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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Simultaneous factor analysis of organic particle and gas mass spectra: AMS and PTR-MS measurements at an urban site" *by* J. G. Slowik et al.

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Response to Comments by Reviewer #3

We thank Reviewer #3 for the helpful comments. A point-by-point response is presented below. For cross-referencing purposes, comments are numbered by reviewer and comment number, e.g. Comment 1.2 is the second comment in the first posted review. A parallel numbering scheme is used for figures and equations.

Comment 3.1:

Slowik et al. present a topical analysis of ambient aerosol- (AMS)/ gas-phase (PTRMS) data by means of PMF (positive matrix factorization). The manuscript is wellwritten and contains novel concepts, e.g. an elaborate technique to combine two and more datasets from different instruments for PMF. The authors give some evidence – for their specific data case – that the factor solution for the unified dataset is superior to the solutions based on isolated AMS and PTR-MS datasets, for example with respect to the identification of secondary/oxygenated organic aerosol, SOA/OOA, a major aerosol component in non-refractory PM1. This latter point is very important and should be stressed even more and supported further (e.g. by rigorously comparing the different OOAs (computed by factor analysis) with time series of AMS inorganics, backwards trajectories, and other auxiliary data). Apart from this open issue, the article is of great interest for ACP readers and it should be published as soon as possible (after considering the technical details mentioned by the other referees and the specific/minor issues below).

Response: We thank the reviewer for the support and agree that the enhanced ability of the unified dataset to distinguish SOA is a central feature of the work. We have augmented the discussion of SOA as follows. The aged SOA factor is now correlated with both particulate nitrate and sulfate. We state that this factor correlates with back trajectories from the densely populated regions to the southwest. We report the m/z 44/total organic ratio for each factor and use this value to estimate an O/C ratio [Aiken et al., 2008]. The implications of the mixed gas/particle nature of the SOA factors are also discussed in terms of the factor model assumptions, as discussed in response to Comments 1.15 and 2.1.

Comment 3.2:
P6740, L15–16: Please rewrite the following sentence: " ... such as apportionment of oxygenated VOCs to direct emission sources vs. secondary reaction products..."

Response:
The revised phrase reads: “The unified dataset provides information on particle and VOC sources and atmospheric processing that cannot be obtained from the datasets of the individual instruments: (1) apportionment of oxygenated VOCs to either direct emission sources or secondary reaction products;. . .”

Comment 3.3:
P6740, L21 sqq.: add some relevant references.

Response:
The following references have been added:

Dockery, D.W., and Pope, C.A.: Acute respiratory effects of particulate air pollution, Annual Review of Public Health, 15, 107-132, 1994.

Driscoll, C.T., Driscoll, K.M., Roy, K.M., and Mitchell, M.J.: Chemical responses of lakes in the Adirondack region of New York to declines in acidic deposition, Environ. Sci. Technol., 37, 2036-2042, 2003.

Jacobson, M.Z.: Strong radiative heating due to the mixing state of black carbon in atmospheric aerosols, Nature, 409, 695-697, 2001.

Pope, C.A., and Dockery, D.W.: Health effects of fine particulate air pollution: lines that connect, J. Air Waste Manag. Assoc., 56, 709-742, 2006.

Ramanathan, V., Crutzen, P.J., Kiehl, J.T., and Rosenfeld, D.: Aerosols, climate, and the hydrologic cycle, Science, 294, 2119-2124, 2001.

Schindler, D.W.: Effects of acid-rain on fresh-water ecosystems, Science, 239, 149-157, 1988.

Watson, J.G.: Visibility: Science and Regulation, J. Air Waste Manag., 52, 628-713,

2002.

Comment 3.4:
P6741, L19: PMF applications on PM compositional measurements date back to the 90ies (e.g. Ramadan et al., 1998, J. Air Waste Manag. Assoc., 50, 1308–1320).

Response:
We have added the following references to the manuscript:

Lee, P.K., Brook, J.R., Dabek-Zlotorzynska, E., and Mabury, S.A.: Identification of the major sources contribution to PM2.5 observed in Toronto, Environ. Sci. Technol., 37, 4831-4840, 2003.

Polissar, A.V., Hopke, P.K., and Poirot, R.L.: Atmospheric aerosol over Vermont: chemical composition and sources, Environ. Sci. Technol., 35, 4604-4621, 2001.

Ramadan, Z., Song, X.-H., and Hopke, P.K.: Identification of sources of Phoenix aerosol by positive matrix factorization, J. Air Waste Manag. Assoc., 50, 1308-1320, 2000.

Comment 3.5:
P6744, L18: what do you mean by "dwell" time?

Response:
“Dwell time” refers to the time spent averaging either ambient or background data. For clarity, “dwell time” has been replaced with “averaging time.”

Comment 3.6:
P6745, L21-L24: This is only true if the two instruments have comparable scaled resid-

uals/errors for all mass channels.

Response:
The concept of instrument relative weight was not clearly defined in the initial manuscript. We use this term to refer to the quality of fit to the sections of the unified **X** matrix, not the contribution of an instrument's data to Q during PMF2 execution. This is clarified in the revised manuscript and discussed further in response to Comment 3.7.

Comment 3.7:
P6746, L4-L7: This sentence might cause some confusion, because if $\Delta\overline{e_{sc}} > 0$ then Q(AMS) > Q(PTR-MS), meaning that the AMS has more "weight" and will determine the factors' shape (because PMF2 strives to minimize large Qs). You probably mean that in the upper case the AMS error is underweighted relative to the PTR-MS error.

Response:
This comment regards the definition of $\Delta\overline{e_{sc}}$ and the concept of instrument relative weight. For clarity, we show the definition of $\Delta\overline{e_{sc}}$ below. This definition has been modified slightly from the original manuscript to reflect the clarified terminology adopted in response to Comment 1.2. Specifically, s'_{ij} (uncertainties generated through the pseudo-robust method, see Comment 1.3) is used instead of s_{ij} to reduce the influence of strong outliers.

$$\Delta\overline{e_{sc}} = \overline{\left(\frac{|e_{ij}|}{s'_{ij}}\right)_{AMS}} - \overline{\left(\frac{|e_{ij}|}{s'_{ij}}\right)_{PTR}} \quad (1)$$

The reviewer correctly notes that PMF2 attempts to minimize Q during the solution process, meaning that, in a qualitative sense, the program strives to improve the fit to sections of **X** containing large Q-contributions. Crucially, these large Q-contributions must be decreased without sacrificing the fit in other parts of the matrix (such that a

larger Q is generated). When PMF2 terminates, some points are better fit than others. Data points with a near-zero $|e_{ij}|/s_{ij}$ are well-represented by the solution; points with a large $|e_{ij}|/s_{ij}$ are poorly-represented. Therefore, $\Delta\overline{e_{sc}} > 0$ indicates a poor fit to the AMS region of **X** relative to the PTR-MS. We refer to such a solution as being overweighted with respect to the PTR-MS, due to higher fit quality of the PTR-MS component of **X**. This has been clarified in the manuscript.

Comment 3.8:
P6747, L20: revise "foolproof"

Response:
"Foolproof" has been replaced with "unambiguous."

Comment 3.9:
P6748, L3–L7: refer to the corresponding figure. As a matter of taste, I would rearrange the figures (factor time series/profiles first, technical Q-plots second).

Response:
The figures are now referenced in the text. The order of the figures has been retained because the Q-plots are used select the "correct" number of factors, which must be done before the factor time series/profiles can be discussed in detail.

Comment 3.10:
P6749, L27: write "strong signals"

Response:

The typo has been corrected.

Comment 3.11:
P6750, L4, L14, L27 etc.: Please indicate the uncertainty associated with this average. Also indicate whether you calculated the percentages for each time stamp first, and then calculated the total average – or if you calculated first the absolute averages (in mass concentrations for each factor) and then calculated the average percentages. (This can make a difference).

Response:
In the original manuscript, averages were calculated using the second method. Because the two methods provide complementary information, both values are tabulated in the revised manuscript, together with their uncertainties.

Comment 3.12:
P6750, L8: replace "HOA-I" by "HOA"

Response:
This typo has been corrected.

Comment 3.13:
P6751, L5: what do you mean exactly by "instrument background"?

Response:
"Instrument background" refers to the signal obtained in the AMS when the particle beam is blocked. This is described in the manuscript as follows: "During operation,

the particle beam is alternately blocked (yielding a background measurement) and unblocked" (P6743/L24-25). We have clarified the discussion on P6751/L5 by explicitly referring to "instrument background signal."

Comment 3.14:
P6751, L6: is it plausible that road salt contributes to PM1 (maybe to PM10)? De-icing salts are mainly NaCl and CaCl2 I believe.

Response:
A significant increase in the AMS chloride signal was observed on 30 Jan immediately following snowfall, suggesting that some road salt particles were small enough to be detected by the AMS (although the majority of the mass is likely PM10). Because the AMS used in this study is very sensitive to potassium (due to the high relative ionization efficiency of potassium), it is possible that potassium from small amounts of KCl in road salt could be detectable. As this is the only period in the study where significant chloride was detected, we have revised the manuscript to note that road salt may affect the potassium measurement specifically during this period.

Comment 3.15:
P6751, L20: does the total aerosol loading depend on wind direction in the same way as the time series of factor 5?

Response:
The time series of factor 5 is not similar to the total aersol loading. As stated in the manuscript, the concentration of factor 5 is elevated only during periods of northerly winds. In contrast, both the total particulate organic and total aerosol mass are elevated by (1) flow from the heavily populated regions to the west/southwest or (2) contributions

from local point sources apportioned to other factors (e.g. charbroiling). This is now noted in the manuscript.

Comment 3.16:
P6752: L27: replace "the similar sources" by "similar sources"

Response:
This typo has been corrected.

Comment 3.17:
P6753, L4 (and at other instances): sort references in chronological order

Response:
The references have been sorted.

Comment 3.18:
P6762, L17-L18: Please note that Ulbrich et al. (2008) did not study charbroiling emissions.

Response:
The reviewer is correct that Ulbrich et al. did not study charbroiling factors. However, their results do indicate that PMF may not reliably distinguish factors with similar mass spectra, e.g. HOA and charbroiling. We have clarified the manuscript to note that the reference to Ulbrich et al. is with regards to correlated spectra, not charbroiling specifically.

Comment 3.19:
P6763, L11: ". . . to the(?) analysis . . . "

Response:
The sentence has been revised: "Analysis of the unified dataset complements that of the individual instrument datasets."

Comment 3.20:
P6755, L14: indicate the convergence criteria used in PMF2.

Response:
Generally, a solution is considered to have converged when 5 iterations within PMF2 produce a change in Q of less than 0.1. The exception to this is the solutions to the unified dataset at $fpeak$ = -1.0 and 1.0, where a change in Q of less than 0.2 is required, as PMF2 was unable to satisfy the more restrictive criteria. This is probably a result of the non-zero fPeak pushing the solution away from the local minimum. This information has been added to the methods section.

References
Aiken, A.C., DeCarlo, P.F., Kroll, J.H., Worsnop, D.R., Huffman, J.A., Docherty, K.S., Ulbrich, I.M., Mohr, C., Kimmel, J.R., Sueper, D., Sun, Y., Zhang, Q., Trimborn, A., Northway, M., Ziemann, P.J., Canagaratna, M.R., Onasch, T.B., Alfarra, M.R., Prevot, A.S.H., Dommen, J., Duplissy, J., Metzger, A., Baltensperger, U., and Jimenez, J.L.: O/C and OM/OC Ratios of Primary, Secondary, and Ambient Organic Aerosols with High-Resolution Time-of-Flight Aerosol Mass Spectrometry, Environ. Sci. Technol., 42, 4478-4485, doi:10.1021/es703009q, 2008.

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