

Review Rattanavaraha et al., ACPD doi: 10.5194/acp-2015-983, 2016

General comments:

The focus of this manuscript is on the relationships between isoprene SOA markers and anthropogenic parameters such as sulfate and NO_x during a field campaign conducted in Birmingham (BHM), Alabama, an urban site in the southeastern USA, where regional isoprene emissions from deciduous trees and local anthropogenic emissions (SO₂ and NO_x) are substantial. The study reveals the complexity and potential multitude of chemical pathways leading to isoprene SOA formation. It is interesting to learn that ozone also plays a role in forming isoprene SOA. It is interesting to learn that ozone also plays a role in forming isoprene SOA. It is very evident from this field study that the IEPOX-related SOA markers contributed by far the most, while the methacrolein-related tracers were rather minor. It is also shown that acidity is not a limiting factor for isoprene SOA formation at the BHM site. Understanding the formation mechanisms of biogenic SOA, especially with regard to anthropogenic emissions, is indeed important for the development of more accurate models that are needed for PM_{2.5} control abatement strategies. I only have some specific issues (mostly minor), which would profit from clarification.

Specific comments:

Lines 229-230: The EIC of *m/z* 199 was used to quantify the MAE/HMML-derived OS. It has been quite well established that the major MAE-derived OS that is present in ambient fine aerosol is 3-sulfooxy-2-hydroxy-2-methylpropanoic acid with a terminal sulfooxy group (Gómez-González et al., 2010). There is, to my knowledge, no chemical evidence for a HMML-derived OS containing a terminal hydroxymethyl group. Therefore, it would be best to be more conservative here and write: “..... to quantify the MAE-derived OS,”

Ref.: Gómez-González, Y., Surratt, J. D., Cuyckens, F., Szmigielski, R., Vermeylen, R., Jaoui, M., Lewandowski, M., Offenberg, J. H., Kleindienst, T. E., Edney, E. O., Blockhuys, F., Van Alsenoy, C., Maenhaut, W., and Claeys, M.: Characterization of organosulfates from the photooxidation of isoprene and unsaturated fatty acids in ambient aerosol using liquid chromatography/(-) electrospray ionization mass spectrometry, *J. Mass Spectrom.*, 43, 371–382, 2008.

Line 238: Mention is also made here of glyoxal-, methylglyoxal and hydroxyacetone-derived OS, but earlier in the introduction nothing is said about the chemical pathways leading to these products. For completeness, I suggest to briefly provide some background information about these pathways.

Lines 335-337: It is mentioned that the IEPOX-derived SOA tracers comprised 92.5% of the total detected SOA tracer mass. To arrive at this value the 2-methyltetrols should not be counted twice, since they are also formed from IEPOX OS in the analytical GC/MS procedure by hydrolysis of the corresponding OS. How was this value of 92.5% estimated?

Line 340: See comment about MAE/HMML-OS above.

Lines 359-361: It is not clear what the authors want to say by writing: “The low isoprene SOA/OM ratio is consistent with the low WSOC/OC reported in section 3.1, suggesting an increased contribution of

primary OA or secondary OM to the total OM at BHM". Some clarification should be given about the secondary OM; perhaps this should be better described as "hydrophobic secondary OM", originating from anthropogenic emissions.

Lines 386-408: Throughout this section, MAE/HMML OS is mentioned several times. See comment about MAE/HMML-OS above.

Section 3.3.2 Effect of O₃: It is very interesting to learn that O₃ has an effect on 2-methyltetrol formation, but not on C₅-alkene triol formation, consistent with a recent study by Riva et al. (2015). What I am missing here is some brief mechanistic information about 2-methyltetrol formation from isoprene by the action of O₃, so that the interested reader does not have to look up the original article. I am also curious to know whether there was an intercorrelation between the 2-methyltetrols and the C₅-alkene triols; a strong intercorrelation would support that they both are formed through the IEPOX multiphase pathway.

Technical corrections:

Line 35: coupled to electrospray ionization high-resolution quadrupole time-of-flight mass spectrometry

Line 148: to measure known or to determine quantities of

Line 176: and NO_x were forecast by

Line 254: baked at 500 °C for (space before "°C")

Line 258: The abbreviation "PTFE" needs to be introduced here.

Line 352: based on recent studies

Line 419: NO₃-initiated oxidation

References: titles of journal articles should not be capitalized; some still are and should be corrected.

Line 807: trans-3-methyl-3,4-dihydroxytetrahydrofuran,

Figure 2 – panel (d): the trace for MAE-OS in light purple/rose color is hardly visible.