Author’s response:

We thank the reviewers for a careful reading and correction of our manuscript. Their suggestions have strongly helped improving the quality of the manuscript.

Following the suggestions of the anonymous referees 2, 3 and 4 we have added in the revised manuscript the description of the meteorological conditions during the measurement periods in both cities. A figure with the time series of wind direction and speed, temperature and precipitation has been added in the supplementary information (Fig. S2) and is described in the methodology section. Moreover, the average wind directions and speed during each measurement loop are now reported in a wind rose plot in Fig. 4 and 5 (spatial distributions for Tartu and Tallinn, respectively) and are fully discussed in the manuscript.

As suggested by anonymous referees 2 and 4, a detailed analysis of the source apportionment diagnostics has been added in the revised manuscript. A figure including (a) Q/Q_{exp} as a function of the number of factors, (b) correlations between OA sources with external factors as a function of the number of factors and the decrease in Q/Q_{exp} time series (c) and profiles (d) for increasing number of factors has been added in the supplementary information (Fig S5). Moreover, a table reporting the correlations between the OA sources from our four-factor solution and literature profiles has been added in the main text.

Moreover, following the suggestion of anonymous referee 4, we have added the correlation coefficients (R^2) between the spatial distributions of all sources and compounds in Tartu in the revised manuscript (Table S1).

Lastly, in order to give an overview of the major local PM sources, we have added emission maps in the revised manuscript (Fig. S1). The wood combustion and industrial sources and the traffic emission rates of the main streets are reported in these maps.

Anonymous Referee #4

Received and published: 29 February 2016

General comments

This paper presents mobile measurements of gas- and particle-phase pollutants at two Estonian cities of Tartu and Talinn. Detail chemical composition of NR-PM2.5 as well as BC and trace gases (CO, CO2, and CH4) were observed in high time resolution and OA characteristics were found to be similar (HOA, BBOA, RIOA, and OOA) at both cities. Primary types of OA (HOA, BBOA and RIOA) were high during the day, whereas secondary OA (OOA) enhanced at night. In summary, the mobile measurements allowed the authors to observe time and spatial distribution of primary and secondary pollutants, as well as influences of long-range transport and local temperature inversion to aerosol and gases pollutants in Tartu and Talinn.

The manuscript is well structured and written. I have some comments regarding research methods, results and discussion as well as suggestions that would improve quality of the manuscript. There are also some typing errors in the text, tables and figures summarized in *technical comments. Overall, I support publication of the manuscript after my comments are addressed.*

Specific comments

OA source apportionment:
I believe the authors have done rigorous analysis in selecting the best PMF factor solution. I expect some of the analysis figures and/or tables are provided in the SI. PMF diagnostic plots, such as those presented by Zhang et al. (2011), are important for understanding the analysis and discussion. Residuals of time series and mass spectra for 3-, 4-, and 5-factor solutions and correlations between factors time series and external tracers (i.e., CO, eBC, SO4, NO3) are useful in understanding selection of the best factor solution. I recommend adding this information in the SI at the least.

Author's response:
As discussed above, a figure with the major source apportionment diagnostic plots has been added in the supplementary information (Fig. S5 in the revised manuscript). This figure includes the Q/Q_{exp} as a function of the number of factors, the correlation coefficients (R^2) of the resolved factors with the external markers for solutions with different number of factors and the change in the residuals time series and profiles for increasing number of factors.

Changes in text: See complete changes in text in comment below regarding the five-factor solution.

eBC source apportionment:
It is not clear why do the authors choose to calculate Angstrom exponent using absorption at 470 and 950 nm. Since Zotter et al. paper has not yet published, I could not verify how the calculation was done. I suggest adding a brief description of this calculation in the main text or SI. Also, brief description of calculation of eBCwb and eBCtr would be a useful addition in the SI.

Author's response: The choice of the wavelengths and of the angstrom exponents used in this work are based on the findings in Zotter et al. (In prep.), where radiocarbon (^{14}C) measurements of elemental carbon (EC) are combined with Aethalometer data to determine the best Angstrom exponents for wood burning (α_{WB}) and traffic (α_{TR}). The best α values were evaluated by fitting the source apportionment results of the Aethalometer (in particular BC_{tr}/BC) against the fossil fraction of EC (EC_f/EC) derived from ^{14}C measurements. This analysis resulted in α_{tr} = 0.9 and α_{wb} = 1.68 fitting best the data when using the attenuation measured at 470 and 950 nm. Other wavelength combinations were also tested but in all cases, especially when 370 nm was used, the residuals of the fit were worse. Moreover it is known that the 370 nm channel of the Aethalometer is more sensitive to artefacts, including response to light absorbing SOA and the adsorption of VOCs on the filter. A brief description of the Aethalometer source apportionment method and the findings in Zotter et al. (In prep.) has been added in the revised manuscript.

Changes in text:
Page 8, Line 9: The Aethalometer measurements can be used to separate eBC from wood burning (eBC_{wb}) and from traffic (eBC_{tr}), by taking advantage of the spectral dependence of absorption, as described by the Ångström exponent (Ångström, 1929). Specifically, the enhanced absorption of wood burning particles in the ultraviolet and visible wavelengths

region (370–520 nm) relative to that of traffic particles is used to separate the contributions of the two fractions. This method is described in detail….

Page 8, Line 19: The absorption Ångström exponent was calculated using the absorption measured at 470 and 950 nm and Ångström exponents of 0.9 and 1.7 were used for traffic and wood burning, respectively.~~,~~ These parameters were chosen following the suggestions in Zotter et al. (In prep.), where the comparison between radiocarbon (^{14}C) measurements of elemental carbon (EC) and the Aethalometer source apportionment results allowed the identification of the best wavelengths and Ångström exponents pairs.

Results and discussion:

Page 10 Ln 1-2: *Could the authors provide approximate uncertainty value of ratio of BBOA and eBCwb relative to change in Angstrom exponent?*

Author's response: As mentioned in the manuscript, the BBOA to eBC_{wb} ratio is very sensitive to the chosen Ångström exponent for traffic. Zotter et al. (in prep.) recommend the use of Ångström exponents for traffic between 0.9 and 1.0, as using 1.1 leads to increased residuals in their method. Therefore, we used an Ångström exponent for traffic of 0.9 and reported the change in the BBOA to eBCwb ratio if an Ångström exponent for traffic of 1.0 had been used. This variability (ratio changed from 4 to 4.8) is an indication of the method uncertainty relative to the choice of Angstrom exponents, which is around 20%.

Page 10 Ln 2-10: *From information provided, it seems reasonable to assign RIOA as COA. The lack of diurnal variability does not mean that the factor is not a COA factor. It is possible that the lack of diurnal variability is due to homogeneous source of cooking emission, or stagnant atmosphere during measurements Have the authors look at meteorological conditions, such as wind direction and speed, when RIOA concentrations were high? I would recommend adding meteorological information in the SI.*
Identification of RIOA or COA could be further assessed by plotting the factor mass spectra side-by-side with reference mass spectra from previous studies, such as by Mohr et al. (2012). The authors will need to provide more evidence to support identification of the RIOA factor.

Author's response:
As previously mentioned, the diagnostic plots included in the revised manuscript support the use of a four-factor solution, where the RIOA factor is resolved. In general, an increase in the correlation coefficient (R^2) is observed when going from a three- to a four-factor solution. As the correlations are not further improved when considering higher order solutions, the four-factor solution is considered the best representation of the data. Also the trend in the model residuals supports the presence of four factors, as the decrease in the residuals time series is important when increasing from three to four factors but is rather low when further increasing the number of factors.

As mentioned above, we have added a time series with the meteorological parameters during the measurement periods (including wind direction and speed, temperature and precipitation) in the supplementary information of the revised manuscript (Fig. S2). We show that in general the wind direction does not influence our measurements significantly (see Fig. 4b and Fig. S14), but the temporal variability of the factor time series, including that of RIOA, are rather driven by their spatial distribution.

A table containing the correlation coefficients (R^2) between the OA profiles from the four-factor solution and literature profiles has been added in the main text of the revised manuscript (New table 2). The high correlation between RIOA and published cooking mass spectra suggests that RIOA may be heavily influenced by cooking processes. However, we could not exclude the contribution from other residential sources (e.g. waste or coal combustion), especially also due to the lack of statistically robust diurnal patterns for cooking that are not affected by the drives. Therefore, we prefer to refer to this factor to RIOA, rather than cooking.

Changes in text: See complete changes in text in the following comment.

Page 10 Ln 16-24: *The 5th factor, LV-OOA, may not show certain process or source, but it can show whether highly oxidized OA is important in the study locations. The LV-OOA can be formed from oxidation of primary OA (e.g., BBOA) or transported into the study location. The authors can discuss this further.*

Author's response:

We now added a thorough analysis for justifying the number of factors selected. We show that the addition of a fifth factor better explains $C_xH_yN_w$ and biomass burning (at *m/z* 60 and 73) related fragments. The additionally extracted factor in the five-factor solution, referred to as 'unknown', has elevated contributions from oxygenated fragments often related to SOA (*m/z* 44) and BBOA (*m/z* 60 and 73), but a time series that unambiguously relates this factor to a spatially variable primary emission source. In effect, the majority (62%) of this factor contribution arises from a split in the BBOA of the four-factor solution (the rest comes from the residuals and the OOA). Consequently, the sum of the contributions of the 'unknown' factor and the BBOA from the five-factor solution matches the BBOA contributions from the four-factor solution (R^2 = 0.97 and slope = 1.15 as shown in Fig. S6). This split in the BBOA is very likely a direct consequence of the variable nature of this combustion source or may potentially represent its very rapid/immediate aging. That is, as the concentrations of this more oxygenated BBOA are highly variable in time and space and coincide with high BBOA concentrations, this factor cannot be transported into the study location, but rather represents an emission from another combustion regime or, less likely, an immediately transformed primary aerosol. As this factor could not be attributed to a specific process and its addition did not significantly alter the contribution from other sources, we have considered the four-factor solution as an optimal representation of our data. This discussion is now added in the text.

Changes in text:

Page 10, Line 31: Some important diagnostic parameters of the source apportionment (including Q/Q_{exp}, factor-marker correlation, and time-series and profiles residuals for solutions with different number of factors) are reported in Fig. S5. The correlation coefficients (R^2) between factors and markers significantly increase when a fourth factor is included, but are not improved when a fifth factor is added. The addition of the fourth factor, which enabled the extraction of RIOA, allows explaining additional structures in the residuals' time series and unsaturated fragments in the residuals mass spectrum. Including a fifth factor also improves the model mathematical quality, by additionally explaining $C_xH_yN_w$ and biomass burning (at *m/z* 60 and 73) related fragments. The additionally extracted factor in the five-factor solution, referred to as 'unknown', has elevated contributions from oxygenated fragments often related to SOA (*m/z* 44) and BBOA (*m/z* 60 and 73), but a time series that unambiguously relates this factor to a spatially variable primary emission source. In effect, the majority (62%) of this factor contribution arises from a split in the BBOA factor from the four-factor solution (the rest comes from the residuals and the OOA). Moreover, the sum of the contributions of the 'unknown' factor and the BBOA from the five-factor solution matches the BBOA contributions from the four-factor solution (R^2 = 0.97 and slope = 1.15 as shown in Fig. S6). This split in the BBOA is very likely a direct consequence of the variable nature of this combustion source, but the two BBOA-like factors extracted in the five-factor solution could not be related to different emission processes. Furthermore, the addition of this factor did not affect the spectral profiles and time series of the other factors and their correlations with their respective markers and did not aid the interpretation of the data. Therefore, we considered the four-factor solution as an optimal representation of our data. Table 2 contains the correlation coefficients (R^2) between the OA profiles from the four-factor solution and available literature profiles (Aiken et al., 2009; Mohr et al., 2012; Setyan et al., 2012; Crippa et al., 2013b). The high correlations obtained in all cases support the use of a four-factor solution and strengthen the link between the RIOA and cooking emissions (R^2 of about 0.8 between RIOA and cooking tracer).

~~If the number of factors is decreased, the RIOA factor is not resolved and the OOA time-series becomes contaminated by local spikes, which is unexpected for a regional component (see Fig. S3 and S4). In contrast, if a five-factor solution is considered an additional highly oxygenated factor is obtained ("unknown" factor in Fig. S3 and S4). The mass spectrum of this additional factor resembles a low-volatility OOA (LV-OOA), as resolved in many previous works (Jimenez et al., 2009), but its time series exhibits the typical characteristics of the primary factors, i.e. strong increases in emission areas. Therefore, this further increase in the number of factors doesn't seem to improve the interpretation of the data, as the new factor cannot be explicitly associated to distinct sources or processes. Accordingly, a four-factor solution was considered as optimal and is utilized below.~~

Page 11 Ln 12-15: *Increase of RIOA in Talinn is relatively small. I think distribution of RIOA in Talinn is more homogeneous compared to Tartu. Thus, enhancement of RIOA in urban area of Talinn is not well supported.*

Author's response: We thank the reviewer for the important remark. We have accordingly modified this paragraph in the revised manuscript.

Changes in text:
Page 12, Line 19: In terms of relative contribution, OOA is dominant during night-time, explaining on average between 42 and 44 % of the OA mass in Tartu and Tallinn, respectively. ~~HOA and RIOA relative contributions to the total OA are higher during day-time (the relative contribution of HOA increases from about 20 to 32% in Tartu and from 11 to 27% in Tallinn; the relative contribution of RIOA increases from 20 to 27 % in Tartu and from 20 to 22 % in Tallinn).~~ The relative contribution of HOA to total OA mass is higher during day-time (32% in Tartu and 27% in Tallinn) than during night-time (20% in Tartu and 11% in Tallinn). RIOA is also enhanced during day-time in Tartu (27% compared to 20% during night-time), and has similar relative contributions for day- and night-time in Tallinn (20 and 22%, respectively). In contrast, BBOA shows similar relative contributions for day- and night-time in Tartu (~~explaining~~ representing about 17 % of the OA mass), and slightly lower contribution during ~~the~~ day-time in Tallinn (20 % during day-time and 25 % at night-time).

Page 13 Ln 1-3: *Spatial distribution of eBC, CO, and CO2 are consistent not only with HOA but also with BBOA. Thus, they may come from BBOA as well. It would be easier to show consistency or inconsistency by correlation coefficient (R^2) between those tracers and HOA and BBOA.*

Also, in general I disagree that CO2 is mostly traffic because it can be emitted from vegetation and other sources. The authors will need to provide more evidence to support CO2 from traffic.

Author's response: We agree that CO_2 sources other than traffic are also present in urban areas (e.g. vegetation, BBOA…). However, our results indicate that these sources don't have a visible effect on the CO_2 enhancements in the urban area, as the spatial distribution of the CO_2 enhancement corresponds best to the one of HOA. These additional sources will indeed have an effect on the CO_2 background concentrations, which are subtracted for the calculation of the enhancements.
Following the suggestion of the referee, we have added a table in the supplementary information of the revised manuscript that contains all the correlation coefficients (R^2) between the spatial distributions of all sources and components in Tartu. This table confirms that the spatial distributions of the enhancements of eBC, CO_2 and CO are in good agreement with those of HOA (R^2 of around 0.6 in all cases), but no correlation is found between these components and BBOA (R^2 of 0.1 or lower).

Changes in text:
Page 13, Line 16: Lastly, the sizes of the points represent the number of measurement points that were averaged in each case. The correlation coefficients (R^2) between the spatial distributions of all sources and components are reported in Table S1.

Page 14, Line 29: The spatial distributions of the eBC, CO_2 and CO (Fig. 4i-k ~~5g-i~~) are consistent with that of HOA (R^2 of 0.61, 0.59 and 0.58, respectively), which indicates that these species originate mostly from traffic.

Table S1: Correlation coefficient (R^2) between the spatial distributions of all sources and components.

Tartu

R^2	HOA	BBOA	RIOA	OOA	SO_4	NO_3	NH_4	Cl	eBC	CO_2	CO	CH_4
HOA		0.02	0.32	0.02	0.04	0.09	0.16	0.10	**0.61**	**0.59**	**0.58**	0.06
BBOA			0.47	0.05	0.28	0.20	0.16	0.47	0.03	0.01	0.10	0.11
RIOA				0.08	0.35	0.14	0.22	0.39	0.24	0.17	0.28	0.07
OOA					0.12	0.09	0.12	0.21	0.01	<0.01	<0.01	0.01
SO_4						0.07	0.10	0.12	0.03	0.02	0.08	0.03
NO_3							**0.60**	0.28	0.08	0.08	0.11	0.11
NH_4								0.24	0.09	0.05	0.11	0.10
Cl									0.07	0.03	0.11	0.13
eBC										**0.77**	**0.75**	0.08
CO_2											**0.78**	0.08
CO												0.14
CH_4												

Technical comments

Page 4 Ln 22: *Add reference for these statements.*

Author's response: Added in the revised manuscript.

Page 5 Ln 10: *Unit for flow rate is m3 s-1 or L min-1*

Author's response: Replaced "flow" by "velocity" in the revised manuscript.

Page 5 Ln 12: *What is the size of particle in the aerosol inlet before particles are divided into different aerosol measurements.*

Author's response: There is no particle size segregation in the inlet of the mobile laboratory. Thus, the size of the measured particles depends on the instrument and inlet system cut-off. The inlet size cut-off is estimated to be at around 5 µm and the AMS lens at 2.5 µm. This information has been added in the revised manuscript.

Changes in text:
Page 5, Line 18: Two different inlet lines connected the main inlet to the aerosol and gas-phase instrumentation. The size cut-off of the inlet system was estimated to be around 5 µm.

Page 5 Ln 28: *eBC has been defined in the introduction.*

Author's response: Corrected in the revised manuscript.

Page 8 Ln 28-30: *The statement about enhancement of negative health impacts is not well supported, as it was not within the scope of this study. I suggest the authors to omit the part or revise the sentence.*

Author's response: We agree with the reviewer and have revised the sentence in the revised manuscript.

Changes in text:
Page 9, Line 11: Such intermittent pollution plumes (expected in some areas in a city) cannot be detected from stationary measurements at an urban background site, but ~~enhance~~ may be associated with negative health impacts.

Page 10 Ln 29: *Delete "secondary" or change it to "secondary source (OOA)"*

Author's response: Changed in the revised manuscript.

Page 11 Ln 24: *"the 5th percentile (P05) of"*

Author's response: Corrected in the revised manuscript.

Page 13 Ln 20: *Add space "… is 4.2 …"*

Author's response: Added in the revised manuscript.

Table 2: *Superscript for the unit µg m-3.*

Author's response: Corrected in the revised manuscript.

Figure 2:
(a) What does the different shade of purple for CO2 mean?
(b) If the average pollutant concentrations exclude those from special events, this needs to be included in the title.

Author's response: (a) The different colors used for the CO_2 time series indicate data from different analyzers. Specifically, the light purple indicates data from the Licor analyzer, which is used in the period in which the Picarro analyzer was malfunctioning. This has been clarified in the figure legend of the revised manuscript.
(b) Yes, the special events were excluded for these calculations. This has been added in the figure caption of the revised manuscript.

Figure 3: *I think mass spectra relative contribution is not in %. For comparison, relative contribution in Figure S3 is unitless.*

Author's response: We apologize for this mistake; the unit has been removed in the revised manuscript.

Figure 8: *Add in the title that the back-trajectories is from 10:00 at 10 March 2014 to 8:00 at 11 March 2014.*

Author's response: Added in the revised manuscript.

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