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 #1

This paper describes an observation of organosulfates (OSs) as well as nitroxyorganosulfates (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 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 NO_3 in urban environments, which appears to be partly responsible for the observed NOSs.

Response: Thanks for your suggestions. The goals and motivation of this study were added or revised as suggested in lines 91-97, 98-105:

Lines 91-97: "Missing knowledge of formation mechanisms, the complexities of ambient aerosol composition and oxidation condition, and the lack of commercially available standards all hinder us from understanding the formation and fate of OSs in ambient atmosphere. Few field studies has been conducted in urban areas dominated by anthropogenic pollutants (e.g. NO_x, SO_4^{2-}). Observations are lacking to illustrate how severe anthropogenic pollutants could influence the OS formation under different physical environmental conditions. This work reports a comprehensive characterization of particulate OSs in summertime Beijing, a location under the influence of both biogenic and severe anthropogenic sources. This study provides direct observational evidence for gaining insights into OS formation."

Lines 98-105:

"…HPLC-MS was then applied to quantify some OSs and NOS species in ambient aerosols using newly synthesized authentic standards and surrogate standards."

"Previously proposed formation pathways of OS or NOS (e.g. acid-catalyzed aqueous-phase chemistry, nighttime NO_3 chemistry) were considered, and the influence of different environment conditions or factors on the formation were comprehensively elaborated."

"It has been suggested that both aqueous-phase chemistry and nighttime NO_3 chemistry play important roles in the heavy haze of Beijing (Wu et al., 2018; Wang et al., 2017b; Wang et al., 2017a). Using OSs and NOSs as examples, this work illustrates SOA formation via acid-catalyzed aqueous-phase chemistry, nighttime NO_3 chemistry under the interaction between abundant anthropogenic pollutants and biogenic emissions."

I found the discussion in sections 3.3 and 3.5 too qualitative. I realize that the data set mat 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 then currently afforded by Figure 4.

Response: The correlation analysis was added in Table S4, Fig. 8 and the main text (lines 331-333, 357-359, 433-434, 452-454,).

Lines 331-333: The OS concentrations generally followed a similar trend to that of sulfate aerosols (Fig. 3). 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.

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

Line 452-454: During daytime, the correlation of isoprene NOSs with NO_2 (r=0.74) was stronger than that with MVK+MACR (r=0.69) (Fig. 8).

Lines 457-459: During nighttime, a strong correlation between isoprene NOS 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).

Here are minor editorial comments.

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

Response: It has been revised as "The sulfate esterification of alcohols could also be a pathway leading to OSs formation, while Minerath et al (2018) predicted that this mechanism was kinetically insignificant under ambient tropospheric conditions. However, this prediction was based on laboratory bulk solution-phase experiments and the applicability to the liquid-phase on particles suspended in the air is unconfirmed." (lines 58-61)

L104: monoterpene -> monoterpenes

Response: Revised accordingly (line 114).

L124: mass resolution -> mass resolving power

Response: Revised accordingly (line 136).

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

Response: The allowed elements and constraints placed on the formulas were described in lines 140-144: "Elements ^{12}C, ^{1}H, ^{16}O, ^{14}N, ^{32}S and ^{13}C were allowed in the molecular formula calculations. The H/C, O/C, N/C and S/C ratios were limited to 0.3- 3.0, 0- 3.0, 0- 0.5 and 0- 2.0. The assigned formulas were also restrained by the double bond equivalent values and the nitrogen rule for even electron ions. More details about the molecular formula assignment have been introduced in Wang et al. (2017c)."

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

Response: Revised accordingly (line 161).

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

Response: Thanks. All similar cases have been corrected throughout the main text.

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.

Response: Related descriptions were added in lines 201-202: "'others' (e.g. CH, CHN, CHS, CHNS) refer to the compounds excluded from the above major compound categories" and line 197: "On average, 62% of the observed peaks in ESI negative mode are assigned with unambiguous molecular formulas."

L202: OSs molecules -> OS molecules

Response: Revised accordingly (line 234).

L202: monoterpene -> monoterpenes

Response: Revised accordingly (line 235).

L203: molecules -> ions

Response: Revised accordingly (line 235).

L205: relatively higher relative intensity -> higher relative intensity

Response: Revised accordingly (line 237).

L206: less -> fewer

Response: Revised accordingly (line 240).

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

Response: Yes, it's the average over all the samples. This sentence was revised as "The average concentration of all the quantified OSs were 41.4 ng/m^3 during the campaign." (lines 256-257)

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

Response: Centreville is located in Alabama, US. The study in Centreville was combined with other studies in Alabama, US to be clear.

L268: monoterpene -> monoterpenes

Response: Revised accordingly (line 315).

L270: were -> was

Response: Revised accordingly (line 317).

L289 and elsewhere in this section: Secondary inorganic aerosols (SIAs) are defined as sulfate, nitrate and ammonium on line 289. However, the ratio of $SO_4^{(2-)}$ *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* $SO_4^{(2-)}/[SO_4^{(2-)}+NO_3^{(-)}]$ *and use it in their discussion instead of the vaguely defined ratio they are currently using.*

Response: The "SO_4^{2-}/SIAs ratios" was revised to "SO_4^{2-}/SIAs mass concentration ratios", to make the definition clear in section 3.3. SIAs (secondary inorganic aerosols) or SNA (sulfate, nitrate, and ammonium) have been commonly used to indicate the secondary inorganic aerosols (sulfate, nitrate, and ammonium) in previous studies (Chen et al., 2016; Wu et al., 2018; Zheng et al., 2016; Aksoyoglu et al., 2017; Choi et al., 2009; Alastuey et al., 2004; Jimenez-Guerrero et al., 2011; Huang et al., 2014). Each of the three secondary ions (i.e., sulfate, nitrate, and ammonium) is important in influencing aerosol liquid water content and acidity (Guo et al., 2015). Thus, we prefer to keep the definition of "SIAs" to indicate different aerosol compositions during the three episodes.

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L304-305: please fix grammar in this sentence

Response: The sentence was revised as following:

Lines 354-356: "During the daytime of May 23, higher aerosol LWC was observed due to the rapid increase of nitrate, however, the aerosol acidity was lower as a result of the less contribution from sulfate."

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".

Response: "nighttime formation" was changed to "elevated nighttime concentrations" (lines 399-400).

"lower production" was deleted in the revised version.

"The lower concentrations of monoterpene NOSs during the daytime could be attributed to the much lower production, as the monoterpene, NO_x and NO_x/BVOCs ratios were much lower than those at night." was changed to "The lower concentrations of monoterpene NOSs during the daytime could be attributed to the lower monoterpene, NO_x and NO_x/BVOCs ratios than those at night." (lines 409-410)

Table 1: some of the OS structures are draw 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

Response: All the OS structures in Table 1 were changed to deprotonated forms.