

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

Anonymous Referee #2

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Summary and recommendation:

In this study, Ye and coworkers report on the abundance of organosulfates in aerosol particles collected on filters in the Arctic, the Antarctic and at two sites in southern China (Guangzhou, rural and urban). The filter samples were extracted, and afterwards analyzed by high-resolution mass spectrometry with direct infusion electrospray ionization in negative mode. From the obtained signals, sum formulas for organic compounds were generated and assigned to certain compound classes (i.e., organosulfates (OSs), nitrooxy-organosulfates (NOSs), organonitrates (ONs), and oxygenated hydrocarbons (OxyCs)). The authors find that aerosol components from the Arctic

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and Antarctic exhibited rather high carbon oxidation states and a large percentage of high molecular weight (HMW) compounds, which they assign to long-range transport of such compounds from stratospheric reservoirs. In comparison to the aerosol samples from China, the authors observe larger fractions of sulfur-containing compounds and lower fractions of ONs, which is assigned to low NO_x levels in the polar atmosphere. Nonetheless, the obtained number fractions of polycyclic aromatic OSs and NOSs and their oxidation states were similar to urban Guangzhou samples, indicating larger anthropogenic influences at the Arctic and Antarctic sampling sites.

Given the quite exotic sampling sites and the potential significance of such a study, I am quite disappointed from this manuscript. The way the samples were taken, processed and analyzed is not appropriate to support any of the hypotheses drawn. This is also why major parts actually remain extremely speculative, inconclusive, or sometimes even contradictory. In my view, a simple, but targeted, LC-MS analysis of the filter samples would have yielded much more (reliable) information on the abundance of OSs and NOSs in aerosol samples from the Arctic and Antarctic. Therefore, I can only recommend either to reject this manuscript or to reconsider it after substantial revisions (as detailed in my comments below).

Major comments:

1) My most pressing concern is the analysis procedure of the filter extracts. Electrospray ionization is known to be prone to matrix effects such as ion suppression and adduct formation. Without any pre-separation of inorganic ions, it is not possible to distinguish organic and inorganic sulfates. Thus, the assigned OSs and NOSs could just represent sulfate adducts of organic molecules. Moreover, I highly recommend including isotopic signals of sulfur in the formula assignment procedure for OSs and NOS. Besides, without any separation technique (e.g., liquid chromatography) and at least some surrogate standards, it is not possible to discuss or compare the abundance of compounds in the aerosol samples.

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2) Merely from reading the abstract, it is obvious that there are some contradicting conclusions drawn in this study. On the one hand, the authors hypothesize that aerosol components are long-range transported to the polar sites. On the other hand, they conclude that oxidation of aerosol precursors under low NO_x levels at the polar sites reduce the amount of ONs. And lastly, they state that local anthropogenic emissions are the source of polycyclic aromatics at these sites. The reasoning for each of these hypotheses is very weak in the corresponding sections.

3) The manuscript is often difficult to read and to understand because of bad language quality. It is possible that some of my specific comments (see below) are actually related to incorrect wording. To improve readability, I would recommend the authors to look for some help either from a native speaker or from a language editing service.

Specific comments:

1) P3L26: Do you have any data on particle size distributions during the sampling period? This would be very interesting to get an impression of the ratio between primary and secondary particles.

2) P3L32: Can the authors estimate the impact from ship exhaust? In particular, regarding the source of polycyclic aromatics in the polar samples, it would be necessary to exclude any influences from the exhaust.

3) P4L11: Why did the authors choose these filter samples? No information is given on the sampling dates or the selection procedure. Are there any additional data available for these samples?

4) P4L14: Did the authors check for compositional changes of the aerosol samples from sonication? Sonication is known to produce OH radicals in aqueous solutions and might therefore induce chemical reactions. Did the authors quantify extraction efficiencies? Why was methanol replaced by acetonitrile after evaporation?

5) P4L18: Why did the sample travel for 3 min through a stainless steel capillary before

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ionization? This could have induced chemical reactions at the steel surface. Did the authors check such potential influences?

6) P4L23: “ppm” is not an absolute value. Moreover, Orbitrap mass spectrometers have much larger mass errors than 0.02 ppm. Typically this should be somewhere between 2 and 5 ppm.

7) P5L13: I don't think that the “ $4s+3n \leq o$ ” criterion is sufficient for the identification of OSs and NOSs. The compounds could also contain other functional groups, such as sulfonates, amines, etc. Moreover, as already mentioned above, the authors should at least include isotopic patterns from sulfur isotopes into their assignment procedure, to decrease the level of uncertainty. (The presence of sulfur isotopes is quite easy to detect in the high-resolution mass spectra.)

8) P6L2: Equation 3 cannot be applied to all heteroatom-containing compounds, as the oxidation states of sulfur and nitrogen are unknown (see also comment 7).

9) P7L13: What do you mean by “aerosol formula types”?

10) P7L16: Figure S1 is only showing back trajectories for one day at each site. What about the other days?

11) P7L20: It is trivial that the authors found compounds between 90–800 Da because this was the instrumental setting of the mass spectrometer.

12) P7L27: Do the authors really believe that high molecular weight compounds are preserved in the stratosphere over several days or weeks and then transported back to the ground? I don't think that such compounds would survive such a transport mechanism. Similarly, why should LMW compounds be more reactive than HMW compounds? From the filter analysis data, none of these statements can be supported.

13) P8L1: What is the meaning of the criterion $(DBE-n) < 4$?

14) P8L6: 80% of the OSs/NOSs are stated to be aliphatic and 10% to be aromatic.

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What about the other 10%

15) It would be very useful to have a list of the observed signals and assigned formulas for the different sampling sites.

16) P8L17: This is very confusing. Do the authors want to say that the O/C ratio given in the discussed Figures is actually not the O/C ratio?

17) P8L25: How do the authors know that biogenic emissions dominate at the rural Guangzhou site?

18) P9L4: The findings for ONs and OxyCs are not discussed.

19) P9L9 – P10L6: In my view this entire approach is invalid. Given that the number of N and S is typically 1 for known OS and NOS, the authors assume that solely from the carbon number they can infer potential precursor. How can they distinguish anthropogenic and biogenic precursors in such an approach (in particular, as many of these precursors have the same number of carbon atoms)? This is all extremely speculative!

20) P10L7: How do you distinguish sea spray derived sulfate from “non-sea-salt-sulfate” when you only collected TSP samples?

21) P10L20 – P11L2: The pH values are never “extremely low” and thus do not support acid-catalyzed reactions. As noted above, it is not possible to assign AVOC and BVOC precursors for certain OSs. Moreover, abundances of single ions do not necessarily correlate with their concentrations. Therefore, they should not be compared directly.

22) P11L8: RH values of 50–65% are not dry, but still quite humid and mostly above the deliquescence point of aerosol particles. Therefore, it seems not possible to draw any conclusion on RH effects here.

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