Atmos. Chem. Phys. Discuss., 15, C12903–C12909, 2016
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Interactive comment on “Characterization of polar organosulfates in secondary organic aerosol from the unsaturated aldehydes 2-E-pentenal, 2-E-hexenal, and 3-Z-hexenal” *by* M. S. Shalamzari et al.

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Received and published: 1 March 2016

We thank this reviewer for thoughtful and detailed comments, and constructive criticism. Our responses to the detailed comments are as follows:

1. The importance of this research, potentially the SOA forming potential of green leaf volatiles (GLV) should be more thoroughly developed in the Introduction as suggested by Reviewer 1. For example, what is the potential impact of GLV relative to the more widely studied isoprene and monoterpenes, particularly in terms of emissions and SOA

yields? How does its potential impact vary with respect to anthropogenic activity, temperature, and season? What is the potential for GLV to contribute to OS?

Response: The request to comment on the importance of this research in the introduction was also made by reviewer #1. See our response to the general comments raised by this reviewer.

2. Please add the following methodological details: a. The supplier and purity of methanol (page 29563, line 8) b. The duration of sonication for extraction (page 29563, line 8) c. Clarify which of the sample aliquots was analyzed (frozen or not) and the purpose of splitting the two aliquots (page 29563, line 16). d. The conditions under which the ambient samples were stored, since their collection in 2006 (section 2.2.3). e. Clarification is needed regarding the similarity/difference between the two columns used (page 29565, line 2). What was chemically different that impacts retention, or are these interchangeable?

Responses:

(a) The supplier and purity of methanol were mentioned in the original text: Page 29562, lines 3-5.

(b) The duration of sonication for extraction has been mentioned in the revised version: “The filters were extracted 3 times with 10 mL of methanol in an ultrasonic bath for 10 min.”

(c) This section has been clarified as follows: “The residue was redissolved in 1 mL of methanol and divided in two portions, because not all analyses could be performed at the same time. A fresh or unfrozen portion was redissolved in . . ...”.

(d) For this information, we refer to a previously published article, where the temperature at which the samples were stored is mentioned (i.e., –25 âĄřC): “Information about the site, sampling campaign and storage of samples can be found in a previous article (Maenhaut et al., 2008).”

(e) The elution order of the targeted compounds was found to be the same but the retention times on the HSS T3 column used for UPLC were shorter. Information on the retention times of the targeted organosulfates has been included. This section has been expanded as follows: Page 29565, line 5: "……which, as the Atlantis T3 column (Waters), contains a stationary phase based on trifunctionally-bonded C18 chains and results in the same elution order for the targeted organosulfates. The retention times on the HSS T2 column were: sulfuric acid, 0.60 min; 2-methyltetrol organosulfates, 0.80 and 0.91 min; 3-sulfooxy-2,4-dihydroxypentanoic acid, 0.62 min; 2-sulfooxy-3-hydroxypentanoic acid, 0.65 min; 3-sulfooxy-2-hydroxypentanoic acid, 0.91 min; 1-sulfooxy-2-hydroxybutane, 1.45 min."

3. The chromatograms shown in Figure 1 (especially A, B, D, and E) reveal early elution of the major organosulfates (OS) products. It is not clear the extent that these compounds retain relative to unretained components (e.g. sulfate). To clarify this point, the authors should provide the retention time of the solvent front / unretained component and briefly discuss the retention of these compounds relative to the solvent front. Notably, the results do not appear to support the rather strong statement that the Atlantis T3 column "provides retention for the organosulfates compounds under investigation" (page 29564, line 20).

Response: We admit that the identified organosulfates only show a limited retention on the Atlantis T3 column. If we would have to start this work all over again we would consider using a HILIC column, as used in a recent study by Hettiyadura et al. (2015). To address this comment, the retention times of the solvent front (containing unretained material) and sulfuric acid have been mentioned in the legend of Figure 1: "The retention times of the solvent front (containing unretained material) and sulfuric acid, which can be seen in the BPC, were 2.0 and 2.3 min." In addition, we have weakened our statement on the retention of the targeted polar organosulfates on the Atlantis T3 column (page 29564, line 20): "provides some retention for the polar organosulfate compounds under investigation."

4. The authors suggest that m/z 213 is an organosulfates unique to GLV (page 29565, line 22; 29560, line 25), overlooking its initial detection in SOA generated from isoprene (Surratt et al. 2008). Because isoprene is a major contributor to biogenic SOA, it is likely also a dominant source of m/z 213 (even if the relative abundance of m/z 215 is lower).

Response: We are well aware of the detection of m/z 213 organosulfates in isoprene SOA, since we were closely involved in the research. However, we failed to detect these compounds in SOA collected from an isoprene/NOx/SO2 photooxidation experiment conducted at the US EPA, which, in our experience better simulated the formation of organosulfates formed under ambient conditions, such as, for example, the m/z 305 organosulfates, which are also discussed in the Surratt et al. (2008) paper. Furthermore, interpretation of the MS data does not suggest a branched isoprene skeleton related to the m/z 215 2-methyltetrol sulfates with a terminal aldehyde but a linear structure. For these reasons, no further attention was paid in the present work to isoprene as a possible precursor for the m/z 213 organosulfates. There was written in the Surratt et al. (2008) paper: "It should be noted that the m/z 213 compounds were not detected by Gómez-González et al. (2008) in the aerosol collected from an isoprene/NOx/SO2 EPA photooxidation experiment."

5. The authors should not use relative abundance to compare m/z 229 formation between 2-pentenal to hexenal, as this depends on the response of other components of the sample. Any quantitative comparison should be done using absolute abundance normalized to the amount of organic carbon extracted.

Response: The sentence has been rephrased as follows: "Selected LC/MS data (m/z 229 EICs and MS2 spectra) for SOA generated from 2-E-hexenal and 3-Z-hexenal, showing that m/z 229 compounds are also formed, are provided in Fig. S1 of the Supplement."

6. The OS formulas in Table 2 and in the results and discussion are anionic and should

be indicated as such with a superscripted negative symbol.

Response: The suggested corrections have been made.

7. Does the MS data (e.g. base peak chromatogram) support that the later-eluting m/z 229 peaks in the 2-E-hexenal SOA have a molecular ion of m/z 229, such that these are isomers (as suggested on page 29567, line 6)? It is also plausible that m/z 229 may be a fragment ion of later-eluting compounds.

Response: It was confirmed that the later-eluting m/z 229 peaks in 2-E-hexenal and 3-Z-hexenal SOA (Fig. S1) have a deprotonated molecule at m/z 229 and were not due to fragment ions of other species. As this is quite a standard practice in MS analysis to perform checks like this, we did not consider it necessary to mention this in the manuscript.

8. The first line of section 3.3 appears erroneous. The chromatogram shows only one m/z 229 peak for 2-E-pentanal, while the text suggests “stereoisomeric forms.”

Response: For clarity, we have deleted the adjective “stereoisomeric” here; however, it should be realized that there are several stereoisomeric forms possible, theoretically eight, which cannot or only partially be chromatographically separated. This feature is discussed earlier in the manuscript (Page 29567, lines 10-15).

9. The structures proposed in Table 2 and described in the text are “tentatively identified” based on MS data and should be clearly noted as such. These structures may only be unequivocally confirmed using structurally-matched standards.

Response: We concur with this criticism and have made appropriate changes in several places in the text and in the heading of Table 2.

10. Figure 4 and section 3.4. The author’s results and conclusions from the quantum chemical calculations are not clear. In particular, the meaning of “accommodated” in the statement in the caption “the negative charge can be accommodated by the carboxyl group” is not clear. Please use chemical terminology and free energies to explain the different behavior of these ions. Without more thorough discussion and clarification, these results have very limited value and should be removed.

Response: Section 3.4 has been thoroughly revised, as suggested. See our reply to the comment made by reviewer #1.

11. Technical comments on Table 1 a. Sample codes should be removed as these are not of use to the scientific community. b. The seed type and concentration should be presented as “AS:SA (1/1, w/w)” as done in the text, instead of 1 2 + 1 2 . c. The footnote should be revised to account for the NO2 contaminant (0.3%).

Response: The sample codes (experiment numbers) have been kept, but the other suggested corrections have been made. The experiment numbers may be meaningless to the average reader, but if a reader wants to request additional information about the experiments, those numbers make it far easier for us to address that request quickly and accurately. Also, if these same experiments are analyzed again and used in another paper, the experiment numbers make it much easier to make connections between the papers.

12. Presentation of Figures a. The MS/MS spectra shown in Figures 2 and 3 may be moved to the supplement, as the relevant data are summarized in Table 2. b. Figure 1 should be removed, as chromatograms in Figure 1c, 1d, 1e are duplicated in Figure 2, 3, and 4. Unique parts of Figure 1 a and b are not discussed in detail and may also be moved to the supplement, or removed.

Response: We prefer to keep all figures. For example, Figure 1 is useful to get an idea about the peak areas of the targeted organosulfates compared to those of the isoprene SOA-related 2-methyltetrol sulfates (m/z 215), which is clearly mentioned in the text, while the base peak chromatogram, shown at the top, also shows all compounds, including unretained material eluting in the solvent front and sulfuric acid. The latter information has been mentioned in the legend to Figure 1 of the revised text. With respect to removing Figures 2 and 3, we also prefer to keep them, because we already present the data obtained for 2-E-hexenal and 3-Z-hexenal in the supplement. Table 2 only provides limited MS/MS information, only m/z values of product ions but no relative abundances.

13. Abstract (page 29557, line 22) “sulfoxy” should be “sulfooxy” 14. Section 3.3 (page 29567, line 27) “is also a” should be “is also an”

Response: The corrections have been made.

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 29555, 2015.