

## ***Interactive comment on “Interpretation of organic components from positive matrix factorization of aerosol mass spectrometric data” by I. M. Ulbrich et al.***

**I. M. Ulbrich et al.**

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### **Response to Comments (cont.) by V. Lanz (Part 2)**

Our response has been divided into two parts to fit within the allowed page length for Author Comments prescribed by ACPD (15 pgs.). This part concludes our response and includes responses from #11 through #22 of V. Lanz’s comments. Excerpts from his comments appear below in italics. Our responses follow each excerpt. Changes to the manuscript appear in bold.

11) *p. 6739, lines 7-8: at this instance, it might be instructive to refer to already published ME-2 based work on organic AMS spectra (Lanz et al., 2008a) or work including organic spectral tracers (Buset et al., 2006).*

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[Response]: The work of Lanz et al. (2008a) using ME has already been cited earlier in the manuscript. This sentence is meant to refer to our own future work. Buset et al. (2006) only used 3 tracers from the AMS, not the whole spectrum, along with various non-AMS tracers, and thus their work is disjoint from the work in this paper.

12) p. 6740, line 26: *what are " 'solid body' geometric rotations"? Please explain or rewrite.*

[Response]: This description of these types of rotations are common for people with an engineering background. This phrase was also mentioned in the comments of reviewer P. Paatero, who said that "the remark is OK but the wording is unusual." We will adopt his suggestion to change the phrase to "orthogonal or 'solid body' rotations".

13) p. 6741, line 15: *I do not understand what is meant by "is still satisfied will little additional error"*

[Response]: We thank V. Lanz for catching this typo. We will change "will" to "with".

14) p. 6742, section 2.2.2 ("*Singular value decomposition*"): *At this point in the text, it is not clear why this subsubchapter was introduced in the manuscript. What about principal component analysis (PCA) etc.? Skip this chapter.*

[Response]: SVD is applied to selected data matrices and residual matrices in later portions of the manuscript. We will keep this section and note this in order to provide the necessary context for results presented later in the paper. PCA is a variant of SVD, but it is not used in this paper. Both of these methods, as well as PMF, are discussed by Paatero and Tapper (1993).

15) p. 6743, line 18: *"the inverse: has also a mathematical meaning and might be somewhat misleading here.*

[Response]: To avoid possible confusion, we will change "the inverse of Eq. (1)," to "**the forward calculation of Eq. (1)**".

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16) p. 6746, line 19 (25): *I would replace "statistics of correlation" by "measures of correlation" as a matter of taste.*

[Response]: Metrics of correlation are called "statistics" in common statistical language. See for example the chapter in Numerical Recipes entitled "Statistical Description of Data", and the Wikipedia pages for correlation (<http://en.wikipedia.org/wiki/Correlation>) and Pearson's R ([http://en.wikipedia.org/wiki/Pearson\\_product-moment\\_correlation\\_coefficient](http://en.wikipedia.org/wiki/Pearson_product-moment_correlation_coefficient)).

17) p. 6749, line 1: *"reduced aerosols such as meat cooking"; seed oil cooking and meat charbroiling aerosols or meat smoke are not fully reduced, but contain oxidized species as well (Schauer et al., 1999a and 1999b, Nolte et al., 1999). It would therefore rather surprising if meat cooking (as AMS determined by Mohr et al., in prep.) had the same spectral fingerprint as diesel combustion particles at all cooking conditions. This could be discussed a little more.*

[Response]: We did not say, nor mean to imply that meat cooking aerosols are completely reduced or that they lack any oxygen in the chemical composition. What we mean here is that meat cooking aerosols are much more reduced than atmospheric OOA, and their spectra are much more similar to HOA than OOA. Indeed the spectra obtained by our group in source experiments with ten different types of meat (Mohr et al., 2008) are very similar to HOA ( $R \sim 0.95$ ) and very different from OOA ( $R \sim 0.45$ ).

This is not surprising, since fatty acids are known to be major components of meat cooking aerosols, and e.g. oleic acid as an atomic oxygen-to-carbon ratio (O/C) of 0.11 and its AMS mass spectrum is very similar to that of HOA (e.g. Morris et al., 2002). Meat cooking can be a large source of PM because the cooking process can lead to the evaporation and recondensation of fatty acids from the meat itself (and sometimes the cooking oils), thus a similar O/C would be expected for meat cooking aerosols which we do not expect to change with different cooking conditions. Indeed the O/C determined by Mohr et al. for meat cooking aerosol is in the range of 0.11-

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0.14, which is similar to O/C ratios of 0.06-0.10 determined for HOA but significantly smaller than the O/C of 0.83-1.02 for OOA-I, 0.52-0.64 for OOA-II, 0.31-0.42 for BBOA determined by Aiken et al. (ES&T, 2008).

Finally, another way to look at these differences is with  $m/z$  44. The meat cooking spectra all show low contribution of  $m/z$  44 (1-2% vs.  $\sim$ 10% for various OOAs). And unlike in ambient air, even the small  $m/z$  44 for meat cooking aerosols was not dominated by  $\text{CO}_2^+$  (typically only 1/3 or less of  $m/z$  44 was due to  $\text{CO}_2^+$  for meat cooking aerosols) (Mohr et al., 2008).

18) p. 6749, lines 14-16: "*the . . . spectrum lies 28 degrees out of the . . . plane*". I am not sure what is meant at this instance? Is the authors' argument a geometrical one (such as: the solution space is three-dimensional)? If this is the case, they could illustrate this (e.g., by a set of suited projections of the samples onto planes - in analogy to Henry, 2003). In any case, it should be specified what is meant by "28 degrees" at this instance.

[Response]: We will add an explanation of this geometric consideration of linear combinations of vectors to the Methods section of the revised manuscript, along the lines described below. This is a projection of a vector onto a plane, but not in the way used by Henry (2003).

The MS can be considered as vectors in a 270-dimensional space. Any two vectors in this space define a plane. We chose here to consider the plane defined by the HOA and OOA-I MS vectors. Any 3rd vector in that 270-dimensional space will have an angle with respect to that plane. Any vector which is the linear combination of HOA and OOA-I would lie exactly in that plane and thus the angle will be zero. Any vector not in the HOA-OOA-I plane is not a linear combination of HOA and OOA-I, and its "distance" from the HOA-OOA-I plane can be quantified by the angle  $\alpha$  between the plane and the vector.

In linear algebra terms, let  $\mathbf{A}$  be a  $270 \times 2$  matrix formed by combining the non-

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orthogonal, non-collinear column vectors  $HOA$  and  $OOA - I$  such that

$$\mathbf{A} = (HOA, OOA - I) \quad (1)$$

and  $\text{rank}(\mathbf{A}) = 2$ . A projection matrix  $\mathbf{P}$  may be constructed by

$$\mathbf{P} = \mathbf{A}(\mathbf{A}^T \mathbf{A})^{-1} \mathbf{A}^T \quad (2)$$

which gives the projection ( $\mathbf{W}$ ) of a third vector ( $\mathbf{V}$ , which is OOA-II in the quoted example) onto the plane by

$$\mathbf{W} = \mathbf{P}\mathbf{V} \quad (3)$$

A right triangle between  $\mathbf{V}$  and the HOA-OOA-I plane can be identified in which  $\mathbf{W}$  is the base (and lies in the HOA-OOA-I plane),  $\mathbf{V}$  is the hypotenuse, and a vector  $\mathbf{Z}$  could be drawn perpendicular to the plane to define the height (Olver and Shakiban, 2006). The cosine of the angle  $\alpha$  between  $\mathbf{V}$  and the plane can be defined by

$$\cos \alpha = \frac{\|\mathbf{W}\|}{\|\mathbf{V}\|} \quad (4)$$

and  $\alpha$  can be calculated with the inverse cosine function.

19) p. 6751, lines 14-15 (and the corresponding passage in the conclusions): I do not understand how the second part of the sentence is related to the first one and our study (Lanz et al., 2007) (please consider specific comment 3). Please explain or write this sentences anew.

[Response]: This item concerns the same topic as V. Lanz's comment 3 (in Part 1 of his comments), and we have already addressed it in our response to that set of

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comments. We will rephrase the sentence to read "**Such factors have been reported in ambient solutions (Lanz et al., 2007). In our experience such factors appeared especially when the noise of a given m/z had been underestimated, but V. Lanz has also observed them when the noise was correctly specified (Lanz, 2008). The reasons for these differences in our results are unclear.**"

20) p. 6766, line 1: *Concerning the identification of OOA-II, it might be instructive to refer to your AAAR poster and/or to Lanz et al., 2007.*

[Response]: We will add a citation to Lanz et al. (2007) at the end of this sentence.

21) p. 6766, line 6: *one could add something like "... or it simply means that distinct profiles of additional sources (not retrieved by PMF) can be approximated by linear combinations of the PMF resolved profiles" (not to be confused by the "mixing artefact").*

[Response]: This idea was already implicit in the text, but to make it more explicit, after the following text (P6766/L3-6):

"There is no clear support for justifying solutions with more than three factors. Note that this does not mean that there are only three sources, but rather that sources with very similar spectra (e.g., gasoline and diesel engine emissions) cannot be separated in this analysis with UMR data."

we will add:

**"Any sources that can be approximated by linear combinations of the PMF factors are likely partitioning among the retrieved factors and are not retrievable separately."**

22) p. 6766, lines 10-12: *structure in the residuals may arise from the ageing, decay etc. of all components (OOA-I, OOA-II, HOA), may arise from minor sources etc.*

[Response]: In general these could be reasons that explain the residuals, but we draw

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this conclusion from the correlation between the TS of OOA-II and HOA and the Q-contribution TS (Fig. 7) and the various residual TS (Fig. S2) (revised figures at <http://tinyurl.com/4klulg>). OOA-I, representing a regional, long-lived organic component, has had a lot of time to change in the atmosphere and appears to have a more stable spectrum, i.e.  $Q/Q_{exp}$  is often near 1 during periods in which OOA-I is dominant. The residual and Q-contribution correlates with both OOA-II and HOA, although there is slightly more similarity in the shapes of OOA-II and the Q-contribution TS during OOA-II events. An expansion of Fig. 7 showing this period can be found at <http://tinyurl.com/5oy8nh> (pg. 5). As discussed above, these variations in the spectra of the components may be caused by "distillation" of a series of semivolatile species (as T and RH change), by changing fractions of different sources with similar spectra (such as diesel and gasoline). A more thorough explanation will be provided with our full response to the review by P. Paatero.

#### References:

- Bein KJ, Zhao YJ, Johnston MV, et al. Interactions between boreal wildfire and urban emissions. *Journal of Geophysical Research – Atmospheres*, 113, D07304, 2008.
- Brinkman, G., Vance, G., Hannigan, M. P., and Milford, J. B. Use of Synthetic Data to Evaluate Positive Matrix Factorization as a Source Apportionment Tool for PM2.5 Exposure Data, *Environmental Science and Technology*, 40, 1892-1901, 2006.
- Cottrell, L.D. et al.: Submicron particles at Thompson Farm during ICARTT measured using aerosol mass spectrometry, *J. Geophys. Res.* VOL. 113, D08212, doi:10.1029/2007JD009192, 2008.
- Chris A. Jakober, M. Judith Charles, Michael J. Kleeman, and Peter G. Green. LC-MS Analysis of Carbonyl Compounds and Their Occurrence in Diesel Emissions. *Anal. Chem.* 78, 5086-5093, 2006.
- Kirchstetter, T.W., et al., On-road measurement of fine particle and nitrogen oxide

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emissions from light- and heavy-duty motor vehicles. *Atmos. Environ.* 33, 2955-2968, 1999.

- Lanz, V. A.: Interactive Comment on "Interpretation of Organic Components from Positive Matrix Factorization of Aerosol Mass Spectrometric Data" by I. M. Ulbrich et al., *Atmospheric Chemistry and Physics Discussions*, 8, S1666–S1667, 2008.

- Lingwall J.W., Christensen W.F., and Reese C.S. (2008) Dirichlet based Bayesian multivariate receptor modeling, *Environmetrics*, in press (DOI: 10.1002/env.902).

- Morris, J. W., Davidovits, P., Jayne, J. T., Jimenez, J. L., Shi, Q., Kolb, C. E., Worsnop, D. R., Barney, W. S., and Cass, G.R. Kinetics of submicron oleic acid aerosols with ozone; a novel aerosol mass spectrometric technique. *Geophysical Research Letters*, 29(9), 2002.

- Murphy D.M., Middlebrook A.M., and Warshawsky M. Cluster analysis of data from the Particle Analysis by Laser Mass Spectrometry (PALMS) instrument. *Aerosol Science and Technology* 37: 382-391, 2003.

- Olver, P.J. and C. Shakiban, *Applied Linear Algebra*. Upper Saddle River, NJ: Prentice-Hall, pp 217-292, 2006.

- Paatero. P. and Tapper U.: Analysis of different modes of factor analysis as least squares fit problems, *Chemometrics and Intelligent Laboratory Systems*, 1993.

- Robinson AL, Subramanian R, Donahue NM, et al. Source apportionment of molecular markers and organic aerosol. 2. Biomass smoke. *Environ. Sci. Technol.* 40: 7811-7819, 2005.

- J.E. Shilling, Q. Chen, S.M. King, T. Rosenoern, J.H. Kroll, D.R. Worsnop, P.F. DeCarlo, A.C. Aiken, D. Sueper, J.L. Jimenez, and S.T. Martin. Loading-Dependent Elemental Composition of  $\alpha$ -Pinene SOA Particles. *Atmospheric Chemistry and Physics Discussions*, 8, 15343–15373, 2008.

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Discussion Paper



- Schneider, J., Weimer, S., Drewnick, F., Borrmann, S., Helas, G., Gwaze, P., Schmid, O., Andreae, M. O., and Kirchner, U.: Mass Spectrometric Analysis and Aerodynamic Properties of Various Types of Combustion-Related Aerosol Particles, *International Journal of Mass Spectrometry*, 258, 37-49, 2006.

- Q. Zhang, D.R. Worsnop, M.R. Canagaratna, and J.L. Jimenez. Hydrocarbon-like and Oxygenated Organic Aerosols in Pittsburgh: Insights into Sources and Processes of Organic Aerosols. *Atmospheric Chemistry and Physics*, 5, 3289-3311, 2005.

- Qi Zhang, M. Rami Alfarra, Douglas R. Worsnop, James D. Allan, Hugh Coe, Manjula R. Canagaratna, and Jose L. Jimenez. Deconvolution and quantification of hydrocarbon-like and oxygenated organic aerosols based on aerosol mass spectrometry. *Environmental Science and Technology*, 39: 4938-4952, 2005, doi:10.1021/es048568l.

- Q. Zhang, M.R. Canagaratna, J.T. Jayne, D.R. Worsnop, and J.L. Jimenez. Time and Size-Resolved Chemical Composition of Submicron Particles in Pittsburgh 8211; Implications for Aerosol Sources and Processes. *Journal of Geophysical Research – Atmospheres*, 110, D07S09, doi:10.1029/2004JD004649, 2005.

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Interactive comment on *Atmos. Chem. Phys. Discuss.*, 8, 6729, 2008.

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