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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.

Anonymous Referee #2

Received and published: 23 December 2015

The manuscript “Characterization of polar organosulfates in secondary organic aerosol from the unsaturated aldehydes...” presents new, qualitative information about organosulfates formed from green leaf volatiles. This adds new information to a growing body of literature about organosulfates formed from biogenic VOC, through the study of three biogenic SOA precursors that have not been previously studied in this regard to organosulfate formation. As noted by Reviewer 1, the atmospheric relevance and particularly their importance in SOA formation, relative to the more widely studied isoprene and monoterpenes, requires further development prior to acceptance. The

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MS/MS results are carefully analyzed and presented. The detailed MS/MS data in Table 2 will likely be useful to other researchers qualitatively identifying organosulfates in ambient aerosol. The quantum chemical calculations, however, are not adequately presented or discussed. The distinction between the two structures is not clear, and the meaning of the negative charge being “accommodated” is unknown. Free energies and chemical terminology should be employed to develop a more robust discussion. Otherwise these data should be removed. Suggestions to improve the presentation of results through the text, figures, and tables are provided in detailed comments below.

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

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?

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

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T3 column “provides retention for the organosulfates compounds under investigation” (page 29564, line 20).

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).

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.

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.

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.

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.”

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.

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

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explain the different behavior of these ions. Without more thorough discussion and clarification, these results have very limited value and should be removed.

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 $\frac{1}{2} + \frac{1}{2}$. c. The footnote should be revised to account for the NO₂ contaminant (0.3%).

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.

Minor comments

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"

Work cited

Surratt, J. D., Y. Gomez-Gonzalez, A. W. H. Chan, R. Vermeylen, M. Shahgholi, T. E. Kleindienst, E. O. Edney, J. H. Offenberg, M. Lewandowski, M. Jaoui, W. Maenhaut, M. Claeys, R. C. Flagan and J. H. Seinfeld (2008). "Organosulfate formation in biogenic secondary organic aerosol." *Journal of Physical Chemistry A* 112(36): 8345-8378.

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