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Atmospheric
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Discussions

Interactive comment on "Source apportionment of submicron organic aerosols at an urban site by linear unmixing of aerosol mass spectra" *by* V. A. Lanz et al.

Anonymous Referee #1

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This manuscript describes the analysis of AMS organic mass spectra acquired from an urban site in Switzerland with PMF. Six source types were identified and their contributions to submicron organic aerosol mass were estimated. This manuscript is overall clearly written and well organized, presenting results that are both new and interesting. However, several aspects of this work need clarification or revision before publication in ACP.

1. Claims of 'first' analysis

The authors claim in several places (p 11682/L5, p 11685/L7-8, p 11706/L5) that this paper is the first to apply PMF to AMS data, and also the first to apply PMF to submicron organic aerosol data. Both claims are incorrect and should be deleted from the final version. Li et al (2004) and Buset et al (2006) have both applied PMF to AMS data, and the second paper applies a more recent version of PMF than that used here (the multilinear engine or ME). Buset et al also include the time series of several individual organic m/z from the AMS in their ME analysis, to derive three different organic sources. These two papers should be cited in the revised manuscript.

2. Credibility on the subject of source quantification.

The use of CE = 1 for this AMS dataset dose not seem well justified. It is elusive to simply say this CE value was validated based on collocated PM10 measurements and OC data. Were the PM10 measurements size resolved? If not, how could it be possible that PM10 mass data can validate the quantification of submicron aerosol mass? For the comparisons with the OC data, what factor was used to convert OC into mass? How was this factor decided? Providing the statistics for these comparisons (even if in the supplementary information) is necessary.

Secondly, the time series of OA components (Fig 6) shows suspicious peaks that suggest possible instrument problems in this AMS data set. For example, the NOx and CO levels were very low (and flat) before the midnight on 30.07.2005, but there were huge spikes in all POA components. The two OOA components also peaked up during this time period. More of such cases can be seen in Fig 6. It is very important that the authors carefully examine them and decide whether the spikes came from sampling artifacts, e.g. due to instrument malfunction. Including artificial peaks may distort results from PMF analysis.

3. Determination of the source number and evaluation of rotational ambiguity

The PMF model solutions are not unique and the “interpretability of G and F” is a subjective criterion. Rigorous validation of the results cannot be bypassed by a simple statement that “the PMF solutions for the data of Zurich-Kaserne were found to be very stable with respect to different ways of modelling the data uncertainty and other input

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options (e.g. EM, FPEAK, lims; Paatero, 2000) Ě” (p. 11692). The variations of the G and F matrices under different input options must be evaluated quantitatively.

Positive FPEAKs force the source composition matrix toward more extremes (larger differences between species) and the source contribution matrix toward less extremes. Negative FPEAK values do the opposite. It is a given that the G and F matrices will vary at different FPEAK values, and results will change significantly for large enough FPEAK. Saying the results are insensitive to different rotational parameter (FPEAK) is misleading. The authors should be clear about the range of FPEAK values tested and the amount of variation in G and F matrices that they see. Also it is important that the authors report the Q values for different FPEAK values.

When discussing the number of factors chosen, the authors rely heavily on the R2 of regressed scores vs. measured organic mass concentration and the max(rotmat) (Fig. 2). Since the AMS organic mass is calculated as the sum of the signals in all m/z’s, positive and negative deviations in individual elements may cancel out. In other words, even a not-so-good fit to the matrix can result in a very high R2 of regressed scores to measured organic mass. The trend of R2 shown in Fig. 2 is not surprising since the linear regression always becomes better when the number of factors allowed to fit increases. For these reasons, I suggest that related statements, such as the one in page 11689 (last paragraph), “all used PMF approaches (2- to 7-factorial) can technically model the data almost perfectly”, be deleted.

My other concern is regarding Max(rotmat), the largest element in the rotational matrix. Conceptually it is hard to believe that this parameter alone can fully represent the rotational ambiguity for all the factors. Also the PMF Users’ Guide (Part 1 Tutorial, page 11) explicitly warns against using PMF in this way. I quote: “Lee at al. (1999) observe how the rotational uncertainties (elements of matrix rotmat) increase when the number of factors is increased over a certain limit. They interpret this increase as one clue for suggesting the best number of factors. It appears that this approach is not of general validity, thus it is not recommended any more.”

4. Naming of the components

This work discusses in due detail how the number of components chosen affects the PMF results, an effort that is no doubt commendable. However, one should keep in mind that PMF, like any factor analysis models, will not give correct answers under wrong model assumptions. Assuming insufficient number of factors will lead to hybrid components that should not be interpreted as sources or components. To avoid confusion, components from different PMF models should be given general names, rather than those that imply sources.

For instance, naming those from 2-4 factorial PMF analysis as HOA, OOA, charboiling, and wood burning, is misleading, giving a false impression that each PMF factors can be associated with one specific source/source type. There is really no basis to force a source name upon a component that is a mixture of unrelated components.

The discussions on possible sources of PMF components in the manuscript rely very heavily on the linear correlations of derived mass spectra to the reference spectra (e.g., Table 1 and section 4.1.). R2, however, is a rather insensitive parameter in the context of mass spectra comparisons. For example, the R2 between fulvic acid and diesel particle mass spectra used in this study is 0.4, yet a mixture spectra of 70

I feel strongly that the components from incorrect number of component analysis should not be named as individual sources. While it is necessary to give cautions on the importance of choosing the right number of components for PMF analysis, in my opinion this paper should emphasize on how to determine the right number and what measure should be taken to evaluate the results. I strongly suggest that Figure 4, section 4.1 and other related discussions be revised. I suggest that only the components of the final best solution are given names, and the components in lower order solutions are just named ‘component 1’, ‘component 2’, etc.

5. Use of fulvic acid as a reference spectrum

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There is no reason why the spectrum of the "true atmospheric OOA" should closely resemble fulvic acid (FA). FA is derived from soil processes, and although it has been proposed as analogous to aerosol HULIS, several recent papers find significant differences in their chemistries (Graber and Rudich 2006, Dinar et al 2006ab). For example Graber and Rudich say that “Major differences between HULIS and humic substances, including smaller average molecular weight, lower aromatic moiety content, greater surface activity, better droplet activation ability, as well as others, are highlighted.” I don’t think it is justified to use the similarity to the FA spectrum as a criterion when analyzing PMF aerosol results. Rather the spectrum of highly aged aerosol at a remote location is what is relevant here.

6. Detailed comments

Page 11683, Line 25: troposphere should probably be replaced by boundary layer

Page 11684, Line 16-17: This is incorrect, in algorithm 2 of Zhang et al. the organic mass cannot be expressed as functions of m/z 44 and 57. That is only true for what those authors call algorithm 1.

Page 11685, Lines 25-26: EV stands for effective variation (absolute value) not variance (quadratic), see PMF User’s Guide, Part 2: Reference, page 27.

Page 11686, Lines 19-20: fireworks periods are included in this analysis. Fireworks can produce high concentrations of aerosols with composition quite different from that of typical urban aerosols (Liu et al 1997, Drewnick et al 2006), which could distort the PMF analysis. Have the authors repeated the analysis with this period excluded. I would expect the main sources to remain the same, and the differences to appear in the smaller sources.

Page 11695, Section 4.2.5: the evidence for the sixth source to be real, and for its association with food cooking appears very weak. It is probably a combined residual. I suggest choosing the 5-component solution instead as the best solution.

Figure 5, will be helpful to show the error patterns for the 4-7 factorial analysis as well.

According to Fig 6, the POA components (HOA, wood burning, and charboiling) covary to a large degree. It will be interesting to know the r2 values between the component time series.

Page 11699, line 7: is there any evidence in the spectrum of OOA II to suggest that it contains oligomers? I would expect that the more aged and non-volatile OOA I would contain more oligomers, while the more semi-volatile OOA II would contain more monomers. For example Kalberer et al see more oligomers as aging proceeds. Despite fragmentation, oligomers are still visible on the spectrum of isoprene SOA with the AMS [Kroll et al 2006], and should also be visible here (depending on the noise level). If there is no evidence to link OOA II with oligomers, this unexpected connection between OOA II and oligomers should be removed from the paper.

Page 11705, line 8, check the equation number.

Various places: the OOA II should be referred to as semivolatile (meaning that it partitions between the gas and particle phases), not volatile (as in VOCs, meaning that it is mostly or exclusively in the gas phase)

7. References

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