

Response to Anonymous Referee # 1

We thank Referee # 1 for the comments and address each below. Our author responses are denoted in blue texts.

Interactive comment on “Assessing the impact of anthropogenic pollution on isoprene-derived secondary organic aerosol formation in PM_{2.5} collected from the Birmingham, Alabama ground site during the 2013 Southern Oxidant and Aerosol Study” by W.Rattanavaraha et al.

Anonymous Referee # 1

Received and published: 16 February 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 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-methyl propanoic 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., Vermeulen, 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.

We agree that only MAE-derived OS can be quantified by the authentic MAE-derived OS synthesized in-house. Thus, we remove the term HMML in the experimental section.

We have revised the sentence as follows on Page 11, Lines 242-243:

“EICs of m/z 215, 333 and 199 were used to quantify the IEPOX-derived OS, IEPOX-derived dimer OS and the MAE-derived OS, respectively (Surratt et al., 2007a).”

We have also revised the sentence as follows on Page 11, Lines 247-249:

“The MAE-derived OS was quantified using an authentic MAE-derived OS standard synthesized in-house by a procedure to be described in a forthcoming publication (¹H NMR trace, Figure S2).

However, as described in the introduction section, recent studies (Surratt et al., 2006; Surratt et al., 2010; Lin et al., 2013a; Nguyen et al., 2015) have shown that isoprene is oxidized under high-NO_x conditions to yield methacrolein, which is then further oxidized by OH radicals in the presence of NO₂ to yield methacryloylperoxynitrate (MPAN). When MPAN is oxidized by OH it

yields at least two SOA precursors, including methacrylic acid epoxide (MAE) and hydroxymethyl-methyl- α -lactone (HMML). MAE and HMML can yield 2-methylglyceric acid (2-MG) and its OS derivative (Lin et al., 2013a; Nguyen et al., 2015). As a result, the MAE-derived OS tracer we measured could likely be derived from both MAE and HMML, even though the existence for HMML has only been indirectly measured by Nguyen et al. (2015). As a result, we will continue using the terminology MAE/HMML-derived OS in the subsequent sections of the manuscript to remind readers about the potential contribution from both MAE and HMML pathways. To be clearer on this issue, we added the following sentences on Pages 11-12, Lines 249-256:

“Although the MAE-derived OS (Gómez-González et al., 2008), which is more formally called 3-sulfoxy-2-hydroxy-2-methyl propanoic acid, has been chemically verified from the reactive uptake of MAE on wet acidic sulfate aerosol (Lin et al., 2013a), the term MAE/HMML-derived OS will be used hereafter to denote the two potential precursors (MAE and HMML) contributing to this OS derivative as recently discussed by Nguyen et al. (2015). It should be noted that Nguyen et al. (2015) provided indirect evidence for the possible existence of HMML. As a result, further work is needed to synthesize this compound to confirm its structure and likely role in SOA formation from isoprene oxidation.”

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.

We agree with the referee’s comment. We have added the following information into the introduction section on Pages 5-6, Lines 111-117:

“In addition to MACR, other key oxidation products of isoprene, including glycolaldehyde, methylglyoxal, and hydroxyacetone, can undergo multiphase chemistry to yield their respective OS derivatives (Olsen et al., 2011; Schindelka et al. 2013; Shalamzari et al., 2013; Noziere et al., 2015). However, the contribution of isoprene on the glyoxal-, methylglyoxal-, and hydroxyacetone-derived OS mass concentrations in the atmosphere remains unclear since these

SOA tracers can also be formed from a wide variety of biogenic and anthropogenic precursors (Galloway et al., 2009, Liao et al., 2015)."

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?

We agree with the point suggested by the referee. Thus, we did additional quality control experiments to investigate the exact impact of the IEPOX-derived OS during the GC/MS procedure and analysis. We directly injected known concentrations (i.e., 1, 5, 10, and 25 ppmv) of the IEPOX-derived OS standard into the GC/MS following trimethylsilylation. We found the signals of 2-methylthreitol and 2-methylerythritol derived from the GC/MS analysis of IEPOX-derived OS were small (1.69% and 2.42%, respectively). We corrected for this effect in the estimation of IEPOX-derived SOA to the total detected SOA tracer mass in our manuscript. The revised estimation is now 92.45%, which did not significantly change from the original value of 92.5%.

However, we decided to use the revised estimation and added this information in the main text as follows in Section 2.2.2, Pages 10-11, Lines 226-231:

"To investigate the effect of IEPOX-derived OS hydrolysis/decomposition during GC/EI-MS analysis, known concentrations (i.e., 1, 5, 10, and 25 ppmv) of the authentic IEPOX-derived OS standard (Budisulistiorini et al., 2015)) were directly injected into the GC/MS following trimethylsilylation. Ratios of detected 2-methyltetrols to the IEPOX-derived OS were applied to estimate the total IEPOX-derived SOA tracers in order to avoid double counting when combining the GC/MS and UPLC/ESI-HR-QTOFMS SOA tracer results."

We also added the following clarifying information in Section 3.2, Pages 16-17, Lines 357-363:

"Our investigation for the potential of OS hydrolysis/decomposition during GC/EI-MS analysis

demonstrated that only 1.7% of 2-methylthreitol and 2.4% of 2-methylerythritol could be derived from the IEPOX-derived OSs. In order to accurately estimate the mass concentrations of the IEPOX-derived SOA tracers, we took this effect into account. Together, the IEPOX-derived SOA tracers, which represent SOA formation from isoprene oxidation predominantly under the low-NO_x pathway, comprised 92.45% of the total detected isoprene-derived SOA tracer mass at the BHM site.”

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

As described above, we decided to use the terminology “MAE/HMML-OS” in the Results and Discussion section to emphasize its formation pathway. We did this as follows on Pages 11-12, Lines 249-256:

“Although the MAE-derived OS (Gómez-González et al., 2010), which is more formally called 3-sulfoxy-2-hydroxy-2-methyl propanoic acid, has been chemically verified from the reactive uptake of MAE on wet acidic sulfate aerosol (Lin et al., 2013a), the term MAE/HMML-derived OS will be used hereafter to denote the two potential precursors (MAE and HMML) contributing to this OS derivative as recently discussed by Nguyen et al. (2015). It should be noted that Nguyen et al. (2015) provided indirect evidence for the possible existence of HMML. As a result, further work is needed to synthesize this compound to confirm its structure and likely role in SOA formation from isoprene oxidation.”

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.

We agree with the referee. The sentence has been revised as follows on Pages 17-18, Lines 385-387:

“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 hydrophobic secondary OM originating

from anthropogenic emissions to the total OM at BHM.”

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

Since this comment was already raised above by the reviewer, please refer to our replies above in how we exactly dealt with this reviewer comment.

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. (2016). 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-alkenetriols; a strong intercorrelation would support that they both are formed through the IEPOX multiphase pathway.

We agree with the referee's comment. We have added brief mechanistic information about 2-methyltetrol formations from isoprene ozonolysis as follows on Pages 22-23, Lines 491-501:

“Previous studies (Nguyen et al., 2010; Inomata et al., 2014) proposed that SOA formation from isoprene ozonolysis occurs from stabilized Criegee intermediates (sCIs) that can further react in the gas phase to form higher molecular weight products that subsequently partition to the aerosol phase to make SOA. Recent work by Riva et al. (2016) systematically demonstrated that isoprene ozonolysis in the presence of wet acidic aerosol yields 2-methyltetrols and organosulfates unique to this process. Notably, no C₅-alkene triols were observed, which are known to form simultaneously with 2-methyltetrols if IEPOX multiphase chemistry is involved (Lin et al., 2012). Riva et al. (2016) tentatively proposed that hydroperoxides formed in the gas phase from isoprene ozonolysis potentially partition to wet acidic sulfate aerosols and hydrolyze to yield 2-methyltetrols as well as the unique set of organosulfates observed (Riva et al., 2016). Additional work using authentic hydroperoxide standards is needed to validate this tentative hypothesis.”

Regarding an intercorrelation between the 2-methyltetrols and the C₅-alkene triols, we observed

a strong correlation ($R^2 = 0.84$) during nighttime suggesting that they both are formed through the IEPOX multiphase pathway. However, a mild correlation ($R^2 = 0.55$) is observed during daytime suggesting that O_3 may contribute some fraction on 2-methyltetrols formation which is in agreement with the key finding from isoprene ozonolysis by Riva et al., 2016.

Technical corrections:

Line 35: coupled to electrospray ionization high-resolution quadrupole time-of-flight massspectrometry.....

We made the correction as the referee suggested on Page 2, Lines 33-37:

“Sample extracts were analyzed by gas chromatography/electron ionization-mass spectrometry (GC/EI-MS) with prior trimethylsilylation and ultra performance liquid chromatography coupled to electrospray ionization high-resolution quadrupole time-of-flight mass spectrometry (UPLC/ESI-HR-QTOFMS) to identify known isoprene SOA tracers.”

Line 148:.....to measure known.....or.....to determine quantities of..... .

We made the correction as the referee suggested on Page 7, Lines 152 - 156:

“The analysis of $PM_{2.5}$ was conducted in order to determine quantities of known isoprene SOA tracers and using collocated air quality and meteorological measurements to investigate how anthropogenic pollutants including NO_x , SO_2 , aerosol acidity (pH), $PM_{2.5}$ sulfate (SO_4^{2-}), and O_3 affect isoprene SOA formation.”

Line 176:..... and NO_x were forecast by.....

We made the correction as the referee suggested on Pages 8-9, Lines 180-184:

“The intensive sampling schedule was conducted on days when high levels of isoprene, SO_4^{2-} and NO_x were forecast by the National Center for Atmospheric Research (NCAR) using the Flexible Particle dispersion model (FLEXPART) (Stohl et al., 2005) and Model for Ozone and Related Chemical Tracers (MOZART) (Emmons et al., 2010) simulations.”

Line 254:..... baked at 500 degrees C for.....(space before degrees C)

We made the correction as the referee suggested on Pages 12-13, Lines 273-275:

“To maintain low background carbon levels, all glassware used was washed with water, soaked in 10% nitric acid, and baked at 500 °C for 5 h and 30 min prior to use.”

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

We made the correction as the referee suggested on Page 13, Lines 278-279:

“Extracts were then passed through a 0.45 μm polytetrafluorethylene (PTFE) filter to remove insoluble particles.”

Line 352:..... based on recent studies.....

We made the correction as the referee suggested on Page 17, Lines 377-379:

“Isoprene SOA contribution to total OM was estimated by assuming the OM/OC ratio 1.6 based on recent studies (El-Zanan et al., 2009; Simon et al., 2011; Ruthenburg et al., 2014; Blanchard et al., 2015).”

Line 419:.....NO₃-initiated oxidation.....

We made the correction as the referee suggested on Page 21, Lines 457-459:

“However, Schwantes et al. (2015) demonstrated that NO₃-initiated oxidation of isoprene yields isoprene nitrooxy hydroperoxides (INEs) through nighttime reaction of RO₂ + HO₂, which upon further oxidation yielded isoprene nitrooxy hydroxyepoxides (INHEs).”

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

We made the correction as the referee suggested in the reference section.

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

We made the correction as the referee suggested on Pages 37-38, Lines 884-887:

“Zhang, Z., Lin, Y.-H., Zhang, H., Surratt, J., Ball, L., and Gold, A.: *Technical Note: Synthesis of isoprene atmospheric oxidation products: isomeric epoxydiols and the rearrangement products cis-and trans-3-methyl-3,4-dihydroxytetrahydrofuran*, *Atmos. Chem. Phys.*, 12, 8529-8535, 2012”

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

We made the correction as the referee suggested for Figure 2 panel (d). The colors in panel (d) were improved for better visibility.

References

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