1 Supplemental Information

Aerosol pH indicator and Organosulfate Detectability from Aerosol Mass Spectrometry Measurements

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18 S1 Analysis of possible impact of amines during ATom

If amines were present in sufficient concentrations, they could affect the thermodynamic calculations by providing another base to neutralize sulfuric acid. We looked at *m/z* 30, 44, 58, and 86, where amines tend to produce distinctive peaks in the AMS, and examined the high resolution spectra for different flights during ATom-1 and ATom-2 (Fig. S5). The objectives were to a) evaluate whether any amine signal could be detected above background and b) if amines were detectable, to quantify their fractional contribution to the aerosol.

We observe in Fig. S5 that amines can be fit above the background during the entirety of one research flight in ATom-1 (within regime I) (here we show the fit for one amine ion, $C_2H_6N^+$) but are much smaller than NH_4^+ (see main text). Thus, we can assume amines are a negligible base for the regions where we use ammonium balance and/or $H_ySO_x^+/SO_x^+$ to estimate aerosol acidity.

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31 S1.5 Quantification of organosulfates from PALMS aerosol measurements

We also compared total sulfate to OS species glycolic acid sulfate (GAS) and IEPOX Sulfate measured by PALMS (Froyd et al., 2019) for ATom-1, shown in Fig. S6.

35 S2 Application of the Song et al. method

The Song (2019) method for estimating OS_f was applied to the the ATom and KORUS-AQ campaigns where data was in Regime II (pH > 0, $AN_f < 0.3$) in Fig. S8 and the entire ATom and KORUS-AQ campaigns, shown in Fig. S9. Results change substantially based on what type of sulfate standard was used to calculate the contribution of OS to total sulfate. When we use ambient data collected from "clean" and "dry" periods (defined in this work as RH < 30% and pressure altitude > 1200 m) with the assumption that they mainly contain AS, the average % OS in the BL is centered around 0%, but fluctuates within $\pm 30\%$. In the FT the distribution narrows for all campaigns, and is centered around a few percent OS. When pure AS standards were used, the estimated percent OS varied widely, from -100% to +50%.

Tables:

Campaign	AN _f	OA _f	Avg. pH
DC3	0.04	0.6	0.75
SEAC ⁴ RS	0.02	0.6	-0.2
WINTER	0.3	0.3	1
KORUS-AQ	0.2	0.4	2
ATom-1	0.01	0.5	-0.7
ATom-2	0.01	0.2	-0.5

48 Table S1. Average AN_{ρ} OA_{ρ} and pH for six campaigns (those shown in Fig. 1D), and DC3

50 Figures:



Fig. S1. Flight paths for the ATom-1, ATom-2, KORUS-AQ, SEAC⁴RS, DC3, and WINTER
aircraft campaigns used in this paper.



Fig. S2. (Left) Chen diagram for the ATom campaigns with and without the periods of higher
MSA concentrations (defined as fMSA > 0.1 and total sulfate > 0.1). (Right) Histograms of fMSA
for ATom-1 and ATom-2.



63 Fig. S3. (A) Variation of the sulfate fragment indicators for pure AS calibration averages for full

64 campaigns. The variability was caused by changes in instrument components (e.g. filaments) and

65 *tuning. (B) Same for individual calibrations during KORUS-AQ, variability caused mainly by* 66 *filament aging.*



70 Fig. S4. (Left two columns) comparison of E-AIM model results to measured $HNO_3(g)$ for six

- 71 campaigns. (Right two columns) comparison of the measured particle inorganic nitrate
- 72 concentrations against the E-AIM model predictions for the same campaigns.
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Fig. S5. Inset: Quantification of amines (green) in the ATom-1 flight RF104 compared to
ammonium (red). Main plot: high-resolution fit of the amine ion at m/z 44 in the ToF-AMS
analysis software



Fig. S6. $fH_ySO_x^+$ ions vs. OA_f colored by total OA concentration (left and bottom right) and top right colored by experiment index. All data are from chamber experiments where SOA was formed on ammonium sulfate seed aerosol from (A, B, C, D) nitrate radical reaction with monoterpenes (where 2014, 2015 represent different series of experiments done in different years and different instruments), and photooxidation of (E) alkanols and (F) toluene. The $fH_ySO_x^+$ ratios have been normalized to the average ratios for the ammonium sulfate seed for each experimental dataset.



94 Fig. S7. Concentration of OS measured by PALMS (only the sulfate moiety) during ATom-1

95 against total sulfate measured by the AMS during ATom-1. The PALMS OS is calculated by

96 summing the concentrations (of the sulfate moieties only) for the IEPOX OS and glycolic acid

97 sulfate mass fractions, and multiplying by total mass from the AMS ($\mu g m^{-3}$) for pH > 0 (bottom) 98 and pH < 0 (top).

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102 Fig. S8. Application of the Song (2019) method for estimating OS_f to ATom campaigns and

103 KORUS-AQ in regime II (pH>0, $AN_f<0.3$) to (A) the free troposphere with "clean and dry"

104 normalization values used, (B) boundary layer with "clean and dry" normalization, (C) free

105 troposphere with pure AS calibration values used, and (D) boundary layer with pure AS values

106 used. Dotted line shows the OS% calculated using data from PALMS during ATom-1.



108 Fig. S9. Application of the Song (2019) method for estimating OS_f to the entire ATom campaigns 109 and KORUS-AQ to (A) the free troposphere with "clean and dry" normalization values used, (B) 110 boundary layer with "clean and dry" normalization, (C) free troposphere with pure AS

111 calibration values used, and (D) boundary layer with pure AS values used. Dotted line shows the

112 OS% calculated using data from PALMS during ATom-1.



Fig. S10. Results from GEOS-Chem v12 simulation for the year 2010 for (A) pH at the surface, (B) pH at 400 hPa, (C) AN_f at the surface, and (D) AN_f at 400 hPa.

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