

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 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 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 NO^+ and 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. We have added discussion in page 17929: **‘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).

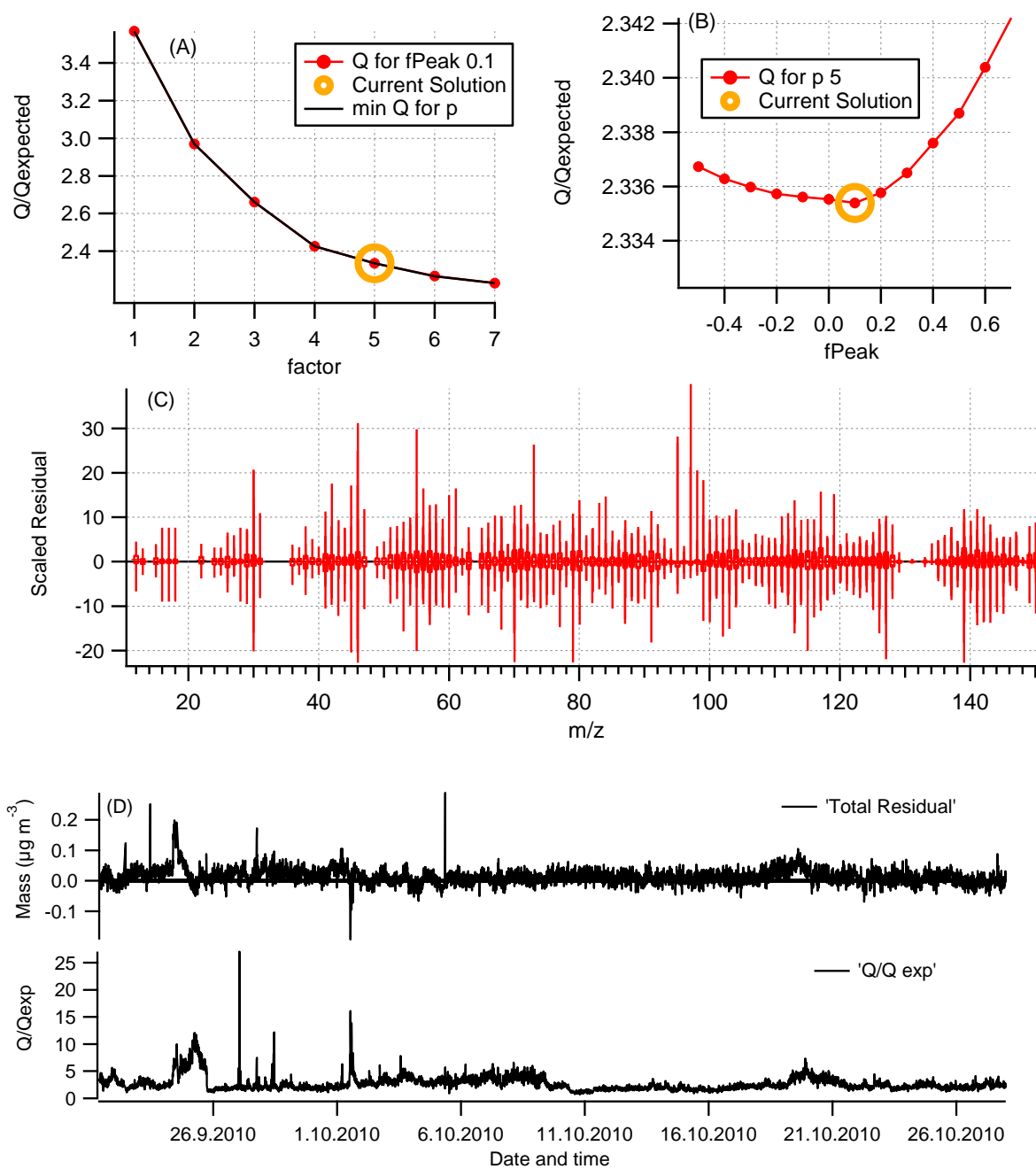


Fig. S1 PMF key diagnostics plots: (A) Q/Q_{expected} varies as function of PMF factor at $F_{\text{peak}} 0.1$; (B) Q/Q_{expected} varies as function of rotational ambiguity; (C) Scaled residual for each mass; (D) time series of the total residual and Q/Q_{exp} contribution for every point during this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

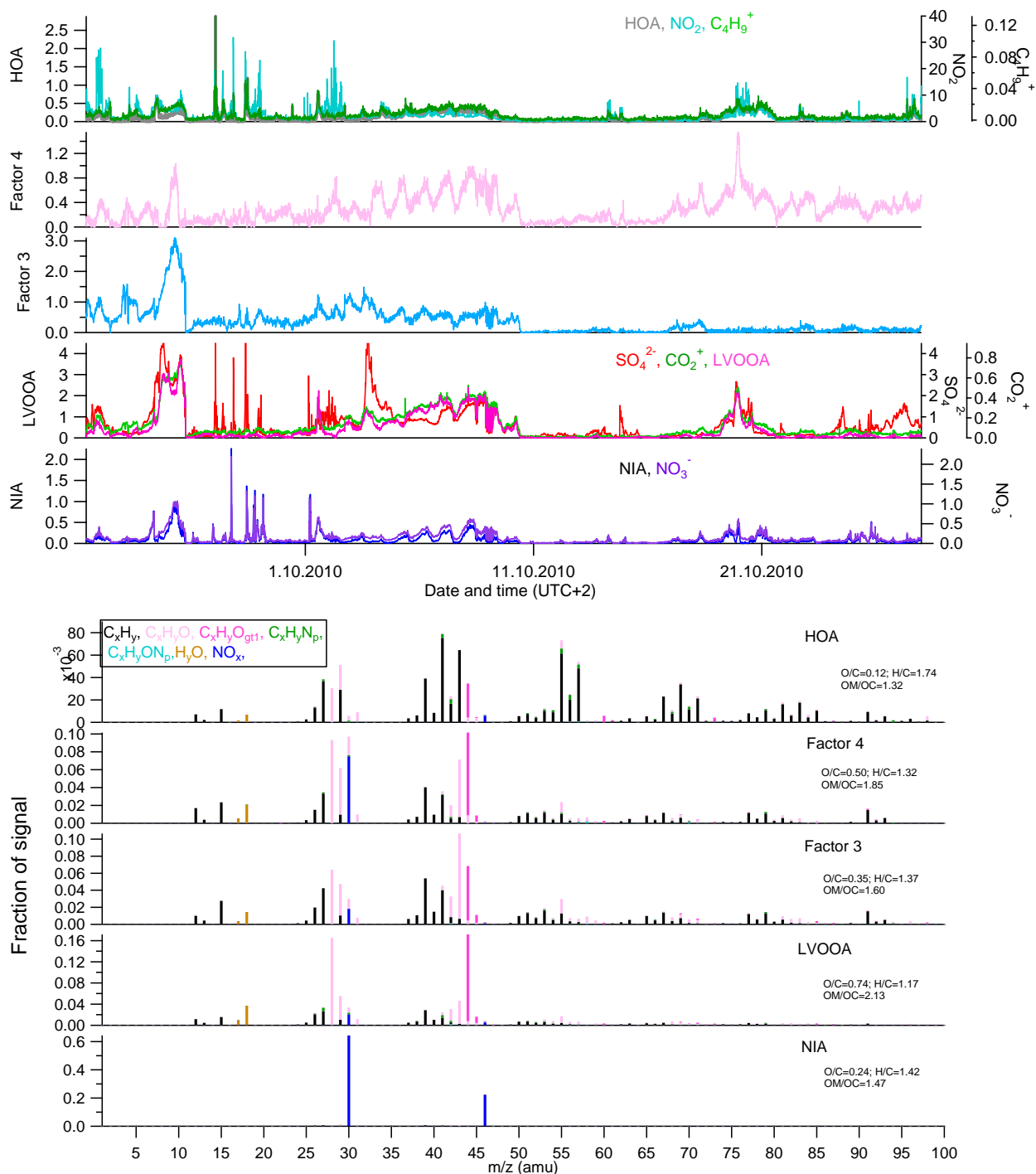


Figure S2. Time series and mass profiles by PMF analysis at 5-factor solution. Factor 3 and 4 were merged to generate a new factor by a mass-weighted combination, which results are reported in the paper. HOA, hydrocarbon-like organic aerosol; LVOOA, low-volatile oxygenated OA; NIA, nitrate inorganic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

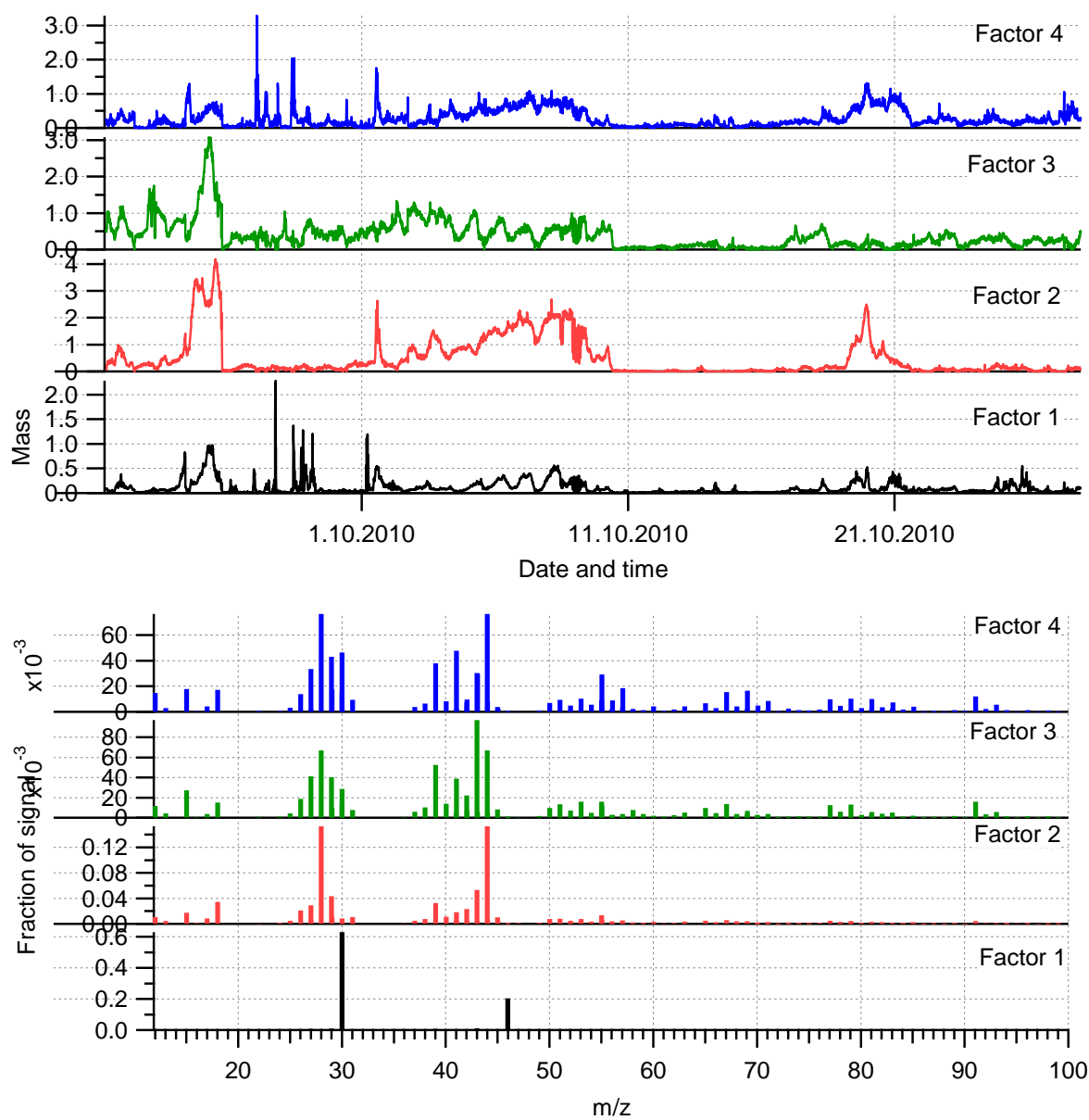


Figure S3. Time series and mass profiles by PMF analysis at 4-factor solution with $F_{\text{peak}} = +0.1$.

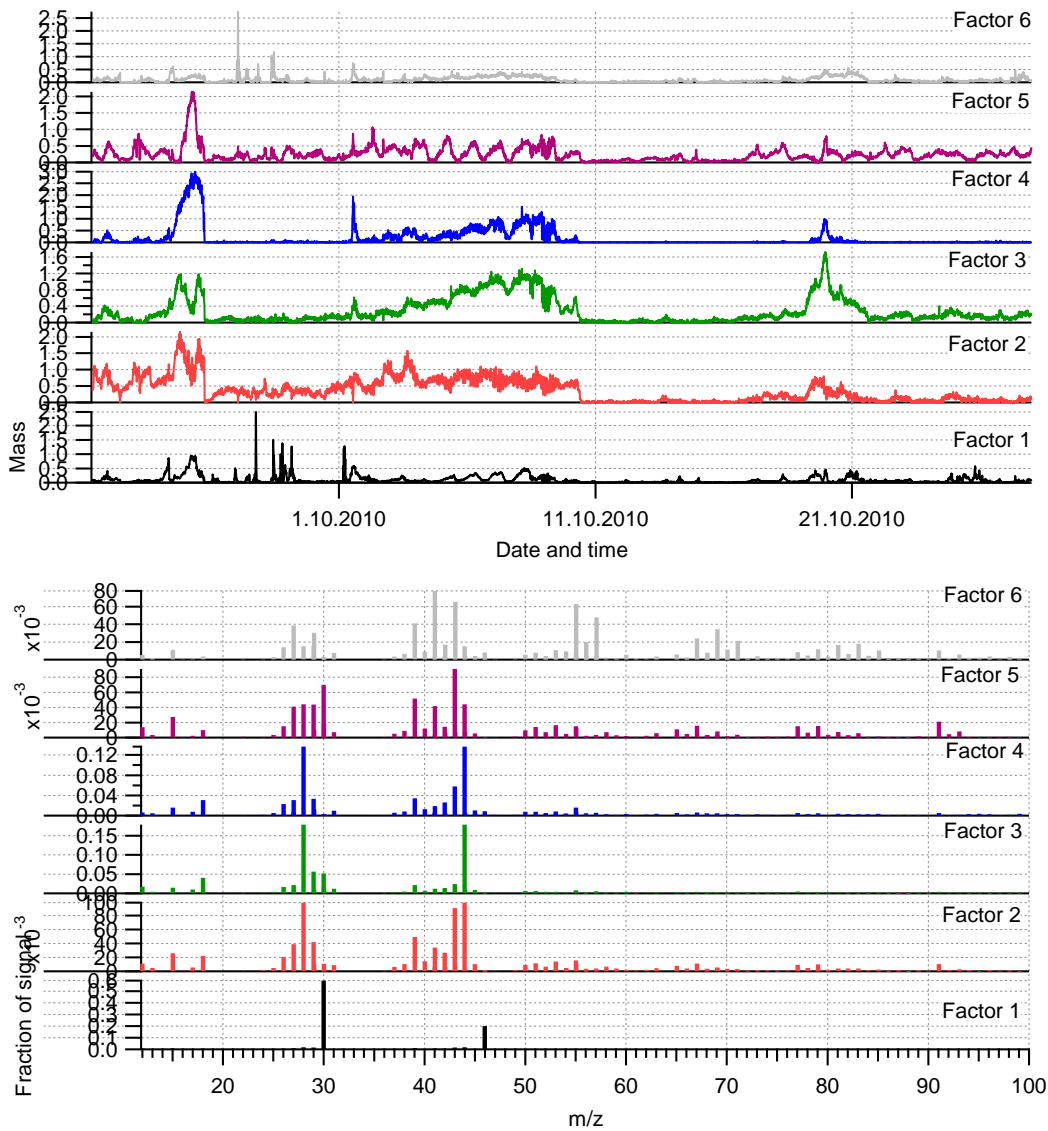


Figure S4. Time series and mass profiles by PMF analysis at 6-factor solution with $F_{peak} = +0.1$.

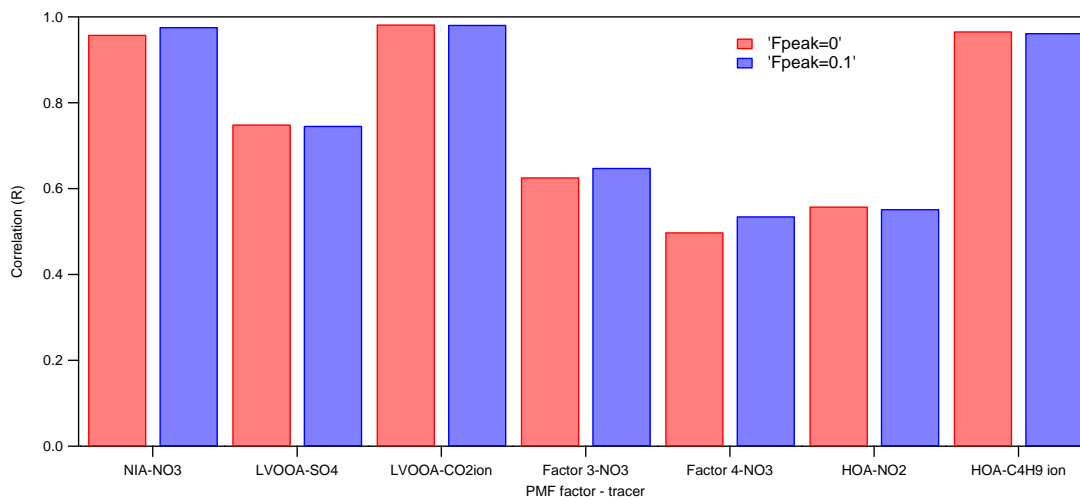


Fig S5 Correction coefficients between the PMF factors and tracers by varying F_{peak} from 0 to +0.1.

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_x 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_x 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_x ions are apportioned to organic factors, indicating these NO_x 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⁺/NO₂⁺ 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.