

Supplementary Information:

Ozone oxidation of oleic acid surface films decreases aerosol CCN activity

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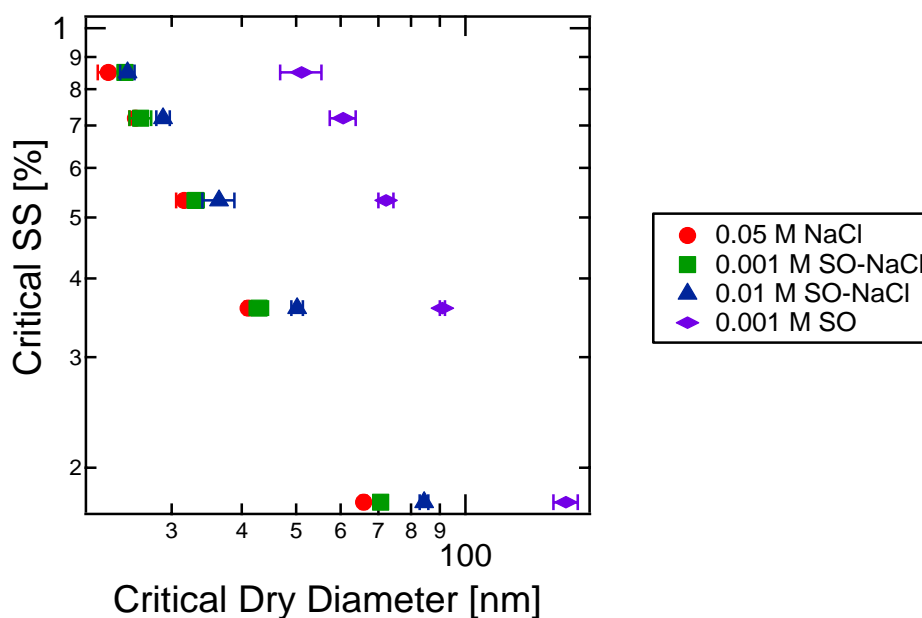


Figure S1. CCN activity of 0.05 M NaCl with increasing concentrations of SO towards pure 0.001 M SO.

Table 1. Power Log Fits and κ parameters of SO/NaCl/Na₂SO₄/H₂SO₄ oxidation experiments

	Power Log Fit	κ (avg)
0.001 M SO, Water, (fit to NaCl SS%)	-1.491	0.118 ± 0.004
0.001 M SO, Water, (fit to Na ₂ SO ₄ SS%)	-1.436	0.119 ± 0.003
NaCl	-1.503	1.378 ± 0.025
NaCl, 1 ppm O ₃	-1.534	1.094 ± 0.045
0.001 M SO, NaCl	-1.474	1.187 ± 0.034
0.001 M SO, NaCl, 0.2 ppm O ₃	-1.505	1.113 ± 0.026
0.001 M SO, NaCl, 1 ppm O ₃	-1.464	1.170 ± 0.027
0.01 M SO, NaCl	-1.296	0.869 ± 0.062
0.01 M SO, NaCl, 0.2 ppm O ₃	-1.368	0.753 ± 0.054
0.01 M SO, NaCl, 1 ppm O ₃	-1.360	0.906 ± 0.041
0.001 M SO, NaCl, H ₂ SO ₄	-1.538	1.138 ± 0.051
0.001 M SO, NaCl, H ₂ SO ₄ , 1 ppm O ₃	-1.473	1.065 ± 0.054
0.01 M SO, NaCl, H ₂ SO ₄	-1.271	0.971 ± 0.079
0.01 M SO, NaCl, H ₂ SO ₄ , 1 ppm O ₃	-1.449	0.786 ± 0.024
Na ₂ SO ₄	-1.503	0.872 ± 0.016
Na ₂ SO ₄ , 1 ppm O ₃	-1.348	0.909 ± 0.044
0.001 M SO, Na ₂ SO ₄	-1.475	0.708 ± 0.037
0.001 M SO, Na ₂ SO ₄ , 1 ppm O ₃	-1.460	0.708 ± 0.024
0.01 M SO, Na ₂ SO ₄	-1.486	0.682 ± 0.025
0.01 M SO, Na ₂ SO ₄ , 1 ppm O ₃	-1.360	0.670 ± 0.032
0.001 M SO, Na ₂ SO ₄ , H ₂ SO ₄	-1.459	0.748 ± 0.011
0.001 M SO, Na ₂ SO ₄ , H ₂ SO ₄ , 1 ppm O ₃	-1.468	0.709 ± 0.026
0.01 M SO, Na ₂ SO ₄ , H ₂ SO ₄	-1.370	0.615 ± 0.029
0.01 M SO, Na ₂ SO ₄ , H ₂ SO ₄ , 1 ppm O ₃	-1.374	0.548 ± 0.024

Calculation for acidification of aerosols with sulfuric acid

The pH of aerosols flowed over a reservoir of sulfuric acid was calculated using the following method:

The amount of H₂SO₄ in the gaseous phase was determined by solving $[H_2SO_4]_{f,gas} = [H_2SO_4]_{i,gas} e^{-k^I t}$

where $k^I = \frac{\gamma \omega S_a}{4}$ and γ is the H₂SO₄ reaction probability, ω is the molecular velocity of H₂SO₄, and S_a is

the aerosol surface area per volume. Using the vapor pressure of H₂SO₄ at 25°C and both 93 and 98% H₂SO₄ (based on the purity of the laboratory H₂SO₄ used), the residence time that the aerosols spent in the H₂SO₄ reservoir (0.8 sec), and an arbitrary $\gamma=0.5$, $[H_2SO_4]_{f,gas}$ was determined. $[H_2SO_4]_{f,gas}$ was converted

from bar to mol cm⁻³ using the ideal gas law, or $c = \frac{P}{RT}$. The amount of H₂SO₄ within the particle was found by $\frac{c}{N_p V_p}$ where N_p and V_p are number density and volume of the particles (using the volume weighted geometric mean diameter) determined by the SMPS. Assuming an initial pH = 8, and determining the number of moles of [H⁺], the final pH of the aerosols was determined.

Calculation for natural acidification of aerosols by formation of organic acids

The natural pH change of the aerosols that could occur through the formation of nonanoic acid, 9-oxononanoic acid and azelaic acid was calculated in the following method:

The pK_a value for each acid was either known or assumed. The K_a for each acid could be written (shown here for nonanoic acid) as $K_a = \frac{[C_9H_{17}O_2^-][H_3O^+]}{[C_9H_{18}O_2]}$, and it was assumed that the concentrations of the dissociated ions were equivalent. Combining the K_a of all three organic acids, $[H_3O^+]VA = \sqrt{K_a[C_9H_{18}O_2]V^2A^2} + \sqrt{K_a[C_9H_{16}O_3]V^2A^2} + \sqrt[3]{K_a[C_9H_{16}O_4]V^3A^3}$ where each K_a describes a unique acid, V is volume and A is Avogadro's number. The final pH was calculated from this point.