Response to Reviewer #2

We kindly thank the referee for taking our manuscript into consideration and we value the comments raised to improve the manuscript. A point-to-point response to the issues raised is enclosed below.

The manuscript describes the use of ME-PMF as source apportionment tool. The data set is composed by the data collected in three sites in London where DRUM impactors have been deployed. The analysis of the DRUM stages by S-XRF has been described in previous papers. ME-PMF is a pretty new topic with still few examples in literature and therefore I recommend the publication of the manuscript. However there are still several points to fix and/or clarify:

Comment #1:

Eq 4, pag. 14742: this way to consider the uncertainties, i.e. neglecting any systematic term, could be acceptable if the DRUM-SXRF data only are used in the statistical analysis. This is only partially true in this case since aethalometer and AMS values are quoted along in the text to comment/clarify the ME-PMF outcomes. Actually, the systematic uncertainties in the DRUM-SXRF approach could be quite large as previous papers shown. I think this point should discussed more in deep and that a systematic term should be added to the final results when compared with other techniques.

Response:

This is a complex issue, and the reviewer's point is well taken. As noted by the reviewer, uncertainties that uniformly affect an entire row or column (time point or element) of the data or uncertainty matrix do not alter the PMF results. However, these uncertainties can be significant when a PMF output is compared to an external measurement.

Systematic errors in the RDI-SR-XRF analysis for this dataset were discussed in detail in a different publication (Visser et al., 2015). In the present analysis, the results are affected only if there are significant biases (1) in the relative calibration of selected elements, which could affect e.g. the elemental ratios used to validate solutions; or (2) the relationship between measurements taken at different times, which could affect the correlations with external data. Possibility (1) was assessed in detail by Visser et al. (2015) and is unlikely to significantly alter the results, while possibility (2) is likely to affect only isolated points or a short sequence (due to e.g. clogging of the RDI inlet) and will not significantly alter overall factor-to-tracer correlations.

As the focus of this paper is on source identification and model sensitivity (rather than e.g. apportionment of total PM mass – see comment #2), we believe that the current method of error reporting is the most directly relevant and clearest for the reader. To clarify this point, we have added the following to the end of Section 2.3: "Note that the errors reported for this analysis deal explicitly with model errors and do not account for systematic errors in the RDI-SR-XRF system that do not affect the PMF model operation (e.g. flow rate, element calibrations). For a detailed discussion of these sources of uncertainty, see Visser et al. (2015)."

Comment #2:

The description of the ME-PMF approach is quite complex and a little bit assertive: the reader understands that many test and trials have been carried out but since this is an innovative procedure more information would be useful. I understand that the available space is limited, however I encourage the Authors to revise this part, maybe adding more information in the supplementary material.

Response:
This issue was also raised by Reviewer #1 (comment #1), and we repeat the response here for clarity. We agree that this section is (by necessity) quite complex, and have made several revisions to improve its readability. Specifically:

The different types of ME-2 analyses have been relabelled with more descriptive names (see also Fig. 1): ME2_seg is now ME2_subset; PROF_nonres is now Profile_unresolved; and SENS is now Sensitivity_test.

Several minor modifications to the text have been added to more clearly explain the (1) use of resolved factor profiles in subsequent analyses and (2) application of criteria to accepted/rejected solutions during sensitivity tests.

In addition, we have rewritten for clarity the descriptions of ME2_subset and Profile_unresolved. The revised text is:

"ME2_subset denotes analysis of a subset of the full dataset in the rows (*i*) dimension. This subset need not be a single continuous block and can be constructed e.g. from separate periods in which a particular source is evident. ME2_subset analyses utilize the basis set built up in previous steps and are considered successful (see Fig. 1) if the entire subset is well explained according to the above criteria. To maximize adaptation of the basis set to the entire dataset (rather than remaining fixed to a previously analyzed and quasi-arbitrary subset), the basis set is allowed to evolve after each successful ME2_subset (or ME2_all) analysis, i.e. the ME2_subset output profiles become the new basis set. Strategies used for selecting subsets may vary with the dataset, however it is critical that the entire dataset be well-investigated, by ensuring that the entire dataset is contained in subsets and/or careful inspection of ME2_all residuals. As an example, in the present analysis high signal-to-noise data at MR and NK were analysed separately (subset #1) from low signal-to-noise data at DE (subset #2). The need for a separate DE analysis was indicated by strong residuals in the ME2_all analysis using the basis set derived from subset #1. This indicated that an additional source (industrial) was needed to fully describe the dataset. Other subset selection strategies could include e.g. size fraction, air mass origin, wind direction, or suspected source influence."

"Profile_unresolved is used to generate an appropriate anchor profile for a factor whose presence is indicated in the solution but cannot be cleanly resolved by ME2_subset. Thus while Profile_unresolved and ME_2 subset may employ similar analytical strategies (e.g. analysis of a data subset), Profile_unresolved is distinguished in that (1) success/failure criteria are applied only with respect to a specific factor; and (2) only the profile of this specific factor is added to the basis set for future analyses. As an example, in the present study, a profile for the $PM_{10-2.5}$ brake wear factor was resolved by analyzing NK data using an excessive number of factors. Although non-brake wear factors exhibited non-interpretable mixing/splitting, the brake wear factor was judged clean based on element ratios consistent with literature, a strong temporal correlation with NO_x, and low overall unexplained variation in the solution. Other Profile_unresolved methods could include e.g. (1) an average profile over periods where the source of interest dominates the total signal or (2) use or estimation of a profile from the literature."

Comment #3:
The significance of the ME-PMF results is limited by the lack of information on important components of the PM (EC/BC, OM, ions, etc). However, the Authors mention and use at least Aethalometer and AMD data which could had been used to fill the gap. Again, I understand that to collect everything in a unique data set and run a "complete" ME-PMF analysis would be quite complicate but this issue should at least be mentioned and commented.

Response:
We agree with the referee that the results are limited to the analysed elements. This is only a minor fraction of the total PM mass. A complete ME-2 analysis requires high time-resolved data of all individual species (elements, EC/BC, ions, OM) with a complete uncertainty analysis at all three sites. First of all this data was not available and second it is very challenging to combine all these different data sets into one ME-2 model due to differences in error propagation. This would mean a complete study by itself and is therefore outside the scope of this manuscript.

We believe that by solely investigating emission sources with ME-2 based on elements, where a method is developed on how to deal with elements measured at several locations in different size fractions, a lot of additional information has been obtained. To clarify this point, we have added the following sentence to the end of Section 3.1: "Although the analysis below includes only trace elements, which constitute a minor fraction of the total mass, the results are important for determining source temporal characteristics and interpreting trends in bulk particle properties such as total PM mass."

Comment #4:
Brake wear, suspended dust and traffic: the "traffic" source with a profile composed by fe only is very suspicious and I believe it is actually the "residual" iron non incorporated in dust and brake wear. Sources should have a physical/chemical meaning and I do not understand which is the process that could produce Fe alone.... This is also related to my previous comment 2: is it really demonstrated that this is the best PMF-solution. Could this depend on the use of common profiles in the three sites (while a different traffic composition could ask for different profiles)?

Response:
We understand the concern of the referee that one should be careful interpreting a source profile composed of mainly one element. In this study, the "Fe-source" is a very strong and consistent source in the ME-2 model. Note that Mn is also significantly apportioned to this source. Iron and manganese are important components in vehicles, leading to the emission of these elements due to vehicle wearing. A minor fraction of both elements is incorporated in the resuspended dust profile. This profile is consistent with existing measurements, suggesting that the major sources of Fe and Mn are correctly accounted for. The absence of both elements in the brake wear profile is also consistent with existing measurements (Amato et al., 2009, 2013; Bukowiecki et al., 2010).

Comment #5:
Sea salt, aged sea salt, reacted Cl: same comment as above. This source with Cl only is a little bit suspicious...here the lack of information on nitrates is important to support the hypothesis considered in the text

Response:
The reacted Cl source is mainly driven by an event at the city sites lasting from 5 February 16:00 to 7 February 2012 04:00 UTC. We believe that the correlation between XRF Cl and a peak in coarse mode aged sea salt, high NO_3^- and NH_3 concentrations and high AMS Cl^- concentrations strongly suggests the presence of NH_4Cl particles. For this species, only the anion is detectable by XRF. This is confirmed by the lack of correlation with combustion related species such as K, Zn, Pb and SO_2, and thus that fine Cl cannot be emitted by combustion sources during this period. We are therefore confident that this reacted Cl source is correctly apportionment.

Comment #6:
S-rich: a mention to the fact that this source likely corresponds to secondary sulphates should be given

Response:
We have clarified this point (page 14752, lines 16-19) in the text as follows: "This factor likely corresponds to secondary sulphates, consistent with the results of many previous source apportionment studies (Mazzei et al., 2007; Viana et al., 2007; Richard et al., 2011)."

Comment #7:
Fig. 5: the correlation with NOx and number of vehicles is quite weak or even absent. While the same plot is not provided for the resuspended dust and the Traffic related (FE only...) sources? Is this the best correlation with independent traffic tracers that could be obtained?

Response:
The emission of gases (NO_x) and particles (elements) as a function of traffic flow on the one hand and the influence of meteorological parameters on the other hand is a complex system in a street canyon. Figure 5 shows the diurnal variations of the brake wear (coarse, intermediate) and other traffic-related (coarse, intermediate and fine) factors at the kerbside site compared to diurnal variations of NO_x and traffic flow (light and heavy duty vehicles separately).

The referee notes that the correlation between NO_x and number of vehicles is quite weak. If we correlate the NO_x diurnal variation with the light and heavy duty vehicles separately, one retrieves Pearson's *R* of 0.77 and 0.94, respectively. This is in line with our statement on page 14749 that NO_x seems more directly related to HDV numbers. The brake wear and traffic-related factors are however more influenced by total vehicle number.

We have not provided a similar plot for resuspended dust, because the processes driving the dust emissions are not directly correlated with traffic intensity and NO_x emissions. They are rather influenced by relative humidity and wind movements in the street canyon as a result of increased traffic flows (see paragraph on page 14750).

Comment #8:
Fig. 12: as above: why the aethalometer data are compared with "solid fuels" only? What about the correlation with the traffic related sources? In Fig. 12 there are several time periods in which the correlation get lost...

Response:
In Fig. 12 the time series of the solid fuel factor at the urban background and rural site are compared to the Aethalometer wood burning absorption coefficient at wavelength 470 nm and to the solid fuel burning organic aerosol factors resolved with AMS-PMF.

In this figure different correlations can be seen between the various solid fuel factors. We clarify this by adding a sentence after line 9, page 14752:
"The solid fuel source is compared to particle light absorption data by Aethalometer measurements ($b_{abs,wb}$ in m^{-1}; not available at MR) and solid fuel factors resolved by AMS-PMF on organic aerosol data (Detournay et al., 2015; Young et al., 2014, 2015). The time series of the various solid fuel tracers are very similar, especially for the light absorbing particles and organic aerosol as shown for NK and DE in Fig. 12 (tracers at MR are similar to NK). The different correlations seen in this figure are caused by the sampling of air containing various burning stages of solid fuel burning, emitting K and other species in different ratios."

We believe that the Aethalometer wood burning absorption coefficient is a good tracer to validate the solid fuel factor obtained with XRF-ME-2 data. The traffic absorption coefficient is more difficult to compare to the traffic factors, because the emission processes are different, and should therefore not necessarily correlate. The traffic factors are mainly influenced by wearing processes, whereas the

Aethalometer measurements are influenced by the emission of elemental carbon from vehicle engines.

References

Amato, F., Pandolfi, M., Viana, M., Querol, X., Alastuey, A., and Moreno, T.: Spatial and chemical patterns of PM10 in road dust deposited in urban environment, Atmos. Environ., 43, 1650–1659, 2009.

Amato, F., Schaap, M., Denier van der Gon, H. A. C., Pandolfi, M., Alastuey, A., Keuken, M., and Querol, X.: Short-term variability of mineral dust, metals and carbon emission from road dust resuspension, Atmos. Environ., 74, 134–140, 2013.

Bukowiecki, N., Lienemann, P., Hill, M., Furger, M., Richard, A., Amato, F., Prévôt, A. S. H., Baltensperger, U., Buchmann, B., and Gehrig, R.: PM10 emission factors for non-exhaust particles generated by road traffic in an urban street canyon and along a freeway in Switzerland, Atmos. Environ., 44, 2330–2340, 2010.

Mazzei, F., Lucarelli, F., Nava, S., Prati, P., Valli, G., and Vecchi, R.: A new methodological approach: the combined use of two-stage streaker samplers and optical particle counters for the characterization of airborne particulate matter, Atmos. Environ., 41, 5525–5535, 2007.

Richard, A., Gianini, M. F. D., Mohr, C., Furger, M., Bukowiecki, N., Minguillón, M. C., Lienemann, P., Flechsig, U., Appel, K., DeCarlo, P. F., Heringa, M. F., Chirico, R., Baltensperger, U., and Prévôt, A. S. H.: Source apportionment of size and time resolved trace elements and organic aerosols from an urban courtyard site in Switzerland, Atmos. Chem. Phys., 11, 8945–8963, doi:10.5194/acp-11-8945-2011, 2011.

Viana, M., Querol, X., Götschi, T., Alastuey, A., Sunyer, J., Forsberg, B., Heinrich, J., Norbäck, D., Payo, F., Maldonado, J. A., and Künzli, N.: Source apportionment of ambient PM2:5 at five Spanish centres of the European community respiratory health survey (ECRHS II), Atmos. Environ., 41, 1395–1406, 2007.

Visser, S., Slowik, J. G., Furger, M., Zotter, P., Bukowiecki, N., Dressler, R., Flechsig, U., Appel, K., Green, D. C., Tremper, A. H., Young, D. E., Williams, P. I., Allan, J. D., Herndon, S. C., Williams, L. R., Mohr, C., Xu, L., Ng, N. L., Detournay, A., Barlow, J. F., Halios, C. H., Fleming, Z. L., Baltensperger, U., and Prévôt, A. S. H.: Kerb and urban increment of highly time-resolved trace elements in PM10, PM2.5 and PM1.0 winter aerosol in London during ClearfLo 2012, Atmos. Chem. Phys., 15, 2367–2386, doi:10.5194/acp-15-2367-2015, 2015.