

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  $\text{NO}_3$  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.  $\text{NO}_x$ ,  $\text{SO}_4^{2-}$ ). 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  $\text{NO}_3$  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  $\text{NO}_3$  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  $\text{NO}_3$  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 may 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 than 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  $\text{NO}_2$  ( $r=0.74$ ) 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  $\text{NO}_2$  ( $r=0.53$ ) 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  $^{12}\text{C}$ ,  $^1\text{H}$ ,  $^{16}\text{O}$ ,  $^{14}\text{N}$ ,  $^{32}\text{S}$  and  $^{13}\text{C}$  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<sup>3</sup> 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<sub>4</sub><sup>(2-)</sup> 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<sub>4</sub><sup>(2-)</sup>/[SO<sub>4</sub><sup>(2-)</sup>+NO<sub>3</sub><sup>(-)</sup>] and use it in their discussion instead of the vaguely defined ratio they are currently using.*

**Response:** The “SO<sub>4</sub><sup>2-</sup>/SIAs ratios” was revised to “SO<sub>4</sub><sup>2-</sup>/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<sub>x</sub> and NO<sub>x</sub>/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<sub>x</sub> and NO<sub>x</sub>/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.

## Referee #2

This study investigates the composition, abundance, and formation pathways of organosulfates during the day and night in the summer of Beijing under the influence of biogenic and anthropogenic emissions. Under various pollution episodes characterized by different aerosol composition and levels of gas-phase pollutants, the authors show that the formation of organosulfates can be largely influenced by the concentrations and relative contribution of sulfate, aerosol acidity and liquid water content. This work provides new field observation data to better understand the abundance and formation of organosulfates in the atmosphere. I support the publication of this paper after addressing the following questions.

### **Major comments:**

*My major comment is the calculation and determination of the aerosol acidity and aerosol phase water content.*

*Line 161, "Aqueous phase  $[H^+]$  and LWC were then calculated with the ISORROPIA-II thermodynamic model. ISORROPIA-II was operated in forward mode, assuming the particles are "metastable" (Hennigan et al., 2015; Weber et al., 2016; Guo et al., 2015). The input parameters included: ambient RH, temperature, particle phase inorganic species ( $SO_4^{2-}$ ,  $NO_3^-$ ,  $Cl^-$ ,  $NH_4^+$ ,  $K^+$ ,  $Na^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ) and gaseous  $NH_3$ ."*

*First, the authors should provide justifications why ambient aerosols can be assumed to be "metastable" in this work. It is important to discuss the physical state of the ambient aerosols (e.g. solid, liquid or solid/liquid) during the field campaign. This information is important for analyzing and interpreting the data given aqueous aerosol-phase reactions have been proposed as one of the major formation pathways for the organosulfates in this work. Some major conclusions are drawn based on this assumption. A detailed explanation is needed.*

### **Response:**

(1) Thanks for the suggestions. The detailed explanation for assuming "metastable" has now been added in Appendix S2.

The ISORROPIA-II thermodynamic model was run for metastable aerosols in this study. It has been suggested in previous studies that "metastable" state often showed better performance than the "stable" state solution, and was commonly applied in previous pH or LWC predictions (Bougiatioti et al., 2016; Guo et al., 2016, 2015, 2017; Weber et al., 2016; Liu et al., 2017a). The verification of thermodynamic prediction by ISORROPIA-II was assessed by comparing the predicted and measured gaseous  $NH_3$  in this study (Fig. S2). Good agreement was reached between the predicted and measured gaseous ammonia concentrations (slope=0.99, intercept= 1.8  $\mu\text{g}/\text{m}^3$ ,  $R^2= 0.97$ ). The result suggested that the "metastable" assumptions are reasonable in this study.

The detailed explanation was added in [Appendix S2](#) and the main text ([lines 188-189](#)).

[Lines 188-189](#): "The thermodynamic calculations were validated by the good agreement between measured and predicted gaseous  $NH_3$  (slope=0.99,  $R^2= 0.97$ ) (see Appendix S2 for details)."

(2) We agree that phase state of ambient aerosols is important for discussing the aqueous

aerosol-phase reactions. The ubiquitous existence of ambient metastable aerosols has been observed in previous studies (Rood et al., 1989). Liquid phase state of ambient aerosols has also been observed during haze episode in winter Beijing (Liu et al., 2017b). Unfortunately, we lack direct evidence to reveal the aerosol phase state in this study. Related discussion was also added in [Appendix S2](#).

### **Appendix S2 The validation of ISORROPIA-II thermodynamic model prediction**

The ISORROPIA-II thermodynamic model was run for metastable aerosols in this study. It has been suggested in previous studies that “metastable” state (only liquid phase) often showed better performance than the “stable” state (solid+ liquid) solution, and was commonly applied in previous pH or LWC predictions (Bougiatioti et al., 2016;Guo et al., 2015;Guo et al., 2016;Guo et al., 2017;Weber et al., 2016;Liu et al., 2017a). Though we lack direct evidence to reveal the physical state of ambient aerosols in this study, indirect evidence is provided to support that the assumption is reasonable. The verification of prediction by ISORROPIA-II was assessed by comparing the predicted and measured gaseous NH<sub>3</sub> in this study (Fig. S2) (Bougiatioti et al., 2016;Guo et al., 2015;Guo et al., 2016;Guo et al., 2017;Weber et al., 2016;Liu et al., 2017a). Good agreement was reached between predicted and measured gaseous ammonia concentrations (slope=0.99, intercept= 1.8 μg/m<sup>3</sup>, R<sup>2</sup>= 0.97). The result suggested that the “metastable” assumptions are reasonable in this study.

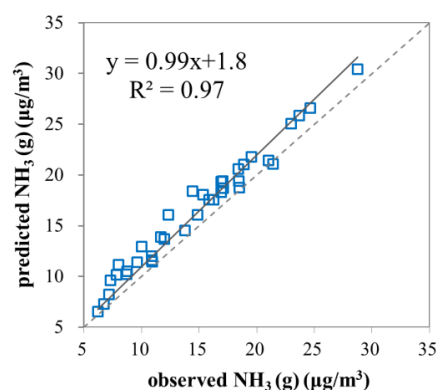


Figure S2 Comparison of predicted NH<sub>3</sub> (g) and measured NH<sub>3</sub> (g)

The ubiquitous existence of ambient metastable aerosols has been observed in previous studies (Rood et al., 1989). Based on our previous study in the winter of urban Beijing (Liu et al., 2017b), the rebound fraction of fine particles was ~0.8 at <20% RH, indicating a semisolid phase of particles. As the RH increased from 20 to 60%, the rebound fraction decreased from 0.8 to 0.2, suggesting transition from semisolid to liquid phase state. The rebound fraction of particles was lower than 0.4 at >40% RH, indicating that the liquid phase as the major phase state of ambient aerosols. RH conditions of < 20% were quite limited during the campaign. RH was usually higher than 40% and could increase to higher than 60% at night. Thus, a nearly liquid phase was likely the major phase state of ambient aerosols at night in this study. It would be desirable to obtain direct observational evidence of aerosol phase state in future studies.

### **References:**



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*Second, given the organic compounds contribute significantly to the total aerosol mass in this work, do the organic compounds being considered when the aerosol acidity and aerosol water content are calculated using the aerosol thermodynamic model. If not, the authors should discuss how the organic compounds would affect the predictions of the aerosol acidity and aerosol water content. Would the findings or conclusions drawn from the data based on inorganic species only affect by the presence of organic compounds? The authors should discuss how they determine the ambient RH and temperature used for their model simulations.*

**Response:** New discussion has been added in main text (lines 189-194, 177-179) and Fig. S3 to address this point.

Lines 189-194: “The contribution of organics to LWC was not considered in this study. Our previous study in Beijing has suggested that LWC associated with organic species was insignificant (<6%), compared to that of secondary inorganic aerosols (Wu et al., 2018) (see Fig. S3 for the comparison between LWC with or without water associated with organic compounds). Previous study also suggested that the predicted aerosol acidity or pH without consideration of organic water could also be sufficient for discussing aqueous SOA chemistry in this study, due to the minor effect on aerosol pH (0.15-0.23) (Guo et al., 2015).”

Thus, the conclusions drawn from the data of inorganic species would not be affected by the presence of organic compounds, due to their minor effects on aerosol water or acidity.

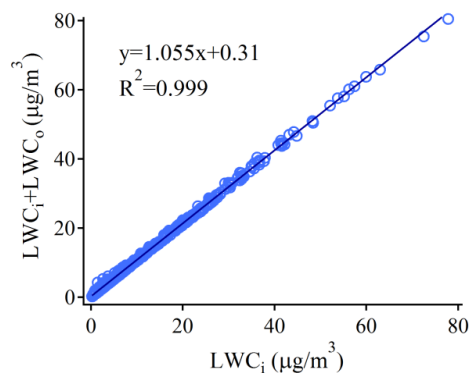


Figure S3 Comparison between aerosol liquid water content with or without water associated with organic compounds. LWC<sub>i</sub> and LWC<sub>o</sub> represent the water contributed by inorganic compounds and organic compounds, respectively. The data is from Fig. S1 in Wu et al. (2018) based on the measurement in Beijing (Wu et al., 2018).

Lines 177-179: “Meteorological parameters, including relative humidity (RH), temperature, wind direction and wind speed (WS) were continuously monitored by a weather station (Met one Instrument Inc.) during the campaign.”

**Minor comments:**

*Line 147* “OSs and NOSs were quantified using authentic standards or surrogates with similar molecular structures (Table 1). Lactic acid sulfate (LAS) and glycolic acid sulfate (GAS) were prepared according to Olson et al. (2011) (Olson et al., 2011). Four monoterpene derived OSs were synthesized according to Wang et al. (2017) (Wang et al., 2017d).” What is the purity of these standards used in this work? What is the recovery or extraction efficiency of these standards?

**Response:** The purity and recovery of OS standards were added in lines 164-168 and table S1.

Lines 164-168: “Lactic acid sulfate (LAS) and glycolic acid sulfate (GAS) were prepared according to Olson et al. (2011). The purity of LAS and GAS are 8% and 15%, determined by 1H NMR analysis using dichloroacetic acid as an internal standard, and the recovery are 89.5% and 94.9%, respectively. Four monoterpene derived OS standards were synthesized and the details are given in Wang et al. (2017). The purity of the four monoterpene OS standards are higher than 99% and the recovery are 80.5%-93.5% (Table S1).”

Table S1 The purity and recovery of organosulfate standards in this study

Organosulfate	Purity (%)	Recovery (%)
lactic acid sulfate	15%	
glycolic acid sulfate	8%	
α-pinene OS	>99%	80.5%
β-pinene OS	>99%	93.5%
limonene OS	>99%	85.4%
limonaketone OS	>99%	82.5%

Line 172, “The OC content in each sample for Orbitrap MS analysis was kept roughly constant to minimize variation arising from matrix ion suppression.” Please elaborate how to achieve this goal.

**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 compositions 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  $\alpha$ -pinene OS. The filter portion size and solvent volume were adjusted to yield solution containing ~100  $\mu$ g or 200  $\mu$ g 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  $\alpha$ -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  $\alpha$ -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  $\alpha$ -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  $\mu$ g OC from the clean sample to 62% in the matrix of 200  $\mu$ g 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  $\mu$ g OC matrix to 32% in 200  $\mu$ g OC matrix for the clean sample and from 45% in 100  $\mu$ g OC matrix to 62% in 200  $\mu$ g OC matrix for the polluted sample. The relative standard deviation (RSD) of  $\alpha$ -pinene OS arising from different OC loadings (100  $\mu$ g and 200  $\mu$ g 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 100 $\mu$ g OC/mL solvent, the intensity of  $\alpha$ -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  $\mu$ g 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  $\alpha$ -pinene OS arising from different chemical composition (clean sample and polluted sample) were 40% and 27% in samples containing 200  $\mu$ g and 100  $\mu$ g 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.

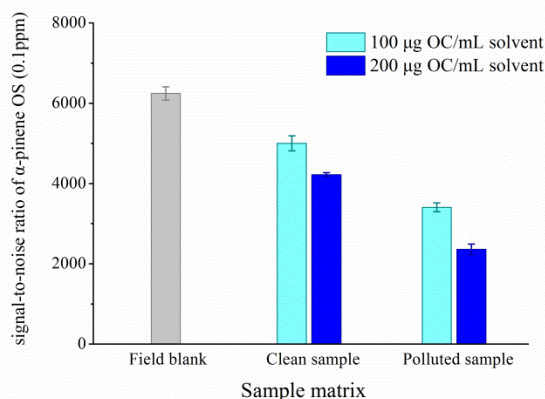


Figure S1 The intensity of  $\alpha$ -pinene OS (0.1 ppm) in different sample matrix (blank sample, clean sample, polluted sample) with different OC loadings. The error bars were derived from three repeat injections of the same sample.

Line 177, “What’s more, the S-containing compounds contributed more to the higher MW formulas than CHO ( $O_1$ - $O_{10}$ ) or CHON ( $O_1$ - $O_{11}$ ) compounds (Fig. 1), due to the existence of more O (CHOS:  $O_1$ - $O_{12}$ , CHONS:  $O_1$ - $O_{14}$ ) atoms and heteroatoms (S, N) in the molecules. They may play more important roles in the increase of SOA mass concentrations during pollution episodes.” Given the concentration of quantified organosulfates is small, the formation of organosulfates is not likely explained the increase of SOA mass. Please elaborate this point.

**Response:**

During pollution episodes, the number and intensity of S-containing compounds (CHOS and CHONS) increased obviously (Fig. S4). Considering the higher MW of CHOS and CHONS than those of CHO or CHON, the S-containing compounds may play more important roles in the increase of SOA mass concentrations. The second sentence was revised to make it clearer: “The increasing trend of S-containing organics (Fig S4), with larger MW than those of CHO or CHON, may play important roles in the increase of SOA

mass concentrations during pollution episodes.” (lines 210-211)

This conclusion was drawn based on the Orbitrap data shown in Fig. S4, rather than the OS concentrations quantified by HPLC-MS. A total of 351 OSs and 181 NOSs formulas were identified during the whole campaign, while only 13 selected OS and NOS species were quantified due to the lack of more standards. Though the quantified OS concentrations were low, the total concentrations of OSs in ambient atmosphere should be higher than those quantified in this study.

*Line 233, “carboxylic acids mainly form via aqueous phase oxidation in cloud or particle water, including both biogenic and anthropogenic sources (Charbouillot et al., 2012; Chebbi and Carlier, 1996). The relatively higher level of hydroxycarboxylic acid sulfate could be attributed to the favorable interaction between sulfate aerosols and carboxylic acids or other precursors in summertime Beijing, while the precursors and mechanisms remain unclear.” The authors should provide more information or field data to support this argument. For example, what are the concentrations of these carboxylic acids if these acids have been measured in this field campaign?*

**Response:**

The concentration of oxalic acid, usually the most abundant dicarboxylic acid in the atmosphere, was added in [lines 273-277](#): “Oxalic acid is usually the most abundant dicarboxylic acid in the atmosphere (Guo et al., 2010; Narukawa et al., 2003). The average concentration of oxalic acid in fine particles was  $0.22 \mu\text{g}/\text{m}^3$ , which was at a relatively high concentration level when comparing with those reported in previous studies ( $0.02\text{-}0.32 \mu\text{g}/\text{m}^3$ ) (Agarwal et al., 2010; Bikkina et al., 2017; Boreddy et al., 2017; Deshmukh et al., 2017; Kawamura et al., 2010; Narukawa et al., 2003).”

*Line 260 “unclear. The concentration of isoprene NOSs ( $\text{C}_5\text{H}_{10}\text{NO}_9\text{S}$ ) was lower than that of individual isoprene OSs. Strong inter-correlations were observed between isoprene OSs and NOSs (Table S2), suggesting their similar formation pathways.” Please elaborate what are the formation pathways.*

**Response:**

The formation pathways were elaborated in [lines 307-309](#): “Strong inter-correlations were observed between isoprene OSs and NOSs (Table S4), suggesting their similar formation pathways via acid-catalyzed epoxide chemistry (Worton et al., 2013).”

*For the 3.3 OS formation via acid-catalyzed aqueous phase chemistry, I understand the authors focus on understanding how the quantified organosulfates form under different pollution episodes. Do the authors observe the same results for the “unquantified” organosulfates (or other detected organosulfates) as well?*

**Response:**

The acid-catalyzed aqueous phase chemistry is suggested to be an important pathway for OS formation, based on the analysis of quantified OSs in section 3.3. The total intensity of OSs also followed similar temporal variation to that of quantified OSs (Fig. S4, Fig. 3(f)). This observation indicated acid-catalyzed aqueous phase chemistry could be an important or major pathway for OS formation, however, it would be too speculative to comment on the formation pathway of the unquantified OSs based on the direct injection measurement. We will learn about the formation pathway of more OS species through expanding

available OS and NOS standards or combining with other techniques (e.g. isotopic analysis) in our future studies.

*Line 294 “Moreover, the higher aerosol LWC encountered during these periods would favor the uptake of gas-phase reactants into particle phase, due to the decrease of viscosity and increase of diffusivity within the particles (Shiraiwa et al., 2011).” These descriptions would be too qualitative. What would be the viscosity of the ambient aerosols expected in this work? How would the aerosol viscosity change with the aerosol composition and environmental conditions (e.g. ambient temperature and RH) in this work?*

**Response:**

We lack direct observation evidence to be more quantitative about the viscosity of ambient aerosols in this study. It has been suggested that the aerosol viscosity would decrease as the increase of ambient RH or temperature (Shiraiwa et al., 2011). Aerosol viscosity is also expected to decrease as the increase of secondary inorganic aerosols (SIAs, sulfate, nitrate, and ammonium), because hygroscopic SIAs would favor the increase of aerosol liquid water (Wu et al., 2018).

A nearly liquid phase (viscosity nearly or lower than  $10^2$ ) was expected based on our previous measurement of aerosol rebound factors in the winter Beijing (Liu et al., 2017b). As the RH increased from 20 to 60%, the rebound fraction decreased from 0.8 to 0.2, meaning that the particles undergo the transition from semisolid to liquid phase state. The rebound fraction of particles was lower than 0.4 at >40% RH, indicating that the liquid phase as the major phase state of ambient aerosols. The conditions with RH < 20% were quite limited during the campaign. The RH was usually higher than 40% and could increase to higher than 60% at night. What's more, the temperature in this study was higher than that in winter, which would decrease the viscosity of ambient aerosols. Thus, a nearly liquid phase (viscosity nearly or lower than  $10^2$ ) was expected at night, while semisolid phase with higher viscosity may occur during daytime when RH was very low. It would be desirable to observe the viscosity of ambient aerosol directly in future studies.

*Line 321, in the section, the authors elucidate the major factors influencing the formation of quantified organosulfates and their interrelations with SIA compositions. Do the authors also observe the same results for the unquantified organosulfates (or other detected organosulfates)?*

**Response:**

The influencing factors for OS formation were drawn based on the analysis of quantified OSs. The total intensity of OSs also followed similar temporal variation to that of quantified OSs (Fig. S4, Fig. 3(f)). This result indicated that the conclusion could be applicable to most of the unquantified OSs. However, we feel it may be overly speculative to draw the conclusion only based on the infusion injection analysis using Orbitrap MS.

## 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<sub>2</sub> (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<sub>4</sub><sup>2-</sup>, NO<sub>x</sub>), 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<sub>x</sub> (NO<sub>2</sub>+O<sub>3</sub>) 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<sub>10</sub>H<sub>16</sub>NO<sub>7</sub>S<sup>-</sup> was recorded on May 27 during episode II (Fig. 5). Besides the high NO<sub>2</sub> 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<sup>3</sup>). 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- $NO_x$  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 summary 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  $\alpha$ -pinene OS. The filter portion size and solvent volume were adjusted to yield solution containing ~100  $\mu\text{g}$  or 200  $\mu\text{g}$  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  $\alpha$ -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  $\alpha$ -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  $\alpha$ -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  $\mu\text{g}$  OC from the clean sample to 62% in the matrix of 200  $\mu\text{g}$  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  $\mu\text{g}$  OC matrix to 32% in 200  $\mu\text{g}$  OC matrix for the clean sample and from 45% in 100  $\mu\text{g}$  OC matrix to 62% in 200  $\mu\text{g}$  OC matrix for the polluted sample. The relative standard deviation (RSD) of  $\alpha$ -pinene OS arising from different OC loadings (100  $\mu\text{g}$  and 200  $\mu\text{g}$  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 100 µg OC/mL solvent, the intensity of  $\alpha$ -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  $\alpha$ -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.

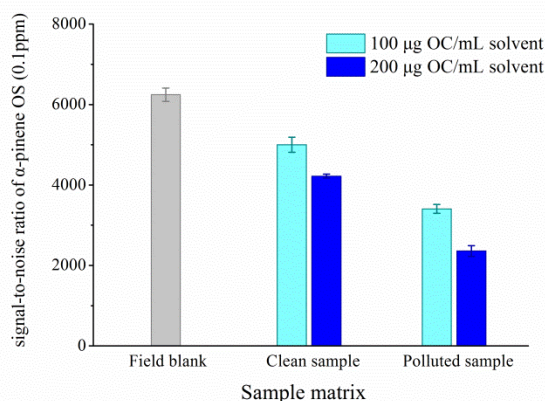


Figure S1 The intensity of  $\alpha$ -pinene OS (0.1 ppm) in different sample matrix (blank sample, clean sample, polluted sample) with different OC loadings. The error bars were derived from three repeat injections of the same sample.

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]<sup>+</sup> 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 sites 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 ( $\text{SO}_4^{2-}/\text{SIAs} > 0.5$ ), both aerosol LWC and acidity ( $\text{pH} < 2.8$ ) 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<sub>2</sub> levels at night...”

**Response:** Revised accordingly (line 490).

## 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  $-\text{ONO}_2$  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  $\text{NO}_3$ -initiated ( $-\text{ONO}_2$  addition) step was the limiting step in isoprene NOSs formation. In other words, the isoprene NOSs did not appear to form via  $\text{NO}_3$ -initiated oxidation as monoterpene NOSs.

# The Secondary Formation of Organosulfates under the Interactions between Biogenic Emissions and Anthropogenic Pollutants in Summer of Beijing

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**Abstract.** Organosulfates (OSs), with ambiguous formation mechanisms, are a potential source of “missing secondary organic aerosol (SOA)” in current atmospheric models. In this study, we analyzed the characterization and formation of OSs and nitrooxy OSs (NOSs) under the influence of biogenic emissions and anthropogenic pollutants (e.g. NO<sub>x</sub>, SO<sub>4</sub><sup>2-</sup>) in summer of Beijing. The ultrahigh-resolution mass spectrometer equipped with electrospray ionization source was applied to examine the overall molecular composition of S-containing organics. The number and intensities of S-containing organics, the majority of which could be assigned as OSs and NOSs, increased significantly during pollution episodes, which indicated their importance for SOA accumulation. To further investigate the distribution and formation of OSs and NOSs, the high performance liquid chromatography coupled to mass spectrometry was employed to quantify ten OSs and three NOS species. The total concentrations of quantified OSs and NOSs were 41.4 and 13.8 ng/m<sup>3</sup>, respectively. Glycolic acid sulfate was the most abundant species among all the quantified species, followed by monoterpene NOSs (C<sub>10</sub>H<sub>16</sub>NO<sub>7</sub>S). The total concentration of three isoprene OSs was 14.8 ng/m<sup>3</sup> and the isoprene OSs formed via HO<sub>2</sub> channel was higher than those formed via NO/NO<sub>2</sub> channel. The OS concentration coincided with the increase of acidic sulfate aerosols, aerosol acidity and

27 liquid water content (LWC), indicating the acid-catalyzed aqueous-phase formation of OSs in the presence of acidic sulfate  
28 aerosols. When sulfate dominated the accumulation of secondary inorganic aerosols (SIAs, sulfate, nitrate and ammonium)  
29 ( $\text{SO}_4^{2-}/\text{SIAs} > 0.5$ ), OS formation would be obviously promoted as the increasing of acidic sulfate aerosols, aerosol LWC and  
30 acidity ( $\text{pH} < 2.8$ ). Otherwise, the acid-catalyzed OS formation would be limited by lower aerosol acidity when nitrate  
31 dominated the SIA accumulation. The nighttime enhancement of monoterpene NOSs suggested their formation via nighttime  
32  $\text{NO}_3$ -initiated oxidation of monoterpene under high- $\text{NO}_x$  conditions. However, isoprene NOSs are supposed to form via  
33 acid-catalyzed chemistry or reactive uptake of oxidation products of isoprene. This study provides direct observational  
34 evidence and highlights the secondary formation of OSs and NOSs, via the interaction between biogenic precursors and  
35 anthropogenic pollutants ( $\text{NO}_x$ ,  $\text{SO}_2$  and  $\text{SO}_4^{2-}$ ). The results imply that future reduction in anthropogenic emissions can help  
36 to reduce the biogenic SOA burden in Beijing or other areas impacted by both biogenic emissions and anthropogenic  
37 pollutants.

## 38 1 Introduction

39 Secondary organic aerosols (SOA), formed by atmospheric oxidation of volatile organic compounds (VOCs), accounts  
40 for a large fraction of organic aerosols (OA) on the global scale (Jimenez et al., 2009; Guo et al., 2014). However, current  
41 models usually underestimate (Kroll and Seinfeld, 2008; Hallquist et al., 2009) or predict the SOA concentration with large  
42 uncertainties (Jimenez et al., 2009; Kiehl, 2007; Shrivastava et al., 2017) in ambient atmosphere. Thus, it is important to  
43 elucidate potential missing groups of compounds or formation mechanisms. Organosulfates (OSs), commonly formed via the  
44 interaction between VOC precursors and acidic sulfate seed particles, could be a potential source of “missing SOA” in  
45 current atmospheric models (Surratt et al., 2010). OSs have been observed in various ambient atmospheres, including urban,  
46 rural, suburban, forest as well as remote environments (Lin et al., 2012; Meade et al., 2016; Stone et al., 2012; Riva et al.,  
47 2015; Brüggemann et al., 2017), which could represent 2-30% of OA (Hawkins et al., 2010; Stone et al., 2012; Frossard et  
48 al., 2011; Tolocka and Turpin, 2012; Surratt et al., 2008; Liao et al., 2015).

49 Many chamber experiments studied try to reveal the precursors and formation mechanisms of OSs (Surratt et al., 2010;

50 Surratt et al., 2008; Liggio and Li, 2006; Chan et al., 2011; Shalamzari et al., 2014; Shalamzari et al., 2016; Zhang et al.,  
51 2012), which remain unclear. Various biogenic VOCs (BVOCs) precursors have been reported, including isoprene (Hatch et  
52 al., 2011; Surratt et al., 2010), monoterpenes (Surratt et al., 2008), sesquiterpenes (Chan et al., 2011), pinonaldehyde (Liggio  
53 and Li, 2006), unsaturated aldehydes (Shalamzari et al., 2014; Shalamzari et al., 2016) and 2-methyl-3-buten-2-ol (Zhang et  
54 al., 2012). OSs originating from isoprene are some of the most studied compounds and could be among the most abundant  
55 OA in some areas (Liao et al., 2015; Chan et al., 2010; Surratt et al., 2010; Lin et al., 2013a; Worton et al., 2013). Isoprene  
56 OSs usually form through ring-opening epoxide chemistry catalyzed by acidic sulfate aerosols (Worton et al., 2013; Froyd et  
57 al., 2010; Paulot et al., 2009). OSs were also proposed to form by reactive uptake of VOCs or their oxidation products that  
58 involves the sulfate radicals (Nozière et al., 2010; Schindelka et al., 2013). [The sulfate esterification of alcohols could also  
59 be a pathway leading to OSs formation, while Minerath et al \(2018\) predicted that this mechanism was kinetically  
60 insignificant under ambient tropospheric conditions. However, this prediction was based on laboratory bulk solution-phase  
61 experiments and the applicability to the liquid-phase on particles suspended in the air is unconfirmed.](#) Nitrooxy  
62 organosulfates (NOSs) were observed to form via the nighttime NO<sub>3</sub>-initiated oxidation of VOC precursors (e.g.  
63 monoterpene), followed by alcohol sulfate esterification (Iinuma et al., 2007; Surratt et al., 2008). Organic nitrate (R-ONO<sub>2</sub>)  
64 could also act as precursors to OSs through the nucleophilic substitution of nitrate by sulfate (Hu et al., 2011; Darer et al.,  
65 2011).

66 Both aerosol acidity and liquid water content (LWC) are key variables influencing the OS formation processes. OS  
67 formation could only happen in the presence of sulfate aerosols, enhanced by increased aerosol acidity, through  
68 acid-catalyzed reactive uptake and multiphase reactions of oxidation products (Riva et al., 2016c; Surratt et al., 2010; Lal et  
69 al., 2012; Riedel et al., 2015). Previous studies also demonstrated the importance of aqueous-phase or heterogeneous  
70 reactions for OS formation (Lal et al., 2012; McNeill et al., 2012; McNeill, 2015; [Riedel et al., 2015](#)). On one hand, the  
71 increased LWC would decrease the aerosol viscosity, which favors the exchange of organics or other gas molecules into the  
72 particles, mass diffusion of reactants and heterogeneous chemical reactions within the particles (Vaden et al., 2011; Booth et  
73 al., 2014; Renbaum-Wolff et al., 2013; [Shrestha et al., 2015](#); [Zhang et al., 2015](#)), and thereby enhance the OS formation. On  
74 the other hand, more LWC would lead to increased pH due to dilution. For example, Riva et al. (2016) and Duporte et al.

75 (2016) found that the OS formation decreased with higher RH, which was attributed to the increased pH as a result of higher  
76 LWC (Duporte et al., 2016; Riva et al., 2016c).

77 To get a comprehensive understanding of the characteristics and formation of OSs in the ambient atmosphere, it is  
78 desirable to simultaneously identify and quantify particulate OSs on the molecular level. Soft ionization techniques coupled  
79 with ultrahigh-resolution mass spectrometer (UHRMS) have been widely applied to identify various and numerous organics,  
80 including OS species, in ambient aerosols or chamber studies (Lin et al., 2012; Blair et al., 2017; Tao et al., 2014; Wang et al.,  
81 2016). UHRMS is a powerful analytical tool in gaining an overall characterization of OSs, however, the quantification  
82 capability is limited without pre-separation. High performance liquid chromatography coupled to mass spectrometer  
83 (HPLC-MS) is suitable for the separation and quantification of different OS compounds. However, one noted limitation is a  
84 lack of commercially available authentic standards. As a result, surrogate standards are often used for quantification (He et  
85 al., 2014; Riva et al., 2015; Zhang et al., 2012), which adds uncertainty to the concentrations (Wang et al., 2017d). Recently,  
86 a few research groups quantified some OS species using synthetic authentic standards (e.g. hydroxyacetone sulfate, glycolic  
87 acid sulfate, lactic acid sulfate, methyltetrol sulfate, aromatic OSs,  $\alpha/\beta$ -pinene OS, Limonene OS and Limonaketone OS)  
88 (Hettiyadura et al., 2017; Hettiyadura et al., 2015; Olson et al., 2011; Wang et al., 2017d; Ma et al., 2014; Budisulistiorini et  
89 al., 2015; Staudt et al., 2014), which was very important for understanding the variation and formation of OSs in ambient  
90 aerosols.

91 [Missing knowledge of formation mechanisms, the complexities of ambient aerosol composition and oxidation condition,](#)  
92 [and the lack of commercially available standards all hinder us from understanding the formation and fate of OSs in ambient](#)  
93 [atmosphere. Few field studies has been conducted in urban areas dominated by anthropogenic pollutants \(e.g. NO<sub>x</sub>, SO<sub>4</sub><sup>2-</sup>\).](#)  
94 [Observations are lacking to illustrate how severe anthropogenic pollutants could influence the OS formation under different](#)  
95 [physical environmental conditions. This work reports a comprehensive characterization of particulate OSs in summertime](#)  
96 [Beijing, a location under the influence of both biogenic and severe anthropogenic sources. This study provides direct](#)  
97 [observational evidence for gaining insights into OS formation. Orbitrap MS coupled with soft ionization source was used to](#)  
98 [identify the overall molecular composition of S-containing organics. HPLC-MS was then applied to quantify some OSs and](#)  
99 [NOS species in ambient aerosols using newly synthesized authentic standards and surrogate standards. Previously proposed](#)

100 formation pathways of OS or NOS (e.g. acid-catalyzed aqueous-phase chemistry, nighttime NO<sub>3</sub> chemistry) were considered,  
101 and the influence of different environment conditions or factors on the formation were comprehensively elaborated. It has  
102 been suggested that both aqueous-phase chemistry and nighttime NO<sub>3</sub> chemistry play important roles in the heavy haze of  
103 Beijing (Wu et al., 2018; Wang et al., 2017b; Wang et al., 2017a). Using OSs and NOSs as examples, this work illustrates  
104 SOA formation via acid-catalyzed aqueous-phase chemistry, nighttime NO<sub>3</sub> chemistry under the interaction between  
105 abundant anthropogenic pollutants and biogenic emissions.

## 106 2 Methods

### 107 2.1 Sample collection

108 This study was a part of the bilateral Sweden-China framework research program on ‘Photochemical smog in China:  
109 formation, transformation, impact and abatement strategies’, focusing on the SOA formation under the influence of  
110 anthropogenic pollutants (Hallquist et al., 2016). An intensive field campaign was conducted at Changping (40.14° N,  
111 116.11° E), a regional site 38 km northeast of the Beijing urban area, China. The campaign was conducted from May 15 to  
112 June 23, 2016, when the site was influenced by high biogenic emissions from vegetation in the nearby mountains and  
113 anthropogenic pollutants from the nearby villages and Beijing urban areas (Tang et al., 2017). During May 17- June 5, the  
114 average concentrations of isoprene, [monoterpenes](#), benzene, toluene and NO<sub>x</sub> were 297, 83, 441, 619 pptv and 22.7 ppb,  
115 respectively.

116 Ambient aerosols were collected from May 16 to June 5. PM<sub>2.5</sub> (particles with aerodynamic diameter less than 2.5 μm)  
117 samples were collected on prebaked quartz fiber filters (Whatman Inc.) and Teflon filters (Whatman Inc.) using a  
118 high-volume sampler (TH-1000C, Tianhong, China) and a 4-channel sampler (TH-16A, Tianhong, China). The sampling  
119 [flow rates were](#) 1.05 m<sup>3</sup>/min and 16.7 L/min, respectively. The daytime samples were collected from 8:30 to 17:30 and  
120 nighttime ones from 18:00 to 8:00 the next morning. Field blank samples were collected by placing filters in the samplers  
121 with the pump off for 30 min. The period May 20 - June 3 will be discussed in this study.

## 122 2.2 Orbitrap MS analysis

123 An Exactive Plus-Orbitrap MS (Thermo Scientific Inc., Bremen, Germany) equipped with a heated electrospray  
124 ionization (ESI) source was used to identify the overall molecular composition of OSs. Details of the extraction and data  
125 analysis have been described in Wang et al. (2017c). Briefly, a portion of filter was extracted with ultrapure water in an  
126 ultrasonic bath for 40 min and the extracts were filtered with 0.45  $\mu\text{m}$  pore size PTFE syringe filter (Gelman Sciences). The  
127 filter portion size was adjusted to yield  $\sim 200$   $\mu\text{g}$  OC in each extract, in order to decrease the variation of ion suppression  
128 arising from varying coexisting organic components. [The influence of ion suppress was illustrated in the Appendix S1](#). The  
129 extract sample was then loaded onto a solid phase extraction (SPE) cartridge (DSC-18, Sigma-Aldrich, USA) to remove  
130 inorganic ions and low molecular weight (MW) organic acids (Lin et al., 2010), followed by elution with methanol. [Some](#)  
131 [selected OS species with low MW would also be removed by the SPE clean-up procedure, which will be discussed in section](#)  
132 [3.1](#). The methanol eluate was dried under a gentle stream of  $\text{N}_2$  and re-dissolved in acetonitrile/water (1:1) solvent for  
133 Orbitrap MS analysis.

134 The Orbitrap MS was operated in negative mode (ESI<sup>-</sup>). The mass calibration was conducted using a standard mixture  
135 of N-butylamine, caffeine, MAFA, sodium dodecyl sulfate, sodium taurocholate and Ultramark 1621, with the scan range set  
136 to be 90-900  $m/z$ . The Orbitrap MS had a [mass resolving power](#) of 140,000 at  $m/z = 200$ . Each sample was analyzed for three  
137 times with at least 100 full-scan spectra acquired in each analysis. The recorded mass spectra were processed and exported  
138 using the Xcalibur software (V2.2, Thermo Scientific). Peaks with a signal-to-noise ratio  $\geq 10$  were exported. All the  
139 mathematically possible formulas for each ion were calculated with a mass tolerance of 2 ppm. Each exported molecular  
140 formula was allowed containing certain elements and limited by several conservative rules (Wang et al., 2017c). [Elements](#)  
141  [\$^{12}\text{C}\$ ,  \$^1\text{H}\$ ,  \$^{16}\text{O}\$ ,  \$^{14}\text{N}\$ ,  \$^{32}\text{S}\$  and  \$^{13}\text{C}\$  were allowed in the molecular formula calculations. The H/C, O/C, N/C and S/C ratios were](#)  
142 [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](#)  
143 [and the nitrogen rule for even electron ions. More details about the molecular formula assignment have been introduced in](#)  
144 [Wang et al. \(2017c\)](#). The background spectra were obtained by analyzing the corresponding field blank sample following the

145 same procedure. Peaks were eliminated from the list if their intensities were lower than ten times of those in the blank  
146 sample.

### 147 **2.3 Quantification of OSs and NOSs using HPLC-MS**

148 An aliquot of 25 cm<sup>2</sup> was removed from each filter sample and extracted in ultrasonic bath three times using 3, 2 and 1  
149 mL methanol consecutively, each time for 30 min. The extracts were then filtered through a 0.25 µm polytetrafluoroethylene  
150 (PTFE) syringe filter (Pall Life Sciences), combined, evaporated to dryness under a gentle stream of high-purity nitrogen and  
151 re-dissolved in 50 µL methanol/water (1:1) containing 1 ppm D<sub>17</sub>-octyl sulfate as internal standard. The solution was  
152 centrifuged and the supernatant was used for analysis, using Agilent 1260 LC system (Palo Alto, CA) coupled to QTRAP  
153 4500 (AB Sciex, Toronto, Ontario, Canada) mass spectrometer. The LC/MS was equipped with an ESI source operated in  
154 negative mode. The optimized MS conditions and details of the method have been described in our previous study (Wang et  
155 al., 2017d). Chromatographic separation was performed on an Acquity UPLC HSS T3 column (2.1 mm×100 mm, 1.8 µm  
156 particle size; Waters, USA) with a guard column (HSS T3, 1.8 µm). The mobile eluents were (A) water containing 0.1%  
157 acetic acid (v/v) and (B) methanol (v/v) containing 0.1% acetic acid at a flow rate of 0.19 mL/min. The gradient elution was  
158 set as follows: the composition started with 1% B for 2.7 min; increased to 54% B within 12.5 min and held for 1.0 min; then  
159 increased to 90% B within 7.5 min and held for 0.2 min; and finally decreased to 1% B within 1.8 min and held for 17.3 min  
160 until the column was equilibrated. The column temperature was kept at 45 °C and the injection volume was 5.0 µL.

161 The quantified OS and NOS species are listed in Table 1. The monoterpene NOSs (C<sub>10</sub>H<sub>16</sub>NO<sub>7</sub>S<sup>-</sup> and C<sub>9</sub>H<sub>14</sub>NO<sub>8</sub>S<sup>-</sup>) were  
162 quantified using the [M-H]<sup>-</sup> ions in the extracted ion chromatogram (EIC) and other species were quantified in  
163 multiple-reaction monitoring (MRM) mode. OSs and NOSs were quantified using authentic standards or surrogates with  
164 similar molecular structures (Table 1). Lactic acid sulfate (LAS) and glycolic acid sulfate (GAS) were prepared according to  
165 Olson et al. (2011). The purity of LAS and GAS are 8% and 15%, determined by <sup>1</sup>H NMR analysis using dichloroacetic acid  
166 as an internal standard, and the recovery are 89.5% and 94.9%, respectively. Four monoterpene derived OS standards were  
167 synthesized and the details are given in Wang et al. (2017). The purity of the four monoterpene OS standards are higher than  
168 99% and the recovery are 80.5%-93.5% (Table S1). OSs with similar carbon chain structures usually have similar MS



169 responses (Wang et al., 2017d). Lactic acid sulfate was employed as a surrogate standard to quantify isoprene OSs due to  
170 their similar structures and retention times (Table 1).  $\alpha$ -pinene OS and limonaketone OS were respectively used to quantify  
171 monoterpene NOSs  $C_{10}H_{16}NO_7S^-$  and  $C_9H_{14}NO_8S^-$  due to the similar carbon structures (Table 1). For the molecule with  
172 isomers, quantification was performed by summing up the peak areas of the isomers, treated as one species (e.g.,  
173 monoterpene NOSs with [M-H] at  $m/z$  294 were treated as one NOS species).

#### 174 **2.4 Other online and offline measurements**

175 A high resolution time-of-flight aerosol mass spectrometer (AMS) was employed to measure the chemical composition  
176 of  $PM_{1.0}$ . The operation procedures and data analysis have been described in Zheng et al. (2017). VOCs were measured by a  
177 proton-transfer-reaction mass spectrometer (PTR-MS). Meteorological parameters, including relative humidity (RH),  
178 temperature, wind direction and wind speed (WS) were continuously monitored by a weather station (Met one Instrument  
179 Inc.) during the campaign. Organic carbon (OC) was analyzed using thermal/optical carbon analyzer (Sunset Laboratory).  
180 The organic matter (OM) concentration was calculated by multiplying OC by 1.6 (Turpin and Lim, 2001). Water soluble  
181 inorganic ions and low MW organic acids (e.g. oxalic acid) were quantified by an ion chromatograph (IC, DIONEX,  
182 ICS2500/ICS2000) following procedures described in Guo et al. (2010). After performing quality assurance/quality control  
183 for IC measurements, the data (ions, pH, LWC) derived from IC measurements in the daytime samples of May 26 and 29  
184 were excluded in the following analysis. Gaseous  $NH_3$  was measured using a  $NH_3$  analyzer (G2103, Picarro, California,  
185 USA) (Huo et al., 2015). Aqueous phase  $[H^+]$  and LWC were then calculated with the ISORROPIA-II thermodynamic  
186 model. ISORROPIA-II was operated in forward mode, assuming the particles are “metastable” (Hennigan et al., 2015;  
187 Weber et al., 2016; Guo et al., 2015). The input parameters included: ambient RH, temperature, particle phase inorganic  
188 species ( $SO_4^{2-}$ ,  $NO_3^-$ ,  $Cl^-$ ,  $NH_4^+$ ,  $K^+$ ,  $Na^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ), and gaseous  $NH_3$ . The thermodynamic calculations were validated by  
189 the good agreement between measured and predicted gaseous  $NH_3$  (slope=0.99,  $R^2=0.97$ ) (see Appendix S2 for details). The  
190 contribution of organics to LWC was not considered in this study. Our previous study in Beijing has suggested that LWC  
191 associated with organic species was insignificant (<6%), compared to that of secondary inorganic aerosols (Wu et al., 2018)  
192 (see Fig. S3 for the comparison between LWC with or without water associated with organic compounds). Previous study

193 also suggested that the predicted aerosol acidity or pH without consideration of organic water could also be sufficient for  
194 discussing aqueous SOA chemistry in this study, due to the minor effect on aerosol pH (0.15- 0.23) (Guo et al., 2015).

### 195 3 Results and discussion

#### 196 3.1 Overall molecular characterization of S-containing organics

197 On average, 62% of the observed peaks in ESI negative mode are assigned with unambiguous molecular formulas. All  
198 the assigned formulas were classified into four major categories based on their elemental compositions, including CHO,  
199 CHON, CHOS and CHONS. As an example, CHONS refers to compounds that contain C, H, O, N and S elements in the  
200 formula. Other compound categories are defined analogously. The percent of different compound categories in terms of  
201 number and intensity are shown in Fig. S4 and Fig. 1, in which 'others' (e.g. CH, CHN, CHS, CHNS) refer to the  
202 compounds excluded from the above major compound categories. During pollution episodes, the number and intensity  
203 percent of S-containing compounds (CHOS and CHONS) increased obviously (Fig. 1, S4). The OC content in each sample  
204 for Orbitrap MS analysis was kept roughly constant to minimize variation arising from matrix ion suppression. Taking the  
205 nighttime sample of May 24 (0524N) as an example of clean days and the nighttime sample of May 30 (0530N) as an  
206 example of polluted days, the mass spectra of different compound categories in each sample are shown and compared in Fig.  
207 1 (a) and (b). The increase in S-containing organics indicated their important contribution to SOA when the pollution  
208 accumulated. What's more, the S-containing compounds contributed more to the higher MW formulas than CHO ( $O_1-O_{10}$ ) or  
209 CHON ( $O_1-O_{11}$ ) compounds (Fig. 1), due to the existence of more O (CHOS:  $O_1-O_{12}$ , CHONS:  $O_1-O_{14}$ ) atoms and  
210 heteroatoms (S, N) in the molecules. The increasing trend of S-containing organics (Fig S4), with larger MW than those of  
211 CHO or CHON, may play important roles in the increase of SOA mass concentrations during pollution episodes.

212 The CHOS formulas with  $O/S \geq 4$  allow the possible assignment of a sulfate group in the molecules (i.e., OSs) (Lin et  
213 al., 2012). Among all the identified CHOS formulas, 60%-99% (93% on average) and 66-100% (96% on average) of them  
214 could be assigned as OSs in terms of number and intensity percent. Analogously, the CHONS formulas with  $O/(S+N) \geq 7$   
215 could likely be NOSs formulas, which account for 22-78% (53% on average) by number and 18-94% (61% on average) by

216 intensity of all the identified CHONS formulas. As OSs and NOSs were assigned based on the molecular formulas alone, we  
217 could not completely exclude the possibility of CHOS being hydroxysulfonates and CHONS being nitro-OSs due to the lack  
218 of MS/MS analysis. According to previous study, the presences of organosulfonate or nitro-OSs were usually limited  
219 compared to those of OSs or nitrooxy-OSs (Lin et al., 2012), thus they were not taken into consideration in this study. A total  
220 of 351 OSs and 181 NOSs formulas were identified among all the samples during the campaign. The temporal variation of  
221 the total number and intensity of OSs and NOSs are shown in Fig. S4. During pollution episodes (nighttime of May 27 - the  
222 nighttime of May 28, nighttime of May 29 - the nighttime of May 30), the total number and intensity of OSs formulas  
223 increased (Fig. S4). The total number of NOSs also showed similar increase trend during pollution episodes, while the total  
224 intensity of NOSs showed nighttime enhancement during the whole observation period (Fig. S4). Previous studies suggested  
225 that some NOS species could form via  $\text{NO}_3$ -initiated oxidation under high- $\text{NO}_x$  conditions at night (Surratt et al., 2008;  
226 Iinuma et al., 2007; Gomez-Gonzalez et al., 2008), which will be further discussed in the following sections.

227 Some of the more abundant OSs and NOS peaks identified in the samples on the clean day (05/24N) or during pollution  
228 episodes (05/30D, 05/30N) are listed in Table S2. For example, deprotonated molecules  $\text{C}_9\text{H}_{15}\text{SO}_7^-$ ,  $\text{C}_{10}\text{H}_{17}\text{SO}_7^-$  and  
229  $\text{C}_9\text{H}_{17}\text{SO}_6^-$  were observed among the highest OS peaks in samples during pollution episodes (Table S2). These compounds  
230 could be derived from the oxidation of alkanes or diesel fuel based on previous chamber studies (Riva et al., 2016c; Blair et  
231 al., 2017). Many OSs previously designated as biogenic origins were also found in the anthropogenic sources (Blair et al.,  
232 2017), which may raise uncertainty when assigning OS sources in field observation studies. OS compounds derived from  
233 anthropogenic VOC precursors were widely observed in ambient aerosols (Table S2), while they were not quantified due to  
234 the lack of standards in this paper. They will be further investigated in our future studies. Other OS molecules (e.g.  
235  $\text{C}_9\text{H}_{15}\text{SO}_6^-$ ,  $\text{C}_{10}\text{H}_{17}\text{SO}_5^-$ ) could be formed via the oxidation of monoterpenes (Surratt et al., 2008). For NOSs, ions  
236  $\text{C}_{10}\text{H}_{16}\text{NO}_7\text{S}^-$ ,  $\text{C}_{10}\text{H}_{16}\text{NO}_9\text{S}^-$  and  $\text{C}_{10}\text{H}_{16}\text{NO}_{10}\text{S}^-$  were among the highest peaks (Table S2). They could form via the nighttime  
237  $\text{NO}_3$ -initiated oxidation of monoterpenes (Surratt et al., 2008). These are just some examples with higher relative intensity  
238 (RI). The RI may not accurately represent their relative concentration levels in each sample, as the MS responses of different  
239 OSs are also influenced by different carbon chain structures (Wang et al., 2017d). The OS species of low MW and short  
240 carbon chain structures (with fewer than 6 carbon atoms in the molecule) are little retained on the SPE cartridges due to their

241 highly water-soluble and more hydrophilic properties (Gomez-Gonzalez et al., 2008; Lin et al., 2012; Lin et al., 2010). As  
242 such, they were largely absent among the OS formulas detected by Orbitrap MS in this work. Hydroxyacetone sulfate  
243 ( $C_3H_5O_5S^-$ ) was detected by Orbitrap MS only in several samples with relatively higher concentrations. Hydroxycarboxylic  
244 acid sulfate ( $C_2H_3O_6S^-$ ,  $C_3H_5O_6S^-$ ) or isoprene OSs ( $C_4H_7O_7S^-$ ,  $C_5H_7O_7S^-$ ,  $C_5H_{11}O_7S^-$ ) are also sufficiently hydrophilic that  
245 little of them would be in the SPE eluate fraction, which was subjected for Orbitrap MS analysis. This explains why these  
246 highly water-soluble OS species with lower MW are absent in Fig. 1. Though these OS species were not detected by Orbitrap  
247 MS, some of them were quantified with high concentrations in the ambient aerosols in the LC/MS analysis (Table 1), as the  
248 sample aliquots for the LC/MS analysis did not involve SPE treatment.

### 249 3.2 Abundance of identified OSs and NOSs in ambient aerosols

250 To further investigate the abundance and formation pathways of OSs and NOSs in ambient aerosols, [some species](#) were  
251 then quantified by HPLC-MS using authentic standards when available or surrogate standards. [The quantified species could](#)  
252 [usually be formed via the interaction between biogenic precursors \(e.g. isoprene, monoterpene\) and anthropogenic pollutants](#)  
253 [\(e.g.  \$SO\_4^{2-}\$ ,  \$NO\_x\$ \), which have been reported in previous chamber studies \(Surratt et al., 2007; Surratt et al., 2008; Surratt et](#)  
254 [al., 2010\). A total of ten OSs and three NOS species were quantified in this study and their concentrations are listed in Table](#)  
255 [1. The molecules with the same molecular formula were treated as one species \(e.g., monoterpene NOSs with  \$\[M-H\]^-\$  at  \$m/z\$](#)   
256 [294 were treated as one NOS species\). The average concentrations of all the quantified OSs were  \$41.4 \text{ ng/m}^3\$  during the](#)  
257 [campaign. The total OSs accounted for 0.31% of OM, with a maximum contribution of 0.65% on the night of May 30. The](#)  
258 [total concentrations of quantified NOSs were  \$13.8 \text{ ng/m}^3\$ , corresponding to 0.11% of OM, with a maximum contribution of](#)  
259 [0.35% on the night of May 23.](#)

260 [The concentrations of each OS or NOS species across this and prior studies were summarized in Table S3. The relative](#)  
261 [contribution of each species to the total OSs or NOSs is shown in Fig. 2. GAS was the most abundant species among all the](#)  
262 [quantified species. The concentrations of GAS were  \$3.9\text{-}58.2 \text{ ng/m}^3\$ , with an average of  \$19.5 \text{ ng/m}^3\$ . The concentrations were](#)  
263 [higher than those observed in Mexico \( \$4.1\text{-}7.0 \text{ ng/m}^3\$ \), California \( \$3.3\text{-}5.4 \text{ ng/m}^3\$ \) or Pakistan \( \$11.3 \text{ ng/m}^3\$ \) \(Olson et al.,](#)  
264 [2011\) \(Table S3\). The GAS concentration level at Beijing was comparable to those reported in summertime Alabama, US](#)

265 (8-26.2 ng/m<sup>3</sup>) (Table S3), a location characterized by high biogenic emissions and affected by anthropogenic pollutants  
266 (Hettiyadura et al., 2015; Hettiyadura et al., 2017; Rattanavaraha et al., 2016). The concentrations of LAS were 0.7-12.0  
267 ng/m<sup>3</sup>, with an average of 4.4 ng/m<sup>3</sup>. The LAS concentrations were also higher than those observed in Mexico (1.2-1.8  
268 ng/m<sup>3</sup>), California (0.6-0.8 ng/m<sup>3</sup>) or Pakistan (3.8 ng/m<sup>3</sup>), while lower than those observed in Alabama, US (16.5 ng/m<sup>3</sup>)  
269 (Olson et al., 2011; Hettiyadura et al., 2015; Hettiyadura et al., 2017) (Table S3). Carboxylic acids mainly form via  
270 aqueous-phase oxidation in cloud or particle water, including both biogenic and anthropogenic sources (Charbouillot et al.,  
271 2012; Chebbi and Carlier, 1996). The relatively higher level of hydroxycarboxylic acid sulfate could be attributed to the  
272 favorable interaction between sulfate aerosols and carboxylic acids or other precursors in summertime Beijing, while the  
273 precursors and mechanisms remain unclear. Oxalic acid is usually the most abundant dicarboxylic acid in the atmosphere  
274 (Guo et al., 2010; Narukawa et al., 2003). The average concentration of oxalic acid in fine particles was 0.22 µg/m<sup>3</sup>, which  
275 was at a relatively high concentration level when comparing with those reported in previous studies (0.02-0.32µg/m<sup>3</sup>)  
276 (Agarwal et al., 2010; Bikina et al., 2017; Boreddy et al., 2017; Deshmukh et al., 2017; Kawamura et al., 2010; Narukawa  
277 et al., 2003). Strong inter-correlations were found among GAS, LAS and hydroxyacetone sulfate (HAS) (Table S4),  
278 indicating their potentially similar precursors or formation pathways. They also showed strong correlations with isoprene  
279 oxidation products (MVK+MACR) and isoprene OSs (Table S4), suggesting isoprene oxidized products as potential  
280 precursors of GAS, LAS and HAS. It is suggested that both hydroxyacetone and carboxylic acids could be produced from  
281 the oxidation of isoprene (Fu et al., 2008; Carlton et al., 2009). GAS, LAS and HAS have been reported to form via isoprene  
282 oxidation in the presence of acidic sulfate (Riva et al., 2016b; Surratt et al., 2008). GAS was also observed to form via  
283 sulfate induced oxidation of methyl vinyl ketone (MVK), oxidation product of isoprene (Schindelka et al., 2013).

284 The concentration of quantified isoprene OSs (C<sub>4</sub>H<sub>7</sub>O<sub>7</sub>S<sup>-</sup>, C<sub>5</sub>H<sub>7</sub>O<sub>7</sub>S<sup>-</sup> and C<sub>5</sub>H<sub>11</sub>O<sub>7</sub>S<sup>-</sup>) was 14.8 ng/m<sup>3</sup>, contributing to 36 %  
285 of the total quantified OSs in this study. The isoprene OSs were lower than those observed in southeastern US, with  
286 substantial isoprene emissions and impacted by anthropogenic pollutants, in which authentic standards were employed to  
287 quantify the isoprene OSs (Rattanavaraha et al., 2016). We used lactic acid sulfate as a surrogate standard to quantify  
288 isoprene OSs on the basis of their similar structures and retention times (Table 1). The isoprene concentration in southeastern  
289 US (1.9 ppb) (Xu et al., 2015) was much higher than that observed during our campaign (297 pptv). Besides the lower VOC

290 precursors and measurement uncertainty, the lower isoprene OSs in this study could be attributed to different atmospheric  
291 conditions in Beijing from those in southeastern US. The IEPOX formation under low-NO<sub>x</sub> conditions (HO<sub>2</sub> channel),  
292 usually with higher yields than the oxidation products under high-NO<sub>x</sub> conditions (NO/NO<sub>2</sub>) (Worton et al., 2013), could be  
293 suppressed under the high-NO<sub>x</sub> conditions (see section 3.4 for the high-NO<sub>x</sub> conditions) in Beijing (Zhang et al., 2017; Hu et  
294 al., 2015). The RH in Beijing was lower than that in southeast US (Xu et al., 2015), which possibly led to an increase of  
295 aerosol viscosity and a decrease of diffusivity within the particles, resulting in lower OS formation (Shiraiwa et al., 2011).  
296 Moreover, the OM-coated particle structures observed in Beijing could reduce the reactive uptake of isoprene oxidation  
297 products (Li et al., 2016; Zhang et al., 2018; Riva et al., 2016a), which may be another possible reason for lower isoprene  
298 OSs in this study. The concentrations were comparable to those observed in suburban area of mid-Atlantic or Belgium and  
299 higher than those observed at the background site of Pearl River Delta (PRD) region, China (Meade et al., 2016;  
300 Gómez-González et al., 2012; He et al., 2014), in which glycolic sulfate ester, ethanesulfonic acid or camphor sulfonic acid  
301 were employed as surrogate standards. The isoprene OSs formed via HO<sub>2</sub> channel (C<sub>5</sub>H<sub>11</sub>O<sub>7</sub>S<sup>-</sup>) were observed to be higher  
302 than that formed via NO/NO<sub>2</sub> channel (C<sub>4</sub>H<sub>7</sub>O<sub>7</sub>S<sup>-</sup>) (Table 1) (Worton et al., 2013). Isoprene had higher mixing ratio during  
303 the daytime (Fig. S5 (b)), when OH radicals dominated the atmospheric oxidation capacity. Furthermore, the yield of  
304 isoprene oxidation via HO<sub>2</sub> channel is proposed to be higher than that via NO/NO<sub>2</sub> channel (Worton et al., 2013). The  
305 concentration of C<sub>5</sub>H<sub>7</sub>O<sub>7</sub>S<sup>-</sup> was comparable to that of C<sub>5</sub>H<sub>11</sub>O<sub>7</sub>S<sup>-</sup> (Table 1). C<sub>5</sub>H<sub>7</sub>O<sub>7</sub>S<sup>-</sup> was suggested to be formed via  
306 isoprene oxidation and related to C<sub>5</sub>H<sub>11</sub>O<sub>7</sub>S<sup>-</sup> (Surratt et al., 2008), while the formation mechanism remains unclear. The  
307 concentration of isoprene NOSs (C<sub>5</sub>H<sub>10</sub>NO<sub>9</sub>S<sup>-</sup>) was lower than that of individual isoprene OSs. **Strong inter-correlations were**  
308 **observed between isoprene OSs and NOSs (Table S4), suggesting their similar formation pathways via acid-catalyzed**  
309 **epoxide chemistry (Worton et al., 2013).**

310 The average concentration of monoterpene OSs ( $\alpha$ -pinene OSs,  $\beta$ -pinene OSs, limonene OSs and limonaketone OSs)  
311 was 0.6 ng/m<sup>3</sup>, lower than those observed in mid-Atlantic (Meade et al., 2016) or the Pearl River Delta in southern China  
312 where more abundant emissions of BVOC precursors are expected (Wang et al., 2017d; He et al., 2014) (Table S3). The  
313 contribution of monoterpene OSs was much lower than that of isoprene OSs or other OSs (Fig. 2, Table 1), as the mixing  
314 ratio of monoterpene (83 pptv) was lower than that of isoprene (297 pptv) during the campaign. Furthermore, the reactivity

315 of **monoterpenes** with OH radical is lower than that of isoprene (Carlton et al., 2009; Paulot et al., 2009; Atkinson et al.,  
316 2006). Different from isoprene OSs, the four monoterpene OS species didn't show strong correlations with each other (Table  
317 S4), which may suggest their different oxidation mechanisms. **While the contribution of monoterpene OSs was low, the**  
318 **monoterpene NOSs ( $C_{10}H_{16}NO_7S^-$ ) were the second most abundant signals among the observed species (Table 1, Table S2),**  
319 **especially in the nighttime samples.** The concentration of monoterpene NOSs ( $C_{10}H_{16}NO_7S^-$ ) was much higher than those  
320 observed in mid-Atlantic or Belgium (Meade et al., 2016; Gómez-González et al., 2012), while lower than that observed in  
321 Pearl River Delta, South China (He et al., 2014).  $C_{10}H_{16}NO_7S^-$  was also identified to be among the highest peaks in the mass  
322 spectra recorded by Orbitrap MS (Fig. 1 (b)), with a RI of 83% in the sample of 05/30N (Table S2). The monoterpene NOSs  
323 could be formed via nighttime  $NO_3$ -initiated oxidation under high- $NO_x$  conditions (Surratt et al., 2008; Iinuma et al., 2007;  
324 Gomez-Gonzalez et al., 2008). During the observation, both monoterpenes and  $NO_x$  showed higher mixing ratios at night  
325 (Fig. S5 (a), (d)), favorable for the  $NO_3$ -initiated formation of NOSs.

### 326 **3.3 OS formation via acid-catalyzed aqueous-phase chemistry**

327 The time series of the total OS concentrations quantified by HPLC-MS are shown in Fig. 3, along with the  
328 meteorological conditions,  $SO_2$ , aerosol LWC, acidity,  $PM_{2.5}$  and the major chemical components. Most OS species showed  
329 similar trends to the total OSs (Fig. S6), except for  $\alpha$ -pinene OSs and  $\beta$ -pinene OSs, observed at very low concentrations.  
330 During the campaign, particles were generally acidic with a pH range of 2.0- 3.7, **favorable for OS formation** (Fig. 3). The  
331 aerosol acidity is indicated by aqueous phase  $[H^+]$  in this study. **The OS concentrations generally followed a similar trend to**  
332 **that of sulfate aerosols (Fig. 3). The total OS concentrations showed strong correlations with sulfate ( $r=0.67$ ) or aerosol**  
333 **acidity ( $r=0.67$ ), suggesting the driving role of acidic sulfate aerosols in the OS formation (Table S4).**

334 During the observation period, three pollution episodes (episodes I, II, III) were identified based on the  $PM_{2.5}$   
335 concentrations, which are marked by gray shadow in Fig. 3. **The back trajectories, average concentrations of VOC precursors**  
336 **and oxidants during each episode are also shown in Table S5.** The most significant increase trend of OSs was observed  
337 during pollution episode III (nighttime of May 29 - the nighttime of May 30). During this episode, the accumulation of  
338 secondary inorganic aerosols (SIAs), referring to sulfate, nitrate and ammonium in this study, was dominated by sulfate.

339 SIAs, especially sulfate and nitrate salts, represent the most important components driving the particle hygroscopicity (Wu et  
340 al., 2018; Xue et al., 2014), thus the aerosol LWC increased with SIAs (Fig. 3). The increase of aerosol acidity was also  
341 observed during this episode (Fig. 3). OSs increased to the highest level ( $129.2 \text{ ng/m}^3$ ) during the campaign under the  
342 condition of high sulfate aerosols, high aerosol acidity and LWC (Fig. 3), suggesting the acid-catalyzed aqueous-phase  
343 formation of OSs in the presence of acidic sulfate aerosols. The higher aerosol LWC encountered during these periods would  
344 also favor the uptake of gas-phase reactants into particle phase, due to the decrease of viscosity and increase of diffusivity  
345 within the particles (Shiraiwa et al., 2011). Moreover, the oxidant levels, indicated by  $\text{O}_x$  ( $\text{NO}_2 + \text{O}_3$ ) in this study (Herndon et  
346 al., 2008), were much higher than the other two episodes, which favored the formation of VOC oxidation products (e.g.  
347 MVK+MACR) (Table S5). This is another reason for higher OSs concentration level during episode III. During pollution  
348 episode II (nighttime of May 27 - the nighttime of May 28), the OS concentration level was lower than that during episode  
349 III. It is noted that the increase of sulfate, aerosol LWC and acidity were also less than that during episode III, indicating less  
350 aqueous-phase formation of OSs. During this episode, the increase of SIAs was attributed to both sulfate and nitrate, the two  
351 with comparable contribution to the total SIAs. Different from episodes II and III, the SIAs accumulation was dominated by  
352 nitrate during episode I (May 21- 23). OS and sulfate aerosols stayed at medium concentration level, lower than those during  
353 the other two episodes. During the daytime of May 21, aerosol acidity increased due to the elevated relative contribution of  
354 sulfate than that of nitrate, thus the OS concentration also increased. During the daytime of May 23, higher aerosol LWC  
355 was observed due to the rapid increase of nitrate, however, the aerosol acidity was lower as a result of the less contribution  
356 from sulfate. Thus, the increase of OS concentration was not very obvious. The OS formation may be limited by the aerosol  
357 acidity, indicating the importance of acid-catalyzed chemistry. Stronger correlations between OSs and sulfate ( $r=0.67$ ) or  
358 aerosol acidity ( $r=0.67$ ) compared with that between OSs and LWC ( $r=0.55$ ) also suggest the importance of acid-catalyzed  
359 chemistry for OSs formation. The back trajectories during episode I were different from those during episode II or III (Table  
360 S5), which could be one reason for different conditions (e.g. SIA composition) during episode I. This episode ended with the  
361 rain elimination event on the afternoon of May 23. The OSs were at low concentrations from May 24 to the daytime of May  
362 27, when sulfate,  $\text{SO}_2$ , aerosol acidity and LWC were noticeably lower than the other periods, restraining the OS formation.

363 The three pollution episodes were characterized by different inorganic aerosol composition and aerosol properties (e.g.



364 acidity, LWC), resulting in different levels of OS formation. The concentrations and relative contribution of sulfate, aerosol  
365 acidity and LWC are important factors influencing OS formation. The OS concentrations generally increased with the  
366 increasing of sulfate, aerosol acidity and LWC (Fig. 3), suggesting more active OS formation via acid-catalyzed  
367 aqueous-phase reactions in the presence of sulfate. These influencing factors were interrelated. Both sulfate and nitrate are  
368 important hygroscopic components (Chan and Chan, 2005; Wu et al., 2018; Xue et al., 2014), favoring the water uptake of  
369 aerosols and thus increasing LWC. The increasing of aerosol LWC with SIAs was observed (Fig. 3). A previous study also  
370 suggested that at a given RH, aerosol LWC was nearly linearly related to the sum of nitrate and sulfate mass concentrations  
371 (Guo et al., 2016). The variation of SIA composition and LWC would then influence the aerosol acidity (Liu et al., 2017;  
372 Guo et al., 2016). In this study, higher aerosol acidity was observed with elevated contribution of sulfate among SIAs (Fig.  
373 3). This is in accord with a previous study suggesting that particle pH was generally below 2 when aerosol anionic  
374 composition was dominated by sulfate ( $\text{NO}_3^-/2\text{SO}_4^{2-}$  mole ratio  $>1$ ) (Guo et al., 2016).

375 To further elucidate the major factors influencing OS formation and their interrelations with SIA compositions, the  
376 distribution of OS concentrations as a function of  $\text{SO}_4^{2-}/\text{SIAs}$  mass concentration ratios and other related factors are plotted  
377 in Fig. 4. The aerosol LWC generally increased with the increasing of the SIA mass concentrations, while the aerosol acidity  
378 was also influenced by the relative contribution of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  to SIAs. When the SIAs were dominated by  $\text{SO}_4^{2-}$   
379 ( $\text{SO}_4^{2-}/\text{SIAs} > 0.5$ ), the aerosol acidity increased obviously as a function of  $\text{SO}_4^{2-}/\text{SIAs}$  mass concentration ratios and the pH  
380 values were generally below 2.8 (Fig. 4 (b, d)). The high aerosol acidity was favorable for OS formation and OS  
381 concentration also increased as a function of sulfate mass concentration and fraction (Fig. 4 (a)). The pollution episode III  
382 (Fig. 3) was the typical case for this condition. When the SIAs were dominated by nitrate ( $\text{SO}_4^{2-}/\text{SIAs} < 0.5$ ), high LWC may  
383 occur due to the high concentrations of hygroscopic SIAs, while the aerosol acidity was relatively lower due to the lower  
384 sulfate fraction than that of nitrate (Fig. 4). The increase trend of OSs as a function of sulfate or  $\text{SO}_4^{2-}/\text{SIAs}$  mass  
385 concentration ratios was not as obvious as the sulfate-dominant condition ( $\text{SO}_4^{2-}/\text{SIAs} > 0.5$ ), as the OS formation may be  
386 limited by lower aerosol acidity. The daytime of May 23 during pollution episode I (Fig. 3) was the typical case for this  
387 atmospheric condition. Overall, the OS formation would obviously be promoted via acid-catalyzed aqueous-phase reactions,  
388 when the SIAs accumulation was dominated by sulfate ( $\text{SO}_4^{2-}/\text{SIAs} > 0.5$ ).

### 389 3.4 Monoterpene NOS formation via the nighttime NO<sub>3</sub> oxidation

390 A recent study suggested that nearly all the BVOCs could be oxidized overnight, dominated by reactions via NO<sub>3</sub>  
391 oxidation, at a NO<sub>x</sub>/BVOCs ratio higher than 1.4 (Edwards et al., 2017). When we roughly estimated the BVOCs  
392 concentration to be the sum of isoprene, MVK+MACR, and monoterpenes, the NO<sub>x</sub>/BVOCs ratios were higher than 10 at  
393 night (Fig. S5). This indicated the dominant nighttime BVOCs loss via NO<sub>3</sub>-initiated oxidation in summer of Beijing. The  
394 oxidation of BVOCs was found to be controlled by NO<sub>3</sub> oxidation rather than O<sub>3</sub> oxidation during the campaign, which  
395 contributed to a total of 90% of BVOCs reactivity at night (Wang et al., 2018). Nighttime enhancement of monoterpene  
396 NOSs was clearly observed under high-NO<sub>x</sub> conditions (Fig. 5). The nighttime concentrations of C<sub>10</sub>H<sub>16</sub>NO<sub>7</sub>S<sup>-</sup> and  
397 C<sub>9</sub>H<sub>14</sub>NO<sub>8</sub>S<sup>-</sup> were respectively 1.3-31.4 (9.8 on average) and 0.9-19.7 (5.8 on average) times larger than daytime  
398 concentrations. Higher mixing ratios of monoterpenes were observed at night (Fig. S5), when the high NO<sub>x</sub> concentrations  
399 (Fig. 5) favored the formation of monoterpene NOSs via NO<sub>3</sub>-initiated oxidation of monoterpenes. The elevated nighttime  
400 concentrations of monoterpene NOSs was also observed in previous studies (Surratt et al., 2008; Iinuma et al., 2007;  
401 Gomez-Gonzalez et al., 2008). High correlation between N<sub>2</sub>O<sub>5</sub> and NO<sub>2</sub> or NO<sub>3</sub> radical production were observed (Wang et  
402 al., 2018), so the NO<sub>2</sub> concentration was employed to investigate NO<sub>3</sub> oxidation during the campaign in this study. Higher  
403 concentrations of monoterpene NOSs (C<sub>10</sub>H<sub>16</sub>NO<sub>7</sub>S<sup>-</sup>) were found with elevated NO<sub>2</sub> levels at night (Fig. 6), indicating the  
404 plausibility of more NOS formation via NO<sub>3</sub>-initiated oxidation. When NO<sub>2</sub> increased to higher than 20 ppb, the NOS  
405 concentration did not further increase obviously with NO<sub>2</sub>, which suggested that NO<sub>2</sub> was in excess and no longer the  
406 limiting factor in NOS formation. The highest nighttime concentration of C<sub>10</sub>H<sub>16</sub>NO<sub>7</sub>S<sup>-</sup> was recorded on May 27 during  
407 episode II (Fig. 5). Besides the high NO<sub>2</sub> concentration (>20 ppb), the high monoterpene level was another primary reason  
408 for the elevated concentration of monoterpene NOSs (Table S5).

409 The lower concentrations of monoterpene NOSs during the daytime could be attributed to the lower monoterpene, NO<sub>x</sub>  
410 and NO<sub>x</sub>/BVOCs ratios than those at night (Fig. S5). What's more, monoterpene NOSs, also as organic nitrate (R-ONO<sub>2</sub>)  
411 compounds, may go through decomposition via photolysis or OH oxidation during the daytime (He et al., 2011;  
412 Suarez-Bertoa et al., 2012). Organic nitrates have been estimated to have a short lifetime of several hours (Lee et al., 2016).

413 Elevation in concentrations of monoterpene NOSs were also observed with the increasing of  $\text{NO}_2$  during daytime, but the  
414 concentrations were much lower and the increase was less prominent than that during the nighttime (Fig. 6). The highest  
415 daytime concentration of  $\text{C}_{10}\text{H}_{16}\text{NO}_7\text{S}^-$  was recorded on May 23 (10.6  $\text{ng}/\text{m}^3$ ), followed by the daytime of May 31 (8.0  
416  $\text{ng}/\text{m}^3$ ). The  $\text{NO}_2$  concentrations were in the range of 20-25 ppb and 10-15 ppb during the daytime of May 23 and 31,  
417 respectively. It is noted that the  $J(\text{O}^1\text{D})$  values during the daytime of May 23 and 31 were much lower than other daytime  
418 periods (Fig. 5), indicating the possibility of less decomposition of monoterpene NOSs. Previous studies also reported that  
419 the organic nitrate have much shorter lifetimes than the corresponding OSs, thus it is possible that organic nitrates derived  
420 from monoterpene would undergo nucleophilic attack by sulfate and form monoterpene OSs or NOSs (He et al., 2014; Darer  
421 et al., 2011; Hu et al., 2011). Monoterpene NOSs could also undergo hydrolysis and form monoterpene OSs (Darer et al.,  
422 2011; Hu et al., 2011). These may be other potential pathways for the loss of monoterpene NOSs and production of  
423 monoterpene OSs. These potential formation pathways of monoterpene OSs were different from the formation pathways via  
424 acid-catalyzed aqueous-phase reactions. This could be another explanation for the different temporal variations of some  
425 monoterpene OSs (Fig. S6) from other OSs.

### 426 3.5 Formation pathways of isoprene OSs and NOSs

427 Different from the day-night variation trend of monoterpene NOSs, isoprene NOSs ( $\text{C}_5\text{H}_{11}\text{NO}_9\text{S}^-$ ) displayed similar  
428 temporal variation to isoprene OSs and the total OSs (Fig. 7). Formation of the isoprene NOSs are supposed to have similar  
429 limiting factors to those affecting isoprene OSs, rather than those limiting the nighttime  $\text{NO}_3$ -initiated formation of  
430 monoterpene NOSs. The strong correlation between isoprene OSs and NOSs also indicated their similar formation pathways  
431 or limiting factors in the formation (Table S4). The oxidation of isoprene could form isoprene epoxydiols (IEPOX),  
432 hydroxymethyl-methyl-lactone (HMML) or methacrolein (MACR) and methacrylic acid epoxide (MAE) (Paulot et al., 2009;  
433 Lin et al., 2013b; Worton et al., 2013; Nguyen et al., 2015). Both isoprene OSs and NOSs showed strong correlations with  
434 isoprene oxidation products (MVK+MACR) (Table S4). The isoprene OSs could be formed through ring-opening epoxide  
435 reactions of isoprene oxidation products, which was shown to be a kinetically feasible pathway (Minerath and Elrod, 2009;  
436 Worton et al., 2013). Isoprene OSs were also proposed to form by reactive uptake and oxidation of MVK or MACR

437 (oxidation products of isoprene) initiated by the sulfate radicals (Nozière et al., 2010; Schindelka et al., 2013). Isoprene  
438 NOSs generally increased with the increasing of isoprene oxidation products (MVK+MACR) and acidic sulfate aerosols  
439 (Figs. 3 and 7, Table S4). It indicates isoprene NOSs form via acid-catalyzed reactions or reactive uptake of oxidation  
440 products of isoprene by sulfate, rather than NO<sub>3</sub>-initiated oxidation pathways. The highest concentrations of isoprene OSs  
441 and NOSs were observed during the nighttime of May 30 during episode III (Fig. 7), with high sulfate, MVK+MACR,  
442 aerosol acidity and LWC (Fig. 3, Table S5). In the formation of isoprene OSs or NOSs, epoxides first form carbocation  
443 intermediates through acid-catalyzed hydrolysis reactions, and then sulfate ions serve as nucleophiles in the subsequent fast  
444 step forming OSs or NOSs (Minerath and Elrod, 2009). The presence of high levels of sulfate may effectively facilitate the  
445 ring-opening reaction of epoxide or reactive uptake of oxidation products and subsequent OSs or NOS formation (Surratt et  
446 al., 2010). The proposed formation mechanisms of isoprene NOSs are needed to be further investigated and validated  
447 through laboratory studies.

448 Although the isoprene NOS formation was not via the NO<sub>3</sub>-initiated oxidation pathways, the NO<sub>3</sub> radical could be  
449 involved in the formation pathways and influence the yield of isoprene NOSs. Considering the different atmospheric  
450 conditions during the daytime and nighttime, we analyzed the variation of daytime and nighttime isoprene NOSs separately  
451 (Fig. 8). Generally, higher concentrations of isoprene NOSs were found with elevated NO<sub>2</sub> or MVK+MACR concentration  
452 levels. During daytime, the correlation of isoprene NOSs with NO<sub>2</sub> (r=0.74) was stronger than that with MVK+MACR  
453 (r=0.69) (Fig. 8). When MVK+MACR was higher than 0.7 ppb, the NOS concentrations did not increase further with  
454 MVK+MACR. It was likely that the biogenic VOCs precursors were in surplus under this condition and the formation of  
455 isoprene NOSs may be limited by the lower daytime NO<sub>2</sub> concentration, sulfate aerosols or other factors. During daytime,  
456 the MVK+MACR concentrations were generally higher and NO<sub>x</sub> was lower (Fig. S5), thus the NO<sub>2</sub> level may limit the  
457 daytime formation of isoprene NOSs. During nighttime, a strong correlation between isoprene NOS and MVK+MACR  
458 (r=0.94) was observed, while the increase trend of isoprene NOSs as a function of NO<sub>2</sub> (r=0.53) was not so obvious and their  
459 correlation was lower (Fig. 8). During nighttime, the NO<sub>x</sub> concentrations were generally higher and MVK+MACR  
460 concentrations were lower (Fig. S5), thus the concentrations of isoprene oxidation products (e.g. MVK+MACR) may be the  
461 limiting factor for the nighttime formation of isoprene NOSs. The threshold (e.g. NO<sub>x</sub>/isoprene ratio, NO<sub>x</sub>/isoprene oxidation

462 products ratio) that makes the transition from NO<sub>x</sub>-limited to isoprene-limited (or isoprene oxidation products) still need  
463 further investigation through laboratory studies.

#### 464 **4 Conclusions**

465 An intensive field campaign was conducted to investigate the characterization and formation of OSs and NOSs in  
466 summer of Beijing, under the influence of abundant biogenic emissions and anthropogenic pollutants (e.g. NO<sub>x</sub>, SO<sub>2</sub> and  
467 SO<sub>4</sub><sup>2-</sup>). The overall molecular characterization of S-containing organics (CHOS, CHONS) was made through ESI-Orbitrap  
468 MS data. More than 90% of the CHOS formulas could be assigned as OSs and more than half of the CHONS formulas could  
469 be assigned as NOSs, based on the molecular formulas. The number and intensity of OSs and NOSs increased significantly  
470 during pollution episodes, which indicated they might play important roles for the SOA accumulation.

471 To further investigate the distribution and formation pathways of OSs and NOSs in complex ambient atmosphere, [some](#)  
472 [species](#) were quantified using HPLC-MS, including ten OSs and three NOS species. The total concentrations of quantified  
473 OSs and NOSs were [41.4 and 13.8 ng/m<sup>3</sup>](#), respectively, accounting for [0.31% and 0.11%](#) of organic matter. Glycolic acid  
474 sulfate was the most abundant species ([19.5 ng/m<sup>3</sup>](#)) among all the quantified OS species. The strong correlations between  
475 GAS, LAS, HAS and isoprene OSs indicated their potential formation pathways via isoprene oxidation in the presence of  
476 acidic sulfate aerosols. The concentration of isoprene OSs was [14.8 ng/m<sup>3</sup>](#) and the isoprene OSs formed via HO<sub>2</sub> channel was  
477 higher than that via NO/NO<sub>2</sub> channel. The contribution of monoterpene OSs was much smaller than other OSs, while the  
478 monoterpene NOSs (C<sub>10</sub>H<sub>16</sub>NO<sub>7</sub>S) were observed at high concentration ([12.0 ng/m<sup>3</sup>](#)), especially in nighttime samples.

479 [OS concentrations](#) generally increased with the increase of acidic sulfate aerosols, aerosol acidity and LWC, indicating  
480 the acid-catalyzed aqueous-phase formation of OSs in the presence of acidic sulfate aerosols as an effective formation  
481 pathway. The sulfate concentration, SIA composition, aerosol acidity, and LWC are important factors influencing the OS  
482 formation. When sulfate dominated the SIAs accumulation (SO<sub>4</sub><sup>2-</sup>/SIAs > 0.5), the aerosol acidity would increase obviously  
483 as a function of SO<sub>4</sub><sup>2-</sup>/SIAs mass concentration ratios and the pH values were generally below 2.8. Thus, the OS formation  
484 would be obviously promoted as the increasing of acidic sulfate aerosols, aerosol acidity and LWC. When the SIAs

485 accumulation were dominated by nitrate ( $\text{SO}_4^{2-}/\text{SIAs} < 0.5$ ), high aerosol LWC may occur, while the OS formation via  
486 acid-catalyzed reactions may be limited by relatively lower aerosol acidity.

487 The  $\text{NO}_3$ -initiated oxidation dominated the nighttime BVOCs loss in summertime Beijing, with the  $\text{NO}_x/\text{BVOCs}$  ratios  
488 higher than 10 at night. Significant nighttime enhancement of monoterpene NOSs was observed, indicating the formation via  
489  $\text{NO}_3$ -initiated oxidation of monoterpene under high- $\text{NO}_x$  conditions. Higher concentrations of monoterpene NOSs were  
490 found with elevated [NO<sub>2</sub> levels at night](#) and  $\text{NO}_2$  ceased to be a limiting factor for NOS formation when higher than 20 ppb.  
491 The lower daytime concentrations of monoterpene NOSs could be attributed to the lower production and the decomposition  
492 during daytime. Different from the monoterpene NOS formation via  $\text{NO}_3$ -initiated oxidation, isoprene NOSs and OSs are  
493 supposed to form via acid-catalyzed chemistry or reactive uptake of the oxidation products of isoprene, which is needed to  
494 be further investigated through laboratory studies. The daytime  $\text{NO}_2$  concentration could be a limiting factor for isoprene  
495 NOS formation, while the nighttime formation was limited by isoprene or its oxidation products. The proposed formation  
496 mechanisms of isoprene NOSs as well as the limiting factors still need further investigation in laboratory studies.

497 This study highlights the formation of OSs and NOSs via the interaction between biogenic VOC precursors and  
498 anthropogenic pollutants ( $\text{NO}_x$ ,  $\text{SO}_2$  and  $\text{SO}_4^{2-}$ ) in summer of Beijing. Our study reveals the accumulation of OSs with the  
499 increase of acidic sulfate aerosols and the nighttime enhancement of monoterpene NOSs under high- $\text{NO}_x$  conditions. The  
500 acidic sulfate aerosols and high nighttime  $\text{NO}_x$  or  $\text{N}_2\text{O}_5$  concentrations were observed in Beijing in our observation and also  
501 other studies (Liu et al., 2017; Wang et al., 2017b; Wang et al., 2017a), which provide favorable conditions for the formation  
502 of OSs and NOSs. The results imply the importance of reducing anthropogenic emissions, especially  $\text{NO}_x$  and  $\text{SO}_2$ , to reduce  
503 the biogenic SOA burden in Beijing, and also in areas with abundant biogenic emissions and anthropogenic pollutants.  
504 Moreover, the OSs or NOSs could be treated as key SOA species when exploring the biogenic-anthropogenic interactions as  
505 well as organic-inorganic reactions.

506

507 *Data availability.* The dataset is available upon request by contacting Min Hu (minhu@pku.edu.cn).

508

509 **The Supplement related to this article is available online**

510

511 *Competing interests.* The authors declare that they have no conflict of interest.

512

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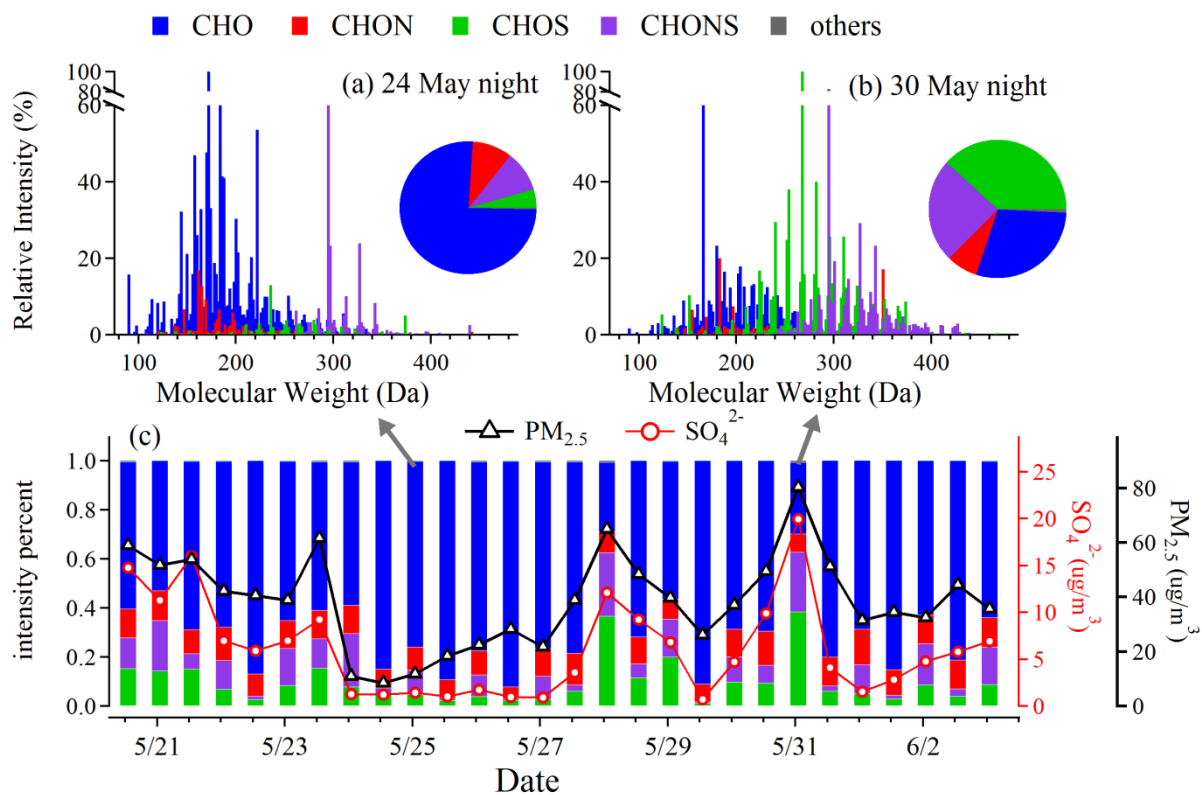
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876 Figure 1 The intensity distribution of different compound categories (CHO, CHON, CHOS and CHONS) (a) on a clean day  
 877 and (b) on a polluted day. (c) Temporal variation of  $PM_{2.5}$ ,  $SO_4^{2-}$  and intensity percentages of different compound categories.

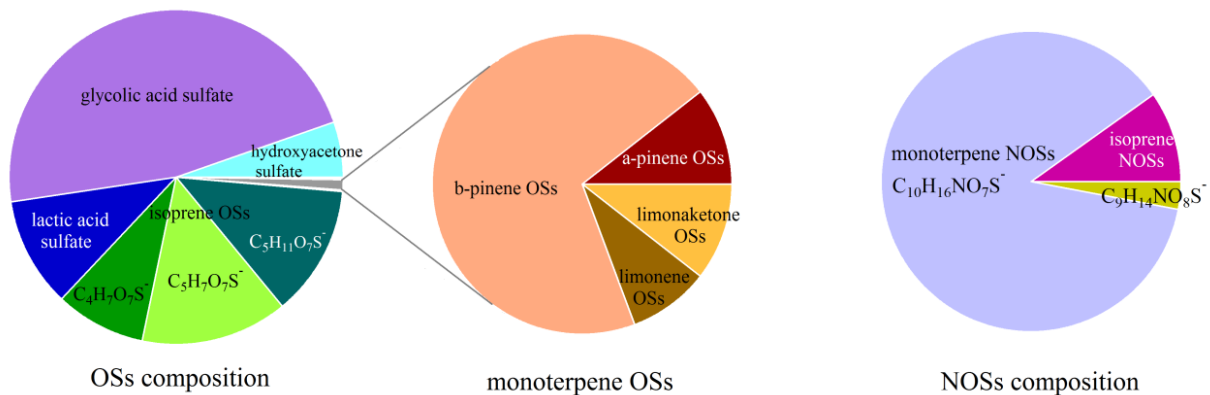
878 The highly water-soluble OS species (e.g. isoprene OSs) with lower MW are absent in these figures and details are described  
 879 in section 3.1.

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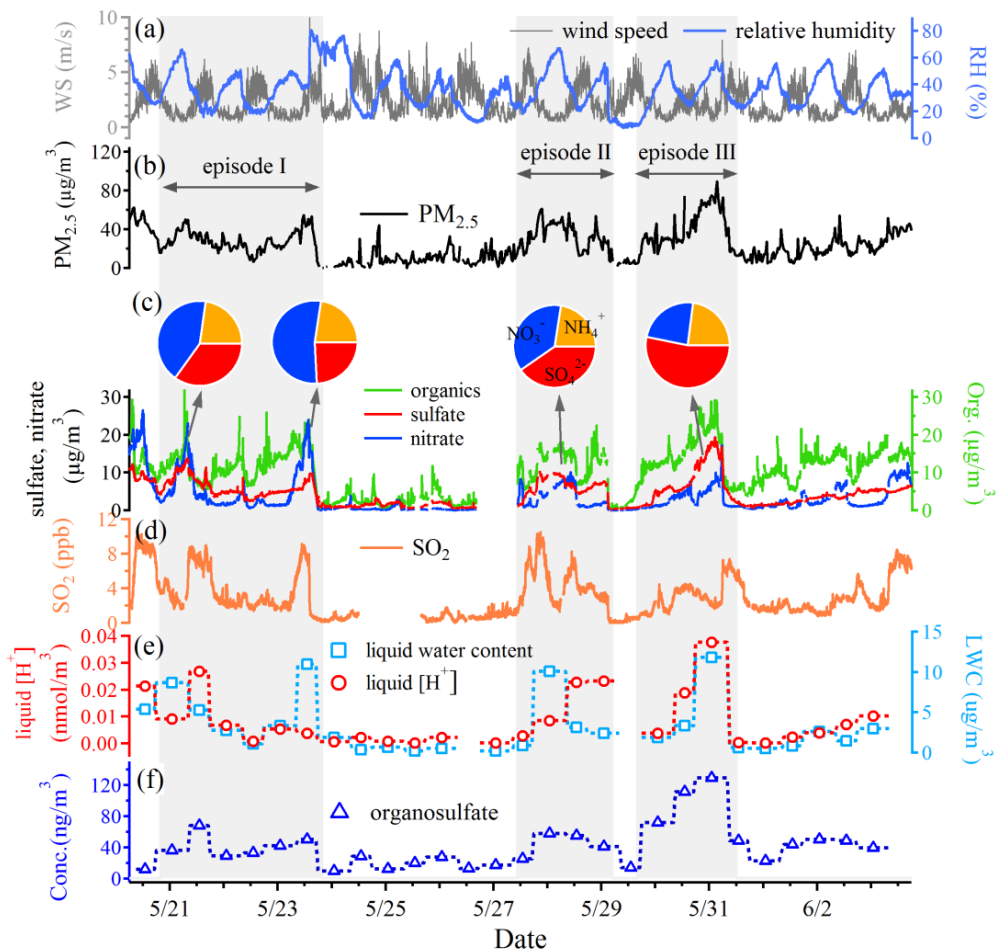
885 Figure 2 The relative contribution of different OS and NOS species. Only the selected species (semi-)quantified by

886 HPLC-MS are included in this figure.

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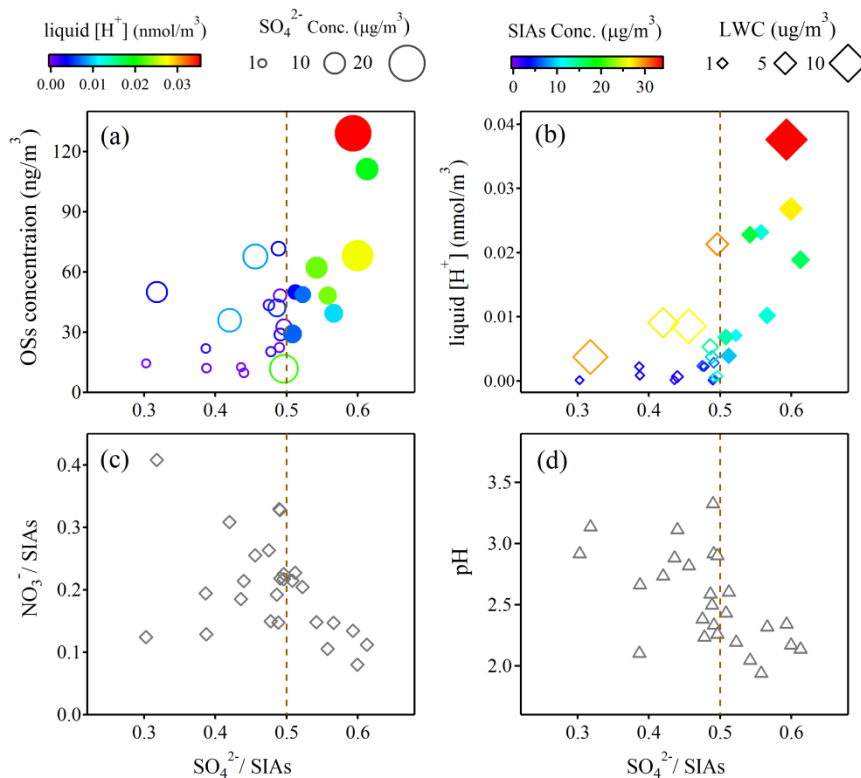
891 Figure 3 Time series of (a) wind speed (WS) and relative humidity (RH), (b) PM<sub>2.5</sub>, (c) mass concentrations of organics,  
 892 sulfate, nitrate and composition of secondary inorganic aerosols during pollution episodes (d) SO<sub>2</sub>, (e) liquid water content  
 893 (LWC) and aqueous phase [H<sup>+</sup>], and (f) the total concentrations of OSs quantified by HPLC-MS. The pollution episodes  
 894 were marked by gray shadow.

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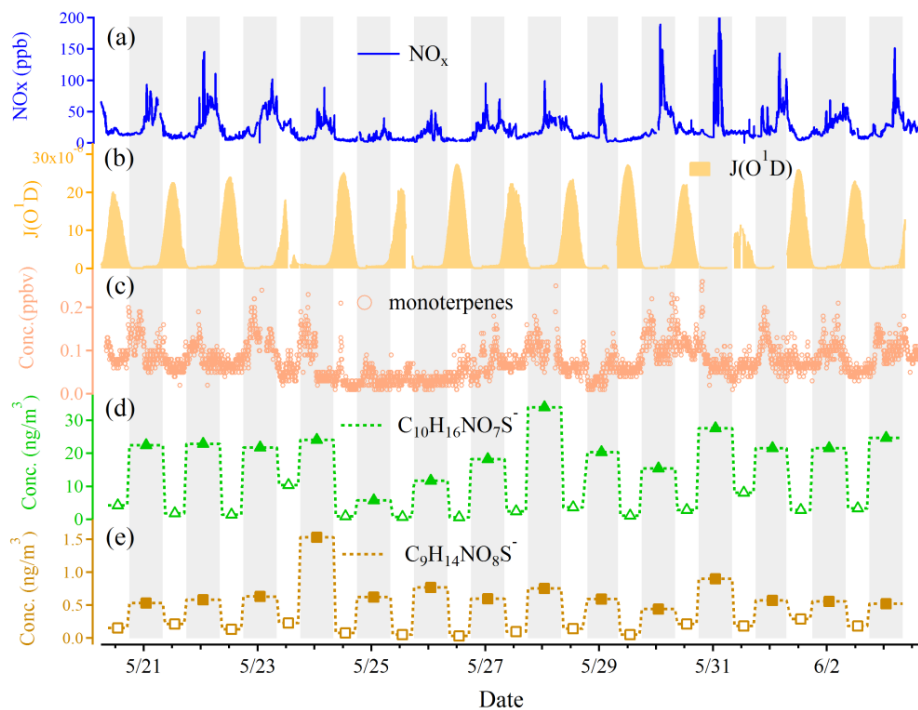
900 Figure 4 (a) The OS concentrations as a function of the  $\text{SO}_4^{2-}/\text{SIAs}$  mass ratios. The circles are colored according to the  
 901 liquid  $[\text{H}^+]$  concentration and the sizes of the circles are scaled to the  $\text{SO}_4^{2-}$  mass concentration. (b) The liquid  $[\text{H}^+]$  as a  
 902 function of the  $\text{SO}_4^{2-}/\text{SIAs}$  mass ratios. The markers are colored according to the SIAs mass concentrations and the sizes of  
 903 the markers are scaled to the liquid water content (LWC). (c) The  $\text{NO}_3^-/\text{SIAs}$  mass ratios as a function of the  $\text{SO}_4^{2-}/\text{SIAs}$   
 904 mass ratios. (d) The aerosol pH as a function of the  $\text{SO}_4^{2-}/\text{SIAs}$  mass ratios. The solid markers represent those among the  
 905 range  $\text{SO}_4^{2-}/\text{SIAs} > 0.5$  and hollow markers represent those among the range  $\text{SO}_4^{2-}/\text{SIAs} < 0.5$  in figure (a) and (b). When  
 906 sulfate dominated the accumulation of secondary inorganic aerosols ( $\text{SO}_4^{2-}/\text{SIAs} > 0.5$ ), both aerosol LWC and acidity ( $\text{pH} <$   
 907  $2.8$ ) increased and OS formation was obviously promoted. In comparison, the acid-catalyzed OS formation was limited by  
 908 lower aerosol acidity under nitrate-dominant conditions.

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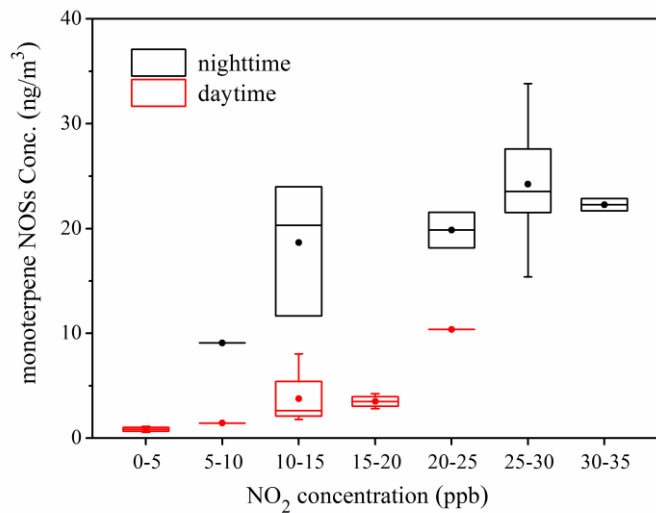
914 Figure 5 Time series of (a) NO<sub>x</sub>, (b) J(O<sup>1</sup>D), (c) monoterpene, (d) monoterpene NOSs (C<sub>10</sub>H<sub>16</sub>NO<sub>7</sub>S) and (e) limonaketone

915 NOSs (C<sub>9</sub>H<sub>14</sub>NO<sub>8</sub>S). The gray background denotes the nighttime and white background denotes the daytime.

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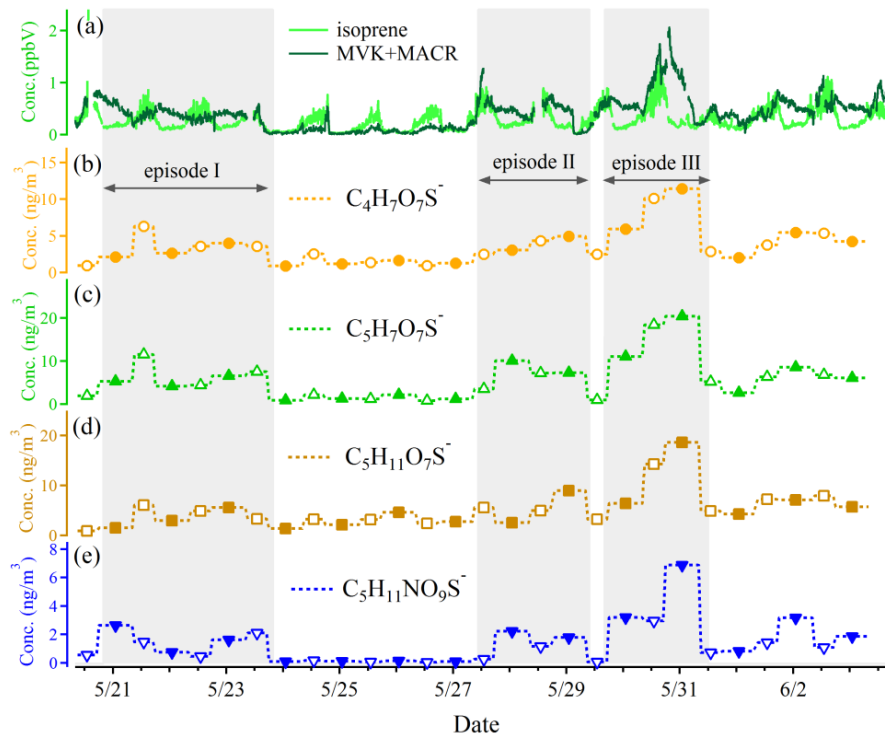


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920 Figure 6 The concentrations of monoterpane NOSs ( $C_{10}H_{16}NO_7S^-$ ) as a function of  $NO_2$  concentration bins (ppb) during  
 921 daytime and nighttime. The closed circles represent the mean values and whiskers represent 25 and 75 percentiles.

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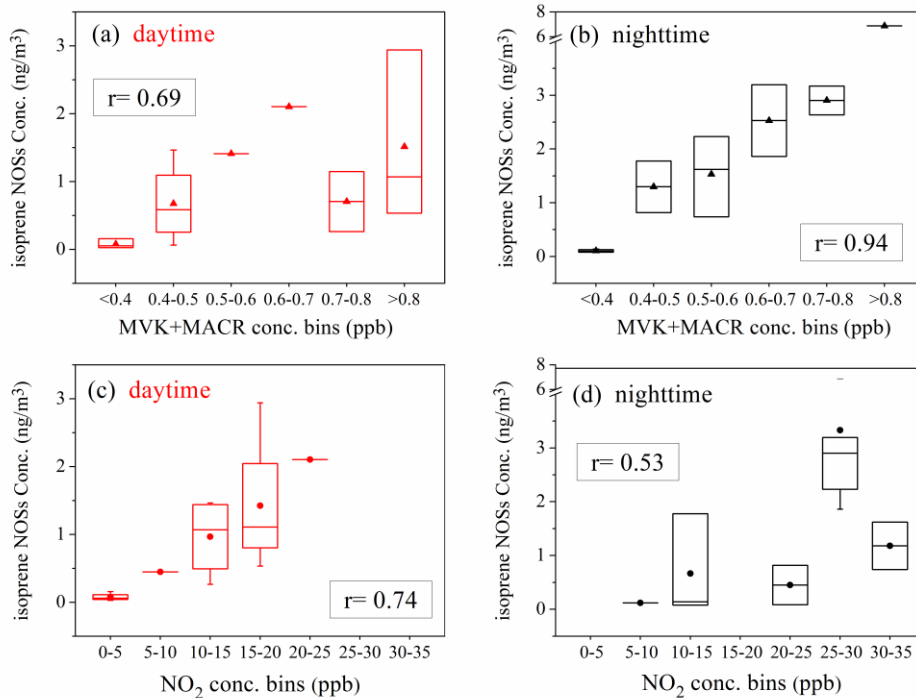
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925 Figure 7 Time series of (a) isoprene and MVK+MACR, isoprene OSs (b)  $C_4H_7O_7S^-$ , (c)  $C_5H_7O_7S^-$ , (d)  $C_5H_{11}O_7S^-$  and (e)  
 926 NOSs ( $C_5H_{11}NO_9S^-$ ). The pollution episodes were marked by gray shadow. MVK and MACR are the abbreviations of  
 927 methyl vinyl ketone and methacrolein, respectively.

928



929

930 Figure 8 The isoprene NOSs ( $C_5H_{11}NO_9S^-$ ) concentrations as a function of  $NO_2$  or MVK+MACR concentration bins (ppb)

931 and the correlations between isoprene NOSs ( $C_5H_{11}NO_9S^-$ ) and  $NO_2$  or MVK+MACR. The closed markers in the box

932 represent the mean values and whiskers represent 25 and 75 percentiles in each concentration bin. The r value in each panel

933 represents the correlation coefficient between isoprene NOSs and  $NO_2$  or MVK+MACR concentrations.

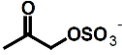
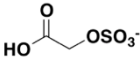
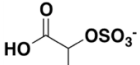
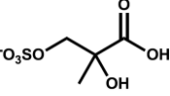
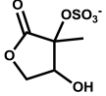
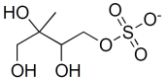
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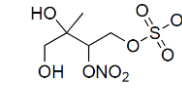
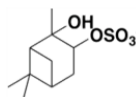
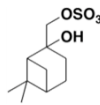
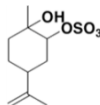
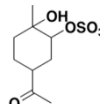
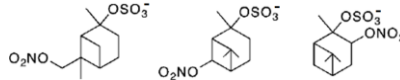
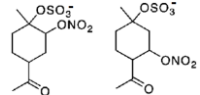
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## Tables

Table 1 Organosulfates and nitrooxy-organosulfates quantified by HPLC-MS

common name	formula	[M-H] <sup>-</sup>	retention time (min)	standard	structure	concentration (ng/m <sup>3</sup> )	
						range	average (n=28)
Hydroxyacetone sulfate (HAS)	C <sub>3</sub> H <sub>5</sub> O <sub>5</sub> S <sup>-</sup>	152.99	1.7, 2.5	Glycolic acid sulfate	 (Hettiyadura et al., 2015)	0.5-7.5	2.2
Glycolic acid sulfate (GAS)	C <sub>2</sub> H <sub>3</sub> O <sub>6</sub> S <sup>-</sup>	154.97	1.6, 2.3	Glycolic acid sulfate	 (Olson et al., 2011)	3.9-58.2	19.5
Lactic acid sulfate (LAS)	C <sub>3</sub> H <sub>5</sub> O <sub>6</sub> S <sup>-</sup>	168.98	1.6, 2.6	Lactic acid sulfate	 (Olson et al., 2011)	0.7-11.9	4.4
	C <sub>4</sub> H <sub>7</sub> O <sub>7</sub> S <sup>-</sup>	198.99	1.5, 2.9	Lactic acid sulfate	 (Lin et al., 2013b; Surratt et al., 2007; Hettiyadura et al., 2015)	0.9-11.4	3.6
Isoprene OSs	C <sub>5</sub> H <sub>7</sub> O <sub>7</sub> S <sup>-</sup>	210.99	1.8, 2.9	Lactic acid sulfate	 (Surratt et al., 2008; Hettiyadura et al., 2015)	0.8-20.4	5.9
	C <sub>5</sub> H <sub>11</sub> O <sub>7</sub> S <sup>-</sup>	215.02	1.6, 2.0	Lactic acid sulfate	 (He et al., 2014; Surratt et al., 2008)	0.9-18.7	5.3

Isoprene NOS	$C_5H_{10}NO_9S^-$	260.01	4.9	Lactic acid sulfate	 (Surratt et al., 2007)	0.03-6.9	1.4
$\alpha$ -pinene OS	$C_{10}H_{17}O_5S^-$	249.08	22.7	$\alpha$ -pinene OS	 (Wang et al., 2017d; Surratt et al., 2008)	0.01-0.5	0.06
$\beta$ -pinene OS	$C_{10}H_{17}O_5S^-$	249.08	22.4, 23.4	$\beta$ -pinene OS	 (Wang et al., 2017d; Surratt et al., 2008)	0.07-0.8	0.4
Limonene OS	$C_{10}H_{17}O_5S^-$	249.08	21.8, 23.8	Limonene OS	 (Wang et al., 2017d)	0.01-0.1	0.05
Limonaketone OS	$C_9H_{15}O_6S^-$	251.06	14.0	Limonaketone OS	 (Wang et al., 2017d)	0.00-0.2	0.06
Monoterpene NOSs	$C_{10}H_{16}NO_7S^-$	294.06	24.8, 26.6, 27.1	$\alpha$ -pinene OSs	 (Surratt et al., 2008; He et al., 2014)	0.6-33.8	12.0
	$C_9H_{14}NO_8S^-$	296.04	21.1	Limonaketone OS	 (Surratt et al., 2008)	0.03-1.5	0.4

1 **Supplement for**

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3 **The Secondary Formation of Organosulfates under the Interactions**  
4 **between Biogenic Emissions and Anthropogenic Pollutants in**  
5 **Summer of Beijing**

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7 Rongzhi Tang,<sup>1</sup> Xiao Li,<sup>1</sup> Ying Liu,<sup>1,5</sup> Michael Le Breton,<sup>2</sup> Zhuofei Du,<sup>1</sup> Dongjie Shang,<sup>1</sup> Yusheng Wu,<sup>1</sup>  
8 Zhijun Wu,<sup>1</sup> Yu Song,<sup>1</sup> Shengrong Lou,<sup>6</sup> Mattias Hallquist,<sup>2</sup> and Jianzhen Yu <sup>\*,3,4</sup>

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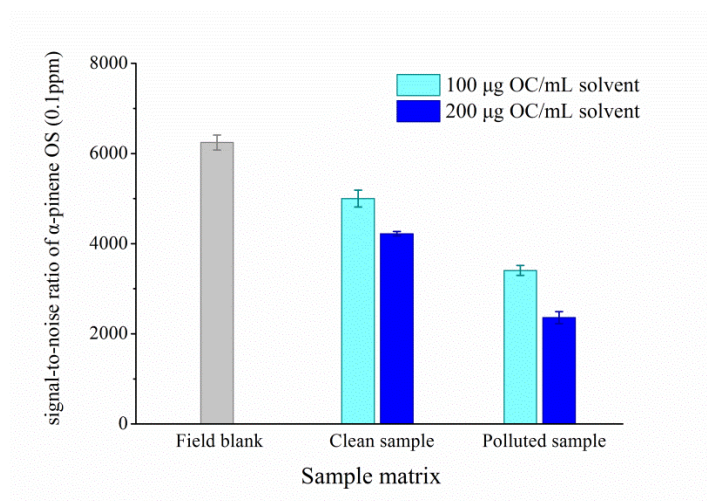
## 31 **Appendix S1 The influence of ion suppression on Orbitrap MS analysis**

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

46 The intensity of 0.1 ppm  $\alpha$ -pinene OS was the highest in the matrix of field blank extract and the lowest in the matrix of  
47 polluted sample extract. The extent of suppression ranged from 20% in the matrix of 100  $\mu$ g OC from the clean sample to 62%  
48 in the matrix of 200  $\mu$ g OC from the polluted sample (Fig. S1). It was clear that the extent of suppression increased with the  
49 OC content of the matrix, from 20% in 100  $\mu$ g OC matrix to 32% in 200  $\mu$ g OC matrix for the clean sample and from 45% in  
50 100  $\mu$ g OC matrix to 62% in 200  $\mu$ g OC matrix for the polluted sample. The relative standard deviation (RSD) of  $\alpha$ -pinene  
51 OS arising from different OC loadings (100  $\mu$ g and 200  $\mu$ g OC/mL solution) were 26% and 12% in polluted and clean  
52 samples, respectively. This result confirmed the benefit of adjusting OC content to a uniform level before Orbitrap MS  
53 analysis in minimizing the impact of matrix ion suppression. We note that when the sample was diluted to 100 $\mu$ g OC/mL  
54 solvent, the intensity of  $\alpha$ -pinene OS in the clean sample was comparable to that in the field blank sample. This indicated

55 that the ion suppression would be insignificant with less than 100  $\mu\text{g OC/mL}$  solution. However, this level of dilution may  
56 limit the identification of species present at low concentrations due to too much dilution.

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



62

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

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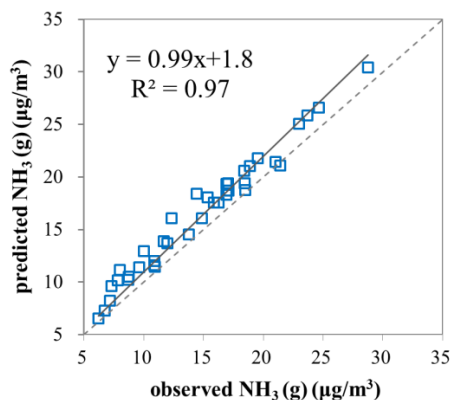
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71 **Appendix S2 The validation of ISORROPIA-II thermodynamic model prediction**

72 The ISORROPIA-II thermodynamic model was run for metastable aerosols in this study. It has been suggested in  
73 previous studies that “metastable” state (only liquid phase) often showed better performance than the “stable” state  
74 (solid+ liquid) solution, and was commonly applied in previous pH or LWC predictions (Bougiatioti et al., 2016;Guo  
75 et al., 2015;Guo et al., 2016;Guo et al., 2017;Weber et al., 2016;Liu et al., 2017a). Though we lack direct evidence to  
76 reveal the physical state of ambient aerosols in this study, indirect evidence is provided to support that the assumption  
77 is reasonable. The verification of prediction by ISORROPIA-II was assessed by comparing the predicted and measured  
78 gaseous NH<sub>3</sub> in this study (Fig. S2) (Bougiatioti et al., 2016;Guo et al., 2015;Guo et al., 2016;Guo et al., 2017;Weber  
79 et al., 2016;Liu et al., 2017a). Good agreement was reached between predicted and measured gaseous ammonia  
80 concentrations (slope=0.99, intercept= 1.8 μg/m<sup>3</sup>, R<sup>2</sup>= 0.97). The result suggested that the “metastable” assumptions  
81 are reasonable in this study.

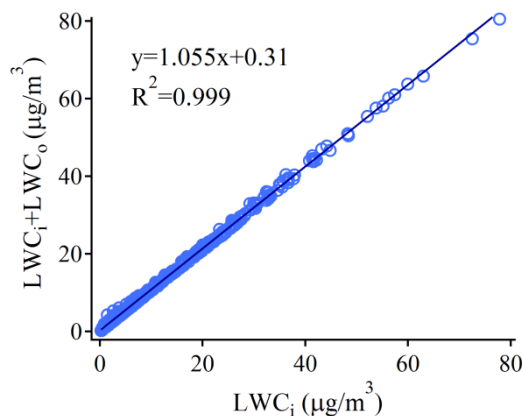


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83 **Figure S2 Comparison of predicted NH<sub>3</sub> (g) and measured NH<sub>3</sub> (g)**

84  
85 The ubiquitous existence of ambient metastable aerosols has been observed in previous studies (Rood et al.,  
86 1989). Based on our previous study in the winter of urban Beijing (Liu et al., 2017b), the rebound fraction of fine  
87 particles was ~0.8 at <20% RH, indicating a semisolid phase of particles. As the RH increased from 20 to 60%,  
88 the rebound fraction decreased from 0.8 to 0.2, suggesting transition from semisolid to liquid phase state. The  
89 rebound fraction of particles was lower than 0.4 at >40% RH, indicating that the liquid phase as the major phase

90 state of ambient aerosols. RH conditions of < 20% were quite limited during the campaign. RH was usually  
91 higher than 40% and could increase to higher than 60% at night. Thus, a nearly liquid phase was likely the major  
92 phase state of ambient aerosols at night in this study. It would be desirable to obtain direct observational evidence  
93 of aerosol phase state in future studies.

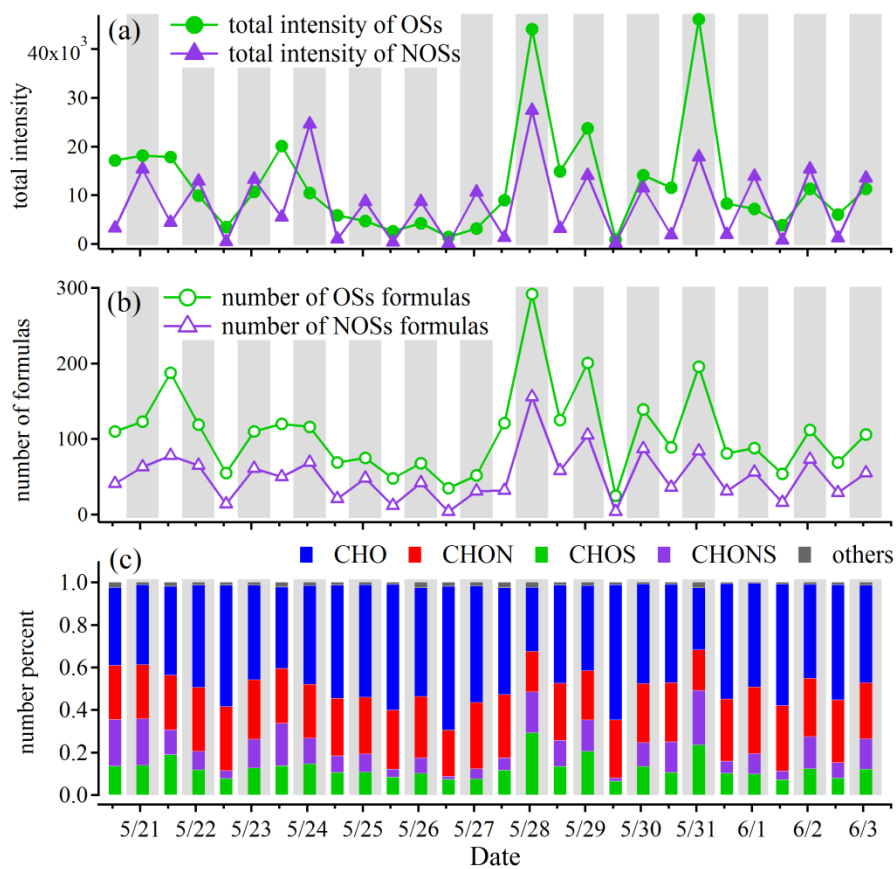
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96 Figure S3 Comparison between aerosol liquid water content with or without water associated with  
97 organic compounds.  $LWC_i$  and  $LWC_o$  represent the water contributed by inorganic compounds and  
98 organic compounds, respectively. The data is from Fig. S1 in Wu et al. (2018) based on the  
99 measurement in Beijing (Wu et al., 2018).

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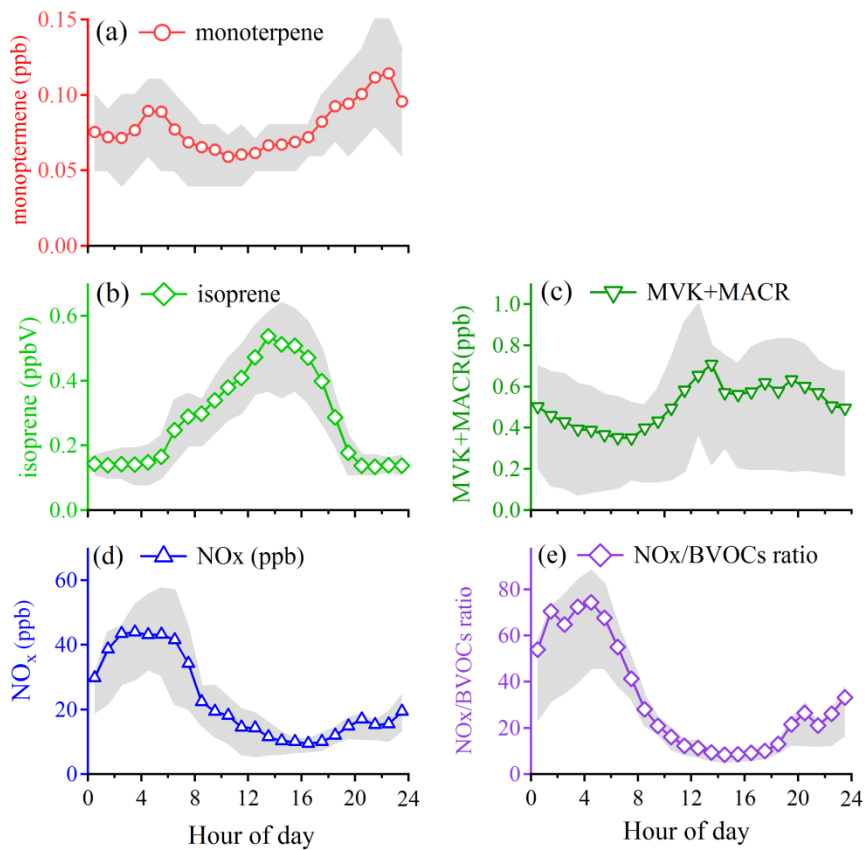
102 Figure S4 Temporal variation of the (a) total intensity and (b) total number of OSs and NOSs, and (c)  
 103 temporal variation of the number percent of different compound categories. The gray background  
 104 denotes the nighttime and white background denotes the daytime.

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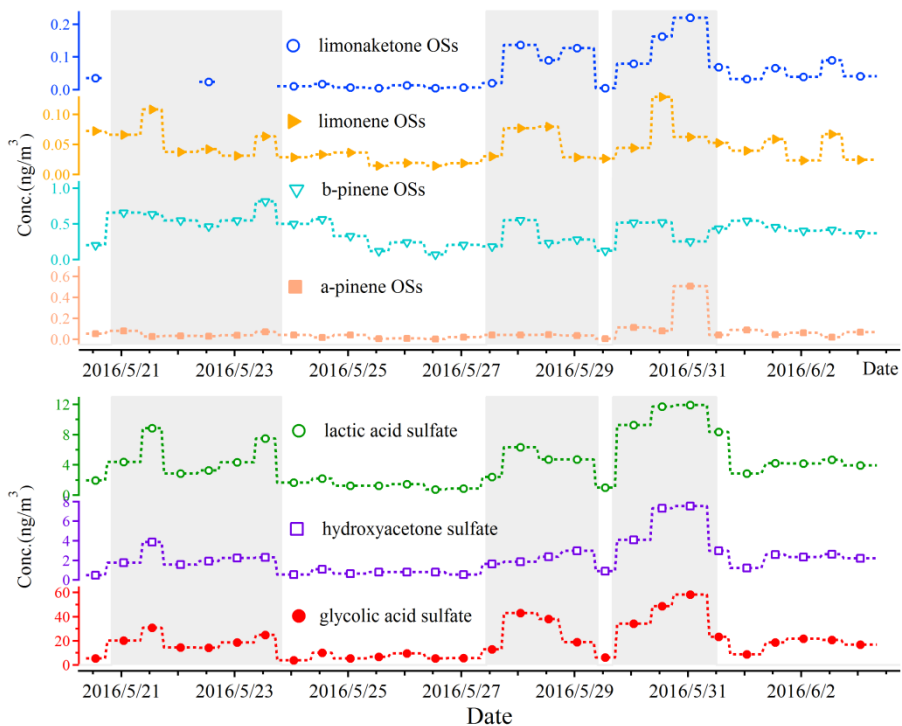
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Figure S5 The diurnal variations of monoterpene, isoprene,  $\text{NO}_x$  and  $\text{NO}_x/\text{BVOCs}$  ratios



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114 Figure S6 Time series of  $\alpha$ -pinene OSs,  $\beta$ -pinene OSs, limonene OSs, limonaketone OSs, lactic acid  
 115 sulfate, glycolic acid sulfate and hydroxyacetone sulfate. The pollution episodes were marked by gray  
 116 shadow.

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Table S1 The purity and recovery of organosulfate standards in this study

Organosulfate	Purity (%)	Recovery (%)
lactic acid sulfate	15%	
glycolic acid sulfate	8%	
$\alpha$ -pinene OS	>99%	80.5%
$\beta$ -pinene OS	>99%	93.5%
limonene OS	>99%	85.4%
limonaketone OS	>99%	82.5%

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Table S2 List of some most abundant OSs and NOSs peaks observed in the mass spectra

No.	m/z [M-H] <sup>-</sup>	Formula [M-H] <sup>-</sup>	relative intensity (%)			precursor/ formation	references
			05/24N	05/30D	05/30N		
<b>organosulfates</b>							
1	151.0071	C <sub>4</sub> H <sub>7</sub> SO <sub>4</sub> <sup>-</sup>	1	4.8	10.3	diesel fuel SOA	(Blair et al., 2017)
2	209.0489	C <sub>7</sub> H <sub>13</sub> SO <sub>5</sub> <sup>-</sup>	1	2.2	7.4	alkane	(Riva et al., 2016b)
3	223.0646	C <sub>8</sub> H <sub>15</sub> SO <sub>5</sub> <sup>-</sup>	3.1	9.7	16.8	diesel fuel SOA	(Blair et al., 2017)
4	225.0438	C <sub>7</sub> H <sub>13</sub> SO <sub>6</sub> <sup>-</sup>	0.4	2.3	14	diesel fuel SOA	(Blair et al., 2017)
5	235.0646	C <sub>9</sub> H <sub>15</sub> SO <sub>5</sub> <sup>-</sup>	12.9	8.7	9.1	diesel fuel SOA	(Blair et al., 2017)
6	237.0438	C <sub>8</sub> H <sub>13</sub> SO <sub>6</sub> <sup>-</sup>	1.4	3.3	10	diesel fuel SOA	(Blair et al., 2017)
7	237.0802	C <sub>9</sub> H <sub>17</sub> SO <sub>5</sub> <sup>-</sup>	2	5.4	9.4	alkane	(Riva et al., 2016b)
8	239.0595	C <sub>8</sub> H <sub>15</sub> SO <sub>6</sub> <sup>-</sup>		11.1	29.4	diesel fuel SOA	(Blair et al., 2017)
9	249.0802	C <sub>10</sub> H <sub>17</sub> SO <sub>5</sub> <sup>-</sup>	2.7	2.6	4.2	monoterpene	(Surratt et al., 2008; Wang et al., 2017)
10	251.0595	C <sub>9</sub> H <sub>15</sub> SO <sub>6</sub> <sup>-</sup>	3.7	9.5	24.7	monoterpene	(Wang et al., 2017)
11	251.0959	C <sub>10</sub> H <sub>19</sub> SO <sub>5</sub> <sup>-</sup>	1.9	5.3	7.5	alkane	(Riva et al., 2016b)
12	253.0751	C <sub>9</sub> H <sub>17</sub> SO <sub>6</sub> <sup>-</sup>	2	11.1	38	diesel fuel SOA	(Blair et al., 2017)
13	265.0751	C <sub>10</sub> H <sub>17</sub> SO <sub>6</sub> <sup>-</sup>	3	7.3	13.9	alkane	(Riva et al., 2016b)
14	267.0544	C <sub>9</sub> H <sub>15</sub> SO <sub>7</sub> <sup>-</sup>	2.1	19.4	100	alkane/ isoprene	(Riva et al., 2016a; Riva et al., 2016b)
15	267.0908	C <sub>10</sub> H <sub>19</sub> SO <sub>6</sub> <sup>-</sup>	1.6	6	13.4	diesel fuel SOA	(Blair et al., 2017)
16	269.0701	C <sub>9</sub> H <sub>17</sub> SO <sub>7</sub> <sup>-</sup>	0.3	4	15.8	alkane	(Riva et al., 2016b)
17	279.0544	C <sub>10</sub> H <sub>15</sub> SO <sub>7</sub> <sup>-</sup>	3.9	4.8	15.9	alkane	(Riva et al., 2016b)
18	279.0908	C <sub>11</sub> H <sub>19</sub> SO <sub>6</sub> <sup>-</sup>	1.9	5.5	13.3	diesel fuel SOA	(Blair et al., 2017)
19	279.1272	C <sub>12</sub> H <sub>23</sub> SO <sub>5</sub> <sup>-</sup>	2.2	3.3	6.5	alkane	(Riva et al., 2016b)
20	281.0701	C <sub>10</sub> H <sub>17</sub> SO <sub>7</sub> <sup>-</sup>	2.6	13.3	40	diesel fuel SOA	(Blair et al., 2017)
21	281.1064	C <sub>11</sub> H <sub>21</sub> SO <sub>6</sub> <sup>-</sup>	0.6	3.6	8.2	diesel fuel SOA	(Blair et al., 2017)
22	283.0493	C <sub>9</sub> H <sub>15</sub> SO <sub>8</sub> <sup>-</sup>	0.4	3.2	12.3	diesel fuel SOA	(Blair et al., 2017)
23	283.0857	C <sub>10</sub> H <sub>19</sub> SO <sub>7</sub> <sup>-</sup>	0.3	3.7	10.1	diesel fuel SOA	(Blair et al., 2017)
24	293.0701	C <sub>11</sub> H <sub>17</sub> SO <sub>7</sub> <sup>-</sup>	0.9		10.1	diesel fuel SOA	(Blair et al., 2017)

25	293.1064	$C_{12}H_{21}SO_6^-$	0.9		9.5		
26	295.0493	$C_{10}H_{15}SO_8^-$	1	2.5	7.1	alkane	(Riva et al., 2016b)
27	295.0857	$C_{11}H_{19}SO_7^-$	1.2	9	25.6	diesel fuel SOA	(Blair et al., 2017)
28	295.1221	$C_{12}H_{23}SO_6^-$	0.7	3.2	6.2	diesel fuel SOA	(Blair et al., 2017)
29	297.0650	$C_{10}H_{17}SO_8^-$		4.2	13.5	alkane	(Riva et al., 2016b)
30	307.0857	$C_{12}H_{19}SO_7^-$	0.6		9.7		
31	307.1221	$C_{13}H_{23}SO_6^-$			7.2		
32	307.1585	$C_{14}H_{27}SO_5^-$	2.1		7.6	diesel fuel SOA	(Blair et al., 2017)
33	309.1014	$C_{12}H_{21}SO_7^-$		11	25.7	diesel fuel SOA	(Blair et al., 2017)
34	321.1014	$C_{13}H_{21}SO_7^-$	0.5		7.5	diesel fuel SOA	(Blair et al., 2017)
35	321.1741	$C_{15}H_{29}SO_5^-$	1.6	6	7.7	diesel fuel SOA	(Blair et al., 2017)
36	325.0963	$C_{12}H_{21}SO_8^-$			10.2	diesel fuel SOA	(Blair et al., 2017)
37	339.0755	$C_{12}H_{19}SO_9^-$			8	diesel fuel SOA	(Blair et al., 2017)
38	351.1119	$C_{14}H_{23}SO_8^-$			9.4	diesel fuel SOA	(Blair et al., 2017)
39	365.1276	$C_{15}H_{25}SO_8^-$	0.3		7.6	diesel fuel SOA	(Blair et al., 2017)
40	373.0963	$C_{16}H_{21}SO_8^-$	5	9.5	8.7	diesel fuel SOA	(Blair et al., 2017)
<b>nitrooxy-organosulfates</b>							
1	276.0184	$C_9H_{10}NO_7S^-$	3.2		9.3		
2	284.0446	$C_8H_{14}NO_8S^-$	6.9	3	10.4		
3	294.0653	$C_{10}H_{16}NO_7S^-$	67.3	5	82.9	monoterpene	(Surratt et al., 2008)
4	296.0446	$C_9H_{14}NO_8S^-$	23.2	1.4	9	monoterpene	(Surratt et al., 2008)
5	300.0395	$C_8H_{14}NO_9S^-$	3.9	2.5	19.2		
6	312.0759	$C_{10}H_{18}NO_8S^-$	10.1		11.5		
7	314.0551	$C_9H_{16}NO_9S^-$	1.9		14.6		
8	326.0551	$C_{10}H_{16}NO_9S^-$	23.9	4	29.2	monoterpene	(Surratt et al., 2008)
9	328.0708	$C_{10}H_{18}NO_9S^-$	3.3	2.5	9.4	monoterpene	(Surratt et al., 2008)
10	342.0500	$C_{10}H_{16}NO_{10}S^-$	8.3	3.3	23.3	monoterpene	(Surratt et al., 2008)

Table S3 Summary of OSs and NOSs concentrations (ng/m<sup>3</sup>) in previous studies and this study

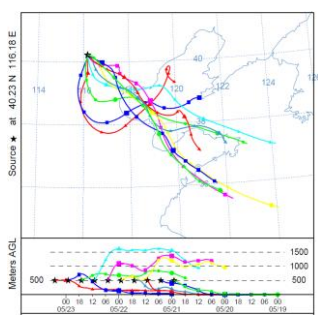
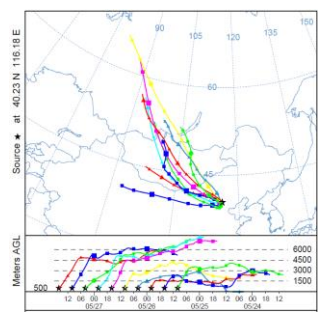
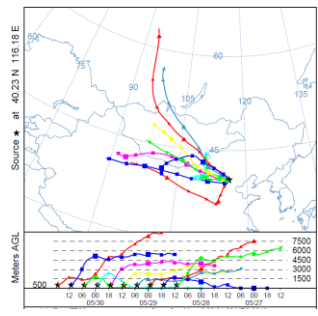
Location	date	Total OSs	HAS	GAS	LAS	Isoprene OSs			Isoprene NOSs	Monoterpene OSs				Monoterpene NOSs		references
						C <sub>4</sub> H <sub>7</sub> O <sub>7</sub> S <sup>-</sup>	C <sub>5</sub> H <sub>7</sub> O <sub>7</sub> S <sup>-</sup>	C <sub>5</sub> H <sub>11</sub> O <sub>7</sub> S <sup>-</sup>	C <sub>5</sub> H <sub>10</sub> NO <sub>9</sub> S <sup>-</sup>	α-pinene OSs	β-pinene OSs	Limonene OSs	Limonaketone OSs	C <sub>10</sub> H <sub>16</sub> NO <sub>7</sub> S <sup>-</sup>	C <sub>9</sub> H <sub>14</sub> NO <sub>9</sub> S <sup>-</sup>	
Riverside, California, US	July, 2005	4.1		3.3	0.8											(Olson et al., 2011)
Cleveland, Ohio, US	July, 2007	2.3		1.9	0.4											(Olson et al., 2011)
Bakersfield, California, US	June, 2010	5.2-6.0		4.5- 5.4	0.6-0.7											(Olson et al., 2011)
Centreville, Alabama, US	June- July, 2013	20.3-42.9	2.7-5.8	8- 20.6	9.6-19											(Hettiyadura et al., 2015;Hettiyadura et al., 2017)
Birmingham, Alabama, US	June- July, 2013	202.5	0.2	26.2	2.7	7.2	1.4	164.5	0.3							(Rattanavara et al., 2016)
Tennessee, US	June- July, 2013	179.5				10		169.5								(Budisulistiorini et al., 2015)
Towson, mid-Atlantic, US	August 2012- June 2013	8.4-33.0	0.3-0.8		0.8-1.3	0.2-4.4		1.6-18.3				0.1-0.4	0.1-2	0.1-0.3		(Meade et al., 2016)
Mexico city, Mexico	March, 2006	5.3-8.8		4.1- 7.0	1.2-1.8											(Olson et al., 2011)
Bavaria, Germany	July, 2002	23.4										23.4				(Iinuma et al., 2009)
Brasschaat, Belgium	June- July, 2007		0.12-36.7					2.0-9.0	0.14-2.3					0.63-3.6		(Gómez-González et al., 2012)
Lahore, Pakistan	Nov., 2007	15.1		11.3	3.8											(Olson et al., 2011)
Pearl River Delta (PRD), China	Sep. 2010	53						0.68						52		(He et al., 2014)
	Nov. 2010	151						0.38						151		
Guangdong, China	Nov.-Dec., 2010	2.71								0.41	0.19	1.14	0.97			(Wang et al., 2017)
Hong Kong, China	Nov.-Dec., 2010	0.88								0.08	0.06	0.36	0.38			
Beijing, China	May-June, 2016	55.2	2.2	19.5	4.4	3.6	5.9	5.3	1.4	0.06	0.4	0.05	0.06	12.0	0.4	this study

Table S4 The pearson correlations between individual OSs and NOSs species quantified by HPLC-MS as well as their correlations with aerosol components, acidity, LWC, VOC precursors and oxidants (n=28)

	total OSs	HAS	GAS	LAS	isoprene OSs			isoprene NOS	$\alpha$ -pinene OSs	$\beta$ -pinene OSs	Limonene OSs	Limonaketone OSs	monoterpene NOSs	
		C <sub>3</sub> H <sub>5</sub> O <sub>5</sub> S <sup>-</sup>	C <sub>2</sub> H <sub>3</sub> O <sub>6</sub> S <sup>-</sup>	C <sub>3</sub> H <sub>5</sub> O <sub>6</sub> S <sup>-</sup>	C <sub>4</sub> H <sub>7</sub> O <sub>7</sub> S <sup>-</sup>	C <sub>5</sub> H <sub>7</sub> O <sub>7</sub> S <sup>-</sup>	C <sub>5</sub> H <sub>11</sub> O <sub>7</sub> S <sup>-</sup>	C <sub>5</sub> H <sub>10</sub> NO <sub>9</sub> S <sup>-</sup>	C <sub>10</sub> H <sub>17</sub> O <sub>5</sub> S <sup>-</sup>	C <sub>10</sub> H <sub>17</sub> O <sub>5</sub> S <sup>-</sup>	C <sub>10</sub> H <sub>17</sub> O <sub>5</sub> S <sup>-</sup>	C <sub>9</sub> H <sub>15</sub> O <sub>6</sub> S <sup>-</sup>	C <sub>10</sub> H <sub>16</sub> NO <sub>7</sub> S <sup>-</sup>	C <sub>9</sub> H <sub>14</sub> NO <sub>8</sub> S <sup>-</sup>
total OSs	1.00													
C <sub>3</sub> H <sub>5</sub> O <sub>5</sub> S <sup>-</sup>	<b>0.96</b>	1.00												
C <sub>2</sub> H <sub>3</sub> O <sub>6</sub> S <sup>-</sup>	<b>0.97</b>	<b>0.88</b>	1.00											
C <sub>3</sub> H <sub>5</sub> O <sub>6</sub> S <sup>-</sup>	<b>0.93</b>	<b>0.92</b>	<b>0.91</b>	1.00										
C <sub>4</sub> H <sub>7</sub> O <sub>7</sub> S <sup>-</sup>	<b>0.95</b>	<b>0.97</b>	<b>0.86</b>	<b>0.86</b>	1.00									
C <sub>5</sub> H <sub>7</sub> O <sub>7</sub> S <sup>-</sup>	<b>0.99</b>	<b>0.96</b>	<b>0.95</b>	<b>0.93</b>	<b>0.95</b>	1.00								
C <sub>5</sub> H <sub>11</sub> O <sub>7</sub> S <sup>-</sup>	<b>0.84</b>	<b>0.91</b>	<b>0.73</b>	<b>0.72</b>	<b>0.93</b>	<b>0.85</b>	1.00							
C <sub>5</sub> H <sub>10</sub> NO <sub>9</sub> S <sup>-</sup>	<b>0.86</b>	<b>0.82</b>	<b>0.83</b>	<b>0.79</b>	<b>0.83</b>	<b>0.88</b>	<b>0.76</b>	1.00						
C <sub>10</sub> H <sub>17</sub> O <sub>5</sub> S <sup>-</sup>	<b>0.67</b>	0.68	0.63	0.59	0.67	0.67	<b>0.71</b>	<b>0.84</b>	1.00					
C <sub>10</sub> H <sub>17</sub> O <sub>5</sub> S <sup>-</sup>	0.18	0.22	0.29	0.44	0.20	0.31	(0.03)	0.26	0.01	1.00				
C <sub>10</sub> H <sub>17</sub> O <sub>5</sub> S <sup>-</sup>	<b>0.64</b>	0.62	0.69	0.71	0.56	0.67	0.37	0.39	0.20	0.44	1.00			
C <sub>9</sub> H <sub>15</sub> O <sub>6</sub> S <sup>-</sup>	<b>0.82</b>	<b>0.84</b>	<b>0.76</b>	<b>0.73</b>	<b>0.82</b>	<b>0.79</b>	<b>0.86</b>	<b>0.74</b>	<b>0.76</b>	(0.04)	0.48	1.00		
C <sub>10</sub> H <sub>16</sub> NO <sub>7</sub> S <sup>-</sup>	0.15	0.11	0.26	0.18	0.13	0.25	0.10	0.48	0.40	0.29	(0.14)	0.10	1.00	
C <sub>9</sub> H <sub>14</sub> NO <sub>8</sub> S <sup>-</sup>	(0.02)	0.02	0.07	0.02	0.02	0.10	0.06	0.26	0.32	0.19	(0.18)	0.07	<b>0.79</b>	1.00
SO <sub>4</sub> <sup>2-</sup>	<b>0.67</b>	<b>0.58</b>	<b>0.69</b>	<b>0.64</b>	<b>0.59</b>	<b>0.69</b>	0.42	<b>0.67</b>	<b>0.57</b>	0.16	<b>0.67</b>	0.44	0.19	(0.03)
NH <sub>4</sub> <sup>+</sup>	0.54	0.42	0.59	0.55	0.43	0.57	0.22	0.58	0.44	0.26	0.62	0.24	0.18	(0.07)
NO <sub>3</sub> <sup>-</sup>	0.22	0.09	0.31	0.32	0.06	0.23	(0.11)	0.36	0.21	0.48	0.39	0.00	0.21	(0.09)
LWC	<b>0.55</b>	0.40	<b>0.61</b>	<b>0.54</b>	0.39	<b>0.57</b>	0.23	<b>0.68</b>	<b>0.57</b>	0.37	0.47	0.29	0.43	0.18
Organics	<b>0.64</b>	<b>0.55</b>	<b>0.65</b>	<b>0.64</b>	<b>0.57</b>	<b>0.65</b>	0.45	<b>0.58</b>	0.42	0.43	<b>0.56</b>	0.48	0.38	0.05
Liquid [H <sup>+</sup> ]	<b>0.67</b>	<b>0.64</b>	<b>0.65</b>	<b>0.57</b>	<b>0.67</b>	<b>0.68</b>	<b>0.60</b>	<b>0.61</b>	<b>0.58</b>	(0.14)	<b>0.57</b>	<b>0.52</b>	0.09	(0.00)

isoprene	0.32	0.34	0.29	0.30	0.34	0.31	0.28	0.03	(0.07)	(0.03)	0.64	0.37	(0.64)	(0.70)
MVK+MACR	0.73	<b>0.72</b>	<b>0.69</b>	<b>0.67</b>	<b>0.71</b>	<b>0.75</b>	<b>0.63</b>	<b>0.69</b>	0.53	0.06	0.64	0.71	0.05	(0.22)
monoterpene	0.35	0.29	0.38	0.36	0.27	0.40	0.11	0.44	0.19	0.34	0.28	0.22	0.55	0.23
NO <sub>2</sub>	0.35	0.27	0.37	0.32	0.29	0.37	0.18	<b>0.58</b>	0.41	0.30	0.01	0.20	<b>0.76</b>	0.39
O <sub>3</sub>	0.45	0.47	0.40	0.39	0.51	0.45	0.44	0.20	0.16	(0.14)	0.67	0.43	(0.59)	(0.57)
O <sub>x</sub> (NO <sub>2</sub> +O <sub>3</sub> )	0.57	0.58	0.53	0.50	0.62	0.59	0.51	0.39	0.29	(0.05)	0.71	0.51	(0.39)	(0.48)

Table S5 The back trajectories, VOC precursors, and oxidants during the three episodes

Episode	Isoprene (ppb)	MVK+MACR (ppb)	Monoterpene (ppb)	NO <sub>2</sub> (ppb)	O <sub>3</sub> (ppb)	O <sub>x</sub> (NO <sub>2</sub> +O <sub>3</sub> ) (ppb)	Back trajectories
episode I (23 May day)	0.36	0.50	0.06	22.51	55.47	77.98	
episode II (27 May night)	0.22	0.43	0.13	24.83	38.27	63.10	
episode III (30 May night)	0.23	1.00	0.08	29.77	87.56	117.33	

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