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 #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+}, Ma^{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 μg/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_3 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^3, R^2= 0.97). The result suggested that the "metastable" assumptions are reasonable in this study.

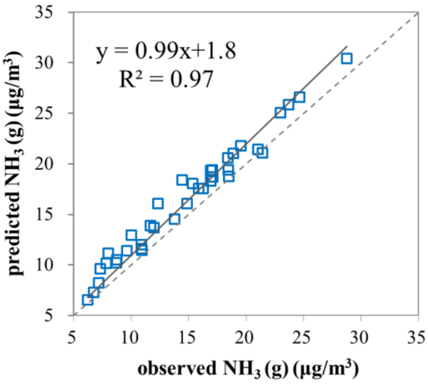

Figure S2 Comparison of predicted NH_3 (g) and measured NH_3 (g)

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:

Bougiatioti, A., Nikolaou, P., Stavroulas, I., Kouvarakis, G., Weber, R., Nenes, A., Kanakidou, M., and Mihalopoulos, N.: Particle water and pH in the eastern Mediterranean: source variability and implications for nutrient availability, Atmos. Chem. Phys., 16, 4579-4591, 10.5194/acp-16-4579-2016, 2016.

Guo, H., Xu, L., Bougiatioti, A., Cerully, K. M., Capps, S. L., Hite, J. R., Carlton, A. G., Lee, S. H., Bergin, M. H., Ng, N. L., Nenes, A., and Weber, R. J.: Fine-particle water and pH in the southeastern United States, Atmos. Chem. Phys., 15, 5211-5228, 10.5194/acp-15-5211-2015, 2015.

Guo, H., Sullivan, A. P., Campuzano-Jost, P., Schroder, J. C., Lopez-Hilfiker, F. D., Dibb, J. E., Jimenez, J. L., Thornton, J. A., Brown, S. S., Nenes, A., and Weber, R. J.: Particle pH and the Partitioning of Nitric Acid during Winter in the Northeastern United States, J. Geophys. Res., [Atmos.], 121, 10355-10376, 10.1002/2016JD025311, 2016.

Guo, H., Weber, R. J., and Nenes, A.: High levels of ammonia do not raise fine particle pH sufficiently to yield nitrogen oxide-dominated sulfate production, Scientific reports, 7, 12109, 10.1038/s41598-017-11704-0, 2017.

Liu, M., Song, Y., Zhou, T., Xu, Z., Yan, C., Zheng, M., Wu, Z., Hu, M., Wu, Y., and Zhu, T.: Fine particle pH during severe haze episodes in northern China, Geophys. Res. Lett., 44, 5213-5221, 10.1002/2017gl073210, 2017a.

Liu, Y., Wu, Z., Wang, Y., Xiao, Y., Gu, F., Zheng, J., Tan, T., Shang, D., Wu, Y., Zeng, L., Hu, M., Bateman, A. P., and Martin, S. T.: Submicrometer Particles Are in the Liquid State during Heavy Haze Episodes in the Urban Atmosphere of Beijing, China, Environmental Science & Technology Letters, 4, 427-432, 10.1021/acs.estlett.7b00352, 2017b.

Weber, R. J., Guo, H., Russell, A. G., and Nenes, A.: High aerosol acidity despite declining atmospheric sulfate concentrations over the past 15 years, Nature Geosci., 9, 282-285, 10.1038/ngeo2665, 2016.

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.

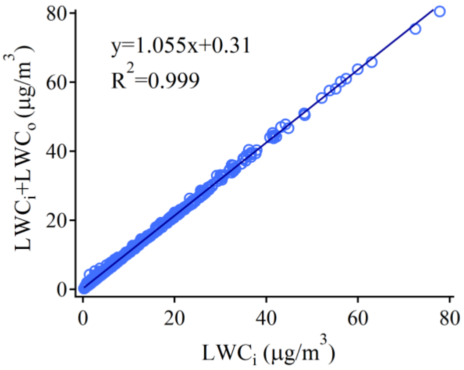

Figure S3 Comparison between aerosol liquid water content with or without water associated with organic compounds. LWCi and LWCo represent the water contributed by inorganic compounds and organic compounds, respectively. The data is from Fig. S1 in Wu et al. (2018) based on the measurement in Beijing (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 dicholoracetic 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 α-pinene OS. The filter portion size and solvent volume were adjusted to yield solution containing ~100 μg or 200 μg OC/mL solvent for the clean sample and polluted sample. The OC concentrations are referred to as the OC loading before the SPE clean-up procedure. Only two concentration levels were examined due to the sample limitation. The intensity (signal-to-noise ratio, s/n) of α-pinene OS (0.1 ppm) in the three different sample matrixes were obtained by deducting the intensity of m/z=249.0802 in the same sample diluted by solvent without α-pinene OS (0.1 ppm) addition. The intensity in each sample was normalized by the ion injection time to make the intensities comparable (Kuang et al., 2016).

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

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

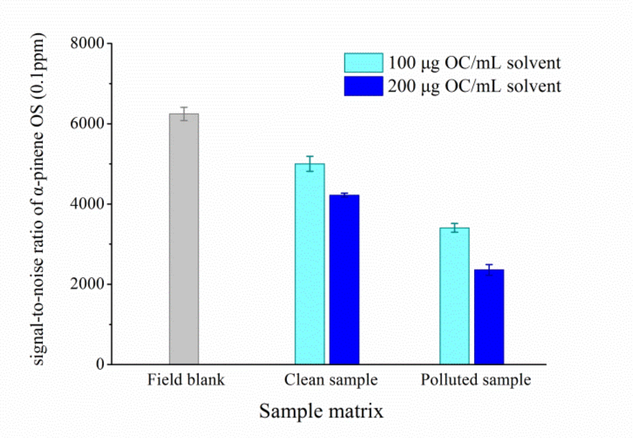

Figure S1 The intensity of α-pinene OS (0.1 ppm) in different sample matrix (blank sample, clean sample, polluted sample) with different OC loadings. The error bars were derived from three repeat injections of the same sample.

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 μg/m^3, which was at a relatively high concentration level when comparing with those reported in previous studies (0.02-0.32μg/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 ($C_5H_{10}NO_9S^-$) 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.