

Interactive comment on “Molecular Characterization of Organosulfates in Arctic Ocean and Antarctic atmospheric aerosols” by Yuqing Ye et al.

Anonymous Referee #1

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Summary and Recommendation:

This study examines the molecular composition of total suspended particles (TSP) collected from Arctic and Antarctic regions as well as from urban and rural areas of China. The focus of the molecular characterization is on organosulfates (including nitrated derivatives of organosulfates) in TSP collected from these regions. The authors rightly justify that more work is needed to understand if organosulfates are present in remote atmospheres like that of the poles. Organosulfates are important compounds present in aerosol, as prior work has shown that these compounds serve as molecular tracers for multi-phase chemistry leading to SOA formation (Surratt et al., 2007, ES&T;

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linuma et al. 2007, Atmos. Environ.). Much of this prior work has shown that biogenic SOA is enhanced by acidic sulfate derived from human activities, and thus, organosulfates can serve as tracers for this biogenic-anthropogenic interaction. However, recent work has shown that anthropogenic VOCs can also yield organosulfate compounds in aerosols (e.g., Staudt et al., 2015, Atmos. Environ.; Riva et al., 2015, ES&T; Riva et al., 2016, ACP; Blair et al., 2017, ES&T). As a result, the molecular characterization results reported in this study are desperately needed in the literature. Another reason for this is that organosulfates may have low-volatilities, allowing them to be transported intact over long distances. Before this manuscript can be accepted into ACP, the authors need to address several specific (major) comments outlined below. One thing I noticed with the manuscript is that the English writing was not the best it could be, and really could use a lot of improvement before publication. The authors may want to consider using an English editing service or reach out to a native English-speaking colleague to edit their manuscript before resubmission. In my technical comments below, I do provide some corrections to the English usage, but I don't feel the burden of English correction should be on the reviewers. Due to the nature of my specific (major) comments below, I must recommend this manuscript be reconsidered after addressing major comments.

Specific (Major) Comments:

1.) I'm curious, could the authors provide a Supplemental Table (or Tables) summarizing all of the most intense OS, NOS, etc. observed in these samples? In this sort of table, you could include the accurate mass measured for each ion, the mass error of the accurate mass fitting compared to the theoretical formula, DBEs, etc. I think this sort of supplement information will be helpful to the wider readership at ACP since it might help to inform future experiments aimed at characterizing the sources of the OSs observed in the polar regions. Also, I'm curious if the authors found isoprene epoxydiol (IEPOX)-derived organosulfates, such as the methyltetrol sulfates (MW = 216 g/mol) (e.g., see Cui et al., 2018, Environmental Science: Processes and Impacts)?

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2.) Sample Collection: During the sample collections in the Arctic and Antarctic regions, did you have any collocated data such as aerosol sizing or total number of particles?

Related to this, I wonder if phytoplankton blooms could also contribute to some of the OSs observed? Work by Claeys et al. (2010, Journal of Aerosol Science) found that organosulfates were observed at Amsterdam Island that appeared to be related to phytoplankton blooms. Did you have any measures of phytoplankton activities onboard your cruise ship? Have you also considered satellite products?

3.) Experimental Section: Was 4 hours of prebaking at 450 degrees C done for both the QFFs used in the Arctic and Antarctic? Please clarify. Also, was 4 hours enough time at this temperature to remove all organics? I'm curious why 4 hours at 450 degrees C was selected?

In addition to prebaking the QFFs, many field studies in the past also prebake the aluminum foil that is used in wrapping and storing the QFFs. Was this also done?

4.) Sample selection for chemical analyses: The authors never discussed the criteria used in selecting the 2 Arctic samples and the 4 Antarctic samples to composite. Why were these selected? Was this due to high aerosol concentrations measured at the same time with other instruments? Please clarify.

5.) Filter Extractions: The authors extract filters in 1:1 v/v mixture of methanol and Milli-q water and dry this down and reconstitute in 1:1 v/v mixture of Milli-Q water and ACN. Why was methanol replaced by ACN? Do you worry some of the components in the initial MQ/water mixture used for extraction may not re-dissolve in the MQ/ACN mixture? Did you test your extraction efficiencies with any standards of OSs?

6.) Direct injection of samples (MY MAIN CONCERN): The reasoning given on Page 3 of the experimental section for selecting direct injection analyses of samples is not very strong. LC separation before ESI-MS analyses helps to minimize matrix effects or

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ion suppression effects in samples. When directly injecting samples without chromatographic separation, one has to worry about salts like sulfate suppressing the ionization of other compounds or causing unwanted cluster ions/artifact ions.

I think if you have any extracts or filter portions remaining from your study, you really might want to consider injecting a few on a LC column to provide further support that many of the ions you detect are indeed real and not simply cluster ions/artifact ions formed in the ESI source when injecting the entire mixture into the ESI source at the same time. LC separations will really help to minimize this potential experimental issue.

Since the authors didn't employ chromatographic separation before ESI-MS analyses, they were not able to be quantitative. I think the authors need to be careful with words like "abundant" in their manuscript. You can't really say which ions are more abundant than others due to the matrix effects of ESI I mentioned above. You may want to be more clear that this is a limitation of your study. Also, be more clear that you are detecting number of formulas only, and thus, can't really be quantitative in your approach.

6.) Aerosol pH calculation: Have the authors considered how organosulfates might affect aerosol pH calculations? Since they likely contribute to the charge balance of aerosols, these components likely contribute to aerosol pH. However, this is an unresolved issue in atmospheric chemistry since the pKas of many organosulfate remain uncertain/unknown. As a result, I don't expect the authors to resolve this issue in this study. However, it might be worth pointing out in the experimental section related to aerosol pH calculations that organosulfates cannot be considered in this calculation at this time.

7.) Page 7, Lines 28-30: I disagree about the possible source of HMW organic molecules coming from the stratosphere. I doubt they would last very long there due to high energy photons breaking them down easily. However, HMW organic molecules tend to have low volatilities. Their low volatilities may allow them to be transported long

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distance before being lost through deposition (wet or dry) or heterogeneous oxidation processes.

8.) For the Arctic Pack Ice Zone, I'm curious what the biological (phytoplankton) activity is there? Do you expect a lot of phytoplankton blooms near this area, especially in summer? If so, could this material be contributing to OS formations?

9.) How did the authors rule out that ship emissions didn't contribute to the OSs/NOSs measured from the filters collected onboard the ship?

10.) Page 10, Lines 28-29: How can you really know if the low pH of the Arctic Pack Ice samples is due to ship emissions? Do you have a tracer of ship emissions to correlate to? Could the low pH of these aerosols really come from continental locations nearby? Thus, if these acidic particles make it to this region from continental locations, they may promote multiphase chemistry of organics derived from the sea surface microlayer.

11.) The authors may be curious about a new article that just came out in ACS Earth and Space Chemistry by Cui et al. (2019, DOI: 10.1021/acsearthspacechem.9b00061) titled "Chemical Characterization of Isoprene- and Monoterpene-Derived Secondary Organic Aerosol Tracers in Remote Marine Aerosols over a Quarter Century." Measured many of the known biogenic SOA tracers in these remote marine aerosols collected from Cape Grim, Australia. Interestingly, many of the known organosulfates associated with biogenic SOA were not found at this site. In addition, they didn't find any anthropogenic-derived OSs at this site. However, they did see some preliminary data (in their SI section) that shows CHONS, CHON, and CHOS that appear to be unique to oceanic aerosol samples. They weren't able to identify these compounds but they appeared to be associated with organics found in the sea surface microlayer.

12.) Finally, due to collecting TSP, can the authors comment on what size fraction the OSs and NOSs are associated with? If associated with SOA processes, I would imagine these components to be associated with PM_{2.5} (or PM₁). However, if they are derived from the sea surface microlayer, they may be more in the PM₁₀ (coarse

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size mode). Did you see association of your compounds with Na⁺ ion concentration? Correlation with Na⁺ may suggest that some of your compounds are derived from bubble bursting processes or photosensitized reactions in the sea surface microlayer (i.e., see the work of Christian George's group in France).

Technical Comments:

- 1.) Abstract, Line 23: Define the acronym HMW.
- 2.) Abstract, Line 25: When you say "atmospheric transmission" do you mean to say "atmospheric transport/fate" instead?
- 3.) Abstract, Lines 27-29: This sentence needs to be rewritten for clarity. Very hard to read.
- 4.) Page 1, Abstract, Line 30, define "nss-SO4"
- 5.) Page 2, Introduction, Line 5: Change "radiation" to "radiative"
- 6.) Page 2, Introduction, Line 12: Change "Researches have been verified SOAs are ubiquitous" to "Prior studies have verified that SOAs are ubiquitous...."
- 7.) Page 2, Introduction, Line 17: Delete ', as well as participate in multiple reactions.' as this isn't really needed.
- 8.) Page 2, Introduction, Lines 19-20: The authors may also want to cite a recent study from the Amazon rainforest that quantified OSs there (Glasius et al., 2018, Environmental Science: Processes and Impacts).
- 9.) Page 2, Introduction, Line 21: Change "information" to "formation"
- 10.) Page 6, Lines 5-6: Please add ", respectively." at the end of this sentence.
- 11.) Page 8, Line 28: Change "long-transported" to "long-range transport"
- 12.) For Figure 1, can you put all of the mass spectra on the same scale for the x-axes?

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13.) For the light green circle and the dark green circle, can you add to the caption of Figures 3 and 4 what these circles mean?

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