

***Interactive comment on* “Photochemical
processing of organic aerosol at nearby
continental sites: contrast between urban plumes
and regional aerosol” by J. G. Slowik et al.**

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Response to Referee #1

We thank the reviewer for their interest and the suggested improvements to the paper. We address the suggestions below on a point-by-point basis.

Comment #1

While the methodologies and observations presented are generally sound, I do not feel that sufficient discussion is given to the implications regarding atmospheric chemistry

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or regional atmospheric composition. For instance, the evolution of the different types of OOA over the course of atmospheric ageing during the case studies is of particular interest, however the quantitative outcomes of this analysis are more or less buried in the discussion. Additionally, the authors do not give the reader any indication of the relevance of the derived quantities from an atmospheric science perspective. The manuscript would be greatly improved if the authors could discuss the overall importance of this work in more detail, with particular attention to the key quantities derived. An example would be the estimate of the timescale of SOA increase at the end of the discussion, but I see no reason why this line of discussion could not be extended to the PMF factors, in particular the apparent conversion between OOA2 and OOA1 seen during the Bear Creek-to-Harrow period. The paper would be improved if the quantitative outcomes of the discussion were given more prominence in the abstract and conclusions.

Response

We agree and have modified the manuscript. We have made the following specific changes:

1. We now compare the observed OOA-2/OOA-1 evolution to changes in the Mexico City plume over similar timescales.
2. The NO_x/NO_y ratio is now used to provide a rough estimate of photochemical age (see Comment #2). This provides approximate values for quantities such as the rate of SOA formation and interconversion between OOA-2 and OOA-1, enabling broader comparison with existing studies.
3. Estimates of the quantities noted by the reviewer and discussed points 1 and 2 are now presented in the abstract and conclusions.

Comment #2

The authors make extensive use NO_x/NO_y ratios as a rough measure of photochem-

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ical age. It would be very useful if they could provide an estimate of the real-world timescales that this metric is thought to represent in this region and time of year. While many assumptions would have to be made and the results would be of questionable accuracy, it would still be useful to the reader to have ballpark figures to contextualise the results. This would in turn allow rough estimates of the timescales of the organic evolution to be made. Again, these would be very rough and would have to have the appropriate caveats, but they would still be more informative and useful to the reader than what is currently presented.

Response

We now provide a crude estimate of the photochemical age based on the NO_x/NO_y ratio. We assume that the major NO_x loss process is the reaction OH+NO₂→HNO₃. The photochemical age Δt can therefore be represented as:

$$([\text{NO}_x]_0 - [\text{NO}_x]_t) / [\text{NO}_x]_0 = A(1 - \exp(-k[\text{OH}]\Delta t))$$

We assume all NO_y originates as NO_x and that there are no significant local sources of NO_x. Therefore [NO_x]₀ = [NO_y] and A = 1. The rate constant k is estimated to be 7.9 × 10⁻¹² cm³s⁻¹ at 1 atm and 300 K using the parameterization of Brown et al. [1999]. The mean daytime [OH] is estimated at 3.6 × 10⁶ molec cm⁻³ from the ratios of toluene and C8 aromatics [Sjostedt et al., 2010]. The estimated photochemical age therefore corresponds to effective daylight hours.

This estimate does not account for nocturnal NO_x loss via N₂O₅ hydrolysis, which is known to be a major NO_x sink in some regions. Diurnal profiles for NO_x/NO_y show that the ratio is stable overnight, but decreases during the day at a rate roughly consistent with the estimated photochemical age. This suggests that photochemical reactions are the primary influence on the NO_x/NO_y, although other influences cannot be ruled out. These diurnal plots will be added to the supplement. The photochemical age estimate also does not account for other NO_x loss processes or reservoirs, e.g. NO_x production by photolysis of HNO₃, nocturnal conversion to HNO₃ by reaction of NO₂ with O₃ and

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H₂O, formation of PAN, etc. Using the above method, we estimate that NO_x/NO_y ratios of 0.9, 0.5, and 0.1 correspond to ~1 hr, ~7 hrs, and ~22 hrs, respectively.

Reference: Brown, S. S., Talukdar, R. K., and Ravishankara, A. R.: Rate constants for the reaction OH+NO₂+M → HNO₃ + M under atmospheric conditions, Chem. Phys. Lett., 229, 277-284, 1999.

Sjostedt, S. J., Slowik, J. G., Chang, R., Mihele, C., Vlasenko, A., and Abbatt, J. P. D.: Diurnally resolved particulate and VOC measurements at a rural site: indication of significant biogenic secondary organic aerosol formation, Atmos. Chem. Phys. Discuss., 27321-27359, 2010.

Comment #3

I feel that the conclusion that the 'UNKN' factor is due to the uptake of biogenic VOCs onto sulphate particles is not adequately supported with the evidence presented and can only be treated as speculative. Taken at face value, the coincident sulphate concentrations could just as easily be due to unique organic sources that happen to be geographically close to the sulphur sources. Without direct evidence or identifying a specific mechanism, it seems unreasonable to refer to uptake mechanisms specifically in the abstract and conclusions sections. Given that this is a relatively minor part of the paper, the authors should consider removing it from these sections, unless they can present additional evidence to support it.

Response

We have modified the abstract and conclusions. In light of the recent findings of Robinson et al. (see Comment #8), we now tentatively relate the UNKN factor to isoprene SOA. However, we emphasize the tentative nature of such attribution. In the discussion of the UNKN factor, we also note that during the case study periods its fractional composition is low and therefore its attribution does not significantly affect the results.

Comment #4

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For the benefit of a reader unfamiliar with the campaign and local geography, a better comparison of the two sites should be given in section 2.1. A map showing the locations and anticipated source regions would be very useful.

Response

A map will be added to the Supplement.

Comment #5

The actual values of the collection efficiencies derived should be stated in section 2.1. If they were significantly different from the usual value of 0.5, the authors should explain why they think this happened.

Response

This information has been added to the manuscript. For the Harrow AMS, the collection efficiency was mostly at ~ 0.6 (similar to estimates obtained using both the light scattering and SMPS comparison techniques at a campaign during the previous month; see Slowik et al., 2010). However, during certain periods it increased to ~ 1 . These increases are believed to be caused by increased water content due to temperature gradients between ambient air and the sampling enclosure. For the Bear Creek AMS, a collection efficiency of 0.57 was estimated, which is similar to values reported in other studies and to the non-humid value estimated for the C-ToF-AMS using the light scattering module.

Reference: Slowik, J. G., Stroud, C., Bottenheim, J. W., Brickell, P. C., Chang, R. Y.-W., Liggio, J., Makar, P., Martin, R. V., Moran, M. D., Shantz, N. C., Sjostedt, S. J., van Donkelaar, A., Vlasenko, A., Wiebe, H. A., Xia, A. G., Zhang, J., Leaitch, W. R., and Abbatt, J. P. D.: Characterization of a large biogenic secondary organic aerosol event from eastern Canadian forests, *Atmos. Chem. Phys.*, 10, 2825-2845, 2010.

Comment #6

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In section 3.1, the authors give no account of why 4 factors were chosen. They should explain why they rejected other numbers of factors. Also, rather than describe the behaviour of the factors when varying f_{peak} , it would be much more informative if graphs could be shown in the supplementary material.

Response

The 4-factor solutions obtained at $f_{\text{Peak}} = 0$ and $f_{\text{Peak}} = 0.5$ are now shown in the Supplement.

We also now discuss the selection of 4 factors. Distinct mass spectral and temporal features of the first 4 resolved factors were discussed in the original manuscript, as were the relationships of these factors to each other and to selected tracer species. We have added a brief discussion of the rejected solutions with higher numbers of factors. At 5 factors, we obtain two HOA-like factors with strong similarities in the mass spectra and time series; a comparison of these factors has been added to the Supplement. While it is possible they contain real differences, we are unable to validate this and the inclusion of additional factors complicates the presentation without providing additional value. Similarly, the 6-factor solution represents the OOA components with 3 factors; we are again unable to justify this resolution. This behavior continues at higher-order solutions: we obtain only factors whose major features are similar to those already resolved and whose differences we cannot satisfactorily explain.

Comment #7

Also in section 3.1, the correlation coefficients between factors and gas phase tracers should be given where relevant.

Response

Correlation coefficients have been added. We also briefly discuss the low R-value obtained for the HOA/NO_x correlation, noting that high HOA concentrations typically correspond to elevated NO_x. The low R-value is due to periods of elevated NO_x with

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low HOA, which would be expected from sources such as gasoline vehicles, which were known to periodically influence the site.

Comment #8

The authors need to explain why they have attributed C₅H₆O⁺ to methylfuran and cyclopentenol, given that there are many other possible structures for this formula (the NIST database lists a total of 17, including isomers), notwithstanding the possibility that it is merely a fragment ion of one or more larger molecules. Is the attribution to methylfuran based on the work of Robinson et al.? <http://www.atmos-chem-physdiscuss.net/10/25545/2010/acpd-10-25545-2010.html> If so, this should be cited. Also, cyclopentenol has the formula C₅H₈O, so it is unlikely to act as a source of C₅H₆O⁺ after electron ionisation. Did the authors really mean to refer to cyclopentenal or cyclopentadienol?

Response

In light of the recent work by Robinson et al., we have modified the discussion of C₅H₆O⁺. In the initial version of the manuscript, we noted the occurrence of the UNKN factor during a period of high isoprene and low aromatics, and that this suggested a biogenic influence. Given the work of Robinson et al. that was published after the submission of our ACPD paper, we now suggest that the observed C₅H₆O⁺ may be due to methylfuran (or a methylfuran fragment from an unidentified larger molecule), but also note that there are other possible structures.

Comment #9

The line of reasoning that the presence of m/z 82 implies the source is local is not completely watertight. While m/z 82 has not been present in previously-studied aged plumes, it has not previously been reported in fresh plumes either (with the recent exception of Robinson et al.), so in this instance, there is no direct empirical evidence to infer the age of the plume. Note that the lack of significant m/z 44 in this factor does

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not necessarily mean anything, as the addition of this signal would be assigned to one of the other factors by PMF (as appears to have happened to a degree, looking at the graphs). While it can be speculated that chemical processing in the atmosphere could progressively remove the 82 signal through oxidation, this will depend on the chemical nature of the organics, which isn't currently known. This is not to say the plume isn't fresh, but the authors need to state their assumptions more clearly.

Response

In light of the work of Robinson et al., we now hypothesize that the UNKN factor is related to isoprene SOA, and therefore no longer discuss whether it is a local source.

Comment #10

Page 25000, line 2: The point about being the first multi-site PMF analysis has already been made, so there is no need to restate it here.

Response

The redundant sentence has been deleted.

Comment #11

The version number of the PMF2 executable should be given.

Response

We are using PMF2 version 4.2. This information has been added to the manuscript.

Comment #12

I would break the first paragraph of section 3.1 up a bit; it currently spans an entire page.

Response

The paragraph has been split in two.

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Comment #13

Page 25001, line 20: “approximately equally convergent” is probably not the best description, as the convergence process is not necessarily linked to the quality of the final solution. I would suggest replacing with something like “of similar goodness of fit”.

Response

We agree and have adopted the suggested wording.

Comment #14

Page 25006, line 1: Comma after “period”.

Response

The typo has been corrected.

Comment #15

Page 25008, line 11: Suggest changing “discrepancy” to “difference”.

Response

We have adopted the suggested change.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 24993, 2010.

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