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Atmospheric
Chemistry
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Discussions

Interactive comment on "Analysis of secondary organic aerosol formation and aging using positive matrix factorization of high-resolution aerosol mass spectra: application to the dodecane low-NO_x system" *by* J. S. Craven et al.

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We gratefully acknowledge Pentti Paatero for his positive support and thoughtful review.

Comment 1:

What was (typically) the size of the matrix analyzed by PMF? Did the columns of the matrix correspond to individual m/z values (or individual fractional m/z values) or to individual identified ions? Did you consider using a mixed matrix, containing both raw (perhaps fractional) m/z values and also a selected set of individual ions?

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Response 1:

The size of the organic signal input matrix for PMF of experiment 2 on Table 1 is 1050 x 325. The columns of the matrix correspond to individual identified ions. High resolution stick intensities for identified ions at fractional m/z's from 12-300 were used. AMS ion identification in the m/z 101 - 300 range was aided by the dodecane low-NOx chemical mechanism, CIMS gas-phase measurements, and MOVI- CIMS aerosol measurements. Not all of the individual ions identified were included in PMF analysis, due to S/N constraint.

This exact discussion is included in the first paragraph of Appendix A.

Comment 2:

Figure A4 shows the behavior of residuals on columns and on rows for different numbers of factors. This is a well-though-of ïňĄgure, much recommended. However, see also suggestions at the very end of this note.

Suggestion at end of note:

Average sizes of residuals on columns and on rows of X were successfully reported in this work. It would be useful to also examine the distribution of negative and positive residuals. Such examination might throw light e.g. on the problem discussed on lines 5-15 on p.16667. I recommend a rectangular "map plot", displaying a dot for each residual element r_ij of X (or of part of X) so that positive residuals r_ij > sigma_ij are plotted with a red dot, and negative residuals r_ij < -sigma_ij are plotted with a blue dot. Small residuals, e.g. -sigma_ij < r_ij < sigma_ij may be omitted from the plot altogether, in order to make the plot less crowded. Alternatively, the command "spy" from matlab might be used. Any regular patterns of red and/or of blue dots may indicate that some assumptions of the PMF model do not hold at that time and/or for those ions. A random pattern indicates a successful model.

Response 2:

The authors found this comment very useful and included map plots of both 2 and 3 factor solutions in the Appendix A. (Added figures, now Figures A5 and A6) A discussion of the map plot figures is added in paragraph five to Appendix A.

Comment 3:

Suggestions for Future Work: Time resolution of the model

Response 3:

A recommendation for averaging data points for PMF analysis on chamber studies was added to the discussion in the appendix. The discussion from the interactive comment from Paatero was cited.

Comment 4:

When modeling speciated aerosol measurements, we may call one certain rotational status "correct". In such a correct rotation, the F factors (rows of F matrix) are identical (within experimental error) with profiles of existing physical sources. Achieving the correct rotation usually requires that in addition to matrix X, some additional information is available.

When modeling the formation of SOA, the situation is different. There are no external profiles to match. It does not make sense to call a rotation "correct" or "incorrect". Each set of G and F factors is equally "right" if they fit matrix X equally well. There is no direct physical interpretation of columns of G or rows of F.

Response 4:

For chamber PMF the source of the aerosol is all coming from the same hydrocarbon (n-dodecane). For long OH exposure oxidation chamber experiments the ‘sources’ of aerosol then become the individual molecules that partition into the aerosol. The type of molecules partitioning or existing in the aerosol change over time due to continued oxidation of the gas phase and perhaps due to reactions in the particle phase.

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In order to match the chamber factor profiles directly to profiles of existing sources, an examination and identification of every compound in the aerosol would have been necessary. This was not possible for the current experiment. For the n-alkane system, the number of species goes up exponentially with carbon number (Aumont et al. 2005), so individual molecular identity in the aerosol is difficult. However, with our chemical knowledge of the gas-phase mechanism and product confirmation with measurements from the gas-phase CIMS of the C12 low-NOX system (Yee 2012), an estimate of products expected to partition into the aerosol phase was possible. We attempted to link the potential aerosol products (single molecules) with AMS ion tracers. An ion tracer for hydroperoxide species in the aerosol were proposed for AMS mass spectra (Table 4 and Figure 9). Also, with the predicted molecular structures from the gas-phase mechanism, additional AMS molecular tracers were developed (Table 2). With these ion tracers in the AMS (Figures 7 and 8) and molecular ions from the MOVI-CIMS (Figure 11), we were able to interpret the factors as groups or clusters of molecules with similar chemical characteristics (similar numbers of C's, H's, and O's) with similar dynamics in the aerosol (i.e. similar generations of gas phase reactions). We attribute most of this to similar products condensing into the aerosol at specific times. Generally speaking, the products that condense sooner have more C's and fewer O's, and products that condense later have fewer C's and more O's (as predicted by the mechanism). In this way we have attempted to physically interpret the source contribution (G) of PMF. The source profile (F) is more difficult, since the external profile to match would have to contain a mixture of mass spectra from several compounds with similar O:C and H:C ratios. However, we made the attempt with ion tracers. PMF with the MOVI-CIMS data will aid in the physical interpretation of F since this instrument retains the molecular information of the aerosol.

Comment 5

The present results are close to violating the non-negativity requirement. If the experiment would be continued for a few hours, the present factor G1 (first time factor) would go negative, as is seen in Figure 8. Of course, if a longer experiment would be performed, a different rotation would be obtained so that G1 factor would again stay positive. The point is, however, that in such longer experiment, the obtained F factor profiles (mass spectra) would be different because of a rotation with respect to present results.

Response 5:

It is plausible that G1 goes down to zero at the end of the experiment from aerosol conversion. However, without having an external molecular tracer to confirm this, there, it is difficult to find an exact solution. The first 17 hours of the G1 time trend is compared to the MOVI-CIMS ion $C_{12}H_{21}O_3^+$ in Figure 11, considered to be the ion tracer for the C12 dihydroperoxide (first greyed product in Channel 2 of Figure 2).

Mathematically, the rotation of this solution can be explored further by explicitly pulling the factor in the desired direction according to the PMF User's Guide and Paatero (2002), which was beyond the scope of this study, but encouraged for future chamber PMF studies.

For future chamber experiment studies, if we have good physical evidence that a factor like G1 should not go to zero, then we will try explicitly pulling the factors in the desired direction.

Comment 6

It is seen that the rotation obtained in present analysis is not "good" because it depends on the length of the experiment. In this work, rotation was controlled by varying the Fpeak parameter, as shown in Figure A7. The alternative rotations shown in Figure A7 appear worse than the 3-factor result in Figure 8. The authors failed to realize that Fpeak is not a precision tool for examining possible competing rotations in any given situation. In so doing, they repeated the very common misunderstanding among PMF users: it is believed that if Fpeak does not provide a competing rotation, then

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no such competing rotation exists. Fpeak examines a onedimensional path in the many-dimensional space of all rotations. (The rotational space is 6-dimensional for 3 factors and 12-dimensional for 4 factors). Only in exceptional cases does one find the desired alternative rotation by using Fpeak.

. . . future colleagues should not be relying solely on Fpeak in the search of alternative rotations. Thus I recommend that the authors should include more detailed discussion of the rotational question in the final version of this work, perhaps adapting some sentences from this note in their presentation.

Response 6

The authors acknowledge that fpeak does not examine all possible rotations, and we have added a more thorough discussion of the rotational ambiguity in the Appendix.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 16647, 2012.

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