

Atmos. Chem. Phys. Discuss., referee comment RC3
<https://doi.org/10.5194/acp-2022-309-RC3>, 2022
© Author(s) 2022. This work is distributed under
the Creative Commons Attribution 4.0 License.

Comment on acp-2022-309

Anonymous Referee #1

Referee comment on "Emission factors and evolution of SO₂ measured from biomass burning in wildfires and agricultural fires" by Pamela S. Rickly et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2022-309-RC3>, 2022

This paper investigates the emissions and chemistry of sulfur in wildfire smoke plumes measured during the FIREX study. The emissions estimates provide addition data to the existing knowledge; the results are consistent with past/published studies. An estimate on the overall contribution of wildfires to atmospheric SO₂/sulfate would be nice to put this in perspective; are these fires an important or only minor source in the regions of the fires and the US as a whole.

The second, and much more speculative part of this study is the investigation, of SO₂ oxidation pathways and fate of the products. The analysis of organo-sulfates, specifically HMS is novel, but highly uncertain since there is actually no HMS data presented so only generalized comparisons to observations are possible, ie, predicted HMS in a flight with highest evidence of organo-sulfates. The HMS analysis is also highly uncertain. As noted, (line 686), pH and LWC have the largest effect on HSM, and the dependance of HMS on pH and LWC is highly non-linear. Furthermore, pH and LWC themselves are uncertain and predicted by a model and no assessment is really shown to assess the pH and LWC predictions. Based on what little data is provided, it appears that the pH can vary substantially within even one smoke plume, making the predicted HMS highly uncertain. Overall, the authors should provide more details on the ISORROPIA predictions of LWC and pH since these are the key variables in the model. Actual HMS data is critical to assess the conclusions of this paper. It is noted that the SAGA MC instrument can detect S(IV) species, but interferences from SO₂ make interpretation difficult. However, SAGA also measured particle ionic composition on filters, which should not have the SO₂ artifact issue (or should be much less). Was that data checked to see if there was an evidence of HMS, or lack of it, on the contrasting flights discussed? It is curious why this is not discussed. Overall, the first part of the paper on emissions seems solid, the secundar part provides some interesting results, but they are really not verifiable and so it is hard to assess their validity and value. Can the authors reference any papers that show evidence that HMS may be present the atmosphere in general or more specifically in regions of fire influence?

Specific Comments.

Lines 85 to 92, what is missing here is some idea on the relative contribution of biomass burning to overall sulfate in various regions. Eg, since this paper is about fires in the US, can references be cited or estimates made on the relative contribution of fires to total S near and long distances from the fires.

Line 160 and on: This measurement technique allows for the speciation of submicron non-refractory particulate mass and the direct separation of inorganic and organic species having the same nominal mass to charge ratio (DeCarlo et al., 2006; Canagaratna et al., 2007). How is separation of inorganic and organic species possible if have same mass to charge?

Line 174 and on. What is the SAGA instrument (from Fig S8 it is the MC), which should be specified in the main text. Also state if both instruments sample over similar particle size ranges or not, and if not, what is the possible effect? What about comparing sulfate from the SAGA MC and Filters to see if there is substantial sulfate at higher particle sizes compared to those measured by the AMS and MC.

Regarding uptake of gases, such as SO₂, HCHO I assume (3.4) & (3.6) is uptake to the dry particles since the LAS reported dry distributions? If so, it is not clear how uptake is to ambient wet particles and equilibrium between gas-LWC is handled. For species that may react slowly in the particle or LWC phase, is equilibrium established between the gas and particles by this model? What are the time scales for equilibrium for the various species and what are the time scales for which concentrations are changing in the plume being modeled? Same applies for calculation of pH where an equilibrium model is used (ISORROPIA). In essence, is equilibrium assumed, and if so, is it that reasonable (ie, provide justifications).

Regarding the pH prediction (lines 290 and on), it would be useful to show the particle phase ammonium predicted and measured (and same for gas phase ammonia), this would give both an idea of the model prediction and the amount of data thrown out due to the 40% criteria. Cations are mentioned, but not in much detail, specifically, what about K⁺, which could be high and seems odd not to be in the pH calculation.

Lines 347 to 362: Maybe the lack of correlation with MCE is that the MCE dynamic range is small? One might try looking at BC/OA ratios, just out of curiosity.

Line 465 and Fig 6a. There are very few data points for T<265K. Please comment on why this is (eg, what is the aircraft altitude) and how this limits conclusions drawn from this plot. One may wish to make a plot of altitude vs SO₂/total S, since alt and T are related. Could this be explained by instrument sampling artifacts as a function of altitude? If this trend is driven by liquid reactions, then test with looking at predicted liquid water vs T or altitude.

Define vertical axis in Fig 7a fig caption.

Line 521, what is the uncertainty here, if uncertainty in pH and LWC are considered? Eg, 30% is stated for the various measurements and chemistry (I assume) for a given pH and LWC, but how sensitive is this to pH and LWC? (This is a common issue with the whole modeling section). The average pH for this smoke plume was 5.3 (range -2 to .8), but the LWC data is not given (at least I did not see it), please provide. It would be interesting to note the ratio of LWC to dry aerosol mass, which could be estimated based on the AMS data. This would give a sense of how wet the particles were.

Why not make plots of pH and LWC vs plume age for all these modeled plumes, given that these are key variables?

Also in Fig 7, what is the relative change in SO₂ and sulfate in the 6 hrs? It appears to be fairly small. Fit the SO₂ and sulfate data vs time with a line and test if the slope is actually not zero. Fig 7b, kind of gives a false sense of the importance of SO₂ oxidation since it shows a huge time dependence, but in reality, there is very little change. It would be more realistic to plot the vertical axis as rate of oxidation divided by total sulfate, or something similar.

Regarding Section 4.2.2. Similar questions apply as noted above regarding sensitivity of predictions to pH and LWC. What species is driving the pH so high (7.2)? Is this a realistic particle pH? The LWC is 10⁻⁷ g/m³; what fraction of dry particle mass is that? Say the particle mass is 100 ug/m³, that is a ratio of 0.1, a small amount of LWC.

Line 595, agree within 40% for what pH and LWC?

In the second pass, how did the pH change relative to the first pass? Was it even higher due to higher LWC (x10)?

The sensitivity analysis is unclear (section 4.2.3.). Figure 11 shows that no HMS will be produced since loss is much larger than production, but the conditions of this flight (Aug 3) showed little organo-sulfate, so I guess there is consistency. Since highest concentrations of organo-sulfate was observed on the second leg of the 7 Aug flight, why not do a sensitivity analysis for this data. In fact, I would focus on this data, showing the predicted pH and LWC in detail and possibly also show how well ISORROPIA does by providing a comparison of the partitioning of ammonia, ammonium, nitric acid, and nitrate for this data. This could provide much more insight than the current analysis.