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Atmospheric Chemistry and Physics Discussions

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.

Anonymous Referee #1

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This paper presents the analysis of a multi-site study in Canada, specifically the PMF analysis of organic AMS data from the BAWS-Met 2007 field campaign. This is an area of much current interest, as there is much still to learn regarding the lifecycle of organic matter in the atmosphere but recent advances in instrumentation and data analysis techniques have allowed many new insights in recent years. The methodology has a degree of novelty to it, in that it applied the PMF analysis to two separate instruments that were making measurements simultaneously. The authors also identify case study periods for inter-site transport for pseudo-Lagrangian analysis.

The paper is well written overall and the diagrams clear. The basic methodology appears to be sound, however the paper is let down by the analysis being a little undersold. As an example, the abstract and conclusions sections seem mainly to be concerned with the measurements and methods. The abstract and conclusions parts that cover the results are largely qualitative and doesn't really convey anything useful, in spite of the fact that there seems to be interesting data contained in the analysis. The paper would be improved greatly if the authors were to deliver more in the way of hard conclusions that would help to further atmospheric science. More detail and suggestions are given below. There are also a number of other comments I would make on specific sections. In particular, section 3.1 is in need of a bit of work. I recommend that this paper can be published subject to minor revisions.

General comments:

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

The authors make extensive use NOx/NOy 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.

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.

Specific comments:

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.

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.

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 fpeak, it would be much more informative if

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graphs could be shown in the supplementary material.

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

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-phys-discuss.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?

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 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.

Technical corrections:

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.

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The version number of the PMF2 executable should be given.

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

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”.

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

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

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

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Interactive Comment