**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "Factor analysis of combined organic and inorganic aerosol mass spectra from high resolution aerosol mass spectrometer measurements" *by* Y. L. Sun et al.

Anonymous Referee #3

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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. How-

ever, 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. Over all, I recommend that this study be published but with the major revisions listed below.

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.

Page 13304, line 9
State the actual version number used and describe how the data changed when the analysis software was upgraded.

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.

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.

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 SO_4-OA and NO_3-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?

Page 13307, line 24 to Page 13308, line 3
More transition is required to put these lines into context with the previous paragraph.

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.

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?

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.

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?

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?

Page 13310, line 10
What happened to the remaining 7%? Is this within the uncertainties?

Page 13310, line 23
Could these be small HOA particles coated with secondary products?

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.

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?

Page 13312, Section 3.4
It is interesting that MO-OOA correlates more with temperature than solar radiation. Is this a coincidence?

Page 13315, lines 2-4
What do you mean by "intrinsically correlate"? Can you graph this correlation?

Page 13315, lines 18
This final paragraph should be its own sub-section since it is an overall discussion of your findings.

Page 13317, line 8
Change cation to ammonium, since the aerosol must be balanced by some type of

cation.

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 SO_4-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"

Page13309, line 11: "the rest of the OA factors"

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

Page 13309, line 19: "The NO_3-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"

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

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

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

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

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

Figure 9: What are the gray circles?

Figure S2
The caption is mis-labelled.

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

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

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).

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.

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

References

Chang, R. Y.-W., Leck, C., Graus, M., Müller, M., Paatero, J., Burkhart, J. F., Stohl, A., Orr, L. H., Hayden, K., Li, S.-M., Hansel, A., Tjernström, M., Leaitch, W. R., and Abbatt, J. P. D.: Aerosol composition and sources in the central Arctic Ocean during ASCOS, Atmos. Chem. Phys., 11, 10619-10636, 2011.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 13299, 2012.