Faiola et al., Atmos. Chem. Phys. Discuss., 14, C8112-C8113, 2014

Response to Anonymous Referee #4

We thank the reviewer for her/his supportive and constructive comments. We have revised the manuscript in several instances to address the reviewer's concerns, and believe the paper is stronger as a result. This response will address the concerns in the order they were raised. Reviewer comments are in bold italics.

General Comments

The manuscript "Chemical characterization of biogenic SOA generated from plant emissions under baseline and stressed conditions: inter- and intra-species variability for six coniferous species" presents an interesting study of how biogenic SOA composition is altered by herbivore stress. The work is novel, well written, and relevant to ACP.

Thank you for these positive comments.

I agree with a previous referee comment that more basic background info on methyl jasmonate is necessary in the introduction or in the supplemental material. Also, do the authors know at what concentrations/rates methyl jasmonate is emitted during typical stressed episodes and how the applied jasmonate concentrations compare?

We have added the following to the description of methyl jasmonate in Section 2.3:

> *"Herbivory stress was simulated by exposing plants to MeJA. This compound is a plant stress hormone with chemical formula* $C_{13}H_{20}O_3$ *that is used in plant-plant communication for defensive purposes (Cheong and Choi, 2003)."*

We have also added an image of its molecular structure to the figure illustrating the SOA mass spectrum that was generated using standard MeJA as a VOC precursor (Figure 4).

Scientists have known for over two decades that plants emit methyl jasmonate and that it plays a role in plant-plant communication (Farmer and Ryan, 1990). However, to our knowledge there are no quantitative measurements of methyl jasmonate emission rates. The highly oxidized structure of this compound means it would not be detected with most common BVOC emission analytical approaches unless the researchers were specifically looking for it. Furthermore, the focus of methyl jasmonate research has primarily been ecological (e.g., the role of methyl jasmonate and induced volatiles in tritrophic signaling (Wasternack & Hause, 2002; Mäntylä et al., 2014)), genetic or biochemical (i.e. the synthesis of methyl jasmonate and its role in biochemical regulation (Cheong & Choi, 2003)), or has simply used the known property of methyl jasmonate to induce other plant volatiles and simulate plant stress (Rodriguez-Saona et al., 2001; Martin et al., 2003; Semiz et al., 2011). These research topics have not prompted the quantitative determination of methyl jasmonate emission rates. Karl et al., (2008) did measure the emission rates of a different plant hormone, methyl salicylate, which is also emitted as a plant defense response. Their measurements showed that emission rates of this plant hormone could equal monoterpene emissions during forest stress events. If methyl jasmonate emission rates were similar to this other plant defense hormone, our results suggest that methyl jasmonate could be a significant SOA precursor in forests under plant stress scenarios. However, we again emphasize that the intent in this study was to induce a strong stress response. We used a MeJA dose that has been shown to induce such a response in previous studies (Rodriguez-Saona et al., 2001; Martin et al., 2003). This exposure is presumed to be significantly higher than what non-infested trees would be exposed to during a herbivory event, but would also likely be a lower level of stress in comparison to an actual herbivore attack.

Why did the authors choose the set of m/z values listed on page 25177 for their correlations? Wouldn't using the whole organic spectra provide almost the same r^2?

> We agree that using the full organic spectra would have produced a very similar r^2 value. However, for some components of the analysis and for many of the plots, it was burdensome to include every *m/z* value in the spectra, particularly when many of them were trivially small. To make the analysis and data visualization more manageable, we chose to screen out *m/z* values that did not ever contribute significantly to a spectrum. The list included on page 25177 is the list of *m/z* values for which there was a significant mass spectral contribution at least once. Note that this list of values has been moved to the supplemental material in the revised manuscript.

It's a bit unclear when GC data is available in the experiments. It's unfortunate that the only GC data presented is in the supplemental section when the differences in BVOCs could be used to interpret the changes in AMS spectra. Do the authors know of other literature where AMS spectra of BVOC SOA has been presented and can be compared?

> As we noted in the manuscript, there is a companion paper to this one that focuses entirely on the VOC measurements for this same set of experiments, i.e., the GC data. The concerns raised by the reviewer are addressed in depth by that paper. The BVOC-focused manuscript was in open discussion for publication in *Biogeosciences* (Faiola et al., 2014) during the same period that this SOA-focused manuscript has been in discussion for *Atmospheric Chemistry & Physics*. The paper focusing on the BVOC emissions has now been accepted for final publication.
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> To avoid similar confusion for future readers, we have revised Table 1 to provide the experiment identifications for the *Biogeosciences* paper. We have also revised the manuscript so that it refers to the companion paper in a few additional spots for the readers' benefit.

Much of the HR-AMS protocol for data analysis on page 25178 can be shortened or moved to supplemental section.

> In the revised manuscript we have moved most of this discussion to the supplemental information.

A-pinene SOA is often the most basic example of BVOC SOA. It would be nice (even if in just the text) to mention how meJA or the other spectra correlate to a-pinene SOA spectra. If they are similar, those spectral fingerprints may be hard to distinguish in the field.

We have added a spectrum from the dark ozonolysis of alpha-pinene (Bahreini et al., 2005) to the supplement as Figure S-4 for qualitative comparison with the typical pre-treatment SOA spectrum presented in Figure 4 (now Figure 7 in the revised manuscript) from experiment AG-2-Pre. We have added the following to refer readers to the alpha-pinene spectra in the supplementary information:

> *"The AG-2-Pre spectrum is more representative of a typical baseline SOA spectrum. The mass spectrum of SOA generated from alpha-pinene dark ozonolysis is shown in supplementary information (Figure S-4, Bahreini et al., 2005) to compare the baseline biogenic SOA spectrum presented in this paper with a typical "model biogenic SOA" spectrum."*

The following discussion has been added to the supplementary information comparing the spectra.

> *"Figure S-4 shows the normalized AMS spectrum of SOA generated from the dark ozonolysis of alpha-pinene. Alpha-pinene has been used as a model compound for investigations of biogenic SOA by the aerosol community. It is provided here for comparison with a pre-treatment SOA spectrum generated from the oxidation of real plant emissions (Figure 7, main text). The dominant peaks in the two spectra are similar, with m/z 43 contributing the greatest organic signal. This is true for most SOA generated from monoterpene precursors in laboratory chambers (Chhabra et al., 2010, 2011). Other dominant peaks in both spectra are m/z 29, 44, 27, 41, 55, 42, 26, and 53. The relative contribution of these peaks between the spectra does vary slightly and there are some major peaks in the alpha-pinene SOA that are not as prominent in the AG-2-Pre spectrum. Some of this variation could be due to differences in fragmentation between AMS instruments, and/or differences in chemistry between chambers. For example, one difference between the two studies is that OH scavengers were used in the Bahreini et al. (2005). This limits our ability to perform a quantitative comparison between alpha-pinene SOA spectra and the biogenic SOA spectra presented in this paper."*

This qualitative comparison with alpha-pinene SOA helps put the AMS spectra we present into context for readers familiar with AMS data.

The authors have SMPS distribution data and HR-AMS PToF data. From those, an aerosol density can be estimated and applied to the volumes listed in Table 2.

We had considered calculating aerosol densities as the reviewer suggests but ultimately decided not to do so. Our primary reason for this choice was that we were not satisfied with the quality of our PToF data for many of the experiments. Providing densities for only some experiments would require explaining our selection criteria for including experiments but not others. In our judgment, the value to be gained from this effort was minimal and the needed discussion would detract from the paper's core arguments. For these reasons we chose not to pursue the density analysis.

Specific Comments

Increase the marker size and text size in Figure 9.

We have modified Figure 9 to improve its readability.

References

Bahreini, R., Keywood, M. D., Ng, N. L., Varutbangkul, V., Gao, S., Flagan, R. C., ... & Jimenez, J. L., Measurements of secondary organic aerosol from oxidation of cycloalkenes, terpenes, and m-xylene using an Aerodyne aerosol mass spectrometer. Environmental science & technology, 39, 5674-5688, 2005.

Chhabra, P. S., Flagan, R. C. and Seinfeld, J. H.: Elemental analysis of chamber organic aerosol using an aerodyne high-resolution aerosol mass spectrometer, Atmospheric Chemistry and Physics, 10(9), 4111–4131, 2010.

Chhabra, P. S., Ng, N. L., Canagaratna, M. R., Corrigan, A. L., Russell, L. M., Worsnop, D. R., Flagan, R. C. and Seinfeld, J. H.: Elemental composition and oxidation of chamber organic aerosol, Atmospheric Chemistry and Physics, 11(17), 8827–8845, 2011.

Cheong, J. J., & Choi, Y. D. Methyl jasmonate as a vital substance in plants. TRENDS in Genetics, 19, 409-413, 2003.

Faiola, C. L., Jobson, B. T. and VanReken, T. M.: Impacts of Simulated Herbivory on VOC Emission Profiles from Coniferous Plants, Biogeosciences Discuss., 11, 13455-13514, doi:10.5194/bgd-11-13455-2014, 2014.

Farmer, E. E. and Ryan, C. A.: Interplant communication: airborne methyl jasmonate induces synthesis of proteinase inhibitors in plant leaves, Proc. Natl. Acad. Sci. U. S. A., 87(19), 7713, 1990.

Karl, T., Guenther, A., Turnipseed, A., Patton, E. G., and Jardine, K.: Chemical sensing of plant stress at the ecosystem scale, Biogeosciences, 5, 1287–1294, doi:10.5194/bg-5-1287-2008, 2008.

Martin, D. M., Gershenzon, J., & Bohlmann, J. Induction of volatile terpene biosynthesis and diurnal emission by methyl jasmonate in foliage of Norway spruce. Plant physiology, 132, 1586-1599, 2003.

Mäntylä, E., Blande, J. D., & Klemola, T. Does application of methyl jasmonate to birch mimic herbivory and attract insectivorous birds in nature?. Arthropod-Plant Interactions, 8, 143-153, 2014.

Rodriguez-Saona, C., Crafts-Brandner, S. J., ParÉ, P. W., & Henneberry, T. J., Exogenous methyl jasmonate induces volatile emissions in cotton plants. Journal of chemical ecology, 27, 679-695, 2001.

Semiz, G., Blande, J. D., Heijari, J., Isik, K., Niinemets, U., & Holopainen, J. K., Manipulation of VOC emissions with methyl jasmonate and carrageenan in the evergreen conifer *Pinus sylvestris* and the evergreen broadleaf *Quercus ilex*, Plant Biology, 14 (Suppl. 1), 57–65, 2011.

Wasternack, C., & Hause, B., Jasmonates and octadecanoids: signals in plant stress responses and development. Progress in nucleic acid research and molecular biology, 72, 165-221, 2002.