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Heterogeneous interactions between SO_2 and organic peroxides in submicron aerosol

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S1. Quantification of sulfate formation for SOA experiments

Particulate sulfate formation upon the reactive uptake of SO_2 onto different types of SOA was monitored using a compact time-of-flight aerosol mass spectrometer (C-ToF-AMS) (Aerodyne Research Inc., Billerica, USA). In this study, the ToF-AMS was operated in the Mass Spectrum (MS) mode with a chopper to regulate particle transmission for aerosol sulfate quantification (DeCarlo et al., 2006). The chopper where the aerosol beam passes is controlled to be alternatively blocked in order to have background corrections for quantification. An aerodynamic lens system selects the particles in a size range of ~35−1000 nm into the vacuum system. The sampling flow rate was 1.26 $cm^3\ s^{-1}$. After the sampling stream passing the sizing chamber, aerosol is vaporized on a heated porous tungsten surface (600 °C) and immediately ionized in electron impact (EI) mode at 70 eV. 300 nm ammonium nitrate (99.999%, Sigma-Aldrich) was used for AMS ionization efficiency (IE) calibration. The collection efficiency (CE) under humid condition was assumed to be 1. The relative ionization efficiency (RIE) of inorganic sulfate was determined to be 1.05 using ammonium sulfate (Canagaratna et al., 2007). The ions are extracted by an orthogonal extractor into the ToF-MS (V-mode), and the MS spectra acquisition was performed under positive mode. Data were analyzed by software “SQUIRREL 1.63” and “PIKA 1.23” in Igor Pro 6.37 (Wavemetrics, Oregon, USA).

For γ_{SO2} measurements of toluene SOA, a strong hydrocarbon interference was observed with the SO_2 analyzer, possibly stemming from the high concentrations of gas-phase aromatic compounds. As a result, the uptake rate was instead estimated by measuring the sulfate production rate using AMS. However, it should also be noted that the sulfate collection and ionization efficiencies of AMS are highly uncertain, since the yield of organosulfate is significant from these reactions (Wang et al., 2019), and AMS has a lower sensitivity towards organosulfates especially under humid conditions in the current study as indicated by ion chromatography and SMPS measurements (Fig.S10-12) (Chen et al., 2019;Farmer et al., 2010). Different RIE for different types of organosulfates were also observed in this study (Fig. S11). As a result, γ_{SO2} of toluene SOA was estimated from rate of sulfate formation measured by AMS and corrected based on the ratio between sulfate formation and SO_2 consumption of limonene SOA (Fig. S12).

S2. Supplemental Table and Figures

Table S1. Summary of experiments in this study.

Figure S1. Schematic of measuring γ_{SO2} onto ammonium sulfate or malonic acid mixed with peroxides.

Figure S2. Experimental schematic of measuring γ_{SO2} onto SOA.

Figure S3. Potential SO_2 loss by peroxides accumulated on the filter before the SO_2 analyzer.

Figure S4. Investigating potential SO_2 decay by losses inside the SO_2 analyzer.

Figure S5. Contribution of wet ammonium sulfate aerosol to the observed SO_2 decay.

Figure S6. Contribution of organic peroxide vapor to the observed SO_2 decay.

Figure S7. Relationship between γ_{SO2} and peroxide characteristics.

Figure S8. Comparison between measured γ_{SO2} and predicted γ_{SO2} in experiments.

Figure S9. Residuals (a) and residual distribution (b) for the multilinear regression.

Figure S10. (a) IC calibration curves for S (VI). (b) Comparison of sulfate quantified by AMS and IC.

Figure S11. Comparison of SMPS measured sulfate and AMS measured sulfate under dry and humid conditions (RH 80%) for both inorganic sulfate and organosulfates.

Figure S12. Time series of sulfate formation monitored by AMS for SOA experiments.

84 **Table S1. Summary of chamber experiments in this study**

Expt.#	**Aerosol**	**Initial SO_2 (ppb)**	**SO_2 decay (ppb)**	**Surface area concentration ($\mu m^2\ cm^{-3}$)**	**γ_{SO2}[a]**	**RH %**
1	25 mM ammonium sulfate	218	-1	7.8×10^3	$(-1.9 \pm 0.08)\times10^{-7}$	52
2	50 mM tert-Butyl hydroperoxide + 25 mM ammonium sulfate	240	3	8.9×10^3	$(2.7 \pm 0.09)\times10^{-6}$	44
3	50 mM tert-Butyl hydroperoxide + 25 mM ammonium sulfate	215	10	7.5×10^3	$(1.4 \pm 0.07)\times10^{-5}$	56
4	50 mM tert-Butyl hydroperoxide + 25 mM ammonium sulfate	250	47	1.4×10^4	$(2.8 \pm 0.7)\times10^{-5}$	67
5	50 mM Cumene hydroperoxide +25 mM ammonium sulfate	201	10	2.9×10^3	$(1.2 \pm 0.09)\times10^{-4}$	47
6	50 mM Cumene hydroperoxide +25 mM ammonium sulfate	167	7	2.0×10^3	$(1.5 \pm 0.3)\times10^{-4}$	52
7	50 mM Cumene hydroperoxide +25 mM ammonium sulfate	207	39	4.4×10^3	$(2.4 \pm 0.3)\times10^{-4}$	61
8	50 mM 2-Butanone peroxide +25 mM ammonium sulfate	108	7	1.6×10^3	$(1.3 \pm 0.1)\times10^{-3}$	25
9	50 mM 2-Butanone peroxide +25 mM ammonium sulfate	201	107	7.4×10^3	$(3.1 \pm 0.2)\times10^{-3}$	47
10[b]	50 mM 2-Butanone peroxide +25 mM ammonium sulfate	153	91	3.5×10^3	$(7.9 \pm 0.4)\times10^{-3}$	53
11[b]	50 mM 2-Butanone peroxide +25 mM ammonium sulfate	107	32	1.7×10^3	$(6.2 \pm 0.7)\times10^{-3}$	54

12[b]	50 mM 2-Butanone peroxide +25 mM ammonium sulfate	98	33	1.1×10^{3}	$(1.0 \pm 0.05)\times10^{-2}$	55
13	50 mM 2-Butanone peroxide +25 mM ammonium sulfate	176	73	1.8×10^{3}	$(9.3 \pm 0.7)\times10^{-3}$	62
14[c]	50 mM 2-Butanone peroxide +25 mM ammonium sulfate	151	133	2.1×10^{3}	$(2.7 \pm 0.4)\times10^{-2}$	71
15	100 mM 2-Butanone peroxide +25 mM ammonium sulfate	100	72	8.1×10^{2}	$(4.8 \pm 1)\times10^{-2}$	52
16	25 mM 2-Butanone peroxide +25 mM ammonium sulfate	175	76	4.1×10^{3}	$(4.2 \pm 0.4)\times10^{-3}$	52
17	5 mM 2-Butanone peroxide +25 mM ammonium sulfate	138	16	4.6×10^{3}	$(8.0 \pm 0.4)\times10^{-4}$	53
18	0.5 mM 2-Butanone peroxide +25 mM ammonium sulfate	180	4	7.3×10^{3}	$(8.3 \pm 0.4)\times10^{-5}$	57
19	100 mM 2-Butanone peroxide +25 mM malonic acid	113	68	3.3×10^{3}	$(1.3\pm 0.2)\times10^{-2}$	52
20	50 mM 2-Butanone peroxide +25 mM malonic acid	157	49	2.3×10^{3}	$(5.1\pm 0.7)\times10^{-3}$	54
21	25 mM 2-Butanone peroxide +25 mM malonic acid	186	32	2.0×10^{3}	$(2.8\pm 0.2)\times10^{-3}$	54
22	5 mM 2-Butanone peroxide +25 mM malonic acid	236	6	1.8×10^{3}	$(4.6\pm 0.5)\times10^{-4}$	54
23	5 mM 2-Butanone peroxide +25 mM ammonium sulfate +0.00002 M HCl	157	25	4.5×10^{3}	$(1.2\pm 0.2)\times10^{-3}$	53

24	5 mM 2-Butanone peroxide +25 mM ammonium sulfate +0.0001 M HCl	152	21	3.4×10^{3}	$(1.3\pm 0.09)\times10^{-3}$	54
25	5 mM 2-Butanone peroxide +25 mM ammonium sulfate +0.001 M HCl	136	30	3.1×10^{3}	$(2.5\pm 0.4)\times10^{-3}$	53
26	α-Pinene SOA	213	12	1.4×10^{3}	$(5.7\pm 0.4)\times10^{-5}$	51
27	Limonene SOA	340	12	4.6×10^{3}	$(2.4\pm 0.1)\times10^{-4}$	54
28	Toluene SOA	-	-	2.7×10^{3}	$(8.3\pm 0.4)\times10^{-4}$	60

[a] Uncertainty of γ_{SO2} in this study was estimated from SO_2 and SMPS measurements. [b] The reproducibility of the γ_{SO2} measurements were estimated from Expt.10-12 to be 26 %. [c] γ_{SO2} measured under high relative humididy condition was corrected by the SO_2 repartioning rate (Fig. S6).

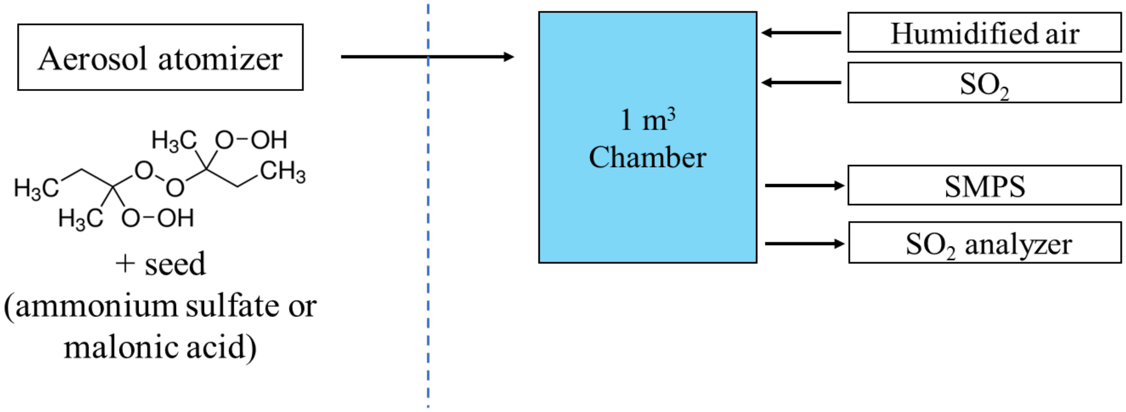

Figure S1. Experimental schematic of measuring SO_2 reactive uptake coefficient onto ammonium sulfate or malonic acid mixed with organic peroxide. Aerosol was generated from the atomizer before being introduced into the chamber.

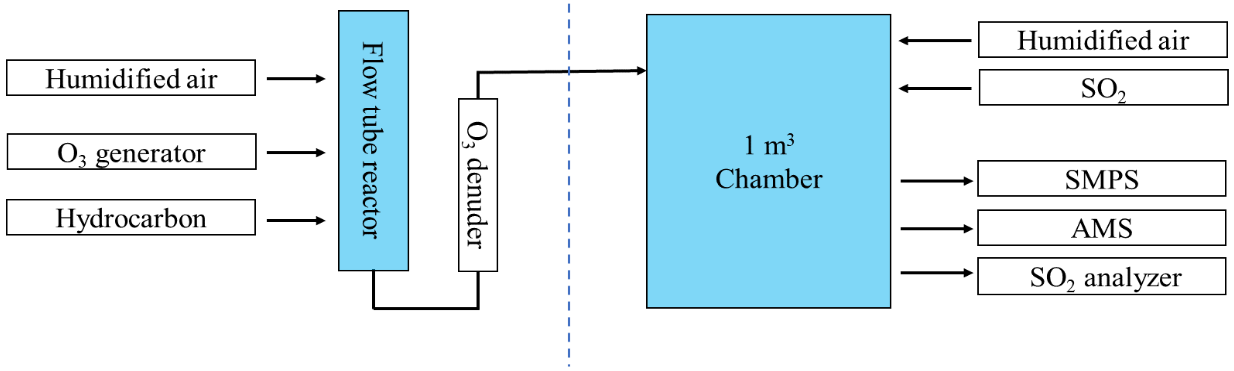

Figure S2. Experimental schematic of measuring SO_2 reactive uptake coefficient onto different types of SOA. Secondary organic aerosol was generated in the flowtube reactor by photooxidation (toluene) or ozonolysis (limonene and α-pinene). Excess amount of O_3 was removed using an O_3 denuder to avoid SO_2 consumption caused by O_3 inside the smog chamber.

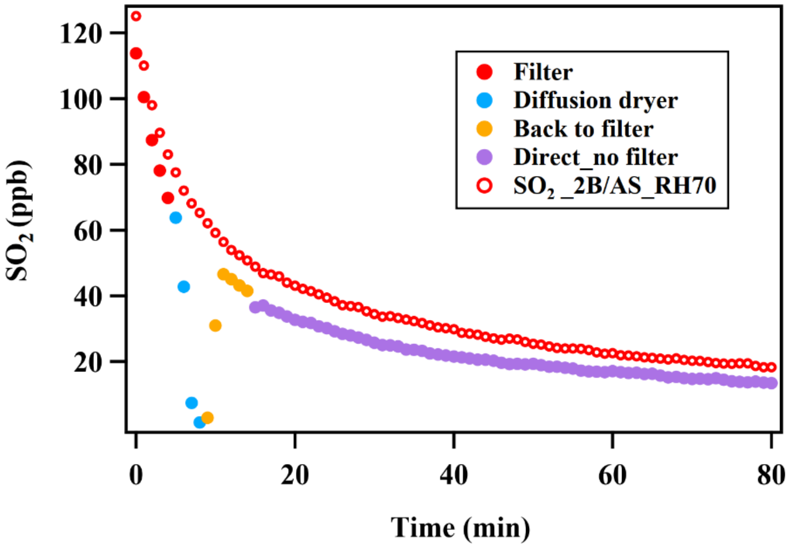

Figure S3. To test whether the observed SO_2 decay is caused by reactions with organic peroxide accumulated on the inline PTFE filter installed in front of the SO_2 analyzer, the first experiment (**solid red circle**) was conducted under the same condition of the second experiment (empty red circle), but the SO_2 measurement was taken with filter (**red**), through diffusion dryer (**blue**), back to filter (**orange**) and eventually direct measurement without filter (**purple**). Measurements taken with/without filter in front of the SO_2 analyzer show the same time series of SO_2 decay during the experiment, except when a diffusion dryer was placed inline (causing SO_2 loss by diffusion). These trends demonstrate that the observed SO_2 decay is not likely caused by reactions with organic peroxides accumulated on the PTFE filter in front of the SO_2 analyzer.

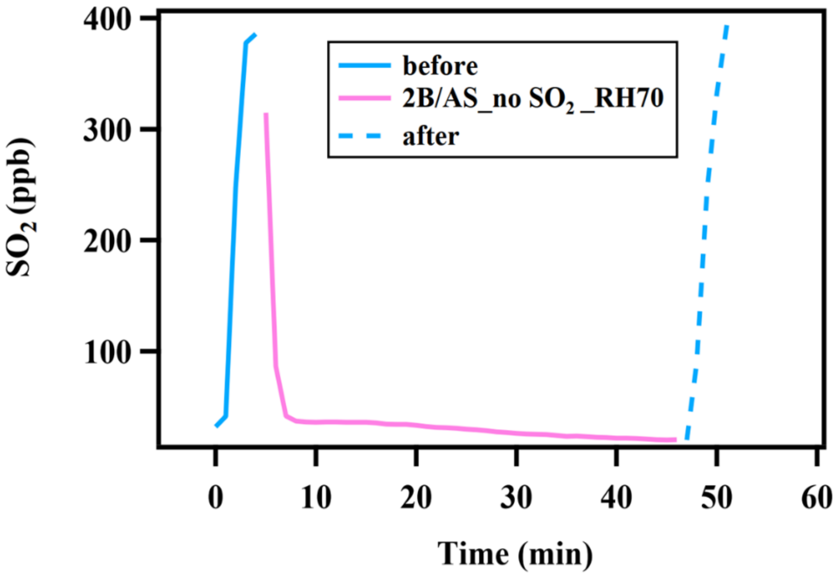

Figure S4. To test whether the observed SO$_2$ decay is caused by the organic peroxide trapped inside the analyzer during monitoring, SO$_2$ analyzer (Model 43i, Thermo Scientific) was directly connected to a stream of standard SO$_2$ gas with a constant SO$_2$ mixing ratio, and then switched to a chamber filled with organic peroxide-containing ammonium sulfate aerosol (no SO$_2$) under RH 70% for 40 minutes. Eventually, the SO$_2$ analyzer was switched back to the standard SO$_2$ gas stream. The response of the SO$_2$ analyzer towards standard SO$_2$ gas shows similar rates before and after measuring organic peroxide-containing ammonium sulfate from the chamber, indicating the significant SO$_2$ decay observed in our study is not caused by any reaction inside the SO$_2$ analyzer.

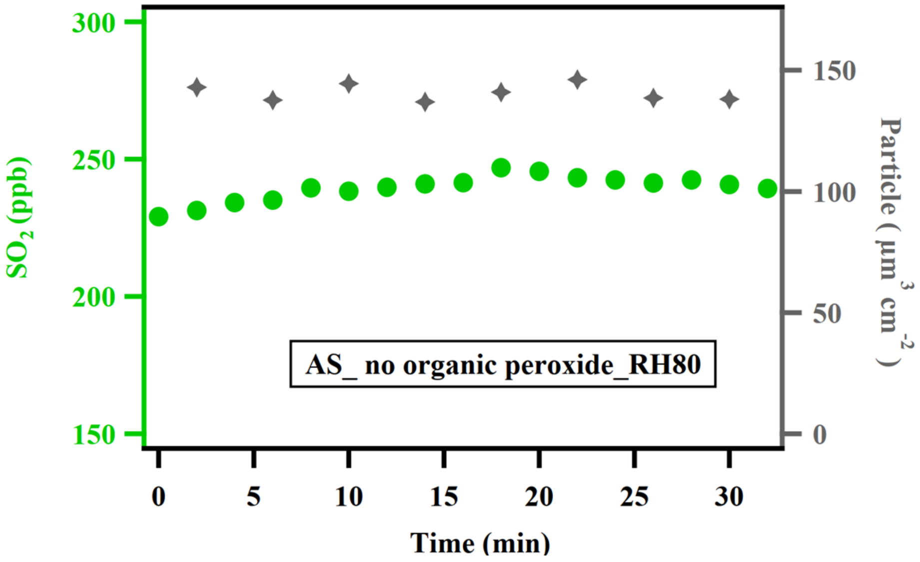

Figure S5. SO_2 time series in a blank control experiment. SO_2 was introduced into a chamber containing 140 µm^3 cm^{-3} of ammonium sulfate aerosol with no organic peroxide at an RH of 80 %. No SO_2 decay was observed. Deliquesced ammonium sulfate aerosol is not a significant contributor to the decay of SO_2 under RH 80 % observed in chamber experiment, indicating the dominant sink of SO_2 during the other chamber experiment is the reaction with organic peroxides.

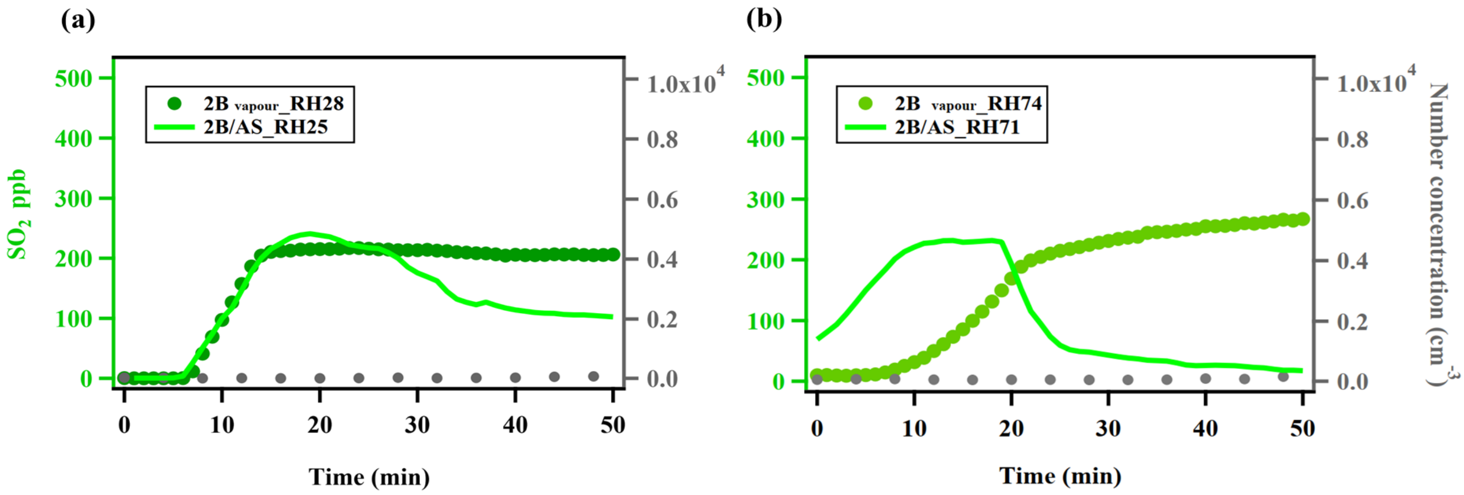

Figure S6. SO_2 consumption by 2-butanone organic peroxide vapor under dry (RH 28 %) and humid (RH 74 %) condition during chamber experiment. Organic peroxide vapor was introduced by placing an inline PTFE filter between the atomizer and chamber in order to remove particle-phase peroxides. No significant SO_2 decay was observed when only organic peroxide vapor was present under both dry and humidity conditions. For comparison, the SO_2 time series with particulate organic peroxide-ammonium sulfate mixture showed significant SO_2 decay. However, we noticed there was SO_2 repartitioning from the chamber wall under high RH (74 %), and this SO_2 repartitioning rate was used to correct the γ_{SO2} measured under high RH conditions (above 70 %, Expt.14).

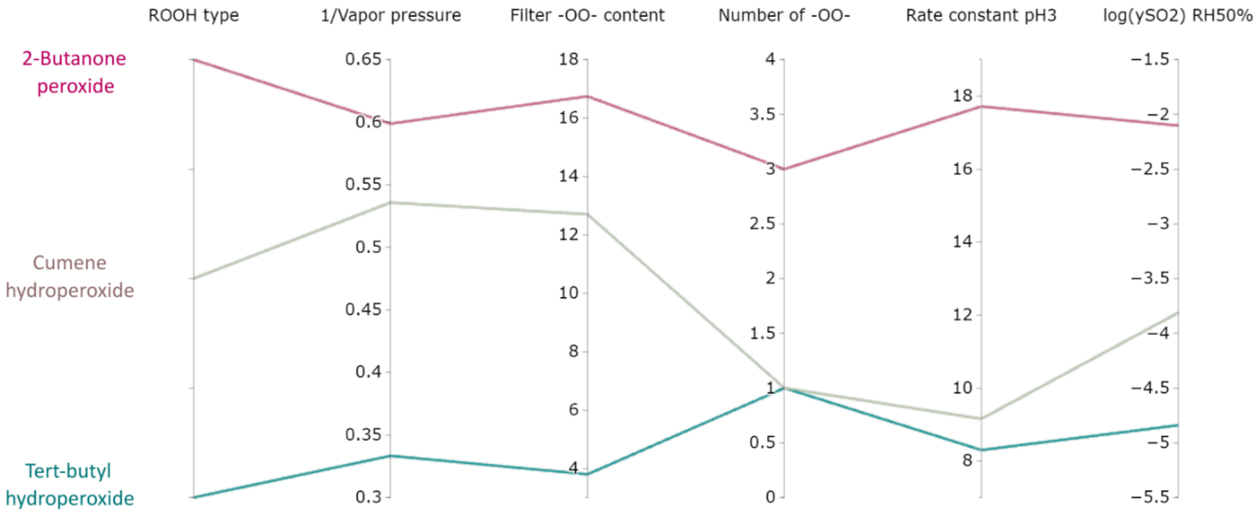

Figure S7. Visualization of organic peroxides' characteristics and γ_{SO2} for chamber experiments at RH 50% and a total peroxide to ammonium sulfate ratio of 2:1. γ_{SO2} is positively related with aqueous phase second order reaction rate constant (M^{-1} s^{-1}) at pH 3 (which is associated with number of -OO- group) and with particulate -OO- content (%) on the filter (which is negatively associated with vapor pressure (kPa)).

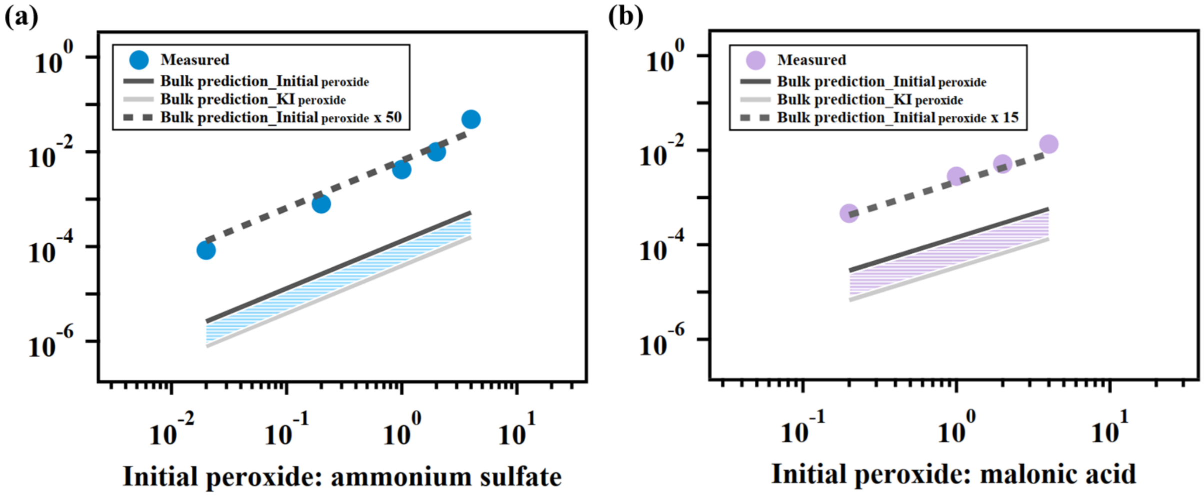

Figure S8. Comparison between measured γ_{SO2} and predicted γ_{SO2} for experiments with different peroxide to ammonium sulfate ratios (a) and peroxide to malonic acid ratios (b). The γ_{SO2} predictions were made based on initial peroxide content assuming no partitioning and off-line KI measured peroxide content, respectively. The shadowed area is the uncertainty in γ_{SO2} prediction in terms of particulate peroxide content. The discrepancy observed for ammonium sulfate aerosol (50 times) is larger than that of malonic acid (15 times) under the same experimental conditions.

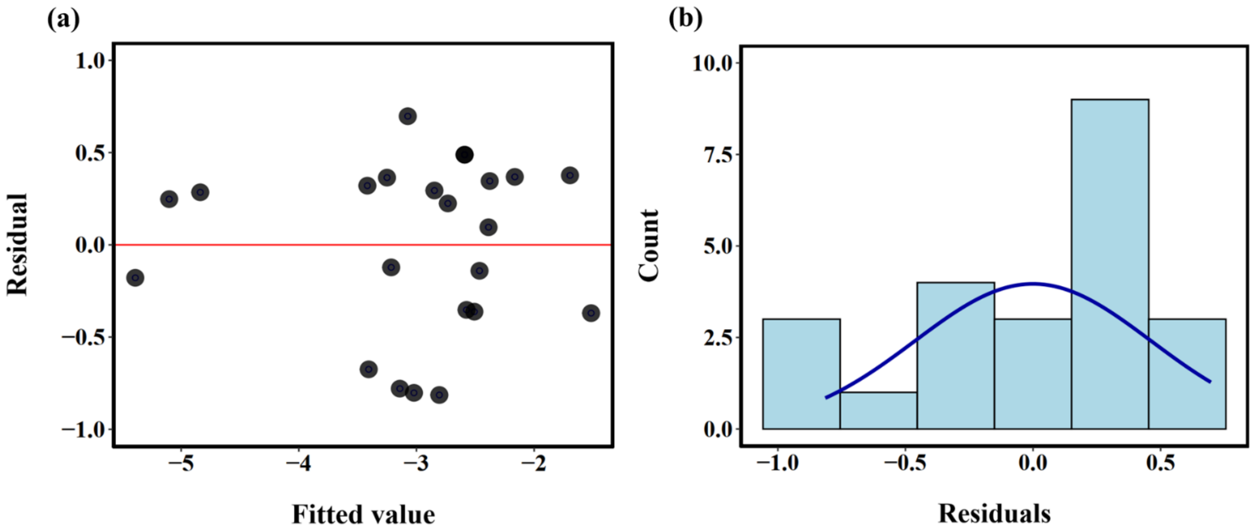

Figure S9. Residuals for individual data points of log γ_{SO2} (a) and the residual distribution (b) from the multilinear regression follows a normal distribution.

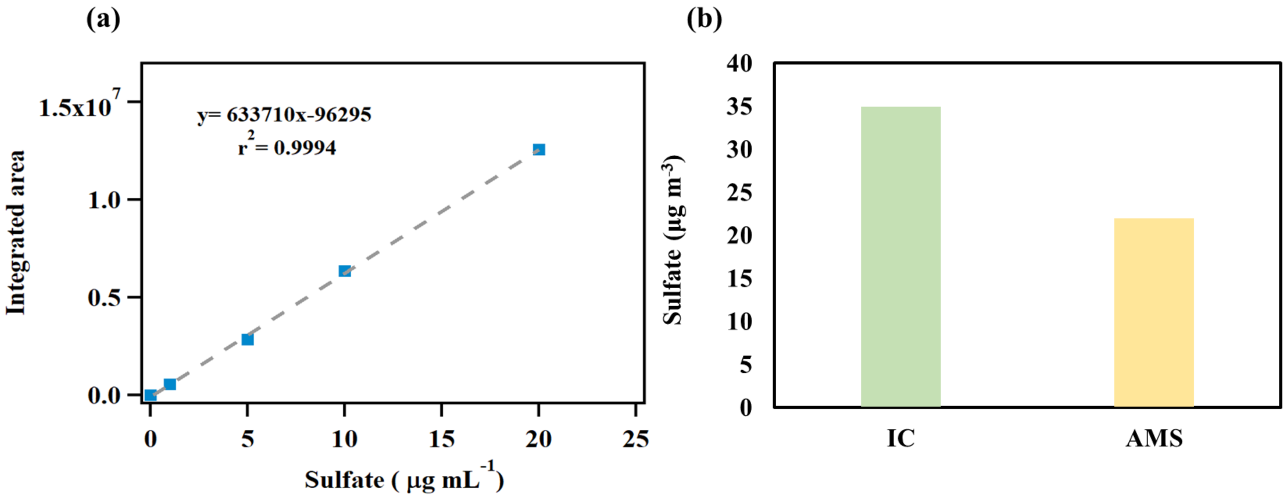

Figure S10. Comparison of sulfate measured by AMS and by ion chromatography (IC). Aerosol from the chamber SO_2 uptake experiments was collected, extracted and measured by an IC (Perkin Elmer, USA). (a) IC calibration curve for SO_4^{2-}. (b) Sulfate quantification comparison between the off-line IC measurement and on-line AMS measurement. Results from AMS presents a lower sensitivity than IC in terms of quantifying total aerosol sulfate during the chamber experiment in this study.

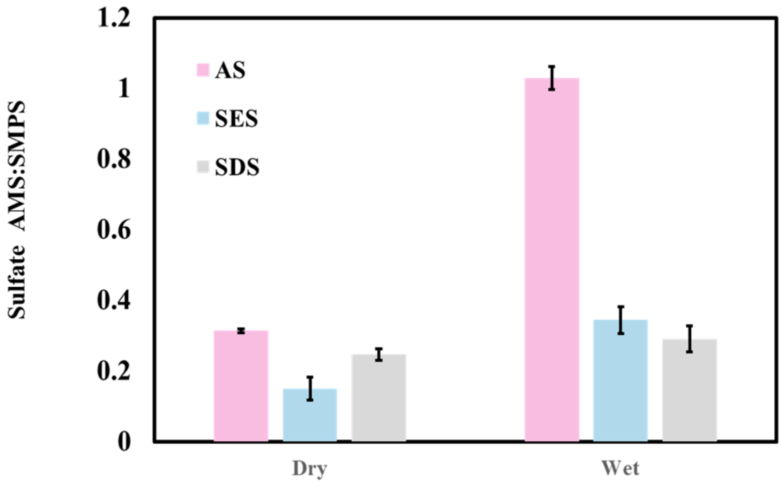

Figure S11. Comparison of SMPS measured sulfate and AMS measured sulfate under dry (with diffusion drier) and humid conditions (RH 80 %) for ammonium sulfate (**AS**), sodium ethyl sulfate (**SES**) and sodium dodecyl sulfate (**SDS**). AMS collection efficiencies for sulfate were considered to be 0.5 and 1 under dry and humid conditions, respectively(Matthew et al., 2008;Middlebrook et al., 2012). Under humid condition, the AMS quantified sulfate can be 3-5 times lower than the SMPS quantified sulfate in terms of organosulfate. The less effective response of AMS sulfate quantification towards organosulfate was also investigated in the work by Chen et al.(2019).

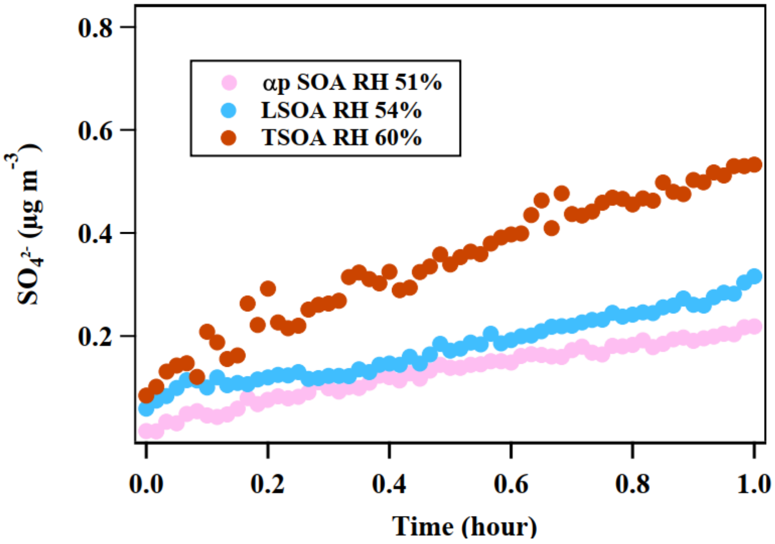

Figure S12. Time series of sulfate formation monitored by AMS during chamber experiments for the α pinene SOA (**αp SOA**), limonene SOA (**LSOA**) and toluene SOA (**TSOA**). The γ_{SO2} of TSOA was estimated from the γ_{SO2} of LSOA, and corrected by the sulfate formation ratio between the two SOA systems, where $\frac{d_{SO2\_TSOA}}{d_{SO2\_LSOA}} = \frac{AMS_{SO4\_TSOA}}{AMS_{SO4\_LSOA}}$.

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