Response to Reviewer #1

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.

Visser and co-authors describe a positive matrix factorization analysis of trace metal SR-XRF data (for rotating drum impactor samples) collected in three size ranges at three sites in London during the ClearfLo campaign in winter 2012. For each size range, data from all three sites were combined into a single dataset prior to analysis by ME2-PMF. This is a nice approach because sources that have high spatial gradients can be identified even if they co-vary temporally when the sites are compared to each other. The Multilinear Engine approach allowed for the introduction of representative "anchor profiles" associated with physically meaningful sources in the analysis. Some of the final factors resolved were constrained to have relative intensities for marker metals within a user defined range of the anchor profiles used. The approach used here involved iterations of ME2-PMF analysis of subsets of the data with high S/N ratios to identify periods where factors are well resolved, and subsequently applying these factor profiles as a basis set when analysing the entire dataset. The methodology is reasonable objective, but with user input in some cases where physically meaningful factors are extracted only at unsatisfactorily high values of p, for example. The final PMF results are used to infer conclusions about the spatial variability of trace metal sources across the three sites, the size dependence of the different sources, and the relative mass contributions of the different sources to total metal mass concentration at all three sites in all three size fractions. The authors identify and apportion sources associated with brake wear, resuspended dust, sea salt, secondary sulphate, solid fuel combustion and industrial emissions. The size dependence, temporality and spatial distribution of the mass contributions of the different factors support their assignments. For example brake wear and resuspended road dust exhibit the highest mass concentrations at the roadside site and lowest at the rural site, while secondary sulphate transported from continental Europe exhibits similar mass concentrations and temporality across all sites. Correlations with relevant tracers for traffic and solid fuel sources are also investigated. Overall, I find this effort to be very well written and scientifically rigorous with extensive sensitivity analysis. It thus represents a useful template for future source apportionment analyses of trace metals. I have only minor suggestions below:

Comment #1:

The description of the modified ME-PMF approach (Section 2.3) is quite dense, and I had to read through it three times to fully grasp the steps. Rewriting parts of this section will almost certainly help. It may be worthwhile to change the naming conventions of the steps to more immediately tangible titles for readers. The meaning of "ME-2 all" is self-evident but "PROF-nonres" and "SENS" are not necessarily useful when examining Fig. 1, for example.

Response:

This issue was also raised by Reviewer #2 (comment #2), and our response is presented in both places 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 ME2_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 #2:
One aspect I'm still not clear on is whether anchor profiles are used for all factors prior to the final ME2 analysis of the total dataset. For example, in Table 1, criteria for only a handful of the factors are listed for each size range. Were there no constraints for the other 3-4 factors in each size range? This should be explained in the text or caption. How was it decided which factors should or should not be constrained in each size range?

Response:
Based on the suggested changes due to comment #1, we believe that we have responded to this comment as well.

Comment #3:
A brief discussion of which factors that could not be resolved or identified using the unconstrained PMF analysis could also be added to the discussion or conclusions section to demonstrate the value of the ME2-PMF approach used here.

Response:
The conclusions section previously included a statement on the additional factors that could be identified with the constrained ME-2 approach on page 14757, lines 22-24. To further clarify this point we will add a sentence to this paragraph:

"The coarse fraction yielded (elements with highest relative contributions in brackets) brake wear (Cu, Zr, Sb, Ba), other traffic-related (Fe), resuspended dust (Si, Ca), sea/road salt (Cl), aged sea salt (Na, Mg) and industrial (Cr, Ni) factors. The intermediate fraction yielded the same factors, except the industrial, and instead yielded an S-rich (S) factor. In the fine fraction a traffic-related factor (Fe, Cu, Zr, Sb, Ba) was found as well as resuspended dust, sea/road salt, aged sea salt, reacted Cl (Cl), S-rich and solid fuel (K, Pb). The other analysed elements (Al, P, Ti, V, Mn, Zn, Br, Sr, Mo, Sn) could not be attributed to a single factor. The brake wear, industrial, reacted Cl and solid fuel factors could only be resolved with the help of anchor profiles retrieved internally in the datasets. Unconstrained ME-2 only led to mixed traffic-related / brake wear, resuspended dust, sea/road salt and aged sea salt factors in the coarse fraction, to mixed traffic-related / brake wear, resuspended dust, sea/road salt and mixed aged sea salt / regional transport factors in the intermediate fraction, and to traffic-related, resuspended dust, aged sea salt, mixed S-rich / solid fuel and mixed sea/road salt / Cl-rich factors in the fine fraction."

Comment #4:

I suggest moving the map from the Supplement to the main manuscript as the site locations are helpful for interpreting Figs 3, 4, 11 and 14. Also changing the map to an image will help to demonstrate how "rural" the DE site is.

Response:

We agree that it would be helpful moving the map from the Supplement to the main manuscript. The following figure will be added as Figure 1 in the manuscript.

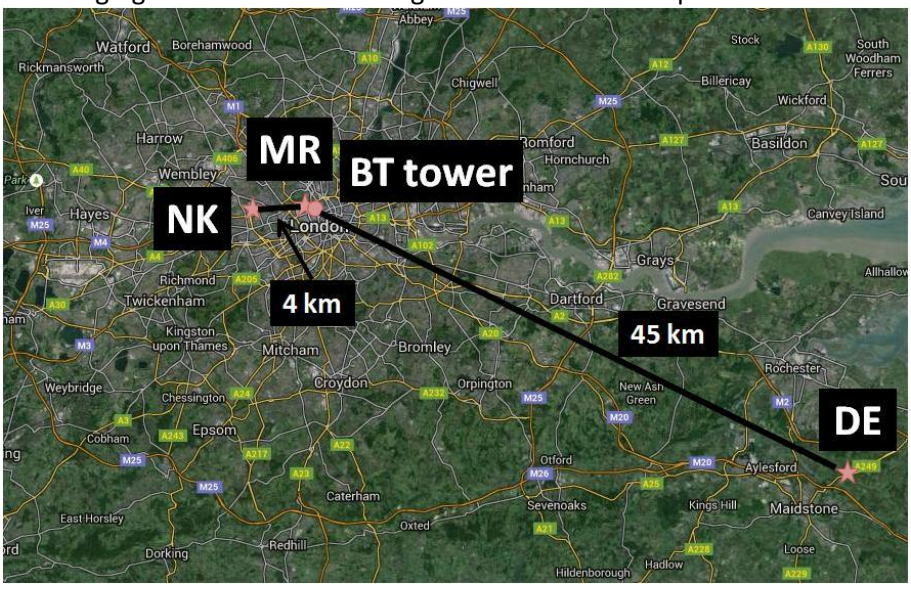

Figure 1. Map of southeastern UK. Indicated are the sampling sites MR (kerbside site Marylebone Road), NK (urban background site North Kensington), DE (rural site Detling), and the elevated BT Tower site for meteorological measurements (adapted from Google Maps).

Comment #5:

Page 14737, line 13: should be "and PM2 data"

Page 14737, line 24: state the limit value

Response:

These points will be adjusted.

Comment #6:
Page 14741, eq 3: But how does one decide how many factors have the "a" constraint applied?

Response:
We would like to refer to Section 2.3 and the suggested changes herein based on comment #1 for this response. We constrain only those factors for which the lack of constraints results in a mixed/unresolved factor. The number of factors with constraints at a particular stage of analysis thus depends on the nature of the dataset and the progress in analyzing it.

Comment #7:
Page 14742, line 14: "e.g."? Were other offset sample numbers investigated?

Response:
We have investigated the number of offsets selected to calculate the uncertainties associated with the energy calibration of an X-ray line as function of detector channel. We tested this in the range 5 to 100, but sensitivity tests indicate that the results do not depend significantly on the number of offsets selected. The specific response depends on the complexity of the peak (line) in question and the precision of the energy calibration.

We would like to clarify this point by changing line 14, page 14742 into:
"From these distributions, several offsets are selected, such that the perturbations are uniformly sampled according to probability, and the XRF spectra are refitted (here 20 offsets)."

Comment #8:
Page 14744, line 2-3: "Consistent with existing measurements"? Do you mean previously reported source profiles?

Response:
The referee refers to the following sentence about the physical criteria of an acceptable ME-2 solution:
"- Attribution of elements to sources and element-to-element ratios within a source are consistent with existing measurements."

"Existing measurements" refers to all published data relevant to the construction of a source profile, including but not limited to previously reported profiles and element-to-element ratios. We have clarified this in the text as follows: " …are consistent with existing measurements (e.g. published source profiles and source-based element-to-element ratios)."

Comment #9:
Page 14753, line 23-28: Rewrite this part for clarity

Response:
We intend to change these lines into:
"Figure 2 shows the source profile and Fig. 13 the time series and diurnal variations. This source is mainly found at DE and consists for 70% of Cr and Ni. The time series at MR and NK show only a few single peaks and can therefore not be attributed to this particular source. The spiky time series at DE are typical indications for influences of one or several point sources close to this rural site. These sources are possibly found in the SW as concentrations were elevated under these conditions (Supplement Fig. S14)."