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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.

Anonymous Referee #1

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General Comments: The authors use ultrahigh resolution mass spectrometry (UHR MS) to present a comparison of the molecular composition of laboratory generated secondary organic aerosols and the organics in two ambient samples, one from a boreal forest, the other from an urban environment. While many studies have identified specific proposed SOA products in ambient samples using UHR MS, the authors have performed a more thorough comparison of the entire . Their comparison found considerable agreement between the laboratory generated SOA and boreal forest organics when restricting the comparison to molecular formulae under 300 Da. These results

provide important confirmatory evidence that the monoterpene volatile organics used in this study are significant sources of the organic aerosols in boreal forests. The paper is clearly written, the subject matter is appropriate for publication in ACP, the methods are clearly understandable and appropriate, and I recommend the paper be accepted subject to technical corrections. I have also provided suggestions/questions for the authors in the following "Specific Comments" section, but I defer to the authors as to whether they feel these comments will improve the manuscript.

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

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

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

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

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