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# The future of airborne sulfur-containing particles in the absence of fossil fuel sulfur dioxide emissions

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Sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), formed from oxidation of sulfur dioxide (SO<sub>2</sub>) emitted during fossil fuel combustion, is a major precursor of new airborne particles, which have well-documented detrimental effects on health, air quality, and climate. Another precursor is methanesulfonic acid (MSA), produced simultaneously with SO<sub>2</sub> during the atmospheric oxidation of organosulfur compounds (OSCs), such as dimethyl sulfide. In the present work, a multidisciplinary approach is used to examine how contributions of H<sub>2</sub>SO<sub>4</sub> and MSA to particle formation will change in a large coastal urban area as anthropogenic fossil fuel emissions of SO<sub>2</sub> decline. The 3-dimensional University of California Irvine–California Institute of Technology airshed model is used to compare atmospheric concentrations of gas phase MSA, H<sub>2</sub>SO<sub>4</sub>, and SO<sub>2</sub> under current emissions of fossil fuel-associated SO<sub>2</sub> and a best-case futuristic scenario with zero fossil fuel sulfur emissions. Model additions include results from (i) quantum chemical calculations that clarify the previously uncertain gas phase mechanism of formation of MSA and (ii) a combination of published and experimental estimates of OSC emissions, such as those from marine, agricultural, and urban processes, which include pet waste and human breath. Results show that in the zero anthropogenic SO<sub>2</sub> emissions case, particle formation potential from H<sub>2</sub>SO<sub>4</sub> will drop by about two orders of magnitude compared with the current situation. However, particles will continue to be generated from the oxidation of natural and anthropogenic sources of OSCs, with contributions from MSA and H<sub>2</sub>SO<sub>4</sub> of a similar order of magnitude. This could be particularly important in agricultural areas where there are significant sources of OSCs.

methanesulfonic acid | sulfuric acid | new particle formation | atmosphere | fossil fuel

Airborne particles play an essential role in many serious environmental issues, including visibility reduction (1) and climate change (2), and have been linked to health problems associated with air pollution (3). On a global basis, sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) is the most significant contributor to new particle formation in air, likely through reaction with ammonia and amines (4–6). In air, the dominant source for H<sub>2</sub>SO<sub>4</sub> is the oxidation of SO<sub>2</sub> from combustion of sulfur-containing fossil fuels. Another source of new particle formation in air is the oxidation of organosulfur compounds (OSCs) generated by biological processes and agricultural activities (7–10). For example, oceans are a significant source of dimethyl sulfide (CH<sub>3</sub>SCH<sub>3</sub>, DMS) (10), whereas a variety of related species such as methanethiol (CH<sub>3</sub>SH, MTO), dimethyl disulfide (CH<sub>3</sub>SSCH<sub>3</sub>, DMDS), and dimethyl trisulfide (CH<sub>3</sub>SSSCH<sub>3</sub>, DMTS) originate from livestock and farming practices (11–15). It has been shown that even human breath contains OSCs (16, 17). Atmospheric oxidation of OSCs generates not only SO<sub>2</sub> (which ultimately converts into H<sub>2</sub>SO<sub>4</sub>) but also methanesulfonic acid [CH<sub>3</sub>S(O)(O)OH, MSA] (18), which also reacts with amines to generate new particles in air in the presence of water vapor (19, 20). Increasing regulations are driving the sulfur content and use of fossil fuels down (21), resulting in

declining atmospheric SO<sub>2</sub> concentration and particulate sulfate concentrations. A key question for understanding future impacts of particles and for the development of cost-effective control policies is the extent to which atmospheric particulate matter can be controlled through regulation of fossil fuel combustion against a background of OSCs. We report here a distinctive multidisciplinary approach that integrates chemical mechanism development, quantum chemical calculations, field measurements, and 3D modeling to examine this issue in the context of a large, urban coastal area, the South Coast Air Basin of California (SoCAB).

## Results and Discussion

The University of California Irvine–California Institute of Technology (UCI-CIT) model domain includes the Pacific Ocean on the west side, heavily populated urban areas, and an agricultural region with large cattle feedlots and associated sources around Chino, California, and constitutes the perfect domain for this study. The model includes spatially and temporally resolved emissions and typical meteorological conditions for this region, as well as a detailed chemical mechanism described as the 2005 base case (22). However, OSCs had not been included in this base case and some adjustments had to be made before running simulations (see *SI Appendix, section 1 and Table S1* and discussion below for detailed OSC chemistry). First, the original emission rates of SO<sub>2</sub>

## Significance

Sulfur dioxide (SO<sub>2</sub>) via its oxidation to sulfuric acid is a major source of airborne particles, which impact visibility, health, and climate. Sources of SO<sub>2</sub> include the combustion of sulfur-containing fossil fuels and the oxidation of organosulfur compounds (OSCs) such as dimethyl sulfide. We show that as fossil fuel combustion is phased out in an urban coastal area, particle formation will decrease substantially but still continue at a reduced rate due to the contribution from OSC oxidation products. Furthermore, methanesulfonic acid generated simultaneously in OSC oxidation will become a significant contributor to particle formation, which should be taken into account in predictive models of air pollution and climate and may be especially important in agricultural areas with significant OSC sources.

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The authors declare no conflict of interest.

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and H<sub>2</sub>SO<sub>4</sub> (3% of total anthropogenic SO<sub>2</sub> emitted) in the model (including emissions, boundary conditions, and initial conditions) were decreased by a factor of 4 compared with the 2005 base case to be consistent with the decrease in measured ambient SO<sub>2</sub> concentrations since 2005 (*SI Appendix*, section 1 and Fig. S1). This scenario is hereafter described as “representative of the year 2011–2013.” A separate scenario was also run corresponding to a best-case futuristic scenario with no fossil fuel SO<sub>2</sub> (emissions, initial conditions, and boundary conditions all set to zero). For the scenario representative of the years 2011–2013, the boundary conditions include anthropogenic sources of SO<sub>2</sub> generated from Asia that are transported across the Pacific Ocean, emissions from ships in shipping lanes, along with sources from other states surrounding the SoCAB. In the zero anthropogenic SO<sub>2</sub> emissions scenario, those were turned off. Lastly, in the standard version of the model, H<sub>2</sub>SO<sub>4</sub> partitions into existing particles or forms new particles if the concentrations exceed those for nucleation (23). However, significant uncertainties remain in quantitatively describing new particle formation from gas phase H<sub>2</sub>SO<sub>4</sub> and MSA, especially given the recently recognized role of amines (4, 5). To compare the relative contributions of H<sub>2</sub>SO<sub>4</sub> and MSA to new particle formation, nucleation and uptake into existing particles were turned off in the model to leave these species in the gas phase. We have shown in a previous study that under certain conditions, MSA and H<sub>2</sub>SO<sub>4</sub> can form new particles at similar rates (20). As long as the processes such as reactions with amines that convert H<sub>2</sub>SO<sub>4</sub> and MSA to new particles are similar for these two acids, their respective concentrations should provide an estimate of their potential relative contributions to new particle formation under different scenarios.

Second, three major contributors to OSCs were incorporated into the model: (i) oceanic emissions, (ii) agricultural activities, and (iii) urban sources. The first was captured by including a typical average emission flux for DMS of 10 μmol S m<sup>-2</sup> d<sup>-1</sup> in the summer months (10) in the model cells that encompass the coastal waters. Agriculture is a second potential source (11–15, 24–26). It was reported in previous studies that both NH<sub>3</sub> and OSC emissions are associated with livestock activities and that their concentrations were correlated (27, 28). Because emission flux measurements were not possible at the time for OSCs, we chose to estimate fluxes of OSCs from agricultural activities in the SoCAB by simultaneously measuring OSC and NH<sub>3</sub> ambient concentrations adjacent to a cattle feedlot in Chino, California (*SI Appendix*, sections 1 and 2) before dawn to avoid photochemistry. Fluxes for the OSCs were then estimated using the ratio of the measured concentrations in air to those of NH<sub>3</sub>, whose emission fluxes are included in the base case of the model as indicated in *SI Appendix*, section 1 and Fig. S2. The average measured concentrations of DMS and DMDS were 1.2 ppb and 28 ppt, respectively, with a ratio of DMS to NH<sub>3</sub> concentrations of  $(7.6 \pm 1.4) \times 10^{-3}$  and of DMDS to NH<sub>3</sub> of  $(1.9 \pm 1.5) \times 10^{-4}$  (1 σ). Applying these to the nine model cells with agricultural activities around the Chino area yields emission fluxes of NH<sub>3</sub>, DMS, and DMDS of 31, 0.24, and  $5.8 \times 10^{-3}$  μmol m<sup>-2</sup> d<sup>-1</sup>, respectively. Finally, heavily populated urban areas represent a third source, which includes emissions from human breath and pet waste. DMS was reported in human breath of healthy subjects at an average concentration of 13.8 ppb (17). The total volume of air inhaled and exhaled per day for an average person is 10,800 L (29), so that one person will typically emit 6.1 μmol of DMS per day. These human-associated emissions of DMS were incorporated into the model based on the population in each cell. Lastly, to assess the potential contribution from pets, measurements using proton-transfer mass spectrometry were made of the headspace of trash bins from a residential area where the bins are used mainly for pet waste. Methanethiol (MTO), DMS, and DMDS were unambiguously detected and quantified (*SI*

*Appendix*, section 2, Fig. S3, and Tables S2 and S3). Emission fluxes were obtained by closing off the top of the container and measuring the increase in concentration of the OSCs with time. These were incorporated into the model on a basis proportional to population density. Potential emissions from other sources such as soils, vegetation (9), biomass burning (30), wetlands, and landfills, as well as emissions of other OSCs, such as hydrogen sulfide and carbonyl sulfide, were not included in the model because of the large uncertainties associated with their emissions estimates.

Third, although many of the individual steps have been established experimentally (18), surprisingly, the mechanism of production of MSA from OSC gas phase oxidation by hydroxyl radicals (OH, daytime) and nitrate radicals (nighttime) remains unclear (31). The CH<sub>3</sub>S(O)(O)O• free radical is likely the key intermediate (*SI Appendix*, section 3 and Fig. S4). The mechanism for the formation of MSA via hydrogen abstraction by CH<sub>3</sub>S(O)(O)O• from water and organic compounds, proposed earlier (18, 32, 33), were explored here using quantum chemical calculations. Results show that the ΔH for the CH<sub>3</sub>S(O)(O)O• + H<sub>2</sub>O reaction is +6 kcal·mol<sup>-1</sup>, consistent with earlier studies showing that the reverse reaction is exothermic (34). On the other hand, reactions of the CH<sub>3</sub>S(O)(O)O• radical with organic compounds such as formaldehyde (HCHO) or methane (CH<sub>4</sub>) are more favorable. Fig. 1 shows that for HCHO, an initial complex (Min-3) is formed, which proceeds through transition state TS-2 and a second minimum Min-4 to form MSA and the HCO radical in what is essentially a barrierless reaction (*SI Appendix*, section 3, Fig. S5, and Table S4). Thus, hydrogen abstraction from aldehydes is fast and provides a feasible pathway to form MSA. As seen in Fig. 1, similar minima and transition states as for HCHO occur for the CH<sub>4</sub> reaction, but the energetics are not as favorable. Given that higher alkanes have weaker C–H bonds, this is a lower limit, and it may be that abstraction of a hydrogen atom from larger hydrocarbons can also contribute to MSA in air. These theoretical studies firmly establish that the mechanism of gas phase MSA formation is occurring via hydrogen abstraction from organics by the CH<sub>3</sub>S(O)(O)O• radical. This chemistry, detailed in *SI Appendix*, section 1 and Table S1, was incorporated into the UCI-CIT airshed model (22). Note that different mechanisms for DMS oxidation have been proposed previously (31, 33, 35–39). The intent of this study was to provide a reasonable mechanism for the oxidation of OSCs and to demonstrate that there are different non-fossil-fuel-related sources of sulfur compounds throughout the SoCAB that will remain as the dominant anthropogenic SO<sub>2</sub> emissions continue to decrease. As

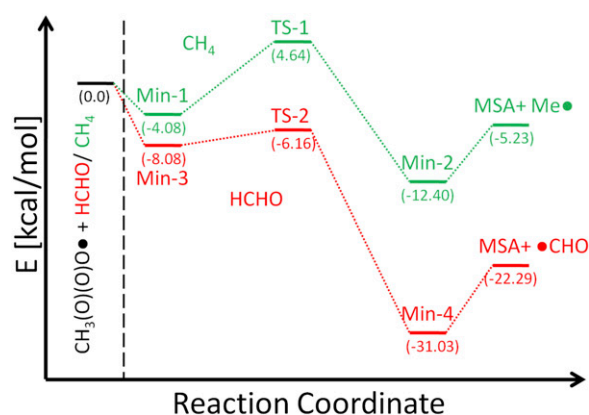
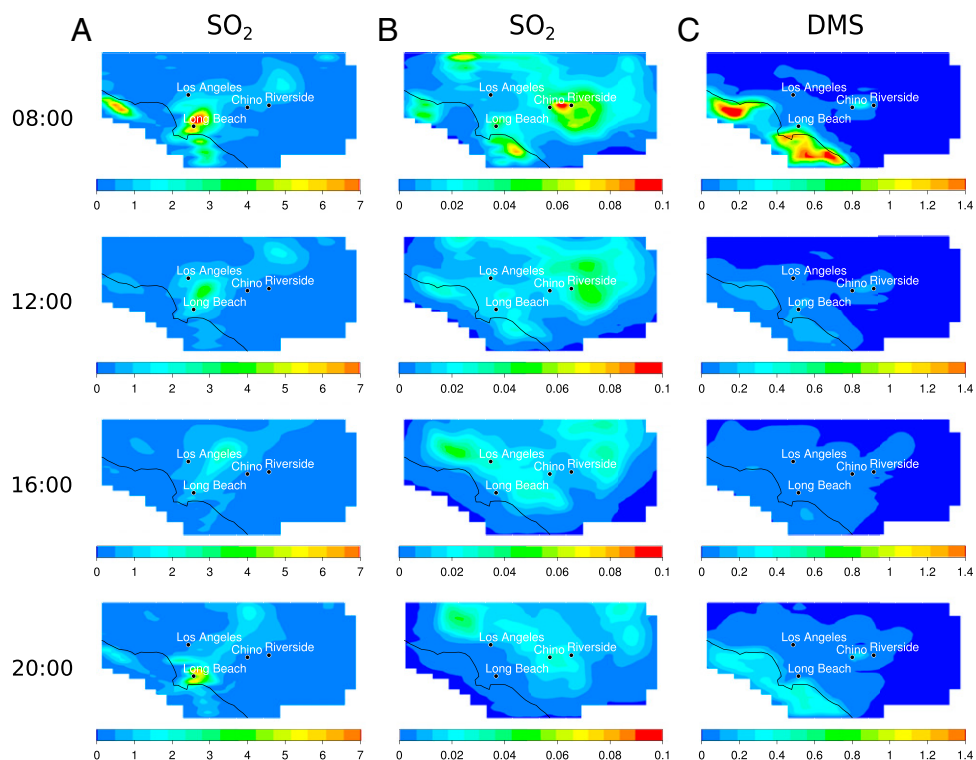


Fig. 1. Potential energy diagram for the reaction of CH<sub>3</sub>S(O)(O)O• radical with methane (CH<sub>4</sub>) or formaldehyde (HCHO). See *SI Appendix*, section 3 for details of the theory applied.







**Fig. 3.** Model-predicted gas phase  $\text{SO}_2$  and DMS concentrations (ppb) in the SoCAB at 08:00 h, 12:00 h, 16:00 h, and 20:00 h with urban, agriculture, and ocean OSCs emission sources included. (A)  $\text{SO}_2$  concentrations (ppb) with  $\text{SO}_2$  and  $\text{H}_2\text{SO}_4$  emissions representative of 2011–2013. (B)  $\text{SO}_2$  concentrations (ppb) with sulfur fossil fuel emissions, boundary conditions, and initial conditions for  $\text{SO}_2$  and  $\text{H}_2\text{SO}_4$  set to zero. (C) DMS concentrations (ppb) with sulfur fossil fuel emissions, boundary conditions, and initial conditions for  $\text{SO}_2$  and  $\text{H}_2\text{SO}_4$  set to zero.

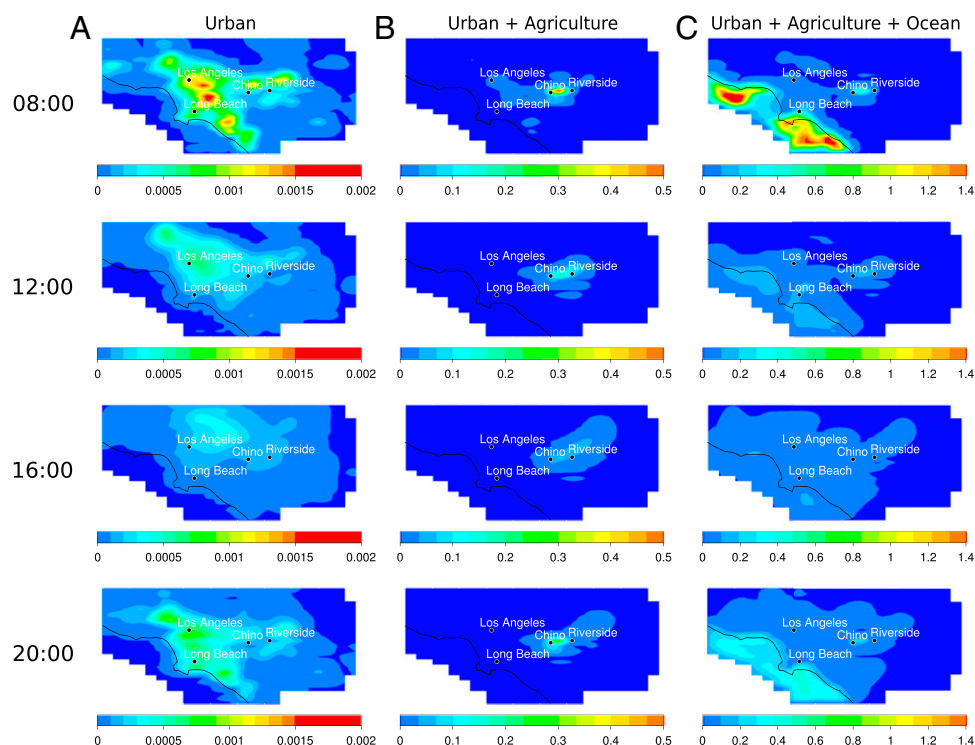
surprising. As described in the mechanism (*SI Appendix, section 3 and Fig. S4*), MSA formation is particularly influenced by  $\text{NO}_x$ . A positive correlation between MSA formation and  $\text{NO}_x$  concentration has been previously reported in laboratory experiments (41). Thus, fresh MSA is formed once the DMS plume encounters enough  $\text{NO}_x$  for the reactions to occur, such as the ports located around Long Beach, as well as urban areas further inland (*SI Appendix, section 4 and Fig. S6*). This explains why the  $\text{SO}_2$  distribution largely follows the DMS plume contour, whereas MSA is present in more localized and concentrated areas associated with higher  $\text{NO}_x$  concentrations. Again, a second hot spot can be seen north of Riverside, which is the residual from the chemistry and meteorology occurring during days 1 and 2. In brief, the localized hot spots for the different species are governed by the emissions, chemistry, and the unique meteorology of the domain.

To investigate the relative source strengths of OSCs, the respective source contributions for DMS are presented in Fig. 4, which indicates the magnitude of the different contributions as well as differences in the spatial distributions of the three types of sources. Results for DMS are presented here as a representative for OSCs, as it is the more abundant species emitted. Fig. 4 clearly shows that the OSCs produced from the ocean overwhelm the other contributions (peak maximum DMS predicted at 1.4 ppb). Agricultural activities also contribute significantly to the total DMS emitted, with up to about a third of the total DMS peak maximum concentration observed from this source localized around the Chino/Riverside area. Urban emissions alone produce a peak maximum DMS concentration of only 0.1% of that seen from oceanic sources. For completeness, corresponding source-specific predicted concentrations for MSA,  $\text{SO}_2$ , and  $\text{H}_2\text{SO}_4$  are presented in *SI Appendix, Figs. S7–S9 (SI Appendix, section 4)*, respectively.

Ambient submicron particle measurements were made with a high-resolution time-of-flight aerosol mass spectrometer (AMS)

at the north campus of the University of California Irvine, which is located in the SoCAB approximately 5 miles inland from the Pacific Ocean. Peaks typical of OSCs were observed on many days; *SI Appendix, section 5 and Fig. S10* show an average mass spectrum of the OSC-specific ion signals identified by high resolution and clearly shows the presence of high-intensity peaks at  $m/z$  78, 79, and 96 corresponding to  $\text{CH}_2\text{SO}_2^+$ ,  $\text{CH}_3\text{SO}_2^+$ , and  $\text{CH}_4\text{SO}_3^+$ , respectively, which are characteristic of MSA (42). Some of these days also show the presence of peaks typical of sea salt chloride. Fig. 5 shows data in which NaCl and MSA are correlated in some cases (Fig. 5A) and uncorrelated in others (Fig. 5B), suggesting that nonoceanic sources of MSA can also be important in this location, despite its proximity to the Pacific Ocean. Previous reports of MSA in particles in Riverside, California were attributed to oxidation of oceanic emissions during transport (43). On the other hand, measurements of MSA in particles in the Central Valley of California, a major agricultural area, were reported to be independent of transport from the coast (42). This finding is in good agreement with our results, indicating that continental sources, especially from agricultural activities, may be significant sources for MSA. Results from this study have particular significance for future air quality in agricultural regions where emissions of OSCs can be much higher than those indicated by the measurements in the current study. For example, *SI Appendix, section 6 and Fig. S11* show DMS in and around a dairy located in the Central Valley (about 28 miles south of Fresno, California), with levels within the dairy itself up to 12 ppb. Exploring alternative agricultural practices that minimize such emissions and their impacts on air quality, visibility, health, and climate may be prudent in such areas in the future.

In summary, removing anthropogenic  $\text{SO}_2$  emissions from a large coastal urban area causes MSA to become relatively more important as a particle source and does not decrease  $\text{H}_2\text{SO}_4$  to zero. For



**Fig. 4.** Model-predicted gas phase DMS concentrations (ppb) at 08:00 h, 12:00 h, 16:00 h, and 20:00 h with sulfur fossil fuel emissions, boundary conditions, and initial conditions for  $\text{SO}_2$  and  $\text{H}_2\text{SO}_4$  set to zero. (A) Only urban OSC emission sources including DMS emissions from humans and DMS, DMDS, and MTO from pet waste. (B) Urban and agriculture OSC emission sources (same conditions as A plus DMS and DMDS emissions from Chino, California). (C) Urban, agriculture, and ocean OSC emission sources (same conditions as B plus DMS from ocean).

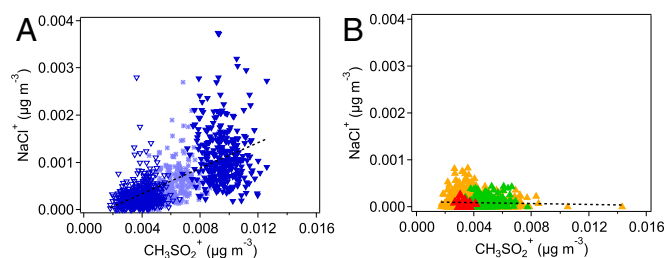
example, the ratio of domain-wide average concentrations of MSA/ $\text{H}_2\text{SO}_4$  changes from 0.005 for the 2011–2013 case to 0.24 for the zero fossil fuel emissions case. Note, however, that these are likely to be lower limits to the MSA/ $\text{H}_2\text{SO}_4$  ratio for the 2011–2013 scenario, as OSC emissions from wetlands, soils, vegetation, and so forth have not been included. Because  $\text{H}_2\text{SO}_4$  and MSA are known precursors to new particles, the number concentration of particles should also decrease significantly, as long as scavenging by existing particles is not important. The predicted 21 ppt and 14 ppt peak concentrations of MSA and  $\text{H}_2\text{SO}_4$  observed, respectively, at 06:00 h and 14:00 h correspond to mass concentrations of only  $0.08 \mu\text{g}\cdot\text{m}^{-3}$  and  $0.06 \mu\text{g}\cdot\text{m}^{-3}$ , respectively, well below current air quality standards for  $\text{PM}_{2.5}$ . However, because of its acidity,  $\text{H}_2\text{SO}_4$  (and potentially MSA) can enhance the formation and growth of secondary organic aerosol (SOA) from organic compounds (5, 44, 45), including those produced by homogeneous nucleation of low-volatility species (46). This process would result in higher particle mass concentrations than those predicted based on the acids alone. The importance of this process is not clear in the SoCAB as amines and ammonia are always present, especially in agriculture areas where they will neutralize the sulfur-containing acid, forming ammonium (or aminium) sulfate salt particles. On the other hand, ammonium sulfate has also been shown to react in particles to yield light-absorbing “brown” carbon (47–49).

## Materials and Methods

Details of the experimental, theoretical, and modeling approaches are found in *SI Appendix*. Quantum chemical calculations were carried out to determine the energy barriers and total energetics of potential reactions of the  $\text{CH}_3\text{S(O)(O)O}^\bullet$  radical to form MSA. The CCSD(T) method used with Dunning’s cc-pV(T+d)Z basis set (50, 51) along with the restricted open-shell approach as implemented in Molpro package (52) was applied to optimize geometries of isolated species. Complexes and transition states were optimized using the multiconfigurational self-consistent field (MCSCF) method. Single point calculations using the CCSD(T)/cc-pV(T+d)Z method were performed to

obtain energies for reaction profiles. The harmonic approximation with the CCSD(T)/cc-pV(T+d)Z method was used to estimate thermodynamic values for the structures.

The atmospheric model calculations were performed using the UCI-CIT regional airshed model (22). The meteorological conditions were identical in all runs and were taken from August 27–29, 1987, for which the model has been tested previously (22, 53–55) and which represent an ideal set of conditions for modeling a pollution episode (22). The 2005 baseline emissions inventory documented in the 2007 Air Quality Management Plan formulated by the South Coast Air Quality Management District (56) was used for all species, except  $\text{SO}_2/\text{H}_2\text{SO}_4$ . Emission rates of all species present in the inventory, including  $\text{NO}_x$ , are kept constant for each run, with the exception of  $\text{SO}_2/\text{H}_2\text{SO}_4$ , as described earlier. Emissions of MTO, DMS, and DMDS from various sources obtained from the literature (10, 17) or from direct measurements as detailed in *SI Appendix, section 2* were incorporated into the model.



**Fig. 5.** Plots of  $\text{Na}^{35}\text{Cl}^+$  ion versus MSA ion ( $\text{CH}_3\text{SO}_2^+$ ). (A) NaCl and MSA are correlated (overall  $r^2 = 0.41$ ) for (light blue  $\star$ ) August 2, 2012 (9:15–14:20), (dark blue  $\nabla$ ) August 27, 2012 (10:00–20:05), and (dark blue  $\blacktriangledown$ ) August 31, 2012 (10:20–16:50). (B) NaCl and MSA are uncorrelated (overall  $r^2 = 0.0023$ ) for (orange  $\blacktriangle$ ) July 28, 2010 (10:10)–July 29, 2010 (15:00), (green  $\blacktriangle$ ) May 14, 2012 (10:35–13:55), and (red  $\blacktriangle$ ) August 26, 2014 (13:50–14:05). Measurements were made in Irvine, California. Mass loading for NaCl is uncorrected for its low sensitivity in the AMS due to inefficient vaporization. Data points represent 1–2-min sampling times. Dashed lines are linear fits to all data points in each plot.

In addition, a detailed oxidation mechanism for OSCs was added to the model (*SI Appendix, sections 1 and 3*), including reactions of the  $\text{CH}_3\text{S(O)(O)}^\bullet$  radical with HCHO and larger aldehydes.

Measurements of gas phase OSCs were made using high-resolution time-of-flight proton transfer mass spectrometry (PTR-ToF-MS 8000, Ionicon Analytik) (57, 58) and gas chromatography coupled with flame ionization detector (Hewlett Packard 6890) of air samples collected in electropolished

stainless steel canisters (59). MSA and markers for sea salt in ambient particles were measured using a high-resolution time-of-flight AMS (Aerodyne) (60).

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