

Interactive comment on “Speciated measurements of semivolatile and intermediate volatility organic compounds (S/IVOCs) in a pine forest during BEACHON-RoMBAS 2011” by A. W. H. Chan et al.

Anonymous Referee #2

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Review: “Speciated measurements of semivolatile and intermediate volatility organic compounds (S/IVOCs) in a pine forest during BEACHON-RoMBAS 2011” by A. W. H. Chan et al. 2015

The manuscript by Chan et al. provides novel methods for the measurements of SVOC/IVOC compounds from the ambient air using an SVTAG-AMS and PTR-ToF-MS instruments. Even though I’m not an expert concerning this particular instrumentation (SVTAG-AMS) I believe this manuscript will bring extremely valuable information on the SVOC/IVOC compounds of the ambient air and shed some light to the complex system behind OA/SOA formation. I definitely recommend this for publication after with a few

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comments have been taken into account. I will not go to details since review #1 covers all my concerns already. I feel that the manuscript is pretty much ready for publication as it is now.

The paper reads exceptionally well and it’s a pleasure to read. I’m especially happy to see the first SQT results of the PTR-ToF compared with the SVTAG-AMS results. Also PMF support nicely the findings made during the campaign. Novelties of this manuscript are following; – you were able to shorten the time resolution compared to filter collection methods and thus decrease uncertainty related to ongoing oxidation reaction during long filter collection periods – the first ambient measurements of SQT202 – speciated PTR-ToF-measurements of SQT204 (I hope you will provide longer time periods in the future for us to read)

Some general comments:

- Introduction and Methods Everyone trying to measure emissions of extremely reactive compounds or their low-volatility reaction products know how hard it is in practice. Especially SQT’s (as SQT204) are known to be “impossible” to measure since they will react with ozone, OH or NO₃ before you get them even close to your detector. Also the information of reaction rates (k) of SQT with oxidants in the literature is limited and full of some very contradictory k-values are determined and published so far because of the difficulties with high SQT reactivity (e. g. Bonn and Moortgat 2003, Winterhalter et al., 2009, Shu & Atkinson 1995, Richters et al., 2015 and so on). What made you choose/believe one of these reaction rate coefficient? SQT also have a tendency to condense after oxidised in the air. I think your introduction is very positive in that sense. Maybe you could highlight the fact a little that what you just measured is really difficult in practice.

When you mention SOA production, I think recent discovery/development in ELVOC (extremely-low-volatility-VOC) should be mentioned (e.g. Ehn et al., 2014). They could be the key of explaining missing SOA and the first models on the matter are already out

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(Jokinen et al., 2015). SQT concentrations may not always be so low as expected (like in Helmig et al., 1994), but they might be even close to MT concentrations (Tarvainen et al., 2005). This would make the measurements of SQT's and their oxidation products even more important at least locally and seasonally.

In the section 2.2. Instrumentation, I (as a non expert user of this particular instrument) had hard time understanding how many instruments you actually use, when you measure gas and when particles (AMS is not the most common detector for gases I assume). Also you mention sample collection and GC analysis that have different time resolutions, which I did not understand why. Please clarify this section.

- Calibrations and GC data: Did you detect any nitrogen containing compounds or are they not separated with this GC column you used? What is the relationship with c^* and RI? Is it only the fact that a longer carbon skeleton effects volatility?

- Throughout the manuscript: You claim that emissions are dependent on sunlight but I would think it is rather the temperature (and also seasonality) this also goes with MT's and isoprene but that isn't the only reason the latter are more abundant at day light hours (p. 22352, r. ~15). Please correct this.

- Figures: Figures 4-7 figure captions seem truncated. Please provide information about the error bars (Fig 4 & 7). Since figures are usually the most read part of articles, I would use some time to clearly state what information is in them. That's all the comments I have regarding your manuscript, All the best: Reviewer #2

references: Bonn, B., and G. K. Moortgat (2003), Sesquiterpene ozonolysis: Origin of atmospheric new particle formation from biogenic hydrocarbons, *Geophys. Res. Lett.*, 30, 1585, doi:10.1029/2003GL017000, 11.

Ehn et al., A large source of low-volatility secondary organic aerosol, *Nature*, 506, 476–479 doi:10.1038/nature13032

Helmig et al. 1994 (cited in the manuscript)

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Jokinen T., Berndt T., Makkonen R., Kerminen V.-M. Junninen H., Paasonen P., Startmann F., Herrmann H., Guenther A., Worsnop D. R., Kulmala M., Ehn M. and Sipilä M. (2015) Production of extremely low-volatile organic compounds from biogenic emissions: measured yields and atmospheric implications, *Proc. Natl. Acad. Sci.*, Early Edition, doi: 10.1073/pnas.1423977112

Richters S, Herrmann H, Berndt T., *Phys Chem Chem Phys.* 2015 May 7;17(17):11658-69. Gas-phase rate coefficients of the reaction of ozone with four sesquiterpenes at 295 ± 2 K. doi: 10.1039/c4cp05542j.

Shu, Y., and R. Atkinson (1995), Atmospheric lifetimes and fates of a series of sesquiterpenes, *J. Geophys. Res.*, 100(D4), 7275–7281, doi:10.1029/95JD00368.

Tarvainen, V., Hakola, H., Hellén, H., Bäck, J., Hari, P., and Kulmala, M.: Temperature and light dependence of the VOC emissions of Scots pine, *Atmos. Chem. Phys.*, 5, 989-998, doi:10.5194/acp-5-989-2005, 2005.

Interactive comment on *Atmos. Chem. Phys. Discuss.*, 15, 22331, 2015.

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