

Response to Anonymous Referee #3

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

This paper presents an interesting set of laboratory experiments investigating the effect of plant stress on SOA composition. The research is original and likely to be of great interest to the research community studying biogenic SOA, and is well within the scope of this journal.

Thank you for these positive comments.

Organization: It feels strange to discuss the "exception" so thoroughly before showing the "typical" plant response. I would suggest reversing the order of sections 3.3 and 3.4, and adding a panel to Fig. 4 showing an AG-Post mass spectrum, so this figure doubles to show a "typical" pre to post change, as well as showing the atypical Pre example.

Thank you for this suggestion. We agree that the paper would flow more logically if we discuss the more general "post-treatment" spectra before discussing the more specific grand fir case. We have reversed the order of sections 3.3 and 3.4. We have also added text to the beginning of the grand fir section to clarify that the "unidentified stress" grand fir experiment discussed in detail in this section may represent a more "typical" plant stress response in the natural environment, which is why we chose to discuss the results in detail. These plants were exposed to a natural stressor outdoors where they were stored, and thus their stress response provided us with a unique opportunity to investigate emissions under naturally-elicited stress conditions as opposed to stress elicited from a plant hormone application. It is difficult to replicate and control natural plant stress responses, and we are not the first to store plants outdoors in their natural environment where they could be exposed to herbivore or pathogen attack and then use those plants to investigate stress effects on BVOC/BSOA (Mentel et al., 2013). The following statement was added to the first paragraph in the grand fir section to clarify this point:

"This experiment provided an opportunity to investigate the effects of a naturally-elicited stressor on BVOC emissions and biogenic SOA composition in contrast to stress elicited from plant hormone application. Furthermore, despite the presence of an external stressor, the MeJA treatment still induced emissions of 1,8-cineol and terpinolene allowing us to investigate the impact of multiple stressors. This scenario is representative of an environmentally-relevant case because the presence of multiple stressors in the natural environment is likely the rule rather than the exception."

This statement aligns with a later statement the authors made in the results summary section on page 25193 line 21, "Consequently, these results were not reproducible but did serve as an opportunity to investigate a plant's response to a natural stressor".

We have also added a panel to the figure (now Figure 7 in the revised manuscript) showing the mass spectrum of a typical post-treatment experiment as suggested and revised the caption to clarify that AG-1-Pre represents a “naturally-elicited stress” condition, AG-2-Pre represents a typical “baseline” condition, and AG-2-Post represents a typical “hormone application stress” condition.

I think it would be useful to add a brief discussion of the motivation for selecting the particular trees investigated here.

The following sentence was added to section 2.2 after listing the tree species used in the study: “All tree species are commonly found in the western mountain ranges of North America.”

The molecular formula and structure for methyl jasmonate should be in the manuscript somewhere, at least in the supplemental, to help readers interpret your results. What is its O:C ratio?

The molecular formula of methyl jasmonate is $C_{13}H_{20}O_3$ with an O:C ratio equal to 0.23. The O:C values from pre-treatment experiments were higher than this, ranging from 0.32-0.41 (page 25192, line 1). The post-treatment SOA had higher O:C ratios, ranging from 0.42-0.46 (page 25192, line 3). Consequently, the methyl jasmonate on its own could not increase the O:C values to match observations.

Thank you for drawing our attention to the lack of detail on methyl jasmonate properties. We have revised the description of methyl jasmonate in Section 2.3 to read:

“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 in the revised manuscript).

I think the fact that you ignore nitrogen-containing ions could introduce some bias and should be discussed more thoroughly (around 25180 lines 6-11). If these come from soil NO_x, they are likely to be NO₃-initiated SOA, which carry a lot of O's with them and could skew your O:C ratios high. NO₃ has highly variable rate constants with terpenoids, often much faster than O₃. If, for example, it's reaction rate with MeJA were anomalously high, this could be a big part of the increase in O:C. Is there any way you can estimate (e.g. from subsequent measurements?) the [NO_x], to report a ballpark guess? Can you put an upper limit on NO₃'s contribution to the O:C change?

Thank you for bringing our attention to this error in our wording on page 25179, lines 6-11. We stated that, “The nitrogen-containing signals were ignored for the analysis presented in

this paper”, but this mischaracterizes our examination of the nitrogen contributions. In fact, for each experiment we fit the same 743 ions using the HR data that passed our quality control assessment (described in Section 2.5). These ions were selected by looking at individual runs in each experiment - if there were measurable peaks present in any of the spectra, we included that ion in the HR fit. Consequently, any nitrogen-containing peaks that were present were accounted for in the elemental analysis. Our statement in the original manuscript was intended to convey that we could not rule out the presence of NO_x due to our experimental set-up, but that we were not focusing on nitrogen-containing ions in our analysis because the nitrogen-containing signal was low. We have revised the wording to reflect this intention more clearly. The paragraph now reads as follows:

“We cannot rule out the presence of NO_x in the reaction chamber because the plant chamber contained saplings potted in soil, and microbial activity in soil can be a source of NO_x. While NO_x was not measured directly, we consistently observed that the contribution of nitrogen-containing peaks to total organic aerosol signal was low— N:C ratios ranged from 0.004 to 0.011. Consequently, the nitrogen-containing signals were not the focus of the analysis presented in this paper.”

With respect to the reviewer’s concern about the potential for nitrate radical chemistry, we do not discount this possibility. However, it was not the intent of this study to investigate how BVOC/ BSOA partitioning for different oxidation mechanisms could impact the AMS spectra. In this work, we sought to provide insight about the inter- and intra- species variability in BSOA composition when using real plant emissions as the VOC precursor source, under baseline and stressed conditions. Certainly there is a need for further study of BVOC oxidation, including for MeJA and other stress-related compounds. Those systematic investigations are left for the future.

I think it would be very useful to report the general trend in total SOA mass pre-post, and the difference in O₃ decay rates, perhaps around 25182 line 25. I’m curious if the addition of MeJA could affect the concentration of O₃ in the pre/post experiments, and hence the total aerosol loading, skewing the volatility distribution of what’s condensing? This could lead to composition shifts even with the same total {gas + aerosol} product distribution, just due to partitioning changes. I know your MeJA MS data suggests that there is some role for the MeJA as an SOA precursor in itself, but this would help think more about what else it could be doing to the gas-phase chemistry.

Table 2 provides the maximum particle volume (proportional to mass) and the initial and final ozone concentrations for each of chamber experiments. It is evident from these data that the particle volumes were substantially higher in most of the post-treatment experiments. This is directly tied to the substantial increases in BVOC emissions observed after treatment. The BVOC emissions and profiles from these experiments are the focus of the companion paper accepted for publication in Biogeosciences (Faiola et al., 2014). To simplify cross-referencing between the two papers, we have added a column to Table 1 in this paper and to the analogous table in the companion paper. This cross-referencing will also help readers compare the BVOC profiles with the matching SOA data.

We recognize that higher BVOC loadings in the post-treatment experiments should shift the partitioning of the condensing compounds to include higher volatility compounds. However, we do not believe this to be the primary effect. If the shift in partitioning were dominant, we would expect the O:C ratios in the post-treatment experiments to be lower. However, the observed O:C ratios in the post-treatment experiments were higher relative to their corresponding pre-treatment SOA. This question merits further investigation, though the study design is complicated by the inherent variability in emissions when working with real plants.

With regard to the comments on ozone, we refer again to Table 2 showing that nearly all post-treatment experiments had excess ozone in the chamber throughout the entire duration of the experiment (see the final ozone measurement). Calculating accurate ozone decay rates during the initial particle formation and growth event would be difficult due to the methods used. In these experiments, the BVOCs were loaded for three hours prior to ozone addition. Once the ozone was added, oxidation chemistry proceeded rapidly and particle formation occurred before ozone addition had ceased.

Can you do elemental analysis of residual spectra? This would be an interesting way to say something more specifically about the non-MeJA SOA stress response composition.

As noted in Section 3.4.2, the residual spectra were calculated by subtracting the optimized combination spectrum (Pre-treatment + MeJA standard spectrum) from the post-treatment spectrum. We believe this method is useful for emphasizing enhanced peaks. However, we are hesitant to apply a quantitative elemental analysis on the residual without a detailed assessment uncertainty. While potentially valuable, we feel that such an assessment is outside the scope of this work.

Based on its vapor pressure, could MeJA condense onto particles and itself contribute to the particle phase?

We considered this possibility. On page 25175, lines 13-20, we report that the vapor pressure of methyl jasmonate at 23 °C is 1.28×10^{-4} mmHg. For comparison, consider a couple of the common oxidation products of alpha-pinene that are known to contribute to SOA formation: pinic acid and pinonic acid. These compounds have vapor pressures of 2.4×10^{-7} and 5.3×10^{-7} mmHg, respectively, at 23 °C (Bilde & Pandis, 2001). Methyl jasmonate is substantially more volatile than these oxidation products of alpha-pinene. Based on this, we think it is more likely that oxidation products of methyl jasmonate would have partitioned significantly to the particle phase in these experiments as opposed to methyl jasmonate partitioning directly to the particle phase.

Specific Comments

I'm puzzled by the climate feedback paragraph in the introduction (25169 lines 20-25). Based on the first 2 sentences of that paragraph, I expected a negative radiative forcing from BSOA. Why is the radiative perturbation then positive?

On page 25169, lines 16-17, we stated that the Carslaw et al. (2010) review paper discussed many feedback processes linking natural aerosol and the rest of the earth system. "These processes include the production of secondary sulfate aerosol from phytoplankton emissions, physical processes that contribute to dust entrainment, and the formation of biogenic SOA from terrestrial plant emissions". The positive overall radiative effect estimated in the Carslaw et al. review includes many more processes than just biogenic SOA formation. The reviewer is correct that the net radiative effect associated with biogenic SOA formation was negative. However, any feedbacks that could decrease natural aerosol production would have a net positive radiative effect. We encourage the reviewer to read the Carslaw et al. review paper for details of their calculations and the individual processes that produced the overall positive radiative perturbation for natural aerosol. The same result was separately reached by Arneth et al. (2010) in their review paper where they investigated many different processes linking the terrestrial biosphere and climate. BSOA formation was one of the many processes they included in their calculation. We did not state that the biogenic SOA formation feedback has a positive radiative perturbation, but that the overall radiative effect (which included the BSOA formation process among other things) was positive. However, the key message of this paragraph was that all these feedbacks are very poorly understood, and we agree with the reviewer that a net positive effect is surprising. These surprising results should motivate future work on natural climate change feedbacks like the work presented in our manuscript.

The format of plant species names is a bit odd and inconsistent: why is it "grand fir" but then "Douglas-fir" with a hyphen?

The Douglas-fir has an unusual common name. It was originally named after a Scottish botanist, David Douglas, making its name a proper noun (personal communication: Chuck Cody, WSU greenhouse manager). Consequently, the common name of this particular tree is normally capitalized whereas other common names are not. Furthermore, in 1867, the Douglas-fir was taxonomically separated from other fir trees and given its own genus name, *Pseudotsuga*, meaning "false hemlock" (http://oregonstate.edu/trees/conifer_genera/douglas_fir.html). The dash in the common name indicates that it is not a "true" fir. We recognize that this common name is structurally different from the others, but this is the correct form for this particular tree.

25175, line 27: is -> in

This has been corrected.

25178, line 23: “1.6 +/- 40%”: why is this error range reported as a %, where the other are all +/- 1 SD? Suggest making consistent.

Thank you for pointing out this inconsistency. This discussion has been moved into the supplementary information based on the suggestion of multiple reviewers and this value has been changed to “1.6 +/- 0.6”.

25180 line 8: Suggest reminding the reader via a brief parenthetical what the negative control experiments were. It was a very brief mention and many sentences previous that it was explained.

We have added the following sentence to section 3.1: “Negative controls refer to experiments where the plants were sprayed with water instead of the MeJA solution.”

After you have introduced the abbreviated MeJA, I suggest using that consistently throughout (e.g. 25182 line 2, 25188 line 19)

This has been corrected.

Top of 25191: two uses of long dashes are strange sentence structure. Use semi-colons?

We have revised this sentence to read as follows:

“One clear outlier was the SOA generated in experiment AG-1-Pre — the unidentified stress (UNID Stress) experiment that was discussed previously. All H:C ratios were similar (~1.5) throughout the pre-treatment experiments. This is consistent with expected H:C ratios for SOA generated from biogenic precursors (Chhabra et al., 2010).”

25191 line 4: insert citation about expected H:C ratios after “ozonolysis reactions.”

We have chosen to revise that sentence to state “this is consistent with expected H:C ratios for SOA generated from biogenic precursors (Chhabra et al., 2010).”

25192 line 29: remove comma after “rich”

We have revised to better represent the original intent of the phrasing to the following:

“The number of experiments and types of tree species examined in this study has provided a rich, but complex, data set”.

Isn't it “van Krevelen”, not “Van Krevelen”?

We followed the precedent set in previous papers that used "Van Krevelen". These papers include the following: Chhabra et al., 2011; Heald et al., 2010; Lambe et al., 2011; Ng et al., 2011. There are possibly other papers that use "van Krevelen", but we chose to be consistent with the format set by these papers that we were most familiar with.

25193 around line 11-14: Make clear that this is true for OZONE-initiated chemistry, not necessarily with different oxidants

We have revised this sentence to read:

"This result, when combined with the diversity in pre-treatment monoterpene emission profiles from these trees presented in Faiola et al. (2014a), suggests that aerosol mass spectra of biogenic SOA formed from ozone-initiated chemistry under baseline conditions all look very similar even with a different mix of monoterpenes used to generate the SOA."

25193 line 19 spectra -> spectrum

This has been corrected.

25194 line 24: couldn't this also be for more highly oxidized C10 products, not necessarily adding other hydrocarbons?

We believe there may have been an error in the line reference here - the question does not seem to correspond to the page and line number given. If the editor chooses to revisit the question with the reviewer, we would be happy to answer.

Aesthetic point: Figs 4, 6, and 8 are all similar but slightly different colors of green and thickness of lines. Make uniform?

The color and line widths of these three figures have been adjusted so they are all uniform.

In Figure 8 caption, recap the key text about these figures omitting negative residual peaks.

We added the following statement to the caption: *"Negative residuals have been removed to focus on the enhanced m/z peaks."*

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