Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2019-939-RC1, 2019

Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Composition and volatility of SOA formed from oxidation of real tree emissions compared to single VOC-systems" *by* Arttu Ylisirniö et al.

Anonymous Referee #1

Received and published: 22 November 2019

Review Ylisirniö et al., ACPD 2019, "Composition and volatility of SOA formed from oxidation of real tree emissions compared to single VOC-systems"

Ylisrniö et al. present a laboratory chamber study on the gas-phase oxidation of biogenic volatile organic compounds from both, pure VOC standards and real plant emissions. The work focusses on the effects of different monoterpene and sesquiterpene precursors (and their ratios) on SOA yield and volatility. They use adequate instrumentation to investigate (1) the VOC precursors by PTR-MS and GC-MS, (2) the secondary organic aerosol mass by SMPS and AMS, and (3) the volatility and molecular chemical composition by FIGAERO-CIMS. Although, there is an intrinsic problem with the

FIGAERO by using a thermal evaporation technique for the detection of highly labile organic compounds (HOMs, hydroperoxides, hydroxy-hydroperoxides, organic peroxides), the technique produces thermograms, which the authors interpreted with the necessary caution.

Studying SOA yields and how physicochemical properties of SOA changes with different single precursors, precursor mixtures, and real plant emissions, enables evaluating chamber experiments against the natural complexity. This is an important work for atmospheric chemistry and hence the paper is clearly within the scope of ACP. As mentioned above, the applied methods are appropriate and the introduction refers to other related work in the field.

However, as outlined below (major comments), the methods section leaves the reader with multiple questions on how the experiments were carried out in detail. Hence, the experimental description is not sufficiently complete and precise allowing for reproduction by other scientists/groups. I think that this can be fixed by going more into detail in the experimental part.

The overall quality of the graphs is good and the language is fluent and precise. The conclusions section should be more on the point in order to leave a clear message. Overall, I can recommend the paper to be published in ACP after addressing the following aspects and improving the information content in the methods section.

Major comments:

l. 25: Bisabolenes also have endocyclic double bonds. Their oxidation would not lead to smaller and more volatile compounds. I suggest rephrasing to "[. . .] is due to exocyclic C=C bond scission [. . .]"

l. 62: not only mixtures of VOCs influence the composition of products, but also trace gases like NOx and CO. Furthermore, ammonia and H_2SO_4 can alter particle phase composition through heterogeneous reactions with organic molecules. It would be good to cite a review at this point (e.g. Ng et al., ACP, 2017, doi:10.5194/acp-17-2103-2017 for the NOx effects).

l. 82: Was the temperature actually monitored/regulated during the experiments, or does 25 °C just mean that experiments were done in the laboratory? I can imagine that the temperature changes in the flow tube when UV lamps are switched or when UV exposure is modulated.

Section 2.1: A more thorough description of the OFR-experiments is urgently needed. With the current description, it would be impossible to replicate these experiments. Instead of mentioning already results in the methods section (l. 84/85, l. 101), the level of information on the setup in the current version is unsatisfactory. As a reader I like to know for example:

How were blank experiments conducted? Was there a carry-over between different experiments when VOC precursors were changed? Did VOCs / SVOCs come back from the wall when switching on UV lamps? What were the flow rates? How were the VOCs flushed into the chamber (material of the tubing?)? Were the source- and sampling-lines heated to avoid condensation of sesquiterpenes? . . .

l. 107: What does the different “use history” of the PAM chambers mean? That statement leaves the reader questioning whether the history of experiments has an effect on the results?

Section 2.2: The level of experimental detail is unsatisfactory. A “suite of instruments” is mentioned in l. 112-115, but the following paragraphs only describe FIGAERO-CIMS and nothing on AMS or SMPS measurements. Concerning AMS, more information is needed in this experimental part, e.g. on the version (HR-AMS or C-ToF), operation mode (V-mode or W-mode) of the AMS, with/without size dependent composition, etc.

Furthermore, key information of FIGAERO-CIMS operation mode are also missing: how were blank measurements conducted? Have the authors evaluated whether gas-

phase adsorption on the particle filter can be an issue? What was the sample flow rate and the duration of particle collection? Until which maximum desorption temperature the ramp was operated? What was the pressure in the ion molecular region? etc.

Figaero data analysis: Why did the authors use tofTools and not Tofware, which offers also a figaero-version? Concerning peak identification: What are the numbers of allowed elements for C, H and O? How were multiple possible sum formulas for one exact mass ranked? Were ratios of H/C or O/C and double bound equivalents used to further constrain sum formula?

l. 167: Was an experiment conducted to measure wall/sampling line loss rates of sesquiterpenes against monoterpenes? E.g. SQT/MT measurements before and after the OFR, without O3 and UV off? L. 171: I disagree with this statement: wall/sampling line losses will be larger for sesquiterpenes than for monoterpenes. Relating this to the observed results, evaluating potential different losses of SQT compared to MT are highly relevant for the conclusions on different SOA yields.

Based on Fig. 2: does it need to be reassessed whether a-pinene is the (globally) strongest emitted monoterpene?

l. 274-276: this has already been shown by Hall et al. (https://doi.org/10.1021/es303891q)

l. 309-316: Is this observation in line with what one would expect from C* estimates based on the sum formula? (Donahue et al., ACP, 2011). It is surprising that oxygenation outweighs fragmentation of e.g. C20-dimers. Does the VBS distribution look different when the VBS bins are filled based on T_max vs. when they are filled based on the sum-formula-derived volatility?

Fig. 6 – SQT mix – mass spec: What are the ELVOCs with molecular mass < 200 Da? Are such compounds formed by thermal fragmentation of larger molecules? If this is the case, a quantitative estimate of the fraction of ion signal that results from thermal

fragmentation would help to evaluate the FIGAERO mass spectra.

l. 418: A comparison FIGAERO spectrum between acyclic and mono/bicyclic SQT would be very interesting. Fig. 4 only shows the spectrum of a SQT mix. More fragmentation products would be expected for the acyclic SQTs.

Minor:

l. 54 add Yassaa et al., ACP, 2012; doi:10.5194/acp-12-7215-2012

l. 119: oxygen or OH-groups: consider to be more specific. Would an ether (a molecule with an oxygen) already give a stable cluster with iodide?

l. 409: Explaining what fragmentation means should not appear in the summary / conclusions.

Technical:

l. 52 replace a-pinene with α-pinene.

l. 62, l. 269 replace Mcfiggans with McFiggans.

Fig. 2: structural formula of farnesene explicitly shows one hydrogen. Either draw all hydrogens or none (preferably none).

Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2019-939, 2019.