

We thank the reviewers for their further comments which help to clarify important details within the manuscript. Below are our responses to each follow-up comment in blue.

#### Follow-up comment #1

Initial Comment #1: 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.

Reply to Comment: To the knowledge of the authors, there are no published observations of how total S biomass burning emissions contribute to overall sulfate for various regions.

New Comment: Eg, even though SO<sub>2</sub> emissions are discussed, the authors claim in the first line of the Abstract that; Fires emit sufficient sulfur to affect local and regional air quality and climate. I am simply asking to assess this. Since a large fraction of the SO<sub>2</sub> goes to sulfate aerosol, and the sulfate is measure and discussed, why can't the sulfate (could include organo-sulfate) in plume be compared to out of plume (eg, data away from the burning regions) for data from this study. A simple statistical result could be given. Or look at in-plume versus studies that report sulfate throughout the US. Please seriously consider the comment. (eg, Hand, J. L., B. A. Schichtel, W. C. Malm, and M. L. Pitchford (2012), Particulate sulfate ion concentration and SO<sub>2</sub> emission trends in the United States from the early 1990s through 2010, Atmos. Chem. Phys. , 12, 10353-10365.)

The following has been added at line 671:

The total S observed for these flights, in terms of SO<sub>2</sub> and sulfate show values of 2-10 ppb on average above the background; however, in the presence of organosulfates, this total S can increase to up to 15 ppb on average above the background.

#### Follow-up comment #2

Initial Comment #3: 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.

Reply to Comment: The SAGA instrument definition has been added at line 173. The size coverage of different instruments is important in intercomparison and has been discussed in detail for these two instruments in Guo et al. (2021) for the ATom aircraft mission on the same airborne platform. Both AMS and SAGA MC/IC sample nominally submicron particles onboard the DC8 through different inlets and agree with each other in general, as shown in multiple comparisons over the years (e.g., Fisher et al. 2011). Despite some nuances between the two, (1) size selection of particles at ambient conditions (SAGA MC/IC) vs. dry (AMS); (2) the cutoff size is on aerodynamic diameter (SAGA MC/IC) vs. vacuum aerodynamic diameter (AMS; due to the aerodynamic lens inlet of the AMS being the main source of large particle loss), (the

following has been added at line 175) both MC/IC and AMS sample submicron particles with very similar effective size cutoffs for the range of altitudes sampled in the FIREXAQ (van Donkelaar et al., 2008; Guo et al., 2021). Supermicron sulfate is rare throughout FIREX-AQ, such as the Aug 3rd flight. However, substantial coarse mode sulfate, especially in the 2nd pass during the Aug 7th flight, was observed and up to several times higher than the submicron MC/IC sulfate.

New Comment: This needs more clarity since very little information is given on what the SAGA MC is reporting. From the wording I assume this is a sulfate, but does the MC-IC analysis also measure S(IV)? I assume the S(IV) is from dissolved SO<sub>2</sub>, but does SAGA MC collected SO<sub>2</sub> in biomass burning plumes affect the measured sulfate? This would be in addition to conversion of particulate organo-sulfates being converted to inorganic sulfate as discussed. It seems it is not a big issue given the good comparison shown in Fig. S8.

What about the SAGA filter measurements of sulfate – the replay above does not address the question? Why are the SAGA filters not used to assess HMS (or S(IV) in general) vs sulfate? Is the data not available? Much of this manuscript is on a model predicting HMS, HMS data may exist, or it may not, and a number of readers of this paper will know that. It is thus strange that this is never mentioned. Adding a sentence or two stating (if it is true) that the SAGA filter data cannot be used to determine HMS would provide clarity (and the reason why or why not). The same applies to the AMS, see (Dovrou, et al, Atmos. Meas. Tech. , 12, 5303-5315). This paper is cited, but it is not explicitly noted why the AMS is not used to directly quantify HMS.

The SAGA filters have similar concentrations and trends of S(IV) as the MC, but they were not frozen after collection and thus we prefer to use the MC measurements as the primary ones.

We have modified the paragraph in the manuscript where the measurements are described to clarify these points including the method description of SAGA filter as follows:

Sulfate measurements were performed by a suite of in-situ instruments: with an Aerodyne high-resolution time-of-flight aerosol mass spectrometer (AMS) (DeCarlo et al., 2006; Canagaratna et al., 2007), with a sampling rate of 1-5 Hz, the online soluble acidic gases and aerosol mist chamber (SAGA-MC) coupled with ion chromatograph (IC) (Scheuer et al, 2003; Dibb et al, 2003), with a sampling interval of 75 s, and SAGA filter collector with subsequent offline IC analysis (Dibb et al., 1999; Dibb et al., 2000). Both SAGA MC/IC and AMS sample submicron particles, while the SAGA filter collects both submicron and supermicron particles up to 4.1 μm with 50% transmission (McNaughton et al., 2007; van Donkelaar et al., 2008; Guo et al., 2021). The AMS instrument 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). The standard AMS data analysis software reports both inorganic and organic sulfate as total sulfate, complicating the quantification of both types of sulfates (Farmer et al., 2010). Both inorganic and organic sulfate fragment similarly in the AMS, mostly to H<sub>x</sub>SO<sub>y</sub><sup>+</sup> ions without carbon. There can be some differences in fragmentation between organic and inorganic sulfur that can in some cases be used to separate organic from inorganic sulfate (Farmer et al., 2010). While in the case of For AMS total nitrate, where the fragmentation pattern is similar (Farmer et al., 2010), techniques for rapid assignment of organic nitrate based on its fragmentation pattern have been successfully developed (Fry et al., 2013; Day et al., 2021). However, the sulfate fragmentation pattern is much more variable and hence

similar approaches have so far had mixed success, depending on the aerosol characteristics (see Schueneman et al., 2021 for a review). While there are some differences in fragmentation between organic and inorganic sulfur that have been used in some cases to separate organic from inorganic sulfate (Chen et al., 2019; Dovrou et al., 2019); the sulfate fragmentation pattern is overall much more variable compared to nitrate and hence such approaches will work only in very specific instances (Schueneman et al., 2021). In this work, we found the ion fragmentation method to produce reasonable results, based on the consistency with the results using positive matrix factorization (PMF, Paatero et al., 1994, Ulbrich et al., 2009) and the measurements of submicron sulfate aerosol by from SAGA-MC, which quantifies only inorganic sulfate. Both MC/IC and AMS sample submicron particles (van Donkelaar et al., 2008; Guo et al., 2021). The correlation between the AMS apportionment inorganic sulfate and SAGA-MC/IC sulfate shows an overall good agreement (Fig. S8), which adds confidence to the AMS apportionment. However, as discussed in section 4.2.2, for certain types of organosulfur compounds, hydrolysis in the liquid phase after capture into the instrument and before analysis might lead to SAGA-MC/IC detecting these as well, hence a larger uncertainty may be reflected by the SAGA-MC/IC sulfate measurements based on the default accuracy estimates for this instrument for inorganic sulfate are likely more uncertain under FIREX-AQ conditions (Dibb et al., 2002; Scheuer et al., 2003).

Both IC (SAGA) instruments detect HMS as S(IV), and the signal interfered with sulfite and bisulfite. There is no unambiguous detection of HMS specifically, either in the IC or in the AMS.

The following text has been added to the discussion of SAGA-MC detection of S(IV):

However, the S(IV) from the SAGA-MC is comparable to the SAGA filter samples, which are unaffected by ambient SO<sub>2</sub> and hence suggests that a large fraction of the S(IV) in the SAGA-MC was present in the aerosol, and that the contribution of the SO<sub>2</sub> artifact to the S(IV) signal is small. This observation further suggests that most of the S(IV) was present in submicron particles, as supermicron particles are not quantified by the SAGA-MC (Guo et al, 2021).

### Follow-up comment #3

Initial Comment #6: 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.

Reply to Comment: Because the range of MCE values presented in Fig. 3 covers a similar range as used in the cited analyses, we believe this range is adequate for the determination of a lack of correlation.

New Comment: In other studies (in fact analysis of this FIREX data), it has been shown that BC/OA is in fact better than MCE for separating out some properties that depend on smoldering vs flaming, I suggest the authors do the calculation to actually test it.

While different analysis might reveal a relationship between sulfur emission factors and a different metric for fire stage, we focus here on MCE because of the historical precedent and widespread use of this parameter, and for comparison with the studies already cited in this paper. Additional analysis is beyond the scope of this work.

#### Follow-up comment #4

Initial Comment #10: Why not make plots of pH and LWC vs plume age for all these modeled plumes, given that these are key variables?

Reply to Comment: We believe that the trends of these variables are clear in the data presented in the supplementary materials.

New Comment: The trends are not clear. For example, I cannot tell from Fig S3 what causes the systematic jump in pH back and forth between two levels, is this due to in vs out of plumes (it is hard to line up with the SO<sub>2</sub> and sulfate data. The pH does seem to increase when the aircraft climbs. Same applies to Fig S4, except in this case the plot shows no pH when the aircraft changes altitude. Some form of plot other than a time series I think would help clarify the odd behavior in pH.

This is correct that the jumps in pH are due to entering and exiting the plume. The peaks are representative of the center of the transect and the troughs are representative of outside of the plume. The values increase and decrease upon entering and exiting the plume, respectively. The plume transects have now been highlighted in Fig. S3 for clarification. A plot that is being described could be shown; however, this would only be representative of the two flights that were modeled. There are, in fact, more data for the remainder of the flights; however, it would take considerable time to analyze each transect for pH, LWC, and plume age which at this time is not feasible. A clear pH shift with altitude was only observed (of the modeled flights) for the 7 August flight as the reviewer has noted. This was likely due to the chemical compounds present and the decreased temperature observed with the changing altitude as well as potentially changing meteorological conditions. With the available data from the two modeled flights, it is believed that a plot of this type with limited data would not add significant insight to the study.

#### Follow-up comment #5

I would like to thank the authors for addressing the comments. I have a minor comment regarding the units of LWC in lines 638-639. The units are provided in g sm<sup>-3</sup> but I assume that they are meant to be g cm<sup>-3</sup>. Please check and correct accordingly.

The units reported in the paper are correct. The LWC values are reported in units of grams per standard cubic meter. These units have now been defined on line 746.

#### Follow-up comment #6

Following up on the previous Comment #5 (regarding the HMS chemistry and the effect of hydroxymethyl hydroperoxide formation) the authors added a sentence stating the potential effect of this chemistry, however a quick test with the model of an average scenario would be useful. I would recommend such a test to be added in the SI with the sentence already presented in the main text in order to have an estimate of the magnitude of hydroxymethyl hydroperoxide chemistry in their system.

Because the main focus of this modeling section is to understand the influence of HMS chemistry on the evolution of SO<sub>2</sub> to sulfate, the authors leave the suggestion of hydroxymethyl hydroperoxide chemistry for future studies to consider.