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## ***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 #1**

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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 co-authors 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.

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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.

General Comments:

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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.

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

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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.

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.

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

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important and valuable contribution to the AMS-PMF literature.

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.

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? Are the whole  $m/z$  signals related to inorganic species (as described in p13304 I21-23) associated with those species or are organic-related signals separated? Please provide sufficient information that other researchers can also use this analysis approach.

The 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 ( $\text{NO}_3\text{-OA}$ ) and the sulfate-related factor ( $\text{SO}_4\text{-OA}$ ) 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

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species onto different particle sizes.

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.

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

P13308 I17: Fig. 2b not Fig. 5a should be referenced here. Figure 5a should be referenced a few lines below, where it is not.

Is it surprising that a good correlation of PMF factors with their own major fragments is found as in p13310 I8/9 and p13311 I5/6? What is the new information we gain from this?

What is a “midnight rush-hour” (p13310 I17)?

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.

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