

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.

V. A. Lanz et al.

Received and published: 21 January 2007

We would like to thank Anonymous Referee #1 and appreciate his comments which are certainly very useful for clarification and improvement of many particular aspects of our work.

1. First analysis

This paper is to our knowledge the first one where non-negativity constraint PMF is applied to highly-time resolved organic aerosol mass spectra measured by the Aerodyne AMS. In contrast, Li et al. (2004) did not include aerosol mass spectra. They included inorganics and OC with a 10-min sampling time interval (Li et al., 2004, p. 6522). Buset et al. (2006) as well as Quinn et al. (2006) did not include aerosol mass spectra either.

In fact, those studies included two to three selected organic fragments in their (ME-2 and PCA based) analysis and not the complete organic aerosol mass spectra as in our work. In the revised version, this issue will be specified and, of course, the three studies mentioned above will be cited.

2. Source quantification

The main focus of this work is source apportionment (see title), i.e. the determination of the relative contribution of sources to the total organic aerosol. Thus, the main results of this study are not dependent on absolute concentrations.

CE is certainly an issue when AMS results are reported as absolute mass concentrations (most of the time, uncertainty is within a factor of 2). We agree with the reviewer that a comparison with a collocated PM10 measurement is not adequate for the estimation of the CE value for this study. We also agree that OC to OM conversion factors add uncertainty to the comparison of AMS organics to organic matter measurements from an EC/OC instrument. Using a factor of 1.4 (commonly used for urban data) yielded a convincing comparison that the CE value for this data set is unity (e.g. Buset et al. (2006; p. 484), mentioned by the referee in item 1, assumed CE = 1 most of the time for their urban study as well). However, this remains subject to the uncertainty of the 1.4 conversion factor. In the light of these comments, we will change the paragraph on collection efficiency in the section “Measurements” as it does, indeed, simplify this issue in its current format. The modified paragraph will read as follow:

“A collection efficiency (CE) value is required for the estimation of aerosol mass concentration measured by the AMS (Alfarra et al., 2004). Due to the lack of collocated PM1 measurements, a value of unity has been used for the results reported in this study. This provides a lower limit estimation of the absolute mass concentrations, but does not influence the findings and the conclusions of this study since major results are reported in percentages of total organic mass.”

In addition, the assumed collection efficiency will be added to the figure captions where

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

Interactive
Comment

absolute concentrations are shown. Uncertainty from collection efficiencies will also be addressed when the calculated emission ratios are discussed, as it is the only aspect within this study where absolute values are reported and CE may be of some concern, even though we expect uncertainty from NO_x reactivity to be at least as large (see our response to referee #3; item 7).

It is certainly correct that it is essential to check any measured data carefully for outliers and indications of instrument problems prior to data analysis. This was done here as well. We do not have indications of instrument problems, i.e. the AMS diagnostics for the time period in question (evening of 30 July) were excellent. The referee was concerned about spurious peaks in the time series of OA components, without corresponding peaks in CO or NO_x. Most importantly, the time series of CO and NO_x are rather poor substitutes for AMS diagnostics to estimate the AMS accuracy and performance. CO and NO_x should be carefully used as indicators for the impact of combustion sources (representing certain temperature ranges of combustion processes). This was done in this study and a good overall agreement between the activity of estimated combustion sources and CO and NO_x was found (see section 4.4.2). However, one should not expect perfect correlation between the tracers such as CO and NO_x and aerosol sources and single mismatching peaks should not be overemphasized, especially as not all organic aerosol generation processes can be fully covered by those trace gases (e.g. events of nucleation, condensation, partitioning of organics into the inorganic aerosol phase etc.). Also the removal processes of the aerosols and the trace gases cannot be assumed to be always correlated.

The referee notes that both OOAs peaked up before midnight. This is not correct. No such peak can be observed for OOA, type II in Fig. 6. In addition, the peak of OOA, type I on 30 July 2005 is not isochronal to the ones of the primary sources and it expands over several hours. Fig. 6 will be enlarged as proposed by P. Paatero to avoid such misunderstandings as much as possible. We also would like to point to our reply to P. Paatero's comments.

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

3.1 choosing the right number of factors

It is true that PMF model solutions are not unique and analyses of data sets using any multivariate receptor model are to some degree subjective. It is therefore very important to validate the model solutions by means of the available PMF diagnostics and - even more important - by interpretability of the PMF solution (see comment of P. Paatero to this manuscript and our reply). As stated in our reply to the comments by P. Paatero, PMF diagnostics have been comprehensively performed in the presented data analysis. In the revised manuscript we will put more emphasis on PMF diagnostics and make clear that checking the PMF diagnostics is an integral part of any PMF analysis. We will also present more numbers, i.e. discuss the development of Q-values with number of factors, FPEAK, and Q contribution per row and column. However, we believe (and will make that more clear in the in the revised version) that the most powerful way to gain confidence (or to validate) the PMF model solution is to link the estimated source profiles and estimated aerosol components to AMS reference spectra. For analysis of AMS data one is in the very comfortable situation that a large (and growing) number of reference spectra is available.

One should also keep in mind that sticking strictly to mathematical criteria (such as the Q-values or $\max(\text{rotmat})$) for choosing the number of factors can be misleading or even detrimental. This can also be derived from this study as the 2-factorial PMF has lowest $\max(\text{rotmat})$ but certainly yields suboptimal source resolution and interpretability. The best approach in our opinion is to show that the chosen solution can explain real-world phenomena and is supported by mathematical diagnostics.

In this study, we chose the number of factors that maximizes the explanatory power of the model. Spectral similarity is an objective and sensitive (see below) criterion for interpretability. Using interpretability is as subjective as the proposed choice of Q-values and other diagnostics. The choice of one such a criterion will always remain subjective. To avoid this general drawback of descriptive models as much as possible, all kinds of mathematical diagnostics such as the model fit (R^2), model error (Q; in

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

the revised version) and rotational ambiguity ($\max(\text{rotmat})$) are shown and discussed along with interpretability.

We investigated the FPEAK range over -0.8, -0.6, -0.4, -0.2, -0.1, 0.0, 0.1, 0.2, 0.4, 0.6, 0.8 and have observed that the resulting Q-value (and interpretability) strongly supports the actual choice of FPEAK = 0.0. It can certainly not be called wrong to report Q values resulting from many different algorithm specifications, we however suggest not to discuss this excessively in the revised paper for several reasons. FPEAK values, as an example, can be in conflict with convergence criteria (“lims”). Then, one also has to present different FPEAK values for different lims. In fact, there are many different input parameters to PMF that can be varied. It is neither instructive nor needed nor considerate towards the reader to show and discuss too many of these results. One can easily calculate a large number of Q-value during the analysis of a data set when different settings are varied. E.g. varying 10 “FPEAK”-values, 2 modes, 4 outlier values, 3 different error models, 4 different “C1”-“C3” values, 6 different “lims”, and up to 10 factors leads to more than 10'000 Q-values (remark: these have not been shown either in most other papers presenting PMF results, including the papers mentioned by the referee in item 1, e.g. Li et al. (2004) did not report even a single Q-value). Another good reason not to include excessive Q values has been mentioned above: mathematical diagnostics for matrix unmixing should not be over-interpreted as it does not guarantee the best solution in terms of representing real atmospheric processes and, moreover, is basically blind to the real-world.

Finally, it is very important to comprehend that PMF is used here to solve a descriptive model. In other words: “Applied science [...] formulates different models according to the needs of the real-world situation. These models can be solved by using different algorithms. The choice of the algorithm usually does not matter as long as the algorithm does what it is supposed to do.” (referee comment by P. Paatero). P. Paatero subordinates the Q-value compared to interpretability as a diagnostic to choose the right number of factors: “If the decrease of Q [...]. Then the new factor should not be

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

included in the model unless the interpretability of the model improved significantly.“ Thus, it can be viewed as state-of-the-art within PMF modelling to use interpretability as a criterion for choosing the number of factors (remark: also the papers mentioned by the referee in item 1 use interpretability as a criterion; there it is called “meaningfulness” and is not expressed by an objective criterion).

3.2 rotational ambiguity

We do not claim that $\max(\text{rotmat})$ can fully represent rotational ambiguity. We also do not derive the number of factors from this parameter, neither. In this study, it is used as one of several PMF diagnostics to show that interpretability is not in conflict with other subjective criteria.

4.1. Naming the factors

We completely agree that wrong model assumptions (i.e. the wrong number of factors) can lead to factors that combine sources and/or aerosol components to unrealistic receptor profiles. The factors derived from models that are considered wrong should therefore not be named in terms of sources or aerosol components. However, naming the factors makes the manuscript much more readable. Since the names in the present manuscript are based on the spectral similarity of the calculated factors to the measured reference mass spectra (expressed by R^2 as similarity measure; see below), we suggest that we name the sources and components derived from “wrong” models with the suffix “-like” (e.g. “wood burning-like”). Only the sources and aerosol components from the correct model will be labelled. We will state this more clearly in the text and in each figure caption in question.

Please note that OOA from the 2-factorial PMF, as an example, can be interpreted as oxygenated organic aerosol, as a chemically specified aerosol component. No specific source can be attributed to it. It is a chemical characterization. However, we have discussed in this study that OOA can not always be equalled to secondary organic aerosol as some oxidized species may be primary in their nature. There is no labelling

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

conflict with the OOA's or HOA. However, it might be too complicated here to distinguish the labelling of sources and components. Therefore, we suggest (as discussed above) to use 'like' for any identified aerosol component or source in "wrong" models.

4.2 Spectral similarity (R2)

Our results are not dependent on the choice of R2 as a measure for spectral similarity. Several other measures (e.g. Euclidian distance) have been considered and applied. The R square (R2) has several advantages over other distance measures between two vectors:

-above all, it is objective.

-it is very sensitive (e.g. the R2 of the mass spectra of diesel and fulvic acid used in this study is $R^2=0.03$. The referee states that this R2 is 0.40, which is not correct.)

-it can be used in a robust way (by additionally choosing masses larger than m/z 44 only a possible leverage effect on R2 from a few high intensity masses can be excluded; e.g. see Table 1).

-it has been applied in similar previous publications (e.g. Zhang et al., 2005a; p. 4950).

-it is widely applicable and commonly used.

-for the present data, it yields the same results as other measures of similarity (e.g. Euclidian distance), but it is more simple to understand.

Using a weighted Euclidian distance, as an example, to express the spectral similarity does not change our results and their interpretation. The reason why not to choose such a measure is that a weighting vector has to be introduced and it is not universally applicable as it varies from AMS instrument to instrument and campaign to campaign. And it would be much less clear to write "calculated spectra X has a weighted Euclidian distance of 3.54 to the measured profile Y" - it is not commonly used and many readers would not be familiar with it.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

5. Fulvic acid

The similarity to the mass spectrum of fulvic acid (FA) is not used as the only criterion to identify highly aged organic aerosol matter: it is one of several spectra used and serves as an illustrative example. Please also note that we have included aged particles from urban and non-urban sites already in the present manuscript (Table 1) and calculated the similarity to aged aerosol from a remote site and many other spectra for aged and secondary aerosols. These similarities evolve in an analogous way as the one for fulvic acid. Aged aerosol from a remote site as a reference spectrum might not be an optimum choice either as this study investigates an urban background site.

6. Detailed comments

Page 11683, Line 25: ‘Troposphere’ will be replaced by ‘boundary layer’ here.

Page 11684, Lines 16-17: We agree that this sentence has to be modified to be more precise and will change it to “In ‘Algorithm 2’, measured data and vectors that initially can be described as a function of m/z 44 and m/z 57 are alternately regressed.”

Page 11685, Lines 25-26: We suggest to use the term “explained variation” (Paatero P., User’s Guide for Positive Matrix Factorization programs PMF2 and PMF3, Part 2: reference, p. 26; last changed on 25 February 2000). In contrast, the term “effective variation” as suggested by the referee is not found there.

Page 11686, Lines 19-20: The PMF analysis was repeated excluding the period from 1 August 21:00 to 2 August 06:00; the spectral similarity to the reference spectra did not change considerably neither for the main (OOAs) nor minor aerosol components.

Page 11695, Section 4.2.5: Concerning the discussion and interpretation of the sixth factor we refer to the comments by P. Paatero and the reply by Ch. Hüglin.

Figure 5: Error patterns for 4- to 7-factorial solutions are similar to the 3-factorial error pattern (at a lower level). This observation can be described introducing an additional sentence in the figure caption.

Figure 6: The correlation coefficients between the different time series of calculated primary OA (i.e. wood burning, HOA and charbroiling) vary from 0.06 to 0.35 if all data points are included and between 0.48 and 0.85 if outliers are excluded.

Page 11699, Line 7: We did not suggest that OOA, type II may contain oligomers; we mentioned oligomers only in the context of OOA, type I (see p. 11699, lines 15-18). It is OOA type I that shows spectral similarity to reference spectra for highly aged organic aerosol (e.g. fulvic acid) indicating that OOA I contains oligomers.

Page 11705, Line 8: equation number '(5)' will be replaced by '(6)' in the revised version.

'Volatile' here is used as an abbreviation and refers to the fact that "OOA, type II is a volatile fraction of OOA" (p. 11700, line 5). Please note that all AMS-aerosol can be described as semi-volatile. Thus, "semi-volatile OOA" would not clarify the role of OOA, type II, in this context.

Finally, we would like to stress the following point: This analysis showed, for the first time, the presence of two different OOA components. When the group of J. Jimenez applied the same PMF analysis to their Pittsburgh data they found exactly the same feature, i.e. an OOA component having a very similar temporal evolution as sulphate, and an OOA component having a very similar temporal evolution as nitrate (J. Jimenez, personal communication and Ulbrich et al., Poster 6G19 presented at the International Aerosol Conference 2006, September 10-15, 2006 St. Paul, Minnesota). This nicely confirms our own results and demonstrates the power of this method in source apportionment of the organic aerosol.

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 11681, 2006.

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)