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Atmospheric Chemistry and Physics
Discussions

Interactive comment on "The Secondary Formation of Organosulfates under the Interactions between Biogenic Emissions and Anthropogenic Pollutants in Summer of Beijing" *by* Yujue Wang et al.

Anonymous Referee #2

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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 (SO42-, NO3-, Cl-, NH4+, K+, Na+, Ca2+, Ma2+) and gaseous NH3."

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

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.

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?

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.

Line 177, "What's more, the S-containing compounds contributed more to the higher MW formulas than CHO (O1-O10) or CHON (O1-O11) compounds (Fig. 1), due to the existence of more O (CHOS: O1-O12, CHONS: O1-O14) 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.

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?

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.

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?

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?

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)?

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