Atmos. Chem. Phys. Discuss., 15, C1358–C1361, 2015
www.atmos-chem-phys-discuss.net/15/C1358/2015/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Examining the effects of anthropogenic emissions on isoprene-derived secondary organic aerosol formation during the 2013 Southern Oxidant and Aerosol Study (SOAS) at the Look Rock, Tennessee, ground site" *by* S. H. Budisulistiorini et al.

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Received and published: 6 April 2015

General comments:

This is a very comprehensive and fine study on the formation of isoprene-derived SOA during an intensive field campaign carried out at Look Rock, a site in the Ozark Mountains in the Eastern USA, where isoprene emissions during summer are known to be

high. The authors have combined on-line measurements using the Aerodyne Aerosol Chemical Speciation Monitor (ACSM) with off-line chemical measurements of a suite of isoprene-related SOA tracers. The isoprene-derived SOA tracers contributed with ∼9% (up to 26%) to the organic aerosol (OA) mass, and almost exclusively were made up by IEPOX-related tracers. An interesting result is that using PMF analysis of the ACSM data an IEPOX-OA factor could be derived that correlates well with off-line measured concentrations of 2-methyltetrols, C5-alkene triols, and IEPOX-derived organosulfates. There is, however, a substantial gap between the IEPOX-OA factor mass (∼25%, up to 47%) accounting for 32% of the total OA, whereas that estimated by off-line isoprene SOA tracer measurements is substantially lower, i.e. ∼9%, which is at present not understood but suggesting that in addition to the IEPOX-related SOA tracers there are other isoprene-related SOA tracers that are not covered by the off-line measurements. As expected, good correlations were found between particle-sulfate with both IEPOX- and MAE-derived SOA tracers and the IEPOX-OA factor, supporting the important role of sulfate in isoprene SOA formation. The authors have also successfully modeled the IEPOX-derived SOA tracers 2-methyltetrols and corresponding sulfates.

Specific comments:

Page 7369/7370 – lines 27 – 5: The only pathway considered for the formation of the sulfate ester of 2-methylglyceric acid is the methacrylic acid epoxide (MAE) pathway (Line et al., 2013b). There is sufficient evidence in my opinion that the pathway involving reactive uptake of methacrolein onto highly acidic aqueous aerosol and reaction with the sulfate radical anion should also be taken into account and mentioned. See, for example, Schindelka et al. (Faraday Discussions, 165, 237-259, 2013). The latter pathway allows to explain the formation of other C2-C5 isoprene-related organosulfates, for example, the sulfate ester of glycolic acid (MW 156), which is difficult to explain otherwise.

Page 7388 – line 1 (and Figure 5): The elemental composition of terpenylic acid (MW 172) should be C8H12O4, instead of C8H12NO4.

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Page 7389 – lines 19-28: Here, oligomeric IEPOX-derived HULIS is mentioned and the suggestion is made that quantification of these compounds could help to close the IEPOX-OA mass budget. Is there already any evidence for the presence of these compounds in ambient fine aerosol from an isoprene-rich site? Other compounds that may help to close the isoprene SOA mass budget are the C2-C5 isoprene-related organosulfates, formed through aqueous-phase reactions of methacrolein or methyl vinyl ketone, first-generation gas-phase oxidation products of isoprene, with the sulfate radical anion (mentioned above).

Page 7390 – line 5: The statement "However, it should be noted that in all previous studies 2-methyltetrols and C5-alkene triols were quantified by surrogate standards structurally unrelated to the targeted analytes." is too general. Authentic standards are a better choice but a surrogate standard used in previous studies is the C4-tetrol erythritol, which is structurally related (homologous) to the 2-methyltetrols (e.g. Kourtchev et al., Plant Biology 10, 138-149, 2008; Claeys et al., ACP 10, 9319-9331, 2010). The situation is different for previous measurements of the sulfate esters of the 2-methyltetrols (MW 216), where indeed a surrogate standard that is unrelated to the analytes (i.e. n-propylsulfate) has been used.

Technical corrections:

Page 7373 – line 13: . . .. a Nafion dryer . . ...

Page 7377 – line 11: . . .. by using a T-piece in . . .. . .

Page 7377 – line 27: the abbreviation "sLPM"should be defined.

Page 7384 – line 28: . . ... higher than those . . ...

Page 7388 – line 27: . . .. the abundance of . . ..

Page 7393 – line 3: . . .. in the predicted IEPOX SOA . . ...

Page 7409 – line 8: 2-methylglyceric acid

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Supplement – page 3 – Table S2: . . ... and reference mass spectra [Note: the abbreviation “MS”stands for “mass spectrometry” and not for “mass spectra”].

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 7365, 2015.