Development of a versatile source apportionment analysis based on positive matrix factorization: a case study of the seasonal variation of organic aerosol sources in Estonia

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Author's response:

We thank Referee #2 for the careful revision and comments which helped improving the overall quality of the manuscript. A point-by-point answer (in regular typeset) to the referees' remarks (in the *italic typeset*) follows. Changes to the manuscript are indicated in blue font.

In the following page and lines references refer to the manuscript version reviewed by anonymous Referee #2.

1) *This manuscript investigates a year of organic aerosol in PM10 at three sites in Estonia. The organic aerosol was characterized by analyzing the watersoluble filter extract with an HR-ToF-AMS. The PM10 samples were 24-hour integrated PM10 quartz fiber filter samples using a high-volume sampler. Source apportionment of the AMS mass spectra was performed using positive matrix factorization. Seven factors were found between the three sites including an oil factor, sulfate-rich factor, summer oxygenated OA, winter oxygenated OA, dust, primary biological OA, and biomass burning OA. The BBOA, PBOA, WOOA, and SOOA factors were all validated with externally measured organic markers. The dust factors were validated with external measurements of Ca2+. A bootstrap analysis is used to analyze the results and factor u ncertainties. The paper thorough in its investigation and very well written. With some minor changes I suggest this paper be accepted.*
   Specific comment: For the estimation of traffic contribution to EC calculation what are the EC/WSOA values used? The ratio of EC/OC measured in biomass burning emissions highly variable (Pokhrel et al., 2016), as is SOA formation in biomass burning plumes (Jolleys et al., 2012; May et al., 2015). Given this range of possible EC/WSOA values, language as to uncertainties regarding this analysis should be added.

We need to add some clarifications about the PMF analysis performed to apportion the EC contribution to the different sources. The analysis includes 4 variables: the time-series of the concentrations of EC, water soluble BBOA (WSBBOA), WSSCOA, and WSOilOA. Four factors are considered only

representing primary anthropogenic sources: traffic, biomass burning, road dust resuspension/tire-wear, and oil related processes. The contribution of EC in all profiles is not constrained (i.e. in none of the profiles is the EC/OA ratio fixed a priori). The contribution of the water-soluble organic aerosol from a certain source is also not constrained in the factor profile representing the source in question, while the organic aerosol from all other sources are set to 0 in this profile. As mentioned in the response to reviewer#1, such setting means that the EC variability is fully explained. In such setting, we do not assume any EC/WSOA in the traffic profile. As mentioned above, we also do not include any factor representing secondary OA. Therefore, uncertainties related to the EC/WSOA in aged biomass burning do not affect the analysis. We indeed agree with the reviewer comment that WSOA/EC is highly variable in primary sources, e.g. biomass burning. Therefore, we have performed a bootstrap analysis to assess the uncertainties in retrieving the contributions of the different sources to EC. These are represented as PDFs in Figure S4.

We have adapted the text in the manuscript as follows (Page 7, line 11):

Here, EC_{bb}, EC_{oil} and EC_{rrd} represent the EC concentration time-series related to the primary sources biomass burning, oil shale industry and resuspension of road dust/tire wear, respectively, while, a, b, and c are the EC/WSOA ratios characteristic of the emissions from the same sources and were obtained as outputs of the model. This new methodology, based on PMF, is especially pertinent as unlike other inversion techniques it sets positive constraints on a, b and c and offers the possibility of resolving the contributions of factors for which no constraints are available, here ECtr.

We found that EC_{tr} contributed 57% ± 5% to the total EC (on a yearly average), while 36% ± 5% of EC was attributed to biomass burning, 4% ± 1% to road dust resuspension and 3% ± 1% to the oil shale emissions (Fig. S4). The contribution of EC from fossil fuel combustion (EC_{ff}) measured at a site similar to Tartu, i.e. an Alpine valley in Southern Switzerland, Magadino in 2014 (Vlachou et al., 2018) was in agreement with our EC_{tr} contribution, with a yearly average of 55% ± 7%. Also in Zurich, an urban site, EC_{ff} ranged from 40% to 55% during winter 2012 (Zotter et al., 2014). From the EC_{tr} contribution, we estimated that the HOC (obtained by multiplication of the EC_{tr} time series with the HOC:EC ratio) contributed 4% to the total OC on a yearly average.

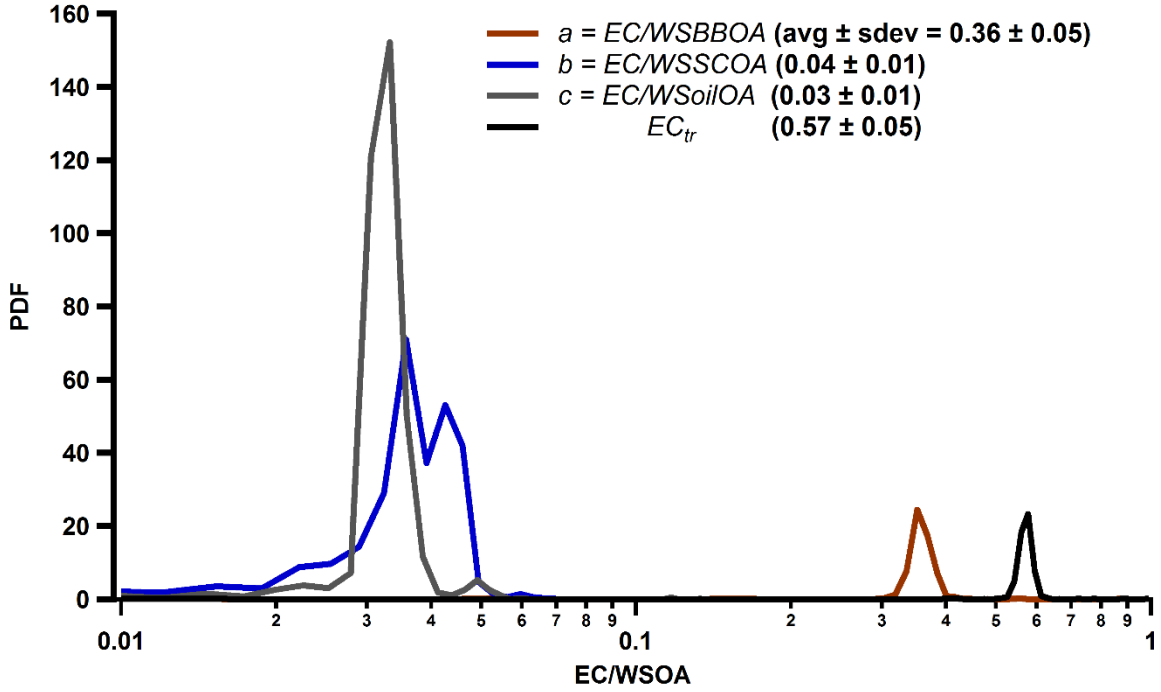

Figure S4. Probability density functions for the EC:WSOA ratios (*a* for WSBBOA, *b* for WSSCOA and *c* for WSoilOA) characteristic of the emissions from the same sources obtained by the 1000 PMF runs.

2) *How many samples per season per site were there?*

We gathered all the information in the following table. We will include it in the supplementary along with Table S1 and Fig. S1 which contain all the dates per site (as mentioned in the response to reviewer#1).

Table S2. Number of samples per season per site.

	Number of samples per season		
Seasons	**KJ**	**Tallinn**	**Tartu**
Summer	11	16	11
Autumn	9	18	10
Winter	10	18	9
Spring	9	17	12

3) *Fig 7. The colours of the two bars are very similar and hard to distinguish.*

We agree with anonymous referee#2 and therefore we changed the colours from light and dark green to red and blue as shown in the plot below.

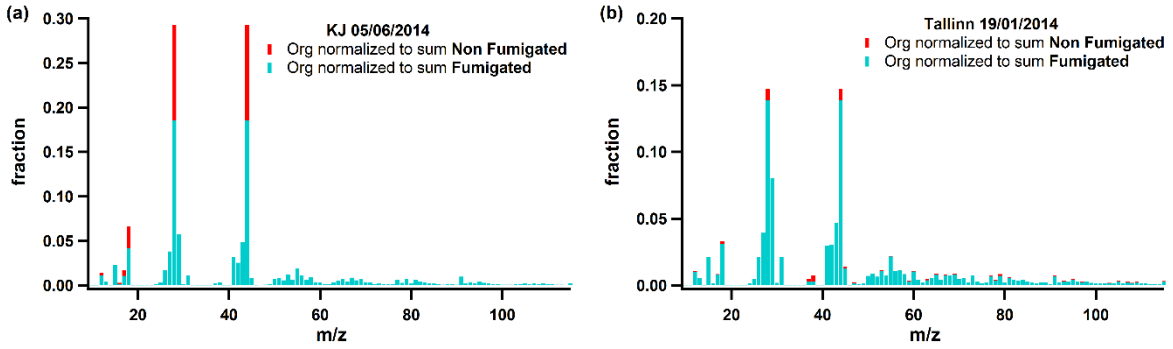

Figure 7. Examples of fumigated and non-fumigated mass spectra from two samples, with a high (KJ 05/06/2014, a), and a low dust concentration (Tallinn 19/01/2014, b).