



**Chemical  
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This discussion paper is/has been under review for the journal Atmospheric Chemistry and Physics (ACP). Please refer to the corresponding final paper in ACP if available.

# Chemical characterization of biogenic SOA generated from plant emissions under baseline and stressed conditions: inter- and intra-species variability for six coniferous species

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Received: 6 September 2014 – Accepted: 16 September 2014 – Published: 1 October 2014

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Published by Copernicus Publications on behalf of the European Geosciences Union.

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## Abstract

The largest global source of secondary organic aerosol in the atmosphere is derived from the oxidation of biogenic emissions. Plant stressors associated with a changing environment can alter both the quantity and composition of the compounds that are emitted. Alterations to the biogenic VOC profile could impact the characteristics of the SOA formed from those emissions. This study investigated the impacts of one global change stressor, increased herbivory, on the composition of SOA derived from real plant emissions. Herbivory was simulated via application of methyl jasmonate, a proxy compound. Experiments were repeated under pre- and post-treatment conditions for six different coniferous plant types. VOCs emitted from the plants were oxidized to form SOA via dark ozone-initiated chemistry. The SOA particle size distribution and chemical composition were measured using a scanning mobility particle sizer (SMPS) and Aerodyne high-resolution time-of-flight aerosol mass spectrometer (HR-AMS), respectively. The aerosol mass spectra of pre-treatment biogenic SOA from all plant types tended to be similar with correlations usually greater than or equal to 0.90. The presence of a stressor produced characteristic differences in the SOA mass spectra. Specifically, the following  $m/z$  were identified as a possible biogenic stress AMS marker with the corresponding HR ion(s) shown in parentheses:  $m/z$  31 ( $\text{CH}_3\text{O}^+$ ),  $m/z$  58 ( $\text{C}_2\text{H}_2\text{O}_2^+$ ,  $\text{C}_3\text{H}_6\text{O}^+$ )  $m/z$  29 ( $\text{C}_2\text{H}_5^+$ ),  $m/z$  57 ( $\text{C}_3\text{H}_5\text{O}^+$ ),  $m/z$  59 ( $\text{C}_2\text{H}_3\text{O}_2^+$ ,  $\text{C}_3\text{H}_7\text{O}^+$ ),  $m/z$  71 ( $\text{C}_3\text{H}_3\text{O}_2^+$ ,  $\text{C}_4\text{H}_7\text{O}^+$ ), and  $m/z$  83 ( $\text{C}_5\text{H}_7\text{O}^+$ ). The first aerosol mass spectrum of SOA generated from the oxidation of the plant stress hormone, methyl jasmonate, is also presented. Elemental analysis results demonstrated an O : C range of baseline biogenic SOA between 0.3–0.47. The O : C of standard methyl jasmonate SOA was 0.52. Results presented here could be used to help identify a biogenic plant stress marker in ambient datasets collected in forest environments.

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## 1 Introduction

Organic material comprises 20–90 % of the mass in atmospheric particles smaller than one micrometer (Jimenez et al., 2009; Zhang et al., 2007). Most of this small organic particulate material is secondary organic aerosol (SOA), and the major fraction of SOA globally is formed from the oxidation of biogenic volatile organic compounds (BVOC) released by vegetation (Hallquist et al., 2009). BVOCs are emitted by plants primarily for defensive purposes (Dudareva et al., 2006; Kesselmeier and Staudt, 1999). BVOC emission rates and emission profiles (i.e., the types of compounds emitted) can change significantly when plants are exposed to biotic and abiotic stressors (Holopainen, 2004; Peñuelas and Staudt, 2010; Pinto et al., 2010). It follows then that plant stress exposure associated with climate change could have significant impacts on SOA formation, and thus could lead to a climate feedback because atmospheric aerosols play an important role in the global radiation budget.

Potential climate change feedbacks resulting from the processes linking naturally produced aerosols and the rest of the Earth system have been summarized by Carslaw et al. (2010). 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. Their simulations estimate that the radiative forcing resulting from these feedbacks could produce positive radiative perturbations up to  $1 \text{ W m}^{-2}$  by the end of the 21st century, amplifying the expected effects of climate change (Carslaw et al., 2010). Another review focused on feedbacks between the terrestrial biosphere and climate, and also included a discussion of the biogenic SOA formation process (Arneth et al., 2010). They estimated that climate feedbacks with the terrestrial biosphere could result in positive radiative perturbations of up to  $1.5 \text{ W m}^{-2} \text{ K}^{-1}$  by the end of the 21st century. Both reviews make clear that more work is required to fully understand these feedbacks, stating that the current level of scientific understanding for them is “poor” (Carslaw et al., 2010) and “very low” (Arneth et al., 2010). Despite the uncertainty in these projections, the assessments of

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both papers are in stark contrast to the previously held assumption that the overall contribution of vegetation to the changing climate system is to act as a sink for increasing CO<sub>2</sub> (Magnani et al., 2007). Carslaw et al. (2010) listed several research topics that need to be addressed in order to reduce the uncertainty in these predictions; resolving BVOC responses to climate change stressors and investigating the subsequent impact on biogenic SOA formation was included as a high priority for future research projects.

Most studies of how BVOC emissions respond to stressors have focused solely on the BVOC emissions themselves. Using these results to infer overall impacts on climate requires highly uncertain assumptions about how different mixtures of BVOCs could impact SOA yields and chemical composition. A few studies have examined SOA formation from real plant emissions more directly. Joutsensaari et al. (2005) were the first to report SOA formation in a laboratory chamber from the oxidation of real plant emissions. They used a methyl jasmonate treatment to induce emissions in order to investigate the role of inducible plant volatiles in particle nucleation and growth. Other studies have focused on SOA production and chemical composition from BVOC emissions under baseline conditions, rather than looking at potential feedbacks between stressors and climate (Hao et al., 2011; Kiendler-Scharr et al., 2009; Mentel et al., 2009; VanReken et al., 2006). Our own recent work showed that SOA can also form from BVOCs emitted from leaf litter, and that this aerosol is chemically very similar to SOA produced from live tree emissions (Faiola et al., 2014b). BVOC emissions from leaf litter were also found to respond to external environmental drivers, raising the possibility of additional pathways for climate feedbacks to occur.

Recently, there have been two studies that compared biogenic SOA yields for baseline emission vs. stressed conditions. Lang-Yona et al. (2010) examined the effect of increased temperature on holm oak (*Quercus ilex*) emissions and subsequent SOA formation, finding that increased temperature led to heightened BVOC emissions and increased SOA production. The BVOC profile was slightly altered with increasing temperature, but this did not impact the resultant SOA mass yields. In another study, Mentel et al. (2013) investigated the impact of herbivory, drought, and heat stress on



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plant enclosure and the on-line analytical gas chromatography (GC) system used to measure BVOC emissions is provided in a separate paper that focuses on the impacts of herbivory stress on plant emissions (Faiola et al., 2014a). The current paper focuses specifically on the composition of biogenic SOA formed from the oxidation of the plant emissions.

The aerosol growth chamber operation and SOA generation methods are similar to those described by Faiola et al. (2014b). Chamber dimensions were 1.6m × 2.2m × 2.2m. All aerosol growth experiments were conducted with the chamber using a batch mode approach. Oxidation of SOA precursors was initiated with ozone that was generated with an Enaly model HG-1500 ozone generator. The chemistry in this chamber is best described as dark “ozone-initiated” chemistry because the chamber was not equipped with UV lights and no OH scavenger was used. Most experiments were unseeded. Experiments where 50 nm ammonium sulfate seed particles were used are marked with an asterisk in the experiment summary table (Table 1). When used, seed particles were produced from a TSI constant output atomizer (model 3076) and then size-selected with a differential mobility analyzer (DMA, TSI, Inc.). Temperature and relative humidity in the aerosol growth chamber were not controlled, but were monitored using a Vaisala HMP110 humidity and temperature probe. Nitrogen oxides were not measured, but the aerosol chamber likely contained some NO<sub>x</sub> due to soil emissions from the plant pots (Davidson and Kingeree, 1997).

## 2.2 Tree description and experimental design

Six different plant species were used as emissions sources to generate biogenic SOA in this study: ponderosa pine (*Pinus ponderosa*), bristlecone pine (*Pinus aristata*), blue spruce (*Picea pungens*), western redcedar (*Thuja plicata*), grand fir (*Abies grandis*), and Douglas-fir (*Pseudotsugas mensiezii*). Saplings were 1–3 years old at the time of the experiments. All specimens were obtained from the University of Idaho forest nursery and were stored outdoors at the Washington State University greenhouse facility

when they were not being used for experiments. Greenhouse staff cared for the specimens, providing regular watering and fertilization.

Plants were transported to the laboratory at least 36 h before the first aerosol growth chamber experiment to allow time for acclimation to laboratory conditions. Three to nine saplings of the same species were placed in the plant enclosure (the number depended on the size of the plants). The only exceptions to this were four experiments performed using a combination of *Abies grandis* and *Pseudotsugas menziesii* specimens rather than just a single plant species (referred to as “mix” experiments). One day before an aerosol growth experiment, the aerosol growth chamber was cleaned with 1 ppm ozone and flushed with zero air for at least 18 h until ozone concentrations were less than 20 ppb (Model 1008-PC ozone monitor, Dasibi) and particle number concentrations were less than 10 cm<sup>-3</sup> (Model 3771 condensation particle counter, TSI, Inc.). Zero air was generated with a pure air generator (Aadco model 737). Chamber flushing was stopped on the morning of the experiment, at which point the chamber was operated in batch mode. Biogenic VOC emissions were pumped from the plant enclosure to the aerosol growth chamber for three hours (flow = 9.5 LPM) using a chemically resistant vacuum pump (KNF Laboport model UN810 FTP) through PFA lines heated to 80 °C. Lines were heated to minimize losses of lower-volatility compounds. During chamber loading, a fan inside the chamber was used to facilitate mixing.

When VOC loading was complete, the oxidation chemistry was initiated by rapidly introducing 130 ppb ozone to the aerosol growth chamber. The mixing fan was turned off immediately following oxidant addition to reduce particle wall loss. Particle growth and composition were then monitored for the next 6–8 h. This process was repeated with the same batch of trees twice in one week – once before treatment was applied and again after the treatment. The treatment was either a stress application or a negative control. Both treatments are described in detail in the next section. The time required to observe maximum plant response to treatment can vary (Copolovici et al., 2011). Consequently, some of the post-treatment aerosol growth experiments were performed the day after treatment and some were performed on the same day as the treatment.

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A list of all experiments with the Experiment ID, date, and treatment approach is provided in Table 1. The naming convention for the Experiment ID is “plant species type” + “experiment number” + “experiment type”. For example, “PA-1-Pre” stands for *Pinus aristata*, first experiment, pre-treatment and “PA-1-Post” stands for *Pinus aris-*  
5 *tata*, first experiment, post-treatment. One pre-treatment aerosol growth experiment performed with *Picea pungens* specimens on 14 May 2013 did not produce enough particle mass for AMS analysis, so it has been removed from this table and will not be considered further. There was also one SOA growth experiment performed that used a single-component standard, methyl jasmonate, as the precursor compound to gener-  
10 ate SOA, rather than using real plant emissions. For this experiment, a 95 % methyl jasmonate standard solution (Sigma-Aldrich part #392707-5ML) was introduced into the aerosol growth chamber using a dynamic dilution system (Faiola et al., 2012).

### 2.3 Stress treatment

Herbivory stress was simulated by exposing plants to methyl jasmonate (MeJA). Methyl jasmonate is a plant stress hormone used in plant-plant communication for defensive  
15 purposes (Cheong and Choi, 2003). Plants emit MeJA into the gas-phase, where it induces the jasmonic acid defense pathway in neighboring plants (Farmer and Ryan, 1990) – a biochemical pathway that leads to changes in the VOC compounds produced and emitted from those plants. Consequently, exposing plants to MeJA alters BVOC  
20 emission rates, their chemical profile, and their concentrations in storage pools (Martin et al., 2003; Rodriguez-Saona et al., 2001). For the 2012 experiments, MeJA was introduced using an exogenous treatment where 20  $\mu\text{L}$  of a 9 : 1 diluted ethanol : MeJA solution was applied to a cotton swab and placed in the biogenic emissions enclosure with the plants, following the methods of Rodriguez-Saona et al. (2001). The 2013 exper-  
25 iments used a foliar application of 10 mM MeJA in nanopure water, following the approach of Martin et al. (2003). The plant foliage was sprayed with 200 mL of this solution. The negative control treatment was a foliar application of 200 mL of nanopure water rather than the MeJA solution.

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The revised MeJA treatment employed in 2013 was intended to promote a maximal herbivory stress response. The goal was to allow us to investigate an upper limit of the potential impacts of herbivory on biogenic SOA composition, something that has not been reported previously. The foliar MeJA stress treatment elevates BVOC emissions and typically leads to much larger mass loadings relative to the pre-treatment experiments. Importantly, the purpose of these experiments was not to quantify changes to the amount of SOA formed under stressed conditions. Rather, this research seeks to fill in current gaps in knowledge by investigating changes to biogenic SOA composition due to stress.

A number of the post-treatment aerosol growth experiments were performed the same day as the foliar MeJA application. In these cases, methyl jasmonate solution remained present on the plants in the plant chamber while the aerosol chamber was being loaded. The vapor pressure of methyl jasmonate at 23 °C is  $1.28 \times 10^{-4}$  mmHg (Acevedo et al., 2003), which corresponds to an effective saturation concentration ( $C^*$ ) for methyl jasmonate of  $1500 \mu\text{g m}^{-3}$ . This puts methyl jasmonate at the lower end of the intermediate volatility range ( $C^*$  range of 1000–100 000  $\mu\text{g m}^{-3}$ ) approaching the semi-volatile range ( $C^*$  range of 0.1–1000  $\mu\text{g m}^{-3}$ ) (Robinson et al., 2007). To compare, the vapor pressure of alpha-pinene, a typical monoterpene, is four orders of magnitude greater, nearly 3 mmHg at 20 °C. Even with MeJA's low vapor pressure, some of the compound sprayed on the trees would volatilize and be subsequently pumped into the aerosol growth chamber. This MeJA could act as an SOA precursor in addition to the VOC emissions from the plant. Consequently, there are two types of post-treatment SOA in these experiments: pure plant emission post-treatment SOA and plant emission + MeJA post-treatment SOA. This latter SOA could still be considered a type of stress SOA because plants do emit significant quantities of plant hormones in forests when exposed to stressed conditions (Karl et al., 2008). The role of plant hormones in SOA formation has typically been ignored in plant SOA experiments. Recently, Richards-Henderson et al. (2014) demonstrated that aqueous phase

oxidation of MeJA had an SOA mass yield of 68 %, suggesting that this is a compound that warrants further investigation.

## 2.4 Analytical instrumentation

SOA microphysical properties were measured with a scanning mobility particle sizer (SMPS, custom built with major components from TSI, Inc.) described previously by Faiola et al. (2014b) and Mwaniki et al. (2014). Aerosol mass spectra were continuously measured using a high resolution time-of-flight aerosol mass spectrometer (HR-AMS, Aerodyne Research, Inc.) described in detail elsewhere (Canagaratna et al., 2007; De-Carlo et al., 2006). Briefly, the HR-AMS collimates sub-micron particles into a narrow beam with an aerodynamic lens. The particle beam is directed onto a vaporizer plate held at 600 °C that volatilizes all non-refractory components. The volatilized fragments are then ionized with a tungsten filament with 70 eV electron impact ionization. These mass fragments are introduced to a ToFwerk high-resolution time-of-flight mass spectrometer where they are separated by size and quantified. The HR-AMS was operated with 1 to 4.5 min sample averaging, alternating between general mass spectrometer (MS) mode and particle time-of-flight (p-ToF) mode. Only v-mode data were used in this study because pre-treatment experiments often did not have sufficient signal for w-mode data to be used. Ionization efficiency calibrations were performed using the brute force single particle technique with monodisperse ammonium nitrate particles generated with a constant output atomizer (TSI Model 3076).

## 2.5 AMS data analysis

The goal of this research was to compare the aerosol mass spectra between SOA formed from the oxidation of emissions from different types of trees and between SOA formed under pre-treatment vs. post-treatment conditions. In the past, unit mass resolution (UMR) data from the Aerodyne HR-AMS has been normalized to the sum of the organic mass to compare spectra between different experiments with different mass

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loadings (Sage et al., 2008). One way these UMR spectra can be quantitatively compared is to calculate the square of the Pearson correlation coefficient ( $r^2$ ), called the coefficient of determination, between the two spectra (Kiendler-Scharr et al., 2009). Using this approach, Kiendler-Scharr and colleagues observed clear differences between biogenic SOA and other types of organic aerosol including biomass burning organic aerosol ( $r^2 = 0.44$ – $0.51$ ), diesel exhaust organic aerosol ( $r^2 = 0.44$ – $0.51$ ), and ambient hydrocarbon-like organic aerosol in Pittsburgh ( $r^2 = 0.16$ – $0.41$ ). For the comparisons presented here, only those  $m/z$  that contributed to 90 % of the HR-AMS UMR organic signal in any of the experiments was used to calculate the correlations. The  $m/z$  values used in the UMR analysis have been listed here: 12, 13, 15, 17, 18, 25, 26, 27, 29, 30, 31, 37, 38, 41, 42, 43, 44, 45, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 77, 78, 79, 80, 81, 82, 83, 84, 85, 89, 91, 92, 93, 94, 95, 96, 97, 98, 99, 100, 101, 103, 105, 106, 107, 108, 109, 110, 111, 113, 114, 115, 117, 119, 120, 121, 123, 125, 127, 129, 131, 134, 135, 137, 152, 155, 157, 202.

The composition of organic aerosol can also be described through the use of elemental analysis (Aiken et al., 2008). Results of such analyses are presented on a Van Krevelen diagram with axes of hydrogen to carbon (H : C) and oxygen to carbon (O : C) ratios. In general, laboratory SOA generation studies produce aerosol that is less oxidized than those found in the ambient atmosphere (Kroll and Seinfeld, 2008). However, laboratory chamber studies have also shown a wide variability in elemental ratios that are dependent on the precursor compounds used to generate the aerosol (Chhabra et al., 2010; Ng et al., 2010). Consequently, differences in the precursor compounds from different sources of BVOCs (e.g., different trees, or pre-treatment vs. post-treatment emissions, or the presence of near semi-volatile plant hormones) could produce differences in biogenic SOA composition that would occupy different locations in Van Krevelen space.

To perform HR-AMS data analysis, it is necessary to carefully correct the particle signals that have significant air interferences. To account for some of these interferences,





a discussion of the inter- and intra-species variation, followed by a discussion of the post-treatment aerosol spectra. In this section, we present the first aerosol mass spectra generated from SOA produced via the gas-phase oxidation of the plant hormone, methyl jasmonate. Finally, we present results of the SOA elemental analysis using a Van Krevelen plot and discuss the inter-species variability along with implications for stress effects on SOA composition.

### 3.1 Negative control summary

Three sets of paired pre-treatment/negative control experiments were performed for which AMS measurements are available- one with grand fir (*Abies grandis*), one with western redcedar (*Thuja plicata*), and one with a mix of grand fir (*Abies grandis*) and Douglas-fir (*Pseudotsugas menziesii*). Scatter plots comparing the normalized UMR organic spectra between the pre-treatment SOA and the corresponding paired negative control SOA are shown in Fig. 1. The signal at  $m/z$  28 was removed to avoid air interferences in the UMR spectra comparisons. The coefficient of determination ( $r^2$ ) for each comparison is shown, calculated from the square of the Pearson product moment correlation coefficient. All paired negative control experiments were very similar, with  $r^2$  greater than or equal to 0.990. The reproducibility of the high correlations between these paired experiments suggest that any correlations less than 0.99 that were observed in other experiments do truly reflect differences in SOA mass spectra. Based on these results, we considered any correlations lower than 0.90 to indicate potentially noteworthy differences between SOA mass spectra.

### 3.2 Summary of UMR comparisons

Correlations ( $r^2$ ) comparing SOA organic UMR spectra from all biogenic aerosol growth experiments are summarized in Fig. 2. Correlations ranged from 0.503 to 0.999. In general, the pre-treatment aerosol mass spectra from all tree types had higher correlation values with respect to each other than they did with respect to post-treatment aerosol

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mass spectra. One pre-treatment experiment, AG-1-Pre (#9), stands out clearly with lower correlation values when compared to all other spectra. During this experiment, plants may have been exposed to an unidentified stress before transport to the laboratory (Faiola et al., 2014a). This pre-treatment experiment will be referred to as the “UNID stress” experiment and will be discussed in detail in a later section. Other than the AG-1-Pre spectra, all other pre-treatment SOA spectra had correlations ranging from 0.806–0.997 when compared to each other across all tree types.

Most of the weakest correlations (excluding the AG-1-Pre spectra) were found between comparisons that included the 2013 post-treatment experiments (#21–30 in Fig. 2). Specifically, the following experiments had the lowest correlations when compared to other SOA spectra: AG-2-Post (#23), TP-1-Post (#24), TP-3-Post (#25), PM-1-Post (#28), PM-2-Post (#29), and Mix-1-Post (#30). This list includes all the experiments where the MeJA treatment and the aerosol growth experiment occurred on the same day (Table 1). In contrast, when these six aerosol spectra were compared to one another, each comparison had  $r^2$  greater than or equal to 0.95. This suggests that the MeJA and its oxidation products may have contributed substantially to SOA formation. This hypothesis and its environmental implications are explored in detail in a later section on methyl jasmonate SOA.

To further investigate trends in the SOA spectra correlations, all comparisons were classified by the type of comparison and binned into six different ranges of correlation values:  $< 0.6000$ ,  $0.6000–0.6999$ ,  $0.7000–0.7999$ ,  $0.8000–0.8999$ ,  $0.9000–0.9499$ , and  $0.9500–0.9999$ . The results of this analysis are presented in Fig. 3. The top bar in the figure shows the results from all types of biogenic SOA comparisons using real plant emission as the VOC precursor for SOA formation ( $N = 561$  total comparisons). This classification did not include any comparisons with the methyl jasmonate standard SOA spectrum. Nearly 50% of all comparisons with biogenic SOA had an  $r^2$  greater than or equal to 0.90. The rest of the comparison types were organized reading top to bottom from highest to lowest number of correlations that fell within the

0.9500–0.9999 correlation bin. The bottom three bars show results from comparisons with the standard methyl jasmonate spectra.

All three comparisons of the paired pre-treatment/negative control SOA spectra were in the highest correlation bin with  $r^2$  greater than or equal to 0.95. The fifteen comparisons between the post-treatment SOA spectra where the methyl jasmonate treatment occurred the same day as the SOA growth experiment (SD, PostT) were all greater than or equal to 0.90. The pre-treatment SOA comparisons were more heavily weighted toward the higher correlation values than the “all comparisons” category, with nearly 80 % of the  $r^2$  values greater than or equal to 0.90. Additionally, the pre-treatment SOA spectra were more similar to one another than the post-treatment spectra were to one another. This suggests there was more variability in VOC emissions post-treatment than there was pre-treatment between the different tree types. The negative control spectra tended to be more similar to the pre-treatment SOA than the post-treatment SOA with nearly 80 % of comparisons with  $r^2$  greater than or equal to 0.90 for the former and only ~30 % of comparisons with  $r^2$  greater than or equal to 0.90 for the latter. SOA spectra from the same tree type were more heavily weighted toward the higher correlation bins than SOA spectra generated from different tree types. Additionally, 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.

Thirteen paired pre-treatment/post-treatment experiments were performed. Six of these had GC-MS-FID data available to investigate whether or not a plant response to the stress treatment had occurred. For several of the intended pre-treatment/post-treatment comparisons, there were no differences in the BVOC profile between the pre- and post-treatment experiment. These paired experiments were excluded from

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Consequently, this is one of the only experiments where emissions actually decreased after MeJA treatment relative to the pre-treatment value. Despite this apparent confounding stress, the MeJA treatment still induced emissions of 1,8-cineol and terpinolene. The BVOC profiles during aerosol chamber loading for experiment AG-1 are shown in Supplement (Fig. S2).

The correlation between the AG-2-Pre SOA mass spectrum and the AG-3-Pre spectrum was very strong, with an  $r^2$  of 0.97. The AG-1-Pre SOA spectrum was less similar to the other two *Abies grandis* pre-treatment SOA spectra with  $r^2$  values of 0.66 (vs. AG-2-Pre) and 0.80 (vs. AG-3-Pre). The aerosol mass spectra for AG-1-Pre and AG-2-Pre are shown in Fig. 4 to highlight some of the  $m/z$  contributing to the differences between the SOA spectra. The AG-1-Pre SOA spectrum has a significant cluster of peaks present around  $m/z$  200 that were not observed in any other aerosol mass spectra including the other SOA spectra produced from *Abies grandis* emissions. This evidence further supports the hypothesis that the AG-1-Pre spectra was not representative of a “typical *Abies grandis* SOA baseline” and that these plants had been exposed to an unidentified stressor.

To investigate differences in the relative  $m/z$  enhancements and reductions generated under the unidentified stress condition and the MeJA stress condition, AG-2-Pre was selected to use as a “typical *Abies grandis* baseline spectrum” for comparison. A stress response plot was generated for both the unidentified stress effect and methyl jasmonate stress effect (Fig. 5). The unidentified stress response was calculated by subtracting the normalized spectrum of the AG-2-Pre experiment (baseline *Abies grandis* SOA) from the normalized spectrum of the AG-1-Pre experiment (unidentified stress SOA). The MeJA stress response was calculated by subtracting the normalized spectra of the same AG-2-Pre experiment (baseline *Abies grandis* SOA) from its paired post-treatment MeJA stress experiment, AG-2-Post (MeJA post-treatment SOA). The changes to the  $m/z$  profile were substantially different between the two stress scenarios. The MeJA SOA stress response spectrum demonstrated the most enhanced  $m/z$  values at 15, 26, 27, 29, 31, 57, 58, 59, 71, and 97. The relative contribution of  $m/z$

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43 was reduced. Recall that these spectra have been normalized to the sum of total organics so a negative value in the stress response spectra does not necessarily mean that the fragment was inhibited. Rather, it demonstrates only that the relative contribution to the total has been reduced. The fragment at  $m/z$  43 is frequently the highest organic fragment in chamber SOA (Chhabra et al., 2010), so it is not unexpected that any increases in other fragments will produce a decrease in the relative contribution of  $m/z$  43. The fragments most enhanced in the unidentified stress response spectrum were different and included 41, 65–69, 77, 79, 81, 91, 93, 95, 105, 109, 117, 119 and 202.

The relative enhancement of most of these  $m/z$  values in the unidentified stress response spectrum could be explained by the partitioning of less oxidized compounds. For example, the two  $m/z$  series 77, 79, 81 and 91, 93, 95 are due to enhancements of the HR ions  $C_6H_5^+$ ,  $C_6H_7^+$ ,  $C_6H_9^+$  and  $C_7H_7^+$ ,  $C_7H_9^+$ ,  $C_7H_{11}^+$  respectively. Compare this to the most enhanced HR ions in the MeJA stress spectrum, which included  $CHO^+$ ,  $C_2H_5^+$ ,  $CH_3O^+$ ,  $C_2HO_2^+$ ,  $C_3H_5O^+$ ,  $C_4H_9^+$ ,  $C_2H_2O_2^+$ ,  $C_3H_6O^+$ ,  $C_2H_3O_2^+$ ,  $C_3H_7O^+$ ,  $C_3H_3O_2^+$ ,  $C_4H_7O^+$ ,  $C_5H_5O_2^+$ ,  $C_6H_9O^+$ , and  $C_7H_{13}^+$ . This list contains many more oxidized fragments than the enhanced HR ions in the unidentified stress response spectrum.

The weaker presence of oxidized HR ions in the unidentified stress SOA spectra could be the result of two possibilities or, possibly more likely, a combination of the two explanations. One explanation is that the unidentified stress induced emissions of large hydrocarbons, which produced a higher proportion of larger, less oxidized fragments in the spectra. This cause is suggested by the cluster of peaks greater than  $m/z$  200, particularly at  $m/z$  202, in the AG-1-Pre spectrum that were not observed in any of the other spectra. The HR ion identified here was  $C_{16}H_{10}^+$ , a large un-oxidized fragment that could have originated from a large stress-induced hydrocarbon BVOC emission. The compounds that contributed to these large  $m/z$  fragments were not detected by the GC system so they cannot be positively identified here. However, large 16-carbon and

18-carbon compounds have been identified following herbivory stress in other studies (De Boer et al., 2004; Mentel et al., 2013).

Another possibility is that the amount of ozone added to the chamber was not sufficient to fully oxidize these particles to the same extent as other experiments because the plant VOC emissions were so high. 114 ppb of ozone was added at the start of the experiment and it had fallen to 9 ppb by the end (Table 2). With the high organic particle loadings generated in this experiment ( $> 500 \mu\text{g m}^{-3}$ ) it is possible that some of these larger emissions and their oxidation products were able to partition to the particle phase in a less oxidized state than would normally occur under lower mass loadings (Kroll and Seinfeld, 2008). Thus, the higher emissions generated a large amount of overall organic particle mass, and the combination of the presence of larger, less volatile emissions (and their oxidation products) and an oxidant-limited system promoted the partitioning of less oxidized components to the particle phase.

The correlations between the two paired pre-treatment/post-treatment *Abies grandis* SOA spectra were 0.86 and 0.77 for AG-1 and AG-2, respectively (Fig. 2). Thus, despite the presence of an unidentified stressor under pre-treatment conditions, the stress treatment still produced some small differences between the pre-treatment and post-treatment SOA spectra in the AG-1 experiment. This is consistent with the BVOC emission profile where emissions of 1,8-cineol were induced after treatment and the relative contribution of beta-myrcene, limonene, and terpenolene increased (Supplement Fig. S2). Five of the top ten most enhanced fragments between the AG-1-Post and AG-1-Pre spectra were also observed in the top 10 most enhanced fragments between the AG-2-Post and AG-2-Pre spectra:  $m/z$  15, 26, 27, 31, and 58. The dominant HR ions corresponding to  $m/z$  15, 26, and 27 were  $\text{CH}_3^+$ ,  $\text{C}_2\text{H}_2^+$ , and  $\text{C}_2\text{H}_3^+$ . These ions are not very specific and could be generated from many organic compounds, so it is unlikely that they alone will provide help in identification of an AMS mass spectral biotic stress SOA “marker”. The dominant HR ions at  $m/z$  31 and 58 were  $\text{CH}_3\text{O}^+$ ,  $\text{C}_2\text{H}_2\text{O}_2^+$ ,  $\text{C}_3\text{H}_6\text{O}^+$ . These ions could provide a little more insight into precursors contributing to their presence in the SOA spectra, and could possibly be the start to identifying AMS

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markers for biogenic stress SOA. This will be discussed further in the following sections while looking at more examples of the post-treatment SOA spectra in detail.

### 3.4 Post-treatment aerosol mass spectra

Thirteen post-treatment SOA experiments were completed for this study. Of those, three were performed in 2012 with the exogenous methyl jasmonate treatment. The PPO-1 experiment exhibited small, likely insignificant, differences between the pre- and post-treatment SOA that could have been due to natural variation in plant emissions. The BVOC profile indicated that any stress response was weak if it existed at all. The other two experiments performed in 2012 may have had a confounding stress effect due to pulling the plants out of dormancy. For these reasons, the 2012 post-treatment experiments will not be the focus of this discussion of post-treatment SOA here. Of the ten post-treatment SOA experiments performed in 2013 with the foliar methyl jasmonate application, four were performed the day after treatment and six were performed the same day as treatment.

The four experiments that were performed the day after MeJA treatment were PPU-1-Post, PPU-2-Post, AG-1-Post, and PA-3-Post. Based on the BVOC profiles, none of the post-treatment experiments where the treatment was performed on a different day than the aerosol growth experiment would work as good candidates for identifying a biogenic stress SOA marker in the AMS spectra. The AG-1-Post SOA spectrum was discussed in detail in the previous section, showing confounding effects on the SOA spectra from an apparent unidentified stress exposure prior to transporting the plants to the laboratory. The PPU-1-Post and PPU-2-Post both appear to be representative of a stress condition for *Picea pungens* based on the BVOC profiles presented in Faiola et al. (2014a). The stress response for the PPU-1 experiment in particular was very high. However, the PPU-1-Pre experiment did not produce enough SOA mass to perform AMS analysis, so there is no baseline *Picea pungens* SOA spectra for comparison. The BVOC results from the PPU-2-Pre experiment suggest these plants may also have been stressed before being brought into the laboratory; their BVOC profile closely

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AG-1-Pre – the unidentified stress (UNID Stress) experiment that was discussed previously. All H : C ratios were similar ( $\sim 1.5$ ) throughout the pre-treatment experiments – this is consistent with expected oxidation products of monoterpenes during ozonolysis reactions. In contrast, the O : C ratios varied between different tree types. In fact, the elemental analysis results demonstrated a higher level of variability between pre-treatment SOA than was expected from the UMR correlation coefficient analysis. This could partially be caused by the exclusion of  $m/z$  28 in the UMR analysis. The  $\text{CO}^+$  ion was accounted for in the elemental analysis but not in the UMR analysis. The contribution from organics at  $m/z$  28 was a substantial fraction of the total signal and is commonly estimated to be around the same magnitude as  $m/z$  44 – a significant peak for all of these spectra contributing between 4–10 % of total organic signal.

Most pre-treatment SOA had an O : C within the range of 0.3–0.38. However, there were some exceptions. Specifically, the *Pinus aristata* SOA had a higher O : C on average than other pre-treatment biogenic SOA generated from emissions of other tree types with O : C ranging from 0.39–0.47. Similarly, one pre-treatment *Picea pungens* experiment and one pre-treatment Mix experiment generated biogenic SOA with higher O : C values than the average. The pre-treatment SOA from the *Picea pungens* emissions could have been more representative of a stress condition based on the BVOC emission profile – stress emissions of 1,8-cineol and beta-ocimene were measured (Faiola et al., 2014a). A second pre-treatment Mix experiment was performed and produced SOA with a much lower O : C than the first, so the high O : C results from the pre-treatment Mix emissions were not reproducible. Two of the three negative control SOA had some of the lowest O : C ratios that were measured (excluding the UNID stress experiment). The *Thuja plicata* negative control had substantially higher O : C than the others, but it was very similar to the other pre-treatment *Thuja plicata* experiments.

A summary of the elemental analysis results from all paired pre- and post-treatment experiments where a plant stress response was observed is presented in Fig. 9b. The pre-treatment SOA that had a paired post-treatment experiment where a stress

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response was observed had O : C that ranged from 0.32–0.41 (excluding the unidentified stress experiment) or 0.32–0.37 if the possible Mix SOA outlier is excluded as well. The paired post-treatment SOA had O : C that ranged from 0.42–0.46. For all experiments, the MeJA SOA shifted the O : C ratio to higher values relative to the paired pre-treatment SOA. Each of these post-treatment experiments were performed the same day as treatment except for the *Abies grandis* unidentified + MeJA stress experiment (AG-1-Post). The unidentified stress post-treatment experiment resulted in an increase of O : C from 0.19 in the pre-treatment SOA to 0.29 in the post-treatment SOA. This effect could have been due to the stress treatment or it could have been due to the unidentified stress waning after the trees were transported to the laboratory – the post-treatment O : C was still not as high as most pre-treatment SOA.

For all the “Same-Day” post-treatment experiments, the increased O : C could be due to the oxidation products of the plant hormone, methyl jasmonate. The elemental ratios from the SOA generated from the oxidation of the single-component methyl jasmonate standard are also shown in Fig. 9b in black. Expected elemental ratios calculated from the optimized linear addition of the baseline spectra and the MeJA standard spectra yielded elemental ratios that were within 10% of those measured for the paired post-treatment experiment (for same day treatment/growth experiment only). This suggests that most of the increase in the O : C may have been due to the methyl jasmonate and its oxidation products rather than the influence of specific stress compounds in the SOA spectra. However, the pre-treatment *Picea pungens* experiment where the plants appeared to be in a stressed condition also had higher O : C in approximately the same Van Krevelen space as these other post-treatment SOA. This suggests there are compounds other than MeJA and its oxidation products that could also produce SOA in this region of the Van Krevelen plot.

### 3.6 Results summary

The number of experiments and types of tree species examined in this study has provided a rich, but complex data set. When experiments are grouped into categories by



lower O : C than any other SOA reported here or reported elsewhere (Chhabra et al., 2010). Other enhanced  $m/z$  in the UNID stress spectra were  $m/z$  31 and  $m/z$  58 corresponding to HR ions  $\text{CH}_3\text{O}^+$ ,  $\text{C}_2\text{H}_2\text{O}_2^+$ , and  $\text{C}_3\text{H}_6\text{O}^+$ .

The other SOA spectra that had the lowest correlation coefficients when compared to pre-treatment SOA were the 2013 post-treatment SOA. We attempted to remove the influence of MeJA, and its oxidation products, on the “Same-Day” post-treatment SOA spectra. The resulting residual spectra highlighted differences to the SOA spectra that were due to the plants response to the stress treatment. The same  $m/z$  that were enhanced in the UNID spectra,  $m/z$  31 and  $m/z$  58 (HR ions  $\text{CH}_3\text{O}^+$ ,  $\text{C}_2\text{H}_2\text{O}_2^+$ ,  $\text{C}_3\text{H}_6\text{O}^+$ ) were also enhanced in each of the residual spectra. Other prevalent  $m/z$  in the residual spectra were  $m/z$  29 (primarily  $\text{C}_2\text{H}_5^+$  enhancement),  $m/z$  57 ( $\text{C}_3\text{H}_5\text{O}^+$ ),  $m/z$  59 ( $\text{C}_2\text{H}_3\text{O}_2^+$  and  $\text{C}_3\text{H}_7\text{O}^+$ ),  $m/z$  71 ( $\text{C}_3\text{H}_3\text{O}_2^+$  and  $\text{C}_4\text{H}_7\text{O}^+$ ), and  $m/z$  83 (primarily  $\text{C}_5\text{H}_7\text{O}^+$  enhancement). The enhancement of these ions in ambient datasets should be investigated to search for this possible biogenic stress marker in aerosol spectra collected in a natural forest environment.

Additionally, our results demonstrate that plant hormones, such as methyl jasmonate, can contribute to SOA formation and produce distinctive SOA mass spectra with peaks at  $m/z$  131 and  $m/z$  157. The standard MeJA SOA was substantially more oxidized than other biogenic SOA as was evidenced by its high relative proportion of  $m/z$  44 to the total organic mass and its high O : C ratio of 0.52. Plant emissions of stress hormones can equal emissions of monoterpenes under stressed conditions, and others have even suggested using ambient measurements of plant hormones to monitor for plant stress at an ecosystem scale (Karl et al., 2008). It is possible that the mass spectral markers associated with either the plants response to the stress treatment or the markers associated with the methyl jasmonate plant hormone directly could also be used to monitor for stress at an ecosystem scale.

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## 4 Conclusions

The baseline aerosol mass spectra of biogenic SOA produced from real plant emissions were similar across six different plant species when comparing UMR results. However, the presence of stress appeared to change the composition of the SOA to the extent that the UMR aerosol mass spectra looked significantly different. This mass spectral biogenic stress marker could be indicative of an herbivory stress aerosol signature in the natural forest environment when stressed conditions produce stress-induced emissions including, but not limited to, plant hormones such as methyl jasmonate.

Future work on this topic should investigate SOA mass spectral fingerprints for other stressors that could induce emissions of non-terpenoid compounds. For example, any stressor that damages plant membranes produces bursts in OVOC products from the lipoxygenase pathway. This could be investigated in the laboratory using real herbivores or pathogens that would damage plant tissues. Additionally, tissue damage can occur under severe heat stress. Future work should also generate SOA from the plant hormone methyl salicylate, which is emitted at higher rates than methyl jasmonate and still has low enough volatility to potentially contribute to SOA formation. To our knowledge, SOA has not been generated from this major plant hormone that has been measured at significant levels in a forest environment. Other future studies should focus on analyzing ambient AMS datasets collected in forest environments to investigate whether or not the biogenic stress marker that was identified here can be observed in field measurements. This could serve as a monitoring tool to identify ecosystem-level plant stress.

**The Supplement related to this article is available online at [doi:10.5194/acpd-14-25167-2014-supplement](https://doi.org/10.5194/acpd-14-25167-2014-supplement).**

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*Acknowledgements.* The authors thank Chuck Cody and the greenhouse staff for taking care of the plants used in this study. Authors also thank Courtney Herring for answering questions about AMS data analysis. This work was supported by the US Department of Energy Early Career Research Program (Award #SC0003899).

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**Table 1.** Experiment Summary. “MeJA” = methyl jasmonate.

Experiment ID	Tree Type (Species)	Common Name	Experiment Type	Date	Treatment Approach		
PPo-1-Pre*	Pinus Ponderosa	Ponderosa Pine	Baseline	7/31/2012	–		
PPo-1-Post*			MeJA	8/2/2012	exogenous, day before		
PPo-2-Pre			Baseline	10/23/2012	–		
PPo-2-Post			MeJA	10/25/2012	exogenous, day before		
PA-1-Pre*	Pinus Aristata	Bristlecone Pine	Baseline	10/9/2012	–		
PA-1-Post			MeJA	10/18/2012	exogenous, day before		
PA-2-Pre			Baseline	4/23/2013	–		
PA-3-Pre			Baseline	5/21/2013	–		
PA-3-Post			MeJA	5/23/2013	foliar, day before		
PA-4-Pre			Baseline	5/28/2013	–		
AG-1-Pre			Abies Grandis	Grand Fir	Baseline	6/25/2013	–
AG-1-Post					MeJA	6/27/2013	foliar, day before
AG-2-Pre	Baseline	9/3/2013			–		
AG-2-Post	MeJA	9/5/2013			foliar, same day		
AG-3-Pre	Baseline	9/10/2013			–		
AG-3-NC	Negative	9/12/2013			foliar, same day		
TP-1-Pre	Thuja Plicata	Western Red Cedar	Baseline	8/14/2013	–		
TP-1-Post			MeJA	8/16/2013	foliar, same day		
TP-2-Pre			Baseline	8/21/2013	–		
TP-2-NC			Negative	8/23/2013	foliar, same day		
TP-3-Pre1			Baseline	9/17/2013	–		
TP-3-Pre2			Baseline	9/19/2013	–		
TP-3-Post			MeJA	9/22/2013	foliar, same day		
PPu-1-Post	Picea Pungens	Blue Spruce	MeJA	5/16/2013	foliar, day before		
PPu-2-Pre			Baseline	7/16/2013	–		
PPu-2-Post			MeJA	7/18/2013	foliar, day before		
PM-1-Pre	Pseudotsugas Mensiezii	Douglas-fir	Baseline	8/27/2013	–		
PM-1-Post			MeJA	8/29/2013	foliar, same day		
PM-2-Pre			Baseline	9/24/2013	–		
PM-2-Post			MeJA	9/26/2013	foliar, same day		
Mix-1-Pre	Mix-Abies Grandis & Pseudotsugas Mensiezii	Grand Fir & Douglas-fir	Baseline	7/24/2013	–		
Mix-1-Post			MeJA	7/26/2013	foliar, same day		
Mix-2-Pre			Baseline	7/30/2013	–		
Mix-2-NC			Negative	8/1/2013	foliar, same day		
MeJA Std	N/A	N/A	Standard	5/8/2014	N/A		

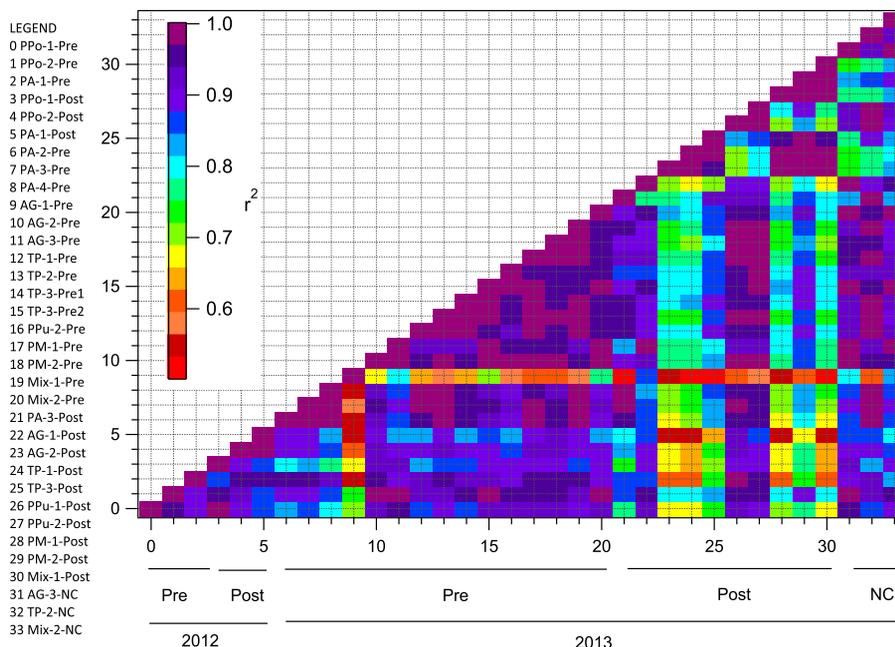
\* 50 nm ammonium sulfate seed was used in this experiment.





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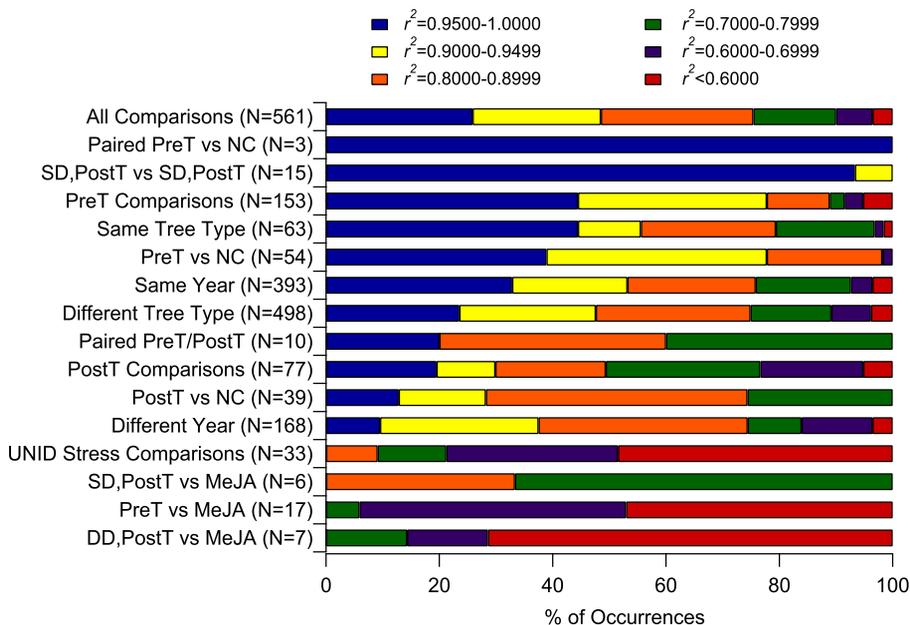
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**Figure 2.** Summary of all comparisons between biogenic SOA spectra. Numbers on the x and y axes refer to each SOA growth experiment, which are listed by experiment ID in the legend (and in Table 1). The color scale denotes the strength of correlation between the two spectra where warmer colors are lower correlations and cooler colors are higher correlations. Due to air interferences,  $m/z$  28 was removed from the spectra for all comparisons. The figure was organized by year followed by experiment type (pre-treatment, post-treatment, negative control) followed by tree type. NC = negative control.

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**Figure 3.** Distribution of correlations classified by type of comparison. The horizontal axis is the percent of total occurrences within a given correlation range for each experiment classification. Each horizontal bar denotes the type of comparison where the *N* value in parentheses refers to the total number of comparisons within that classification. PreT = Pre-Treatment; PostT = Post-Treatment; NC = Negative Control; SD, PostT = Post-Treatment where treatment and SOA growth experiment occurred on the same day; DD, PostT = Post-treatment spectra where treatment and SOA growth experiment occurred on subsequent days; MeJA = comparisons with SOA spectra of aerosol formed from the oxidation of a methyl jasmonate standard. The bottom three horizontal bars comparing the standard MeJA SOA spectra to different types of biogenic SOA are discussed in Sect. 3.4.

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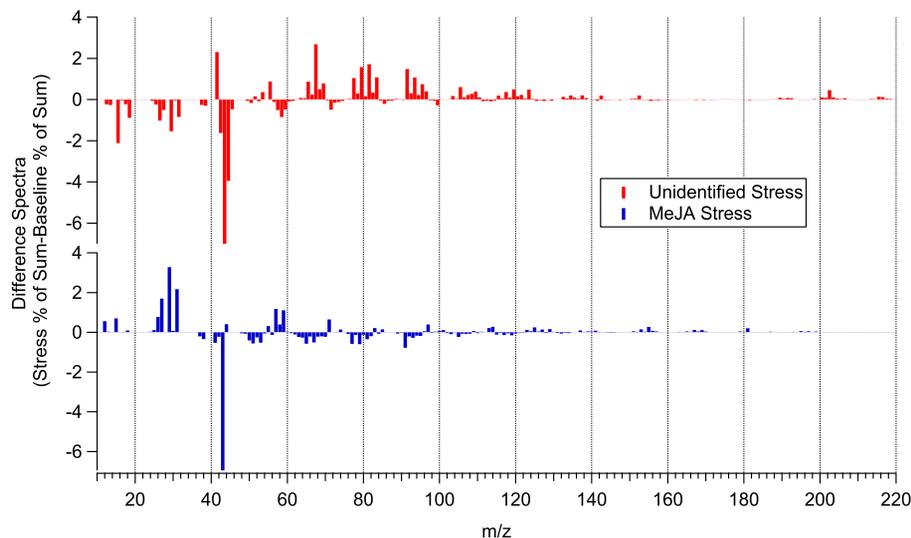
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**Figure 5.** Stress response spectra comparing the effects of two different types of stress – an unidentified stress (red) and a MeJA treatment (blue). The  $x$  axis shows the  $m/z$  values and the  $y$  axis denotes the difference between the normalized stress spectrum and the normalized baseline spectrum.

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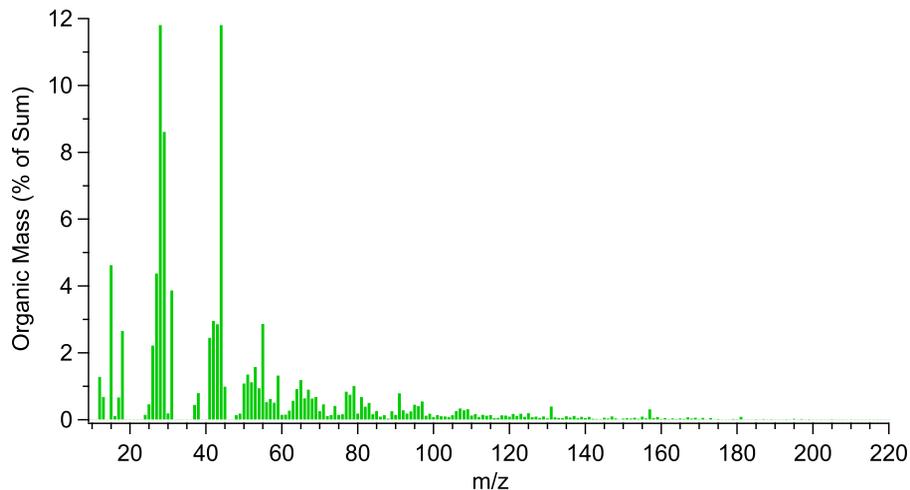
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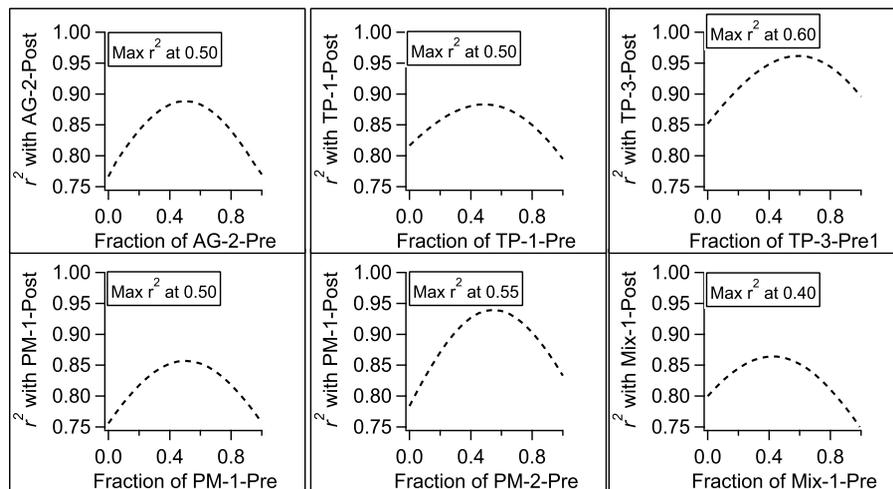


**Figure 6.** Normalized mass spectra of SOA generated from the oxidation of a methyl jasmonate standard. The  $x$  axis shows the  $m/z$  value and the  $y$  axis denotes the percent contribution of each  $m/z$  to the total organic mass.

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**Figure 7.** Results from the linear addition optimization for all six experiments where the post-treatment aerosol growth experiment was performed the same day as the foliar methyl jasmonate treatment was applied. The  $x$  axis denotes the fraction of the pre-treatment experiment that was included in the linear addition of the pre-treatment and MeJA standard SOA spectra. The  $y$  axis is the correlation of the linear addition spectra with the paired post-treatment SOA spectra. The fraction of pre-treatment SOA included in the linear addition spectra that produced the highest correlation with the paired post-treatment is shown in the box on each graph.

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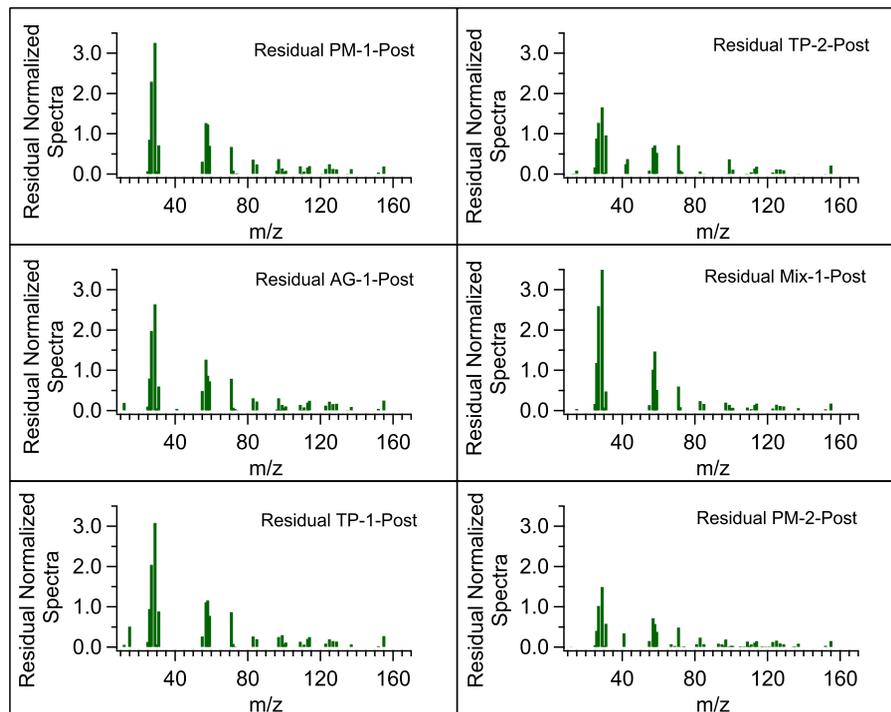
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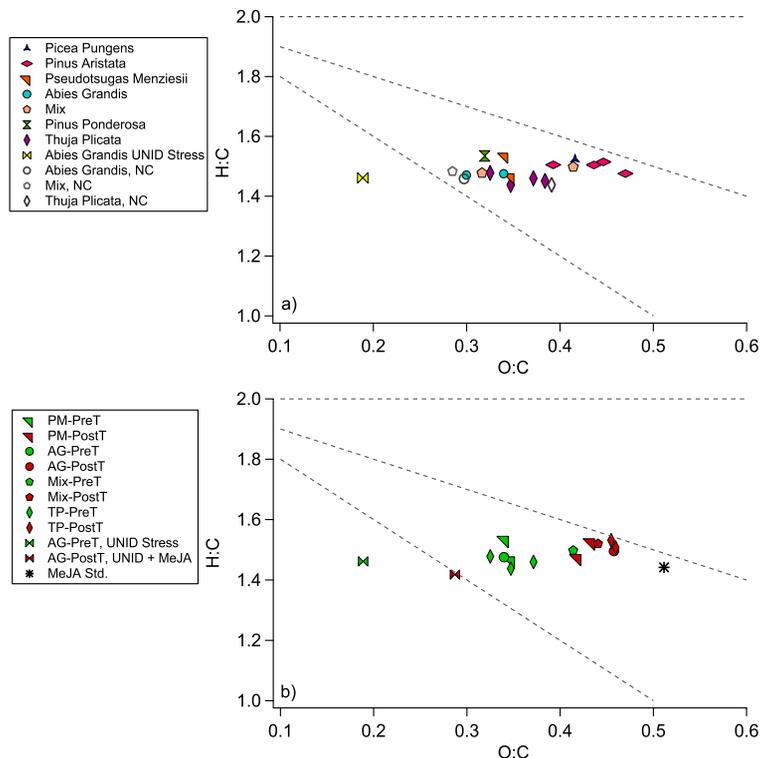


**Figure 8.** Residual stress spectra calculated by subtracting the optimized linear addition of the paired baseline + MeJA standard spectra from the post-treatment stress spectra. The x axis is the  $m/z$  value and the y axis is the residual.

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**Figure 9.** (a) Summary of the elemental analysis results from all pre-treatment SOA and negative control SOA. The pre-treatment experiment, AG-1-Pre, is labeled as an unidentified stress (UNID Stress) experiment. NC=Negative Control. (b) Summary of elemental analysis results from all experiments with paired pre-treatment/post-treatment SOA where a MeJA plant stress response was observed. Green markers denote pre-treatment SOA. Red markers denote post-treatment SOA. The black asterisk illustrates the results from the MeJA single-component standard SOA.