

Interactive comment on “The Secondary Formation of Organosulfates under the Interactions between Biogenic Emissions and Anthropogenic Pollutants in Summer of Beijing” by Yujue Wang et al.

Anonymous Referee #1

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This paper describes an observation of organosulfates (OSs) as well as nitroxy-organosulfates (NOSs) in Beijing over a summer period. A number of OSs and NOSs are detected by direct infusion electrospray mass spectrometry. In addition, several OSs are quantified by HPLC-ESI methods using authentic standards or surrogates. The measurements are very done and cover a meaningfully long period of time making it possible to qualitatively correlate the presence of OSs or NOSs with other environmental conditions, such as precursor concentrations, liquid water content, particle acidity etc. The paper should be published after some minor improvements described

C1

below.

In my opinion, the introduction section does not explain the motivation of the study sufficiently well. The introduction sections states that OSs are important, were observed many times, can form by mechanisms that are affected by environmental conditions, and can now be in some cases quantified with authentic standards. However, it does not explain what this study is trying to accomplish and how it builds on all the previous field and lab work on OSs and NOSs. There is a clue about what authors want to accomplish in the sentence on lines 89-90, but this is not enough. Ideally, a testable hypothesis or a clear set of goals should be posed in the introduction.

Another issue I have with the introduction is that it motivates the study by saying that we cannot predict the amount of SOA correctly. The implication is that formation of rather involatile OSs and NOSs should help resolve this discrepancy. However, the mass concentrations of OSs reported here are rather small compared to the mass concentration of organic matter in particles. Since OSs and NOSs are minor species, it is better to motivate the study by our quest to understand the acid-catalyzed chemistry in particles, of which formation of OSs is an example, and the night time chemistry of NO₃ in urban environments, which appears to be partly responsible for the observed NOSs.

I found the discussion in sections 3.3 and 3.5 too qualitative. I realize that the data set may be not long enough to make more definitive conclusions. Tied to this is Figure 4, the data in which are too scattered to make any reliable conclusions. I am not sure what the authors can do about it under the circumstances. Is Figure 4 the best way to look for correlation in the data? Have the authors tried correlating the amount of observed OSs to, for example, a product of sulfate, organic mass, and hydronium ion concentrations that might be expected to describe an acid-catalyzed reaction? I would encourage them to come up with more convincing ways of presenting the data than currently afforded by Figure 4.

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Here are minor editorial comments.

L57-58: this is an unclear sentence, please revise

L104: monoterpene -> monoterpenes

L124: mass resolution -> mass resolving power

L128: please be more explicit about the allowed elements and constraints placed on the formulas

L145: OSs and NOS species -> OS and NOS species

L149: Olson et al. (2011) (Olson et al., 2011) -> Olson et al. (2011). Similar corrections may be needed in other places in the manuscript, for example, on line 153

L171: please clarify what are "compounds excluded from the above major compound categories". Would it be CHS? Or peaks that could not be assigned within the imposed constraints? It would also be useful to know what fraction of peaks was assigned.

L202: OSs molecules -> OS molecules

L202: monoterpene -> monoterpenes

L203: molecules -> ions

L205: relatively higher relative intensity -> higher relative intensity

L206: less -> fewer

L221: does the "total concentrations of quantified OSs" refer the average over all the samples?

L227: Where is "Centreville" located? (Unlike the other locations mentioned, it is not a country or state)

L268: monoterpene -> monoterpenes

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L270: were -> was

L289 and elsewhere in this section: Secondary inorganic aerosols (SIAs) are defined as sulfate, nitrate and ammonium on line 289. However, the ratio of $\text{SO}_4(2-)$ to SIAs above or below 0.5 is then used to separate conditions into sulfate and nitrate dominated regimes. The exact definition of this ratio is not clear. To be more precise the authors should define a molar ratio $\text{SO}_4(2-)/[\text{SO}_4(2-)+\text{NO}_3(-)]$ and use it in their discussion instead of the vaguely defined ratio they are currently using.

L304-305: please fix grammar in this sentence

L345 and 352: the "nighttime formation" and "lower production" are not plausible explanations. The diurnal profile of monoterpenes may be peaking at night because they are removed more slowly at night and/or boundary layer height is changing. It should say "nighttime peak in concentrations" instead of "nighttime formation".

Table 1: some of the OS structures are drawn as ionized (deprotonated) and some are not. Since the formulas are given for the ionized forms, it would be good to draw the structures for the ionized forms as well for consistency

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