Emission factors and evolution of SO₂ measured from biomass burning in wild and agricultural fires

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Abstract. Fires emit sufficient sulfur to affect local and regional air quality and climate. This
study analyzes SO_2 emission factors and variability in smoke plumes from US wild and
agricultural fires, and their relationship to sulfate and hydroxymethanesulfonate (HMS)
formation. Observed SO_2 emission factors for various fuel types show good agreement with the
60   latest reviews of biomass burning emission factors, producing an emission factor range of 0.47 –
1.2 g SO_2 kg^{-1} C in the emissions. These emission factors vary with geographic location in a way
that suggests that deposition of coal burning emissions and application of sulfur-containing
fertilizers likely play a role in the larger observed values, which are primarily associated with
agricultural burning. A 0-D box model generally reproduces the observed trends of SO_2 and total
65   sulfate (inorganic + organic) in aging wildfire plumes. In many cases, modeled HMS is
consistent with the observed organosulfur concentrations. However, a comparison of observed
organosulfur and modeled HMS suggests that multiple organosulfur compounds are likely
responsible for the observations, but that the chemistry of these compounds yield similar
production and loss rates to that of HMS, resulting in good agreement with the modeled results.
70   We provide suggestions for constraining the organosulfur compounds observed during these
flights and we show that the chemistry of HMS can allow for organosulfur to act as a S(IV)
reservoir under conditions of increased pH (>6) and liquid water content (> 10^{-7} g m^{-3}). This
can facilitate long-range transport of sulfur emissions resulting in increased SO_2 and eventually
sulfate in transported smoke.

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1 Introduction

Sulfate is a major component of PM$_{2.5}$, contributing significantly to adverse air quality and
severe haze events (Chan and Yao, 2008). A severe haze event in Beijing, China showed PM$_{2.5}$
80   sulfur concentrations reaching 100 μg/m^3 with aerosol optical depths over 1 (Moch et al., 2018).
Sulfate aerosols are produced through the oxidation of sulfur dioxide (SO_2) which was estimated
to have a global emission rate of approximately 113 Tg S yr^{-1} in 2014 (Hoesly et al., 2018).
Approximately 67% of global SO_2 emissions are due to anthropogenic sources, primarily fossil
fuel combustion and smelting (Lee et al., 2011; Smith et al., 2011; Feinberg et al., 2019).
85   While biomass burning is expected to contribute a smaller portion to global sulfur
emissions (1.22 Tg S yr^{-1}), the effects of climate change and land use change are expected to
increase biomass burning events in both frequency and duration (Westerling et al., 2006;

Heyerdahl et al., 2002; Lee et al., 2011). Biomass burning SO_2 emissions can influence air quality through sulfate aerosol production in regions thousands of kilometers away from the burn site due to meteorological long-range transport (Fiedler et al., 2011). In extreme cases, pyro-cumulonimbus formation injects biomass burning aerosol – including sulfate – into the upper troposphere and lower stratosphere (Fromm et al., 2005).

Biomass burning produces both primary and secondary aerosols, with sulfate aerosols mostly from secondary production, but also a smaller primary component in some cases (Lewis et al., 2009). The chemical composition of aerosols produced during biomass burning is highly dependent on the environmental conditions and type of combustion occurring, flaming or smoldering. For example, elemental carbon and NO_x are mainly emitted during the flaming stage, while emissions of VOCs and (mainly organic) $PM_{2.5}$ are larger during the smoldering phase (Pandis et al., 1995; Lobert et al., 1991; Burling et al., 2010). Fuel composition also influences SO_2 emissions. This is demonstrated in a recently published compilation of biomass burning emission factors utilizing only data from young smoke to limit conversion during chemical aging, reducing the variability within the published measurements (Andreae, 2019). This compilation shows savanna and grassland SO_2 emission factors to be 0.47 ± 0.44 g g SO_2 kg^{-1} C and agricultural residues to be 0.80 ± 0.71 g SO_2 kg^{-1} C with a full fuel type range of 0.2 to 0.87 g SO_2 kg^{-1} C.

Oxidation of SO_2 in both the gas and aqueous phase produces sulfate, with a typical SO_2 lifetime of 0.6 – 2.6 days (Pham et al., 1995; Koch et al., 1999). However, the importance of some conversion mechanisms of SO_2 to sulfate remains poorly understood, resulting in the frequent underprediction of sulfate concentrations in atmospheric models by up to a factor of two for regional models (Wang et al., 2016; Shao et al., 2019; Wang et al., 2014). This underprediction has been reported for industrialized pollution where limited photochemistry is observed as a result of aerosol dimming (Cheng et al., 2016; Shao et al., 2019). While no known studies have reported on the modeling of SO_2 and sulfate chemistry in biomass burning smoke plumes, it is possible that similar phenomenon could occur because biomass burning plumes can have very high aerosol loading and thus dimming. However, the chemistry is likely to be different as a result of differing emissions. In addition, it has been suggested that unaccounted-for hydroxymethanesulfonate (HMS) formation may explain the discrepancy between measured and modeled sulfate values (Dovrou et al., 2019; Song et al., 2021).

In this study, we quantify SO_2 emissions and examine the production of sulfate using airborne observations within a variety of smoke plumes. These measurements provide insight into the variable emission factors observed during biomass burning and allow for a comprehensive analysis of the conversion of SO_2 to sulfate and HMS including both gas- and aqueous-phase conditions. Smoke is a highly dynamic environment, and we examine how S chemistry is affected by radiation attenuation, enhanced aerosol liquid water content (LWC), and variable pH.

2 Methods

2.1 Mission and measurements

FIREX-AQ was a joint NASA-NOAA mission to study multiple aspects of fire emissions, chemistry, and impacts. Here we utilize observations from the NASA DC-8. The base locations for this aircraft campaign were Boise, ID from 21 July to 17 August and Salina, KS from 18

August to 5 September, 2019. The Boise, ID location allowed for the measurement of western
135   U.S. wildfires, with sampling occurring in the late afternoon through evening. Salina-based
flights focused on prescribed burns, primarily of croplands, within the midwestern and southern
regions of the U.S. with measurements typically occurring in the afternoon. A subset of these
measurements including seven different fuel types from over 80 fires is reported here.

Flight paths differed between the wildfire and cropland measurements. A typical flight
140   path through the wildfire smoke plumes consisted of two "lawnmower" patterned passes
consisting of about 10 staggered downwind transects perpendicular to the plume (Fig. 1). The
closest transects were generally 10-15 km downwind due to flight restrictions, with the pattern
extending as far as 200 km downwind resulting in smoke ages (based on Lagrangian trajectory
analysis) ranging from 10's of minutes to several hours. In contrast, sampling of smaller
145   agricultural fires typically involved 1-2 plume intersections per fire.
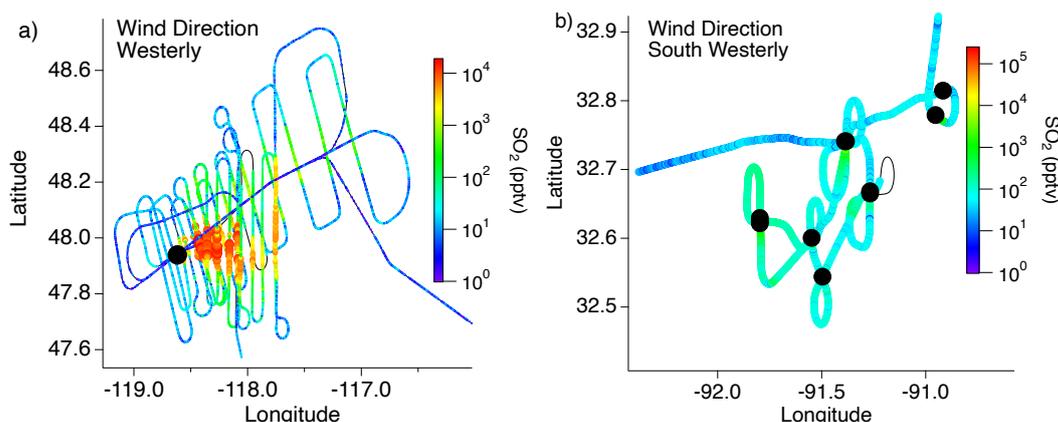
*Figure 1. Typical flight path through (a) wildfire and (b) agricultural fire smoke plumes with the
color and size of the markers indicating the SO$_2$ mixing ratio and the black markers indicating*
150   *the fire locations.*

In situ measurements of SO$_2$ were performed using laser induced fluorescence (LIF SO$_2$)
in which SO$_2$ was excited at 216.9 nm by a custom-built fiber laser system with the red-shifted
fluorescence detected between 240 and 400 nm. An intercomparison performed between the LIF
155   SO$_2$ and Caltech CIMS instrument during FIREX-AQ showed good agreement between the two
measurement techniques (Rickly et al., 2021). The accuracy of the LIF SO$_2$ measurements is
$\pm 9\% + 2$pptv, primarily dictated by uncertainty in the calibration standard concentration and
spectroscopic background.

Sulfate measurements were performed with an Aerodyne high-resolution time-of-flight
160   aerosol mass spectrometer (AMS) (DeCarlo et al., 2006; Canagaratna et al., 2007). 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). The standard AMS data analysis
software reports both inorganic and organic sulfate as total sulfate, complicating the
165   quantification of both types of sulfates (Farmer et al., 2010). While in the case of AMS total
nitrate techniques for rapid assignment of organic nitrate based on its fragmentation pattern have
been successfully developed (Fry et al., 2013; Day et al., 2021), 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). 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 inorganic sulfate speciation provided by the SAGA instrument. As an additional constraint, the AMS apportionment can be compared with ion chromatography measurements reported by the SAGA instrument (Dibb et al., 2002; Heim et al., 2020), which quantifies only inorganic sulfate. The correlation between the AMS apportionment and SAGA measurements of inorganic sulfate shows an overall good agreement (Fig. S8). 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 detecting these as well, hence the SAGA sulfate measurements can be considered an upper limit on inorganic sulfate under FIREX conditions.

In situ CO concentrations were measured via wavelength modulation spectroscopy (Sachse et al., 1991), with an uncertainty of 2-7% over the dynamic range of the measurements. In situ CO_2 concentrations were measured using non-dispersive infrared spectrometry using a modified commercial spectrometer (Model 7000, LI-COR) similar to Vay et al., (2009), with uncertainties varying between 0.25 ppm and 2% of the measurements (whichever is larger) over the range of the measurements.

2.3 Emission factor calculation

Emission factors (EF) are defined as the mass of compound X relative to the mass of fuel burned; however, this can be substituted with the mass balance method which approximates the fuel mass by the sum of emitted carbon (Andreae, 2019). In accordance, the emission factors for SO_2 and sulfate were calculated as the enhancement ratio of each compound relative to the enhancement ratio of total carbon emitted per fire in units of g kg^{-1} (Eq. 3.1). Because CO and CO_2 comprise approximately 95% of total carbon emissions, the summation of these values was used to represent total carbon.

$$EF(X) = \frac{X}{CO+CO_2} \cdot \frac{MM_X}{MM_C} \cdot F_C \cdot 1000 \qquad (3.1)$$

The orthogonal distance regression slope of compound X to total carbon ($\frac{X}{CO+CO_2}$) was determined for each transect through the smoke plume with a smoke age <1 hr to limit the influence of chemical processing due to atmospheric aging. Only emission ratio values with $R^2 >$ 0.5 were included in the EF analysis. It is shown in sections 3.3 and 3.7 that no significant aging of SO_2 occurs within this length of time. In addition, only measurements $\geq$ 25% enhanced from the background were used, which allowed for the background mixing ratios to be neglected. MM_X and MM_C represent the molar mass of compound X and the summation of CO and CO_2, respectively. The approximated value of 45% is used to represent the carbon fraction (F_C) of the fuel emitted during these biomass burning events as outlined by Susott et al. (1996) and allows for a more direct comparison to the compilation of EF data prepared by Andreae (2019).

2.4 Modified combustion efficiency

The modified combustion efficiency (MCE) is a metric for combustion stage. The MCE is defined as the enhancement of CO_2 from the background in relation to the summation of the enhanced CO and CO_2 mixing ratios (Eq. 3.2). Traditionally, MCE > 0.9 is indicative of the flaming stage and an MCE < 0.9 is representative of the smoldering stage (Ferek et al., 1998; Sinha et al., 2003; Zhang et al. 2018). In reality, smoke sampled from large wildfires likely reflects a combination of variable fractions of flaming and smoldering combustion.

$$MCE = \frac{CO_2}{CO + CO_2} \tag{3.2}$$

2.5 Box Model

The Framework for 0-D Atmospheric Modeling (F0AM) was used to evaluate the evolution of SO_2 downwind of the fire location (Wolfe et al., 2016). Within F0AM, the Master Chemical Mechanism (MCM) version 3.3.1 was used to describe the evolution and chemistry of the gas-phase SO_2 and oxidant species. An additional mechanism describing the conversion of SO_2 to sulfate was implemented to address aerosol oxidation processes of sulfur compounds based on an establishment of equilibrium of the S(IV) compounds and oxidant species with relation to pH (Tang et al., 2014; D'Ambro et al., 2016; Seinfeld and Pandis, 2006). A complete list of the aqueous phase reactions and measurements used for model input is included in Tables S1-2 and the mechanism code is provided in the Supplementary Section 2.

The model was implemented to investigate the chemistry that occurred during the Williams Flats fire which was started 2 August 2019 through lightning ignition of timber/slash fuels in Keller, WA. Two separate flight days, 3 and 7 August, were modeled here using measurements acquired by the DC-8 in which two passes of lawnmower pattern paths were completed. These flights were analyzed by applying a Lagrangian model approach. The measurements were corrected for dilution by normalizing to CO (Müller et al., 2016) as follows:

$$\Delta_{dil} X = \frac{(X - X_b)}{(CO - CO_b)} \cdot CO_i \tag{3.3}$$

in which $\frac{X}{CO}$ represents the ratio of compound X at each transect with respect to CO, X_b and CO_b are the background concentrations, and CO_i represents the carbon monoxide mixing ratio at the source of the fire determined from the extrapolation of the transect average CO values. This extrapolation method was also applied to the dilution-normalized mixing ratios in order to initialize the model back to the fire source (t=0). The model was constrained to these initial concentrations, then allowed to run freely through the remainder of the flight time. The dilution rate was determined by matching the modeled CO to the measured CO decay using a Gaussian fit. However, CO_i, used to determine the dilution normalized mixing ratio values, was based on the extrapolated CO initial value based on all transect CO values (core and edge).

Measurements were acquired through aircraft smoke plume penetration, which provided pseudo-Lagrangian observations by not entirely following the same air parcel. Comparison to a Lagrangian simulation is challenging because the aircraft measured different parts of the plume (core vs edge) and at different emission times. As a result, an exponential fit applied to the SO_2 and sulfate dilution-normalized mixing ratios against plume age is used to represent the measurement trend for comparison to the model results. While the model is not expected to

precisely reproduce the measurements based on plume age, due to variations in altitude between transects and subsequently varied pressures and temperatures, it does allow for the comparison of the overall trends of SO_2 and sulfate downwind of the source using averaged meteorological constraints.

Uptake of SO_2 and the oxidant species (O_3, NO_2, H_2O_2, and HCHO) to aerosol was represented within the model mechanism as a first-order loss (Seinfeld and Pandis, 2006):

$$khet = 0.25 \cdot \gamma \cdot c \cdot \nu \qquad (3.4)$$

where γ represents the uptake coefficient, c is the mean molecular speed of SO_2, and ν is the aerosol surface area based on average particle size distributions measured by a Laser Aerosol Spectrometer 3340. To account for the gas-phase diffusion limitation, γ was calculated by the following equation:

$$\gamma = \frac{1}{\alpha} + \frac{0.75 + 0.286 Kn^{-1}}{Kn \cdot (Kn+1)} \qquad (3.5)$$

where α represents the mass accommodation coefficient and Kn is the Knudsen number. Mass accommodation and gas diffusion coefficients used for deriving Kn and γ are listed in Table S3.

To represent equilibrium partitioning between the gas and aqueous phases, rates of condensation and evaporation were applied as described by D'Ambro et al. (2016):

$$k_{cond} = khet \qquad (3.6)$$

$$k_{evap} = \frac{khet}{H \cdot LWC} \qquad (3.7)$$

where H represents the Henry's Law constant of the species being adsorbed and LWC is the liquid water content of the cloud or aerosol. Because S(IV) production is pH dependent, individual equilibrium constants in relation to the H^+ produced by each reaction are required as an additional factor in the k_{evap} denominator as described by Seinfeld and Pandis (2006). As a result, the model accurately reproduces the S(IV) pH dependence (Fig. S1a) in which HSO_3^- is the dominant form between the pH range of 2-7 and SO_3^{2-} becomes the dominant form at pH > 7. Table S1 lists all aqueous phase reactions.

The rate of S(IV) oxidation exhibits a pH dependence based on the available oxidant species (Table S1) (Cheng et al., 2016). Using our model and the initial conditions from Guo et al. (2017), we reproduced very similar pH dependent oxidation rates to those shown in that study. However, initializing the model with the higher concentrations observed during FIREX-AQ increases the rates of oxidation as shown in Fig. S1b. This results in S(IV) oxidation being dominated by reaction with hydrogen peroxide at pH values < 5 which is within the range that aerosol sulfate production most commonly occurs in the U.S. For pH values approaching 5, there may be some competition amongst H_2O_2, O_3, and HCHO depending on the oxidant concentrations. As pH values increase above 5, O_3, NO_2, and HCHO become the dominant oxidants with H_2O_2 and NO_2 oxidation declining rapidly. Although the reaction of HCHO with S(IV) results in HMS production rather than inorganic sulfate, it has been included here to demonstrate its role in S(IV) oxidation. HCHO oxidation follows a very similar trend to O_3 oxidation, becoming a major S(IV) oxidant at higher pH. Further discussion of the HMS reactions listed in Table S1 can be found in the supplement.

300   In this study, aerosol LWC and pH were determined via ISORROPIA-II thermodynamic modeling (Fountoukis and Nenes, 2007) in forward mode based on the AMS measured aerosol composition (SO_4, NO_3, NH_4, Cl) and collocated gas-phase measurements of NH_3 and HNO_3 from PTR-MS and CIMS, respectively. NH_3-NH_4 is the most important species pair for constraining pH because it was not completely in either the gas or particle phase in the fire plumes or the background air mass. To improve the accuracy in thermodynamic modeling

305   predictions, we removed the outliers when the predicted particle phase fraction of the NH_3-NH_4 partitioning is off by more than 40% compared to the observation. Because these calculations are based on the inorganic aerosol concentrations, the LWC could potentially be up to several times greater due to the dominant organic portion in the fire plumes despite the lower hygroscopicity compared to the inorganics (Kreidenweis et al., 2008; Guo et al, 2015; Brock et al, 2016). The

310   mixing state of inorganic and organic for the particles in the early phase plumes remains to be investigated but is likely to be phase separated given the low oxidation state of the organics (Sullivan et al., 2020). The current modeling can be interpreted as assuming a phase separation of inorganic vs. organics, with the chemistry studied occurring only in the inorganic-dominated phase and its associated water, with no kinetic limitations due to a potential core/shell or micelle

315   like structures present in the particles. Due to the dominant organic fraction of sulfate signals in the fire plumes investigated in this study, addition bias and uncertainty derive from using the total AMS SO_4 signals and zero non-volatile cations (e.g. not accounting for the potential contribution of soluble ions from ash, Adachi et al, 2022) in estimating LWC and pH. This is of particular concern when the uncertainties are larger than the estimated free acidity based on ion

320   balance, as often happens near the neutralization point.
   Most importantly, the modeling work presented in this study assumes an ideal solution. Given the relatively high ionic strength conditions observed for the 3 Aug (89.5 ± 19.3 M) and 7 Aug (83.2 ± 25.3 M) flights due to the overall rather low RH, this can potentially lead to high deviations in the actual gas uptake coefficients, aqueous phase rate coefficients and to a lesser

325   extent, pH (calculation of which does account for ionic strength, but is fairly under constrained under these conditions).

3 Results and discussion

3.1 Emission factors

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The elemental sulfur EFs calculated for FIREX-AQ are comparable to previous reports. As described in section 2.4, flaming and smoldering delineation was determined by an MCE value of 0.9. For consistency with other FIREX-AQ reports, the fuel types listed remain as subcategories, but are combined for comparison to the comprehensive biomass burning fuel

335   types listed in Andreae (2019). The FIREX-AQ agriculture category comprises measurements of residual burns of rice, corn, and soybean fields. Across the fuel types measured during FIREX-AQ (Fig. 2), we find that SO_2 is consistently larger than sulfate when calculated as EFs of elemental sulfur, indicating that, at most, a minor fraction of SO_2 (20-25%) is converted to sulfate within 1 hr downwind (or emitted directly as primary sulfate). Where data is not reported,

340   this is due to either missing data or a low correlation with total carbon ($R^2 < 0.5$). The total sulfur EFs agree reasonably well with those reported by Andreae et al. (1988), measured in the Amazon basin, in the range of 0.24-0.66 g S kg^{-1} C.

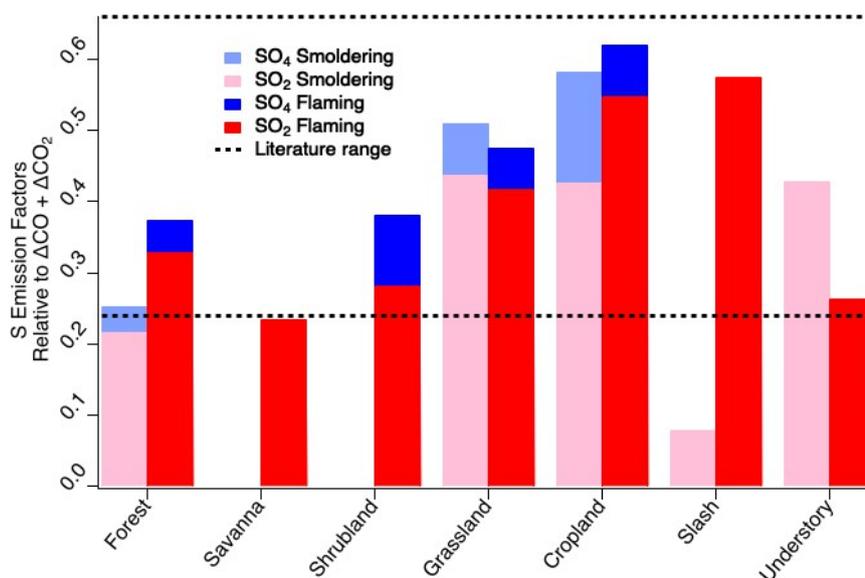
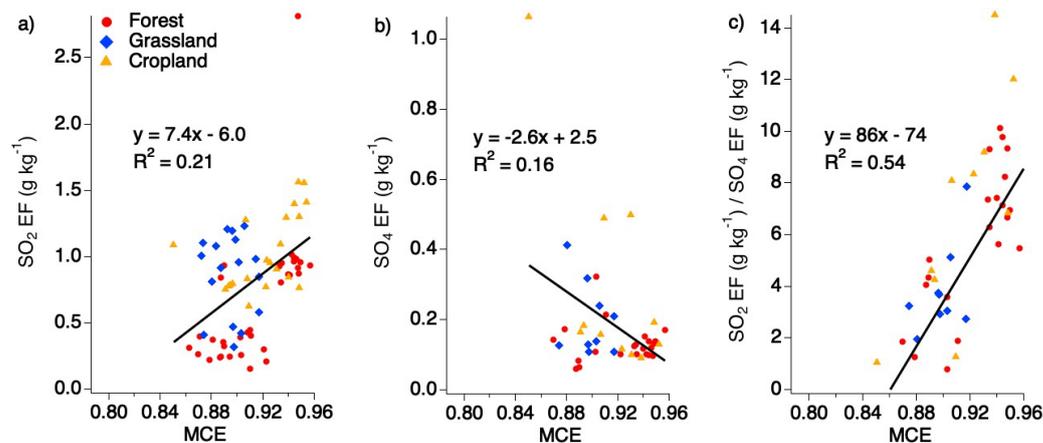



Figure 2. Elemental sulfur *emission factors of SO₂ and sulfate by fuel type and combustion stage*
345   *within 1 hr downwind compared to literature values of total sulfur emission factors.*

       No trend with MCE is observed for SO_2 EFs when separated by the various fuel types
when considering fuel types with measurements of smoldering and flaming conditions as well as
SO_2 and sulfate measurements above MCE 0.85 (Fig. 3). It has previously been suggested that
350   EFs can be calculated based on MCE for use by the global climate modeling community. There
have been conflicting opinions around this suggestion with some species showing relevant
correlations while other species do not (Yokelson et al., 1996; Burling et al., 2011; Akagi et al.,
2013). Considering all the EFs for SO_2, sulfate, and the ratio of SO_2 to sulfate under one hour
shows that, individually, SO_2 and sulfate do not show strong correlations with MCE (Fig. 3).
355   However, the ratio of the two produces a stronger correlation suggesting there may be a
relationship in which more sulfate may be produced during smoldering combustion and more
SO_2 emitted during flaming combustion. One possibility is that the smoke plumes from
smoldering fires are more conducive to rapid conversion of SO_2 to sulfate such that the ratio of
SO_2 and sulfate has significantly decreased by the time it is sampled. This could be due to a
360   number of factors, including higher aerosol EF which, depending on the aerosol composition,
could allow for more rapid aqueous phase oxidation. It is also possible that more primary sulfate
is emitted from those plumes.
       Averaging the flaming and smoldering EFs produces an overall SO_2 EF of 0.73 ± 0.43 g
SO_2 kg⁻¹ C. This is within the combined variability of the Andreae (2019) compilation of flaming
365   and smoldering EFs of 0.62 ± 0.75 g kg⁻¹ C, which excludes peat and laboratory fires. Separating
the SO_2 EFs by combustion stage results in a flaming stage value of 0.80 ± 0.46 g kg⁻¹ C (0.62 ±
0.61 g kg⁻¹ C from Andreae, 2019) and a smoldering stage value of 0.62 ± 0.36 g kg⁻¹ C (0.61 ±
0.27 g kg⁻¹ C from Andreae, 2019). While the FIREX-AQ flaming stage value is considerably
higher than the Andreae (2019) compilation, the two are within the combined variability of the
370   observations. However, this higher average EF for the flaming stage FIREX-AQ measurements

is strongly influenced by the large number of measurements of longleaf pine and agricultural fuels which had high EF values.

375 *Figure 3. Scatter plots of EFs for SO₂ (a), sulfate (b), and the ratio of SO₂ to sulfate (c) (within 1 hr downwind of each fire source) vs. MCE based on combined fuel types.*

Looking more closely at the different fuel types in comparison to the categories compiled by Andreae (2019), we see good agreement within the combined variability (Table 1 and Fig. 4).
380 While the fuel types are categorized differently in this study, many still fit the characteristics of the categories listed in the compilation report allowing for comparison. Of the FIREX-AQ categories that allow for comparison with Andreae (2019), all EF data available are for the flaming stage.

The generally strong agreement between FIREX-AQ EFs and those in published
385 inventories lends confidence to the quality of EFs underlying model emissions. Agricultural burns exhibit the highest EFs. This was reported by Andreae (2019) as 0.80 ± 0.71 g kg⁻¹ C in the flaming stage, similar to 1.1 ± 0.30 g kg⁻¹ C reported here. The temperate forest category, comprised here of forest and slash, produces a combined EF of 0.70 ± 0.51 g kg⁻¹ C which is in excellent agreement with the Andreae (2019) value of 0.7 ± 0.48 g kg⁻¹ C. Combining savanna,
390 shrubland, grassland, and understory, into the savanna/grassland category produces the largest difference in which the FIREX-AQ value of these combined fuels is 0.70 ± 0.26 g kg⁻¹ C, whereas, Andreae (2019) reported a value of 0.47 ± 0.44 g kg⁻¹ C; however, these values fit within the standard deviation.

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Table 1. Comparison of the flaming stage SO$_2$ EFs (g kg^{-1} C) by fuel type as measured during FIREX-AQ (left) to the compiled values reported in Andreae (2019) (right).

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Fuel Type (FIREX-AQ)	EF	StDev	Num tran[+]	Combined Categories	EF	StDev	Num stud[*]	Fuel Type (Andreae, 2019)
Forest	0.66	0.49	35	0.70 ± 0.51	0.7	0.48	5	Temperate forest
Slash	1.15	0.38	3					
Savanna	0.47	0.06	2	0.70 ± 0.26	0.47	0.44	12	Savanna/grassland
Shrubland	0.56		1					
Grassland	0.83	0.29	6					
Understory	0.53		1					
Cropland	1.09	0.30	16	-	0.8	0.71	10	Agriculture

[+]Num tran indicates the number of transects measured within 1 hr downwind of the fire source measured during FIREX-AQ.
[*]Num stud indicates the number of studies included in the Andreaa (2019) compilation.

410   The categories measured during FIREX-AQ that do not overlap with the Andreae (2019) compilation reflect smoldering conditions. For the most part, the majority of the smoldering stage SO$_2$ EFs exhibit lower values than the flaming stage by approximately 21-63% (Fig. 4). The two FIREX-AQ categories (grassland and understory) which show smoldering SO$_2$ EFs to be larger than the flaming stage suggest the need for additional measurements to build statistical
415   confidence.
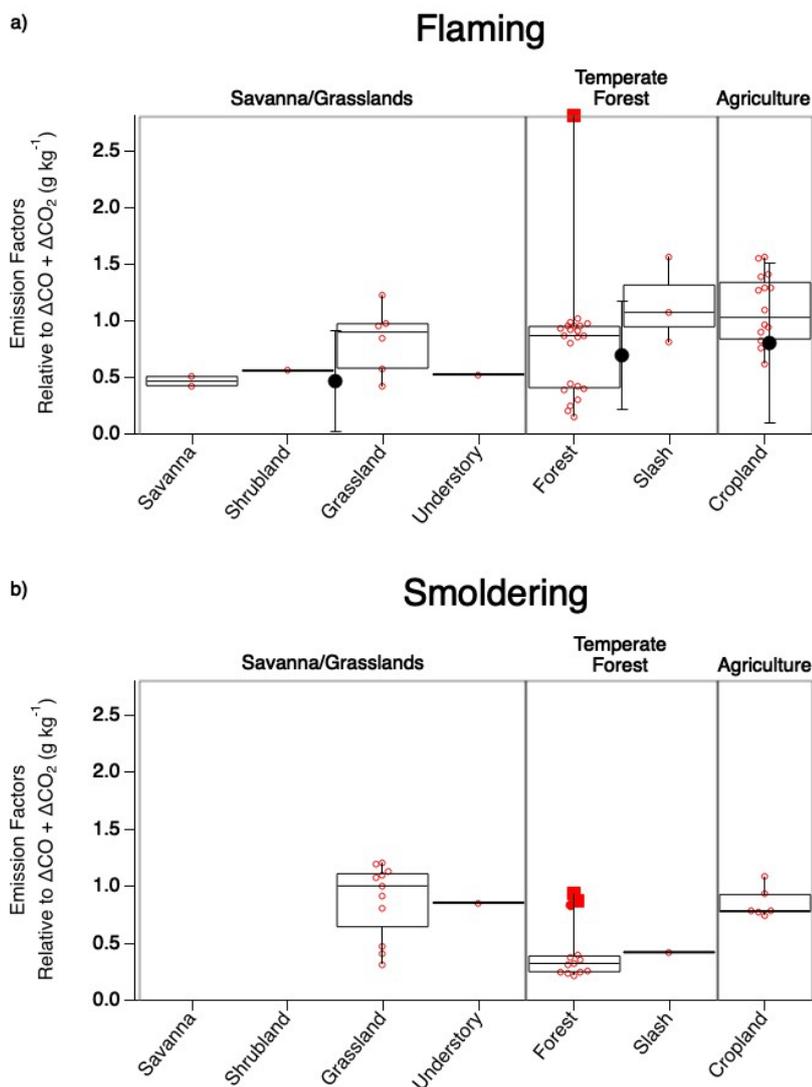
Figure 4. Comparison of SO₂ EF values observed during flaming (a) and smoldering (b) combustion across fuel types sampled during FIREX-AQ. The box upper edge represents the 75th percentile and the lower edge the 25th percentile with the median shown by the middle line. The whiskers represent the minimum and maximum observed values with the open circles representing each observation and the solid red circle representing a potential outlier. The large solid black circles with error bars depicting 1 standard deviation in panel (a) show corresponding average Andreae (2019) values.

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3.2 Emission factor variability

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The variability observed amongst the different fuel types may partly reflect variability in surface S content stemming from wet and dry deposition. Although this source of sulfur has significantly decreased in the U.S. over the last two decades, the highest emission factors during FIREX-AQ were observed within the regions of the U.S. that typically experience the largest sulfur
435 deposition rates as reported by the National Atmospheric Deposition Program (2022) (Fig. 5).
Sulfur-containing fertilizers may also enhance S content in smoke. Sulfur aids plant uptake of nitrogen, and decreasing sulfur deposition over the last two decades has led to an increased use of sulfur additives in fertilizers (Hinckley et al., 2020). Hinckley et al. (2020) report this sulfur application to range from around 20-300 kg S ha^{-1} yr^{-1}, which occurs in the form
440 of inorganic sulfate or elemental sulfur (Solberg et al., 2011). Given that the average yield of corn within the U.S. is 168 bushels per acre, a sulfur application of 20 kg S ha^{-1} yr^{-1} would result in 12 g S kg^{-1} C in its composition. Assuming 10% of this added sulfur remains after harvest and runoff and is present in the residual material that is burned, the remaining 1.2 g S kg^{-1} could in part explain the enhanced emission factors in those regions (U.S. Department of Agriculture,
445 2020). Therefore, the observed variability in emission factors throughout the U.S. may be in part explained by the sulfur availability to the plants and soils, either from deposition or fertilizer use, resulting in larger emission factors from certain locations when burned.
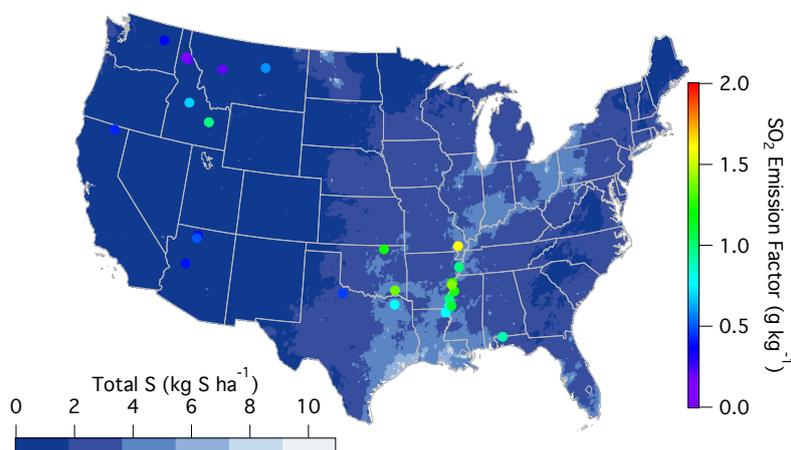
Figure 5. National Atmospheric Deposition Program (2022) reported sulfur deposition rates
450 *(https://nadp.slh.wisc.edu/committees/tdep/#tdep-maps) compared to SO$_2$ EFs (closed circles) by geographical location as measured during FIREX-AQ for all fuel types.*

4 Chemical Evolution of Sulfur

455 After emission, SO$_2$ oxidizes to sulfate via both gas and condensed-phase processes. Discrepancies reported by previous studies of modeled sulfate compared to measurements suggest that the conversion chemistry of SO$_2$ to sulfate is not fully understood. In this section, we combine FIREX-AQ observations with a detailed chemical box model to evaluate the chemical mechanisms of SO$_2$ to sulfate conversion.

460

4.1 Temperature dependence of sulfate production efficiency

The balance of gas and particle phase sulfur between SO_2 and sulfate exhibits a marked temperature dependence amongst the cumulative flights while remaining generally constant

465 during individual flights (Fig. 6). Sulfate is >90% of the sum at temperatures below 265K, while above 285 K SO_2 and sulfate are equally balanced which is likely due to the quasi-second order process of heterogeneous oxidation in a plume (Freiberg, 1978). The noisy, but overall positive trend between 265-283 K suggests rapid chemistry after emission. Conversion of SO_2 to sulfate generally increases with decreasing temperature due to increased aerosol water content and SO_2

470 and oxidant solubility, but the rapid change observed in this temperature regime also requires aqueous phase sulfur oxidation (Pattantyus et al., 2018).

 The majority of sulfur oxidation occurs in the aqueous phase. As observed during the 3 August flight, calculation of the contribution of OH to the decrease in SO_2 by applying an OH concentration of 2×10^6 cm^{-3} (Liao et al., 2021) produces a negligible SO_2 decay compared to

475 the dilution normalized mixing ratio of SO_2 (Fig. S2). Similar behavior is expected for other flights due to similar conditions of limited photolysis near the center of the smoke plume.

 Recent studies have suggested HCHO to be an important aqueous phase oxidant at reduced temperatures (Moch et al., 2018; Song et al., 2021). However, HCHO is also an indicator of smoke age with mixing ratios typically being largest nearest to the fire source (Liao

480 et al., 2021). Considering measurements acquired when the HCHO mixing ratio is high (>25 ppb), implicitly filtering out aged smoke, the slope of the SO_2 to total sulfate ratio over the 265-283 K temperature regime (0.04) shows a stronger correlation with temperature (R^2=0.74) (Fig. 6b, black line). Further limiting the effect of chemical aging by analyzing only those measurements within 1 hr of the fire source, the conversion of SO_2 to sulfate is observed to be

485 approximately 65% slower (Fig. 6b, red line) in the 265-283 K temperature range. This is consistent with heterogeneous chemistry in that aging occurs more rapidly at higher temperatures. While sulfate measurements within 1 hr of the fire source could be due to primary emission, this is expected to be a small fraction compared to SO_2 as shown in Fig. 2 and primary emission would not exhibit the temperature dependence observed here.

490  Other sulfate species are contributing to sulfur conversion during this temperature regime. There were several periods identified during these flights in which organosulfur species were recognized to be a significant fraction of the AMS sulfate measurement. These measurements only occurred within the temperature range 270-285 K. When organosulfur was present in plume transects within 1 hr downwind of the fire source, the SO_2 to total S ratio

495 decreased with decreasing temperature 23% faster than in transects of fresh plumes when organosulfur was not present.

 These findings emphasize the importance of temperature in combination with smoke age and organosulfur production on the conversion of SO_2 to sulfate and is further investigated in section 4.2.1.

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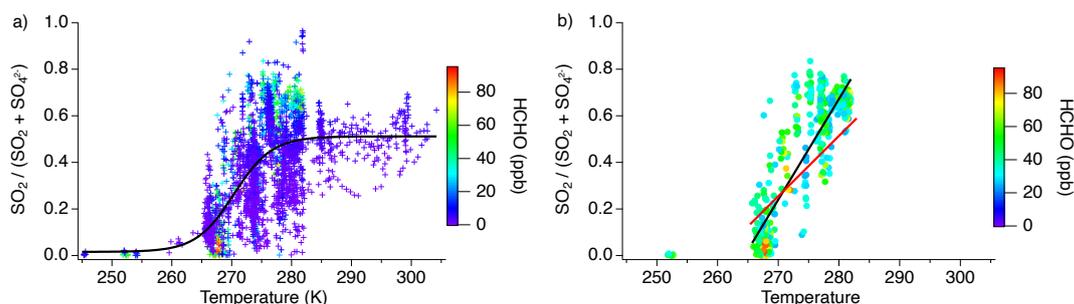


Figure 6. Fractional sulfur conversion as a function of temperature a) including all smoke ages with a sigmoid fit and b) only measurements with HCHO > 25 ppb with the black line indicating the linear fit through the data at all ages between 265-283 K and the red line indicating the
505   *linear fit through the measurements within 1 hr of emission in the same temperature regime.*

4.2 Model results

4.2.1 Williams Flats 3 August 2019 flight

510

Select time series relating to the conversion of SO_2 to sulfate for the 3 August 2019 flight are shown in Fig. S3. Altitude and temperature were constant, around 3 km and 280 K, for both passes of about 10 transects each. Actinic fluxes trended downward for the second pass as dusk approached. Thermodynamic modeling suggests an average pH value of 5.3 (range of -2 to 8)

515   over the length of the plume transects, but a possible increase in LWC by a factor of 2-3 during the second pass. Because the conditions of this flight are relatively consistent between passes, the measurements of both passes are combined for comparison to the model with pH and LWC held constant. Modeling results of this flight with the inclusion of all known gas- and aqueous-phase S(IV) oxidation pathways (Table S1) are shown in Fig. 7 with a conservatively assumed 30%

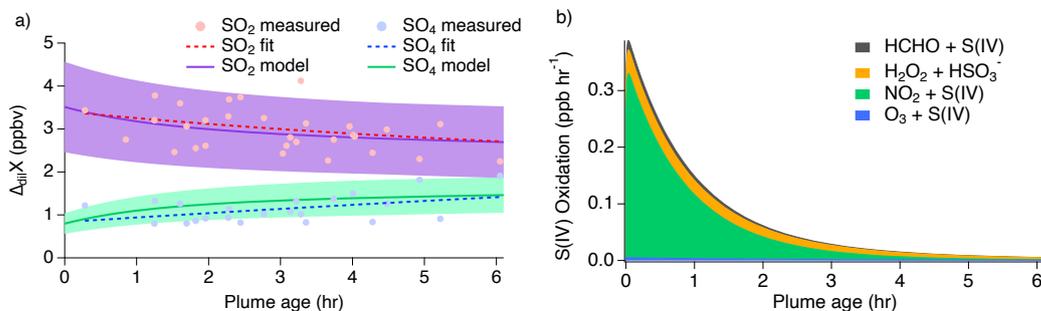
520   uncertainty shown. This uncertainty range encompasses the uncertainties associated with the mechanism of aqueous phase uptake and chemical rate constants occurring at the specified LWC and pH.

525

Figure 7. (a) Measurements of 3 August 2019 shown by the markers and measurement fits shown by the dashed lines compared to the SO_2 and sulfate model results represented by the solid lines with shading denoting an estimated 30% model uncertainty. The sulfate (SO_4) measurements

represent total sulfate which potentially includes organosulfur. (b) Stacked modeled S(IV)
530   *oxidation rates leading to sulfate and HMS production.*

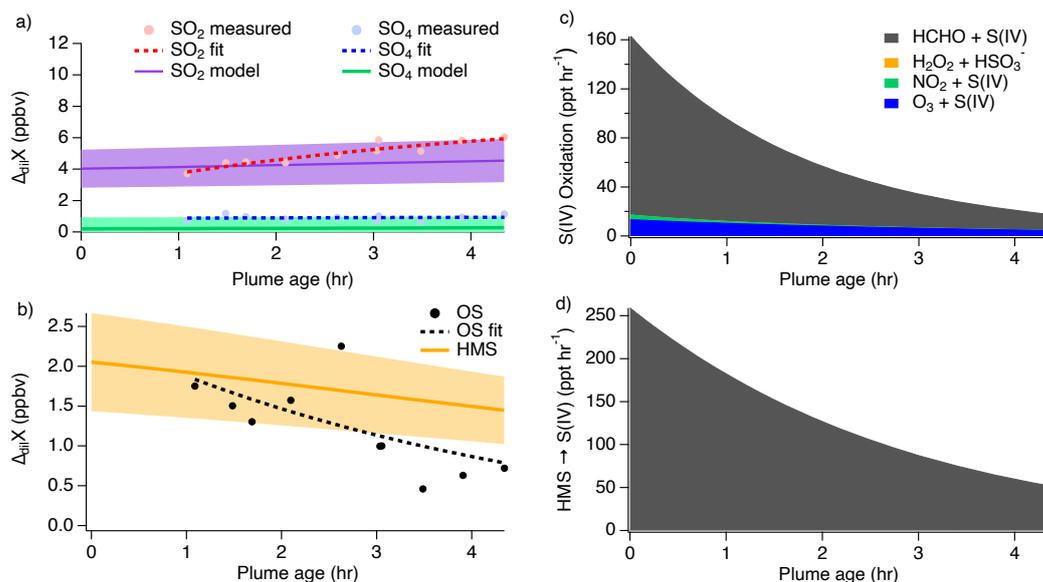
      The model reproduces the general measurement trend of the 3 August flight for both SO_2 and sulfate (Fig. 7a). Model results for NO, NO_2, NO/NO_2, O_3, HCHO, and H_2O_2 are compared to the measurements for each model in Fig. S4 showing good agreement for the 3 August flight.
535   In accordance with the sulfate measurements, the modeled sulfate represents the sum of sulfate and HMS (the latter representing OS). Under the conditions of this flight, the model indicates that aqueous phase oxidation by NO_2 and H_2O_2 are the dominant pathways leading to inorganic sulfate formation with little S(IV) oxidation by HCHO and O_3 (Fig. 7b). This is in contrast to what has been previously expected of aerosol S(IV) oxidation which has been thought to be
540   dominated by ozone oxidation. However, the higher NO_2 oxidation rate constant with increased pH reported by Liu and Abbatt (2021) for non-ideal solutions increases the significance of this reaction.

4.2.2 Williams Flats 7 August 2019 flight
545

The 7 August 2019 flight shows distinct differences between the two passes (Fig. S5); therefore, the flight has been differentiated into the first pass (first full set of transects) and second pass (second full set of transects). It is also during this flight that the largest OS contribution has been reported for the AMS measurements during the FIREX-AQ wildfire flights.
550   The first pass was measured around 4 km and 276 K with an estimated dilution factor of approximately 8×10^{-5} s^{-1} and limited cloud presence. A pH of around 7.2 was estimated for this flight with an aerosol LWC of approximately 1×10^{-7} g m^{-3}. Both NO_2 and CO decrease at similar rates while HCHO remains relatively stable around 40 ppb and O_3 shows a decrease compared to the air outside of the plume for the first six transects (Fig. S6). SO_2 and sulfate are
555   fairly similar with a few instances of sulfate surpassing SO_2 in addition to a moderate fraction of OS observed during this pass.
      The rise in altitude for the second pass is associated with an 8 K decrease in temperature relative to the first pass. The dilution factor for this pass was determined to be slower at around 3×10^{-5} s^{-1}. The difference in these dilution factors could be due to measuring at different
560   altitudes or the result of a sampling artifact due to measuring in different sections of the plume, however, there is not enough information available to determine the exact cause. NO_2 appears to decrease more slowly in comparison to CO which remains relatively constant after the plume has moved away from the clouds. In addition, ozone, which shows the same trend as O_x, appears to be consumed more quickly in transects in which clouds were observed, suggesting rapid uptake
565   within the clouds, in addition to the fast reaction with NO producing the additional NO_2. This additional NO_2 in combination with limited photochemistry as a result of decreasing actinic flux (Fig. S7) due to approaching dusk conditions slows the decreasing NO_2 trend observed during this pass. Furthermore, ISORROPIA calculations indicate a 10-fold increase in aerosol LWC in the presence of clouds compared to the first pass. This is likely due to the decrease in
570   temperature (268 K) and larger relative humidity. The presence of clouds decreases downwind concurrently with a decrease in relative humidity, but aerosol LWC remains high. Lastly, this pass shows SO_2 is nearly depleted in the center of the plume (Fig. S5) while sulfate increases substantially with a rather significant fraction of OS being observed (Fig. S8).

Due to these distinct differences between passes, each pass was modeled separately with
575   the OS contribution reported independently from the sulfate measurements and model results.
The modeled oxidation compounds (Fig. S4) show generally good agreement with the
measurements for these passes; however, some discrepancies are observed due to measuring
different parts of the plume. Results of the first pass are shown in Fig. 8 and the second pass
shown in Fig. 9, both showing good agreement between the model and measurements with ozone
580   and NO$_2$ as the largest contributors to sulfate production during this flight. However, the
majority of modeled S(IV) oxidation occurs through the HCHO pathway rapidly producing
HMS.

The first pass shows SO$_2$ increasing downwind, which is unexpected because SO$_2$ is
considered to be a primary emission which typically decreases downwind as it is removed
585   through oxidation. In addition, the measurements show a large OS mixing ratio following the
first hour after emission before gradually decreasing downwind. This suggests that OS is either
directly emitted from the fire source or very rapidly produced.

Clouds and large LWC were present throughout the majority of the second pass
measurements (Figs. S5 and S6), significantly shifting the chemistry from that of the first pass.
590   Figure 9 shows that modeled SO$_2$ is quickly taken up into the aqueous phase under these higher
LWC conditions with approximately 1.5 ppb going directly into sulfate production and the
remaining 3 ppb of the initial SO$_2$ concentration being converted into HMS. These oxidation
processes occur promptly after emission, but they rapidly slow once all of the available initial
SO$_2$ is depleted within the first 1-2 minutes. The exponential trends of the sulfate and OS
595   measurements agree with the model results to within approximately 40%.

600   Figure 8. *First pass measurements shown by the markers and measurement fits shown by the
dashed lines compared to the model results represented by the solid lines with shading denoting
an estimated 30% model uncertainty for SO$_2$ and sulfate (a) and OS (b). Stacked modeled S(IV)*

*oxidation rates (c) leading to sulfate and HMS production. HMS reverse reaction rate (d)
reproducing S(IV).*

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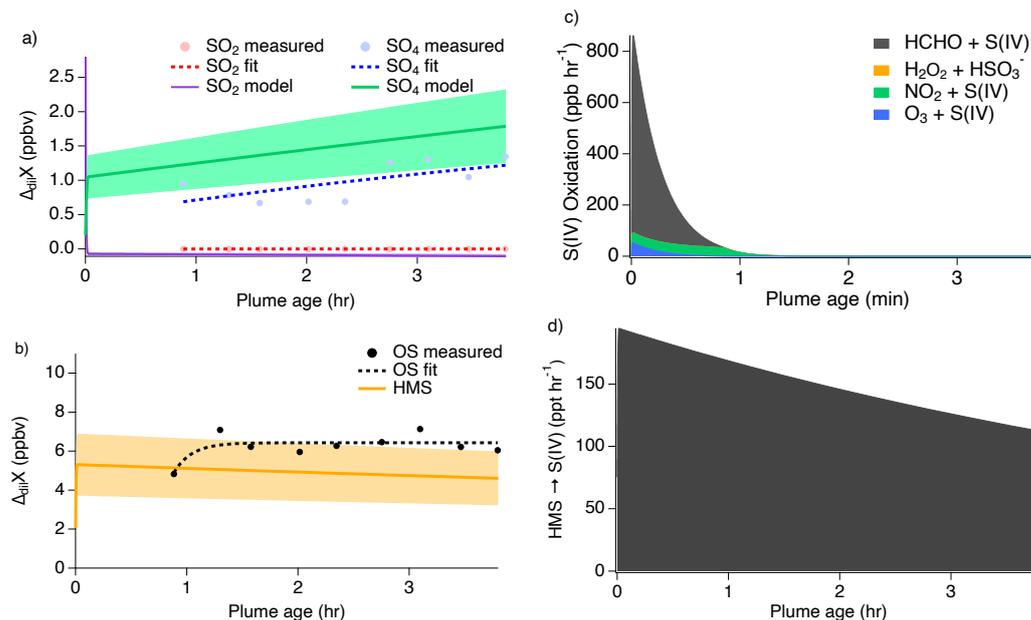


*Figure 9. Second pass measurements shown by the markers and measurement fits shown by the
dashed lines compared to the model results represented by the solid lines with shading denoting
610   an estimated 30% model uncertainty for SO₂ and sulfate (a) and OS (b). Stacked modeled S(IV)
oxidation rates (c) leading to sulfate and HMS production. HMS reverse reaction rate (d)
reproducing S(IV).*

The importance of HMS as a S(IV) reservoir and its conversion into sulfate or into gas-
615   phase SO₂ largely depends on the varying conditions of LWC. Under neutralized conditions
(7.2), the model reproduces the observed trends of all three compounds for the first pass at low
aerosol LWC (1×10^{-7} g m⁻³) and for the second pass at LWC conditions typical of wet aerosol
(1×10^{-3} g m⁻³). As discussed further in section 4.2.3, the higher pH of this flight increases the
rate of HMS reversal back into S(IV) by a factor of six. Because of the low LWC of the first
620   pass, heterogeneous uptake is limited and causes the rates of S(IV) oxidation to significantly
decrease. S(IV) evaporation then enhances gas phase SO₂ in transported smoke, consistent with
similar rates of HMS decay and SO₂ growth. As a result, very little sulfate is produced during
this pass at a rate of approximately 4 ppt hr⁻¹ primarily due to S(IV) oxidation by ozone.
However, the higher LWC conditions of the second pass allow S to remain in the aqueous phase.
625   The small increase in sulfate of approximately 500 ppt over the course of the flight can be
explained by a small fraction of HMS, on the order of 120-190 ppt hr⁻¹, which undergoes a
reverse reaction decomposing back into S(IV) before being oxidized to produce sulfate (Fig. 9d).
The SAGA instrument detects HMS as S(IV), which cannot be separated from HSO₃⁻ and
SO₃⁺ and is therefore subject to interference from high concentrations of gas-phase SO₂. As
630   shown in Fig. S8, MC sulfate measurements show similar concentrations to the AMS
organosulfur portion of the total sulfate measurements during the first pass, but a considerably

smaller value in comparison during the second pass. This suggests that HMS may have been the majority of the organosulfur concentrations measured during the first pass but that an additional unknown organosulfur was much more abundant than HMS during the second pass. Therefore, it
635 appears that the modeled HMS exceeds measurements on the second pass.

There are two potential explanations for the good agreement between the observed organosulfur concentration from the second pass and the modeled HMS. It is possible that during the very rapid uptake of SO_2 into the aqueous phase, (1) additional organosulfur species may be produced or (2) the additional organosulfur species are the result of further reactions of HMS
640 suggesting that the model is correctly reproducing the HMS formation chemistry, but indicating that the model aqueous phase chemistry is incomplete. Both of these potential explanations require that the measured organosulfur species behave similarly to HMS in their rates of formation and termination in order to explain the good agreement between the modeled HMS and measured organosulfur concentrations. In addition, these explanations would require that the
645 organosulfur species are not identified as S(IV) in ion chromatography measurements. While the modeling allows for significant insight into the identity and formation mechanisms of aerosol sulfur, there is not enough evidence available from these measurements to conclusively explain all of the AMS and SAGA sulfur observations.

650 **4.2.3 Model HMS sensitivity analysis**

We performed a model sensitivity analysis to investigate the relevance of organosulfur behavior under the conditions of the HMS rates of production and termination in different environments by varying the model LWC (10^{-6} - 1 g m^{-3}), pH (1-8), temperature (260-280 K), and HCHO (10-
655 90 ppb) individually while holding the other parameters constant at the 3 August flight conditions (T = 280 K, pH = 5.3, and LWC = 2×10^{-4} g m^{-3}) due to the more simplified chemistry occurring during this flight.

Variations in LWC (Fig. 10a) show that aerosols with less LWC produce minimal amounts of sulfate and HMS, but that HMS makes up between 5 and 45% of the combined
660 concentrations. The HMS fraction shows the largest contribution as LWC increases into the cloud regime at which point sulfate production begins to decrease with a rapid increase in HMS. While the typical LWC range estimated for these fires is $10^{-7} - 10^{-2}$ g m^{-3}, this indicates that the chemistry of the smoke will change substantially with cloud interactions. LWC is shown to be an important variable in the ratio of the formation of HMS to sulfate; however, this ratio trend
665 is indicative of conditions at pH 5.3 and will vary under differing pH conditions.

The pH dependence of the ratio of HMS / (SO_4 + HMS) is shown in Fig. 10b in which HMS formation is more active as the acidity decreases. At acidic pH values, representative of typical tropospheric aerosol (Nault et al., 2021), a negligible amount of HMS contributes to the combined concentrations. Above pH 4, HMS contribution begins to increase followed by a more
670 rapid increase after pH 6. The maximum HMS contribution is reached around pH 7.3 before rapidly decreasing at higher values.

The ratio of HMS production and reverse reactions varies with pH with the reverse reaction becoming more substantial at higher pH (Fig. 11). Under aerosol LWC conditions, the rate of the HMS reverse reaction is up to 3 times larger than the rate of HMS production. As
675 LWC increases into the cloud regime, the rate of the HMS reverse reaction increases further to approximately two orders of magnitude larger than HMS production around pH 7. However, a

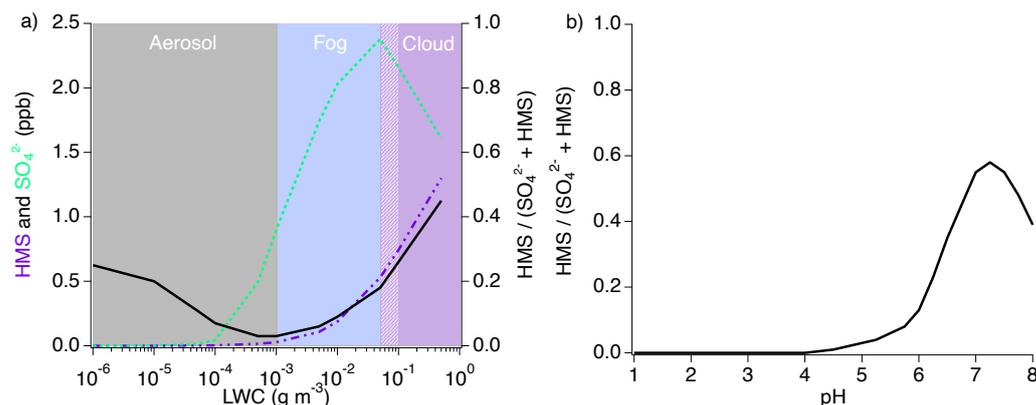
reduction in temperature shifts this dependence to higher pH decreasing the rate of HMS reversal at the same pH.

680   While temperature and HCHO concentration are key factors controlling HMS production, these factors alone under low LWC and pH result in minimal HMS (Fig. S9). HMS production increases with decreasing temperature; however, under the conditions of the 3 August flight, HMS only reaches a maximum value of 5 ppt at 260 K which is approximately 5% of the modeled sulfate. Similarly, a minimal amount of HMS is produced with varied HCHO, but the ratio of HMS to the sum of HMS and sulfate increases linearly with HCHO at a rate of 1.5 ppt

685   ppb^{-1} HCHO.

    The conditions that most largely affect HMS are LWC and pH. Due to the significance of LWC to HMS production and reversal, it is likely that aqueous aerosols, fog, cloud droplets, and possibly ice crystals will be most impactful on HMS production. Because the rainwater pH of areas such as the Western U.S. and Eastern China can reach much less acidic pH levels due to

690   increased ammonia emissions, it is likely that these areas will be more susceptible to HMS production (Keresztesi et al., 2020; Qu and Han, 2021). Together, these conditions indicate that highly polluted areas which experience higher pH and greater LWC will likely be influenced by this chemistry. Therefore, the production of HMS should be an important consideration for air quality in areas such as agricultural regions which experience enhanced emissions of ammonia,

695   likely increasing the pH, as well as geographical locations which may promote fog formation. This would include areas such as Beijing, the Uintah basin, and Bakersfield, CA which have observed severe haze formation and have the potential to be affected by HMS.

700   Figure 10. *Sensitivity analysis of HMS formation under individually varied LWC and pH conditions. The black line in each figure represents the ratio of the modeled HMS mixing ratio to the sum of the modeled inorganic sulfate and HMS. The shading in b) reflects the typical rainwater pH for each region.*

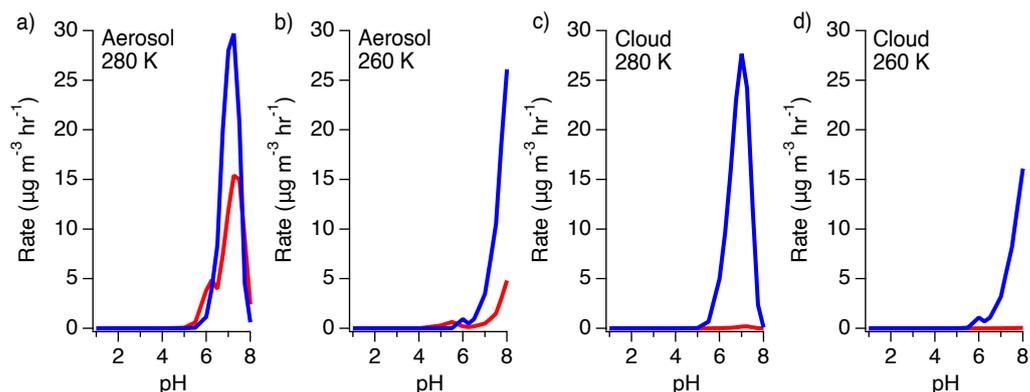



Figure 11. *Rates of HMS production (red) and reversal (blue) under aerosol and cloud conditions at 280 K and 260 K.*

5. Conclusions

SO_2 plays an important role in sulfate aerosol formation and thus air quality and climate forcing. Therefore, understanding the sources and evolution of SO_2 emissions in a changing climate are essential. The emission factors determined from the FIREX-AQ mission under flaming conditions show good agreement with the compilation reported by Andreae (2019). This provides confidence for the same categories under smoldering conditions for which there are no reported measurements from previous studies. No distinct correlation is observed for SO_2 emission factors based on MCE; however, it remains unclear if fire MCE influences the ratio of SO_2 and sulfate emission factors. With biomass burning events increasing worldwide, this study suggests that the resulting SO_2 emission factors will be more dependent on geographical location and land use, and less dependent on combustion phase and fuel type. Areas that incur more sulfur deposition from coal burning or application through fertilizer use, will likely produce larger SO_2 emission factors.

Modeling with inclusion of the HCHO oxidation chemistry, producing HMS, shows good agreement with the measurements. However, the differentiation of HMS from sulfate through the SAGA measurements indicates that HMS can be over-predicted. While HMS is potentially directly emitted from the fire source, a large organosulfur concentration is observed that has not yet been identified. Because the modeled HMS is similar to the measured organosulfur fraction, it is expected that the additional organosulfur species likely exhibit similar rates of production and termination as HMS. The importance of the HMS, or similar species, reverse reaction is also made apparent by the ability to act as an S(IV) reservoir. This allows these species to produce sulfate or SO_2 further downwind depending on the LWC and pH.

Environments that experience high LWC and pH are expected to be the most influenced by this chemistry. This includes regions that experience higher ammonia emissions and are geographically or meteorologically subject to greater cloud or fog formation. As a result, this chemistry should be considered when assessing severe haze events as a result of either biomass burning or industrial pollution.

Plain Language Summary

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Biomass burning sulfur dioxide (SO_2) emission factors range from 0.27–1.1 g kg-1 C. Biomass burning SO_2 can quickly form sulfate and organosulfur, but these pathways are dependent on liquid water content and pH. Hydroxymethanesulfonate (HMS) appears to be directly emitted from some fire sources, but is not the sole contributor to the organosulfur signal. It is shown that

745   HMS and organosulfur chemistry may be an important S(IV) reservoir with the fate dependent on the surrounding conditions.

Keywords

750   Sulfur dioxide, hydroxymethanesulfonate, emission factors, biomass burning

Data and code availability. The data collected for FIREX-AQ are available from the NASA/NOAA FIREX-AQ data archive: https://www-air.larc.nasa.gov/cgi-bin/ArcView/firexaq. The Framework for 0-D Atmospheric Modeling code is available from the AirChem/F0AM

755   archive: https://github.com/AirChem/F0AM (doi.org/10.5281/zenodo.5752566).

Author contribution. The research was designed by PSR and AWR. Measurement contributions were provided by all authors. The modeling was performed by PSR and GMW. The paper was written by PSR with contributions from all coauthors.

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Competing interests. The authors declare that they have no conflict of interest.

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