

Atmos. Chem. Phys. Discuss., referee comment RC2  
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## Comment on acp-2022-309

Anonymous Referee #2

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Referee comment on "Emission factors and evolution of SO<sub>2</sub> measured from biomass burning in wild and agricultural fires" by Pamela Rickly et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2022-309-RC2>, 2022

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The manuscript investigates the sulfur dioxide (SO<sub>2</sub>) emissions, and sulfate and hydroxymethanesulfonate (HMS) formation from US wild and agricultural fires. The study includes a combination of field data, collected during the course of two flights (one in Boise, ID and the other in Salina, KS) and modeling, using a 0-D box model. The authors provide SO<sub>2</sub> fuel emission factors in agreement with previously literature reported values and provide evidence that HMS acts as S(IV) reservoir under higher pH and liquid water content conditions. This new role of HMS provides valuable insight on the role of sulfur-containing species under biomass burning conditions. I believe that the authors have conducted an analytical work that is of interest to the readers of ACP, however there are some points that need to be addressed. Please find below some comments that I believe need to be addressed in order to clarify specific results and the model mechanism used in this work.

- The authors provide an HMS loss rate constant of:  $6.2 \times 10^8 \times \exp(-11400 \times (1/T - 1/298)) + 4.8 \times 10^3 \times (K_w/H + ) \times \exp(-4700 \times (1/T - 1/298))$ , while Song et al. (2021, ACP), which is used as the reference of the rate, provide a rate constant of:  $6.2 \times 10^{-8} \times \exp(-11400 \times (1/T - 1/298)) + 4.8 \times 10^3 \times (K_w/H + ) \times \exp(-4700 \times (1/T - 1/298))$ . I assume that this is a typo, but please clarify.

Assuming that the HMS loss rate has a typo, additional comments are:

- The role of HMS as S(IV) reservoir is very interesting, especially since this result is mainly under conditions of pH > 6 and high LWC, in which HMS has been shown to be unstable and prone to additional reactions. In the model, the formation and decomposition of HMS is included (Table S1), however its reactions with OH and H<sub>2</sub>O<sub>2</sub>, which has been shown to occur at pH > 6 (Kok et al., 1986. J. Geoph. Res.; Martin et al., 1989, Atmos. Environ.; Chapman et al., 1990, Atmos. Environ.) are not included. How

are the results affected upon inclusion of these reactions?

- The model represents efficiently the field data of August 3<sup>rd</sup>, however it does not capture the trend of all the field data for the case of August 7<sup>th</sup>. Since both days are within the same campaign in Boise, ID, what was the main differences between these days? It would be interesting to provide a brief explanation on why the two days differ, as provided for the two passes of the 7<sup>th</sup> of August.
- Field data are provided for mainly August 3<sup>rd</sup> and 7<sup>th</sup>, which correspond to the Boise flights. It would be beneficial to provide field data and the model performance for the Saline flights. Are the main results the same for both flights? This is not very clear.
- It is stated in the manuscript that HMS can be over-predicted and that additional organosulfur species can be “the result of further reactions of HMS suggesting that the model is correctly reproducing the HMS formation chemistry, but indicating that the model aqueous phase chemistry is incomplete” (lines 639-641). The inclusion of HMS oxidation via OH and H<sub>2</sub>O<sub>2</sub> might improve the HMS prediction for the cases that pH>6, however for more acidic conditions there is another pathway that can lead to sulfate formation but also add to the HCHO loading and potentially affect the HMS chemistry. HCHO can react directly with H<sub>2</sub>O<sub>2</sub> forming hydroxymethyl hydroperoxide, which can then decompose to reform HCHO and H<sub>2</sub>O<sub>2</sub> (Dovrou et al., 2022, PNAS). Since H<sub>2</sub>O<sub>2</sub> and HCHO are observed via the flight measurements, could this pathway be useful for the model representation of these species as well as the organosulfur chemistry (as it provides further information regarding HCHO (source of HMS))?