

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.

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RE: A point-to-point response to referee #2'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 #2 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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The manuscript presents results from high-resolution mass spectrometric analysis of 8 particle samples collected in three Chinese cities, and the main objective of the study is to investigate occurrence of organosulfates and nitrooxy-organosulfates. As such, the study should be very interesting, but unfortunately the presentation needs to be improved in order to communicate the findings adequately. There are numerous grammatical errors, which need to be corrected carefully before resubmission. The study is interesting and should be published once the authors have improved it according to the comments of all reviewers.

Reply: We are very grateful to referee #2 for his/her positive viewing of our study and we revised the manuscript thoroughly according to the comments of all reviewers.

General comments:

1. The study is based on eight samples, which is OK, given that the authors remember this limitation in their discussion of the findings. Examples where this need to be improved are found e.g. on pages 21428 and 21431 as well as the discussion of Fig. 5 on page 21433.

Reply: The manuscript has been thoroughly edited and improved to limit the conclusions about seasonal trends and urban variations, preferentially highlighting the nature/variety of the detected OSs rather than their temporal and spatial variations. For example, new section 3.5 is now titled with “Comparison of OSs in the SH samples” (Page 17, Line 460).

2. The introduction should refer to the first findings of organosulfates and nitrooxy-organosulfates before more recent papers (first paragraph).

Reply: We now state, before other recent papers, that “Surratt et al. (2007) were the first to identify isoprene- and α -pinene-derived OSs in ambient aerosols in the southeast US using high-performance liquid chromatography coupled with electrospray mass spectrometry” (Page 3, Line 46–48).

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3. I support the discussion brought forward by other reviewers regarding use of the word “identification”. This word should only be used, when the finding has been supported by analysis of an authentic standard.

Reply: We revised our title into “Molecular Characterization of Atmospheric Particulate Organosulfates in Three Megacities at the Middle and Lower Reaches of the Yangtze River”. In addition, we now state in our revised manuscript (Page 4, Line 85-86) that “Recently, ultra-high-resolution mass spectrometry has been applied for tentative determination of the molecular formulas of OSs in atmospheric aerosols samples” to avoid any misinterpretation of the term “identification”.

4. Number of isomers: It is not clear what the scientific explanation and interpretation is of these numbers, and why this is relevant (text + Fig. 2).

Reply: The number of isomers for a tentatively determined OS is based on the number of chromatographic peaks with the same m/z value. It corresponds to the number of molecular structures detected for a given molecular formula, and reflects another dimension of the complexity of the aerosol composition, hidden by more common direct high resolution MS analysis. In the revised manuscript, we started our discussion with chromatograms that show the presence of different numbers of isomers of C₅H₁₀O₅S (neutral mass 182.0251 Da) in seven ambient samples. In addition, the retention times of isomers for all observed OSs have been included in the supplement for future comparison (new Table S3).

Specific comments:

1. page 21418 line 7: Find a better reference than Lee et al, 2013 for this statement.

Reply: Two new references have been cited (Page 3, Line 40-42). Magari, S. R., Schwartz, J., Williams, P. L., Hauser, R., Smith, T. J., and Christiani, D. C.: The association of particulate air metal concentrations with heart rate variability, *Environmental Health Perspectives*, 110, 875-880, 2002 Ostro, B., Feng, W. Y., Broadwin, R., Green,

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S., and Lipsett, M.: The effects of components of fine particulate air pollution on mortality in California: Results from CALFINE, *Environmental Health Perspectives*, 115, 13-19, doi:10.1289/ehp.9281, 2007

2. BS -> OS several places: particulate matters -> particulate matter Materials and methods: Please add some more information on the cities and the surrounding areas.

Reply: “BS” is the abbreviation for benzyl sulfate. “particulate matters” has been replaced by “particulate matter” throughout the manuscript (Page 5, Line 103, 113). We added the population and typical metrological conditions of the three cities. The detailed information on the surrounding areas of the three sampling sites can be found in the previous studies (Zheng et al., 2015; Xiao et al., 2015; Ma et al., 2014).

3. 21422 lines 4 + 5: Ficher -> Fischer

Reply: “Ficher” has been replaced by “Fischer” throughout the manuscript (Page 6, Line 153, Page 7, Line 158, 159, 173,174).

4. 21422 line 14: Please state at least the recovery percentage here. Use of the word daily: In most places it should be replaced by “daytime”.

Reply: We have stated (Page 6, Line 163-167) that “The efficiency and the repeatability on three replicates of the extraction protocol were checked using four standards: methyl sulfate, octyl sulfate, dodecyl sulfate, and camphor sulfonic acid. The results showed that their average extraction efficiencies were 71.4, 95.0, 97.7, and 94.0%, respectively (Table S2)”. In the present manuscript, “daily sample” has been replaced by the sample IDs.

5. 21426 line 18: Do you mean that C (C₆H₁₀O₃SO₄) could come from isoprene with 5 C-atoms?

Reply: C (C₆H₁₀O₃SO₄) could be derived from 3-Z-hexenal (Shalamzari et al., 2014). The manuscript has been revised accordingly (Page 12, Line 319).

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6. 21428 line 7: “so closed values” – do you mean so similar or?

Reply: The term “so closed values” has been replaced by “The values of the oxidation states for OSs and nitrooxy-OSs on a same sample (0.01 to 0.14 units of difference) suggest that the presence of the sulfate and/or nitrate groups is not determinant.” (Page 13, Line 357).

7. 21428 lines 10-25: This discussion should focus on differences between samples not cities (due to the very low number of samples).

Reply: Please refer to our reply to the 1st general comment from referee #2.

8. 21429 line 26: Add reference to Fig. 3 here.

Reply: The manuscript has been revised accordingly (Page 15, Line 401).

9. 21432 line 1-2: This statement seems out of context and should be elaborated further, preferably with reference to relevant sources.

Reply: We now state that “In summary, the molecular characteristics of tentatively assigned OSs between NJSD+NJSN and SHSD+SHSN shared better similarity, probably because NJ and SH are geographically closer at the lower reach of the Yangtze River, whereas WH is at the middle reach of the Yangtze River” (Page 16, Line 432-436).

10. 21433 line 4-5: This statement is too strong (given the few samples) and should be softened.

Reply: As stated in our reply to comments from other referees, the manuscript have been thoroughly edited to limit the conclusions about seasonal trends.

11. 21434 line 11: How can these pathways lead to low abundance of CHONS during daytime? A better statement would be that they lead to a higher abundance during night.

Reply: The statement refers to the potential photochemical pathway of nitrooxy-OS

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formation. This pathway should thus contribute to daytime N-OS, detected here at relatively low abundances. We thus maintain our statement but it is now clarified to avoid any misinterpretation: “This photochemical pathway could contribute to the formation of the nitrooxy-OSs detected during daytime, even if they showed only relatively low abundances in this study (Page 18, Line 490-492).”

Reference: Shalamzari, M. S., Kahnt, A., Vermeylen, R., Kleindienst, T. E., Lewandowski, M., Cuyckens, F., Maenhaut, W., and Claeys, M.: Characterization of polar organosulfates in secondary organic aerosol from the green leaf volatile 3-Z-hexenal, *Environmental science & technology*, 48, 12671-12678, doi:10.1021/es503226b, 2014.

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

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