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

Response to Anonymous Referee #2

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 overall manuscript shows innovative and certainly interesting research, which fits well within the scope of the journal.

Thank you for these positive comments.

Statistically significant differences are observed in the mass spectra of SOA generated in 2012 or in 2013. While such difference is clearly shown, there isn't in the manuscript a proper discussion on why it was so. P. 25182. L.20 hypothesis the cause to be related to different plant age, whereas P.25187 L.10 states that it could be explained by confounding stress effects. It is clear that this discussion must be better aligned throughout the manuscript and, furthermore, that the reason for these differences has not been completely elucidated. The fact that it was not completely elucidated has to be clearer in the manuscript.

As suggested in one of the reviewer's later comments, we have substantially revised Figure 3 and moved the results comparing same year and different year SOA to the supplementary information. The text accompanying the new figure has been revised to summarize all our hypotheses for these differences into a single paragraph, and to clearly state that we cannot conclude with certainty what the real cause could be. The supplementary text reads as follows:

> *"SOA spectra generated the same year were more similar to one another than SOA generated in different years. We hypothesize that some of difference between years could be attributed to differences in tree types and tree maturity from 2012 to 2013. In the 2012 experiments, only* Pinus ponderosa *and* Pinus aristata *were used and they were 2-3 years of age at the time of the experiments. In contrast, in 2013 all tree types except for* Pinus ponderosa *were used and most of the experiments were performed with trees that were 1 year of age. Furthermore, two of the 2012 PreT/PostT experiments were performed in October after the plants had already entered their winter dormancy period. As a result, there could have been confounding effects impacting SOA composition in four of the six biogenic SOA spectra from 2012. We are unable to explain with confidence why there were differences in SOA spectra between different years."*

While the experimental setup used allows a rich and extensive analysis of SOA formation from BVOCs, it covers a very specific type of chamber experiment (dark ozone-initiated). While the authors suggest a few m/z's from AMS that could act as biogenic stress markers (i.e. under

ambient conditions), I feel that it lacks a proper discussion on how representative one would expect that such measurements are of actual ambient measurements, and what would be expected for a wider range on chamber experiments.

The dominant atmospheric oxidant for many of the terpenoid compounds emitted by vegetation is ozone (Atkinson and Arey, 2003). Furthermore, chamber chemistry initiated by ozone in the absence of OH scavengers results in the formation of HOx and ROx radicals. We did not use any OH scavengers to suppress radical chemistry so it is likely that OH chemistry was occurring in the chamber as well. Consequently, the results presented here could be representative of ambient SOA. Based on our results, we suggest a number of *m/z* values for which the presence of signal in ambient measurements could indicate the stress-affected SOA. We do not assert with certainty that these markers would be found in ambient datasets- that is left to future investigations.

We have added text to clarify this point in section 3.6 (Results Summary):

"*Ozone is the dominant atmospheric oxidant for many of the terpenoid compounds emitted by vegetation (Atkinson & Arey, 2003). Furthermore, no OH scavenger was used to suppress OH chemistry. Consequently, these AMS results could be representative of what one would expect in ambient conditions.*"

Specific Comments

Although several references of size distribution using an SMPS are found throughout the manuscript, no actual SMPS measurements are shown. Please remove those references, in particular from the abstract.

The authors chose not to show any size distribution data or time series of particle growth because we did not believe it would add significant value to the manuscript's major arguments. However, we do present SMPS data in Table 2. Please refer to the column labeled "Max Particle Volume", which was calculated from SMPS measurements. We have added a sentence to the table caption to clarify this: "*Particle volume was calculated from SMPS measurements.*"

Section 2.2: It is unclear, by this section alone, how many experiments were actually carried out and how often each experiment was repeated (if at all). Also, please attain to absolutely essential information within the scope of the manuscript.

The authors refer the reviewer to the paragraph in section 2.2 beginning on page 25174, line 1. The paragraph begins: "*A list of all experiments with the Experiment ID, date, and treatment approach is provided in Table 1*." Table 1 lists each experiment that was conducted and orders the experiments by plant type and experiment type. Readers can find the number of experiments and the number of replicates using this summary table.

Table 1: Change date format into dd-mmm-yyy. Furthermore I'd suggest including a column indicating the experiment number showed in Fig. 2

We have revised the dates in Table 1 to be compliant with ACP guidelines (example: 25 July 2007). The numbers shown in Figure 2 are index numbers that refer to the figure axes and do not refer to an experiment number. We believe the experiment ID is sufficient for cross-referencing the figure with the tables. The Figure 2 caption has been revised for clarity. The caption now begins:

> *"Summary of all comparisons between biogenic SOA spectra. Each number on the x and y axes refers to a single SOA growth experiment. The legend provides a key to match the axis number with its corresponding experiment ID. Details of each experiment are listed by experiment ID in Tables 1 and 2."*

P. 25176 L. 4: Please replace "microphysical properties" with "number size distribution" if SMPS reference is kept.

This has been changed as the reviewer suggests.

Section 2.5: This section is far too descriptive and most of the usual data correction procedure can be referenced and/or moved into the supplemental material. Please move the list of used m/z's in a table format to supplemental material as well.

We have moved much of the data analysis discussion to the supplemental material, including the UMR *m/z* values used in our analysis, the HR air interferences, the water interferences, and the CO/CO_2 ion considerations.

Caption Fig. 2: Please remove color-code explanation, as it is already shown in the legend.

The relevant sentence in the caption has been revised so that it now reads: *"The color scale denotes the strength of correlation between the two spectra."*

Fig. 3: Overall this figure is highly informative, however it requires few modifications. I think the most relevant information is somewhat lost among all different constraints and the number of bars could be reduced, making it easier for the reader to extract most of it. For example, I'd strongly suggest the authors to remove references as "same year" or "different year" from this figure and include in a separated section, or supplemental material, linked not to the actual results, but pointing out the differences between 2012 and 2013 measurements. Also, color selection can be improved, blue and purple are too similar, please change it.

Thank you for these helpful comments. We have simplified Figure 3 to direct the reader's focus to the most relevant points. Specifically, we have eliminated the bars showing results for different year and same year comparisons as well as the bars showing comparisons with the methyl jasmonate standard spectra. We added a sentence to the paragraph introducing

Figure 3 that reads, *"Comparisons between experiments performed different years and comparisons with the standard MeJA spectrum are discussed in the supplementary information (Figure S-2)."* We have made a new figure with these results and discuss them in more detail in the supplementary material.

New results suggest a significant revision of O:C and H:C calculation (Canagaratna et al., 2014). The authors should consider whether directly adopting the new parameterization or just referring to it (discussing newly calculated O:C and H:C ratios) as it is still under discussion.

The two objectives of elemental analysis in this research were to 1) compare with previously published literature and 2) compare the different biogenic SOA to one another. For the first objective, we found it best to use the same approach that has been used previously. For the second objective, the updated approach would adjust all ratios from each experiment similarly, and thus should not have a major impact on our comparison. We thank the reviewer for bringing to our attention the recently published updated approach. We have added a few sentences to the Section 2.5 to discuss the implications of the new approach within the context of the results presented in this paper:

> *"Substantial revisions to the Aiken et al. (2008) approach to elemental analysis have recently been proposed by Canagaratna et al. (2015). These revisions have not been incorporated into this analysis. A major motivation for performing elemental analysis in this work was to compare with previously published results, which used the earlier methods. Another objective was to compare results between the different experiments conducted here; the new approach would affect all ratios similarly and thus would not influence the conclusions from these comparisons. Other technical considerations related to the HR data analysis are described in more detail in the supplementary information."*

Section 3: I find this section quite difficult to read, please consider changing the order on how the sections are organized. Consider combining all subsections entitled "summary" into a single one, and move some of the discussion of 3.6 to conclusions as well.

We have reordered Section 3 as was suggested here and by another reviewer. Specifically, we have moved the section describing the *Abies grandis* case so that it follows the section on post-treatment spectra. We have also modified the titles of subsections to avoid calling them 'summaries'. We have chosen not to make further changes to the organization of this section; we believe that the current structure presents our results clearly and effectively.

More on Section 3: A too large fraction of this section details the results of the unidentified external stress on the Abies Grandis emissions. By detailing almost four pages of this results, it actually diminishes strongly the main contribution of the manuscript, SOA spectra (and its markers) obtained under actually controlled conditions. Consider reducing it not to lose focus of the manuscript.

As noted above, we have revised the order of the sections so that the *Abies grandis* "unique" case is discussed after the section on post-treatment spectra. We believe this effectively addresses this comment also by improving the focus on the controlled experiment results.

References

Atkinson, R. and Arey, J.: Gas-phase tropospheric chemistry of biogenic volatile organic compounds: a review, Atmospheric Environment, 37(Supplement 2), 197–219, doi:10.1016/S1352-2310(03)00391-1, 2003.

Canagaratna, M. R., Jimenez, J. L., Kroll, J. H., Chen, Q., Kessler, S. H., Massoli, P., Hildebrandt Ruiz, L., Fortner, E., Williams, L. R., Wilson, K. R., Surratt, J. D., Donahue, N. M., Jayne, J. T., and Worsnop, D. R.: Elemental ratio measurements of organic compounds using aerosol mass spectrometry: characterization, improved calibration, and implications, Atmos. Chem. Phys., 15, 253-272, doi:10.5194/acp-15-253-2015, 2015.