

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 #4

This ACPD article characterizes the amount of organosulfates (OSs) and nitrooxy organosulfates (NOS) through ESI-Orbitrap and HPLC-MS during a field campaign near Beijing, China. By using standards or surrogates, the manuscript breaks down organosulfates into isoprene-derived OSs and monoterpene derived OSs, and shows isoprene-derived OSs dominated the total OSs.

By analyzing inorganic aerosol composition, acidity, and liquid water content, the author concludes that due to acid catalyzed chemistry, the production of isoprene-derived OSs was strongly correlated with the acidity of the particles, which was governed by sulfate percentage in secondary inorganic aerosols.

The monoterpene-derived NOSs and isoprene-derived NOSs were measured mainly by the HPLC-MS and their concentrations were used to correlate with the ambient NO<sub>x</sub> concentration. Monoterpene NOSs were greatly enhanced during night time due to high NO<sub>x</sub> concentration.

As written in the manuscript, through measurements of OSs and NOSs, this study describes the interaction between biogenic emission and anthropogenic pollutants. The data of this kind are valuable and fits into the scopes of ACP. Overall, the manuscript is sound and after addressing the following issues, it is suitable to be published on ACP.

### Comments

*Line 145: This part was not very clear. How did the author obtain the monoterpene NOSs for quantification? Was it synthesized or commercially available? Please illustrate in detail.*

#### Response:

Monoterpene NOSs were quantified using  $\alpha$ -pinene OSs or limonaketone OS as surrogates due to their similar structures shown in Table 1. The monoterpene OSs were synthesized and the details are reported in Wang et al. (2017). These have been illustrated in lines 166-167, 170-171.

Line 166-167: “Four monoterpene derived OS standards were synthesized and the details are given in Wang et al. (2017).”

Lines 170-171: “ $\alpha$ -pinene OS and limonaketone OS were respectively used to quantify monoterpene NOSs  $C_{10}H_{16}NO_7S^-$  and  $C_9H_{14}NO_8S^-$  due to the similar carbon structures (Table 1).”

*Line 239: The manuscript describes the strong correlation between GAS, LAS, and HAS with isoprene OSs. Then the author concludes that “isoprene or its oxidized products as potential*

precursors of GAS, LAS and HAS.” The logic here is flawed. Isoprene OSs are correlated with sulfate concentration. Therefore, it is very much likely that GAS, LAS, and HAS are just correlated with sulfate concentration. The correlation of GAS with isoprene OSs does not mean isoprene oxidation products may be precursors of GAS, LAS, and HAS. I suggest changing this part to: “They also showed strong correlations with isoprene OSs (Table S2), suggesting GAS, LAS, and HAS can be potential tracers for organosulfates.”

**Response:**

The sentence has been revised as below to improve the clarity:

Lines 278-280: “They also showed strong correlations with isoprene oxidation products (MVK+MACR) and isoprene OSs (Table S4), suggesting isoprene oxidized products as potential precursors of GAS, LAS and HAS.”

It has been suggested that GAS, LAS and HAS could form via isoprene oxidation in the presence of acidic sulfate (Fu et al., 2008; Carlton et al., 2009; Riva et al., 2016a; Surratt et al., 2008; Schindelka et al., 2013). (as described in lines 280-283) Thus, we indicate here that isoprene oxidized products could be potential precursors of GAS, LAS and HAS.

*Line 250: The author raised a very interesting point here. The Southeast U.S. has an isoprene OSs concentration of 165 ng cm<sup>-3</sup> (Rattanavaraha et al., 2016). The isoprene concentration in Beijing is only 5 times lower than Southeast U.S, but the isoprene-derived OS is 10 times lower. The average RH in Beijing is also lower than Southeast U.S. Maybe the author should provide this evidence to further support the statement that organic coatings and their phase can play an important role.*

**Response:** Thanks for the suggestions. This was added in lines 294-295: “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).”

*There are a few important references that I would suggest adding to the manuscript:*

*Line 69: I suggest adding Shrestha et al., 2014; Zhang et al., 2015 to provide more evidence for how RH and LWC affect aerosol viscosity.*

**Response:** The references were added in lines 73.

*Line 66: I suggest adding Riedel et al., 2015 to show acid-catalyzed reactive uptake reactions in forming isoprene-derived OA.*

**Response:** The reference was added in lines 70.

*Line 250: I suggest adding Riva et al., 2016 to show the effects of pre-existing organic loading on isoprene-derived SOA formation. Riva et al. was the first to show the effect of OA on isoprene SOA formation, and Zhang et al. 2018 was the first to quantify such effects.*

**Response:** Thanks for the reminding. The reference (Riva et al., 2016a) was added in line 297.

*Line 164: Oxford comma is suggested here.*

**Response:** Revised as suggested (line 188).

*Line 371-372: Are there any evidence to show that isoprene NOSs are formed via similar pathways (or multiphase reactions) as isoprene OSs? To my knowledge there is limited*

*experimental evidence to show the isoprene NOSs are formed through multiphase reactions. The author should provide more evidence to support the argument.*

**Response:**

The sentence was revised to be accurate: “Formation of the isoprene NOSs are supposed to have similar limiting factors to those affecting isoprene OSs”. ([lines 428-429](#))

NO<sub>3</sub>-initiated oxidation was proposed as the limiting step in the formation of monoterpene NOSs, supported by the observation of nighttime enhancement under high-NO<sub>x</sub> conditions. Acid-catalyzed chemistry was proposed to be a limiting step in the formation of isoprene OSs. We lack direct evidence to discern whether -ONO<sub>2</sub> group in isoprene NOSs was added in gas-phase or multiphase-phase reaction processes. However, we note isoprene NOSs showed similar temporal variation and good correlations with sulfate, aerosol acidity and isoprene OSs. This led us to propose that acid-catalyzed step, rather than NO<sub>3</sub>-initiated (-ONO<sub>2</sub> addition) step was the limiting step in isoprene NOSs formation. In other words, the isoprene NOSs did not appear to form via NO<sub>3</sub>-initiated oxidation as monoterpene NOSs.