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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Are sesquiterpenes a good source of secondary organic cloud condensation nuclei (CCN)? Revisiting <i>beta;</i>-caryophyllene CCN" *by* X. Tang et al.

Anonymous Referee #1

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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^{-1} (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 (O3) 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.

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

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

3) 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

Specific comments

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

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 ?

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

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

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

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

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 ?

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

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 ?

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.

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 f44 vs O/C relationship does not hold. It is possible that in those cases other masses contribute to O/C more than CO2+. 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.

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 ?

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 ?

Page 16, lines 336 - 347: Figure 4 highlights that different masses other than mz 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 CxHy, CxHyO1 or CxHyOgt1 ion families ? For example, mz 43 has a contribution from both C3H7 and C2H3O. 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).

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