Ni and V loading was not able to be resolved in the 9-factor PMF_{Full} solution. As stated in Line 15-22, Page 11, the deconvolution of the Ni-V factor was also unstable in the PMF_{metal} analysis. Through this statement we acknowledged a possible limitation of the PMF_{Full} analysis, which may not good at the identification of factors associated with minor elements with high analytical uncertainty.

Table R5. Comparison of error estimation diagnostics for PMF_{metal} and PMF_{org} analyses.

	PMF _{metal}	PMF _{org}
# of Factors	8	5
Robust Mode	Yes	Yes
Seed Value	Random	Random
# of Bootstraps in BS	100	100
R2 in BS	0.8	0.8
BS block size	157	440
DISP active species	All non-weak species	All non-weak species
BS mapping	All: 99-100%	BBOA: 80%, HOA: 81%, LVOOA: 99%, COA: 100%, OOA: 100%
Average BS mapping	99%	92%
DISP %dQ	<0.1%	<0.1%
DISP swaps	none	none

15) p 13 l- 29-35 The combination in the PMF of stable markers like K with unstable markers (at higher temperatures) like the organics may be problematic. This could explain the different correlations.

Lee et al. (2016) observed a strong ion signal for K with mass spectra characterized by low molecular weight organic species during a biomass burning event in Toronto using single-particle measurements from a Soot-Particle Aerosol Mass Spectrometer coupled with a light scattering module (LS-SP-AMS). Furthermore, a combination of K and organic carbon fractions has been used to identify biomass burning factors in many filter based PMF studies.

Minor comments:

1) Which program was used to fit the X-Ray spectra?

The Xact metals monitor (625, Copper Environmental) uses XRS-FP to process the raw X-ray spectra.

2) *How were the raw aethalometer data were corrected (e.g. which mass absorption coefficient was used?)*

A 7-wavelength Aethalometer (AE-33) is incorporated with real-time loading effect compensation algorithm based on dual spot measurements of optical absorption. BC concentrations calculated from the change in optical attenuation at 880 nm using the mass absorption coefficient of 7.77 m²/g (manufacturer default value).

This description has been added in the revised manuscript.

3) *What does it mean that "only good species" (p 5 l. 13) were taken into account when calculating the Q/Qexp ratio? This is a number that is given by the program considering the results as a whole*

The theoretical Q (Q_{exp}) can be estimated and given by

$$Q_{\text{exp}} = (n \times m) - p(n+m)$$

where n is the number of samples, m is the number of input elements, and p is the number of sources. The number of species, m should be only good species determined by the signal/noise ratio as clearly described in the EPAPMF guide (<https://www.epa.gov/air-research/epa-positive-matrix-factorization-50-fundamentals-and-user-guide>).

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