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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Qualitative and Quantitative Analysis of Atmospheric Organosulfates in Centreville, Alabama" *by* Anusha P. S. Hettiyadura et al.

Anonymous Referee #2

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The manuscript by Hettiyadura et al. presents measured organosulphate (OS) concentrations in aerosol from the South East US from a four-day period during the SOAS campaign in the summer of 2013 at Centreville, Alabama. OS are an important contributor not necessarily due to their contribution to PM mass, but because they are the result of multi-phase processes and anthropogenic influence. The stated goals of the study are (i) quantification of OS (for which authentic standards are available) in PM2.5, (ii) assessment of filter sampling artefacts, and (iii) identifying major OS in Centreville.

The analytical work is very thorough using state-of-the-art methods and the finding on the filter artefacts will be important for future work on OS. Similarly, the progress toward identifying/ruling out isomers/functional groups is an important contribution. The main

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concerns I have that should be addressed before publication is considered are clearer statements on the broader impact/significance beyond the analytical approach/work.

Major comments:

1. In order for the measurements to have significance beyond the very nice analytical method and artefact description and not simply be an anecdotal note of specific OS, it is critical to describe to what degree the very limited 4 day period was representative. As there was a plethora of measurements obtained at the Centreville site this should be easy. For example, where temperature, photochemical conditions, NOx conditions, amount of PM typical and, even more importantly, how variable were these conditions and is there any correlation with the observed OS variability shown in figure 1 (see point 2). Such a description of putting the measurements within the broader context of the SOAS campaign would help readers evaluate the broader significance of the observations described here.

2. It is stated that the work is complementary to that of Riva et al. 2016. However, it would be helpful if the similarities and differences with both the work/findings by Riva et al. 2016 and Rattanavaraha et al. 2016 would be stated more explicitly. For example, which OS were not observed by the two mentioned studies and how are the results similar and different? In fact, the time series in the Riva et al. 2016 (figure 4 of that manuscript) has a much longer dataset and it shows dramatic variability for organosulfate concentrations, which directly relates to point 1. In fact, a strong recommendation would be to collaborate with the Surratt group and use their much more extensive set of filter samples for the work described here.

3. It is stated that the work provides new insights for the major OS species in the SE US. Again, it would be helpful to explicitly state what the new insights are. For example, which of the major OS had not been identified before, and if they had been identified it would be useful to describe what additional new insight is gained for each of the major species. Clearly, such new insights exist, e.g., resulting from the analytical

approach such as ruling out carboxylic acid functional groups for some OS. Ending the manuscript by stating that there are new insights but not mentioning what they are could then be improved.

In summary, it would be helpful to make it easier for readers to identify clearly the novelty of the work/findings and the significance. To this end it may make sense to reorganize findings, e.g, (i) first show the 10 major OS, (ii) highlight the work to identify functional groups and isomers, which is a very nice and important contribution, and (iii) then discuss insights/recommendations. I think this may make it easier to recognize the significance, as the interesting new findings would not be interspersed within the "long" list of ten major OS. My second recommendation is to collaborate with the Surratt group using their extensive filter sample range, if possible.

Minor comments:

P.1 line 5: "from biogenic volatile. . ." As written it implies that only BVOCs form OS?

p.1 Line 13-4: "their VOC precursors" is a little vague, as isoprene is one of the VOC precursors for OS, but I don't think the authors are implying that isoprene reacts on the filters to form SO. It would be useful to clarify.

p.1 line 19: "Most of the ten. . ." Please be specific. How many?

p.2 line 2: "PM adversely affects . . . climate" This is a matter of debate. Some would say that PM positively affects climate due to counteracting greenhouse gas radiative effects. I would consider rephrasing

p.2 line 6-7: The authors could also consider the work of Liao et al. 2015 as it discusses acid effects. Currently, only ground based studies are cited.

p.2 line 12: I think it would be more specific to state that OS may be useful markers for one type of anthropogenic influence on SOA formation from biogenic VOCs, as there surely must be aspects of anthropogenic influence that the sulphate does not represent.

p.3 line 28: My understanding is that it is not clear whether the organosulfate is from methacrylic acid epoxide (MAE)or from hydroxymethyl-methyl-alpha-lactone (HMML), see Rattanavaraha et al. 2016?

p. 3 line 31-32: I think follow-up studies (Gallowy et al. 2011 and Liao et al. 2015) showed that glycolic acid sulphate was unlikely to result from (photochemical formation) from glyoxal and that the mechanism/source was unknown? Similarly, the formation of lactic acid sulphate from methylglyoxal seems mechanistically challenging.

p. 4 line 25: Please state the total organic carbon content as resistivity does not address the content of uncharged organic compounds.

p. 5 line 7: front QFF. Although it is fairly clear, defining better what the front QFF is would be useful (actual sample QFF?)

p. 6 line 29-30: If the mass range was 400 Da, why consider up to 500 carbon atoms, corresponding to 6000 Da?

p.7 line 18-20. Please put these results in context with the ones previously mentioned by Tolocka and Turpin 2012).

p.8 line 24-27. I don't understand how the second sentence follows from the first: (i) there is some OS formation on the acidified filters, (ii) SOA is acidic enough and has high enough sulphate that these are not limiting factors. Are the authors implying that the gas-phase is already depleted of precursors or what is then limiting?

p. 9 line 3: Does "negative sampling artefact" imply destruction of the OS in question? It would be helpful to clarify and explain

p.9 line 23-24. Does this mean that not all condensed-phase is evaporated when using water with little acetonitril, i.e., that liquid water remains or just a few H2O molecules on the OS and are such signals seen? Could it be that the water takes some of the charge and that or in some other way suppresses/reduces the ionization efficiency of the OS? Please explain this effect better.

p.11 line 20. Given the very high vapour pressure of MVK and MACR is it reasonable to assume that they are present in any significant concentration in PM in the first place to be able to oligomerize?

Technical comments:

There are some grammatical errors, e.g., noun-verb agreement, and the manuscript could benefit from some proof reading. Some examples: p.2 line 13: “SAO accounts for a significant . . . and suggested. . .” p.2 Line 25 : “Among them are most abundant organosulfate has been . . .” p.2 Line 31-32: “In the absence of authentic standards, surrogate standards are commonly instead, but can” p.3 line 9: “have been discussed”, “are discussed” is perhaps more suitable p.8 line 20 “14-15: “the potential . . . were assessed” p.11 line “forms” instead of “form” p. 14 line 9. “of” instead of “to”?

There are some places where it is not quite clear what is meant, e.g.:

p.2 line 16-17: Stating that high sulphate etc. make the atmosphere subject to anthropogenic influence sounds a little odd to me. Do they actually not directly represent the anthropogenic influence?

p.8 line 9-11: “The very minor influence of . . . may be promoted . . .” I am not sure what promoting a minor influence means, and the “and possibly temperature” also seems a little out of place.

p. 3 line 8: MS2 has not been defined, I think. Some explanation of this method would be useful for readers to understand the following statements.

Galloway, M. M., Loza, C. L., Chhabra, P. S., Chan, A. W. H., Yee, L. D., Seinfeld, J. H., Keutsch, F. N.: Analysis of photochemical and dark glyoxal uptake: Implications for SOA formation, Geophys. Res. Lett. 38, L17811, doi:10.1029/2011GL048514, 2011.

Liao, J., Froyd, J. K. D., Murphy, D. M., Keutsch, F. N., Yu, G., Wennberg, P. O., St. Clair, J. Crounse, J. D., Wisthaler, A., Mikoviny, T., Jimenez, J.-L., Campuzano Jost, P., Day, D. A., Hu, W, Ryerson, T. B., Pollack, I. B., Peischl, J., Anderson, B. E., Ziemba, L. D.,

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