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Comment

## ***Interactive comment on “Campholenic aldehyde ozonolysis: a possible mechanism for the formation of specific biogenic secondary organic aerosol constituents” by A. Kahnt et al.***

**A. Kahnt et al.**

ariane.kahnt@ua.ac.be

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We thank the anonymous reviewer #1 for useful comments which helped to improve our manuscript. Our responses to the comments raised by the reviewer are as follows:

Title: The title is a bit vague and rather long. Also, I don't think the “possible” is really needed.

Re: The title was changed to: “Campholenic aldehyde ozonolysis: A mechanism leading to specific biogenic secondary organic aerosol constituents”

Page 22489, line 10: Insert “the prevailing”

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Interactive Discussion

Discussion Paper



Re: It was changed accordingly.

Page 22491, line 13: Would be clearer as “composition of the inorganic salt solutions used”

Re: The sentence was changed accordingly.

Page 22491, line 25: Remove “added”

Re: It was changed accordingly.

Page 22492, line 12: I don't think moisturised in the correct word. I think you can just say “was purchased as a 50 % solution in water”. Also is the v/v or w/w?

Re: The sentence was modified as follows: “The DNPH reagent ( $\geq 99\%$ , HPLC grade) was purchased from Sigma-Aldrich as a 50% solution in water and was recrystallised twice in acetonitrile (HPLC grade, Sigma Aldrich) before usage.”

According to the Sigma-Aldrich webpage there is no information given if the water content is v/v or m/m; however, we presume it is v/v.

Page 22493, line 16: The filters were baked out at 105 C. This seems very low. Are the filters sufficiently blank with this pre-treatment method?

Re: The applied method for the pre-heated quartz filter samples used in this study was shown to be a good compromise, as especially OC values were higher when filters were baked at higher temperatures. This is most likely due to adsorption of organic contaminants during the cooling process.

Page 22494, line 21: Replace “,” with “and” after reagent

Re: It was changed accordingly.

Page 22495, line 13: Remove the “also”

Re: It was changed accordingly.

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Interactive Discussion

Discussion Paper



Page 22499, section 3.3.1: This section is rather confusing. You start talking about a single compound and then mention lots of other ions and how you interpret the data. I think the whole section from line 23-29 needs to be before the start of section 3.3.1 i.e.

Re: The section was modified for better clarity.

in 3.3 Page 22500, line 17: For completeness, it might be prudent to include a sentence stating that this product is not identified at present

Re: The sentence was modified accordingly.

Page 22502, line 8: This wording is not clear.

Re: The sentence was changed for a better clarity.

page 22503, line 4: Replace “could thus be” with “was”. Line 21: Swap round to be “both appeared”

Re: Both sentences were changed accordingly.

Page 22504, line 14: There is not discussion here about the fact that this peak really is very minor in the a-pinene and k-pushta samples. I think there could be more discussion, either here or in the conclusions about why some peaks are very prominent in the ambient samples and some are not.

Re: For the non-derivatised filter samples the abundance of the m/z 215 compound was comparable to the a-pinene ozonolysis SOA sample but was rather low in the ambient filter (see Figure SI-17). It seems that for this compound formation pathways are favoured under laboratory conditions that can explain the difference in abundances observed from chamber-generated SOA and the ambient filter samples.

A short discussion about this issue was added to the section 3.3.4. as follows: “The current study enabled the identification of campholenic aldehyde as a possible precursor compound for specific biogenic aerosol constituents, which are commonly observed in ambient aerosol. Other, yet unknown formation routes or pathways that could

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Interactive Discussion

Discussion Paper



be favoured under chamber conditions can explain the observed differences in abundances for some of the oxidation products detected in the atmospheric and the chamber SOA samples.”

Page 22504, line 24: The sentence starting “these highly functionalised...” Is unclear, I am not sure what your point is.

Re: The phenomenon that chamber SOA usually exhibits not the extensive degree of oxidation that is observed in atmospheric organic aerosol can be explained by e.g. the duration of chamber studies. Starting from the first-generation oxidation products such as campholenic aldehyde can lead to laboratory-generated aerosol that resembles more closely the ambient SOA.

Page 22505, Replace “enabled to explain” with “could be used to explain”

Re: The sentence was modified accordingly.

Table 2: I think the CO should be in brackets. It looks like one formula

Re: A slash was added for better readability.

Table 3: There is a 541a but no b

Re: The “a” was removed.

Table 4: For the hydrazones 381 a-c, it is not clear which peaks the two structures relate to. Just a spacing issue.

Re: For the detected DNPH-derivatives at  $m/z$  381 three peaks were observed from the HPLC/TOFMS analysis, which contain one carbonyl and two carboxylic acid groups based on the derived elemental composition. From the HPLC/ITMS analysis even more  $m/z$  381 isomers were detected, but based on the matching peak at the same retention time in the  $\alpha$ -pinene oxide / O<sub>3</sub> / acidic seed experiment, only the compound at 27.4 min was further investigated in terms of MS<sup>2</sup> experiments. As shown in Figure SI-16 (right), the loss of water and CO<sub>2</sub> was observed during the fragmentation of the

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Interactive Discussion

Discussion Paper





DNPH-derivatised compound that corroborates the proposed structure as a carbonyl-containing dicarboxylic acid. Based on the campholenic aldehyde ozonolysis mechanisms the formation of different carbonyl-containing dicarboxylic acids with MW 202 are possible. We provided two possible structures in Table 4 but cannot relate them to the individual peaks. For a better clarity, the synthesis of authentic standard compounds would help to assign and establish their exact structure, and we believe that is something to be examined in a future study.

Table 5: Why are no product ions given for terpenylic acid?

Re: The information on product ions of terpenylic acid were added.

Figure 2a: What does the shaded area represent?

Re: The shaded area represents a particle as the acid-catalysed rearrangement of  $\alpha$ -pinene oxide with the formation of oxonium-ion and carbocations can only proceed on or in the particle phase.

Figure 2b. The molecular formulae are very hard to read

Re: The figure was changed for better readability.

Figure 6: You do not mention the very different intensities in the text. Why are they so different?

Re: For the DNPH-derivatised samples a highly complex matrix was obtained and indeed a very abundant product ion at  $m/z$  291 was detected from the fragmentation of the DNPH-derivative  $m/z$  335 in the ambient sample. We believe that due to possible interferences the ionisation efficiency is affected leading to different abundances for the product ions.

Supporting info: Figure SI-1: Is the peak in k-puszt a single compound or co-eluting ones? It is very large in comparison to the very small peak in the  $\alpha$ -pinene SOA

Re: The compound is co-eluting with other  $m/z$  335 isomers but only one of them

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Interactive Discussion

Discussion Paper



fragments to the diagnostic product ion  $m/z$  171. For clarity, the chromatogram from the MS3 experiment ( $m/z$  335  $\rightarrow$   $m/z$  171) is added in the revised Supporting Information (Figure SI-1, right).

Text under SI-12: “e” missing from diverse

Re: The text was corrected.

Text under SI-15: remove the “also” after Nevertheless

Re: The text was corrected accordingly.

Section 1.7: This  $m/z$  is not mentioned in the main text. It is rather strange to discuss it here, when it is not in the actual paper. The last line is unclear. I think you mean “have different chemical structures”? Also, in Figure SI-19, why is the k-pusztá chromatogram not scaled to 100%? The peak is tiny and I wonder if it is actually very relevant? But if you scaled it 100% the reader could determine the size of the peak compared to the raised baseline.

Re: The  $m/z$  229 compound is briefly mentioned in the main manuscript (see Section 3.3.1, Table 5). The compound was included because it was reported as a campholenic aldehyde oxidation product in a recent publication (Linuma et al., 2013), with matching retention time from an ambient filter sample collected in Seiffen, Germany. The authors reported comparable signal intensities of the  $m/z$  229 compound to cis-pinic acid and based on its intensity the  $m/z$  229 compound was discussed. In contrast to the latter study, a later eluting compound with low abundance was observed in the K-pusztá sample in the present investigation. It seems that at the K-pusztá sampling site the formation conditions for the  $m/z$  229 compound observed in the study of Linuma et al. (2013) were not met. Figure SI-19 was modified and a scaling to 100% was performed, accordingly. Based on the observed differences in the chromatographic and fragmentation behaviour, a different structure for the observed  $m/z$  229 compound in the K-pusztá sample was proposed. The last sentence was modified for better clarity.

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Interactive Discussion

Discussion Paper



Figure SI-25: Do you think the a-pinene SOA and k-pushta MS2 are from a different compound than the campholenic aldehyde SOA or is it that 2 compounds are overlapping in those samples? Since the MS3 data look similar, the latter seem very plausible. This section needs some sort of conclusion.

Re: The unknown MW 232 compound in the a-pinene SOA and the ambient filter sample seems to be formed from a different precursor than campholenic aldehyde but their structure seems to be related to the compound observed from the campholenic aldehyde ozonolysis based on a similar product ion spectrum from their MS3 product ions ( $m/z$  231  $\rightarrow$   $m/z$  199).

A short conclusion for this section was added to the revised Supporting Information as follows: "Based on the slightly distinctive fragmentation behaviour, the unknown MW 232 compound seems to be related to the compound observed in the ambient sample and the one detected from a-pinene ozonolysis. It likely originates from another precursor compound than campholenic aldehyde and further studies are warranted to elucidate the structure of and gain insight into the formation mechanism of this yet unidentified oxidation product."

References: Iinuma, Y., Kahnt, A., Mutzel, A., Böge, O., and Herrmann, H.: Ozone-driven secondary organic aerosol production chain, *Environ. Sci. Technol.*, 47(8), 3639–3647, 2013.

Please also note the supplement to this comment:

<http://www.atmos-chem-phys-discuss.net/13/C9614/2013/acpd-13-C9614-2013-supplement.pdf>

Interactive comment on *Atmos. Chem. Phys. Discuss.*, 13, 22487, 2013.

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