

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 #2

We appreciate the suggestions submitted by Reviewer #2. A point-by-point response is presented below to the comments by Reviewer #2. At times we reference comments by another reviewer. For cross-referencing, comments are numbered by reviewer and comment number, e.g. Comment 2.1 is the first comment in the second posted review.

Comment 2.1:

Implicit in the combining of the two datasets is the assumption that the organic parti-

C4325

cle/gas system can be described by chemical profiles containing coupled particle and gas phase tracers, with fixed concentrations relative to each other. While this could conceptually occur, at the same time there may be reasons why it would not. For instance, many gas and particle phase species are contained within generalised primary emissions, but may not be emitted at consistent concentrations relative to each other and will have different lifetimes within the atmosphere, so measured concentrations would not necessarily be expected to correlate exactly. A similar argument could be applied to the precursors, formation and destruction rates of secondary species, which would lead to the relative concentrations varying depending on the photochemical age and initial sources of the emissions. It could also be speculated that there may be a chemical coupling between gas phase VOCs and aerosol organic matter, e.g. through semivolatile partitioning. While none of these would necessarily invalidate the work presented, these issues and how they affect the assumptions, results and interpretation should be dealt with much more thoroughly than it is currently.

Response:

A related issue was raised in Comment 1.15, and portions of the response are duplicated here.

The reviewer raises an important issue regarding the assumptions inherent in applying a factor model such as PMF to an ambient dataset. As discussed below, many of the specific considerations raised here apply equally to analysis of gas-only, particle-only, and gas/particle datasets. However, the question of specific gas-particle decoupling is an interesting one, and can be partly addressed through the current study. We have augmented the discussion of these issues in the revised manuscript.

Implicit in the application of a receptor model such as PMF to an ambient system is the assumption that that system can be represented by a linear combination of a finite number of static factors. Clearly this provides only an approximation of the ambient system. However, as the literature shows, such approximations have proven useful in

C4326

describing the composition of the ambient system.

In a fundamental sense, incorporation of particle and gas data into a single dataset for analysis is no different from analyzing gas and particle data separately. The reviewer correctly notes differences in reactive lifetimes and variable emissions sources as issues that PMF cannot fully address. However, both these issues also arise in the analysis of gas or particle-only datasets; they are not unique to the unified dataset. For example, reactive lifetimes of co-emitted aromatic VOCs vary from minutes to hours, and the dependence of VOC and particle composition on engine load is well-documented. In practice, some sources and lifetimes are “similar enough” to be approximated as identical by PMF (e.g. traffic emissions, long-range transport of oxygenated aerosol and VOCs). The criteria for being “similar enough” vary from dataset to dataset, though some recurring trends are evident, e.g. the similarity between OOA-1, OOA-2, HOA, and BBOA PMF factors across datasets.

The reviewer alludes to the possibility of situations in which chemical reactivity and/or partitioning may explicitly cause different time trends for VOCs and particles. We note that, although gas and particle data has been combined into a single dataset, it is not required that every factor contains both VOC and particle data. The UN-oxygenated POA and UN-Local Point Source factors provide examples of VOC-dominated factors (as the AMS mass fraction is too low to be reliable).

Finally, we note situations in which the factor model assumptions prove inadequate are reflected by increases the residuals. This is evident in the present dataset, as variable local source profiles are believed to be a major cause of outliers in the PMF solution (see response to Comment 1.3).

Comment 2.2:

One specific example of a shortcoming in the discussion is in the comparison presented in figure 13. There are many reasons why it may be expected that the rela-

C4327

tionship between OOA and the benzene/toluene ratio may break down, an important one being the contribution from biogenic VOCs. It may be that instead of improving the fit to OOA, the inclusion of PTR-MS data has simply pulled the time trend of the factor towards certain combustion-related gas phase markers and further away from the concentration of ‘true’ OOA. Under these circumstances, the approach would in fact be detrimental to the accuracy of the results.

Response:

The reviewer is correct in noting the potential contribution from biogenic VOCs. However, because the study was conducted in downtown Toronto in late January/early February, biogenic VOCs are expected to be negligible. This is supported by the PTR-MS measurement of isoprene, which never increased above the detection limit. Under these conditions, it is reasonable to expect SOA precursors to be dominated by anthropogenic emissions, notably aromatics, and the toluene/benzene ratio to be a reasonably accurate indicator of photochemical age.

The reviewer also raises the question of whether the fit of OOA/organics vs. toluene/benzene improves because of an improvement in the characterization of OOA, or a pulling of the OOA fit away towards aromatic gas-phase markers. To address this point, an additional panel has been added to Fig. 13, plotting (OOA-1-like) Aged SOA/total organics vs. toluene/benzene. As the figure shows, the improved correlation is due to the extraction of an additional OOA-like factor (“Local SOA”) rather than a distortion of the Aged SOA time series. The revised figure is shown below as Fig. 2.1.

Comment 2.3:

I would echo the other reviewer’s request that results be presented in the form of tables as it is difficult to see from the paper in its current form what the quantitative atmospheric implications of the results are.

C4328

Response:

As discussed in response to Comment 1.12, several tables have been added to the manuscript. For clarity, we repeat the response here.

Figures 7 and 12 (fraction of m/z or AMS total mass apportioned to each factor) have been replaced by tables, and an additional table has been added for the AMS dataset. These tables contain all of the following that apply to the given dataset, as a function of factor: AMS mass fraction, PTR-MS m/z mass fraction, toluene/benzene ratio, ratio of AMS m/z 44 to total organics, and estimated AMS O/C ratio. For the mass fractions, two complementary calculations of this fraction and the associated uncertainties are presented, as discussed in response to Comment 3.11. Average fractional composition is calculated by (1) calculating the fraction at each time stamp, then calculating the average concentration; and (2) calculating the average concentration across the study, then determining the fraction.

We have also added a table summarizing analysis parameters: matrix dimensions, α , and the range of p , f_{peak} , and seed values analyzed.

Another new table summarizes output values for the selected solution to each dataset: C_{PTR} (unified only), p , $Q/Q_{expected}$, $Q_{pseudo}/Q_{expected}$, and the percent of points in \mathbf{X} classified as outliers (see response to Comment 1.3).

Comment 2.4:

Furthermore, it is also important to communicate how much uncertainty the inherent ambiguities associated with the analysis introduce and how this could affect arising conclusions. While this is discussed, it is difficult to pull the information out of the text as it is currently.

Response:

The uncertainties in this analysis are illustrated primarily in the dependence of the solu-

C4329

tion on $\Delta\bar{e}_{sc}$, rotational ambiguity, the overall model fit quality. The analysis of solutions as a function of $\Delta\bar{e}_{sc}$ has been substantially expanded, as discussed in response to Comments 1.14, 4.4, and 4.16. We compare the 6-factor solution at $\Delta\bar{e}_{sc} = 0.052$ ($C_{PTR} = 10$), with 6-factor solutions at $\Delta\bar{e}_{sc} \sim \pm 0.25$, $\Delta\bar{e}_{sc} \sim \pm 0.50$, and $\Delta\bar{e}_{sc} \sim \pm 1.0$. Rotational ambiguity is analyzed through the f_{peak} parameter. We compare solutions at $f_{peak} = -1.0, 0.0, \text{ and } 1.0$ for each dataset, as discussed in response to 1.7 and 4.15. Finally, the quality of fit as a function of time can be evaluated through the plots of the $Q_{contribution}$ time series included in the original manuscript. A discussion of these uncertainties has been added to the manuscript.

Comment 2.5:

In a more general sense, the paper does seem to lack overall context beyond the analysis itself. While the introduction gives a very generalised motivation, the paper does not explicitly define how this work addresses the issues at stake.

Response:

The Introduction has been modified to highlight the apportionment of gas and particle concentrations to primary emission and secondary reaction processes. We also emphasize the need for methods capable of holistic analysis of combined gas/particle systems. We note the utility of this method as a tool for investigating gas/particle coupling, as discussed in response to Comments 1.15 and 2.1. Finally, because this manuscript is in large part concerned with the introduction of a new analysis method applicable to a variety of datasets, the benefits of the method will vary with the characteristics of the selected dataset.

Comment 2.6:

Additionally, the site description is very brief and does not contain any information regarding surrounding buildings, land use, how heavily used nearby roads are, etc.

C4330

Response:

The site description has been expanded: "The sampling inlet consisted of a 4 in. diameter circular duct located 5 m above ground and 15 m north of College Street. College Street has a weekday traffic volume of approximately 33 000 vehicles per day, similar to other major roadways in Toronto [Godri et al., 2009]. The site is situated in a mixed commercial/residential area. Known local particle emissions sources include automobile traffic, street food vendors, and restaurants."

References:

Godri, K.J., Evans, G.J., Slowik, J.G., Knox, A., Abbatt, J.P.D., Brook, J.R., Dann, T., and Dabek-Zlotorzynska, E.: Evaluation and application of a semi-continuous chemical characterization system for water soluble inorganic PM_{2.5} and associated precursor gases, *Atmos. Meas. Tech.*, 2, 65-80, 2009.

Interactive comment on *Atmos. Chem. Phys. Discuss.*, 9, 6739, 2009.

C4331

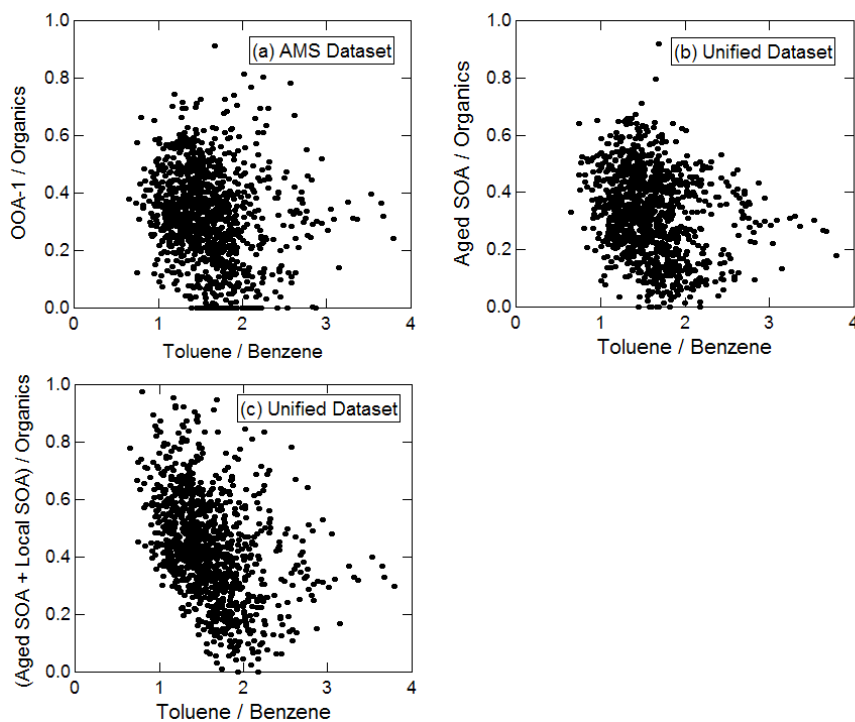


Fig. 1. Mass fraction of oxygenated aerosol as a function of the toluene/benzene ratio. Oxygenated aerosol is calculated as: (a) AMS-OOA-1, (b) UN-Aged SOA (OOA-1-like), and (c) UN-Aged SOA + UN-Local SOA.

C4332