

## ***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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We would like to thank the reviewer for thoughtful and constructive comments. Our responses to the detailed comments are as follows:

General comments: My main criticism of the paper is that it is difficult to really understand the impact of this chemistry on a wider scale. The paper is very technical and describes the analysis well. But at the end I'm left wondering whether these are actually important or if they are just well suited to the analysis method. Do the authors

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think this is a large source of SOA? Is it a global source, regional or local? There is no mention of the potential for anthropogenic emissions of GLV from grass cutting in domestic and within cities (i.e. could they be more important than isoprene OS in these environments?). Do the authors think these species are likely to be found in cities where biogenic and anthropogenic emissions mix. What are the potential impacts of this source?

Response: It is still too early to understand the impact of this GLV chemistry on a wider scale. Unfortunately, there is very little information about emissions of GLVs compared to those of isoprene and terpenes in different environments and even less about SOA formation. However, we believe that GLV chemistry can be of a regional and local importance. GLV emissions in agricultural areas where crops are harvested could be important as well as those in urban residential areas where grass is mown. It has also been reported that lawn mowing contributes to atmospheric aerosol levels in American suburbs (Harvey et al., 2014). It should be noted that the investigated ambient aerosol was from K-puszta, Hungary, a rural area with intensive agriculture, where at the time that the samples were collected (May-June) hay was harvested and crops were cultivated. It is known that herbivory, mechanical injury or pathogen infestation to vegetative tissue of cereal grasses can induce VOC production (Piesik et al., 2011; Brilli et al., 2012). As to urban residential areas, we have some data about a site in Belgium (i.e., a polluted residential/forest site in Brasschaat, Antwerp), where a MW 226 organosulfate, originating from 3-Z-hexenal (Shalamzari et al., EST 2013), could be detected with a substantial relative abundance: the concentration of this compound was on average  $6.8 \pm 10.1 \text{ ng m}^{-3}$  versus  $9.0 \pm 11.6 \text{ ng m}^{-3}$  measured for the isoprene SOA-related 2-methyltetrol sulfates (Gómez-González et al., ACP 2012). It is thus well possible that in urban residential areas GLV chemistry might be as important as isoprene chemistry. However, more research is necessary to support this hypothesis. The introduction has been expanded with the following sentences: “It should be noted that the investigated ambient aerosol was from K-puszta, Hungary, a rural area with intensive agriculture, where at the time that the samples were collected (May-June) hay was harvested and

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crops were cultivated. GLV chemistry might be important on a regional and local scale where emissions such as from grasses and cereal crops are substantial. It is also well possible that in urban residential areas GLV chemistry might be as important as isoprene chemistry. A field study conducted at a site in Belgium (i.e., a polluted residential/forest site in Brasschaat, Antwerp) indicated substantial concentrations of a m/z 225 organosulfate, originating from 3-Z-hexenal, i.e.,  $6.8 \pm 10.1 \text{ ng m}^{-3}$  versus  $9.0 \pm 11.6 \text{ ng m}^{-3}$  for the isoprene SOA-related 2-methyltetrol sulfates (Gómez-González et al., 2012).

Specific comments:

Abstract: This needs some text on the relevance of the findings. (see comments above).

Response: The abstract has been expanded as follows taking into account the above general comments: "This chemistry could be important on a regional and local scale where GLV emissions such as from grasses and cereal crops are substantial."

Page 29559, line 27: Change to "reaction of sulphuric acid with epoxide containing"

Response: Suggested correction has been made.

Page 29560, line 17: Here and throughout there are a lot of sentence that start with "AS to". This makes the sentences rather long and hard to follow. Often the sentence just needs to be reversed to be clearer i.e. "It was shown that. . . . . bulk sulphur mass at K-puszta in Hungary"

Response: Suggested changes have been made.

Page 29560, line 27: What do mean by "magnitude"? Is this ion abundance?

Response: With "magnitude" we mean here the peak area observed in the extracted ion chromatogram. This has been clarified in the revised text.

Page 29561, line 11: I think it needs to be clearer here that you are actually character-

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izing OS from E-pentenal in particular and that the other VOC precursors fall apart to give E-pentenal. I was confused reading this why you were only talking about one set of OS but 3 precursor.

Response: This section has been clarified as follows: "In order to chemically characterize the unknown OSs from 2-E-pentenal, 3-Z-hexenal and 2-E-hexenal in detail laboratory smog chamber experiments were conducted in the present study, and the organosulfate profiles were compared with those of ambient fine (PM2.5) aerosol collected from K-puszta, Hungary, a rural site with mixed deciduous-coniferous vegetation. Only the results obtained for 2-E-pentenal SOA are discussed, because it was found that 2-E-hexenal and 3-Z-hexenal SOA contains the same OSs."

Line 18: Change "resorting" to "using". Page 29562, line 8, sentence doesn't make sense – preparing used twice. Line 15: I am not sure you need to explain which VOCs you are using again. Take out "selected". Page 29563, line 24: Change to "some adaptations". Page 29564, line 4: Change to "and the 2-E-pentenoic acid reaction products were

Response: Suggested changes have been made.

Page 29565, line 25: I think it needs to be clearer what you mean by "substantial relative abundance" Do you mean peak area, ion intensity?

Response: By "substantial relative abundance" we mean "peak area" here.

Page 29567, line 28: watch tense, only 1 reaction 1.

Response: Correction has been made.

Page 29568, line 3 plus figure: This reaction scheme seems unlikely. Surely the second attack of this molecule will take place at the double bond? Do the authors have an explanation of the reaction adjacent to the unsaturated bond.

Response: We have done an attempt here to explain the formation of MW 230 OSs

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from 2-E-pentenal but have to admit that it is somewhat speculative. Unfortunately, we could not come up with an alternative explanation to accommodate the second hydroxyl group at the C-4 position in the identified MW 230 OS.

Page 29569, line 10: I am not entirely convinced by this explanation. Why is this seen for this peak only? The retention time is not much different but the shape is much worse.

Response: We have tried to find a possible explanation for the unusual chromatographic behavior of the m/z 213 isomers present in 2-E-pentenal SOA. We have thoroughly reflected on this phenomenon and have to admit that we cannot come up with a more convincing explanation. In our experience the 2-E-pentenal SOA was much more hydrophobic than the ambient extract in the sense that it was more difficult to dissolve it in the solvent mixture used for LC/MS analysis (i.e., methanol:water; 1:1, v/v). We also have injected the 2-E-pentenal SOA sample in a more diluted form but the peak shapes did not improve.

Line 17: give retention time for second isomer.

Response: The retention time of the second isomer has been provided: 3.7 min.

Line 23-27: I don't think this section is explained particularly well. And the reasoning is hard to follow. Needs more.

Response: The reasoning becomes easier to follow if in addition to Figure 4 (revised) also Scheme 3bis consulted. This section has been revised as follows, also taking into account the concerns of reviewer #2, who requested a thorough discussion using chemical terminology and free energies: "The distinctly different fragmentation behavior of the two isomers was addressed through quantum chemical calculations. Figures 4a and 4b display the lowest-energy conformers of the acid with the sulfate group at C-3 and C-2, respectively. Transfer of the carboxyl proton to the oxygen atom linked to C-3 and C-2, respectively, followed by geometry optimization leads to loss of SO<sub>3</sub> by

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breaking the relevant sulfur-oxygen bond, for both isomers: the resulting structures are presented in Figs. 4c and 4d, respectively. However, the energetics of both processes are different: while for the C-3 isomer (Figs. 4a and 4c) this is accompanied by an energy increase of 85.30 kJ.mol<sup>-1</sup>, the corresponding value for the C-2 isomer (Figs. 4b and 4d) is 128.41 kJ.mol<sup>-1</sup>, or just over 50% higher. This suggests that the loss of SO<sub>3</sub> is considerably less unfavorable for the C-3 isomer than for the C-2 isomer, in agreement with the observations from the mass spectra."

Page 29571, line 12: Don't think you need to explain the structure of methacrolein.

Response: Correction has been made.

Page 29581, table 2: The top section is confusing, making you think it is somehow related to the rest of the table. I would remove this. I don't think you need to give the structures of the precursors. I would like to see Rt in this table.

Response: The top section has been deleted and RTs have been added.

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

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