

We are thankful to the three referees for their comments and suggestions. We have revised the manuscript accordingly. In particular, we expanded the details on 1) the preparation of high resolution data and error matrices for PMF analysis, 2) the selection and evaluation of PMF factors, and 3) the procedures for size-resolved mass spectra analysis. Listed below are our point-by-point responses in blue to each reviewer's comments

Response to referee#1

In their manuscript “Factor analysis of combined organic and inorganic aerosol mass spectra from high-resolution aerosol mass spectrometer measurements” Y.L. Sun and coworkers present a re-analysis of a high-resolution aerosol mass spectrometer dataset obtained in New York City. Here they use an extended approach to perform positive matrix factorization (PMF) in order to separate potential organic contributions to the mass spectra. The same dataset was analyzed earlier also using PMF and results from this first study were published by the same author and several of the coauthors of this manuscript before. Within this paper the authors often refer to the previous analysis and compare the new results with those of the former paper.

The major step forward presented within this manuscript – compared to the previous analysis – is the implementation of AMS inorganic species signals into the PMF analysis of the high-resolution mass spectra. As a consequence of this new approach the authors present the identification of eight different organic aerosol factors while in the previous study only five different factors have been found, associated with either different types of organic aerosol or different aerosol sources. The authors thoroughly describe mass spectra, diurnal cycles and size distributions of all factors and discuss potential sources and processes associated with all factors.

In general, the inclusion of inorganic species signals into the PMF analysis of aerosol mass spectra seems to be a logical step towards a more complete analysis of the mass spectra with the potential of delivering additional information on the ambient aerosol and therefore definitely merits publication. Similar approaches have been presented by other authors who included results of co-located measurements with other instruments into the PMF analysis. However, the authors should decide about the major focus of their publication, which is not really clear so far. If they want to present a new method to analyze high-resolution aerosol mass spectrometer data by including inorganic species information into the PMF analysis the method must be characterized much more in depth and in multiple perspectives, including a discussion of potential and limitations of this approach and the resulting factors. If the focus of the paper is the deeper characterization of the New York City aerosol this kind of investigation must be much deeper and include external information from other measurements and account for the meteorological situation and air mass transport.

In the present form I do not recommend publication in ACP. However, after major revisions which present the selected focus of the paper more clearly and in more depth I am confident that this manuscript can be published in ACP. In order to support this recommendation I

provide more general as well as several more detailed comments below.

The main objective of this manuscript is to gain new insights into the sources and evolution processes of aerosol particles in New York City using two new data analysis approaches, i.e., PMF analysis on the combined high resolution mass spectra of organic and inorganic aerosols and multiple linear regression analysis for determination of the size distribution of OA factors. Compared to our previous analysis reported in Sun et al. (2011), new results, e.g., the formation of organic nitrates, the acidity of OA components, and the evolution of the size distributions of OA factors, are discussed in this study. In response to the reviewer's comments, we substantially expanded section 2.3 and 2.4 to provide more details on the two approaches. However, given that most of the collocated measurements and the relation of aerosol sources with meteorological variables and air masses have been reported in Sun et al. (2011) and Lin et al. (2012), we didn't go into detail further in this study.

General Comments:

Is this manuscript a corrigendum for the Sun et al. 2011c paper? Here the same data set was analyzed using the same method (PMF), however with slightly different input (including also inorganic signals in the mass spectra). In both papers the organic aerosol was described as being composed of different types of organic aerosol as a result of the PMF analysis. However, in the present manuscript 8 organic aerosol types were found while in the previous paper the same aerosol was described to consist of 5 different organic aerosol types. Even those organic factors that are explicitly named to be identical in both analyses (HOA, COA and NOA) are presented with significantly different concentrations in the new manuscript compared to the 2011 paper. For example NOA had more than 90% larger mass concentrations in the previous publication. So the question whether this previous analysis was "wrong" and this new analysis is "correct", such that the present paper is a corrigendum for the previous one seems to be reasonable (especially since all results were presented without any uncertainties as if they were absolutely correct). However, I do not think this is the case. Contrary, these two manuscripts are an excellent example that shows how random and undefined PMF analysis results often can be. PMF provides a POSSIBLE mathematical separation of the observed variations in the mass spectra which can reasonably be explained by different aerosol types. However, it does not provide a separation into aerosol types that directly reflect the ambient aerosol composition – as it is typically implicitly assumed in the papers. Therefore both analyses (Sun et al. 2011c and this manuscript) are not wrong or incorrect, but both of them do only present a possible "view" of the ambient aerosol.

This manuscript is not a corrigendum of Sun et al. (2011). The differences between the results from this study and those reported Sun et al. (2011) are the outcome of enhanced variance in the combined inorganic and organic mass spectral matrix which allows PMF to distinguish more physically-meaningful factors, i.e., 8 factors vs. 5 factors previously. Increasing the number of factors would lead to redistribution of signals among different OA factors. For example, the LV-OOA reported in Sun et al.

(2011) clearly represents the sum of the LV-OOA and the SO₄-OA determined in this study (Fig. 1d and Fig. S7d). Comparisons of the other OA factors also show overall consistencies between this study and the Sun et al. (2011) (e.g., Fig. 1 and Fig. S7). In terms of the observation of lower NOA mass loading in this study, a main reason was that part of the C_xH_yO_z⁺ signals in the NOA spectrum reported in Sun et al. (2011) was apportioned to other factors. Nevertheless, the time trends of the two NOA factors correlate tightly ($r^2 = 0.98$) and their mass spectral patterns, especially for the nitrogen-containing ions (C_xH_yN_p⁺), are very similar. These results indicate that the two sets of PMF solutions give overall consistent results. In fact, the results of this study demonstrate that by introducing additional chemical information in the combined mass spectral matrix, we are able to identify a larger number of OA factors and thus gain more insights into the sources and processes of aerosol particles.

In this manuscript yet two more new types of oxidized organic aerosol are introduced into the AMS-PMF literature (LO-OOA and MO-OOA). They are introduced as if these “types” of organic aerosol really exist. Since the AMS always performs an analysis on an “ensemble”, which is more or less a “small bulk”, one can expect that a continuous variation of mass spectral fingerprints from less oxidized to more oxidized organics can be found in the mass spectra of ambient aerosol. Therefore it would also be possible to separate each of the “identified” PMF factors into several more or less oxidized ones: e.g. to have a LO-LO-OOA and MO-LO-OOA, etc. Whether such factors can be observed within the mass spectra is less a question whether they really exist but a question of noise in the data and mathematical uncertainty.

It is true that PMF factors may undergo “splitting” when solving for more factors, but there are multiple criteria for determining the optimum number of factors, and the signs of “split” factors can be identified via examining the correlation of mass spectra and time series of factors in the same solution (Zhang et al., 2011). In addition, increasing the number of factors for PMF does not necessarily lead to more OOA factors of different oxidations. For example, we found that it was the ammonium sulfate factor split into two in the 9-factor solution (Fig. S4). In this study, the 8-factor solution was selected based on a thorough evaluation of different PMF solutions and careful interpretation of the mass spectral patterns, ion compositions, and the temporal and diurnal variation patterns of individual factors, including comparing the factor profiles with source component spectra and the factor time series with those from external measurements.

I do not doubt that PMF analysis of AMS mass spectra provides additional information and insight into atmospheric processes. However, it should be discussed more clearly what the resulting factors really mean, how they can be interpreted and how robust or uncertain a selected analysis result really is. The 90% discrepancy between the aerosol type NOA found in this study and in the previous analysis (by the same researchers using the same tool) already show that there is significant uncertainty associated with such results. Unfortunately very rarely PMF results are presented with any direct information about their uncertainty.

Often alternative results are presented in the supplementary material together with arguments why the selected result was chosen as the correct one. And this one is presented without any uncertainty.

The robustness of the PMF solution and the reasons for choosing the 8 factor solution are now discussed in the revised manuscript (e.g., Section 2.3, Table S1, Fig. S2c, Fig. S5, and Fig. S6). Table S1 gives a summary of the fractional contributions of the PMF factors associated with the rotational ambiguity. The interpretation of individual PMF factors with a focus on new insights into the sources and processes of aerosols are detailed in section 3.1 – 3.5. In terms of the observation of lower mass loading of the NOA factor in this study compared to the NOA reported in Sun et al. (2011), a main reason was that part of the $C_xH_yO_z^+$ signals in the NOA spectrum reported in Sun et al. (2011) was apportioned to other factors. The spectral patterns of the nitrogen-containing ions ($C_xH_yN_p^+$), however, are almost identical in the two NOA spectra. The time trends of the two NOA factors also correlate tightly ($r^2 = 0.98$).

I do not want to discredit PMF analysis of AMS data in general. As mentioned above, I think this approach can provide valuable information on atmospheric conditions, processes and aerosol sources. However, this manuscript is an excellent example that it has to be thought more about what PMF factors really mean and how certain a selected and presented analysis really is – and this has to be clearly discussed within the related manuscripts. Otherwise they can leave the impression that repeated analyses are not in agreement with each other as in the current case. In the worst case continuing this practice of “identifying” new types of organic aerosol which are at the first place mathematical factors that describe some of the variation within a mass spectra matrix and which are not based on a basis of chemical analysis, and if factors that have the same name but different mass spectra are continued to be treated as if they were identical, the community is in danger of losing credibility. Therefore I suggest that the authors of this manuscript use the opportunity to discuss the issues mentioned above openly and thoroughly as they became relatively obvious due to the comparison with their previous publication. If the authors decide to do so, this paper can become a very important and valuable contribution to the AMS-PMF literature.

In response to the reviewer’s comments, we have expanded the discussions on PMF uncertainties, e.g., rotational ambiguity, in the revised manuscript. Also, the reasons for the differences between these two studies are further explored. Given the ensemble mass spectra reported by AMS represent a linear superposition of the spectra from individual species, the deconvolution of aerosols components through PMF algorithms are actually based on chemical information, e.g., sources, composition, and atmospheric processes. The PMF solution must be carefully evaluated through the comparisons with other external measurements, and the results should be well interpreted, particularly, when new factors are resolved. The name of OA components represents a group of organic species with similar composition, properties, and temporal variations that are indicators of different sources and/or atmospheric processes, but this does not necessarily mean that they must be the same in different environments. Indeed, the OA components often vary as a function of sites, seasonality, and time.

More specific comments:

The authors should revise their manuscript regarding the language. Several statements are hard to understand or are misleading due to inadequate use of the English language.

Some statements have been re-worded in the revised manuscript for clarity.

The authors should describe their analysis procedure more clearly. In order to allow the reader to understand how this new approach works a clear description of it is needed. For example it is not very clearly stated that HR-PMF was performed. All the procedures to include the inorganic signal into the PMF analysis are not described with any detail. Since this is a new method and not standard analysis this is definitely needed. For example are the individual m/z signals for the inorganic species down or up-weighted in any way? What kind of effect would such a treatment have, how would it affect the results?

Following the reviewer's suggestions, the details for preparation of high resolution data and error matrices, and the subsequent PMF analysis were substantially expanded in section 2.2 and 2.3, respectively. For example, the "bad" ions with signal-to-noise (S/N) ratio < 0.2 were removed from the data and error matrices, and the "weak" ions with S/N between 0.2 and 2 were downweighed by increasing their error values a factor of 2. While removing the "bad" ions may improve the differentiation of OA factors, it has minor impact on the mass concentrations since they together account for $< 2\%$ of total OA signal. The downweighting of the "weak" ions will lower the calculated Q-values, but won't hurt much to the results. The details for such treatments and their impacts on PMF results have been given in Paatero and Hopke (2003) and Ulbrich et al. (2009).

Are the whole m/z signals related to inorganic species (as described in p13304 l21-23) associated with those species or are organic-related signals separated? Please provide sufficient information that other researchers can also use this analysis approach.

The HR-AMS, particularly the high resolution "W-mode", allows us to distinguish different fragment ions at one integer m/z . With a mass resolution of ~ 5000 - 6000 for "W-mode", the organic and inorganic fragment ions can be relatively well separated due to their large differences in mass defects. The m/z in the brackets (p13304 L21-23) refers to the integer mass-to-charge ratio for the ion. In fact, these m/z 's might also have the contributions of organic ions, e.g., m/z 81 has $C_4HO_2^+$, $C_5H_5O^+$, and $C_5H_9^+$ in addition to the inorganic ion HSO_3^+ . Such analysis is performed with the AMS standard analysis software (PIKA) and the details are given in DeCarlo et al. (2006).

The authors claim in their abstract and more specifically in the main text that "the new approach is able to study the mixing of organic aerosols (OA) and inorganic species". I doubt that this is possible. The fact that for the nitrate-related organic factor (NO_3 -OA) and the sulfate-related factor (SO_4 -OA) different diurnal trends have been observed is not at all an indication for external mixture of these species! It is well-known that ammonium nitrate partitions more into the gas phase as temperatures increase and partitions back into the

particle phase when temperatures decrease again. However, this does not exclude the possibility that the ammonium nitrate evaporates off the mixed ammonium nitrate/ammonium sulfate particles and later on condenses onto such particles again. Even differences in size distributions between different aerosol factors would not prove external mixture but just shows a different distribution of the individual species onto different particle sizes.

The term “mixing” in the manuscript refers to the relative contribution of organic and inorganic species in each factor. It was not meant to refer to the mixing states (e.g., externally or internally mixed).

Several statements in the introduction regarding PMF analysis are misleading regarding the capabilities of PMF and the interpretation of the factors. PMF is a bilinear model that constrains the factors to be non-negative (P13302 line 16/17). This avoids physically meaningless negative concentrations, however, this does not constrain the results to physically meaningful ones as claimed in the rest of the same sentence. The results are potentially meaningful, but not necessarily meaningful.

We agree. “and physically meaningful” was removed from the sentence.

The instrument that was used during the measurements is commonly named “HR-ToF-AMS”, not “HR-AMS”.

The “HR-AMS” was changed to “HR-ToF-AMS”

P13308 117: Fig. 2b not Fig. 5a should be referenced here. Figure 5a should be referenced a few lines below, where it is not.

It was fixed

Is it surprising that a good correlation of PMF factors with their own major fragments is found as in p13310 18/9 and p13311 15/6? What is the new information we gain from this?

The fact that a specific ion correlates especially well with a given PMF factor indicates that this ion can be used as a tracer ion for this factor, allowing rapid and real-time estimation of the mass concentrations of the factor. For example, m/z 44 (mainly CO_2^+) and $\text{C}_3\text{H}_5\text{O}^+$ -subtracted m/z 57 (C_4H_9^+) can be used for the first-order estimates of the mass concentrations of OOA and HOA, respectively (Aiken et al., 2009; Ng et al., 2011).

What is a “midnight rush-hour” (p13310 117)?

The statement “both mid-night and morning rush hours” refers to the time of “mid-night” and “morning rush hours”. To avoid confusion, we revised this sentence as “both mid-night time and morning rush hours”.

The discussion of the LV-OOA factor (section 3.5) sounds very interesting. Especially the separation of different LV-OOA contributions (local and regional) is a very interesting result. However, regarding the obvious uncertainties of the PMF analysis which become apparent for example in the large differences of nominally identical organic aerosol types between the previous and this analysis, I wonder how robust or how uncertain these results are. In the

view of abovementioned uncertainties in both the analysis method/procedure as well as the interpretation of PMF factors the robustness and uncertainty of such results should be well discussed and quantified.

The robustness of PMF solution was explored by varying fPeak values, which was included in the revised manuscript. The mass spectra and time series of factors for selected fPeak values are shown in Fig. S5. While the factor profiles and time series are reasonably robust for most PMF factors, the NOA and MO-OOA appear to show relatively higher uncertainties than the other factors. A detailed summary of the rotational ambiguity on the fractional contributions of the PMF factors is given in Table S1. The PMF solution was further justified through the comparisons of factor time series with those of tracer species, which is shown in Fig. S6.

Response to referee #2

General comments:

This paper presents the re-analysis of an existing AMS dataset previously presented by the same first author, using PMF on the whole high-resolution mass spectrum rather than simply the organic peaks in isolation, which is the common practice. This produces a larger number of factors than the previous analysis, featuring many inorganic peaks. While some of the results are expected (identification of ammonium nitrate and ammonium sulphate), this analysis gives some interesting insights into the role of organic nitrates and amines and this technique will probably prove useful to others in the future.

This paper stops short of over-analysing the results, so no major advances in atmospheric chemistry are gained and most of what is said could be considered incremental on previous works. However, the new results in themselves do represent novel observations of particulate composition (particularly with respect to the organic nitrates and amines) and tantalising hints as to the roles of some of these hard-to-measure species, so these in their own right make this paper worthy of publication in ACP (rather than a technical journal).

The paper is well-written overall, although I do have a few reservations (see below). But given that taken at face value, the results are hard to argue with and the authors provide sufficient information for someone to repeat the analysis, none of these should be considered potential showstoppers. I therefore recommend this be published subject to minor revisions.

Specific comments:

The authors neglect to provide a time series of the basic AMS data products or the derived factors. While some of these are available in previous publications, they would be highly informative and should be given here.

Following the reviewer's suggestion, the time series of mass concentrations of PMF factors were added in Fig. 2 and Figs. S3&S4 in the revised manuscript.

Not enough detail is given as to why a solution with 8 factors with an fPeak of 0 was chosen. The authors need to explicitly give their reasons for why the other potential solutions were rejected. They should also have tested the numerical stability of the solution through seed variation or bootstrapping.

In response to the reviewer's comments, we substantially expanded the discussions on how we chose the PMF solution in section 2.3. The evaluation of the robustness of PMF solution by varying the initial fPeak value, and the determination of fPeak through the comparisons of factor time series with external tracer species were also included in the revised manuscript.

The authors seem to have been very selective in their treatment of the different factors when attempting to recreate size distributions. A general concern is that species that vaporise on slower timescales (tens of milliseconds) may not be adequately represented in pTOF space, which distorts the relative contributions of various components. It could be that this is happening here, so for the sake of general technical interest and for those attempting this

technique in the future, they should go into more detail in the supplementary material regarding the problems encountered. It would also be useful to know how much normalisation the different factors required.

We derived the size distributions using both the six-factor solution from the PMF analysis of OA only spectra and the eight-factor solution from the analysis of the combined OA and inorganic OA spectra. While the size distributions of six OA factors (HOA, COA, NOA, LO-OOA, MO-OOA, and LV-OOA) from the two methods are similar, the size distribution of SO₄-OA from 8-factor analysis was quite different from that of sulfate (Fig. S9 in supplementary). Given that SO₄-OA is dominated by ammonium sulfate, similar size distributions between SO₄-OA and sulfate are expected. Such differences might be due to the uncertainties of linear regression analysis when two factors with very similar spectra patterns, i.e., SO₄-OA and LV-OOA, are included. For these reasons, we presented the results from multiple linear regression analysis of six OA from PMF analysis of only OA. These points are now clarified in section 2.4 in the revised manuscript.

We agree with the reviewer that the measured size distributions may be affected by vaporization time. In fact, the measured particle sizes may be affected by: 1) PToF time from the chopper to the vaporizer, e.g., time change due to particle bounce; 2) vaporization and ionization time, e.g., different vaporization rates for different aerosol species; and 3) the transfer time between ionization region and ToF mass spectrometer. The effects of these factors on the particle sizes have been detailed in Ulbrich et al. (2012). Considering that the technical details are beyond the scope of this manuscript, we didn't go into much detail on it.

We normalized the size distribution of each OA factor by integrating the signals between 50 – 1200 nm to the corresponding mass concentration of OA factor. This information is now given in the revised manuscript.

P13308, L21: Given the long timescale for gas-phase production of sulphuric acid, it would not necessarily be expected that a pronounced lunchtime peak would be manifested. There may be other explanations, such as the formation of organosulphates.

We agree with the reviewer that the noon peak might also be associated with organosulfates. Such possible explanation was added in the revised manuscript as “It should be noted that photochemical production of organosulfates might also have played a role for the noon peak.”

Also, the phrase “the sulfate in the rest of OA factors shows a pronounced noon peak” should be reworded as “the other OA factors containing sulfate showed a pronounced noon peak” because the diurnal profiles only show the behaviour of the factor as a whole, not the sulphate in isolation.

We revised this sentence as “In comparison, the sulfate in the rest of the OA factors shows a pronounced noon peak (Fig. 5a)”. The diurnal profiles in Fig. 5a refer to the isolated sulfate from OA factors.

Section 3.1: Given that sulphate and nitrate give strong signals at completely different m/z channels and their lack of correlation extends to periods where each of the species approach zero independently of the other (seen in Fig. 1 in Sun et al., 2011c), PMF assigning these to distinct factors isn't so much an observation as a mathematical certainty. Therefore, this separation does not contribute anything new to the science beyond what can be seen with a simple time series and statements such as "PMF analysis results clearly indicate their different formation and evolution processes" massively overstate the significance of this result. The lack of correlation between sulphate and nitrate is already well-documented and fairly well understood, but what is perhaps more scientifically significant is the organic matter associated with them.

We revised our statements in the revised manuscript, and now it reads:

“Note that the majority of the nitrate and sulfate signals are apportioned into two different factors, i.e., NO₃-OA and SO₄-OA, respectively, due to their different formation mechanisms and evolution processes. Of importance, the OA mixed within these two factors are quite different with different spectral patterns and oxidation states, supporting their different sources and processes. In comparison, previous PMF analysis of filter-based fine particle composition in New York offered much less information of OA although separate factors of secondary sulfate and secondary nitrate were also identified (Li et al., 2004;Qin et al., 2006).”

P13315, L16: The authors should explain what they mean by 'similar aging properties and internally mixed characteristics'.

We have removed this sentence from the revised manuscript.

P13332: More detail should be given on the smoothing used and the reasons why this was used.

The binomial smooth algorithm automatically switches to a nearly equivalent. While the boxcar smoothing algorithm detects and ignores NaNs in the input data, the binomial smoothing algorithm does not. More details on binomial smoothing is given in “*Marchand, P., and L. Marmet, Binomial smoothing filter: A way to avoid some pitfalls of least - squares polynomial smoothing, Review of Scientific Instruments, 54(8), 1034-1041, 1983.*” Given that the smoothing was just used to reduce the noise, we didn't give much detail on the smoothing algorithm here.

Technical corrections:

P13304, L4: The time zone should be defined relative to UTC

It was revised as “EST = UTC – 5 hr”

P13308, L23: The phrase “These results suggest the different sources of sulfate in SO₄-OA and other factors” does not make sense. Suggest rewording.

It was re-worded as “These results suggest different sources of sulfate in SO₄-OA compared to other factors.”

P13310, L13: It should be noted that conventional wisdom considers a portion of sulphate to be primary, however the adoption of low sulphur fuels has all but eliminated this.

We agree with the reviewer. Indeed, a very small amount of sulfate was observed in the HOA factor, which might be from the direction emission of fuel combustion.

P13313, L21: Replace 're-look' with something more formal.

It was revised as “Further investigation of the case study on 22 July”

Response to referee#3

General comments

This paper re-analyses AMS measurements made in New York City during the summer of 2009. Positive matrix factorisation (PMF) is performed on the entire mass spectrum of organics + inorganics and eight factors are found. Compared to the previous analysis, where PMF was performed on only the mass spectrum of the organic aerosol, the current study is able to associate different organic fractions to nitrate and sulphate and identifies an additional organic factor due to additional data being made available since the previous publication.

The results from this analysis are not greatly different than the previous study. However, two relatively new techniques are employed: PMF on the entire mass spectrum and determining the size distribution of the resulting factors. The former has never been published for an urban site and the latter is done here in a more simple way than other studies. Unfortunately, neither of these methods is described with enough detail for someone to reproduce these calculations (I see that this is in disagreement with Reviewer 2 but see my specific comments below), and a comparison with existing size distribution factor analysis should be included. Parts of the text would also greatly benefit from English editing. Some suggestions are included in the technical corrections. However, the manuscript could be made much clearer. Overall, I recommend that this study be published but with the major revisions listed below.

In response to the reviewer's comments, more details on PMF analysis and size distribution analysis were included in section 2.2 and section 2.4, respectively. In addition, the results of size distribution analysis were further evaluated and discussed in the revised manuscript. Unfortunately, at present we have difficulties to do 3-dimensional PMF analysis (Ulbrich et al., 2012). Some English editing was also performed in the revised manuscript.

Specific comments

Page 13303, line 14

Refer to Chang et al. (2011) who performed PMF on the entire spectrum (organic + inorganic) for a unit-resolution AMS.

Thank the reviewer for pointing this reference out. Chang et al. (2011) was cited in the revised manuscript.

Page 13304, line 9

State the actual version number used and describe how the data changed when the analysis software was upgraded.

The version we used in this study is PIKA v1.10H and SQUIRREL v1.51H. Compared to the version (PIKA v1.06) used in our previous study, a major update of the new version is the calculation of ion counting errors, especially at the higher

masses. Also, the baseline errors are included into ion counting errors. Such update affects the Q/Q_{exp} , but appears to show minor influences on factor profiles and time series. For example, the spectral patterns of OA factors in these two studies are very similar ($r^2 = 0.99 - 1.0$; slope = $0.97 - 1.02$). Following the reviewer's suggestion, we added the related information in the revised manuscript.

Page 13304, Section 2.2

The details for preparing the matrices for PMF are very vague. For example, did you simply add the errors together from the different species? Or did you add them in quadrature? Did you include the relative ionization efficiency? Or did you change them to nitrate equivalent mass / ion signal? Can you even include the RIE when adding the errors and mass spectra? I.e. should PMF be performed on the detected signal or an interpreted signal? Did you have to discard any m/z due to weak S/N? Since the processing required to perform PMF on the entire mass spectrum is still in its infancy, it is vital that all these details be included so that other groups doing the same analysis can compare and learn from them.

We significantly expanded the details for preparing the HR data and error matrices for PMF analysis in section 2.2.

The error for each ion was determined as the sum of quadrature of Poisson counting statistics and electronic noise for each ion (Allan et al., 2003). The “bad” ions with signal-to-noise (S/N) ratio < 0.2 were removed from the HR data and error matrices, and the “weak” ions with S/N between 0.2 and 2 were downweighed by increasing their error values a factor of 2 as discussed in Ulbrich et al. (2009),

Both the HR data and error matrices were converted from ion signals (Hz) to mass concentrations before PMF analysis, thus, the relative ionization efficiency was already considered.

All the details were clarified in the revised manuscript.

Page 13307, Section 2.4

On page 13307 lines 5-7 you mention that Ulbrich et al. (2012) used 3D factor analysis to determine size distributions of OA factors. However, you do not use any of the methods described in that study. This should be clearly stated in this section. How does your method compare to those of Ulbrich et al.? At least the PARAFAC model which still uses PMF.

We thank the reviewer for pointing this out. It was clearly stated in the revised manuscript. Given that we have difficulties to perform such analysis, we cannot compare our results with those of Ulbrich et al. (2012). As a result, we compared our results with those determined from tracer- m/z based method. No doubt, this is a good point and should be investigated in the future.

In addition, when using MLR, did you use the mass spectra from your PMF results from only

the OA (described on page 13306 line 25), or are the six factors on page 13307 line 10 the factors from the results of the combined organic + inorganic PMF? If the latter, did you first subtract the organic contribution associated with SO₄-OA and NO₃-OA? Or are you trying to fit the entire organic component with only the six OA, and how much error would this introduce? What do the residuals and uncertainties look like?

The six OA factors used in MLR analysis was PMF results from only the OA. We also tried MLR analysis with eight OA factors from PMF analysis of combined organic and inorganic aerosols. The results are now presented in supplementary and compared with those from six OA factor analyses. As shown in Fig. S9, the average size distributions of HOA, COA, NOA, LO-OOA, MO-OOA, and LV-OOA from the two analyses agree reasonably. Considering the SO₄-OA and NO₃-OA factors are primarily ammonium sulfate and ammonium nitrate, respectively, similar size distributions between sulfate and SO₄-OA, and nitrate and NO₃-OA are expected. However, we note that the size distribution of SO₄-OA is quite different from sulfate while that of NO₃-OA is somewhat similar to nitrate. One explanation is that the OA mass spectrum in SO₄-OA resembles to that of LV-OOA. The similar spectral patterns and the dominated two large peaks of m/z 28 and 44 peaks in the spectrum might have increased the uncertainties for linear regression coefficients. For the reasons above, we presented the results from MLR analysis of six OA which were resolved from PMF analysis of only OA. All these information was clarified in the revised manuscript.

Page 13307, line 24 to Page 13308, line 3

More transition is required to put these lines into context with the previous paragraph.

The whole paragraph was rewritten, and the transition was more readable in the revised manuscript.

Page 13307, line 24-25

Did you have tracer- m/z for each factor? If so which m/z did you use? Or did the tracer- m/z method only yield HOA and OOA and you are comparing COA+HOA and NOA+LV-OOA+LO-OOA+MO-OOA? Please clarify in your text.

Because AMS uses electron impact ionization which results in extensive fragmentation, it's difficult to find specific tracer- m/z for each OA factor. However, two m/z 's, i.e., m/z 44 (mainly CO₂⁺) and m/z 57 after subtracting its OOA contribution (mainly C₃H₅O⁺) have been proved to be good surrogates for OOA and HOA, respectively, at urban sites in many previous studies (e.g., Zhang et al., 2005; Aiken et al., 2009). Thus, we evaluated the MLR results with the 2-factor solution, i.e., HOA and OOA, from PMF analysis of the OA-only spectra by comparing with those derived from the tracers of m/z 57 and 44. The HOA and OOA here are approximately the sum of HOA+COA and LV-OOA+MO-OOA+LO-OOA+NOA, respectively, from the 6-factor solution of PMF analysis of the OA-only spectra. In response to the reviewer's comments, the descriptions on the comparisons were clarified in section 2.4 in the revised

manuscript.

Page 13308, lines 1-3

What does the difference in the tracer- m/z method and MLR tell you? Why is the HOA different? What are the uncertainties like in either of these methods? Would you not say that the slight differences observed in the two methods are within the uncertainties?

Both the tracer- m/z based method and the MLR method have their own assumptions. For example, we assume that the mass spectra of OA factors are constant across the whole size ranges in the MLR analysis. For the tracer- m/z based method, we assume that the size distribution of OOA is the same as that of m/z 44 (mainly CO_2^+). In fact, we note that the HOA spectrum also has contribution of m/z 44. These assumptions might be the reasons for the differences. Despite this, the two methods provide reasonably good agreements in size estimates.

The size distribution of HOA derived from the tracer- m/z based method is generally higher than that from MLR at D_{va} below ~ 100 nm. This can be explained by the fact that the signal of m/z 44 below 100 nm is very low and often close to zero, the tracer- m/z (m/z 44 and 57) based method would output dominant HOA below 100 nm while some OOA with low m/z 44 signals would be neglected. This suggests that the tracer- m/z based method might slightly overestimate the contribution of HOA at small size ranges, while such overestimation is tempered in MLR method. Since the two methods provide reasonable estimate of the size distributions, we could say that the differences are within the uncertainties.

Page 13308, line 5-9

A time series for each factor for the entire campaign would be helpful in order to understand when contributions of each factor were greatest.

The time series of PMF factors for the entire campaign are presented in Fig. 2 in the revised manuscript.

Page 13308, lines 15-16

What are the uncertainties associated with your O/C calculation? Can you say that one is significantly higher than the other?

The uncertainty for O/C calculation is 31% based on previous analysis from laboratory standards (Aiken et al., 2008). The difference between the O/C values of LV-OOA (0.63) and SO_4 -OA (0.69) does not indicate that one is significantly more oxidized than the other

Page 13309, line 17

Does that mean that NH_4Cl and NO_3 -OA have a similar source? Can you elaborate on what you think it is?

The NO_3 -OA factor is primarily composed of NH_4NO_3 . Both NH_4Cl and NH_4NO_3 are semi-volatile and share similar gas-to-particle partitioning mechanism

$(\text{NH}_3 + \text{HCl} \leftrightarrow \text{NH}_4\text{Cl}; \text{NH}_3 + \text{HNO}_3 \leftrightarrow \text{NH}_4\text{NO}_3)$ which favors the formation of particles under conditions of lower temperature and higher relative humidity. This may explain the similar variation patterns of NH_4Cl and NH_4NO_3 . The correlation between NH_4Cl and NH_4NO_3 does not necessarily suggest that they have similar sources. While an important source of ammonium chloride is combustion emissions, nitrate is also from daytime photochemical production (e.g., $\text{NO}_2 + \text{OH}$) and nighttime heterogeneous reaction (e.g., $\text{N}_2\text{O}_5 + \text{H}_2\text{O}$).

Page 13310, line 10

What happened to the remaining 7%? Is this within the uncertainties?

The sum of HOA and COA in this study is ~7% lower than those reported in Sun et al. (2011), mainly because part of COA was apportioned into other OA factors, most likely to LO-OOA. Indeed, the diurnal profile and mass spectrum of LO-OOA show some similarities to that of COA and the O/C of COA (O/C = 0.18) reported in Sun et al. (2011) is between that of the COA (O/C = 0.13) and LO-OOA (O/C = 0.27) in this study. Also consistently, the sum of MO-OOA and LO-OOA in this study is 7% higher than that of SV-OOA reported in Sun et al. (2011).

Page 13310, line 23

Could these be small HOA particles coated with secondary products?

We thank the reviewer for pointing this out. It has been revised as: “likely from the emissions of large HOA particles and/or the growth of small HOA particles which are coated by secondary organic and inorganic species (Massoli et al., 2012)”

Page 13311, line 7

*Your previous study only discussed the possibility of the amine factor originating from marine and industrial sources and did not **show** it.*

We revised this sentence, and now it reads: “Our previous analysis indicated that the NOA is likely from amines...”

Page 13311, line 19-23

In your previous study, the NOA factor was almost neutralised. How did including the inorganics in the PMF change this?

The acidity in our previous study refers to the acidity of bulk aerosol particles. We found that aerosol particles during the periods with high concentration of NOA appear to be slightly acidic (Sun et al., 2011), however, we are unable to investigate the acidity of the NOA factor directly in our previous study. In this study, after incorporating inorganic species into PMF analysis, we are able to characterize the acidity of each OA factor. The NOA shows a high deficit of ammonium, indicating its acidic properties. Yet, the acidity of NOA should not significantly affect the acidity of bulk aerosol particles given that NOA contributes only a small fraction of total aerosol mass.

Page 13312, Section 3.4

It is interesting that MO-OOA correlates more with temperature than solar radiation. Is this a coincidence?

It's hard to tell such correlation is a coincidence or not. But it should be noted that solar radiation at night was zero, which was not included in the correlation analysis. This might explain the weaker correlation of MO-OOA with solar radiation compared to temperature.

Page 13315, lines 2-4

What do you mean by “intrinsically correlate”? Can you graph this correlation?

It was reworded as “appears to be associated with” to avoid confusion.

Page 13315, lines 18

This final paragraph should be its own sub-section since it is an overall discussion of your findings.

Following the reviewer's suggestion, we listed the final paragraph as sub-section “3.6 Evolution of OA” in the revised manuscript.

Page 13317, line 8

Change cation to ammonium, since the aerosol must be balanced by some type of cation.

It was fixed

Technical corrections

Page 13301, line 26: “rely on measurements”

Page 13301, line 27: “making it difficult”

Page 13302, line 22: “source emissions”

Page 13302, line 24: “understanding of the sources”

Page 13302, line 27: “allows us to determine the oxidation state”, otherwise find some other rewording.

Page 13303, line 14: “only performed on AMS”

Page 13303, line 20: “we re-analyze the three-week”

Page 13303, line 22: Remove the “(QC)” since you never use it.

Page 13305, line 8: “approach, PMF”

Page 13305, line 17: “PMF solves Eq. (1)”

Page 13306, line 14: Remove “respectively”. Check your use of respectively throughout the text. It is often wrong.

Page 13306, line 26: “The results of this six-factor solution”

Page 13308, line 1: Remove the leading “As”.

Page 13308, line 8: “likely from regional transport”

Page 13308, line 21-22: “In comparison, the sulphate in the rest the OA factors”

Page 13308, line 23-24: “These results suggest different sources of sulphate in SO4-OA

compared to the other factors.”

Page 13308, line 25: Change “though” to “although” throughout the text.

Page 13309, line 1: “ammonium nitrate is more volatile, which is less favourable for long-range transport.”

Page 13309, line 3: “dominantly composed of”

Page 13309, line 6: “when the temperature”

Page 13309, line 8: “shows a minimum”

Page 13309, line 11: “the rest of the OA factors”

Page 13309, line 16: “contains the majority of the total chloride”

Page 13309, line 19: “The NO₃-OA factor includes 17% fresh OA”

Page 13309, line 24: “appear to not mix with each other.”

Page 13309, line 27: “resembling those from”

Page 13310, line 8: “with most of the tracers”

Page 13310, line 13: “This is evidence for different sources of primary”

Page 13310, line 21: “during daytime while the contribution of the large mode correspondingly increases”

Page 13311, line 9: “by the on-line measurement of atmospheric”

Page 13311, line 19-23: This sentence is awkward. Please improve.

Page 13313, line 10: “is from isoprene oxidation”

*Page 13313, line 17: “(MV-OA-*lv*) fraction during”*

Page 13313, line 29 and Page 13315, line 1: Replace “till” with “until”

Page 13315, line 6: “does not mix much with ammonium sulphate”

Page 13315, line 8: “from the new PMF analysis”

Page 13315, line 21: “As aging progresses”

Page 13316, line 6: “appears to follow a trend”

We are thankful to the reviewer for the detailed technical corrections. We have implemented all the corrections in the revised manuscript.

Figure 3: What is the grey shaded line in Figure 3E?

The grey shaded line in Fig. 3e was used to distinguish primary and secondary OA. It was removed in the revised manuscript.

Figure 4: Include the charges for sulphate and nitrate on the x-axis.

The charges for sulfate and nitrate were included.

Figure 6: Please include the size distributions of sulphate and nitrate so that they can be compared to the OA distributions.

Following the reviewer’s suggestion, we included the size distributions of sulfate and nitrate in Fig. 6 in the revised manuscript.

Figure 7: It is very difficult to distinguish between all the green lines. Please make them more distinct.

We changed the thickness of the green lines, which makes them clearer than before.

Figure 8: What do the vertical lines in the Pearson R panel represent?

The vertical lines are the gridlines added to assist reading the plot.

Figure 9: What are the gray circles?

The grey circles are the hourly averaged f44 and f43 for the entire study.

Figure S2 The caption is mis-labelled.

It was fixed

Please include more labels on panel (b) so that the tick marks can be interpreted.

It was revised

Please change the colour of the residual fraction since I cannot differentiate it from the HOA fraction.

The mass fraction of residual for different f_{peak} values is ~0.6%. It's difficult to see even if we change the color. So we described it in the caption.

Can you make the numbers clearer on panel (d)? You could label certain groups with letters and list them out. Also, what do these numbers refer to? Which factors correspond to which numbers? Perhaps you can include this in the legend in panel (c).

The numbers refer to different OA factors in panel (c). They were all clarified in the revised Figure S2.

Figure S7: Please change the order of the times so that 00:00-01:00 starts in the upper-left and 23:00-24:00 is in the bottom-right.

It was revised

Figure S9: What happened to COA and NOA? The caption and the legend do not agree.

They were not shown for the purpose of clarity. However, to avoid confusion, we included them in the revised manuscript and also fixed the caption and the legend.

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