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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Molecular composition of biogenic secondary organic aerosols using ultrahigh resolution mass spectrometry: comparing laboratory and field studies" *by* I. Kourtchev et al.

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We would like to thank Referees #1 for very helpful comments and suggestions. All of the comments and suggestions have been considered. Point by point responses to these comments are listed below.

Referee #1 comments: 1) The authors require that a peak have a signal to noise ratio of 10 to be considered for molecular formula assignment. This is a quite conservative requirement that ensures that only peaks that ionize efficiently and/or are in high con-

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centration in the sample are detected. As a result, I have confidence that the identified molecular formulae are representative, but I wonder if how much information is lost by not including peaks at lower signal to noise ratios. Authors often report data at a much lower signal to noise.

Authors Response: The signal to noise ratio (10) was established experimentally. The direct infusion ESI technique is susceptible to ion suppression and competition for the charge between the components with high and low ionisation efficiencies thus resulting in a fluctuation of the ion intensities. This phenomenon is more pronounced for ions with relatively low intensities (especially in the presence of matrix compounds present in the ambient samples). We do agree that by increasing signal to noise level to 10 we might lose some molecules but at the same time we are more confident about the ions that passed the S/N threshold applied in this study.

2) Do the authors have a reason for not considering phosphorous as an elemental constituent?

Authors Response: We agree that phosphorous is an important element in certain environments (e.g., marine). We reanalysed a few selected samples by including phosphorous in the formulae assignment model. However, the number of chemically realistic formulae in the examined ambient samples did not change and no P-containing formulae were detected.

3) The cluster analysis technique is well explained and demonstrates differences among the samples. The authors used a binary presence/absence matrix for input which is useful. The authors correctly note that the technique used here is not quantitative and that peak intensities should be viewed with caution, but I suggest that the relative magnitude of each peak is still useful information. (See, for example, Sleighter et al. (2010).) Patterns in the relative magnitudes of peaks present across many samples may reveal differences among samples that can not be detected using a binary matrix.

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Authors Response: As mentioned in the response to Comment 1, the direct infusion ESI method suffers from competitive ionisation of the ions especially in complex mixtures such as ambient aerosol resulting in rather high fluctuation of ion intensities. Thus, we refrained from using relative intensities for the interpretation of our results.

4) I think an important part of this study is that the authors restrict their analysis to <300 Da (the monomeric region). The authors note that the absence of dimers in ambient samples requires further study which is certainly true. Another way of interpreting these results is that the laboratory generated SOA methods used here (and in several other studies) do a fairly good job of describing what happens in nature (as indicated by the high agreement between the SOA and the boreal forest sample). But these procedures are not replicating the environment when it comes to these dimers which either don't form or have a very short half-life in nature.

Authors Response: We would like to thank the reviewer for this valuable remark. The following statement has been added to the text (p. 29613, line 17): 'Thus it appears that while the laboratory experiments performed here and in other studies do a fairly good job of simulating biogenic SOA formation (as indicated by the high level of agreement between the laboratory SOA and the boreal forest samples), they do not completely replicate the processes occurring in the ambient atmosphere.

5) Figure 5 shows the fraction of common formulae relative to the total number of formulae in the ambient samples. Has the opposite comparison been made (relative to the SOA formulae)? And if so, are there formulae present in the SOA that just don't appear to be important in nature? This, again, could have important information for how well SOA experiments are replicating what happens in nature.

Authors Response: The inverse comparison of the fraction of common formulae relative to the total number of formulae in the laboratory generated samples indicated that laboratory generated SOA contained 20-25% formulae that were not observed in the boreal samples. We suggest that these molecules are first generation products that

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are possibly oxidised with time in the atmosphere resulting in aged oxidation products. A respective statement has been added to the text (p. 29612, line 5): 'The inverse comparison of the fraction of common formulae relative to the total number of formulae in the laboratory generated samples in the monomeric region indicated that laboratory generated SOA contained 20-25% formulae that were not observed in the boreal samples. We suggest that these molecules are first generation products that are possibly oxidised with time in the atmosphere resulting in aged oxidation products.'

6) I would include Figure S2 in the manuscript. I think it is useful information.

Authors Response: Figure S2 has been added to the manuscript as suggested.

Technical Corrections:

1) Page 29602, line 12: 0.3<=H/C>=2.5 is confusing to read. I suggest separating this into the two groups that are being excluded, 0.3<=H/C and H/C>=2.5.

Authors Response: As suggested by the reviewer, the expression has been separated into the groups.

2) Page 29603, lines 1 and 3: The authors refer to "compounds" where formulae is the accurate term because the formulae could represent several isomeric compounds. In general, the authors were careful not to use compound, but the rest of the manuscript should be checked.

Authors Response: We agree with this statement, the word 'compounds' has been replaced with 'molecules'.

3) Page 29608, line 18: "indicated" is misspelled.

Authors Response: The word "indicated" has been corrected.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 29593, 2013.