Atmos. Chem. Phys. Discuss., 15, C6597–C6598, 2015
www.atmos-chem-phys-discuss.net/15/C6597/2015/

Atmospheric Chemistry and Physics Discussions

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.

Anonymous Referee #1

Received and published: 6 September 2015

The work by Wang et al. describes molecular composition of PM2.5 samples from three megacities i.e., Wuhan 15 (WH), Nanjing (NJ), and Shanghai (SH) determined by an UHPLC Orbitrap MS. The authors identified significant number of organosulfates and nitrooxy-organosulfates and discussed their contribution to the PM at these locations.

Unfortunately the authors ignored a majority of the very important comments that were given at the initial ACPD review stage. I strongly believe that they have to be addressed before the manuscript could be published in ACP. Unfortunately I cannot support this work for publication in this current form. The methodology section is still confusing. Considering a very large number of detected molecules (>200), I assume the whole

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results and discussion section is based on the direct infusion analysis. If not, please show the LC/MS chromatogram and describe the methodology more clearly. Please add a citation for the LC/MS method. It is not clear whether the mass spectra were blank corrected. If yes, please describe how. What was the signal to noise threshold for keeping the formulae for further evaluation? Orbitrap MS is known to result in the formation of shoulder ions, which significantly increase a number of identified molecules. Were the shoulder ions removed from the mass spectra? Were the analytical replicates considered? Were the C, N, P and S isotopes considered for the correct molecular formulae assignment? What was the mass scan range of the Orbitrap analysis? Orbitrap is known to have mass dependant ion transmission. Therefore, by selecting either low or high mass range one can miss out high or low molecular weight compounds. The mass error of 2ppm for formulae assignments is rather high, especially considering that the majority of the assigned OSs have MW >200 (see Figure 2). Kind and Fiehn (2007) demonstrated that even at 1 ppm error a very large number of chemically realistic formulae is possible in this mass range. Please mention reproducibility of the ion appearance in the mass spectra for the ions with low intensity in the replicates. Please also clarify whether the mass spectra (Figure 2) was obtained by integration of chromatographic area of the LC chromatogram or from a direct infusion analysis.

It is important that all extracts have comparable OC or PM load, overwise the comparison of molecular composition in the samples from different sampling locations is highly speculative as such differences could be attributed to the analytical artefacts (e.g., ion suppression which is known to be an issue in the ESI direct infusion analysis). Please justify it.

Reference:

T. Kind, O. Fiehn. Seven golden rules for heuristic filtering of molecular formulas obtained by accurate mass spectrometry. BMC Bioinform. 2007, 8, 115.

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