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Aerosol pH indicator and organosulfate detectability from aerosol mass spectrometry measurements

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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.

S2 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.

S3 Application of the Song et al. method

The Song (2019) method for estimating OS_f was applied to the ATom and KORUS-AQ campaigns where data was in Regime II (calculated pH > 0, $AN_f < 0.3$) in Fig. S9 and the entire ATom and KORUS-AQ campaigns, shown in Fig. S10. 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 ± 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. calculated pH
DC3	0.04	0.6	0.8
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

Table S1. Average AN_f, OA_f, and calculated pH for six campaigns (those shown in Fig. 1D), and DC3

Figures:

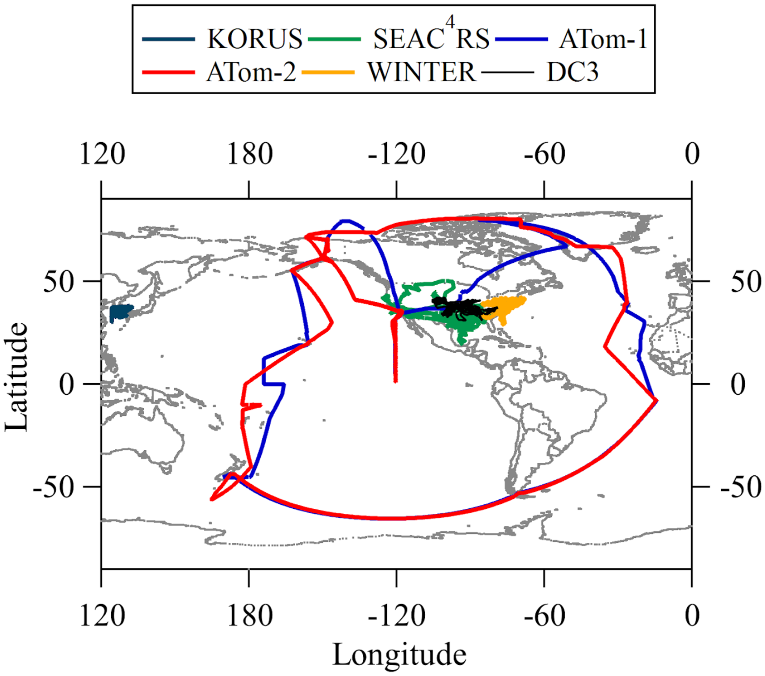

Fig. S1. Flight paths for the ATom-1, ATom-2, KORUS-AQ, SEAC^4*RS, DC3, and WINTER aircraft campaigns used in this paper.*

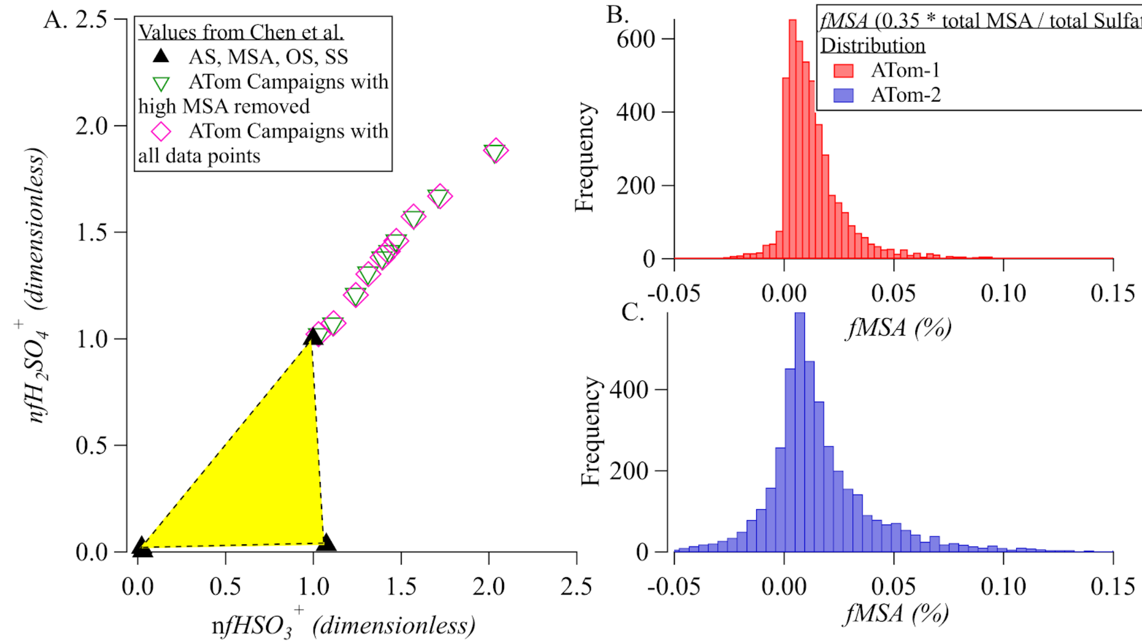

Fig. S2. (Left) Chen diagram for the ATom campaigns with and without the periods of higher MSA concentrations (defined as fMSA > 0.1 and total sulfate > 0.1). (Right) Histograms of fMSA for ATom-1 and ATom-2.

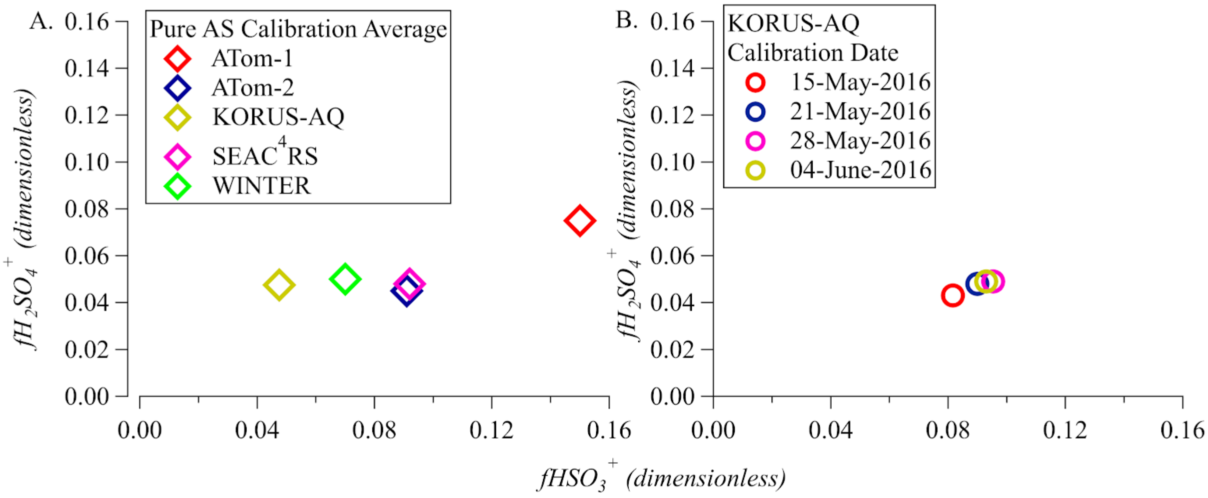

Fig. S3. (A) Variation of the sulfate fragment indicators for pure AS calibration averages for full campaigns. The variability was caused by changes in instrument components (e.g. filaments) and tuning. (B) Same for individual calibrations during KORUS-AQ, variability caused mainly by filament aging.

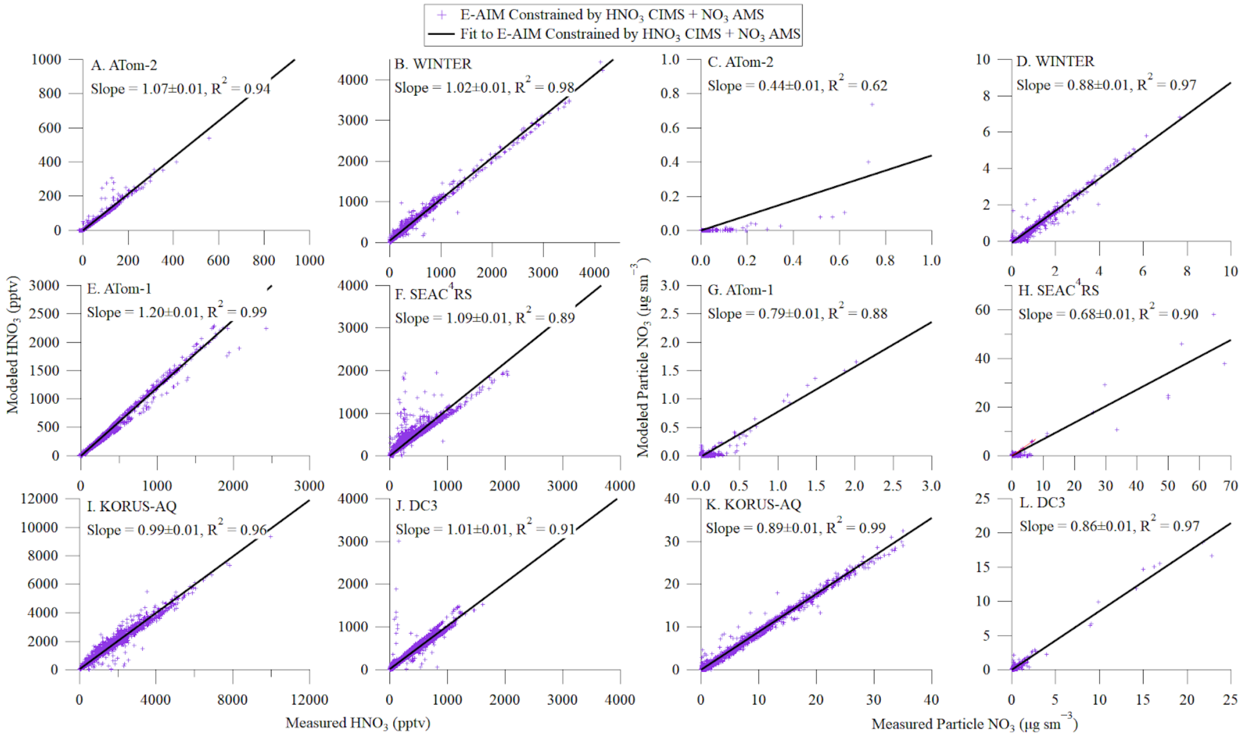

Fig. S4. (Left two columns) comparison of E-AIM model results to measured HNO$_3$(g) for six campaigns. (Right two columns) comparison of the measured particle inorganic nitrate concentrations against the E-AIM model predictions for the same campaigns.

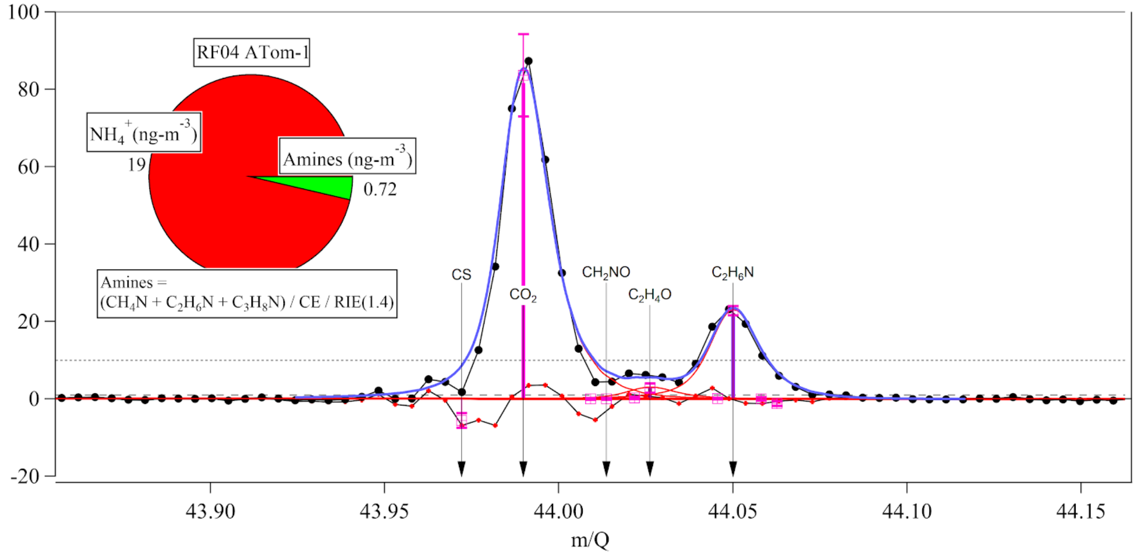

Fig. S5. Inset: Quantification of amines (green) in the ATom-1 flight RF104 compared to ammonium (red). Main plot: high-resolution fit of the amine ion at m/z 44 in the ToF-AMS analysis software

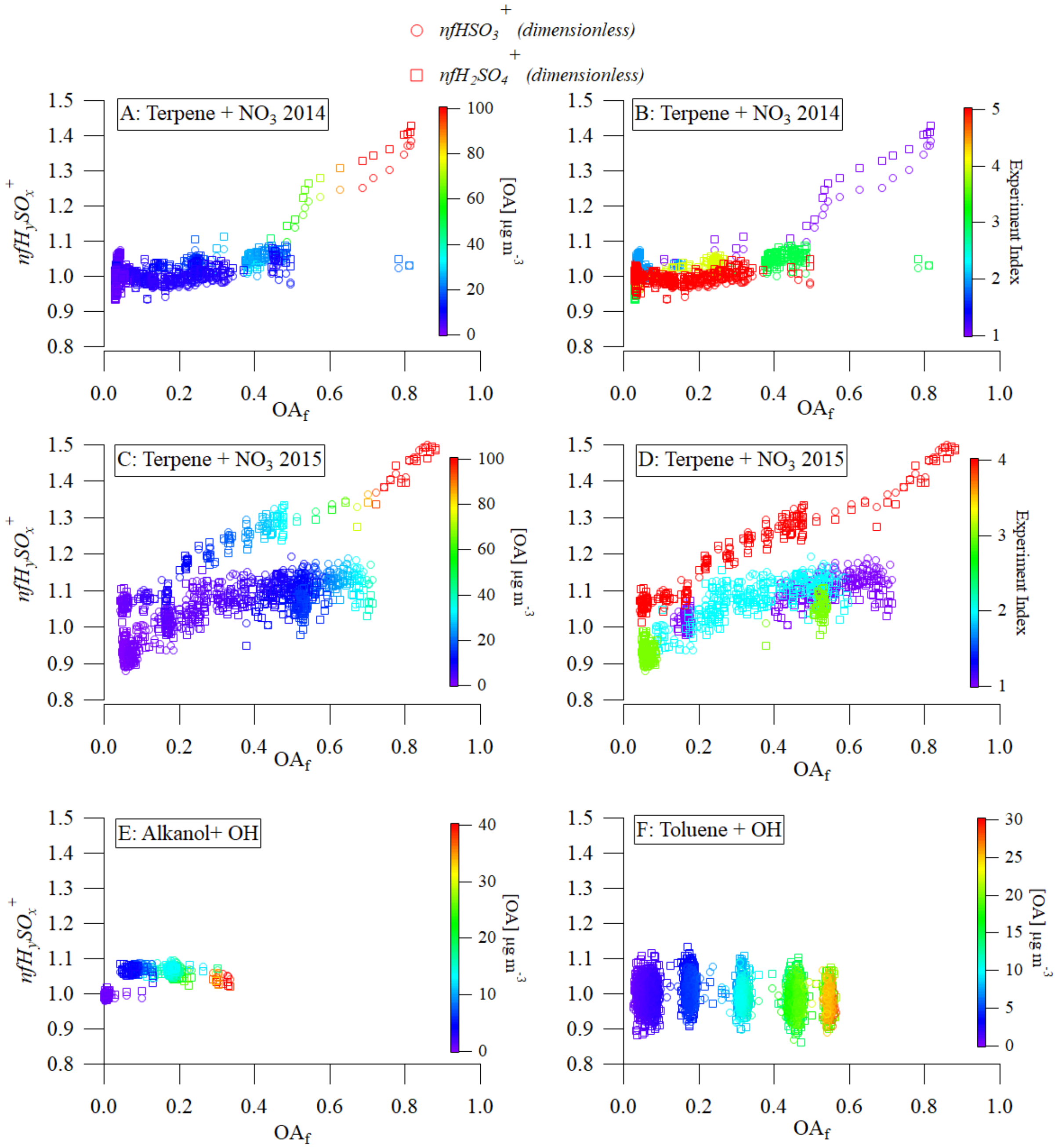

Fig. S6. $fH_ySO_x^+$ ions vs. OA_f colored by total OA concentration (left and bottom right) and top right colored by experiment index. All data are from chamber experiments where SOA was formed on ammonium sulfate seed aerosol from (A, B, C, D) nitrate radical reaction with monoterpenes (where 2014, 2015 represent different series of experiments done in different years and different instruments), and photooxidation of (E) alkanols and (F) toluene. The maximum [OA] concentrations observed in (A) and (C) are 204 and 206 μg m^{-3}, respectively. The $fH_ySO_x^+$ ratios have been normalized to the average ratios for the ammonium sulfate seed for each experimental dataset.

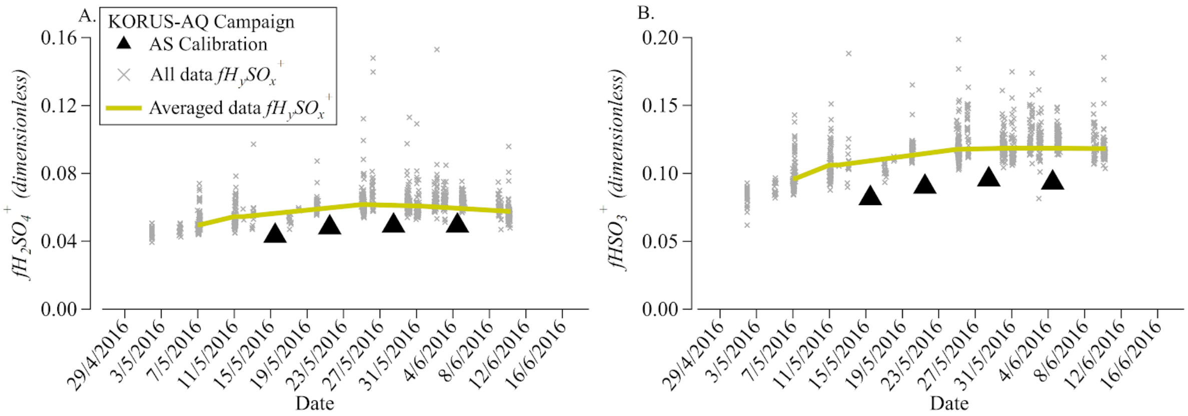

Fig. S7. $fH_ySO_x^+$ *ions (not normalized) vs. time for AS calibrations and ambient sampling for the KORUS-AQ campaign. (A) shows* $fH_2SO_4^+$ *and (B) shows* $fHSO_3^+$*. The yellow line shows smoothed, average data for the campaign, and the grey points show the non-averaged ambient data. Black triangles show the average* $fH_ySO_x^+$ *values for four pure AS calibrations done during KORUS-AQ.*

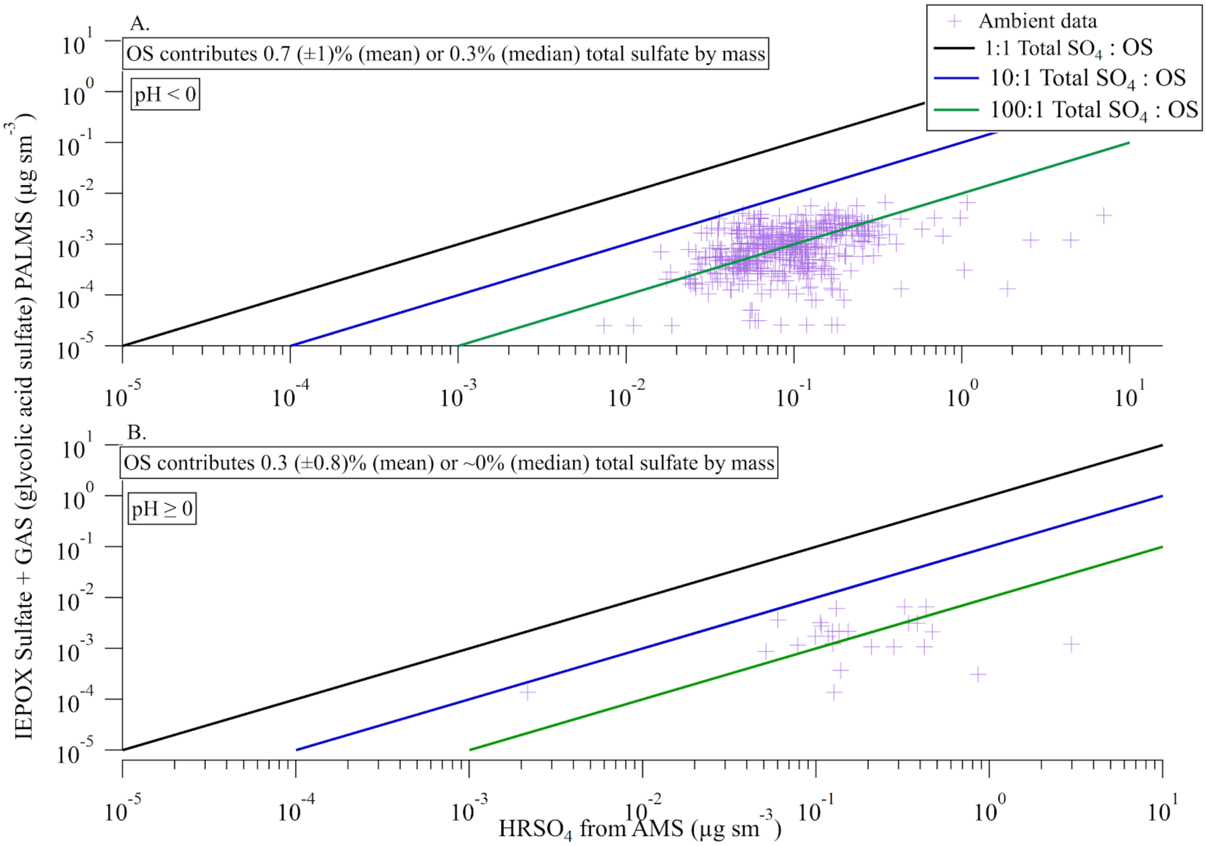

Fig. S8. Concentration of OS measured by PALMS (only the sulfate moiety) during ATom-1 against total sulfate measured by the AMS during ATom-1. The PALMS OS is calculated by summing the concentrations (of the sulfate moieties only) for the IEPOX OS and glycolic acid sulfate mass fractions, and multiplying by total mass from the AMS (μg m^{-3}) for calculated pH > 0 (bottom) and calculated pH < 0 (top).

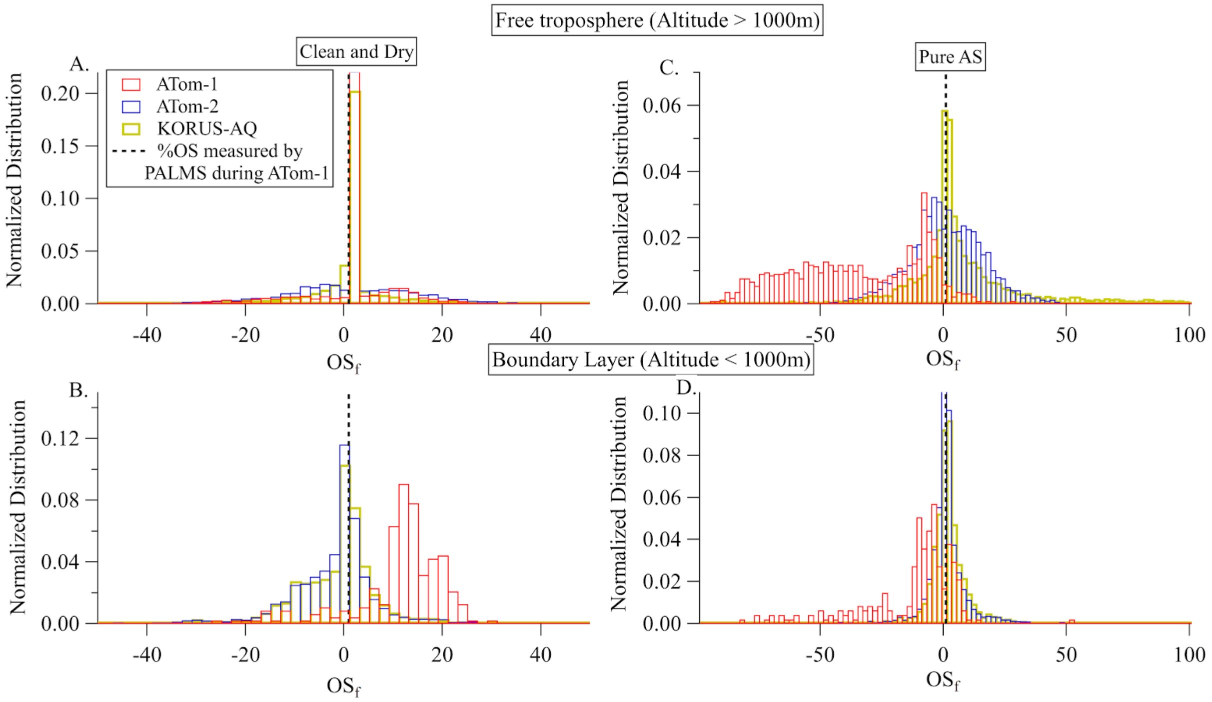

Fig. S9. Application of the Song (2019) method for estimating OS_f to ATom campaigns and KORUS-AQ in regime II (calculated pH>0, AN_f<0.3) to (A) the free troposphere with "clean and dry" normalization values used, (B) boundary layer with "clean and dry" normalization, (C) free troposphere with pure AS calibration values used, and (D) boundary layer with pure AS values used. Dotted line shows the OS% calculated using data from PALMS during ATom-1.

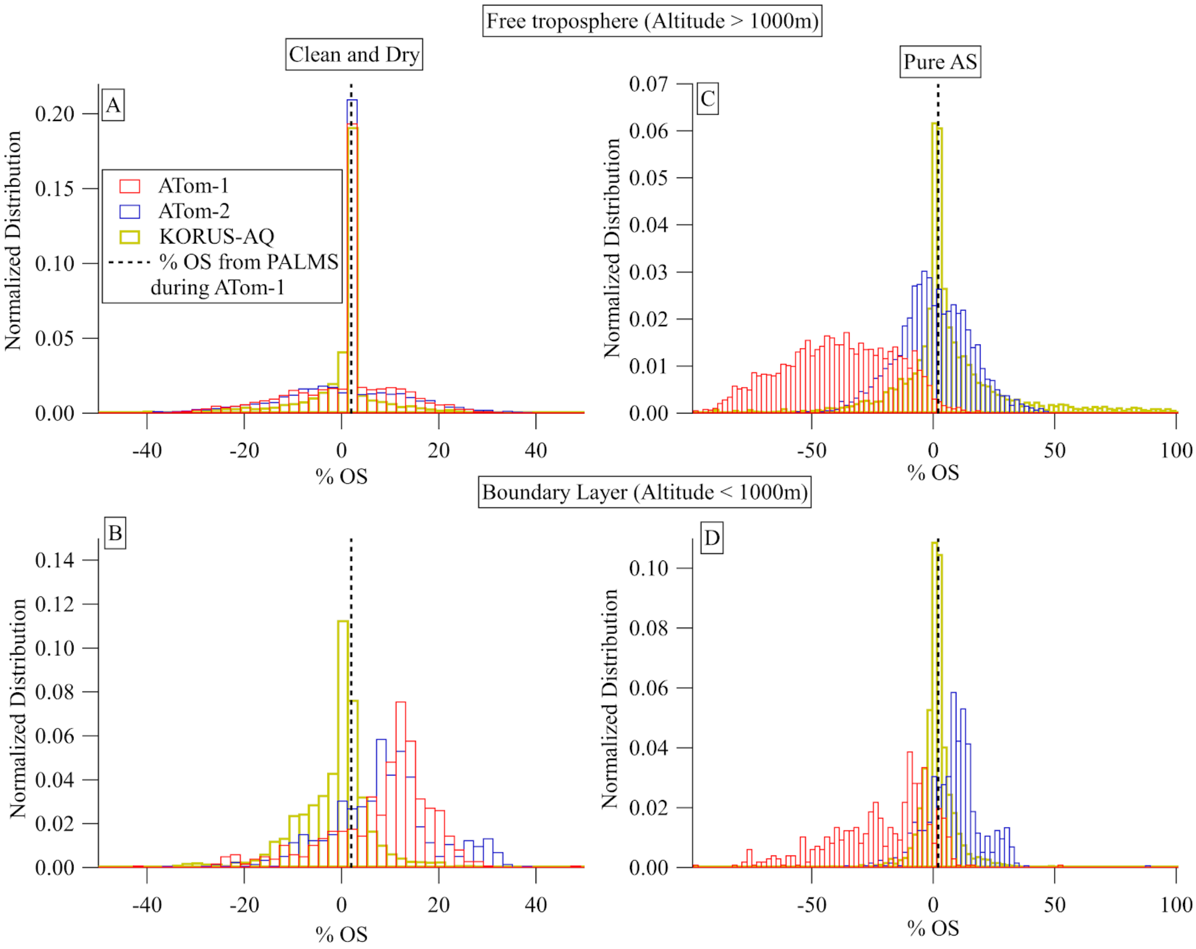

Fig. S10. Application of the Song (2019) method for estimating OS_f to the entire ATom campaigns and KORUS-AQ to (A) the free troposphere with "clean and dry" normalization values used, (B) boundary layer with "clean and dry" normalization, (C) free troposphere with pure AS calibration values used, and (D) boundary layer with pure AS values used. Dotted line shows the OS% calculated using data from PALMS during ATom-1.

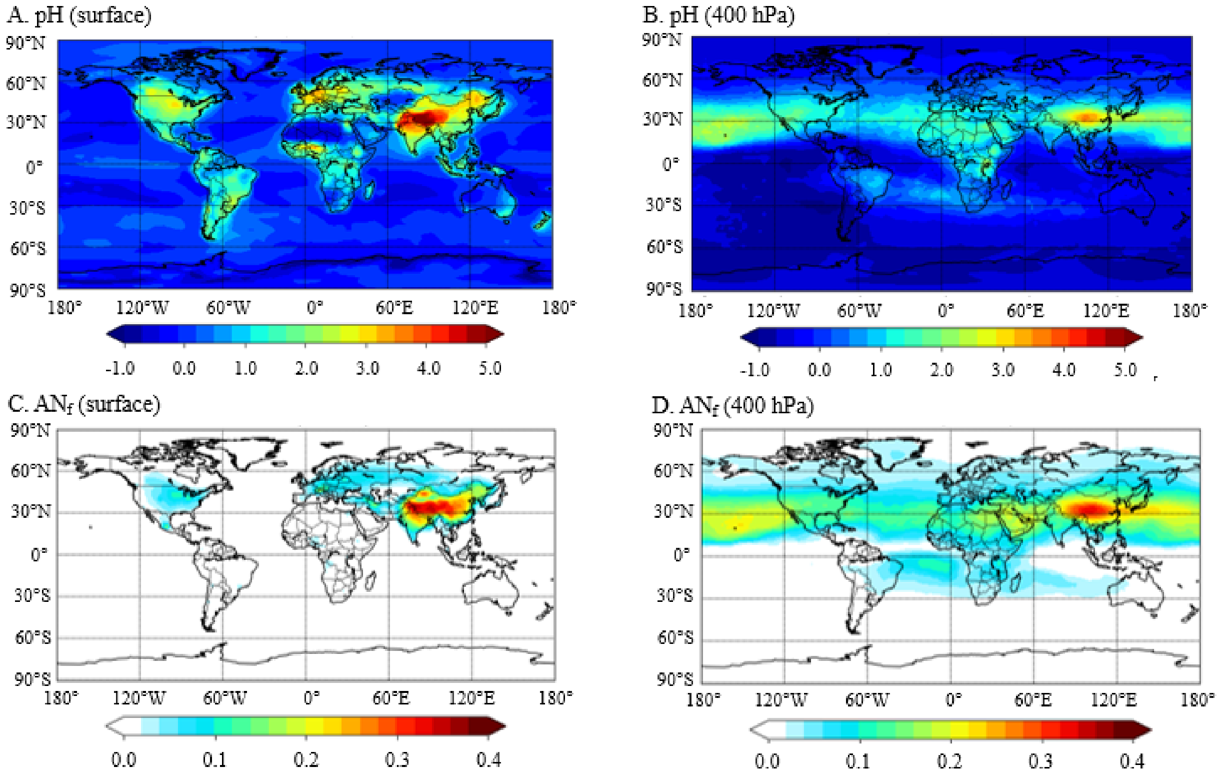

Fig. S11. Results from GEOS-Chem v12 simulation for the year 2010 for (A) calculated pH at the surface, (B) calculated pH at 400 hPa, (C) AN_f at the surface, and (D) AN_f at 400 hPa.

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