

## *Authors Response*

The authors thank the posted anonymous reviewers and Dr. McGillen for their comments. We have compiled the responses as follows. Reviews are in **bold**. Author responses are numbered with [A0, A1, A2 ...]. Line numbers in the responses are consistent with those in the reviews.

### **Short comment by M. McGillen**

As outlined in the introduction of this article, one of the main motivations of this work comes from the apparently extremely rapid rate ( $1.16 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) with which  $\beta$ -caryophyllene reacts with ozone, which is reportedly so fast that it is the dominant oxidation pathway in the atmosphere (Shu and Atkinson, 1995). If true, the resulting oxidation products of the ozonolysis reaction would likely have a dominant effect on the aerosol-forming processes associated with this sesquiterpene. However, there are several lines of evidence which would suggest that the rate coefficient reported by Shu and Atkinson (1995) may be overestimated by several orders of magnitude:

- 1.) A recent study by Ghalaieny et al. (2012) measured the rate of ozonolysis of  $\beta$ -caryophyllene at an elevated temperature of 366 K, where the effects of aerosol formation can be minimized. Experimental difficulties precluded the measurement of Arrhenius parameters for this reaction, however, when a structural analogue was used to estimate the activation energy of this reaction, extrapolation to room temperature yielded a rate coefficient of  $3.62 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , a factor of 320 smaller than the determination of Shu and Atkinson (1995). Furthermore, the rate coefficient for the formation of first-generational products of Winterhalter et al. (2009) appears to be more consistent with a smaller rate coefficient of ozonolysis for  $\beta$ -caryophyllene.
- 2.)  $\beta$ -caryophyllene possesses a low saturation vapour pressure at room temperature and its oxidation products are likely to possess much lower vapour pressures. The hypothesis is that heterogeneous reactions may therefore influence the results of experiments conducted at room temperature for certain species. This has been tested in an analogous system at high temperature with large terminal alkenes (McGillen et al., 2011a) and the results suggested that the previous literature data possesses an artifact which leads to an overestimate in the gas-phase rate coefficient.
- 3.) It has been demonstrated by SAR analysis of the aliphatic alkenes and dialkenes that the rate of ozonolysis is largely dictated by the counteractive effects of induction and steric hindrance (McGillen et al., 2008, Leather et al., 2010, McGillen et al., 2011). The results of these studies suggest that gas-phase ozonolysis rate coefficients of alkenes ought not to exceed the rate with which 2-butene, 2,3-dimethyl reacts with ozone ( $1.24 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) With these points considered, if the rate of ozonolysis of  $\beta$ -caryophyllene is taken to be  $3.62 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  instead of  $1.16 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , the atmospheric lifetime with respect to ozone increases from 1 minute to 7 hours, implying

**that reactions with NO<sub>3</sub> and OH are likely to play a far more important role in determining the atmospheric processing of this compound. Given this reduced role of ozonolysis in the atmosphere how does this impact on the paper's conclusion that  $\beta$ -caryophyllene ozonolysis SOA is a potentially important contributor to biogenic CCN?**

This study does not explicitly investigate the reaction rate of  $\beta$ -caryophyllene ( $\beta$ -c) ozonolysis and its contribution to biogenic CCN. However,  $\beta$ -c ozonolysis SOA may still be a potentially important contributor to biogenic CCN. The low vapor pressure of  $\beta$ -c precursor generates even low vapor pressure products of  $\beta$ -c ozonolysis that can contribute to secondary organic aerosol formation. This occurs quite rapidly in our chamber system under realistic atmospheric conditions (5 ppb  $\beta$ -c concentrations in 90m<sup>3</sup> reactor system). Since there appears to be some scientific discussion about the gas-phase rates we have included the Ghalaieny et al. (2012) to our manuscript. In regards to the CCN, very low hygroscopicities ( $\kappa < 0.1$ ) of  $\beta$ -c SOA have been observed in previous studies compared to other terpene counterparts. In this paper, we achieve greater  $\kappa$  values that indicate that SOA formed via ozonolysis can uptake water and can contribute significantly to biogenic CCN.

**Anonymous Referee #1**

#### **General comments**

**The paper addresses the potential for cloud condensation nuclei (CCN) activity of a specific class of secondary organic aerosols (SOA) of biogenic origin (sesquiterpenes) by means of laboratory chamber experiments. The CCN activity of both single sesquiterpene gaseous compounds (beta-caryophyllene) and mixtures of terpene and sesquiterpene precursors (isoprene and beta-caryophyllene, respectively) are investigated. As pointed out in the introduction, isoprene is well known to be likely the most abundant non-methane hydrocarbon emitted into the atmosphere with a global emission of 500 Tg yr<sup>-1</sup> (Guenther et al., 1995; Guenther et al., 2006). Conversely, longer chain sesquiterpenes are less abundant, however beta-caryophyllene SOA may be relevant for the global SOA budget. The hygroscopic properties of biogenic SOA in both subsaturated and supersaturated regimes has been the object of increasing attention in the last few years for improving the understanding of the global role of biogenic SOA potential as CCN. The topic of this paper is appropriate for ACPD, and it has the potential of adding useful information to the existing (yet small) pool of literature work regarding the CCN activity of biogenic SOA. The study is based on a well known method, i.e., generating SOA in a environmental chamber experiments. The methods are presented clearly and the paper is overall sufficiently well written and organized in the various sections. However, some aspects need to be revised in a major way before publication on ACP. My main concerns are listed below**

**1) The question raised by Dr. McGillen on the rate coefficient for the reaction of beta-caryophyllene with ozone (O<sub>3</sub>) is a critical point that needs to be addressed. The authors need to somehow incorporate this information in the paper, discuss their results in such context and revise their conclusions if necessary. Generally speaking, it appears to me that the beta-caryophyllene SOA behave as it has been seen in the case of other SOA systems, i.e., they are less CCN active**

**when generated from larger precursor concentrations, which probably correspond to larger SOA mass.**

[A1] We agree with the reviewer that without presence of OH scavenger,  $\beta$ -c of larger concentration formed less hygroscopic SOA. Response to Dr. McGillen's comments can be found above.

**2) The SOA yields and / or mass should be added in Tables Ia and Ib.**

[A2] SOA yields have been added in Table 1a and 1b.

**3) The correlation between f44 and O/C (Figure 3b) raises some major questions and data need to be verified. See details in the specific comments below**

[A3] Responses can be found below.

**4) A figure elucidating the relationship between the hygroscopic parameter kappa and O/C should be added. Such information would help the reader putting the paper into context with the recent literature showing that type of correlation**

[A4] The relationship between  $\kappa$  and O/C was examined and no correlation was found (including the line where this is stated in the text). As there are already a significant number of plots, we did not show the figure.

#### **Specific comments**

**Page 3, line 50: the term "natural VOCs" could be eliminated**

[A5] **Changed to:** Isoprene, monoterpenes, and sesquiterpene dominate BVOC emissions.

**Page 4, lines 77-79: can a reference to this statement regarding the O/C values (and perhaps even the O/C values) be added?**

[A6] The reference is added in the revised manuscript.

**Page 5, line 89: delete the repetition of "Kleindienst et al."**

[A6] The two citations are separated by a full stop. The first citation refers to the values reported for SOA yield. The second term "Kleindienst et al." is the subject of the sentence "*Kleindienst et al. (2007) observed lower aerosol mass with the presence of OH scavenger for ...*".

**Page 6, line 114: should be specified that the hygroscopicity in that paper is for subsaturated conditions (or growth factor, GF)**

[A7] This change is made in the revised manuscript (Page 6, line 114).

**Page 6, lines 120: the more recent work of Massoli et al., GRL, 2010; Lambe et al, ACP, 2011 should be also cited for the k vs O/C relationships**

[A8] The two references are added in the revised manuscript.

**Page 10, line 214: have the authors tried to generate mixtures with comparable precursor amounts (ppb) instead of adding isoprene in ppm?**

[A9] No, we investigated mixtures of atmospheric relevance. This is the first study of SOA mixtures of this kind; our reported results confirm that these terpene mixtures are of importance. In future studies, incremental additions of isoprene may be of interest.

**Page 11, line 220-226: how the authors think that these possible issues might affect the final yields and the conclusions on the effect of isoprene on the hygroscopicity of beta-caryophyllene?**

[A10] We have accounted for the first three possible causes (chamber wall loss, actual density and reacted isoprene amount) when calculating final yields in this study. Previous study in the same chamber have also proved that aerosol yield is not influenced by the presence of inorganic seed (not published). Therefore, there should be negligible effects on the reported final yields and the conclusion on effects of isoprene.

**Page 11, line 228: add the standard deviation to density value**

[A11] The average standard deviation for our density measurements is  $\pm 3\%$ .

**Page 11, lines 227-235: a statement related to the possible changes in observed O/C (if any) with density should be added - e.g., did O/C go up with density?**

[A12] The statement regarding to relationship between O/C and density is added to Page 12, line 263-265.

**Page 12, Paragraph 2.3: the authors could make a more extended use of the HR-ToF AMS data. If the AMS data have been analyzed to the point of extracting O/C and H/C, then the high resolution mass spectral features (MS) should be readily available. Some key MS could be shown in supplementary material. For example, it would be good to have a high resolution MS of both unoxidized isoprene and beta-caryophyllene systems. Other high resolution MS could be added for specific experimental conditions (e.g. for the highest oxidation levels) or for systems that behave in a unexpected way (e.g., do the authors see changes in the MS even if the O/C does not change significantly?). See Chaabra et al., ACP, 2010 for examples of high resolution mass spectra. At a minimum, a statement regarding the presence (or lack) of additional information in the AMS mass spectra should be added.**

[A13] Mass spectra of SOA formed under different conditions have been added in the supplemental material. No obvious change of mass spectra has been observed.

**Page 13, line 278 and Figure 3b: I have some issues with the f44 vs O/C correlation plot. The f44 seems too high for those O/C values. I have seen papers where for oxidized enough system (O/C > 0.2), the Aiken et al. slope holds very well (for example, see Figure 15 of Chaabra et al., ACP, 2010 reporting chamber SOA systems). I assume that f44 was correctly calculated as org44/org - was this done by using UMR or HR data? Have the authors looked at the f43 vs f44 plot? Once this aspects are clarified, I can see the reason for showing at the correlation between f44 and O/C for different systems. I think it is relevant to point out that some correlations hold and some others do not. Probably here it would be worth showing some high resolution mass spectra for the systems where**

**the  $f_{44}$  vs O/C relationship does not hold. It is possible that in those cases other masses contribute to O/C more than  $\text{CO}_2^+$ . That could be related to different products generated via ozonolysis vs OH photo oxidation products at least for isoprene. The authors should look at high resolution mass spectra and report on possible differences that are relevant for the interpretation of the results.**

[A14] (1)  $f_{44}$  was calculated using UMR data, while  $m/z$  44 only contained  $\text{CO}_2^+$  fragment. Figure 3b has been replaced and now  $f_{44}$  values are within reasonable range. (2) We did not look at  $f_{43}$  vs  $f_{44}$  plot, because we did not see the contribution to our understanding of  $\beta$ -c SOA hygroscopicity. (3) Figure 3b showed that only reaction between  $\beta$ -c and OH radicals produced SOA with a strong correlation between  $f_{44}$  and O/C. High resolution mass spectra indicated the  $f_{44}$  of  $\beta$ -c/OH SOA was much lower than that of  $\beta$ -c/ $\text{O}_3$  SOA, which is consistent with our inference in the paper that high  $f_{44}$  may be one reason for the failure of correlating  $f_{44}$  and O/C.

**In the caption of Figure 3a (lines 620-621) the authors state that they see formation of first and second generation products. How is this information supported? Did the authors find features in the high resolution mass spectra?**

[A15] Li et al. (2011) contained a list of identified second generation products, while first-generation products of  $\beta$ -c ozonolysis have been studied relatively more extensively (e.g. Jaoui et al., 2003; Nguyen et al., 2009; Winterhalter et al., 2009). HR-AMS data suggested that  $m/z$  43 ( $\text{C}_2\text{H}_3\text{O}^+$ ) and  $m/z$  44 ( $\text{CO}_2^+$ ) of second generation products contributed more to the total organic signal, which should be responsible for the observed higher O/C.

**Page 15, lines 322-329: there is a contradiction here. How can the authors first state that the equation 2 is unrealistic, and then say that (based on this formulation) small amounts of beta-caryophyllene have significant contribution to the kappa values of the mixtures?**

[A16] Perhaps the word unrealistic is too harsh? It has been removed from the text. The method of calculating the fractional contribution of organic aerosol to  $\kappa$  values has been applied in several studies (e.g., Lambe et al., 2011; Moore et al., 2012) to look at hygroscopicity of different aerosol components separately. The “unrealistic” aspect of this method assumes that the aerosol formed can be simulated as a mixture of  $\beta$ -c SOA and isoprene SOA formed in different experiments. Our results suggest that this is not true. Estimation based on the additive  $\kappa$  formulation reveals that the SOA formed from the precursor mixture behaves more like  $\beta$ -c SOA than isoprene SOA even though the contribution of  $\beta$ -c in the gas-phase is significantly less. We have clarified this in the text.

**Page 16, lines 336 - 347: Figure 4 highlights that different masses other than  $m/z$  44 might correlate better with kappa. Have the authors look at the high resolution mass spectrum and determined if those signals are dominated by ions of the  $\text{C}_x\text{H}_y$ ,  $\text{C}_x\text{H}_y\text{O}$  or  $\text{C}_x\text{H}_y\text{Ogt1}$  ion families? For example,  $m/z$  43 has a contribution from both  $\text{C}_3\text{H}_7$  and  $\text{C}_2\text{H}_3\text{O}$ . I strongly recommend to re do Figure 4 using the HR information that is available to the authors. Finally, I stress again that a figure of kappa vs O/C is made to compare with the trends observed for other studies (e.g., Chang et al., ACP, 2010; Massoli et al., GRL, 2010; Lambe et al., ACP, 2011).**

[A17] The major peaks in the mass spectrum of 5 ppb  $\beta$ -c/ $O_3$  reaction with OH scavenger present in Figure 4 were listed below with the corresponding ions. Most fragments consist of only one ion in the  $C_xH_y$  ion family, except for  $m/z$  43, 44 and 55. The two ions making up  $m/z$  55 showed similar time trend, so that the correlation of each ion with  $\kappa$  would also be to the same extent. As a result, even with UMR data, Figure 4 demonstrated the weak  $\kappa$  versus  $m/z$  correlation for  $\beta$ -c and isoprene SOA and the effect of OH scavenger on  $\beta$ -c SOA.

$m/z$	43	44	51	55	56	65	67	69	77	79	81	91	95
Ions	$C_2H_3O^+$	$CO_2^+$	$C_4H_3^+$	$C_3H_3O^+$ $C_4H_7^+$	$C_4H_8^+$	$C_3H_5^+$	$C_5H_7^+$	$C_5H_9^+$	$C_6H_5^+$	$C_6H_7^+$	$C_6H_9^+$	$C_7H_7^+$	$C_7H_{11}^+$

### Anonymous Referee #2

This manuscript presents experimental data regarding the potential of one of the most important sesquiterpene emitted into ambient atmosphere (beta-caryophyllene) as a source of secondary organic aerosol cloud condensation nuclei (CCN). This study focuses on the effects of hydroxyl radicals, light and the presence of isoprene for bcaryophyllene/  $O_3$  SOA formation and Cloud Condensation Nuclei (CCN) characteristics. The authors use a series of experimental techniques to evaluate the chemical and physical parameters of the resulting SOA (CCN activity). The results and conclusions regarding the role of light, OH and isoprene on CCN activity of the SOA generated are presented. These results are of great interest to atmospheric scientists and are appropriate for ACP. In fact, this study represents a significant advance for biogenic hydrocarbons emitted into the atmosphere and their global role as source of SOA CCN. However, I have some concerns with the organization and technical aspects of the paper.

It's important to emphasis that these conclusions are specific to this system and the presence for example of other compounds/oxidants with b-caryophyllene may leads to different conclusions. There may be hundreds or thousands of different HCs/oxidants present at the same time and their role on SOA CCN activity will be difficult to understand. It will be beneficial if some structural/quantitative information about some key compounds (e.g. b-caryophyllinic acid, methyltetrols or methyl glyceric acid) were identified and reported that may play a critical role in the b-caryophyllene SOA CCN activity. The role of ozone rate constant as reflected by Dr. McGillen comment should be addressed in the revised manuscript. There are several issues that I found and are also reported in comments made by referee #1. The authors need to address these comments. For example, HR AMS data need to be re-analyzed and addressed as suggested by referee #1. The paper need to be carefully edited for errors, and to check for area where some statements need references. As I said, the topic of this manuscript is of great interest and appropriate to ACP. The paper should be published after the authors address the comments raised above.

[A18] We agree with the reviewer that structural/quantitative information on some key compounds would be beneficial, however, necessary instruments were not available at the time we conducted this study.

In addition to the comments from our reviewers we would like to thank Dr. Imad El Haddad for his interest and discerning comments to our paper. In response to Dr. Haddad's comments, we corrected errors in the figure captions and removed AMS data points with low signal-to-noise ratio (< 100%). Furthermore, in Fig. 3b the x and y-axis of a data set was switched. As a result of our changes the O/C ratios are within reasonable range of SOA. All the above changes have been made in the revised manuscript and have been highlighted in the submitted revisions.

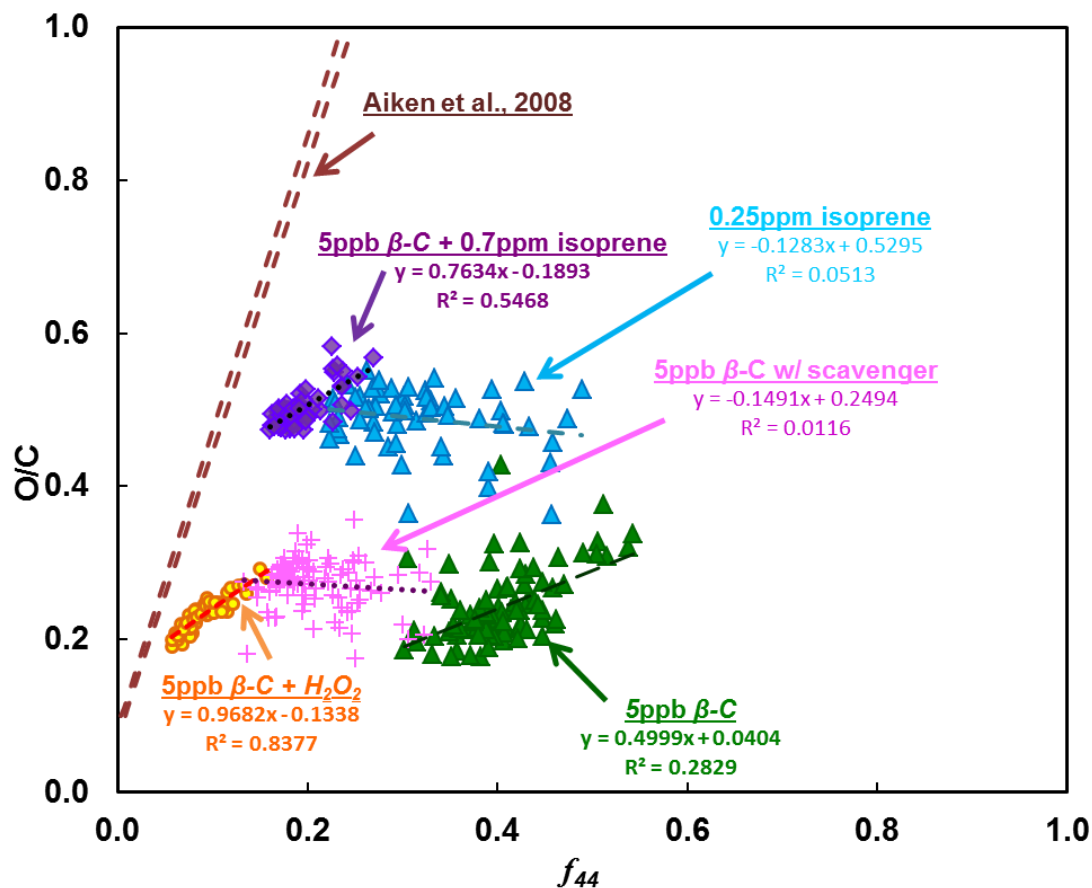


Fig.1. Revised version of Figure 3b