Author Response to Referees of "Oligomer and highly oxygenated organic molecule formation from oxidation of oxygenated monoterpenes emitted by California sage plants" by Archit Mehra et al.

General Response

We thank the reviewers for their comments for helping us to improve the paper. Referee #1 states that the interpretation of the results is sound, while offering helpful comments which have allowed us to improve the paper through suggesting ways in which we might discuss caveats to our conclusions in the light of instrumentation, calibration and experimental setup. Referee #2 states that this study is new and original, and provides interesting and fruitful results with their major concerns surrounding the experimental setup. Upon the request of Referee #2, we have added a more detailed description of the plant experiments and their measured or estimated VOC mixing ratios. With the exception of eucalyptol, the experiments were all carried out at similar VOC mixing ratios, with oligomers also observed in the plant experiments at relatively low VOC mixing ratios. We agree that the inclusion of the measured VOC mixing ratios during the single component experiments would have been a valuable addition. Unfortunately, the PTR-MS was not functioning properly during this study and we could not use any of that data, which was intended to provide us with information about the inlet mixing ratios during the single component standard experiments. We have, however estimated these concentrations, and include them in the revised manuscript. We believe that the measurements we present in this paper provide novel information on the SOA from previously uncharacterised precursors and plants and we have identified new products which may be important under atmospheric conditions. Whilst we cannot confirm their atmospheric importance, we know from the biology literature that many common plant types emit oxygenated monoterpenes. Thus, this paper serves to highlight that these systems should be considered and may be relevant for ambient SOA chemistry, and provides data for understanding their contributions in ambient measurements. Below the referee comments are in black, our responses indented and in blue, and additions to the manuscript indented and in green.

Anonymous Referee #1

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This manuscript presents measurements of VOC emissions from California sage plants and the chemical composition of subsequently formed SOA. The major finding is that highly oxygenated organic molecules (HOMs) and oligomer contribute to a larger fraction of SOA. This manuscript fits in the scope of the Atmospheric Chemistry and Physics, and the interpretation of the results is sound. While I suggest publication after major revision, I hope that the authors will consider the following comments.

1. What is the VOC concentration in the OFR? Is the high oligomer content caused by high concentrations of VOC and RO2? In other words, is the RO2 fate in the OFR representative of that in the atmosphere?

> During this study, VOC concentrations were successfully measured for the plant experiments but not for the single component experiments. Of the single component experiments, the concentration for eucalyptol can estimated to be 115 ppb by its injection rate through the syringe pump into the OFR. However, the concentrations of camphene and camphor cannot be determined by this approach as they were sublimed at room temperature into the OFR.
>
> For the plant experiments, total VOC concentrations from the plants ranged from 27 - 34 ppb during the averaging intervals used for FIGAERO-CIMS analysis in this paper. Approximately 80 %, by mass, of the VOC emissions were oxygenated monoterpenes. Under low-NO, no seed conditions, an approximate SOA mass yield was determined of 8 % for mass loadings ranging from 4 – 19 µg m^{-3}. This value is consistent with the typical ~5-20% yields measured at similar mass loadings for other monoterpenes, such as α-pinene (Donahue et al., 2012, Figure 2a; Shilling et al., 2008, Figure 3). The SOA mass yield in this study was

estimated by assuming all measured terpenes at the inlet reacted (ΔVOC, µg m^{-3}) and using AMS data for organic aerosol mass generated (ΔC_{oa}, µg m^{-3}) as SOA mass yield = ΔC_{oa} / ΔVOC. A new table has been added to the text summarizing the measured and estimated VOC mixing ratios at the OFR inlet. The aerosol mass concentrations measured during the single component studies were approximately 30 µg m^{-3} for camphor and 66 µg m^{-3} for eucalyptol. With an 8% yield, this would correspond to an estimated 60 ppb of camphor, which is still on the lower end of VOC mixing ratios used for SOA experiments historically. An 8% yield from eucalyptol would correspond to an estimated 130 ppb at the inlet, which is similar to the theoretical 115 ppb calculated based on syringe pump rate and dilution. This mixing ratio is substantially higher than the VOC mixing ratios in the camphor and plant experiments. The aerosol mass concentrations measured for camphene was 20 µg m^{-3}, to which a 12 % yield was applied based upon a literature aerosol yield of β-pinene from similar PAM-OFR experiments, owing to its structural similarity to that of camphene (Friedman and Farmer, 2018). This gave an estimated VOC concentration of 30 ppb, similar to that of the plant experiments. As highlighted in the manuscript, AMS measurements during the medium-NOx experiments had an interference and thus are not presented in the table. However, the VOC mixing ratios are expected to be the same as under low-NOx conditions, owing to the same injection conditions.

It could be the case for eucalyptol that the higher oligomer in the single component experiments was influenced by higher VOC concentrations employed in this experiment. However, camphor and camphene had similar VOC mixing ratios to that of the plant experiments alongside similar aerosol mass loadings, with camphor showing higher oligomer content which is thus unlikely to be related to VOC mixing ratios. In addition, the increased oligomer content was also observed in the plant experiments which had lower VOC mixing ratios, SOA mass loadings and SOA mass yields which suggests that the observation of oligomers was associated with the VOC itself, though contributions from the higher VOC concentrations cannot be ruled out in the case of eucalyptol.

We have added an additional section (2.5 – Summary of Experiments) containing the following text into the manuscript alongside a table of experimental conditions.

> “During this study, the VOC mixing ratios were measured for the plant mixture experiments by TD-GC-FID/ToF-MS and ranged from 27-34 ppb as shown in Table 2, with approximately 80 % by mass from oxygenated monoterpenes. Of the single component experiments, VOC mixing ratios were estimated for eucalyptol, by its injection rate through the syringe pump to be 115 ppb, while camphor and camphene could not be estimated by this approach due to their introduction through sublimation. VOC mixing ratios for camphor is thus estimated as 61 ppb on the basis of the SOA mass yields from the plants, which under low-NO, no-seed conditions which were approximately 8 % for mass loadings ranging from 4 – 19 µg m^{-3}, similar to that for other monoterpenes such as α-pinene (Donahue et al., 2012; Shilling et al., 2008). An 8% yield from eucalyptol would correspond to an estimated 130 ppb at the inlet, which is similar to the 115 ppb calculated based on syringe pump injection rate and dilution. For camphene, the VOC mixing ratios are estimated to be 30 ppb, based on a reported yield from β-pinene from PAM-OFR experiments (Friedman and Farmer, 2018). Calculations of remaining VOC for the single component experiments shows that all VOC is reacted under under the OH exposures employed in this study, thus validating the use of aerosol yield itself to estimate VOC concentrations.”

> Table inserted:

Precursor	NO_x Condition	VOC Mixing Ratios (ppb)	AMS Aerosol Mass Concentrations (µg m-3)	OH Exposure (x 10^{11} molecules cm^{-3})		NO ppb	NO_2 ppb	VOC /OH	VOC/ NO_x
				With VOC	Without VOC				
Artemesia	Low	27^*	9.35	10.02	-	0	0	48.7	
	Med	28^*	-	5.29	-	2.1	51.8	97.7	0.52
Sage	Low	28^*	18	7.32	-	0	0	70.6	
	Med	34^*	-	4.09	-	1.7	48.5	154	0.68
Camphene	Low	$30^\$$	20	10.14	10.1	0	0	48.7	
	Med		-	4.57	4.16	2.2	58.4	121	0.49
Camphor	Low	$61^\#$	30	9.33	8.58	0	0	121	
	Med		-	4.67	3.77	2.2	57.0	241	1.03
Eucalyptol	Low	$115^\wedge$	66	7.16	5.51	0	0	296	
	Med		-	3.54	2.11	1.9	57.9	600	1.93

Table 1 Summary of Experimental Conditions, where VOC mixing ratios denoted by * are measured by TD-GC-FID/ToF-MS, those denoted by $^\wedge$ are estimated from syringe pump injection, $^\$$ are estimated from SOA yields of β-pinene and $^\#$ are those estimated from SOA yields of plant experiments .

2. The uncertainty of the contribution of HOMs and oligomers to SOA should be discussed. Firstly, the SOA product signal is represented by the sum of FIGAERO-CIMS signals. However, this by no means represents the total SOA concentration. Thus, the reported contribution likely represents an upper bound.

We agree with the referee that the sum FIGAERO-CIMS signals does not represent the total SOA concentration, and have added clarification in the manuscript that this study did not aim to relate the composition to total SOA concentration but instead compare the distribution of the SOA products detected by the different VOC systems to one another.

We have added the following text to the manuscript for clarification:

> "The products detected by I-CIMS are typically multifunctional oxidised species, which do not fully represent the SOA formed from a given system. Thus the I-CIMS signal represents only a portion of the SOA and the reported contributions of this portion are likely to be an upper bound of the contribution of oligomers and HOM to total SOA. This study aims to compare the relative contributions of different SOA components across the different single precursor and plant experiments rather than quantify the absolute contributions of any of the components. Owing to the similarity in composition across these systems, we expect that the ratios described here are not significantly affected by uncertainties in quantification."

Secondly, the same instrumental sensitivity is assumed for all ions. I understand the challenges in instrumental calibration, but the associated uncertainty should be considered, even qualitatively, based on previous understanding on the general relationship between compounds chemical properties and sensitivity (Lopez-Hilfiker 2016 AMT).

We agree that the uncertainty associated with calibrations should be considered, and have added a statement discussing the potential impact of these differences:

> "Iodide is more sensitive to oxidised organic species and thus is likely to overestimate the relative contribution of the more oxidised compounds and underestimate the relative contribution of the less oxidised compounds to SOA. However, given the comparison here is between VOC and oxidant systems that yield similar products, we expect that these sensitivity differences will not influence the relative contributions of different compounds classes, though estimates of absolute contributions may be an upper bound."

3. In Figure 5, how is the "% of HR signal" defined? Is this based on number or abundance? Please specify.

This and all other figures have been changed to the same y-axis labelling of "Contribution to MS Signal (%)" for clarity.

4. Is the VOC emission profile in Figure 1 measured by I- CIMS or TD-GC-FID/ToF-MS? I would guess the latter is used, but the description in Line 175-176 ("measured with I- CIMS") is ambiguous.

The sentence has been replaced with:

> "Figure 1 shows a single snapshot of VOC composition from these plants as measured by TD-GC-FID/ToF-MS to note the main features relevant for the SOA composition measured with I-CIMS."

Anonymous Referee #2

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The authors describe a study in a PAM/OFR reactor. They oxidized emissions from two plant species and three of the major single VOC in the emissions, two of them oxidized. They studied the importance of oligomers and highly oxygenated organic molecules (HOM) for SOA formation. The focus was on oxygenated MT emitted by the Californian sage species. The study is new and original, and provided interesting and fruitful results within the scope of ACP. So the manuscript could be published in ACP. However, there are some major issues that need improvement/extension. The manuscript is relatively short so there should be room for that. In summary:

1.) Experimental details are scarce: one would need to know about the applied VOC concentrations, VOC/NOX ratios, and VOC/ oxidant ratios. I guess experiments were performed at high VOC and high oxidant concentration. In this context it should be discussed in the conclusions under which conditions and in how far the results mean anything under atmospheric conditions.

As outlined in our response to referee 1, we have added a new section titled "Summary of Experiments" which contains additional details on the applied VOC mixing ratios for the plant experiments, and includes a table of the OH exposure, VOC/NOx ratios and VOC/OH ratios the experiments. For camphor, where measurements of VOC mixing ratios are unavailable, we assume an 8 % SOA yield based upon the yields determined from the plant experiments, to estimate the VOC mixing ratios. While, for camphene, we apply a literature yield of 12 % based on that of β-pinene to estimate the VOC mixing ratios. These show that with the exception of eucalyptol experiments, the remaining experiments were carried out at relatively low mixing ratios.

We have additionally included a discussion of the remaining uncertainties with respect to the relevance of these results to ambient SOA in the conclusions:

> "This study shows that HOM and oligomer formation is potentially important for SOA formed from the oxidation of oxygenated monoterpenes. These compounds are commonly emitted by woody shrubs, but have not been the subject of previous SOA studies. Owing to the potential of these VOCs to form HOM and oligomer products, future laboratory studies should encompass a broader

> range of VOC/OH and VOC/NOx ratios, owing to the potential influence this has on the proportion of oligomers formed (Kourtchev et al., 2016), alongside seed acidity and humidity dependence. In addition, there are uncertainties pertaining to the absolute contributions of HOM and oligomer products to the SOA from these plant and precursor systems owing to challenges calibrating for these oxidised products for which no standards exist. These may influence the absolute magnitude of the contributions of these compound classes to SOA. This study provides insights into the SOA formation from VOC systems not previously studied for their SOA formation potential and these results should be taken as a basis upon which to study their potential importance for ambient SOA formation in more detail."

2.) **There is no information on the reproducibility or the significance of the findings, although differences between the different chemical systems are stated as results.**

This comment has been addressed in a later response where more specific questions pertaining to the significance of findings were given.

Further there is no attempt to discuss "missing calibrations" although the relative importance of different two compound classes is presented as a important result.

Though there were no direct calibrations, the relative sensitivity of the different compound classes between the different experiments would be expected to be the same. Thus, though the absolute contributions of compound classes of HOM and oligomer may be an overestimation, we feel the relative proportions of them for the different VOC systems are a valid comparison. We have added the following into the manuscript:

> "Iodide is more sensitive to oxidised organic species and thus is likely to overestimate the relative contribution of the more oxidised compounds and underestimate the relative contribution of the less oxidised compounds to SOA. However, given the comparison here is between VOC and oxidant systems that yield similar products, we expect that these sensitivity differences will not influence the relative contributions of different compounds classes, though estimates of absolute contributions may be an upper bound."

Major comments in detail: Kourtchev et al. (2016) showed that oligomer content in SOA depends on the precursor concentration and simulation experiments tend to overestimate oligomer formation compared to atmospheric situations. What were VOC/OH ratio and VOC/NOX ratio in your experiments. A table giving an overview on experimental conditions and number of replications per system will be helpful. Were experiments performed at different VOC and the results compared? If so are there any trends with VOC/OH and VOC/NOX?

As discussed above, the VOC concentrations in the plant experiments were relatively low and similar between the plant systems. In addition, the single component experiments had similar aerosol mass loadings to that of the plant experiments, with the exception of eucalyptol. Thus, though the higher oligomer content in the case of eucalyptol could be influenced by the higher VOC concentrations, the presence of oligomers in the camphor, camphene and plant experiments, where VOC mixing ratios were lower suggests that oligomer formation estimations were not significantly influenced by high VOC concentrations. We have added clarification of this to manuscript:

> "It should be noted that VOC concentrations were higher in the case of eucalyptol compared with the other single component and plant studies, and this could influence the extent to which oligomers contribute to SOA (Kourtchev,. 2016). However, the estimated VOC mixing ratios for the other single component and plant experiments were more similar to one another. Furthermore, oligomer content observed in the plant experiments which had lower VOC mixing ratios than that of the single component experiments are comparable to that of camphor."

A table has also been added to the manuscript describing experimental conditions along with a discussion of the experimental conditions, as outlined in detail in our response to referee #1, with the following text added as a result:

> "During this study, the VOC mixing ratios were measured for the plant mixture experiments by TD-GC-FID/ToF-MS and ranged from 27-34 ppb as shown in Table 2, with approximately 80 % by mass from oxygenated monoterpenes. Of the single component experiments, VOC mixing ratios were estimated for eucalyptol, by its injection rate through the syringe pump to be 115 ppb, while camphor and camphene could not be estimated by this approach due to their introduction through sublimation. VOC mixing ratios for camphor is thus estimated as 61 ppb on the basis of the SOA mass yields from the plants, which under low-NO, no-seed conditions which were approximately 8 % for mass loadings ranging from 4 – 19 µg m-3, similar to that for other monoterpenes such as α-pinene (Donahue et al., 2012; Shilling et al., 2008). An 8% yield from eucalyptol would correspond to an estimated 130 ppb at the inlet, which is similar to the 115 ppb calculated based on syringe pump injection rate and dilution. For camphene, the VOC mixing ratios are estimated to be 30 ppb, based on a reported yield from β-pinene from PAM-OFR experiments (Friedman and Farmer, 2018). Calculations of remaining VOC for the single component experiments shows that all VOC is reacted under under the OH exposures employed in this study, thus validating the use of aerosol yield itself to estimate VOC concentrations."

Experiments were not carried out at different VOC concentrations, and thus there are no trends with VOC/OH and VOC/NOx to discuss in this manuscript. As this is a potentially useful body of future work, we have included the following in the conclusions:

"Owing to the potential of these VOCs to form HOM and oligomer products, future laboratory studies should encompass a broader range of VOC/OH and VOC/NOx ratios, owing to the potential influence this has on the proportion of oligomers formed (Kourtchev et al., 2016), alongside seed acidity and humidity dependence."

Line 206-211: Isn't that statement kind of trivial? One can only observe molecules with smaller carbon number in the particulate phase when they are more oxidized and vice versa larger molecules can make it into the particulate phase even if they are less oxidized? So what do we really learn from this? Only that camphene fragments stronger in thermodesorption?

This discussion is relating to the relative importance of carbon backbone retaining oxidation reactions compared with those that lead to fragmentation of the carbon backbone, an additional statement has been added for clarity:

> "The presence of oxidised fragmentation products in the case of camphene potentially shows that there is an increased prevalence of fragmentation pathways during the oxidation of camphene while the oxidation of camphor and eucalyptol proceed via pathways which retain their carbon backbone more readily. In eucalyptol SOA, for example, a large proportion of signal can be attributed to oxidised C10 products which form with no fragmentation of the carbon backbone, and there is a larger contribution from oligomers (≥ C11)."

Line 212: **Was the concentration of eucalyptol higher than the other species? I understand this is a laboratory study, which has its own right. Although not really stated, I guess the VOC input was high. Therefore I am wondering about OH lifetime for the (single) VOC as a measure of VOC/oxidant, and the VOC/NOX ratio. And, I am wondering in how far and under which conditions the results can be transferred to atmospheric situations?** This is also in context with the missing information on errors and significance for the discussed differences Low NOX / medium NOX, single compounds vs mixture, MT vs. oxidized MT.

The concentrations have been discussed in previous responses, and further details of the VOC/oxidant, VOC/NOx ratio and OH lifetime are provided in the table. In addition, other comments above and discussion in the conclusions have discussed the potential relevance of these results to atmospheric situations. As the significance of the results are also highlighted in the following question, a detailed response on this aspect will be provided below.

Table 2 and line 229 -242: How many experiments were performed per VOC (mixture)? How significant are the differences, discussed in the text? Which differences are really significant? And if the differences are significant, what does it eventually mean? The paragraph is difficult to follow and should be structured clearer. E.g. I don't see some of the points made so clearly in the table.

As is typical for chamber and OFR experiments, a single experiment was performed per VOC and plant mixture under a given set of conditions (Huang et al., 2018; Wang and Hildebrandt Ruiz, 2018; Ylisirniö et al., 2019). In this case, this corresponds to aerosol sample collected over a 20 to 30-minute period over which aerosol mass concentration and OFR conditions remain stable. The results presented in this manuscript are thus an average of the aerosol generated over this time period. Though not a true replicate, this is typical in OFR and chamber studies where it is challenging to get each experimental variable identical between experiments, for example in Table 1 in Chhabra et al., 2015. Thus the majority of studies generate SOA under various conditions just once and compare all the experiments, as we have done in this study. We have added clarification of this approach to the manuscript:

> "The intervals presented in Table 2 represents aerosol which was collected over a period of 20 – 30 minutes after aerosol mass concentrations stabilised, so each setting represents an integrated average that was analysed as a single mass spectrum. One averaging interval was used to characterize aerosol composition for each VOC system under low and medium-NOx conditions."

Regarding the significance of the differences between SOA composition, typically this is established in other fields (such as plant metabolomics) by comparing the statistical differences between the mass spectral profiles using multivariate statistical analyses (for example, PERMANOVA). However, this is not a typical approach for FIGAERO-CIMS papers published in this field with many papers comparing mass spectra in a similar manner to this study, and thus we feel that this analysis is not required for our manuscript (Huang et al., 2018; Wang and Hildebrandt Ruiz, 2018; Ylisirniö et al., 2019). In general, SOA experiments are incredibly laborious and often have low replicates, which makes multivariate statistical analyses to compare composition much more difficult than in other fields where, for example, hundreds of plant leaves can be easily sampled at one time. This is one of the primary reasons these types of analyses are not regularly performed in SOA composition studies.

We have restructured the paragraph to make the points clearer and easier to follow:

> "The table shows average O:C of I-CIMS calculated by averaging across molecular formulas and bulk O:C determined from AMS for the low NOx conditions. The average molecular formula for each condition, obtained by averaging over the distributions for each element, are also shown in the table. Table 2 indicates that increasing NOx results in a slight increase in O:C across most of the systems. The average molecular formulae indicate that this increase is caused by both a slight decrease in the average C# and an increase in the average O#."

Line 264-269: I am sorry but this comparison is empty. Didn't you made some a-pinene reference experiments under same conditions, so that you could connect your new findings with something better established?

We did not carry out experiments of α-pinene under the same conditions as the focus of this study was to characterise the SOA from novel systems. We agree that this may have helped to relate the products to something more established, however given the small contribution of α-pinene to the emission profile of the plants, we focused on those VOCs which were more abundant (camphor and eucalyptol) and unique (camphene). We understand that including this comparison with α-pinene from literature may be confusing to the reader and have thus removed it from the revised manuscript.

Section 4: Please, put your results in perspective to the atmosphere, explicitly considering the experimental conditions under which they were achieved. (A few sentences: what can be learned, where one should be careful.)

We have added a discussion in the conclusions to contextualise these results and highlight potential uncertainties:

> "This study shows that HOM and oligomer formation is potentially important for SOA formed from the oxidation of oxygenated monoterpenes. These compounds are commonly emitted by woody shrubs, but have not been the subject of previous SOA studies. Owing to the potential of these VOCs to form HOM and oligomer products, future laboratory studies should encompass a broader range of VOC/OH and VOC/NOx ratios, owing to the potential influence this has on the proportion of oligomers formed (Kourtchev et al., 2016), alongside seed acidity and humidity dependence. In addition, there are uncertainties pertaining to the absolute contributions of HOM and oligomer products to the SOA from these plant and precursor systems owing to challenges calibrating for these oxidised products for which no standards exist. These may influence the absolute magnitude of the contributions of these compound classes to SOA. This study provides insights into the SOA formation from VOC systems not previously studied for their SOA formation potential and these results should be taken as a basis upon which to study their potential importance for ambient SOA formation in more detail. "

Line 140, 275, and 281: I understand that calibrations are inherently difficult. However, since you are comparing two different types of SOA contribution: do you have any idea about the relative sensitivity? Please, discuss in section 2.2 your estimate and in section 4 the limitations of your findings, because of missing (possibility for) calibrations.

The following has been added to section 2.2:

> "Iodide is more sensitive to oxidised organic species and thus is likely to overestimate the relative contribution of the more oxidised compounds and underestimate the relative contribution of the less oxidised compounds to SOA. However, given the comparison here is between VOC and oxidant systems that yield similar products, we expect that these sensitivity differences will not influence the relative contributions of different compounds classes, though estimates of absolute contributions may be an upper bound."

And the following to section 4:

> "This study shows that HOM and oligomer formation is potentially important for SOA formed from the oxidation of oxygenated monoterpenes. These compounds are commonly emitted by woody shrubs, but have not been the subject of previous SOA studies. Owing to the potential of these VOCs to form HOM and oligomer products, future laboratory studies should encompass a broader range of VOC/OH and VOC/NOx ratios, owing to the potential influence this has on the proportion of oligomers formed (Kourtchev et al., 2016), alongside seed acidity and humidity dependence. In addition, there are uncertainties pertaining to the absolute contributions of HOM and oligomer products to the SOA from these plant and precursor systems owing to challenges calibrating for these oxidised products for which no standards exist. These may influence the absolute magnitude of the contributions of these compound classes to SOA. This study provides insights into the SOA formation from VOC systems not previously studied for their SOA formation potential and these

results should be taken as a basis upon which to study their potential importance for ambient SOA formation in more detail."

Minor comments: In general, figures and tables need to be adapted to ACP format.

Tables and figures have been checked against ACP format, and labelling of (a) and (b) in Figure 2 changed accordingly.

Line 35: Bianchi et al. 2019 is a review, one should give the authors of the original articles also credits. I suggest to add at least e.g. Ehn et al. , Nature, 2014 here.

An additional reference to Ehn 2014 has been added to the manuscript.

Line 88: A short description of the plant-chamber and /or a reference is missing.

Inserted:

"The plant enclosure was constructed from Teflon sheets and was approximately 45" x 14" x 14"."

Line 250 Figure 6 -> Figure 5

Changed in Line 250 and a few additional instances.

Figure 2 Venn -> Venn diagram

Changed.

Figure 2b and 3: legend should not cover information

Changed Figures.

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Oligomer and highly oxygenated organic molecule formation from oxidation of oxygenated monoterpenes emitted by California sage plants

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Abstract

Plants emit a diverse range of biogenic volatile organic compounds (BVOC) whose oxidation leads to secondary organic aerosol (SOA) formation. The majority of studies of biogenic SOA have focused on single or simple multi-component BVOC mixtures thought to be representative of Northern Hemispheric deciduous or mixed forest conditions. Gaps remain in our understanding of SOA formation from complex mixtures of real plant emissions in other environments.

Towards the goal of understanding SOA in other regions, we conducted the first comprehensive study of SOA from oxygenated monoterpenes. These are the dominant emissions from the most common plant species in southern California's coastal sage ecosystem: black sage (*Salvia mellifera*) and California sagebrush (*Artemisia californica*).

Emissions from sage plants, and single compounds representing their major emissions (camphor, camphene and eucalyptol), were oxidised in an Aerodyne potential aerosol mass oxidation flow reactor (PAM-OFR). The chemical composition of SOA was characterised using a high-resolution time-of-flight iodide-anion chemical-ionization mass spectrometer equipped with a Filter Inlet for Gases and AEROsols (FIGAERO-I-HR-ToF-CIMS) under low and medium-NO_x conditions.

SOA from oxygenated monoterpenes showed higher order oligomer content and a greater presence of highly oxygenated organic molecules (HOM) than non-oxygenated monoterpenes, with HOM contributing 27 – 47 % and 12-14 % of SOA product signal from oxygenated and non-oxygenated monoterpenes, respectively. This study highlights the potential importance of oxygenated monoterpene emissions for SOA formation in woody shrub ecosystems.

1. Introduction

Secondary organic aerosol (SOA) formed from the oxidation of volatile organic compounds (VOCs) contributes 50-85 % of organic aerosol in the atmosphere (Jimenez et al., 2009). VOCs from biogenic emission sources (BVOCs) are estimated to contribute 75 – 90 % of total VOC (Guenther et al., 1995; Lamarque et al., 2010, Carlton et al., 2009; Claeys et al., 2004). BVOC oxidation by reaction with ozone, hydroxyl radical or nitrate radical has been estimated to contribute up to 50 % of SOA worldwide (Chung and Seinfeld, 2002; Hoffmann et al., 1997) having implications for air quality, climate and human health (Chung and Seinfeld, 2002; Fiore et al., 2012; Forster et al., 2007; Lohmann and Feichter, 2005).

Formation of highly oxygenated organic molecules (HOM) has been identified as a pathway for new particle formation and growth of SOA (Bianchi et al., 2019; Ehn et al., 2014). Recent work has shown that alongside HOM formation from ozonolysis (Quéléver et al., 2019), hydroxyl radical oxidation of monoterpenes is a large source of HOM (Berndt et al., 2016). Oligomerisation is another key pathway to formation of SOA and has been identified as important for monoterpenes including α-pinene and limonene (Hall and Johnston, 2011; Kourtchev et al., 2016; Kundu et al., 2012; Putman et al., 2011; Tolocka et al., 2004). Uncertainties remain in the relative importance and sensitivity to anthropogenic conditions of the different SOA formation pathways alongside their relevance in other BVOC systems.

Isoprene and α-pinene are globally the most abundant aerosol forming BVOCs emitted from vegetation and forests and thus have been the focus of many studies on SOA formation and composition (Carlton et al., 2009; Després et al., 2012; Guenther et al., 2012; Kroll, 2006; Zhang et al., 2015). However, these are only a subset of over 1700 BVOCs which have been identified from plant emissions (Dudareva et al., 2006). Though most of these are thought to have a negligible contribution on the global scale, they could be a major contributor in specific ecosystems and thus important on local scales. Despite this diversity, chemical composition of SOA from the majority of these BVOCs remains unknown. Real plant emissions are mixtures of many BVOCs, yet it remains unclear if the compounds currently used as proxies for BVOCs are adequate to describe SOA chemistry of plants globally (Faiola et al., 2018).

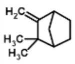
Real plant emissions have been used as atmospherically relevant VOC mixtures in various studies (Faiola et al., 2015, 2019; Hao et al., 2009, 2011; Joutsensaari et al., 2005, 2015; Mentel et al., 2009; Vanreken et al., 2006; Yli-Pirilä et al., 2016; Ylisirniö et al., 2019; Zhao et al., 2017), however, most of these used conifers or broad-leaved trees. Comparison of pine species has shown that thresholds of new particle formation (NPF) from plant emissions are lower than that for α-pinene alone, and plants with a larger proportion of oxygenated VOCs (OVOCs) have the lowest thresholds (Mentel et al., 2009). For mainly isoprene emitting plants, SOA yields from co-emitted VOCs were less than expected from single-VOC data, suggesting that isoprene inhibits SOA formation (Wyche et al., 2014). Furthermore, recent incorporation of terpene complexity into a box model has demonstrated enhancements of 1.5-2.3 in SOA mass yields from Scots pine, relative to the commonly used model monoterpene α-pinene (Faiola et al., 2018). Though studies of SOA from real plant emissions are limited, all results show pronounced differences between plants and single components. This suggests that simplification of BVOC complexity may be responsible for model under-estimates of organic aerosol mass loadings in dry shrubland areas of the western United States (Carlton et al., 2018).

The impact of mixing BVOCs on SOA has been recently studied using mixtures of α-pinene and isoprene, and results have shown that isoprene can suppress the mass yield derived from monoterpenes through oxidant scavenging (McFiggans et al., 2019). Utilisation of detailed chemical composition enabled attribution of this effect to a reduction in yield of low volatility HOM products which form SOA, relative to their yields during single VOC oxidation (McFiggans et al., 2019). This study demonstrates the utility of detailed chemical composition for deconvolution of SOA from complex mixtures. Despite these findings, studies to date have lacked adequate characterisation of differences in chemical composition between SOA from plants and single precursors.

Relative proportions of different BVOCs in the atmosphere is a function of both the plant species and environmental factors. Thus VOC mixtures vary regionally and globally, making the need to understand SOA formation from different precursors and mixtures vital for application in regions with different BVOC source profiles (Guenther, 2013). For example, at some agricultural locations in California, oxygenated monoterpene emissions and ambient concentrations were higher than anthropogenic and monoterpene VOCs (Gentner et al., 2014) suggesting that they may be important for SOA formation in this region.

In this study we investigate the VOC emission profile of two species of plant native to California: black sage (*Salvia mellifera*, Sage herein) and California sagebrush (*Artemisia californica*, Artemisia herein) and subsequent SOA formation from hydroxyl radical oxidation of these VOCs in an oxidation flow reactor (OFR) under low and medium NO_x conditions. On the basis of the measured emission profiles of these species, we also studied SOA formed from individual VOCs which were major contributors, camphene, camphor and eucalyptol (Table 1).

Though terpenoid emissions of sage plants into the atmosphere were reported in the mid-1970s (Tyson et al., 1974) and they have been considered by plant scientists for their ecological function (Karban et al., 2014), these are the first detailed SOA composition measurements from these plants and the first study of woody shrubs, which are the dominant vegetation type in many landscapes including coastal sage scrub, shrub lands and chaparral. Atmospherically relevant studies of the VOC precursors alone have focused on gas phase reaction rates and chemistry but not looked into the SOA (Ceacero-Vega et al., 2012; Gaona-Colmán et al., 2017a). Our results show high HOM and oligomer formation from oxygenated monoterpenes which dominate the emission profile of California sage plants.

Precursor	**Formula**	**Structure**	**kOH (cm^3 molecule^{-1} s^{-1})**
Camphene	$C_{10}H_{16}$		5.95 x 10~~E~~$^{-11}$ (Gaona-Colmán et al., 2017b)

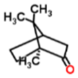
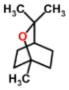
Camphor	$C_{10}H_{16}O$		3.8 x 10~~E~~$^{-12}$ (Ceacero-Vega et al., 2012)
Eucalyptol (1,8-cineole)	$C_{10}H_{18}O$		1.11 x 10~~E~~$^{-11}$ (Corchnoy and Atkinson, 1990)

Table 2 VOCs investigated in this study

2. Experimental Methods

2.1. Oxidation of VOCs and SOA Production

SOA particles were generated by the OH oxidation of VOCs in an Aerodyne Potential Aerosol Mass (PAM) oxidation flow reactor (OFR) (Lambe et al., 2011) affording short experimental timescales and the ability to generate consistent and reproducible oxidation conditions. Plant emissions were sampled from an external plant chamber into the OFR using an eductor. The plant enclosure was constructed from Teflon sheets and was approximately 45” x 14” x 14”. Eucalyptol was injected into the OFR through a length of Teflon tubing using a syringe pump, prior to evaporation into N_2 carrier gas. Camphene or camphor vapour were introduced by flowing N_2 over solid camphene or camphor placed in a Teflon tube.

In the OFR, OH, HO_2 and NO were generated via the following reactions:

~~$O_2 + h\nu_{185} \rightarrow 2O$ **(R1)**~~

~~$H_2O + O_2 + h\nu_{185} \rightarrow OH + HO_2$ **(R2)**~~

~~$N_2O + h\nu_{185} \rightarrow O(^1D) + N_2$ **(R3)**~~

~~$O + O_2 \rightarrow O_3$ **(R4)**~~

$O_3 + h\nu_{254} \rightarrow O(^1D) + O_2$ **(~~R5~~R1)**

$O(^1D) + H_2O \rightarrow 2OH$ **(~~R6~~R2)**

$O(^1D) + N_2O \rightarrow 2NO$ **(~~R7~~R3)**

All experiments were carried out at room temperature (approximately 26 ℃), relative humidity of 35 % and constant gas flow of 10 standard litres per minute (SLM) through the OFR, including injection of ~3 % N_2O at the inlet to generate NO in a subset of experiments (Lambe et al., 2017; Peng et al., 2018). The OFR was run in ~~OFR185~~ OFR254 mode which uses ~~185~~ 254 nm photons to generate radicals by the reactions outlined above, and under these conditions the estimated OH exposures ~~were in the range of (1.5-1.7) E^{12} molecules cm^{-3} s^{-1}~~are outlined in 2.5. In experiments where N_2O was added to the OFR, the NO:HO_2 ratio was approximately 0.5 as calculated using an adapted version of the OFR photochemical box model described in (Li et al., 2015) and (Peng et al., 2015). Between experiments, the flow reactor was flushed with humidified synthetic air at full lamp power for 12-36 hours until the particle mass generated was reduced to background concentrations (< 0.5 µg m^{-3}), measured by a scanning mobility particle sizer (SMPS) and an aerosol mass spectrometer (AMS). Instrument and OFR backgrounds were determined using N_2 + O_2 injection under lights off/on, with/without precursor injection. The results presented here are for low NO_x ([NO] < 0.1 ppb) and medium NO_x ([NO] > 1 ppb, [NO]: [HO_2] = 0.5) conditions.

2.2. FIGAERO-I-HR-ToF-CIMS Measurements

A time of flight chemical ionisation mass spectrometer (Lee et al., 2014) using an iodide-anion ionisation system was coupled with a filter inlet for gases and aerosols (FIGAERO) (Lopez-Hilfiker et al., 2014) for detection of both gas and particle phase composition (I-CIMS herein). The gas phase inlet consisted of a piece of 0.5 m long ¼” O.D. PFA tubing from which the I-CIMS sub-sampled 2 SLM. The aerosol phase inlet consisted of 0.5 m stainless steel tube through which 2 SLM were pulled over a Teflon filter. The sample flow (gas or aerosol) enters an ion molecule reaction region (IMR) which was maintained at a pressure of 100 mbar using a pump fitted with a pressure controller. I^- reagent ion was made by flowing N_2 over a permeation tube containing methyl iodide (CH_3I), mixing that flow with a humidified N_2 flow from a bubbler, and then ionising with a Po-210 source. Particle mass concentrations were monitored using a TSI Scanning Mobility Particle Sizer (SMPS, TSI, Model 3080) and collection time on the FIGAERO filter was varied to ensure hundreds of nanograms of aerosol in each sample for the different precursors. The FIGAERO thermal desorption cycle consisted of a 15-minute temperature ramp to 200 °C, a hold at that temperature for 10 minutes and then cooling down over 15 minutes.

Data analysis is performed using the Tofware package (version 3.1.0) running in the Igor Pro (WaveMetrics, OR, USA) environment. Time of flight values were converted to mass-to-charge ratios in the I-CIMS data using a calibration curve based on the times for I^-, $I.H_2O^-$ and I_3^- . The instrument was operated at a ~ 4000 Th/Th resolving power. Further analysis was carried out in custom Python 3 procedures using the packages Pandas, Matplotlib and Numpy.

While the FIGAERO is capable of providing information about both gas and particle phases, the gas phase I-CIMS spectra obtained during the medium NO_x experiments were complicated by the presence of high nitric acid formed in the OFR from the N_2O precursor (Lambe et al., 2017; Peng et al., 2018). High nitric acid depletes the I^- reagent ion to form NO_3^-, which subsequently acts as an additional reagent ion and complicates interpretation of the observed CIMS spectra. Thus, the gas phase measurements are deemed unsuitable for the comparison of medium and low NO_x conditions and the HR analysis of the I-CIMS spectra has been carried out only for the particle phase FIGAERO data. -This data provides thermal desorption profiles which have been previously used to draw conclusions about the volatility distribution of ions. However, in this study we do not make use of this owing to the additional complexity associated with calibration of the volatility and uncertainties with thermal decomposition (Bannan et al., 2019; Schobesberger et al., 2018; Stark et al., 2017) and instead integrate these desorption profiles in order to compare the overall composition of the different precursors. For all plant and VOC experiments, > 70 % of observed product signal was assigned with molecular formulae and these ions are used for analysis herein.

Quantification of highly oxidised species measured by I-CIMS is challenging due to the lack of availability of standards for many of the observed products. Previous attempts at quantification have used functional group dependencies, collision limit sensitivities or those derived from ion-adduct declustering scans (Lopez-Hilfiker et al., 2016). Experimental limitations exist in the use of these techniques, meaning that quantification remains a challenge (Riva et al., 2019) thus in this study we utilise observed ion signal intensities without accounting for species-dependent differences in instrument sensitivity. Iodide is more sensitive to oxidised organic species and thus is likely to overestimate the relative contribution of the more oxidised compounds and underestimate the relative contribution of the less oxidised compounds to SOA. However, given the comparison here is between VOC and oxidant systems that yield similar products, we expect that these sensitivity differences will not influence the relative contributions of different compounds classes, though estimates of absolute contributions may be an upper bound.

2.3. TD-GC-FID/ToF-MS VOC Measurements

Gas-phase VOC profiles observed during the SOA experiments using real plants were characterized at the inlet of the PAM flow reactor. Samples were collected by trapping VOCs onto multi-bed adsorbent cartridges containing Carbograph 5TD and Tenax TA adsorbents (Markes International, part # C2-AXXX-5149). Sampling lines were conditioned for a minimum of 10 minutes to minimize VOC line losses before attaching adsorbent cartridges. Air was pulled through duplicate cartridges with a sampling pump at 300 cm^3 min^{-1} for 20 minutes. On days where experiments were run using real plant emissions, duplicate cartridges were collected at the PAM inlet at least twice per day. Cartridges were shipped overnight to UCI on ice for offline analysis on a thermal-desorption gas chromatograph interfaced with a flame ionization detector and a time-of-flight mass spectrometer (TD-GC-ToF-MS: TD-Series 2 Unity + Ultra, Markes International; 7890B Agilent GC-FID; BenchToF-Select MS, Markes International). Compounds were identified using the 70 eV MS spectra by comparing them with compounds in the NIST library. Terpene mixing ratios at the PAM inlet were quantified using the FID signal as described elsewhere using the effective carbon number concept (Faiola et al., AMT, 2012).

2.4. AMS Measurements

SOA composition was continuously measured at the PAM outlet with a high-resolution time-of-flight aerosol mass spectrometer (HR-LToF-AMS; Aerodyne Research, Inc.) described in detail elsewhere (Canagaratna et al., 2007; DeCarlo et al., 2006). Briefly, the HR-LToF-AMS collimates sub-micron particles into a narrow beam with an aerodynamic lens. The particle beam is directed onto a vaporizer plate at 600 °C to vaporize non-refractory components. Volatilized fragments are ionized with 70 eV electron impact ionization and detected with a Long-ToF mass spectrometer (Tofwerk, resolving power 4000 Th/Th) where the ionized fragments are separated by mass. The detection efficiency was calibrated with monodisperse ammonium nitrate particles generated with a constant output atomizer (TSI, Model 3076) and a differential mobility analyser (DMA, TSI, Model 3080). AMS data was analysed using the Squirrel (v1.60P) and Pika (v1.20P) ToF-AMS toolkits in Igor Pro (v6.37; Wavemetrics, Inc.). Medium NO_x experiments had a large N_2O interference with CO_2 and thus O:C are not presented.

2.5. Summary of Experiments

During this study, the VOC mixing ratios were measured for the plant mixture experiments by TD-GC-FID/ToF-MS and ranged from 27-34 ppb as shown in Table 2, with approximately 80 % by mass from oxygenated monoterpenes. Of the single component experiments, VOC mixing ratios were estimated for eucalyptol, by its injection rate through the syringe pump to be 115 ppb, while camphor and camphene could not be estimated by this approach due to their introduction through sublimation. VOC mixing ratios for camphor is thus estimated as 61 ppb on the basis of the SOA mass yields from the plants, which under low-NO, no-seed conditions which were approximately 8 % for mass loadings ranging from 4 – 19 µg m^{-3}, similar to that for other monoterpenes such as α-pinene (Donahue et al., 2012; Shilling et al., 2008). An 8% yield from eucalyptol would correspond to an estimated 130 ppb at the inlet, which is similar to the 115 ppb calculated based on syringe pump injection rate and dilution. For camphene, the VOC mixing ratios are estimated to be 30 ppb, based on a reported yield from β-pinene from PAM-OFR experiments (Friedman and Farmer, 2018). Calculations of remaining VOC for the single component experiments shows that all VOC is reacted under under the OH exposures employed in this study, thus validating the use of aerosol yield itself to estimate VOC concentrations.

A summary of the measured and estimated VOC concentrations are included in Table 2, along with aerosol mass concentrations, OH exposures, modelled NO$_x$ conditions, VOC/OH and VOC/NO$_x$ ratios. The OH exposure with VOCs accounts for reductions in OH exposure following additions of VOC (Li et al., 2015). The intervals presented in Table 2 represents aerosol which was collected over a period of 20 – 30 minutes after aerosol mass concentrations stabilised, so each setting represents an integrated average that was analysed as a single mass spectrum. One averaging interval was used to characterize aerosol composition for each VOC system under low and medium-NOx conditions.

Precursor	**NO$_x$ Condition**	**VOC Mixing Ratios (ppb)**	**AMS Aerosol Mass Concentrations (µg m-3)**	**OH Exposure (x 10^{11} molecules cm^{-3})**		**NO ppb**	**NO$_2$ ppb**	**VOC /OH**	**VOC /NO$_x$**
				With VOC	**Without VOC**				
Artemesia	Low	27^*	9.35	10.02	-	0	0	48.7	
	Med	28^*	-	5.29	-	2.1	51.8	97.7	0.52
Sage	Low	28^*	18	7.32	-	0	0	70.6	
	Med	34^*	-	4.09	-	1.7	48.5	154	0.68
Camphene	Low	$30^\$$	20	10.14	10.1	0	0	48.7	
	Med		-	4.57	4.16	2.2	58.4	121	0.49
Camphor	Low	$61^\#$	30	9.33	8.58	0	0	121	
	Med		-	4.67	3.77	2.2	57.0	241	1.03
Eucalyptol	Low	$115^\wedge$	66	7.16	5.51	0	0	296	
	Med		-	3.54	2.11	1.9	57.9	600	1.93

Table 3 Summary of Experimental Conditions, where VOC mixing ratios denoted by * are measured by TD-GC-FID/ToF-MS, those denoted by $^\wedge$ are estimated from syringe pump injection, $^\$$ are estimated from SOA yields of β-pinene and $^\#$ are those estimated from SOA yields of plant experiments .

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3. Results & Discussion

3.1. VOC emissions from Plants

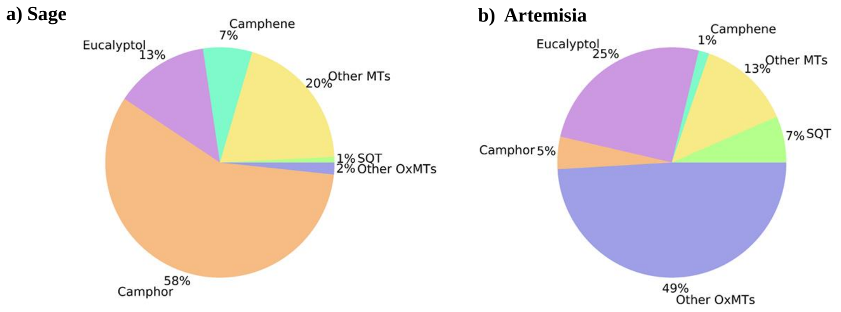

Figure 1 VOC emission profiles of a) Sage and b) Artemisia where OxMTs are oxygenated monoterpenes, MTs are monoterpenes and SQT are sesquiterpenes.

Figure 1 shows a single snapshot of VOC composition from these plants, measured by TD-GC-FID/ToF-MS, to note the main features relevant for the SOA composition measured with I-CIMS. Both Sage and Artemisia plant emission profiles are dominated by oxygenated monoterpenes (73 and 79 %, respectively), the least studied BVOC type (Goldstein and Galbally, 2007), while other monoterpenes have a small contribution (20 and 13 %, respectively). For Artemisia, eucalyptol contributes a larger proportion of the signal than camphor (25 and 5 %, respectively) while camphor alone dominates the emission profile of Sage (58 %). Artemisia has a large contribution (49 %) from other oxygenated monoterpene species. Speciation of VOC emissions vary between the two plants and the detailed VOC profiles and SOA yields will be presented in a separate paper. Of the monoterpenes, composition of SOA from camphene is least well characterised due to its low reactivity with ozone, however it is highly reactive with hydroxyl radical (Gaona-Colmán et al., 2017a) and is thus studied in detail in this paper. The following section focuses on characterisation and comparison of SOA from photooxidation of camphor, camphene and eucalyptol alongside SOA produced from photooxidation of the Sage and Artemisia plant emissions under low and medium-NO_x conditions.

3.2. Overview of SOA Composition

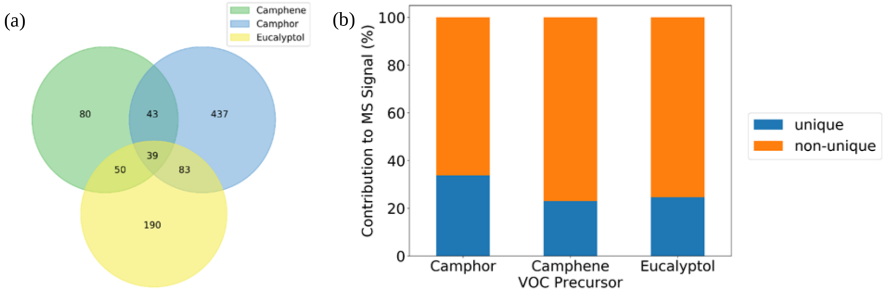

Figure 2 (a) Comparison of ions from peak lists of individual VOC precursors (no. of ions shown in Venn diagram) and (b) contribution of unique and non-unique products to total signal derived from Venn diagram under low-NOx conditions

Here we utilise the ions identified in each experiment to carry out a qualitative comparison of SOA composition between the different VOC precursors and plants. Figure 2a shows a Venn diagram of the number of distinct molecular formulas used in the high-resolution ion peak lists for camphene, camphor, and eucalyptol spectra. A majority of the assigned ions are unique to each of the precursors, and a small number of ions are non-unique (i.e. are present in the mass spectra of all 3 of the precursors). The relatively small number of non-unique ions (39) formed from all the precursors contributes to > 70 % of the product signal observed (Figure 2b). Unique ion signal is minor and is distributed across many more ions (80-437) (Figure 2a). Due to the relatively low signal intensity of these individual unique ions, it is not deemed suitable to use them as markers, particularly as there is ambiguity in their assignment under the limited resolution of the mass spectrometer and potential artefacts due to thermal decomposition caused by the FIGAERO. The percentage of signal from the 20 highest intensity ions (Figure 3) shows that the complexity of SOA from plants is greater than that of single components where up to 40 - 60 % of the product signal can be attributed to the top 20 ions. The top 20 ions observed under low and medium-NO_x conditions are listed in Table S1 and S2, respectively.

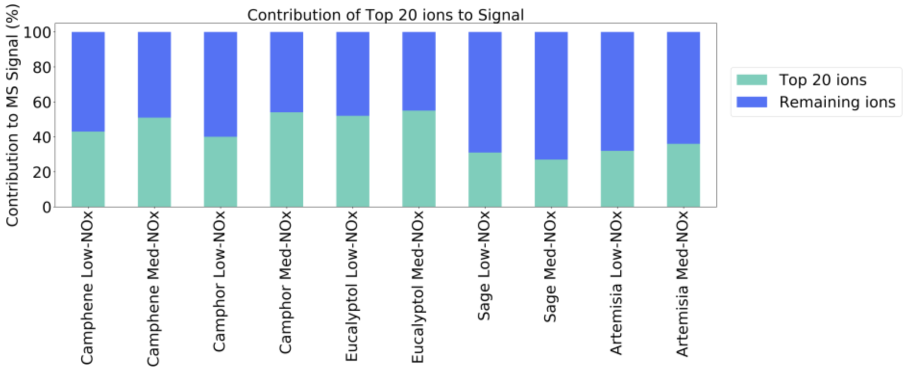

Figure 3 Contribution of Top 20 ions to observed product signal

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3.3 HOM & Oligomer Formation

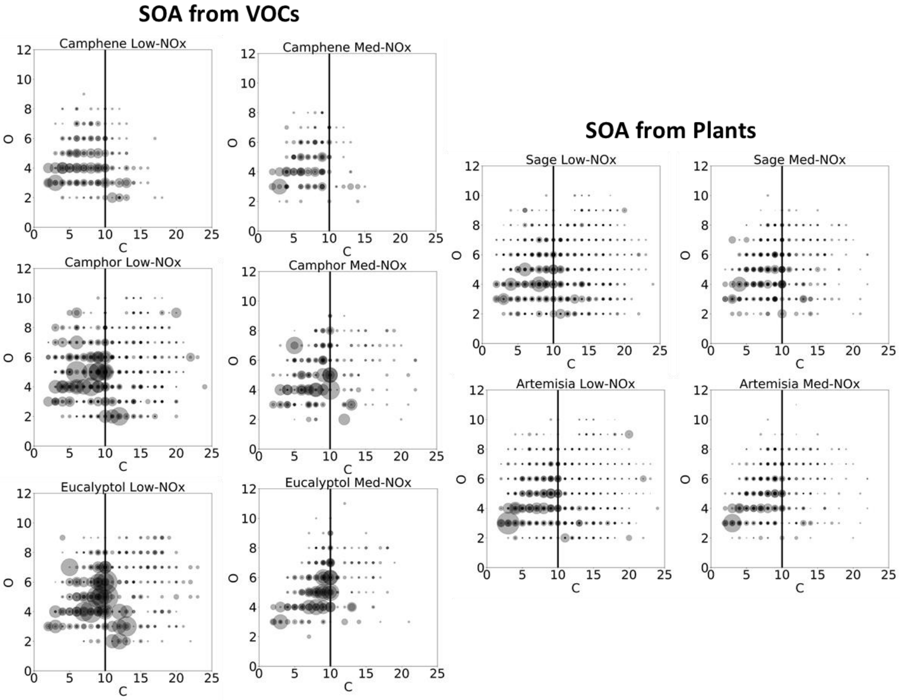

Figure 4 Carbon vs. Oxygen Plot for Aerosol Phase Composition under low and medium NO_x conditions for VOC precursors and plants (vertical black line separates monomers and oligomers in carbon number space and symbols are proportional to ion intensity).

Figure 4 plots the ions observed during all experiments according to their carbon and oxygen numbers. This figure highlights some of the differences in the SOA spectra between the single precursors and the plant emissions. ~~SOA from the oxygenated monoterpenes (camphor and eucalyptol) haappears at higher m/z (Figure S1)sand has lower O:C than that of camphene (Table 2), although their products are generally higher mass (Figure S1).~~ Oxidation of camphene yields mainly small, low mass (Figure S1), molecular fragmentation products (<C_{10}) as compared with camphor and eucalyptol which have many more products at higher carbon numbers. The bulk of the signal for camphene SOA is spread amongst fragmentation products, while for camphor it is a mixture between fragmentation and those retaining the carbon backbone of the precursor (Figure 2, vertical black line). The presence of oxidised fragmentation products in the case of camphene potentially shows that there is an increased prevalence of fragmentation pathways during the oxidation of camphene while the oxidation of camphor and eucalyptol proceed via pathways which retain their carbon backbone more readily. In eucalyptol SOA, for example, a large proportion of signal can be attributed to oxidised C_{10} products which form with no fragmentation of the carbon backbone, and there is a larger contribution from oligomers (≥ C_{11}).

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Precursor	Condition	O:C I-CIMS	O:C AMS	$C_XH_YO_Z$
Camphene	Low NO_X	0.69	0.70	$C_{7.26}H_{9.85}O_{4.03}$
	Medium NO_X	0.74	-	$C_{6.63}H_{9.7}N_{0.12}O_{4.21}$

Camphor	Low NO_X	0.66	0.64	$C_{8.97}H_{12.34}O_{4.8}$
	Medium NO_X	0.66	-	$C_{8.34}H_{11.98}N_{0.07}O_{4.71}$
Eucalyptol	Low NO_X	0.58	0.52	$C_{9.45}H_{13.09}O_{4.85}$
	Medium NO_X	0.65	-	$C_{8.47}H_{12.37}N_{0.01}O_{5.06}$
Sage	Low NO_X	0.74	0.78	$C_{9.54}H_{13.30}O_{4.52}$
	Medium NO_X	0.66	-	$C_{8.42}H_{12.34}N_{0.09}O_{4.66}$
Artemisia	Low NO_X	0.67	0.74	$C_{8.51}H_{11.79}O_{4.58}$
	Medium NO_X	0.71	-	$C_{7.62}H_{11.07}N_{0.06}O_{4.65}$

Table ~~2~~ 3 Bulk Composition of SOA from single component standards and plants

Despite different species contributing to the emissions profiles for the two plants, bulk composition and average molecular formulae are similar (Table ~~2~~3). A potential explanation for this is the similar contributions from oxygenated monoterpenes (Figure 1), which may have similar SOA characteristics despite different speciation. The monomer region of plant SOA (≤ C_{10}) can be attributed to fragmentation products from all VOCs. However, the presence of oligomers (≥ C_{11}) in the plant SOA is likely to be from products associated with the oxygenated monoterpenes as camphene shows few oligomer products (Figure 4).

The table shows average O:C of I-CIMS calculated by averaging across molecular formulas and bulk O:C determined from AMS for the low NOx conditions. The average molecular formula for each condition, obtained by averaging over the distributions for each element, are also shown in the table. Table 3 indicates that increasing NOx results in a slight increase in O:C across most of the systems. The average molecular formulae indicate that this increase is caused by both a slight decrease in the average C# and an increase in the average O#. ~~Under medium NO_x conditions the O:C of SOA was higher than under low-NO_x conditions for camphene, eucalyptol and Artemisia (Table 2). Though smaller carbon number SOA products are observed under medium-NO_x conditions for all except camphene, average molecular formula show that the average oxygen content is not altered, suggesting that further oxidation of fragmentation products continues under elevated NO_x (Table 2). It is also noted that oxidation of eucalyptol under low NO_x conditions yields larger products, and higher NO_x conditions give more similar SOA to other precursors.~~ Fewer high carbon number products are observed under medium-NO_x conditions for all precursors, however this effect is more notable in the single component experiments than the plant SOA, where low and medium-NO_x conditions look largely similar (Figure 4). Under medium NO_x conditions, nitrogen containing products are observed, with largest contributions to signal in camphor (35 %), followed by Sage (30 %), camphene (28 %), Artemisia (19 %) and eucalyptol (7 %).

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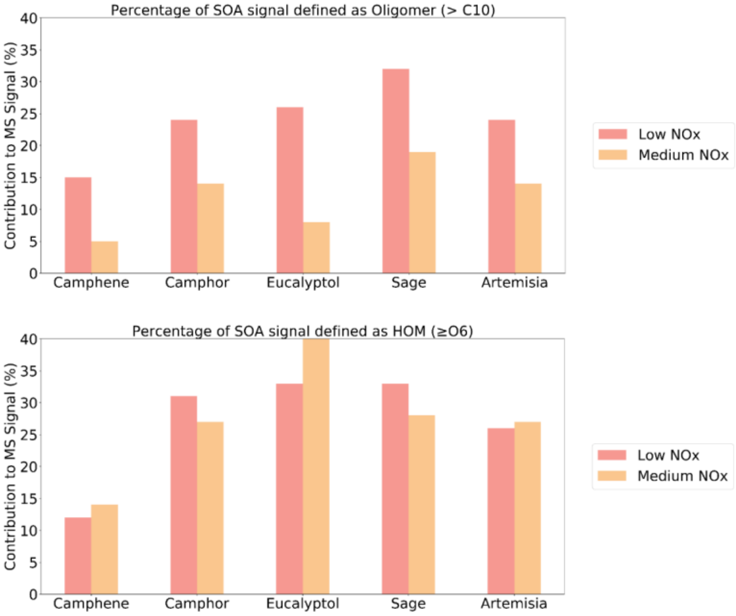

Figure 5 Comparison of the proportion of signal attributable to oligomeric species (top) and HOMs (bottom)

Two key pathways of SOA formation from BVOCs have been identified; formation of highly oxygenated organic molecules (HOM) (Bianchi et al., 2019; Ehn et al., 2014; Jokinen et al., 2014; Tu et al., 2016) and oligomerisation (Hall and Johnston, 2011; Kourtchev et al., 2016; Kundu et al., 2012; Putman et al., 2011; Tolocka et al., 2004). HOMs are defined here as ions which contain six or more oxygen atoms (Bianchi et al., 2019). Figure ~~6~~ 5 shows the relative contributions of HOM and oligomer products to observed signal for the different precursors and plants, aiding in evaluation of the relative importance of different SOA formation pathways under low and medium NO_x conditions. The products detected by I-CIMS are typically multifunctional oxidised species, which do not fully represent the SOA formed from a given system. Thus the I-CIMS signal represents only a portion of the SOA and the reported contributions of this portion are likely to be an upper bound of the contribution of oligomers and HOM to total SOA. This study aims to compare the relative contributions of different SOA components across the different single precursor and plant experiments rather than quantify the absolute contributions of any of the components. Owing to the similarity in composition across these systems, we expect that the ratios described here are not significantly affected by uncertainties in quantification.

Our results show large contributions of HOM to total product signal from the oxygenated monoterpenes of up to 40 %, while contributions of HOM to camphene SOA are as low as 12-14 % (Figure ~~6~~5). HOM show minimal differences in contribution to signal between low and medium-NO_x conditions, whereas oligomers show a decrease in all cases with NO_x addition. This suggests that HOM formation itself, a rapid intramolecular process, is not hindered by NO_x under these conditions, while NO hinders oligomerisation. Figure ~~6~~ 5 also indicates that the oligomer content in SOA is highest for oxygenated monoterpenes. Previous studies of mixtures have shown oligomer content to be similar to that of α-pinene alone (Kourtchev et al., 2016). However, our results suggest that in low α-pinene emitting plant species such as Sage and Artemisia, other VOCs such as camphor and eucalyptol may become important for oligomer formation. It should be noted that VOC concentrations were higher in the case of eucalyptol compared with the other single component and plant studies, and this could influence the extent to which oligomers contribute to SOA (Kourtchev,. 2016). However, the estimated VOC mixing ratios for the other single component and plant experiments were more similar to one another. Furthermore, oligomer content observed in the plant experiments which had lower VOC mixing ratios than that of the single component experiments are comparable to that of camphor.

~~Recently Ylisirniö et al. (2019) have published FIGAERO-CIMS studies of α-pinene SOA from PAM-OFR experiments. The proportion of HOM signal calculated from the α-pinene SOA spectra presented in (Ylisirniö et al., 2019) ranges from 41 % HOM at low OH exposure to 62 % at higher OH exposure. These HOM values are higher than those obtained in our experiment.~~

~~However, there are differences in experimental conditions that complicate these comparisons. The conditions utilised in Ylisirniö et al (2019) used OFR254, which utilises both 185 nm and 254 nm photons, as opposed to OFR185 which was used in our experiments. In OFR254, HO$_2$ concentrations are lower than in OFR185; increased HO$_2$ under the OFR185 conditions utilised during our experiments may suppress HOM formation and explain the differences between the two experiments. Therefore, though more HOM is observed for α-pinene in Ylisirnio et al (2019), a true comparison would require these precursors to be run under the same conditions.~~

4. Conclusions & Implications

Emissions of VOCs from sage and Artemisia plants, widespread in California and much of the western United States, are different from that of other commonly studied plants such as conifers and broad-leaved trees, since emissions of oxygenated monoterpenes are the largest fraction. Here we have presented detailed chemical characterisation of SOA from Sage and Artemisia plants, from 2 oxygenated monoterpene precursors emitted by these species (camphor and eucalyptol) and from a monoterpene (camphene). Results show up to 40 % of product signal was from HOMs for the oxygenated monoterpene precursors and clear oligomerisation was observed. Under elevated NOx conditions, HOM formation did not change significantly. However, oligomerisation was reduced for all precursors and plants.

This study shows that HOM and oligomer formation is potentially important for SOA formed from the oxidation of oxygenated monoterpenes. These compounds are commonly emitted by woody shrubs, but have not been the subject of previous SOA studies. Owing to the potential of these VOCs to form HOM and oligomer products, future laboratory studies should encompass a broader range of VOC/OH and VOC/NOx ratios, owing to the potential influence this has on the proportion of oligomers formed (Kourtchev et al., 2016), alongside seed acidity and humidity dependence. In addition, there are uncertainties pertaining to the absolute contributions of HOM and oligomer products to the SOA from these plant and precursor systems owing to challenges calibrating for these oxidised products for which no standards exist. These may influence the absolute magnitude of the contributions of these compound classes to SOA. This study provides insights into the SOA formation from VOC systems not previously studied for their SOA formation potential and these results should be taken as a basis upon which to study their potential importance for ambient SOA formation in more detail.

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Sage plants emit a mixture of BVOCs, and SOA formed from their emissions shows greater complexity than single components, though the majority of ions observed are generic monoterpene oxidation products emitted from all the investigated VOCs. Thus, constraining VOC contributions to SOA in complex mixtures remains a challenge. Our results clearly show that in the plant emission mixtures, HOMs can contribute up to 33 % of signal and oligomerisation continues to be a significant fraction of the SOA. This indicates that oxygenated monoterpenes may be key to understanding SOA in regions with many sage plants or other high oxygenated monoterpene emitting plant species.

This is the first detailed study of oxygenated monoterpene SOA chemistry using both single component standards and real plant emissions. Eucalypts, dominant emitters of eucalyptol, are present globally with many different species, and it is likely that they are globally important for SOA formation. Previously reported low thresholds of new particle formation from species containing high proportions of oxygenated monoterpenes (Mentel et al., 2009) could be explained by the high oligomer content of the SOA we have observed for these VOCs and in the mixtures. High oligomer content has been shown to influence particle viscosity by intra- and inter-molecular hydrogen bonding between oligomers (Huang et al., 2018), and thus our results could indicate very different physicochemical properties for SOA generated from plants which contain high proportions of oxygenated monoterpenes.

5. Author Contributions

CF designed the experiments. Instrument deployment and operation were carried out by CF, AM, JEK, CS, LW and FK. AMS analysis was carried out by CF. AM carried out I-CIMS analysis and wrote the paper. AG and CS ran the volatile sample analysis. All co-authors discussed the results and commented on the manuscript.

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7. Competing Interests

The authors declare they have no conflicts of interest.

8. Data Availability

Data is available upon request from corresponding authors.

9. Supplement

Supplement is included.

10. References

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