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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 JDS Surratt and M Riva, and have carefully revised our manuscript accordingly.

1. Although I am not a reviewer for this paper, when my Postdoctoral Scholar (Matthieu Riva) and I saw this published online in ACPD we read this with very high interest. I think the intentions of the authors are very good and this kind of data from China are highly needed in the literature.

Reply: We are very grateful to JDS Surratt and M Riva for their positive viewing of our

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study.

2. I strongly agree with the reviewer comments on the technical aspects they raised in their reviews. Specifically, I do want to point out that I agree that comparing seasonal and site trends really requires more filters, so these comparisons probably need to be modified with this in mind.

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 will now be entitled with "Comparison of four OS". In addition, the technical aspects, and especially the LC-MS coupling, will be clarified and underlined. Bearing in mind the availability of instruments having resolutions better than 1 ppm, and the availablity of the environmental samples as those considered here, we do believe having conducted our study according to the best available standards.

3. However, the degree of characterization provided in this manuscript is very interesting and potentially useful, especially the supplemental tables listing the detailed list of organosulfates (OSs) (including nitrated derivatives) identified from these samples. From carefully reviewing these detailed tables, it is clear that a lot of biogenic VOCs contribute to these OSs.

Reply: We gratefully thank Mrs. Surratt and Riva for their support.

4. "However, the authors should be aware that a new study by Riva et al. (2015, ES&T) recently published from my group (in collaboration with Professor Eric Villenave's group and Professor Betsy Stone's group) revealed that organosulfur compounds (both organosulfates and sulfonates) form from the photooxidation of PAHs in the presence of sulfate aerosol. Several of the laboratory-generated PAH organosulfur compounds were identified in ambient samples collected from Pasadena, CA, USA and Lahore, Pakistan. Notably, many of the ions you report in your supplemental tables were recently characterized as sulfonates (i.e., m/z 201 [C₇H₅O₅S⁻], 215 [C₈H₇O₅S⁻], 227

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[C₉H₇O₅S-], 229 [C₉H₉O₅S-]) and organosulfates (i.e., m/z 231 [C₉H₁₁O₅S-], 257 [C₁₀H₉O₆S-], 274 [C₁₀H₉O₇S-]) from PAH (naphthalene and 2-methylnaphthalene) oxidations in presence of sulfate aerosol (Riva et al., 2015, ES&T). In addition, we noted that many of the OSs you identified were recently observed in Riva et al. (2015, Atmos. Environ.). In that study, OSs distinct to isoprene ozonolysis were identified. Many of these OSs previously observed from isoprene ozonolysis were also identified in your supplemental tables, including m/z 181 [C₅H₉O₅S-], 197 [C₅H₉O₆S-], 199 [C₅H₁₁O₆S-], 213 [C₅H₉O₇S-], 227 [C₆H₁₁O₇S-], 249 [C₉H₁₃O₆S-], and 267 [C₉H₁₅O₇S-]. One lesson we learned from the isoprene ozonolysis study is that some of the OSs can have similar elemental formulas as monoterpene OSs, and thus, reporting retention times or showing extracted ion chromatograms (as suggested by one of the reviewers) will be very helpful. I also wonder if the authors agree if adding another column to their supplemental tables listing the potential VOC precursor(s) and relevant study(studies) that supports this is useful? The authors may want to add a cautionary note that even if an OS has a C₅ or C₁₀ backbone (based on accurate mass measurements), these might not necessarily come from isoprene or monoterpenes as our recent work has shown that PAHs might have similar compositions or nominal masses as these products.”

Reply: This comment on your recent study on the formation of OSs, and more particularly to organo-sulfonates, from PAH is of high interest regarding the determination of the nature of sulfur compounds as SOA components and the determination of their formation pathways. In our manuscript, compounds that present a number of oxygen greater than, or equal to, $4s + 3n$ (s being the number of sulfur atoms and n the number of nitrogen atoms) were tentatively regarded as OSs or nitrooxy-OSs, ignoring the fact that a compound with a number of oxygen atoms greater than, or equal to, $3s$ could also correspond to a sulfonate. This assumption was similarly used by Lin et al., 2012a and 2012b, for example. We think that it should be kept in the present manuscript for data processing and comparison purposes. However, specific mentions to the possibility of the presence of sulfonate groups instead of sulfate ones will be added all along the

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text appropriately, especially when discussing compounds with high DBE values (i.e., potentially aromatic species), according to your comment. Mention to possible PAH precursors will be also added. Besides, the highly relevant cautionary note that even if an OS has a C5 or C10 backbone these might not necessarily come from isoprene or monoterpenes will be introduced. Both of the previous studies, Riva et al. (2015, ES&T) and Riva et al. (2015, Atmos. Environ.), will be of course cited appropriately. We will add statements such as “in summer samples, C5 and C10 were the most abundant. Isoprene and monoterpenes could be the main precursors for most of those C5 and C10 OSs (Riva et al., 2015a; Surratt et al., 2008). On the other hand, a recent work (Riva et al., 2015b) suggests that a number of the observed C10 OSs might be derived from PAHs”. As requested, we will also show more extracted ion chromatograms (Figure S1) and add retention times, possible precursors and corresponding references in the compounds’ tables (Table S3-S10) in the supporting information.

Reference: Lin, P., Rincon, A. G., Kalberer, M., and Yu, J. Z.: Elemental composition of HULIS in the Pearl River Delta Region, China: results inferred from positive and negative electrospray high resolution mass spectrometric data, *Environmental science & technology*, 46, 7454-7462, doi: 10.1021/es300285d, 2012a. Lin, P., Yu, J. Z., Engling, G., and Kalberer, M.: Organosulfates in humic-like substance fraction isolated from aerosols at seven locations in East Asia: a study by ultra-high-resolution mass spectrometry, *Environmental science & technology*, 46, 13118-13127, doi: 10.1021/es303570v, 2012b. Riva, M., Budisulistiorini, S. H., Zhang, Z., Gold, A., and Surratt, J. D.: Chemical characterization of secondary organic aerosol constituents from isoprene ozonolysis in the presence of acidic aerosol, *Atmos. Environ.*, doi:10.1016/j.atmosenv.2015.06.027, 2015a. Riva, M., Tomaz, S., Cui, T., Lin, Y.-H., Perraudin, E., Gold, A., Stone, E. A., Villenave, E., and Surratt, J. D.: Evidence for an Unrecognized Secondary Anthropogenic Source of Organosulfates and Sulfonates: Gas-Phase Oxidation of Polycyclic Aromatic Hydrocarbons in the Presence of Sulfate Aerosol, *Environ. Sci. Technol.*, 49, 6654-6664, doi:10.1021/acs.est.5b00836, 2015b.

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