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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 #1

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Summary and Recommendation:

This manuscript summarizes quantitative and semi-quantitative data obtained for organosulfates chemically characterized from PM2.5 samples collected from the main ground site (Centreville, AL) during the 2013 Southern Oxidant and Aerosol Study (SOAS). This study had 3 major goals: (1) to quantify select organosulfates that had authentic standards available using HILIC interfaced to ESI-triple quadrupole mass spectrometry; (2) assess for potential positive filter sampling artifacts of organosulfates; and (3) identify other major organosulfates that should be targets for future quantification once authentic standards are available. Analytically, this paper is very solid. The authors make a serious effort in understanding potential positive artifacts of organosul-

fates and find that they have fairly small artifacts. This is good to have these results in the literature.

This paper will certainly be of interest to the broader readership of ACP since organosulfates are good indicator compounds of mulitphase chemical reactions! However, there are some weaknesses that need to be improved upon before full publication in ACP. (Weakness 1) In some parts of the manuscript the writing is unclear or not explicit enough. I will point these out in my specific comments below. (Weakness 2) If your goal was to identify the major organosulfates at CTR during the 2013 SOAS study, I'm curious as to why only 4 days of sampling were considered? Why weren't the periods of intensive sampling included? From what I understand from this campaign (Budisulistiorini et al., 2015, ACP), chemical forecasts were made when biogenic VOCs and anthropogenic pollutants (sulfate) would be high. I believe the period chosen falls outside of these periods. Further, wouldn't analyzing most of the days for organosulfates also provide stronger statistics? (Weakness 3) In section 3.1 of the results and discussion, why wasn't more work done to investigate the potential sources (VOCs and/or their oxidation products as well as reactions) of these quantified organosulfates, especially since CTR had a wealth of gas and aerosol phase data? Since you focus on the quantification of these 4 organosulfates, it seems to me it would be interesting to at least examine potential correlations with other data sets to test previously proposed mechanisms for these products. That would add some more "beef" to the scientific discussion of these organosulfates. (Weakness 4) Have the authors considered adding into their discussion of the mass contribution of organosulfates quantified previously using authentic standards to the total OC/PM mass the data from Rattanavaraha et al. (2016, ACP, Table 5). That paper included the average MAE- and IEPOX-derived OSs quantified using the authentic standards for the CTR site. I think you can use these numbers to provide further insights into the potential overall mass contribution of these organosulfates (with yours here) to the total OC/PM2.5 mass. That seems like an important thing to do here. Once you add these in, how much closer do you get to the mass fractions of organosulfates reported by Tolocka and Turpin (2012, ES&T)?

(Weakness 5) For your qualitative discussion of other major organosulfates present at CTR, what about OSs that do not fragment to the m/z 97 ion in MS2? Prior work has shown that other important organosulfates, especially from monoterpenes (like m/z 294), may produce only the m/z 96 product ion (Surratt et al., 2008, JPCA) in MS2 spectra. I would at least acknowledge that you may be missing some important organosulfates since you focus your analyses only on those that produce the m/z 97 product ion in MS2 analyses.

Specific Comments:

1.) Abstract, Page 1, Lines 18-19: You should probably emphasize that this organosulfate is derived from mulitphase chemistry of IEPOX (Surratt et al., 2010, PNAS; Lin et al., 2012, ES&T).

2.) Introduction, Page 2, Lines 2-5: Should you be more specific and emphasize that PM2.5 has these adverse effects on human health and climate as well as contains most of the SOA?

3.) Introduction, Page 2, Line 4: I would insert "atmospheric oxidation" before "reactions"

4.) Introduction, Page 2, Lines 5-6: You should rephrase this sentence to be more correct. Maybe something like: "Organosulfates, which are produced from acid-catalyzed particle-phase reactions of gaseous oxidation products, such as epoxides (Lin et al., 2012, ES&T) and hydroperoxides (Mutzel et al., 2015, ES&T), contribute to SOA."

5.) Introduction, Page 2, Line 13: Now you switch to PM2.5. You should define this since this is its first use.

6.) Introduction, Page 2, Line 25: The beginning of this sentence should be reworded, possibly to "The most abundant organosulfates to be previously quantified include....."

7.) Introduction, Page 2, Line 32: change "instead" to "used"

8.) Introduction, Page 2, Line 32: Define the acronym "(-) ESI" for the first time here.

9.) Introduction, Page 3, Line 9: change ", however" to "; however, "

10.) Introduction, Page 3, Lines 18-19: Not sure how relevant this sentence is to the discussion here. I believe the Ehn et al. (2010, ACP) study could measure extremely low vapor pressure products in the gas phase (there still of course is an equilibrium between the gas and aerosol phase) such as the glycolic acid sulfate due to the high sensitivity of their CIMS instrument.

11.) Page 3, Line 27: Change "epoxides" to "epoxydiols"

12.) Section 2.2: In this section, I would be clear on which samples were analyzed. You should also be clear on why on these samples were extracted and analyzed for this study.

13.) Page 7, Line 12: Is this an average glycolic acid sulfate concentration from this BHM study or the upper limit? Please clarify.

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