Dear co-editor and referees,

We appreciate all your detailed and valuable comments on our manuscript of "acp-2018-262". Please see the point-by-point response below and changes are marked blue in the revised manuscript.

Referee #3

This manuscript describes measurements of organosulfates and related compounds in Beijing during May-June 2016. Emphasis is placed on understanding the factors that influence organosulfate and nitrooxyorganosulfate formation, particularly during three pollution episodes. The manuscript concludes that sulfate, liquid water content, and acidity are important factors in their formation.

The measurements appear to be carefully conducted and well-described. However, there are some shortcomings in the presentation of the data that should be addressed prior to publication.

Major comments:

1) The discussion of the trends in organosulfates and co-located measurements in section 3.3 is limited to qualitative descriptions. Correlation analysis (like that conducted between observed organosulfates, Table S2) should be extended to include co-located measurements of sulfate, nitrate, ammonium, liquid water content, aerosol acidity [H^+], VOC precursors, oxidants, etc. to provide quantitative support for the associations (or lack thereof) that are discussed in this section.

Response:

The correlation analysis in Table S4 is now extended to include sulfate, nitrate, ammonium, liquid water content, aerosol acidity [H^+], VOC precursors and oxidants. The related descriptions or analysis have also been added in the main text (lines 332-333, 357-359).

Lines 332-333: "The total OS concentrations showed strong correlations with sulfate (r=0.67) or aerosol acidity (r=0.67), suggesting the driving role of acidic sulfate aerosols in the OS formation (Table S4)."

Lines 357-359: "Stronger correlations between OSs and sulfate (r=0.67) or aerosol acidity (r=0.67) compared with that between OSs and LWC (r=0.55) also suggest the importance of acid-catalyzed chemistry for OSs formation."

2) Correlation analysis should also be conducted and presented to support the discussion in section 3.5.

Response:

The correlations between isoprene OSs/NOSs and the co-located measurements are now in Table S4. The correlations between isoprene NOSs and MVK+MACR or NO_2 are shown in Fig. 8. The related descriptions or analysis have also been added in the main text (lines

433-434, 452-454, 457-459).

Lines 433-434: "Both isoprene OSs and NOSs showed strong correlations with isoprene oxidation products (MVK+MACR) (Table S4)."

Lines 452-454: "During daytime, the correlation of isoprene NOSs with NO_2 (r=0.74) was higher than that with MVK+MACR (r=0.69) (Fig. 8). When MVK+MACR was higher than 0.7 ppb, the NOS concentrations did not increase further with MVK+MACR."

Lines 457-459: "During nighttime, a strong correlation between isoprene NOSs and MVK+MACR (r=0.94) was observed, while the increase trend of isoprene NOSs as a function of NO_2 (r=0.53) was not so obvious and their correlation was lower (Fig. 8)."

3) The phrase "representative organosulfates" is used in several instances (line 22, 218, 411) although the authors do not indicate what these species represent. Rather than using this vague language, the authors should more explicit in describing why the selected compounds were quantified and semi-quantified.

Response:

These species were selected as their precursors or formation mechanisms have been proposed in previous chamber studies and their formation represent the anthropogenic-biogenic interactions. The proposed mechanisms could be applied in the field observation. "representative" was deleted in the revised version (lines 22, 250, 471-472). New text given below is added to improve the clarity on this point.

Lines 251-255: "The quantified species could usually be formed via the interaction between biogenic precursors (e.g. isoprene, monoterpene) and anthropogenic pollutants (e.g. SO_4^{2-}, NO_x), which have been reported in previous chamber studies (Surratt et al., 2007; Surratt et al., 2008; Surratt et al., 2010). A total of ten OSs and three NOS species were quantified in this study and their concentrations are listed in Table 1."

4) The discussion in the paragraph beginning at line 209 implies that the only difference between the three air pollution episodes was their inorganic ion content (which affected aerosol acidity and liquid water content). Do back trajectories, VOC concentrations, and other co-located measurements support this? If not, how could variations in other atmospheric conditions explain the organosulfate observations?

Response:

The back trajectories, VOC and oxidant concentrations during each episode are now included added in Table S5. Description for the related analysis has been added in the main text (lines 335-336, 345-347, 359-360, 406-408, 440-442).

Lines 335-336: "The back trajectories, average concentrations of VOC precursors and oxidants during each episode are also shown in Table S5."

Lines 345-347: "Moreover, the oxidant levels, indicated by O_x (NO_2+O_3) in this study (Herndon et al., 2008), were much higher than the other two episodes, which favored the formation of VOC oxidation products (e.g. MVK+MACR) (Table S5). This is another reason for higher OSs concentration level during episode III."

Lines 359-360: "The back trajectories during episode I were different from those during episode II or III (Table S5), which could be one reason for different conditions (e.g. SIA composition) during episode I."

Lines 406-408: "The highest nighttime concentration of $C_{10}H_{16}NO_7S^-$ was recorded on May

27 during episode II (Fig. 5). Besides the high NO_2 concentration (>20 ppb), the high monoterpene level was another primary reason for the elevated concentration of monoterpene NOSs (Table S5)."

Lines 440-442: "The highest concentrations of isoprene OSs and NOSs were observed during the nighttime of May 30 during episode III (Fig. 7), with high sulfate, MVK+MACR, aerosol acidity and LWC (Fig. 3, Table S5)."

5) The overall concentration of organosulfates observed in Beijing seems to be very low (~150 ng/m^3). In encourage the authors to discuss this observation and include it in their comparison to prior studies.

Response:

The key species and total quantified OS concentrations in this and prior studies are summarized and compared in Table S3. Related description or analysis was also added in the main text.

The low OS concentrations in Beijing compared with that in southeast US was mainly attributed to the low concentrations of isoprene OSs, especially $C_5H_{11}O_7S^-$ formed via HO_2 channel under low-NO_x conditions (Table S3). The related discussions were added in lines 287-298. The reasons include: 1) The isoprene concentration in southeastern US (1.9 ppb) (Xu et al., 2015) is much higher than that observed during our campaign (297 pptv). 2) The IEPOX formation could be suppressed by the high-NO_x conditions in Beijing (Zhang et al., 2017; Hu et al., 2015). 3) The RH in Beijing was lower than that in southeast US (Xu et al., 2015), which possibly led to an increase of aerosol viscosity and decrease of diffusivity within the particles, resulting in lower OS formation (Shiraiwa et al., 2011). 4) The OM-coated particle structures observed in Beijing could reduce the reactive uptake of isoprene oxidation products (Li et al., 2016; Zhang et al., 2018; Riva et al., 2016a), which may be another possible reason for lower isoprene OSs in this study. 5) Lactic acid sulfate was employed as a surrogate standard to quantify isoprene OSs, which may also be one possible reason for low isoprene OSs in this study.

Lines 287-298: "We used lactic acid sulfate as a surrogate standard to quantify isoprene OSs on the basis of their similar structures and retention times (Table 1). The isoprene concentration in southeastern US (1.9 ppb) (Xu et al., 2015) was much higher than that observed during our campaign (297 pptv). Besides the lower VOC precursors and measurement uncertainty, the lower isoprene OSs in this study could be attributed to different atmospheric conditions in Beijing from those in southeastern US. The IEPOX formation under low-NOx conditions (HO_2 channel), usually with higher yields than the oxidation products under high-NO_x conditions (NO/NO_2) (Worton et al., 2013), could be suppressed under the high-NO_x conditions (see section 3.4 for the high-NO_x conditions) in Beijing (Zhang et al., 2017; Hu et al., 2015). The RH in Beijing was lower than that in southeast US (Xu et al., 2015), which possibly led to an increase of aerosol viscosity and a decrease of diffusivity within the particles, resulting in lower OS formation (Shiraiwa et al., 2011). Moreover, the OM-coated particle structures observed in Beijing could reduce the reactive uptake of isoprene oxidation products (Li et al., 2016; Zhang et al., 2018; Riva et al., 2016a), which may be another possible reason for lower isoprene OSs in this study."

6) A table comparing key species and total organosulfate concentrations across this and prior studies would be a useful addition to the supplement to support the comparison of data.

Response:

A summery table (Table S3) is now added in the supplement to compare the key species and total OSs concentrations in prior studies and this study.

7) In two places (line 117 and 173) the authors indicate that the organic carbon concentration was held constant across samples analyzed by Orbitrap, in order to decrease ion suppression. The authors should provide a reference to support this statement and/or evidence to support that ion suppression did not occur.

Response: The variation of different sample matrix would influence the responses of different species (Furey et al., 2013). A previous study suggested that the extent of ion suppression showed good linearity with the concentrations of urine extracts (Chen et al., 2015).

A set of experiments were also conducted to evaluate the influence of sample matrix and ion suppression in this study. With constant OC loading, the variation of ion suppression extent arising from different chemical compositions was lower than 40% in this study. Overall, the extent of ion suppression was proposed to be comparable for samples with similar OC concentrations in this study, though the variation of ion suppression caused by different sample composition cannot be eliminated. The related description has been added in the supplement (Appendix S1).

Appendix S1 The influence of ion suppression on Orbitrap MS analysis

The overall molecular composition of S-containing organic species was measured using ESI-Orbitrap MS analysis. Sample matrix would influence the MS responses of different species, which cannot be eliminated (Furey et al., 2013). A previous study showed the extent of ion suppression was in good linearity with the concentrations/dilution factors of urine extracts (Chen et al., 2015). We conducted a set of experiments to evaluate the influence of sample matrix on MS response for OSs. A field blank sample, a clean sample and a polluted sample were extracted following the same procedures described in section 2.2. The sample collected during the nighttime of May 24 and 30 were selected to represent the clean sample and the polluted sample, respectively. Sample extracts were dried and re-dissolved either in acetonitrile/water (1:1) solvent or solvent containing 0.1 ppm α-pinene OS. The filter portion size and solvent volume were adjusted to yield solution containing ~100 μg or 200 μg OC/mL solvent for the clean sample and polluted sample. The OC concentrations are referred to as the OC loading before the SPE clean-up procedure. Only two concentration levels were examined due to the sample limitation. The intensity (signal-to-noise ratio, s/n) of α-pinene OS (0.1 ppm) in the three different sample matrixes were obtained by deducting the intensity of m/z=249.0802 in the same sample diluted by solvent without α-pinene OS (0.1 ppm) addition. The intensity in each sample was normalized by the ion injection time to make the intensities comparable (Kuang et al., 2016).

The intensity of 0.1 ppm α-pinene OS was the highest in the matrix of field blank extract and the lowest in the matrix of polluted sample extract. The extent of suppression ranged from 20% in the matrix of 100 μg OC from the clean sample to 62% in the matrix of 200 μg OC from the polluted sample (Fig. S1). It was clear that the extent of suppression increased with the OC content of the matrix, from 20% in 100 μg OC matrix to 32% in 200 μg OC matrix for the clean sample and from 45% in 100 μg OC matrix to 62% in 200 μg OC matrix for the polluted sample. The relative standard deviation (RSD) of α-pinene OS arising from different OC loadings (100 μg and 200 μg OC/mL solution) were 26% and 12% in polluted and clean samples, respectively. This result confirmed the benefit of adjusting OC content to a uniform level before Orbitrap MS analysis in minimizing the impact of matrix ion suppression. We note that when the sample was diluted to 100μg OC/mL solvent, the intensity of α-pinene OS in the clean sample was comparable to that in the field blank sample. This indicated that the ion suppression would be insignificant with less than 100 μg OC/mL solution. However, this level of dilution may limit the identification of species present at low concentrations due to too much dilution.

It is also apparent that chemical composition of the OC matrix also played a role in ion suppression. The RSD of α-pinene OS arising from different chemical composition (clean sample and polluted sample) were 40% and 27% in samples containing 200 μg and 100 μg OC/mL solution, respectively, which could represent the biggest differences of ion suppression arising from chemical composition. This source of difference in ion suppression could not be controlled with the infusion injection mode.

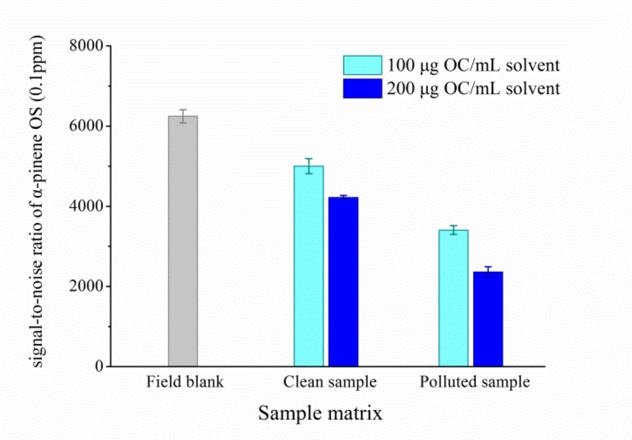

Figure S1 The intensity of α-pinene OS (0.1 ppm) in different sample matrix (blank sample, clean sample, polluted sample) with different OC loadings. The error bars were derived from three repeat injections of the same sample.

8) The SPE method described at line 118 indicates that select compounds are removed by the SPE process. However, there is no mention until line 207-215 what effect the SPE has on organosulfates. I suggest making a note at line 120 indicating that further discussion of the impact of this clean-up procedure on organosulfates is discussed in section 3.1.

Response:

A note was added in lines 130-132.

Line 130-132: "Some selected OS species with low MW would also be removed by the SPE clean-up procedure, which will be discussed in section 3.1."

9) Line 150 – please explain how semi-quantification is achieved for a surrogate standard that appears to be comprised of a mixture of compounds (e.g., "alpha-pinene OS").

Response:

This point was explained in lines 171-173: "For the molecule with isomers, quantification was performed by summing up the peak areas of the isomers, treated as one species (e.g., monoterpene NOSs with $[M-H]^-$ at m/z 294 were treated as one NOS species)."

10) The discussion at lines 198-202 implicates long-chain alkanes and diesel/biodiesel emissions as the source of several organosulfates. Can the authors please comment on the (un)certainty of these assignments and the possibility that they may derive from monoterpenes (given the similarities in the molecular formulas to the monoterpene derived organosulfates mentioned later in the same paragraph)?

Response:

The comment on the uncertainty when assigning OSs sources was added in lines 231-232: "Many OSs previously designated as biogenic origins were also found in the anthropogenic sources (Blair et al., 2017), which may raise uncertainty when assigning OS sources in field observation studies."

11) Line 225-227, please include the city, state, and country for each of the measurement sides discussed. Centreville and summertime Alabama are presented as though they are different locations, when they are one in the same.

Response:

The studies reported in Alabama were combined together. The city, state, and country were included in the summery table (Table S3), and the state or country information were included in the main text.

12) I encourage the authors to consider their use of significant figures in reporting their data. Many organosulfate concentrations are listed to four significant figures, while their contributions to organic carbon have only one. The former seems to be too many (considering measurement uncertainties and use of surrogate standards) and the latter seems to be not enough.

Response:

Revised. The OS concentrations are now presented to show three significant figures while the contributions of OS to OM are shown with two significant figures.

13) In Table S2, please label which compounds are "isoprene OS" that are mentioned at line 238.

Response: "isoprene OSs" is labelled in Table S4.

14) In several places, the wording should be adjusted so as to better reflect that many species were semi-quantified and absolute concentrations remain unknown. At line 244: "The concentration of quantified isoprene OS…" At line 271 "…were the second most abundant signals among the observed species…"

Response: They were revised accordingly (lines 284, 318).

15) In Figure 1, please write out the dates "24 May night" and "30 May night" rather than "0524N" and "0530N".

Response: Revised accordingly.

16) In the figure 2 caption, please point the reader to the specific section where the information about the missing water-soluble OS can be found (3.1)

Response: Do you mean the figure 1 caption? It was revised as "…, details are described in section 3.1".

17) In the Figure 2 caption, please explain that these plots only include the select species quantified or semi-quantified by LCMS.

Response:

The caption was revised as "The relative contribution of different OS and NOS species. Only the selected species (semi-)quantified by HPLC-MS are included in this figure."

18) There is a lot going on in Figure 4. Can this be simplified? Or perhaps broken into multiple graphs that do not have so much overlap? Also, because there is so much going on, adding the key findings / takeaway messages from the graphs to the caption would help the reader.

Response:

Figure 4 was broken into four graphs and takeaway message was added: "When sulfate dominated the accumulation of secondary inorganic aerosols (SO_4^{2-}/SIAs> 0.5), both aerosol LWC and acidity (pH<2.8) increased and OS formation was obviously promoted. In comparison, the acid-catalyzed OS formation was limited by lower aerosol acidity under nitrate-dominant conditions."

19) Figure S1 – delete 2016 from the date on the x-axis (as this takes up unnecessary room). It would be helpful to designate what is daytime and nighttime in this figures as is done in many of the other figures.

Response:

Revised as suggested. '2016' was deleted from the date on x-axis. The gray background was added to denote the nighttime and white background was used to denote the daytime.

20) Table S1 would benefit from organization by m/z so that the table can be easily navigated by other researchers who are likely to look up the data in this way.

Response: Revised as suggested. The formulas in Table S2 have been organized by m/z in the revised version.

Technical/editorial comments

21) Line 20: "the majority"

Response: Revised accordingly (line 20).

22) Line 22: "mass spectrometry was employed"

Response: Revised accordingly (line 22).

23) Define LWC at line 27

Response: LWC was defined in line 27.

24) Define SIA species at line 28

Response: SIAs was defined in line 28.

25) "0.02%" of OA at line 46 seems too small, is this reasonable?

Response: Thanks very much for your careful reading. The percent "0.02%" should was "2%". It has been corrected (line 47).

26) Line 109: "flow rates were"

Response: Revised accordingly (line 119).

27) Line 164: Mg^{2+} *(rather than* Ma^{2+}*)*

Response: Thanks. It was corrected (line 188).

28) Line 172: do not need to say "percent" in either instance, since it is earlier in the sentence.

Response: Revised accordingly (line 202-203).

29) Line 283: "favorable for OS formation"

Response: Revised accordingly (line 330).

30) Hettiyadura et al. (2015) propose a mechanism for the formation of the isoprene organosulfate with m/z 211 that is consistent with the hypothesis presented by Surratt et al. (2008).

Response: Thanks for the reminding.

31) Line 343: "times larger than daytime"

Response: Revised accordingly (line 397).

32) Line 349: "levels at night…"

Response: Revised accordingly (line 403).

33) Line 351: "was in excess and no longer the limiting factor in NOS formation.

Response: Revised accordingly (line 405-406).

34) Line 380: "NOSs form via"

Response: Revised accordingly (line 439).

35) Line 382: "formation of isoprene OSs or NOSs, epoxides first form…"

Response: Revised accordingly (line 442).

36) Line 393: "increase further with MVK+MACR."

Response: Revised accordingly (line 453-454).

37) Line 419: "OS concentrations"

Response: Revised accordingly (line 479).

38) Line 430: "NO_2 *levels at night…"*

Response: Revised accordingly (line 490).