Responses to Reviewers

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

Author(s): C.-H. Jeong et al.

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 #3

The study investigated the sources of the main elements of the PM2.5 based on hourly resolved particulate matter (PM) speciation during two campaign periods by means of Positive Matrix Factorization (PMF) analysis. Separate PMF analyses were conducted using the trace metal only data (PMFmetal) and organic mass spectra only (PMForg), and compared with the PMFFull results.

The results presented here are not so innovative for the scientific community working on air quality studies and of difficult understanding because there are many problems to interpret the results. The PMF analysis needs to be performed with a study based on PM filters sampled every 24 h to identify and apportion the emissive sources present on a given area and to compare also the obtained results even with similar source apportionment studies performed in other sites.

Unlikely other source apportionment studies using 24-hr integrated filter data, hourly data for the chemical species of PM2.5 can be advantageous to identify short-lived sources that have high temporal variations. In addition, PMF is widely used for organic aerosol (OA) mass spectra measured by aerosol mass spectrometer (AMS, Aerodyne) or aerosol chemical speciation monitor (ACSM, Aerodyne) to resolve types of complex OA, one of a large group of compounds in PM2.5. However, without additional information it is not possible to identify the origins of OA in relation to other PM2.5 sources and apportion various OA factions (i.e., low-volatile, semi-volatile organics) to these PM2.5 sources. Metal speciation data have also been used for source apportionment studies (e.g., Dall'Osto et al, 2013). Trace metal based chemical profiles can be very useful for resolving and identifying sources more effectively in the PMF analysis. However, due to the minor contributions of trace metals on total PM2.5 mass (i.e., ~1% of total PM2.5 mass), it is impossible to quantify source contributions of the identified PM2.5 sources using metal data only.

To the best of our knowledge, this is the first reported study to combine OA, inorganic species (sulphate, nitrate, ammonium), black carbon, and trace metal data measured at high time resolution for source apportionment. Furthermore, the effectiveness of the PMF solutions was evaluated in this study by comparing and contrasting three PMF solutions using the combined data, OA only, and metal only. Thus,

we respectfully argue that our methodology and findings are certainly novel and quite innovative. Further the results of this study provide additional insight into PM2.5 sources related to their high temporal variations, various OA fractions, and metal-rich factors. This new knowledge should support the development of control strategies for these sources and thus is of value to the air quality community.

A chemical mass closure is not performed due to the lack of a complete chemical speciation of the PM2.5 on the same filters: the measured elemental concentrations represent a minor fraction of PM.

Chemical mass closure was performed as shown in the Supplement (Line 23-30, Page 2, Fig. S2) of the original manuscript. In this study, organics aerosol, sulphate, nitrate, ammonium, black carbon, and trace metals were used in analysis. As shown in Fig. S2, good correlation and agreement were found between the reconstructed mass and total PM2.5 mass measured by a collocated SHARP during the entire period (4234 hourly samples).

Certainly the metals alone represented a minor fraction of the PM which is why these data were combined with the data from the other instruments in the full analysis. No mass closure was performed for the PMF_{metal} for this reason. However, three PMF analyses, PMF_{Full}, PMF_{org} and PMF_{metal} were separately conducted and mass closure was done for two out of three of these analyses. These solutions were also compared to evaluate and illustrate the capability of the combined data to identify sources more effectively.

The sum of the estimated source contributions and the simultaneous comparison with total measured PM mass is not possible.

As discussed previously, there was good agreement between the sum of the components used in the PMF_{Full} analysis and the measured total PM2.5 mass. Besides, the modelled contributions of PMF_{Full}-resolved sources were regressed against the total PM2.5 mass using a multi linear regression method as described in Line 27-29, Page 5. The modelled and measured PM2.5 showed a high correlation (r^2=0.83) and agreement with a slope of 0.94. The correlation has been added in the revised manuscript.

The study seems to be quite constrained. The meaning of some paragraphs is unclear and I advise the authors to carefully revise the paper to check for clarity before the resubmission. Therefore, in my opinion, the manuscript is not suitable for publication as current version due to the major deficiencies described above.

This is a novel and complex analysis that introduces new concepts requiring more explanation than a traditional PMF paper. We expect that PMF studies with similar combinations of high time resolution data will become more common in the future thus we wanted to help lay down an initial foundation. We have worked to clarify these explanations and interpretations in the revised manuscripts.

Specific comments

2.2 Trace metal measurements Lines 15-20: It could be useful to write what kind of filters are used for this analysis.

In this study, the continuous metal concentrations were measured by the Xact metals monitor on an hourly basis. The Xact used a Teflon reel tape (manufacturer's recommendation) to sample and analyze simultaneously. In the revised manuscript, the statement has been modified as follows:

"In brief, the Xact instrument pulls ambient air through a section of filter tape (Teflon tape roll) at a flow rate of 16.7 lpm using a PM2.5 sharp cut cyclone (BGI)."

3.1 PMF of combined data, PMFFull It could be useful to report the parameters of the good quality of the source apportionment study. The comparison between reconstructed and measured mass is not present, the Bootstrap analysis and the evaluation of the errors regarding the contributions are missing too.

As shown in the caption of Fig. 1, the error bars in the source profiles were estimated by the standard deviations of the 100 bootstrap (BS) runs.

The quality of the 9-factor solution was also discussed in Section 3.1.1. In the revised manuscript, detailed diagnostics of error estimation in the PMF$_{Full}$ solution using the bootstrap and displacement analyses have been added in the Supplement of the revised manuscript. Please refer to the responses for Reviewer 2. The comparison of PMF-modelled PM2.5 mass and measured PM2.5 mass has been added in the revised version as well.

3.1.2 Road dust Lines 5-10: the organic component of PM is considered among the variables input of the PMF analysis in the Figure 1 as m/z ratio and not as measure of OC by thermo-analysis instrument. In my opinion, this evaluation should be better explained; anyway, is not enough to apportion the total PM2.5 mass without this kind of measure. Moreover, the BC concentration is considered in the PMF analysis without a correction for EC measure; is true? Are there any kind of evaluation in this field? I would like to understand the way to apportion in this case the organic component of the PM.

Organic carbon (OC) typically determined in 24h filter based PMF studies by thermal/optical techniques (i.e., Sunset Lab OCEC analyzer) is converted to equivalent OA total mass by multiplying by a conversion factor (i.e., 1.4~2.5). This factor accounts for additional mass, mainly hydrogen, associated with organic carbon present in the particle phase. To achieve a proper mass closure, the conversion factor for OC is required and mostly has to be assumed. Thus thermal OC analysis, although very useful, is by no means an absolute or definitive method for determining organic aerosol mass or composition.

In this PMF study we used detailed and more compositionally relevant OA data (as OA mass spectra) measured by the ACSM. With PMF the OA mass spectra can be decomposed into specific groups of m/z

fragments, which are used to identify differences between OA sources (i.e., hydrocarbon-like OA, oxygenated OA, biomass burning OA, low-volatility oxygenated OA). Thus, source apportionment using measured OA fragments can be more effective than the PMF analysis using bulk OC mass to identify sources related to OA. PMF is routinely applied to mass spectra data so as to apportion the organic components in PM (see relevant references within the manuscript).

Due to a different time resolution (1 hr vs. 2 hr interval) and a lower data availability for EC measurements, hourly BC data were used in this study. The optically based BC concentrations measured by the Aethalometer were converted to mass based concentrations using a mass absorption coefficient. Thermally based measurements of EC were not used in the study due to their 2h time resolution but they were available. As shown in Fig. R10, there was good agreement between 2-hour averaged Aethalometer BC and EC measured by a Sunset Lab OCEC analyzer.
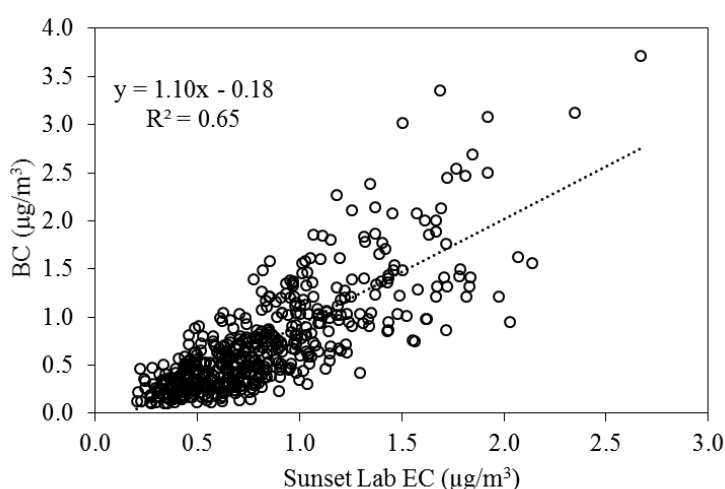

Figure R1. Comparison of 2-hr averaged Aethalometer BC (880 nm) with EC measured by a collocated Sunset Lab OCEC analyzer from May 8 to July 2, 2013.

3.1.5 Industrial Sector Lines 25-30. I would like to understand why Pb and As are considered as marker elements of industrial sector; were considered some meteorological parameters as velocity and direction of the wind link to this kind of source?

The correlations of the Industrial factor with meteorological parameters (i.e., temperature, RH, wind speed) and the wind sector analysis (i.e., CPF) are shown in Table 2 and Fig. S9 in the original manuscript. Overall, there was no distinct correlation with meteorological parameters. However, the directionality of CPF pointed to the location of a once heavily industrialized sector and a wastewater-treatment facility, indicating the influence of local industrial sources. Recently, Sofowote et al. (2015) also found a similar Pb-As factor associated with non-ferrous metal smelting using 6-year chemical speciation data in Toronto.

3.2 Comparison of results for the PMFmetal and PMForg analysis Lines 10-15. For this aspect, the comparability with other V/Ni ratios reported in literature is not shown to distinguish the different sources of Heavy oil combustion due to ship or industrial emissions.

The ratio of V to Ni is generally used as an indicative of ship emissions or residual oil combustion. Viana et al. (2014) reviewed the V/Ni ratios of ship emissions in Europe, which were found that the ratios ranged from 3 to 4. Jeong et al., (2011) reported the V/Ni ratio of 3.7 for ship emissions in Halifax, Canada. Oil combustion from mainly heating for residential and commercial buildings is enriched with Ni and thus the V/Ni ratio for residual oil combustion is typically lower than the ratio for ship emissions (Peltier et al., 2008). In the study, the V/Ni ratio in the PMF_{metal} solution was 1.6, which was much lower than the typical ratio for ship emissions. This may suggest that residual oil combustion for heating purpose is a likely source of the Ni-V factor in this study as Toronto is not a major shipping port.

We have added a statement for the V/Ni ratio in the revised manuscript.

Figure 1. Factor profiles of the nine-factor solution (Road Dust, Primary Vehicle Emissions, Tire Wear, Industrial Sector, Cooking, Biomass Burning, Oxidised Organics, Sulphate and Oxidised Organics, Nitrate and Oxidised Organics) from PMFFull analysis including ACSM organic mass spectra, ACSM inorganics, Xact metals, and Aethalometer black carbon. The plots presented in this way show the chemical profiles but they are not completely clear. I suggest the author to find a more simple way to show the results.

We have added a new summary table exhibiting the explained variations of key marker species for each factor in the Supplement of the revised manuscript.

Figure 4. I suggest the authors to show the different contribution in percent and absolute terms one next the other one figures.

Thank you for this suggestion. We felt that placing the two figures on top of each other facilitated comparison for each of the factors. We will leave it to the journal to determine if presenting these figures beside each other or on top of each other fits more easily within the manuscript

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