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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.***

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We would like to thank the anonymous Referee #2 for the time taken to provide helpful comments and discussion of our paper. Our responses to the comments raised by the reviewer are as follows:

... My only concern with this mechanism is would this be the main mechanism to occur in atmospheric aerosols, as many groups find that when they try to estimate aerosol acidity by E-AIM (Simon Clegg et al.) or charge balance approaches that atmospheric aerosol appear to be more or less neutralized? Furthermore, alpha-pinene oxide is

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considered a minor product based on recent work by Eddingsaas et al. (2012, ACP) and based on past work conducted by some of the authors present on this manuscript. Thus, I wonder does this aldehyde form from a more direct pathway that doesn't rely on several steps (including heterogeneous chemistry)? That is, could campholenic aldehyde form almost immediately in the gas phase by some unknown gas-phase mechanism (such as radical rearrangements)? For example, in isoprene oxidation chemistry, radical rearrangements, such as RO<sub>2</sub> rearrangements (Peeters et al., 2009, PCCP; Crouse et al., 2011, PCCP), are proving critical to consider for the formation of previously unrecognized gas-phase oxidation products.

Re: We agree that the described mechanism of  $\alpha$ -pinene oxide to campholenic aldehyde on acidic seed particles represents only one of the possible routes leading to campholenic aldehyde as a SOA precursor compound. This mechanism was shown to occur in laboratory studies (Iinuma et al., 2013; Bleier and Elrod, 2013), and was hence discussed only in this study as we wanted to avoid too much speculation about other possible reaction mechanisms. Based on the recent publication on the aqueous phase reaction of  $\alpha$ -pinene oxide its lifetime was estimated to be less than 5 min in neutral solution, and it was speculated that water can act as a general acid catalyst (Bleier and Elrod, 2013). Thus, the mechanism can be of atmospheric relevance also for neutral conditions. Other chemical formation mechanisms, both for  $\alpha$ -pinene oxide and campholenic aldehyde are certainly possible. Reaction mechanisms, which are not yet identified can be involved, such as the mentioned radical rearrangement processes as they are operating in isoprene chemistry. Possible reaction mechanisms were discussed from  $\alpha$ -pinene NO<sub>3</sub> reactions in the past and an independent formation of  $\alpha$ -pinene oxide and campholenic aldehyde was proposed (Berndt and Böge, 1997). In the latter study, it is described that  $\alpha$ -pinene oxide can form from the unimolecular decomposition of the excited adduct radical that results from NO<sub>3</sub> addition to the  $\alpha$ -pinene double bond. This route for epoxide formation has also been reported from other alkene NO<sub>3</sub> reactions (Berndt and Böge, 1995; Benter et al., 1994; Wille and Schindler, 1993), but also campholenic aldehyde was proposed to result from the

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decomposition of the excited adduct radical during the  $\alpha$ -pinene NO<sub>3</sub> reaction (Berndt and Böge, 1997).

A modification to the manuscript was made to emphasize possible multiple sources of campholenic aldehyde, including a direct formation from yet unidentified processes and its potential to understand specific reaction mechanism leading to SOA components.

#### References:

Bleier, D. B. and Elrod, M. J.: Kinetics and thermodynamics of atmospherically relevant aqueous phase reactions of  $\alpha$ -pinene oxide, *J. Phys. Chem. A*, 117, 4223–4232, 2013.

Berndt, T. and Böge, O.: Products and mechanism of the gas-phase reaction of NO<sub>3</sub> radicals with  $\alpha$ -pinene, *J. Chem. Soc. Faraday Trans.*, 93, 3021–3027, 1997.

T. Berndt and O. Böge, *J. Atmos. Chem.*, 1995, 21, 275.

Th. Benter, M. Liesner, R. N. Schindler, H. Skov, J. Hjorth and G. Restelli, *J. Phys. Chem.*, 1994, 98, 10492.

U. Wille and R. N. Schindler, *Ber. Bunsen-Ges. Phys. Chem.*, 1993, 97, 1447.

1.) Introduction, Lines 10-13: Wouldn't these prior lab SOA yields from monoterpenes already have campholenic aldehyde chemistry included? That is it was already contributing to SOA mass but it wasn't yet recognized.

Re: We agree that the campholenic aldehyde chemistry is included in older literature that reported  $\alpha$ -pinene O<sub>3</sub> SOA yields. Despite this fact, a lot of uncertainties are associated with these studies as for example higher precursor and oxidant concentrations were used, and a high variation in SOA yield data is described (yield data range between 0.022 – 0.543 as described in section 3.1). The usage of selected first-generation oxidation products (e.g. campholenic aldehyde) and the study on their oxidation can provide valuable insights into possible reaction pathways. Some abundant oxidation products in ambient aerosol could be related to campholenic aldehyde

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in this study for which challenging issues have been reported, such as a disagreement in product distribution from laboratory and ambient SOA samples (e.g. MW 188 compounds) as described by Vogel et al., 2013. These discrepancies can be associated with certain experimental conditions but probably also with analytical challenges, as it is especially the case for highly functionalised and hydrophilic compounds. This relates also to the relatively new biogenic SOA tracers terebic acid and terpenylic acid, which could not be detected with GC/MS analysis prior trimethylsilylation in the past (Claeys et al., 2012), likely owing to their thermal instability, and require other strategies for their characterisation.

## References

Vogel, A. L.; Äijälä, M.; Corrigan, A. L.; Junninen, H.; Ehn, M.; Petäjä, T.; Worsnop, D. R.; Kulmala, M.; Russell, L. M.; Williams, J.; Hoffmann, T., In-situ submicron organic aerosol characterization at a boreal forest research station during HUMPPA-COPEC 2010 using soft and hard ionization mass spectrometry. *Atmos. Chem. Phys. Discuss.* 2013, 13 (7), 17901-17952.

Claeys, M.; Szmigielski, R.; Vermeylen, R.; Wang, W.; Shalamzari, M. S.; Maenhaut, W., Tracers for biogenic secondary organic aerosol from  $\alpha$ -pinene and related monoterpenes: an overview. In *Role of oxides and acids of nitrogen in atmospheric chemistry*, NATO Science for Peace and Security Series - C, Environmental Security, Barnes, I.; Rudziński, K. J., Eds. Springer: Dordrecht, The Netherlands, 2012; 227-238.

2.) Experimental section, Chamber Experiments: Why is no wall-loss corrections applied to report SOA yields? This doesn't reflect the "true" values due to chamber wall losses of semivolatiles or lower volatility products as well as aerosol losses. I worry that if you report SOA yields here that modelers will use them. Maybe some clarification is warranted here, especially for the benefit of modelers?

Re: We agree that in general wall loss corrections should be applied to derive better estimations for true SOA yields. However, aerosol mass yields are highly sensitive

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to experimental conditions and to the applied corrections and assumptions made for chamber wall losses. Furthermore, deviations from SOA yield data have also been observed when different techniques were used to determine the SOA mass, which is necessary to calculate the SOA yield. Discrepancies have been reported from AMS and DMPS measurements, and differences in the aerosol sampling were proposed as a possible reason (Alfarra et al., 2012). Also the usage of a SMPS system was shown to result in uncertain SOA mass data, especially when organic aerosol loading and/or the ratio of suspended organic mass to inorganic mass is low (Hildebrandt et al., 2009). Furthermore, the treatment for losses of particles and vapours to the wall require certainly additional studies, especially as the mass transfer of vapours to the chamber wall is hard to measure experimentally. We believe that due to multiple challenging issues regarding the used techniques (for determining SOA mass) and the individual system (campholenic aldehyde/O<sub>3</sub>) additional research is necessary to enable a “correct” treatment of wall losses (which is actually on-going research in the Leipzig aerosol chamber). A correct treatment of the organic aerosol and an evaluation of wall loss rates for this system, which is dependent on particle size, charge distribution and turbulences in the chamber needs to be evaluated and require more data. We are aware of the possible problems and made modifications to the manuscript to emphasize that non-corrected gas and particle phase data are provided so that the reported SOA yield data represents lower limit values.

## References

Alfarra, M. R.; Hamilton, J. F.; Wyche, K. P.; Good, N.; Ward, M. W.; Carr, T.; Barley, M. H.; Monks, P. S.; Jenkin, M. E.; Lewis, A. C.; McFiggans, G. B., The effect of photochemical ageing and initial precursor concentration on the composition and hygroscopic properties of beta-caryophyllene secondary organic aerosol. *Atmospheric Chemistry and Physics* 2012, 12 (14), 6417-6436.

Hildebrandt, L.; Donahue, N. M.; Pandis, S. N., High formation of secondary organic aerosol from the photo-oxidation of toluene. *Atmos. Chem. Phys.* 2009, 9 (9), 2973-

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3.) Ambient Filter Samples Section: What does "rural background site" really mean? Can you be more specific? Does that mean a certain threshold of NO<sub>x</sub>, O<sub>3</sub>, or sulfate particles?

Re: The sampling site in Seiffen, Germany is located in a mid-level mountain area in East Germany and is surrounded by mixed forest. It is true that a clear classification is hard to make as no threshold values have been reported for this sampling site. We used filter samples from this site as high biogenic emission from the surrounding forest was expected in the summer month to proof the atmospheric relevance of campholenic aldehyde oxidation products. Most of the campholenic aldehyde oxidation products were compared with a pooled ambient filter sample collected in the K-pusztá, Hungary. This site is an established EMEP and GAW sampling site, classified as a rural measurement station.

4.) Ambient Filter Samples Section: Can the authors comment on how good filters are after 5-7 years of archiving them presumably in a freezer at -20 degrees C? Someone might ask: "Did long-term storage after these campaigns cause changes in the "true" composition of the aerosols?" Have the authors conducted tests to confirm how things change over storage time, especially with regards to the compounds of interest described in this study?

Re: We agree that problems can be associated with long-term storage of filter samples. This is indeed an important issue that should be investigated in future aerosol research studies. As also aerosol samples are highly spatial in time and space, together with sampling-related problems (e.g. negative and positive artefacts), individual filter samples need to be studied for extensive investigations on this issue. The filter samples were treated as careful as possible in this study (storage at -18/20°C in the dark, relatively quick analysis after extraction), but no tests were conducted to derive conclusions for effects of the storage time on the product distribution. Filter samples

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collected from two different sampling sites were thus investigated in this study. Only qualitative analysis was carried out to characterise specific compounds related to campholenic aldehyde oxidation and we believe that for such an approach the used filter samples can still be used. For quantitative analysis, the analysis of older filter samples are not recommended.

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