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Interactive comment on “Identification of particulate organosulfates in three megacities at the middle and lower reaches of the Yangtze River” by X. K. Wang et al.

X. K. Wang et al.

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RE: A point-to-point response to referee #3's comments

“Identification of Particulate Organosulfates in Three Megacities at the Middle and Lower Reaches of the Yangtze River” (acp-2015-393) by X. K. Wang , S. Rossignol , Y. Ma, L. Yao, M. Y. Wang, J. M. Chen , C. George, and L. Wang

We are grateful to referee #3 for his/her valuable comments, encouraging us to further improve our manuscript. A point-to-point response to this reviewer's comments is given below.

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This is the first study combining UPLC separation with UHRMS (Orbitrap) to characterize organosulfates (OSs) present in ambient samples. The UPLC separation allows detection of isomers, which offers another dimension of information in comparison with the previous fused-injection UHRMS studies of OSs. Such data is valuable in advancing our understanding of OSs, although the authors could have done a better job exploring information derived from this unique combination of information (see details in specific comments).

Reply: We are very grateful to referee #3 for his/her positive viewing of our study and we revised and improved the manuscript thoroughly according to his/her comments.

General comments

The uses of wording such as “seasonal” and “diurnal” are misleading as a very small number of samples (a total of 8 samples spread over three cities and two seasons) were characterized and it is over-stretched to argue these snapshots represent seasonal and diurnal variation for a location. The authors also noted that the NJ daytime sample was different from other (pp21425, lines 18-19), illustrating the danger of using one single sample to represent one type of atmospheric conditions). In related to this concern, the abstract needs re-phrasing to indicate sample-to-sample variation, instead of generalizing as seasonal or diurnal variation.

Reply: Our point of view was not to infer any general conclusion about seasonal or diurnal trends of OSs in China but more to describe our observations and suggest some explanations. Nevertheless, we agree that seasonal/diurnal comparisons from average values in Table 1 are not so relevant and should come along with moderate conclusions. For the Shanghai samples and corresponding manuscript section, even if we do agree that no definitive conclusion can be made about seasonal/diurnal trends with such a small dataset, we think that describing our results this way is informative and could help future more complete field campaign to identify specific points to clarify, as the presence of nitrooxy-OSs during daytime or the importance of the precursors’ seasonality

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in different locations. The manuscript was nevertheless be thoroughly edited to limit the conclusions about seasonal trends preferentially highlighting the nature/variety of the detected OSs rather than their seasonal/diurnal trends. For example, new section 3.5 is now entitled with “Comparison of OSs in the SH samples” (Page 17, Line 460) The abstract was revised accordingly

Specific comments:

1. Abstract: “. . . detection of about two hundred particulate organosulfates (OSs), including dozens of nitroxy-organosulfates. . .”. This statement appears to refer to the number of unique formulas, not counting isomers sharing the same formula. This needs to be clarified. It will also be good to indicate the number of OS chromatographic peaks detected (i.e, counting the isomers).

Reply: We now state that “. . . allowed for detection of about 200 formulas of particulate organosulfates (OSs), including dozens of formulas of nitrooxy-organosulfates. . .” (Page 2, Line 21-22).

2. Abstract: winter versus summer comparison for WH and SH is better removed or rephrased as sample-to-sample variation instead of generalizing as seasonal variation considering the small number of samples at each location and in each season (as there is only one 24-h summer sample and one 24-h winter sample in WH, one day sample and one night sample in SH in each season).

Reply: Please refer to our reply to the general comment from referee #3.

3. Considering the ability of detecting isomers is a unique result with this work, Fig. S1 deserves to be shown in the main text. I also suggest that the authors include example chromatograms showing isomer presence for a few monoterpene-derived OSs that have been reported in the smog chamber experiments and other ambient studies. For example, [M-H]⁻ at $m/z = 251.0595$ (or neutral mass 252.0673) could be a limonene derived OS. In current work, 5-7 of isomers at this neutral mass were detected, possibly

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indicating VOCs other than limonene could also be precursors. Such information is useful in guiding future LC/MS quantification of common OSs.

Reply: In the revised manuscript, we start our discussion with chromatograms that show the presence of different numbers of isomers of C₅H₁₀O₅S₁ (neutral mass = 182.0251 Da) in seven samples. Some more extracted ion chromatograms have been included in the supplement (Figure S1), including those for species H (neutral mass=295.0729 Da) derived from monoterpenes.

4. For the abundant OS formulas shown in Fig. 2 (i.e., A, B... J, K), I suggest including a table to show the isomer ratios in the samples and possible VOC precursors for these abundant OS formulas. Also comment on the ratio variability among different samples. This information can be useful for LC/MS quantification studies of OSs with lower mass resolution instruments.

Reply: This table has been added in the Supplement (new Table S4). Discussion on the isomer ratios has been added in the manuscript (Page 12, Line 332-334).

5. Figure 2 caption, line 4: a given species -> a given formula

Reply: “species” has been replaced by “formula” (Page 25, Line 11).

6. Re-organize Tables S3-S10 to list the formulas from the three sites side by side. I suggest combining into one single table to facilitate cross-sample comparison. Also include the retention time data as this also offers information on the compound polarity. It will be also helpful to label the formulas that match those reported in the smog chambers of known precursors.

Reply: Tables S3-S4 and S6-S10 were combined into one single table (new Table S3 in the supplement), to facilitate cross-sample comparison. However, data for the Nanjing daytime sample is not included because a large amount of injection (50 ul) led to corruption of peaks and hence inaccurate retention times and worse peak resolution.

7. As sulfate is the common precursor for all the OSs, the level of sulfate in each

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sample could be useful to understand the sample-to-sample variation of OSs detected. I suggest including sulfate data in the manuscript.

Reply: Unfortunately, the concentration of sulfate is not available.

8. Figs. 3 and 4: please add a brief note in the caption to indicate what the series (1, 2, 3, ...) are.

Reply: We have added “The molecular formula of the homologue series 1 to 15 can be written as $C_nH_{2n+2}SO_4$, $C_nH_{2n+2}O_1SO_4$, $C_nH_{2n}O_1SO_4$, $C_nH_{2n}O_2SO_4$, $C_nH_{2n-4}O_1SO_4$, $C_nH_{2n-2}O_2SO_4$, $C_nH_{2n}O_3SO_4$, $C_nH_{2n-4}O_2SO_4$, $C_nH_{2n-2}O_3SO_4$, $C_nH_{2n-4}O_3SO_4$, $C_nH_{2n-2}O_4SO_4$, $C_nH_{2n-4}O_4SO_4$, $C_nH_{2n-2}O_5SO_4$, $C_nH_{2n-4}O_5SO_4$, and $C_nH_{2n-4}O_6SO_4$, respectively ($n>4$)”, and “The molecular formula of the homologue series 1 to 10 can be written as $C_nH_{2n+1}NO_3SO_4$, $C_nH_{2n-1}NO_3SO_4$, $C_nH_{2n+1}ONO_3SO_4$, $C_nH_{2n-1}ONO_3SO_4$, $C_nH_{2n-1}O_2NO_3SO_4$, $C_nH_{2n-5}ONO_3SO_4$, $C_nH_{2n-3}O_2NO_3SO_4$, $C_nH_{2n-1}O_3NO_3SO_4$, $C_nH_{2n-3}O_3NO_3SO_4$, and $C_nH_{2n-3}O_4NO_3SO_4$, respectively ($n>4$)”, in the captions of Figs. 3 and 4, respectively.

9. Fig. 4 (f): series (3) appear twice but series (2) is missing.

Reply: This typo has been corrected. One mis-labelled “3” in the Fig. 4 (f) has been replaced by “2” (Page 30).

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 21415, 2015.

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