

Atmos. Chem. Phys. Discuss., author comment AC2  
<https://doi.org/10.5194/acp-2022-13-AC2>, 2022  
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## Reply on RC2

Haoyu Jiang et al.

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Author comment on "Formation of organic sulfur compounds through SO<sub>2</sub>-initiated photochemistry of PAHs and dimethylsulfoxide at the air-water interface" by Haoyu Jiang et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2022-13-AC2>, 2022

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*In this work, the authors investigated the formation of compounds including organosulfur compounds through SO<sub>2</sub> initiated photochemistry of PAHs and DMSO. Mass spectrometric data and reaction mechanisms supported by theoretical calculations are given to support the formation of observed products in the gas and aqueous phase. The results of this work provide greater insight into the sources of atmospheric sulfur compounds formed through light induced heterogeneous processing of SO<sub>2</sub> with PAHs/DMSO at air/water interface. I support the publication of this work with a few minor comments below.*

### **We would like to thank the reviewer for the constructing and encouraging comments.**

*Line 145, "The applied mixing ratio of 800 ppb would probably amplify the intensity of the detected product compounds, but the formation profiles would still remain the same as in the case of smaller SO<sub>2</sub> mixing ratios." In addition to the reaction pathways, can the authors further elaborate if the formation and volatilization of reaction products (e.g. the detection of the gas phase products) would be affected by the high concentrations of the reactants applied in the study?*

**The mixing ratio applied in this study of 800 ppb is similar with the mixing ratio of 500 ppb in the previous study. However, even if much lower SO<sub>2</sub> mixing ratios were applied the same compounds would be formed but probably with lower signal intensities. Future model studies should reveal the levels of the formed organic sulphur compounds under realistic environmental conditions i.e. SO<sub>2</sub> concentration, PAHs and DMSO concentrations etc.**

**As we mentioned above the goal was to suggest an alternative formation pathway of organic sulfur compounds in the atmosphere. The suggested reaction mechanism tentatively describes the process of formation of these compounds in the gas and in the aqueous phase.**

**We are currently estimating the importance of the suggested chemistry here under environmentally relevant conditions. We added the following paragraph in the section "Atmospheric Implications":**

**"Based on the observed emission rates of Oss in this study, we estimate emission fluxes of MSA, and MSIA, among others, considering realistic environmental conditions, SO<sub>2</sub> mixing ratios ranging between 2 ppb and 50 ppb,**

**surface UV-VIS irradiation, realistic surface microlayer coverage with PAHs/DMSO, and surface wind speeds, (Brüggemann et al., 2018) to account the potential impact of the heterogeneous SO<sub>2</sub> (photo)chemistry with PAHs/DMSO, on the aerosol production in marine boundary layer, which results will be published elsewhere."**

*Line 221, " we tentatively identified a number of unsaturated multifunctional molecules and OSs released in the gas phase from the reaction of SO<sub>2</sub> with either DMSO or PAHs/DMSO, which are summarized in Table S5." Again, will the detection of gas-phase products be affected by the choice of the reactant concentrations?*

**We performed test experiment by using 50 ppb of SO<sub>2</sub> and the same product compounds with similar profiles were obtained. However, we are unable to carry out experiments with lower DMSO concentration and for this reason we are currently modeling the laboratory data by using environmentally relevant conditions. The model outcomes will be published elsewhere.**

*Line 234, Figure 1, please check the resolutions of the figures and the reaction scheme.*

**The resolutions of figures and reaction scheme have been updated.**

*Line 239, "In this study, we observed rapid formation of MSA, MSIA, MSM, EMS, MSAOH, and ESAOH (Figure 2 and Figure S2)." What are the concentrations of these gas-phase products (e.g. ppb or ppm) and their aqueous phase concentrations?*

**It is challenging to quantify the observed product compounds because of the lack of standards. However, with the calibrations of EPA TO15 standard gas established before the experiments, we could relatively quantify the products by using benzene as the reference standard. The concentrations of these gas-phase products were 15-20 ppb for MSA, 96-230 ppb for MSIA, 47-240 ppb for MSM, 1.4-2 ppb for EMS, 2-2.3 ppb for MSAOH and 8-18 ppb for ESAOH in the reactions of SO<sub>2</sub> and PAHs/DMSO under light irradiation. Usually, their concentrations were higher in the reactions of light-excited SO<sub>2</sub> and DMSO (around 25 ppb MSA, 210 ppb MSIA, 285 ppb MSM, 2.3 ppb EMS, 3 ppb MSAOH and 23 ppb ESAOH). As these values are based on semi-quantitative analysis we did not add these values in the manuscript.**

*Line 261, " Here, we show that during daytime the reactions of light-excited SO<sub>2</sub> and aqueous DMSO or DMSO/PAHs could represent an important source of gaseous MSA in the atmosphere near the water (ocean, lake and river) surface" What are the yields of the gasoues MSA in different systems?*

**We are currently modeling the measured emission fluxes to evaluate their importance in the real-life environment. The results will be published elsewhere.**

*Line 271, "The intensities of the product compounds (Figure 2 and Figure S2) decrease after one hour most probably due to their reaction with SO<sub>2</sub> and/or their photodegradation" Please elobarate or show these reactions. What are the kinetics or rates of these reactions?*

**Determining the kinetics of SO<sub>2</sub> induced degradation of PAHs/DMSO was out of scope in this study. The rates of photochemical degradation of PAHs/DMSO are reported in our previous study by Jiang et al. published in JGR: Atmosphere.**

*Line 284, "Numerous unsaturated multifunctional molecules and OSs were identified in the liquid phase during the reaction of SO<sub>2</sub> with either DMSO or PAHs/DMSO by using FT-ICR-*

*MS. The number of detected product compounds in the aqueous phase was significantly higher compared to those detected in the gas phase, due to very high sensitivity of FT-ICR-MS." What are the concentrations of these aqueous-phase products detected by the FT-ICR-MS? Are they volatile or non-volatiles in the reaction systems?*

**The same as above. Due to the lack of standards and the limitations of FT-ICR-MS, it is challenging to quantify the observed product compounds. Based on ionization efficiency and the concentrations of target compounds, only relative abundance was acquired by the semi-quantification of ESI FT-ICR-MS. Thus, we are unable to give the concentrations of aqueous-phase compounds. The detected compounds are soluble and they are detected in the aqueous phase. It is not excluded that some of these compounds partition in the gas phase as well. The compounds released in the gas phase were detected in real-time by the use of SPI-TOF-MS.**

*Line 398, "3.5. Reaction Mechanism of the Gaseous Compounds" As mentioned above, will there be other volatile and gaseous compounds that want to be considered?*

**Depending on the vapor pressure of the compounds it is not excluded that some other compounds would partition in the gas phase.**

*Line 416, "These observations highlight the importance of the SO<sub>2</sub> oxidation reactions of DMSO and/or PAHs/DMSO at the freshwater and sea surface, or in the liquid films of the aerosol particles, which would represent important source of OSs." What would be the formation yields of these products through SO<sub>2</sub> oxidation reactions of DMSO and/or PAHs/DMSO?*

**We are not sure we can give the formation yields for the aqueous products through SO<sub>2</sub> oxidation reactions of DMSO and/or PAHs/DMSO due to the lack of standards and the limitations of FT-ICR-MS.**