

## Response to Referee #1

The authors thank the reviewer for his/her constructive and helpful comments:

*This paper presents the PMF analysis of AMS data in a semi-urban location in Finland. This type of deployment and analysis is not particularly new, however the authors go into some detail exploring an apparent organic nitrate signature. The results are possibly a little ambiguous, but given the potential importance of this chemical category, this result is relevant to ACP and still worth reporting. The manuscript is generally well written and scientifically sound, with only two major problems (see below), however fixing these merely entails caveating and toning down the conclusions and providing more supporting data from the PMF analysis, so I would recommend this be published subject to minor corrections.*

Answer:

We thank the reviewer for his/her positive comments on the manuscript.

General comments:

*The method of calculating organic nitrate on page 17278 is not quantitatively sound. To begin with, the authors are not explicit as to whether they are calculating the mass of the nitrate functional group present or the mass of organic molecules containing nitrate.*

Answer:

We are sorry to confuse the reviewer with terminology of organic and inorganic nitrate. In this study, we are calculating the mass concentration of nitrate species in form of functional groups both from organic and inorganic chemical species. To make this clearer, we rephrased the sentence in page 17279 ‘The fact that  $\text{NO}_x$  ions distribute between organic and inorganic PMF factors indicates that nitrate has both organic and inorganic chemical forms. Based on this observation, we can estimate the masses of organic nitrate and inorganic nitrate in this study’ to **‘The fact that  $\text{NO}_x$  ions distribute between organic and inorganic PMF factors indicates that nitrate (in the form of functional group) has both organic and inorganic chemical forms. Based on this observation, we can estimate the mass concentrations of nitrate in different chemical forms. The nitrate in organic molecules thereafter refers to organic nitrate and in inorganic molecules refers to inorganic nitrate’.**

*But regardless of this detail, the authors omit to discuss the relative ionization efficiency (RIE) of organic nitrate, which is not very well constrained in general, owing to the complications associated with thermal desorption and the dearth of laboratory data. This is discussed in more detail in Aiken et al. (doi: 10.1021/ac071150w) and Farmer et al. (2010), but it basically means that the mass concentration analysis presented here cannot be viewed as quantitatively accurate. I would regard the quantitative outcomes of these calculations as highly uncertain and they should be presented as such. However, they are still of interest in a qualitative sense.*

Answer:

To our knowledge, ionization of nitrate species (in inorganic or organic chemical compounds) affects the fragmentation of nitrate in a way that it only changes the ratios of  $\text{NO}^+$  and  $\text{NO}_2^+$  ions (e.g. Farmer et al., 2010), but we haven’t seen any reports on the ionization efficiency of nitrate species that is dependent on their chemical form (inorganic VS. organic species). Thus in this study, the same RIE is applied both for organic and inorganic nitrate. Anyhow, we have added discussion in page 17278, L22: **‘Since the RIE value for organic nitrate is not specified, we applied the same value of 1.1 as for inorganic nitrate. This might cause uncertainty in determining the organic nitrate mass.’**

*The authors must provide more data in the supplementary material to justify their choice of PMF solution. Specifically, why the 4-factor and 6-factor solutions were rejected and why a nonzero value of  $f_{peak}$  was used, given that Paatero et al. (doi:10.1016/S0169-7439(01)00200-3) recommends that  $f_{peak}=0$  is used for environmental data.*

Answer:

Following the reviewer's comments, we added one section in the supplementary materials to describe the selection of PMF factor solution and rotational ambiguity.

#### S2.1 PMF factor solution

Fig. S1 shows Positive Matrix Factorization (PMF) key diagnostics in this study. 5-factor solution  $F_{peak} +0.1$  were selected. Fig S2 shows the time series and profiles of PMF 5-factor solution at  $F_{peak}=+0.1$ . Factors 3 and 4 produced meaningful time series and mass profiles but we could not find other gas or particle phase observations that correlate with them during the measurement. Thus these two factors were merged to generate a new factor by a mass-weighted combination. After merging, the four factors are NIA (nitrate inorganic aerosol), LVOOA (low-volatile oxygenated OA), SVOOA (semi-volatile oxygenated OA), HOA (hydrocarbon-like organic aerosol). In 4-factor solution the factor 4 from 5-factor solution was divided between factor 5 and factor 2 and made HOA factor meaningless. In 6-factor solution the LVOOA from 5-factor solution was split into LVOOA1 (Factor 3) and LVOOA2 (Factor 4) without reasonable reason and doesn't give any better interpretation on the data (Fig. S4). Thus a 5-factor solution was selected.

The rotational ambiguity of 5-factor solution was explored by varying  $F_{peak}$  between -1.0 and +1.0. The choice of  $F_{peak} < -0.1$  gives periods of zeros in factor 4 that don't correspond to any events in observations. Increasing  $F_{peak}$  to +0.1 improves the corrections of SVOOA and NIA to nitrate compared to  $F_{peak}$  value of 0 whilst it does not affect the correlations of other factors to the external tracers. Thus  $F_{peak} = 0.1$  was selected (Fig. S5).

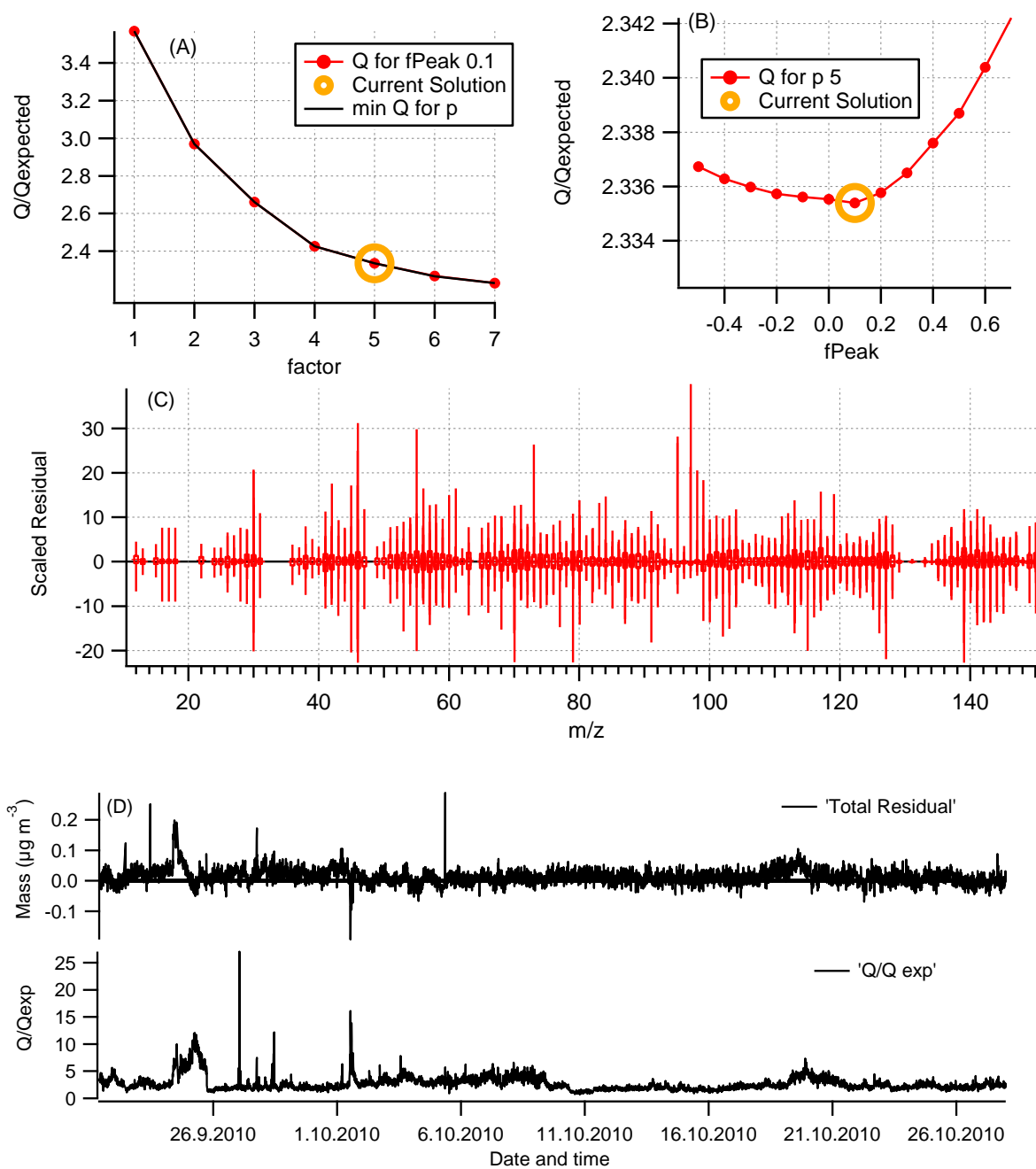


Fig. S1 PMF key diagnostics plots: (A)  $Q/Q_{\text{expected}}$  varies as function of PMF factor at  $F_{\text{peak}} 0.1$ ; (B)  $Q/Q_{\text{expected}}$  varies as function of rotational ambiguity; (C) Scaled residual for each mass; (D) time series of the total residual and  $Q/Q_{\text{exp}}$  contribution for every point during this study. For more details on PMF and the interpretation of these plots see Ulbrich et al. (2009).

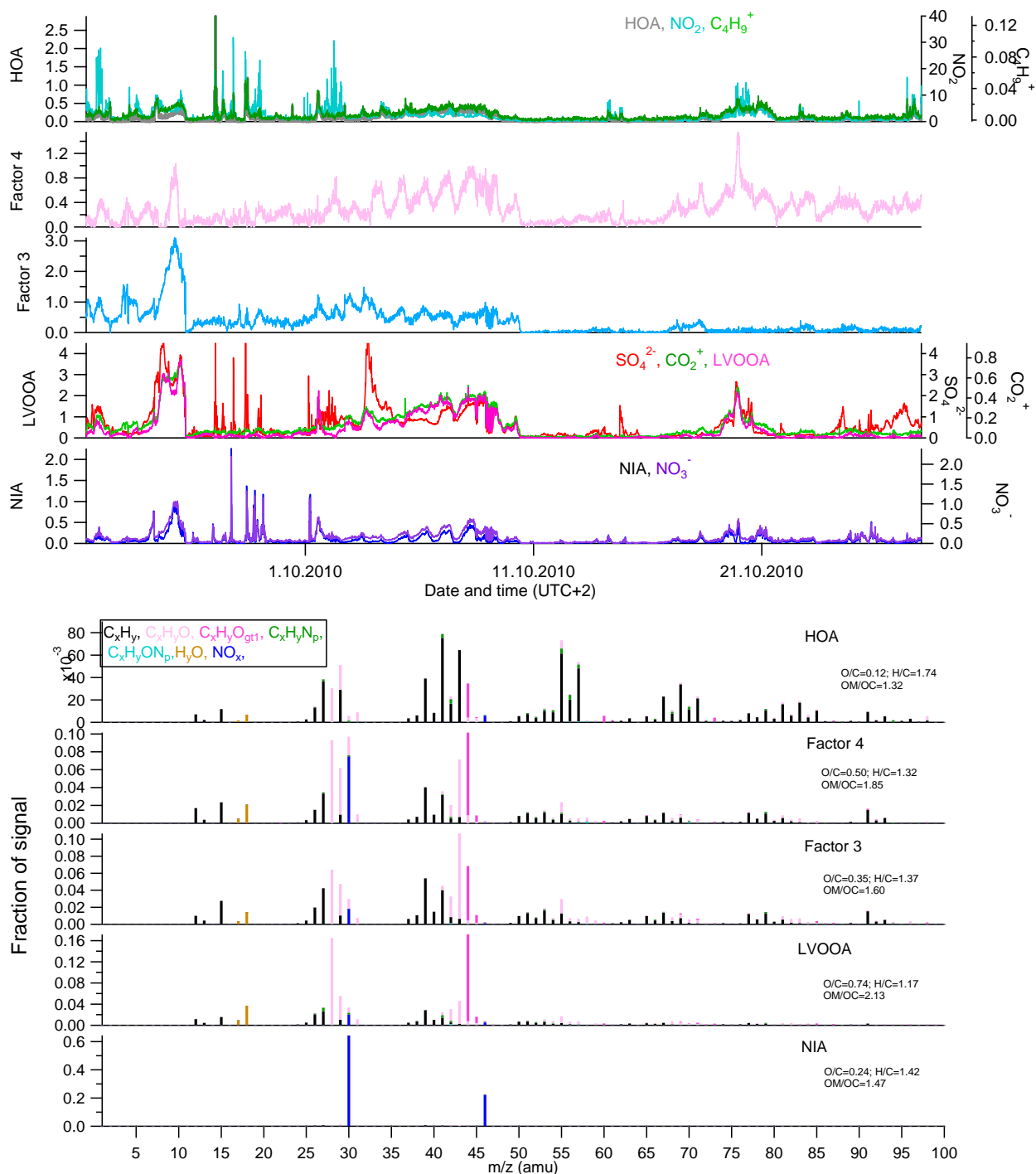


Figure S2. Time series and mass profiles by PMF analysis at 5-factor solution. Factor 3 and 4 were merged to generate a new factor by a mass-weighted combination, which results are reported in the paper. HOA, hydrocarbon-like organic aerosol; LVOOA, low-volatile oxygenated OA; NIA, nitrate inorganic aerosol

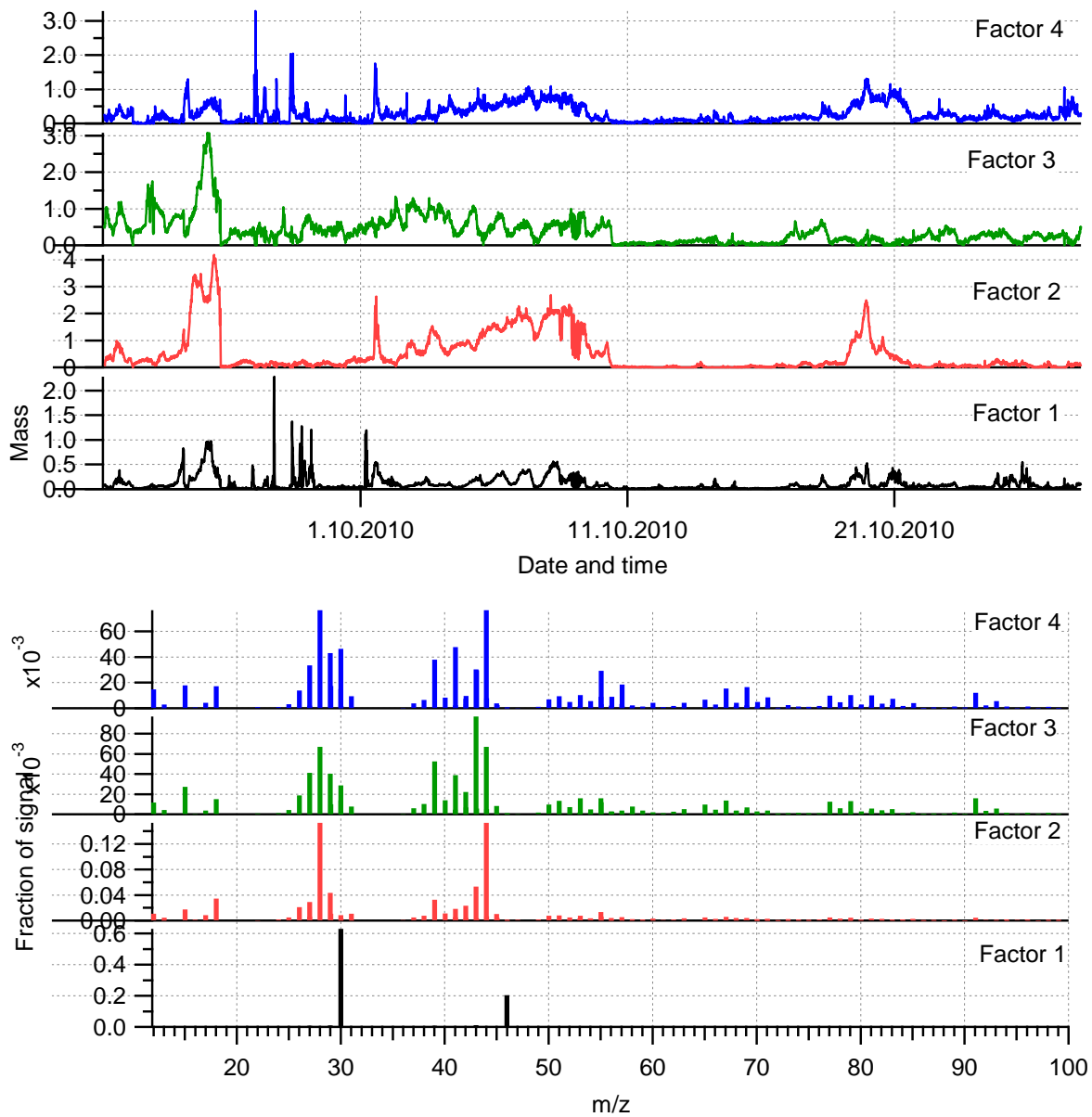


Figure S3. Time series and mass profiles by PMF analysis at 4-factor solution with  $F_{\text{peak}} = +0.1$ .

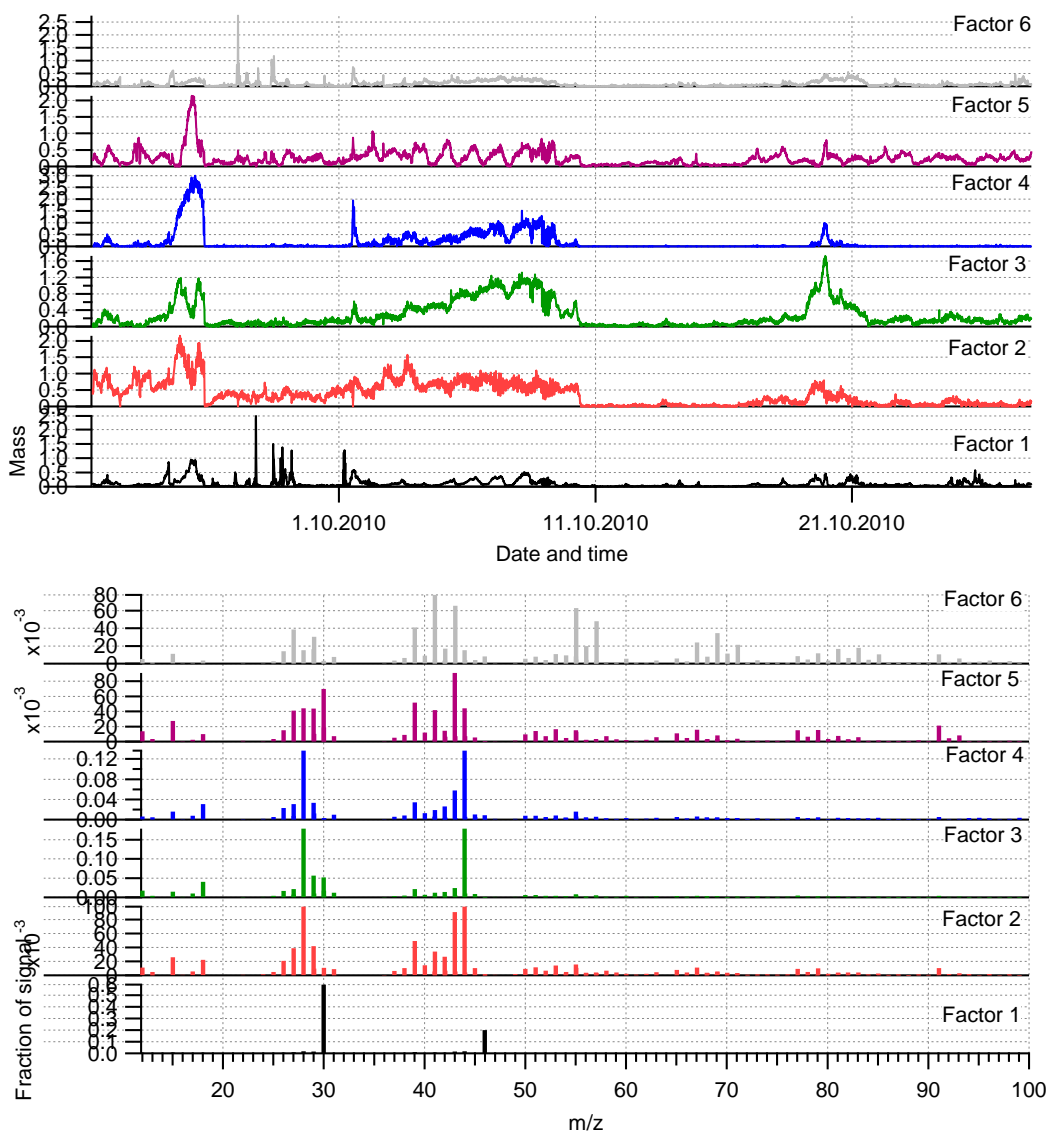


Figure S4. Time series and mass profiles by PMF analysis at 6-factor solution with  $F_{peak} = +0.1$ .

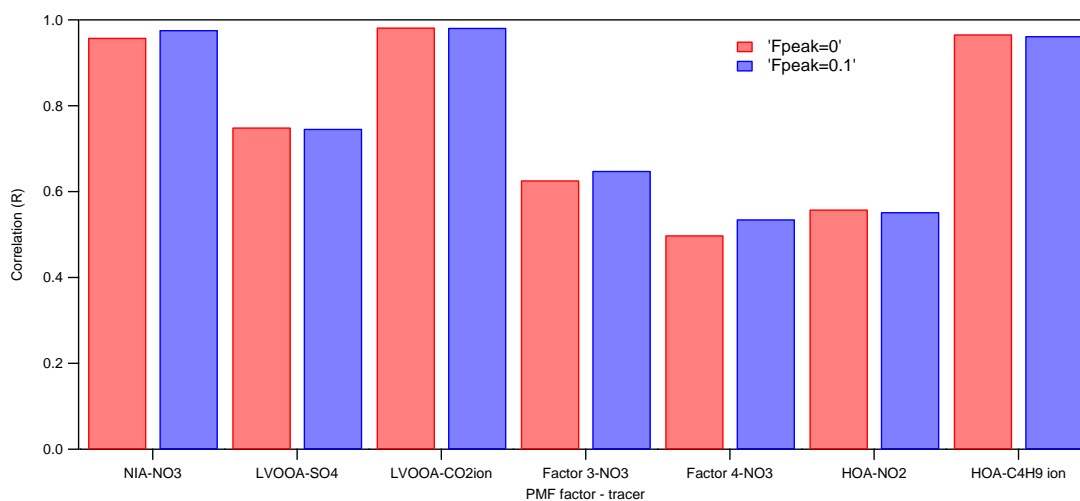


Fig S5 Correction coefficients between the PMF factors and tracers by varying  $F_{peak}$  from 0 to +0.1.

*Specific comments:*

*Page 17275-6: One cannot apportion OOA to biogenic and anthropogenic this way. What is reported by PMF as 'LV' and 'SV' OOA do not represent organic types in themselves but end members in a continuum of a highly complex chemical composition that is entirely dependent on the range of organic aerosols observed at a specific location and time. As such, their exact nature will vary dataset to dataset and no quantitative inferences regarding precursors can be derived from their abundances.*

Both reviewers raised their concerns on the calculation of anthropogenic OA contribution to the total OA and we admit that our analysis was not built on a solid base. Following the reviewers' comments, we deemphasized this particulate possible explanation. Accordingly we also revised the text:

P17275 L29 –P17276 L3: we rephrased the sentences 'Based on the measurement results in the boreal forest in Hyytiälä, where the SVOOA and LVOOA were observed in equal proportions (Raatikainen et al., 2010), biogenic SVOOA mass fraction can be approximately as 24% as LVOOA in Puijo tower. Thus the mass contribution from the anthropogenic VOCs to the OOA can be approximated as 40% (difference between 65.7% and 23.9%) in this study.' to '**Setyan et al., (2012) characterized the properties of atmospheric aerosol in a mixed biogenic and anthropogenic emission area. They observed that more oxidized OOA originates from biogenic VOC's, whereas less oxidized OOA is sourced to urban emission photooxidation products. However, the quantitative discrimination of biogenic and anthropogenic OOA species in this study is still a challenge based on the present measurement results because the forestland and urban areas surrounding the measurement site are intertwined.**'

P17277 L9-11: we also reworded the sentences 'HOA originated from the city emissions and contributed 10.4% to the mass of organic aerosols. Based on a rough approximation, the urban emissions also contributed more than 40% of OOA species by mass.' to '**HOA originated from the city emissions and contributed 8.9% to the mass of organic aerosols. Contribution of urban emission to the OOA species in this study is still uncertain and need further investigation.**'

Summary and conclusions: we also toned down the conclusions. We revised 'Compared to the measurement performed in a similar boreal forest environment in Hyytiälä, Finland, the anthropogenic emissions approximately contribute more than 50% to the total organics, highlighting the city as the local anthropogenic emission source to the atmospheric aerosols. The influence of anthropogenic activity on the biogenic OOA formation still requires further investigation in this study.' to '**Compared to the measurement performed in a similar Finnish boreal forest environment in Hyytiälä, the measurement in a forest-urban mixed region distinguished an extra HOA factor, which dominantly originated from urban emissions and comprised 8.9% of total organic aerosols. However, the quantitative discrimination of biogenic and anthropogenic OOA species and the influence of anthropogenic activity on the biogenic OOA formation still require further investigation.**'

*Page 17278, line 4: The mere presence of NO<sub>x</sub> ions in an organic PMF factor alone does not prove that they are organic in origin, as there could be a level of covariance between an organic component and inorganic nitrate for whatever reason, although the high 30/46 ratio in factor 4 in particular would indicate that it is not ammonium nitrate.*

Answer:

Using the presence of NO<sub>x</sub> ions in PMF organic factors to determine whether they are organic in origin is based on: (1) the PMF principle which works in a way that it collects the species with similar chemical properties into a same factor. In this study, 38% of NO<sub>x</sub> ions are apportioned to organic factors, indicating these NO<sub>x</sub> ions are the constituents of the organics or related to organics. The determined organic nitrate also shows good correlation to SVOOA ( $R^2=0.78$ ). (2) The ratio of NO<sup>+</sup>/NO<sub>2</sub><sup>+</sup> ions for the determined organic

nitrate is 10.4 in this study, being consistent with the values of 10-15 for the organic nitrates in the previous reports. This gives us confidence that our method holds.

*Technical corrections:*

*Page 17265, line 16: The technique employed by Zhang et al. (2005) was not strictly PCA.*

Answer:

We corrected the sentence to **‘The AMS-derived organics can be further investigated to track their different sources and processes by multivariate linear regressions (Zhang et al., 2005a; Zhang et al., 2005b) or multiple component analysis (MCA) (Zhang et al., 2007a).’**

*Page 17269, section 2.3: The instrument models should be specified for the supporting Measurements*

Answer:

Done.

*Page 17270, line 7 (and elsewhere): ‘motorway’ does not need hyphenating*

Answer:

Fixed

*Page 17274, line 15: Fix “Allan et all.” to “Allan et al.”*

Answer:

Fixed.

*Page 17275: It is not clear why there are bracketed numbers in this paragraph. I recommend making this clearer or removing them.*

Answer:

We have removed them.



## Response to Referee #2

The authors thank the reviewer for his/her constructive and helpful comments:

*This paper describes aerosol mass spectrometer (AMS) measurements and source apportionment using positive matrix factorization (PMF) made during fall in a boreal forest region which had moderate impacts from various local pollution sources. Submicron aerosol was half organics, a quarter sulfate and the remainder nitrate, ammonia and black carbon. PMF results showed ~90% percent of organics was oxidized organic aerosol (OOA) with a small contribution from hydrocarbon-like organic aerosol (HOA). In addition to including the standard practice of including explicitly organic ions in the AMS PMF analysis, the NO<sup>+</sup> and NO<sub>2</sub><sup>+</sup> ions, which can be from both inorganic nitrate and organic nitrate aerosol components as seen in the AMS, were included. This produced a fourth factor which was almost purely representative of inorganic nitrate. One-third of the NO<sup>+</sup> and NO<sub>2</sub><sup>+</sup> ions were apportioned to the one of the OOA factors, the semivolatile one (SVOOA), indicating that organic nitrates are at least one component of the SVOOA and related to its formation. It is hypothesized that the organic nitrate, peaking at night to early morning, may be produced from NO<sub>3</sub> radical + biogenic VOC -initiated reactions. Several hypotheses are presented as to why the OOA contribution is so large, particularly compared to other measurements in the region. The manuscript is generally well written and describes a clear and straightforward analysis of AMS/PMF results in an important environment (boreal forest with anthropogenic influences). The authors demonstrate the ability to expand the capability of AMS/PMF to quantify contributions of organic nitrates and their association with organic aerosol sources or processes. This manuscript warrants publication in ACP after relatively minor revisions.*

Answer:

We thank the reviewer for his/her nice summary and positive comments on this manuscript.

*General comments followed by a detailed list of comments are below.*

*General/Main Comments:*

*- Two key numbers, SVOOA and LVOOA contributions to OA appear to be grossly inconsistent in the text and figures on which a major conclusion rests (anthropogenic contribution to OOA). It raises concern that other mistakes may have been made in the analysis and interpretation that are not so transparent.*

Answer:

We thank the reviewer for careful examination of the data. We checked the data again and noticed the mistake in the calculation on the average mass fractions of SVOOA and LVOOA. After correction, SVOOA and LVOOA components accounted for 54.8 and 36.3% of the total organic aerosol mass, respectively. The results don't change the conclusions, but we apologize to this fault.

*- The authors appear to have overstated/overinterpreted the tenuous conclusion that because there is more SVOOA compared to LVOOA compared to measurements at a more remote location, that all the "extra" SVOOA comes from anthropogenic emissions. While an interesting speculation, the evidence doesn't warrant the level of certainty that the authors appear to place on it. The authors need to provide stronger evidence in their analysis otherwise assign a more appropriate level of certainty (probably doesn't belong in the conclusions, at least in present form). See more detailed comments on this aspect below.*

Answer:

Both reviewers raised their concerns on the calculation of anthropogenic OA contribution to the total OA and we realized that our analysis was not built on a solid base. Following the comments, we deemphasized this particulate possible explanation and leave the problem for future studies. Accordingly we also revised the text:

P17275 L29 –P17276 L3: we rephrased the sentences ‘Based on the measurement results in the boreal forest in Hyytiälä, where the SVOOA and LVOOA were observed in equal proportions (Raatikainen et al., 2010), biogenic SVOOA mass fraction can be approximately as 24% as LVOOA in Puijo tower. Thus the mass contribution from the anthropogenic VOCs to the OOA can be approximated as 40% (difference between 65.7% and 23.9%) in this study.’ to ‘**Setyan et al., (2012) characterized the properties of atmospheric aerosol in a mixed biogenic and anthropogenic emission area. They observed that more oxidized OOA originates from biogenic VOC’s, whereas less oxidized OOA is sourced to urban emission photooxidation products. However, the quantitative discrimination of biogenic and anthropogenic OOA species in this study is still a challenge based on the present measurement results because the forestland and urban areas surrounding the measurement site are intertwined.**’

P17277 L9-11: we also reworded the sentences ‘HOA originated from the city emissions and contributed 10.4% to the mass of organic aerosols. Based on a rough approximation, the urban emissions also contributed more than 40% of OOA species by mass.’ to ‘**HOA originated from the city emissions and contributed 8.9% to the mass of organic aerosols. Contribution of urban emission to the OOA species in this study is still uncertain and need further investigation.**’

Summary and conclusions: we also toned down the conclusions. We revised ‘Compared to the measurement performed in a similar boreal forest environment in Hyytiälä, Finland, the anthropogenic emissions approximately contribute more than 50% to the total organics, highlighting the city as the local anthropogenic emission source to the atmospheric aerosols. The influence of anthropogenic activity on the biogenic OOA formation still requires further investigation in this study.’ to ‘**Compared to the measurement performed in a similar Finnish boreal forest environment in Hyytiälä, the measurement in a forest-urban mixed region distinguished an extra HOA factor, which dominantly originated from urban emissions and comprised 8.9% of total organic aerosols. However, the quantitative discrimination of biogenic and anthropogenic OOA species and the influence of anthropogenic activity on the biogenic OOA formation still require further investigation.**’

*- Throughout the manuscript articles are often omitted or inserted incorrectly. Best to have a native English speaker proofread before submitting, if needed.*

Answer:

We will proofread the article and ACP also has language check before publishing.

*Detailed Comments:*

*P17265, L12: delete “the”*

Answer:

Fixed.

*P17266, L7-9: Suggests adding “may” before “enhance biogenic emissions”. Most of these studies provide evidence that this appears to be happening, but rarely, if at all, is the evidence demonstrative.*

Answer:

Fixed.

*P17266, L20-21: Why cite only older studies showing that quantifying organic nitrates is challenging but not mention more recent studies where it has been done well in the field (e.g. Rollins et al. Science 2012, Liu et al. JGR, 2012, Fry et al., ACP, 2013)? Omitting them appears as cherry picking, ignoring more recent advances in detection of particle-phase organic nitrates.*

Answer:

We have updated the cited references in the revised manuscript.

*P17267, L9: need “the” before “city”*

Answer:

Fixed.

*P17267, L25: Provide reference for SQUIRREL and PIKA. No one outside the AMS community would know what these are.*

Answer:

We have added a webpage link: <http://cires.colorado.edu/jimenez-group/ToFAMSResources/ToFSoftware/index.html> as a reference for SQUIRREL and PIKA in the revised manuscript.

*P17268, L6-8: Why was CE=0.5 chosen? Why not use the Middlebrook et al. (AS&T, 2012) chemical-dependent CE algorithm? What was the slope of the AMS vs SMPS after a constant CE=0.5 was applied (Fig. 2c seems to show that sometimes the AMS is high and other times the DMPS is higher). Does applying the chemically dependent CE improve the correlation coefficient? Also, the application of CE correction is for particle bounce on the vaporizer only, not for the lens transmission. For a properly-aligned lens, the transmission should be 100% between 50-600 nm and then decrease outside that range. So accounting for lens transmission effects would be a size-dependent correction. See Middlebrook et al. for discussion and references.*

Answer:

The AMS CE depends on the particle bounce on the vaporizer, which is subject to the relative humidity, acidic sulfate particles, and ammonium nitrate mass fraction (Middlebrook et al. AS&T, 2012). Particle losses in the lens transmission are minor (Middlebrook et al. AS&T, 2012). Our AMS in this work was running with a sil-gel dryer in front of the inlet, and the particles are basically neutralized (refer to Fig. S8), thus the effects of relative humidity and acidity on CE variations can be negligible. A constant CE can be used for the mass fraction of ammonium nitrate <0.4 and a linear CE increase with CE>0.4 ((Middlebrook et al. AS&T, 2012). In this work the mass fraction of ammonium nitrate over 99.94% of time is <0.4 (see Figure C1), and thus a constant of CE=0.5 is applied. The measured AMS total mass concentration plus BC mass concentration shows a nice consistence with DMPS measurement (Figure C2,  $R^2=0.95$ , slope=1.1).

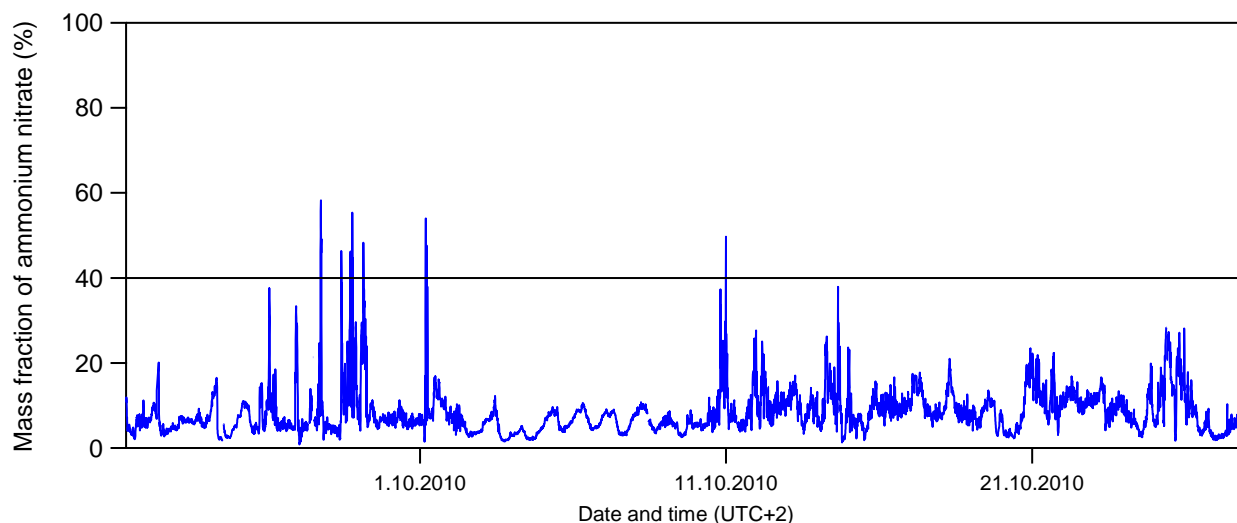


Figure C1 Mass fraction of ammonium nitrate in the study.

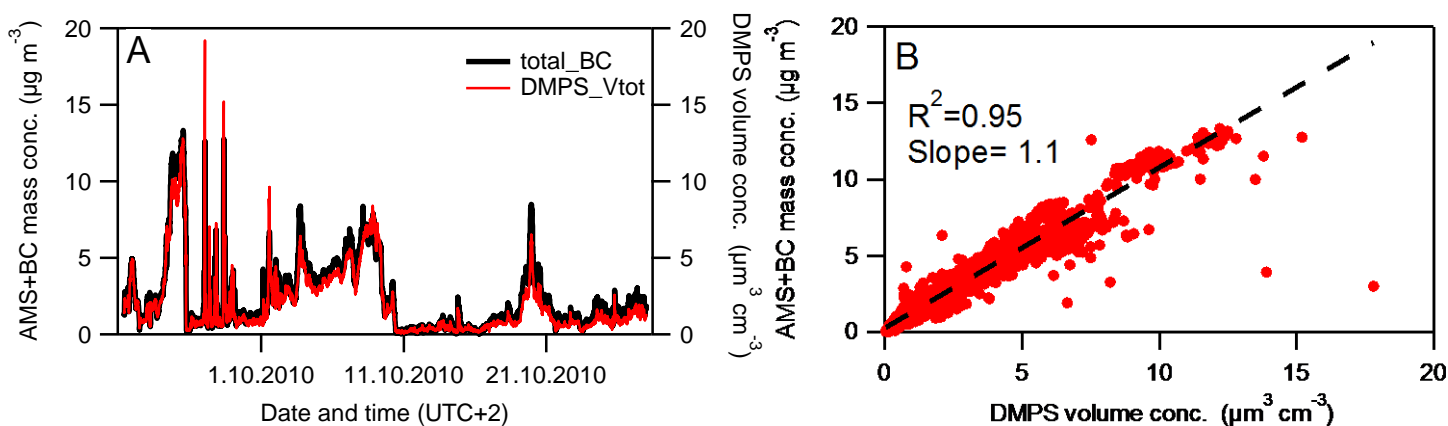


Figure C2 Comparisons between AMS total mass+BC concentration and DMPS volume concentration.

*P17268, L27-29: What happened for the 4-factor solution? It seems equally relevant to comment on that as for the problem with the 6-factor solution (especially since the 5-factor solution was combined to 4 factors).*

Answer:

In 4-factor solution the factor 4 from 5-factor solution was divided between factor 5 and factor 2 and made HOA factor meaningless. In 6-factor solution the LVOOA from 5-factor solution was split into LVOOA1 (Factor 3) and LVOOA2 (Factor 4) without reasonable reason and doesn't give any better interpretation on the data (Fig. S4). We have added one section to describe the selection of PMF factor solution and rotational ambiguity in the supplementary materials. Please also refer to our reply to Review 1.

Accordingly, we added one sentence in Line 2, Page 17270 that **'A discussion of the PMF results is presented in Sec. 3.2 and Sec. S2.1 in the supplementary materials.'**

*P17270, L4: missing "the" before "northern direction".*

Answer:

Fixed.

*P17270, L5: Note the typical durations of the high sulfate peaks (can't tell from Fig. 2)*

Answer:

A zoomed figure is supplied in Fig. S7 to show the duration of the high sulfate peaks. We also mentioned in the manuscript in P17270 L5 that **'A few high concentration peaks of sulfate, nitrate and organic species during Sep. 27- 28 (e.g., the gray bar in Fig. 2 and the zoomed figure in Fig. S7) were also observed.'**

*P17270, L11: "Pearson's", not "Person"; Also, please report the slope too.*

Answer:

Fixed and slope=1.1.

*P17271, L1: "Major aerosol mass" is vague and should be reworded to clarify what is meant.*

Answer:

We reworded 'major aerosol mass' to 'the high mass concentration'.

*P17271, L2: Need "the" before "paper mill".*

Answer:

Fixed.

*P17271, L13: “The cycle [of sulfate] does not display dramatic variations” is a bit strong language as it’s very much an understatement. There is very little average diurnal variation so better to state from that angle.*

Answer:

We rewarded this sentence to ‘**On average, the diurnal variations are small**’

*P17271, L20: Add “a” before “similar”. There are several instances throughout the manuscript where articles (the, a) are left out or included when not needed. I’ll leave it up to the authors or ACP to carefully proofread and correct these and will not list them all here.*

Answer:

Fixed.

We will proofread the article and ACP also has language check before publishing.

*P17271, L28: “observed to distribute around a peak in the northwest direction” is odd wording. Consider rewording.*

Answer:

We reworded to ‘**The particulate nitrate demonstrates a peak in the northeast direction.**’

*P17271, L29: “which is believed to be due to emissions from the paper mill”. Give a reference for this or explain reasoning.*

Answer:

We explained that ‘**As locally formed chemical species, the high concentration from that direction is consistent with the locations of paper mill and motorway and therefore is believed to be attributed to the emissions from the sources.**’

And also on P17278, Line24-27, we have other explanations that ‘The inorganic nitrate aerosol in this study shows high concentrations from the northeast direction (Fig. 10B), which is believed to be due to the emissions from the paper mill and motorway. The high concentration of inorganic nitrate aerosol from the southwest follows a similar pattern to that of gaseous NO<sub>2</sub> (Fig. S11); therefore, this nitrate can be attributed to secondary conversion of urban emissions.’

*P17271-72: Why is the diurnal cycle of sulfate discussed here but nothing about the other species? Seems incomplete (even if there is more detailed discussion of nitrate later).*

Answer:

We added discussion on the nitrate diurnal cycles:

P17271-17272, we rephrased the paragraph ‘Particulate nitrate species were observed to distribute around a peak in the northeast direction (Fig. 3F), which is believed to be due to the emissions from the paper mill and motor-way. The nitrate species were separated into organic and inorganic sub-components in this study and will be discussed more in Sec. 3.2.3.’ to ‘**The particulate nitrate concentration demonstrates a peak in the northeast direction (Fig. 3F). As locally formed chemical species, the high concentration from that direction is consistent with the location of paper mill and motorway and therefore is believed to be attributed to the emissions from both sources. The nitrate species were separated into organic and inorganic sub-components in this study. The diurnal cycle of nitrate shows a very small peak in the morning and a decrease in the afternoon (Fig. 4). Such a diurnal behavior can be explained by the facts that the relatively low temperature and higher relative humidity favor the gas to particle partitioning of nitrate during the night-time and morning. The slight decrease of nitrate in the**

afternoon is attributed to the dilution of nitrate concentration caused by the increase in the boundary layer height and also the possible evaporation of particulate nitrate species due to increasing temperature. More discussion is provided in Sec. 3.2.3’.

For BC diurnal cycle, we added on Page 17272 that ‘The diurnal cycle of BC peaked at 10:00, displaying a similar cycle as HOA factor. The cycle behavior is the outcome of traffic and city life in a relatively small- city and will be discussed more in Sec. 3.2.1.’

P17271, Line 24-26, we also have descriptions on organic diurnal cycle that ‘The diurnal pattern is the interplay of HOA, Semi-volatile oxygenated organic aerosol (SVOOA) and low-volatility oxygenated organic aerosol (LVOOA) components that are extracted from organic spectra by PMF analysis. A more detailed explanation will be provided in Sec. 3.2.’

*P17272, L3-9: In investigation/discussion of the ammonium balance and acidity it would be appropriate to exclude the organic nitrate fraction of the total AMS-measured nitrate. It probably doesn’t make a lot of difference since sulfate is » nitrate but nonetheless this point should be made here since the authors have this information.*

Answer:

We agree with reviewer. But the idea here is to investigate the neutralization of particles in a routine way as has been conducted in the AMS community, which takes all nitrate and sulfate species into account. The overpredicted ammonium can be explained by acidic sulfate and organic nitrate. Thus we don’t make any change in the manuscript.

*P17273, L13-15: Showing a high correlation of the HOA factor with the saturated m/z 57 ion peak doesn’t really seem meaningful, in that, if all the m/z 57 was in the HOA factor, clearly one would expect them to correlate. Pointing out that the HOA factor looks like other HOA factors and combustion spectra would be more relevant and convincing. Correlation with other combustion factors such as BC would also be more relevant to the discussion. Also, correlation with NO<sub>x</sub> is weak. Can the authors comment on that?*

Answer:

The HOA mass spectra in this study showed high similarity to other HOA factors determined in other measurement sites. Correlation coefficient with BC is 0.44. If we check the time trends of HOA and NO<sub>x</sub>, they are following each other in most of the time (shown in the following figure). Occasionally, NO<sub>x</sub> had strong local sources, e.g. from paper mill, which weakened the correlation with HOA.

We have added the discussion on Page 17273, L12

‘The HOA profile shows high similarity to other HOA mass spectra determined in Pittsburgh ( $R^2=0.91$ , Ulbirsch et al., 2009 and  $R^2=0.84$ , Zhang et al., 2005a) and also the averaged HOA spectra on a global scale ( $R^2=0.88$ , Ng et al., 2010) (Fig. S9).’ and Page 17273, L15 ‘HOA also correlates with other combustion tracers such as and BC ( $R^2 = 0.44$ ) and NO<sub>x</sub> ( $R^2 = 0.31$ ) (Fig. 5 and Fig. S9).

we also supplied the following figures in the supporting materials:

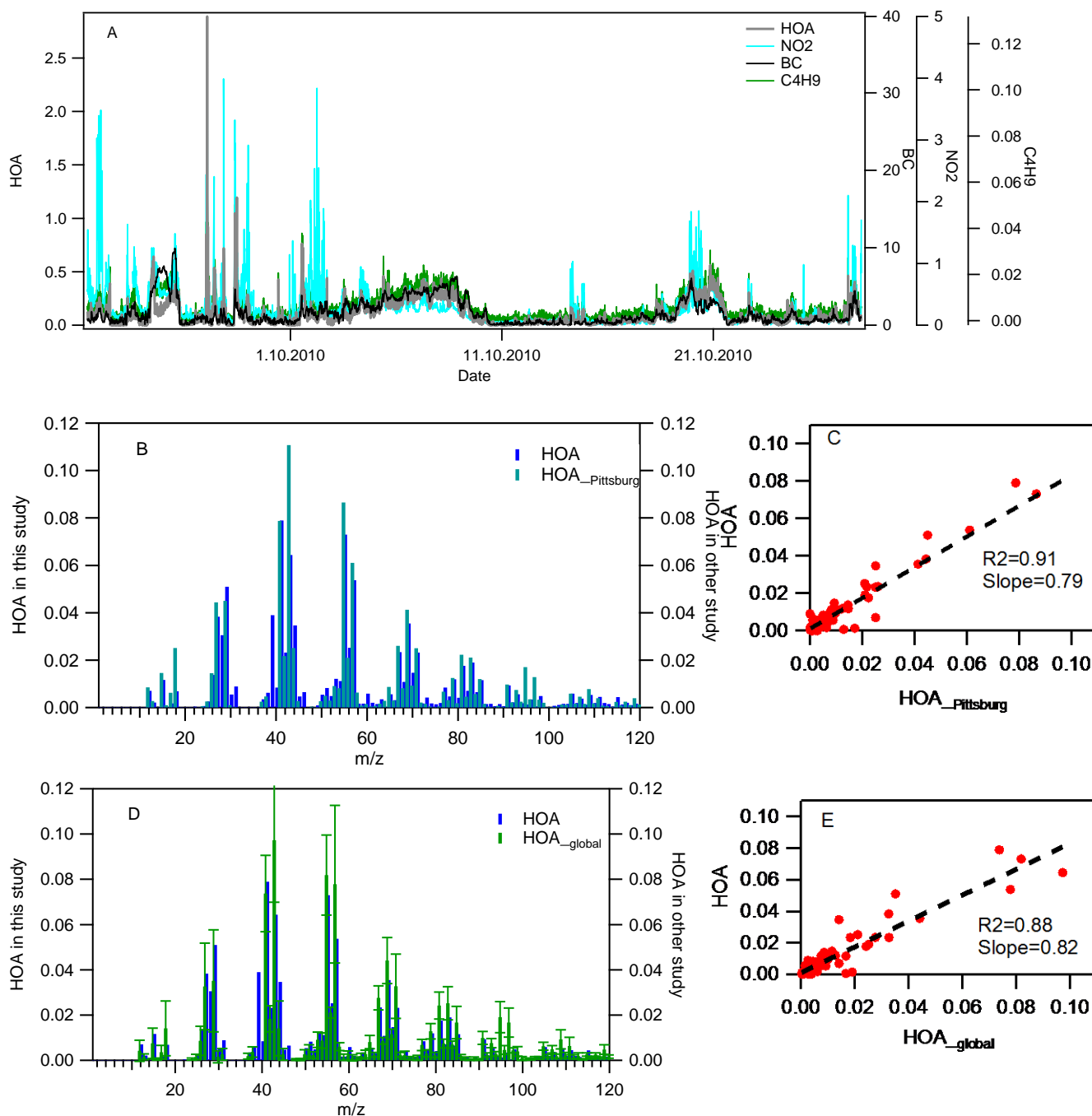


Figure S9 (A) Correlations of HOA time series with tracers; (B) Comparison of HOA mass spectrum from HOA determined in Pittsburg (Ulbrich et al., 2009); (C) a scatter plot of HOA mass spectrum between this study and Pittsburg; (D) Comparison of HOA mass spectrum from HOA determined on a global scale (Ng et al., 2010); (E) a scatter plot of HOA mass spectrum between this study and on a global scale;

*P17274, L24: Sentence doesn't make sense (non sequitur). What is being compared?*

Answer:

We have rephrased to this sentence to ‘A survey of correlation relationships shows that SVOOA correlates with nitrate ( $R^2=0.55$ ) and sulfate ( $R^2=0.48$ ), whilst LVOOA shows a good correlation with sulfate ( $R^2=0.56$ ).’

*P17275, L2: “are representative of SOA” is unclear. Elaborate.*

Answer: we revised to ‘are formed as SOA’

*P17275, L11: “SVOA and LVOA components account for 65.7% and 23.9% of the total organic aerosol mass”. Looking at Figure 8A, it appears the average SVOOA is  $\_0.6$  ug/m<sup>3</sup> and LVOOA is  $\_0.45$  ug/m<sup>3</sup> which means that SVOA is only 30% higher than LVOOA. Yet the percentages in the text suggest it’s 2.7 times higher? Discussion on the following page and a statement in the conclusions is based on these percentages. This is a bit worrisome since while this apparent error is obvious to the reader, it raises the concern that there are other major calculation errors that are not possible for a reader to discern.*

Answer:

See earlier reply, we found a mistake in calculations and the numbers are now corrected.

*P17276, L1: change “approximately” to “approximated” and “in” to “at the”*

Answer:

Fixed.

*P17277, L6: “component” should be plural*

Answer:

Corrected.

*P17277, L7: “one more HOA factor”? Do the authors really mean “one more factor, which was a HOA factor”?*

Answer:

The reviewer is correct. We have revised it.

*P17277, L10-12: The authors have concluded that urban emissions “contributed more than 40% of OOA species by mass” based simply on comparing the SVOOA contribution to the LVOOA contribution and that to the relative ratio at a more remote site in the region and then assigning the “extra” SVOOA to SOA from anthropogenic SOA. This result also appears in the conclusions (apparently adding in the HOA to get the total contribution of anthropogenic OA to total OA of 50%). The authors give several other reasons in that section why there may be high OOA mass fraction during this study, e.g. anthropogenic-biogenic interactions, cooler temperatures, etc. (pages 17275, 17276). In fact, looking at the wind roses in Fig 7A, it appears that SVOOA is a larger fraction of OOA when the wind is from the northern wind sector hemisphere rather than from the south of southwest where the urban center is. It is not clear why the authors have picked this particular one out as the explanation that they seem to assign considerable certainty (i.e. repeated in end of section and conclusions). The reasoning and support for this is tenuous at best (albeit certainly possible). Other reports of anthropogenic biogenic interactions appearing to show enhanced SOA typically have shown that most of the carbon is modern, not fossil. It seems unlikely that 50% of the carbon was of fossil origin at this site (which this claim would suggest). It would seem more appropriate for the authors to de-emphasize this one particular possible explanation for their observations, probably giving it equal weight to the other 6 possibilities presented in Section 3.2.2. Unless, of course, they can present more convincing support.*

Answer:

We thank the reviewer for the very detailed explanation on this point. The interpretation to Fig. 7 is that even the mass fraction of SVOOA is much greater in the northern direction than in the southern (Fig 7C), but the absolute mass concentration is much lower than in southern (Fig. 7B). Both reviewers raised their concerns on the calculations of anthropogenic OA contribution to total OA and we realized that our analysis was not built on a solid base. Following the comments, we deemphasized this one particulate possible explanation and leave more detailed investigation for future studies. Detailed reply please refers to prior answer.



*.P17278, L27-28: Authors state: “organic nitrate shows a good correlation with SVOOA, suggesting that it could be Semi-volatile” Like the m/z57 correlation with HOA (see above), this statement seems a bit circular or indirect logic. 75% of the organic nitrate has been attributed to the SVOOA PMF factor (Fig 9) so clearly we’d expect them to correlate. Isn’t the fact that 75% of the organic nitrate is in the SVOOA factor the most direct evidence that it may be semivolatile? Likewise, don’t the results suggest that 25% is not SV?*

Answer:

Yes, we agree that 75% fraction of organic nitrate in SVOOA is indicative of its semi-volatile property. We also observed 24% of organic nitrate in LVOOA and 1% in HOA, which indicate that they are not semi-volatile.

Following the reviewer’s comment, we changed our argument on P17278, L26 ‘Organic nitrate shows a good correlation with SVOOA ( $R^2=0.78$ , Fig. S13), suggesting that it could be semi-volatile’ to ‘**For organic nitrate aerosol, 74.4% of mass was assigned in SVOOA, suggesting that it is semi-volatile in nature, whilst we also observed 24.3% of organic nitrate in LVOOA and 1.3% in HOA.**’

We also deleted Fig. S7.

*P17279, L13: add “been” before “observed”*

Answer:

Fixed.

*P17280, L5: I think the authors mean organic nitrate “fractions of nitrate”, not “concentration” based on the preceding discussion of other observations.*

Answer:

The reviewer is correct and we have fixed it accordingly.

*P17280, L6: Should qualify as organic nitrate “functional group” since technically the whole molecule is an organic nitrate which is not what is reported here.*

Answer:

Both reviewers commented the terminology of organic nitrate which is widely used in the manuscript. Both reviewers are correct that we are quantifying the nitrate species in form of function groups. To make this clearer, we rephrased the sentence in page 17279 ‘The fact that  $\text{NO}_x$  ions distribute between organic and inorganic PMF factors indicates that nitrate has both organic and inorganic chemical forms. Based on this observation, we can estimate the masses of organic nitrate and inorganic nitrate in this study’ to ‘**The fact that  $\text{NO}_x$  ions distribute between organic and inorganic PMF factors indicates that nitrate (in the form of functional group) has both organic and inorganic chemical forms. Based on this observation, we can estimate the mass concentrations of nitrate in different chemical forms. The nitrate in organic molecules thereafter refers to organic nitrate and in inorganic molecules refers to inorganic nitrate.**’

*P17280, L18: It doesn’t seem useful to report the total contribution of the highest two species (organic and sulfate) since that is a common result and they have very different sources. Reporting their contributions separately would be more informative. Ditto for abstract. Same goes for the 89.6% for SVOA + LVOOA a few sentences below (but in that case also noting that together as OOA they comprise 90% of the OA mass may be appropriate).*

Answer:

Following the reviewer’s comment, we rephrased the sentence on P17280, L18 ‘On average, the submicron aerosols in the study are dominated by organic and sulfate species, contributing 76.9% of total observed

aerosol mass.’ to ‘**On average, the submicron aerosols in the study are dominated by organic and sulfate species, contributing 48.2% and 28.7% of total observed aerosol mass, respectively.**’ We also did the same change in the Abstract.

We also changed in Abstract ‘For organic factors, the semi-volatile oxygenated organic aerosol (SVOOA) and low-volatile oxygenated OA (LVOOA) accounted for 89.6% of total organic masses,’ to ‘**For organic factors, the semi-volatile oxygenated organic aerosol (SVOOA) and low-volatile oxygenated OA (LVOOA) accounted for 54.8% and 36.3% of total organic masses, respectively,**’.

*P17281, L6: delete “as”*

Answer:

Fixed.