Response to Reviewer #1

We are grateful to the reviewer for the thoughtful comments on the manuscript. Our point-to-point responses to each comment are as follows (reviewer comments are in black, our responses are in blue, and revised texts that appear in the manuscript are in quotes and underlined).

Comments:

General Comments:

The article entitled "Organosulfates in atmospheric aerosols in Shanghai, China: seasonal and interannual variability, origin, and formation mechanisms" by Wang et al., presents the OS that are quantified across the 4 seasons in 2015/2016 and 2018/2019, before and after reduction of anthropogenic pollution in the Eastern China, giving valuable insights to their formation mechanisms. They have shown that Ox level (O_3+NO_2) plays a key role in OS formation particularly in summer, while sulfate, aerosol acidity, ALWC are also important factors. Overall, this study is well executed, and the article is well written. The authors have provided sufficient evidence to support their results and conclusions. I recommend acceptance of this manuscript after minor revision listed below.

Specific Comments:

Line 21: Indicate the reason for the observed decrease in OM in 2018/2019 with compared to 2015/2016 upfront

Response: we have indicated the reason for the decrease in OM in the revised manuscript.

"We find that while the concentration of organic aerosol (OA) decreased by 29% from 2015/2016 to 2018/2019, mainly a result of the reduction in anthropogenic pollutant emissions in eastern China, the annually averaged concentrations of 35 quantified OS were overall similar in two years"

Line 22: Indicate percent contribution of OS to OA in 2015/2016 and 2018/2019 next to their average concentrations

Response: We have added the percent contribution of OS to OA in 2015/2016 and 2018/2019, i.e., 0.57%±0.56% and 0.66%±0.56%, respectively, to the revised manuscript.

Line 24, 29-30, 32-34: Is this the average contribution (%) in 2015/2016 and 2018/2019 of each species? If yes, indicate it clearly here as well as in the main text

Response: Yes, there are average contributions. We have clearly indicated this in both the abstract and the main text.

Line 55-56: Replace POM with FPOM to denote "fine particulate organic mass"

Response: We have revised this.

Section 2.1: Give the coordinates of the sampling site

Response: We have added the coordinates (31.201°N, 121.429°E) of the sampling site to the revised manuscript.

Line 137: Indicate the temperature at which the sonication took place

Response: The temperature of the sonication bath was maintained at 4 ℃. We have indicated this in the revised manuscript.

Line 140: Indicate time and speed of centrifugation. Also include the model of the centrifuge used

Response: We have included this information in the revised manuscript by rephrasing the sentence here.

"The resulting extracts were mixed with ultrapure water (milliQ, 18.2 M·cm) of the same volume and then centrifugated at 12000 rpm and 4 ℃ for 20 min using a centrifuge (Cence, TGL-16M) to get supernatant for analysis."

Line 145-147: Revise water as (A) and methanol as (B) to match with the gradient elution procedure, as in reversed phase separation starts with high aqueous and then elution progressed with increasing organic mobile phase

Response: Thanks for the suggestion. We have revised this.

Line 155: Indicate why the purities of LAS and GAS are very low.

Response: Because LAS and GAS which are C_2-C_3 OSs are too small, we were not able to find a promising stain and use thin layer chromatography (TLC) on silica gel to purify these standards. Instead, we employed ^{1}H NMR and internal standards to determine their purities.

We have added above sentences to the revised manuscript.

Line 153-158: Indicate the chemical formula of all the standards in parentheses next to their names

Response: We have added the chemical formulas of all the standards, i.e., glycolic acid sulfate (GAS, $C_2H_3O_6S^-$), lactic acid sulfate ($C_3H_5O_6S^-$), limonaketone sulfate ($C_9H_{15}O_6S^-$), α-pinene sulfate ($C_{10}H_{17}O_5S^-$), methyl sulfate ($CH_3O_4S^-$), octyl sulfate ($C_8H_{17}O_4S^-$), and phenyl sulfate ($C_6H_5O_4S^-$).

Section 2.3: Add table S3 to section "2.3 Auxiliary measurements" and change the order of table S2 and S3 in the SI and throughout the main text

Response: We have revised this.

Line 186: Indicate the spike concentration/s

Response: We have added the spike concentrations to Table S2.

Line 187: Indicate that in addition to these standards d-carene sulfate, b-caryophyllene sulfate, camphor sulfate were also used in QC.

Response: We have indicated this by rephrasing the following sentence in the manuscript.

"The extraction efficiency of OS species in filter samples was evaluated by measuring the recovery of ten different OS standards (see Table S2)."

Line 191-193: Indicate briefly how the matrix effect is evaluated for those that were already present in the samples, whether the response is neglected if it is very small compared to the spike concentration or subtracted from the total (sample + standard) before calculating the ratio

Response: As for the standards that were already present in the samples, we subtracted the response in the sample from the total (sample + standard) before calculating the ratio. We have added this statement to the manuscript.

Line 148: Indicate the ESI source was operated in negative ion mode

Response: We have indicated this in the following sentence.

"The ESI source was operated in the negative ion mode under optimum conditions as follows…"

Line 230: Is it high MW CHOS (>400 Da?) or high MW S-containing compounds (>400 Da? CHOS+CHONS) and what is the size range?

Response: It is CHOS in the mass range of 400-700 Da. We have revised "The high-MW CHOS species…" as "The high-MW CHOS species (400-700 Da)…".

Line 231: Indicate what anthropogenic sources

Response: The high-MW CHOS (400-700 Da) consists of a bunch of compounds, and the major ones are listed in Table S4. These species showed a large abundance in winter than in summer, indicating that they were more likely to arise from anthropogenic sources than biogenic emissions. However, the specific anthropogenic sources are currently unclear and need to be further studied.

Line 246: What about $C_{27}H_{53}O_{11}S^-$?

Response: We have performed MS^2 analysis for $C_{27}H_{53}O_{11}S^-$ and found that this species basically did not produce sulfur-containing fragments even under the maximum collision energy (50 eV). We have also noticed that the ion signal originally assigned to $C_{27}H_{53}O_{11}S^-$ is also consistent with a sulfur-free ion ($C_{30}H_{49}O_{11}^-$) with a relative mass error of 4.3 ppm, which is only slightly larger than the mass error for $C_{27}H_{53}O_{11}S^-$ (-1.5 ppm). Therefore, we now do not consider this species to be an organosulfate (it may not even be a sulfur-containing organic compound) and exclude it from the analysis and discussion in

the manuscript.

Line 255-256: Revise the sentence "The quantified OS and NOS accounted for 14-18% and 47-67% by intensity of identified CHOS and CHONS, respectively, in polluted winter days and 15-37% and 58-87%, respectively, in polluted summer days (Fig. 3c)." to read "The quantified OS and NOS accounted for 14-18% and 47-67% by intensity of identified CHOS and CHONS in polluted winter days and 15-37% and 58-87%, in polluted summer days (Fig. 3c), respectively."

Response: Thanks. We have revised this.

Line 274: Replace the values of quantified OS in Centreville, AL using the values given in Hettiyadura et al., 2019 and revise the sentence accordingly

Response: We have replaced values and revised the sentence accordingly.

"…but significantly lower than those observed in Atlanta (2366.4 ng m^{-3}, 16.5% of OC) and Centreville, AL (812 ng m^{-3}, 7.3% of OC) (Hettiyadura et al., 2019)…"

Line 274-275: OC%, instead of OM% is given in Hettiyadura et al. indicate it as follows e.g Atlanta, GA (2366.4 ng m-3, 16.5% of OC) (Hettiyadura et al., 2019)

Response: Thanks. We have revised this.

Line 314-316: Also add Chen et al., 2020, which gives evidence for formation of m/z 211 and 213 from 2-MT-OS

Response: We have added this reference to the manuscript.

Section 3.4: How well the OS correlates with individual Ox species (O_3 and NO_2 separately)?

Response: The OS showed a correlation with NO_2 in all seasons (r=0.40 in spring, autumn and winter, and r=0.60 in summer), but it was correlated well with O_3 only in summer (r=0.73 in summer and r=0.19 in other seasons), likely because of the strong titration of O_3 by NO in spring, autumn, and winter when the solar radiation (and photochemistry) was relatively weak.

Line 416-421: I suggest also discussing this result in the context of "Multiphase buffer theory explains contrasts in atmospheric aerosol acidity" by Zheng et al, Science, 2020 (https://science.sciencemag.org/content/369/6509/1374)

Response: Thanks for the suggestion. We have added the following discussions to the manuscript.

"A recent study by Zheng et al. (2020) has suggested that aerosol pH levels in populated continental regions including eastern and northern China are widely buffered by ammonium/ammonia, where the variation in aerosol pH is mainly driven by the variation in ALWC and temperature. Therefore, we infer that the lower aerosol pH in summer than in other seasons in Shanghai was mainly a result of decreased ALWC (Figs. 5 and 6c, d) and enhanced temperature (Fig. 2a)."

Tables and Figures

Figure 1: Indicate the coordinates of the sampling site

Response: We have added the coordinates of the sampling site to the figure.

Figure 1: Increase the symbol size of sampling site or use a star to show the sampling site

Response: We have used a star to show the sampling site.

Figure 2 and 4: Indicate the 4 seasons in the time series either in the figure or in the caption

Response: We have indicated the four seasons in both figures.

Figure 2: Indicate the whole Y axis scale of [H+] concentration in scientific notation (10-x..)

Response: We have revised this.

Figure 5: Indicate what is Ox in the figure caption

Response: We have replaced "the O_x concentration" with "the concentration of O_x (O_x = O_3 + NO_2)" in

the figure caption.

Figure S1: Indicate collision energy of each

Response: The collision energy was 6-10 eV for $C_5H_8NO_8S^-$, 12-25 eV for $C_3H_5O_4S^-$, $C_2H_3O_5S^-$, $C_4H_5O_5S^-$, and $C_{10}H_{16}NO_{10}S^-$, 20-50 eV for $C_6H_5O_4S^-$, and 10-35 eV for the rest. We have added the collision energy of each OS to the figure caption.

Figure S1: Revise the caption to indicate that the S-containing fragments are labeled or label all the fragment ions

Response: We have revised the figure caption as "Figure S1. The MS^2 spectra of quantified OS with the S-containing fragments being labeled."

Table 1: Add retention times

Response: We have added retention times of quantified OS to the table.

Table S1: Indicate the spike concentration/s

Response: We have added spike concentrations to the table

Table S1: Add spike recoveries of LAS and GAS

Response: We have added recoveries of LAS (72.5%) and GAS (77.8%) to the table

Table S2: Clearly indicate the spike concentration of individual OS and/or add the information presented in the table caption to the table

Response: We have added the spike concentration of individual OS, as well as concentrations of OM, NO_3^-, SO_4^{2-}, and OS ambient aerosol samples to the table.

Table S2: Indicate the dates of the samples used

Response: We have indicated the dates of the samples in the table.

Technical corrections

Table 1: Adjust the column width to indicate anthropogenic in one line

Response: We have revised this.

Line 86, 138, 142, 144: Define all acronyms where it first appears (OM, PTFE, UPLC, BEH...)

Response: We have revised this.

Line 116: PRD should be corrected as YRD

Response: Thanks, we have corrected it.

Line 144: Add 'Waters' in parentheses

Response: We have revised this.

Line 169: Organic matter is already defined at line 86, use acronym

Response: We have used acronym here.

Line 288: Correct "($C_7H_9O_7S$)" as "($C_7H_9O_7S^-$)"

Response: We have corrected it.

Line 297: Use 2-MA-OS, as the acronym is introduced before
Use acronyms consistently e.g. OS_i instead of OSI (line 394) and Ox or Ox (subscripted) consistently
Add GA after Atlanta and AL after Centreville (e.g. Atlanta, GA and Centreville, AL)

Response: We have corrected all of these technical issues.