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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.

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We are grateful to the helpful comments from anonymous referee #4, and will carefully revised our manuscript accordingly.

General comments:

1. "I feel that the manuscript is not suitable for publication in its current form for a number of reasons. My first concern is lack of chromatograms and mass spectra in the manuscript or supporting information. I understand that showing a large number of extracted ion chromatograms is not practical. However, the authors need to show at least



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chromatograms from major peaks in the main manuscript or supporting information. The authors can discuss about the differences in organosulfates at different locations directly using chromatograms. That is far more effective than descriptive texts."

Reply: We do share with the referee, his/her concern about the practical aspects of adding too much chromatograms, but we will indeed add some more selected (major) peaks (to be included as Figure S1) and start our discussion around those. In addition to showing more extracted ion chromatograms, we will also add retention times in the tables in the supporting information (new Table S3-S10). Nevertheless, figure such as Figure 3 or Figure 6 appears more appropriated to discuss the complete dataset.

2. "Second, the authors discuss about seasonal and diurnal variations from extremely small sets of data. While the authors can discuss about the differences in these sampling days, they should not be discussed as seasonal or diurnal patterns."

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 for. 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 in different locations. The manuscript will nevertheless be thoroughly edited to milden the conclusions about seasonal trends i.e., preferentially highlighting the nature/variety of the detected OSs rather than their seasonal/diurnal trends. For example, section 3.4 will now be entitled with "Comparison of four OS samples".

3. "Third, I find the manuscript extremely difficult to follow. It is extremely densely written. The authors should seek a language editing service to make sure that the

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manuscript can be read smoothly."

Reply: The manuscript will be lightened and clarified as much as possible and reviewed by a language editing service. Naturally all technical comments will be implemented in the revised version.

Technical comments: 4. Page 21419 line 13 onwards: The authors should also address Kahnt et al (2015) here. Kahnt, A., Behrouzi, S., Vermeylen, R., Shalamzari, M. S., Vercauteren, J., Roekens, E., Claeys, M., and Maenhaut, W.: One-year study of nitroorganic compounds and their relation to wood burning in PM10 aerosol from a rural site in Belgium, Atmos. Environ., 81, 561-568, Doi 10.1016/J.Atmosenv.2013.09.041, 2013.

Reply: The reference will be addressed. We will now state in our revised manuscript (Page 3, Line 82-85) that "For example, the a-pinene-related nitrooxy-organosulfates (MW 295) were detected in high concentrations during the winter period, followed by autumn, spring, and summer, at a rural background site in Hamme, Belgium (Kahnt et al., 2013)."

5. Page 21420 line 10: Do the authors mean 'OS' measurements instead of identification? I am not aware of a study dealing with OS identification from Shanghai aerosols.

Reply: Ma et al. (2014) have identified seventeen OSs in SH with the corresponding authentic standard compounds.

6. Page 21421 line 4: Do the authors mean 24 h samples? Daily samples mean a sampling was performed every day. I can only find two 24 h samples in the Table 1.

Reply: The term "24 h sample" has been used throughout the manuscript.

7. Page 21422 line 11: 'Th' and 'm/z' are used simultaneously. Both are a unit of massto-charge ratio, and it is redundant here. I recommend using 'm/z' as recommended by IUPAC.

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Reply: Only "m/z" is used in the revised manuscript.

8. Page 21423 line 1 and throughout the manuscript: A term 'identification' should be reserved for a compound that is positively identified from the comparison to an authentic standard compound. 'Pseudo-molecular ion' should be 'quasi-molecular ion'.

Reply: We will now state in our revised manuscript (Page 4, Line 92-94) that "Recently, ultra-high resolution mass spectrometer has been applied to the identification of OSs, i.e., tentative determination of the molecular formulas of OSs, in atmospheric aerosols samples" to avoid any misinterpretation of the term "identification". "Pseudo-molecular ion" has been replaced with "quasi-molecular ion" throughout the manuscript.

9. Page 21423 line 16: The authors claim the detection of about 200 organosulfates from the UHPLC/(-)ESI-MS analysis but I am a little skeptical if these compounds eluted from the column as peaks. The authors mush show more extracted ion chromatograms in the main manuscript and supporting information. In supporting information, the authors show only four extracted ion chromatograms for an m/z value range between m/z 351.1849 and m/z 351.1853 without showing their mass spectra. From the description of the data processing, the authors did not seem to consider an isotope distribution of a detected compound, and relied solely on the ratio of H/C, O/C, N/C, S/C, and DBE. The authors should show corresponding mass spectra to assure readers that the compounds shown here are indeed organosulfates.

Reply: We will add some more ion chromatograms in the supplementary information (new Figure S1). Showing additional ion chromatograms and mass spectra are just overwhelming and unpractical. However, retention times, potential precursors, and corresponding references for the identified OSs have been included in the supplement (new Tables S3-S10). Molecular formulae assignment was performed including the following elements: C, H, N, S and O. Isotopes are a classical way to confirm molecular formulae assignments when the resolution of the instrument is not sufficient. Here, in most cases, the isotopic peak is not detected due to the low intensity of the related

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quasi-molecular ion. Nevertheless, we are confident in our assignments as, within an error of 2 ppm, only one molecular formula is generally chemically relevant.

10. Pages 21422-21423: In connection to the previous concern, how did the authors calibrate m/z values? Have the authors used a lock mass function or were they calibrated externally? This should be clearly stated in the manuscript.

Reply: We apologize for not having provided this information and will amend the manuscript by adding the corresponding information i.e., the Q-Exactive mass spectrometer was mass calibrated using commercial Calmix solutions (Thermo Scientific, USA), but also and mainly with sodium acetate for smaller masses.

11. Figure S1 in supporting information: Figure S1 should show the intensity of the peak.

Reply: Figure S1 is shown to illustrate the separation of various OSs. Due to the different PM loadings in the samples, the intensity of the peaks in Figure S1 varies significantly but does not deliver additional useful information. Therefore, in our opinion, relative abundance is retained for the y-axis.

12. Page 21425 line 10: How do the authors know that they are all nitrooxyorganosulfates? They are other structures that can contain nitrogen such as heterocyclic compounds, nitrophenolic compounds, etc.

Reply: MSn experiments were not performed in our study, and hence we cannot exclude other possibilities such as heterocyclic compounds, nitrophenolic compounds, etc. We will now state (Page 7, Line 199-203) that "In this study, compounds that satisfy the above criteria and present a number of oxygen atoms greater than 4s+3n (4s+3n \leq o) were tentatively regarded as OSs or nitrooxy-OSs. However, a few other S-and N-containing compounds, such as sulfonates, may be also included (Riva et al., 2015b)."

13. Figure 2. The authors should caution the readers that these are a number of

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isomers separated by the authors' method. For example, the C10H17O7N1S1 compounds show only three isomers for a certain method but it can be separated into six isomers when the method is further optimized.

Reply: We will now state in our revised manuscript (Page 6, Line 176-178) that "Note that the obtained number of isomers may vary significantly when the separation method is further optimized"

14. Page 21426 line 27-29 and throughout manuscript: Is it a nitrate group or nitrooxy group? How do the authors know without MSn experiments?

Reply: please refer to our reply to the 12th comments from the referee #4..

15. Page 21427: The authors cannot discuss seasonal differences from such a limited number of samples.

Reply: The manuscript will nevertheless be thoroughly edited to milden the conclusions about seasonal trends i.e., preferentially highlighting the nature/variety of the detected OSs rather than their trends. For example, section 3.4 is now entitled with "Comparison of four OS samples". In addition, air quality and meteorological data on the sampling days have been compared with the seasonal averages in the supplement (Table S2), indicating that those parameters on the sampling days are quite close to the seasonal average.

16. Page 21429 onwards about KMD and VK diagrams: I find this section very difficult to read and get information out of it. I recommend the authors summarizing most important information here instead of describing every single detail about the diagrams.

Reply: The manuscript will be lightened and clarified as much as possible and reviewed by a language editing service.

17. Page 21432: These isoprene originating organosulfates tend to elute very early in the chromatogram, and their MS intensities can be potentially influenced by co-eluting compounds in this region (ion suppression). How have the authors corrected for this?

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If not, how do the authors know that they are not affected by the ion suppression?

Reply: No correction has been made. We do agree that co-eluting compounds may lead to ion suppression. However, the samples were not analyzed here by ESI direct infusion. LC separation allowed to minimize artifacts due to the matrix, diluting the low amount of sample injected (5μ L) in the LC solvent flow (300 μ L min-1) and resolving most the matrix components (these latter being previously solvent extracted and filtered). Please also refer to our reply to the 8th comment from referee #1.

15ïijŐPage 21433 onwards: Seasonal and diurnal variations cannot be discussed when the number of sampling day is so limited even they are similar to average seasonal conditions

Reply: please refer to our reply to the 2nd comment from referee #4..

Reference: Ma, Y., Xu, X., Song, W., Geng, F., and Wang, L.: Seasonal and diurnal variations of particulate organosulfates in urban Shanghai, China, Atmospheric Environment, 85, 152-160, doi:10.1016/j.atmosenv.2013.12.017, 2014.

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