Supporting Information

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SI Text

Reaction of Surface-Adsorbed HONO with HCl. The flow system described in the text was used to study the adsorption of nitrous acid to fumed SiO_2 and the potential of surface-adsorbed HONO to form ClNO when exposed to gaseous HCl. A stream of nitrogen containing HONO (5–6 ppm) and water vapor [(4.1–4.7) $\times$ 10^{16} molecules per centimeter)] was flowed through a borosilicate glass reaction tube containing a bed of 1.0 g of SiO_2 pellets, or bypassed through an empty tube on its way to the IR cell. As shown in the top part of Fig. S1, HONO is effectively removed when the nitrogen stream is diverted over a bed of SiO_2 (indicated by the shaded regions of the graph). In this experiment, the SiO_2 was exposed to HONO for a total of 1.75 h. The reaction chamber was closed off from the gas stream between t = 165 and t = 175 min. At t = 180 min a stream of HCl ($\approx$200 ppm) and water vapor (6% RH) was flowed through the empty reactor, then diverted through the SiO_2-filled reactor between t = 185 and t = 195 min. Nitrosyl chloride was not observed in the reactor effluent. A possible explanation for the absence of ClNO in these experiments is that HONO is converted into NO_2 and NO on the SiO_2 surface (1) and then quickly removed by the stream of nitrogen flowing over the SiO_2. In this case, the concentration of NO^+ on the SiO_2 surface would be insufficient to produce a detectable signal from ClNO. However, the concentration of NO and NO_2 were always below the detection limit of 1 ppm in these experiments. Future work is focused on understanding the fate of HONO upon adsorption to SiO_2 surfaces.

Effect of Water on ClNO Hydrolysis. Previous studies have shown that hydrolysis on aqueous solutions may be a loss process for ClNO in the atmosphere (2, 3). The surprising stability of ClNO in our experiments, even under conditions of high water vapor concentrations and high surface area, warranted further investigation of the kinetics of ClNO loss in our system. Experiments were performed in which ClNO (120–180 ppm) was added to a 10-cm path length IR cell containing 1.0 g of fumed SiO_2 pellets that had been evacuated overnight at $\approx 10^{-4}$ Torr and heated at 125 °C. After cooling to room temperature, water vapor was introduced to the IR cell from an attached 493-cm^3 bulb to give a gas-phase equilibrium water vapor concentration of (0.7–1) $\times$ 10^{17} molecules cm^{-3} (relative humidity of 9–13%) and the decay of ClNO was monitored by FTIR. Least squares fit of the decay of [ClNO] vs. time to an exponential function yielded a first order rate constant of (0.2–4) $\times$ 10^{-5} s^{-1} depending on the water concentration, indicating that the decay of ClNO due to hydrolysis was negligible under conditions of experiments reported here. Assuming that fumed-SiO_2 is a surrogate for mineral oxide surfaces, this suggests that loss of ClNO to aerosol particles and surfaces at the terrestrial-air interface may be much slower than what is expected to occur in bulk water. This is not surprising because water adsorbed on surfaces is very different chemically and physically from bulk liquid water (4–6).

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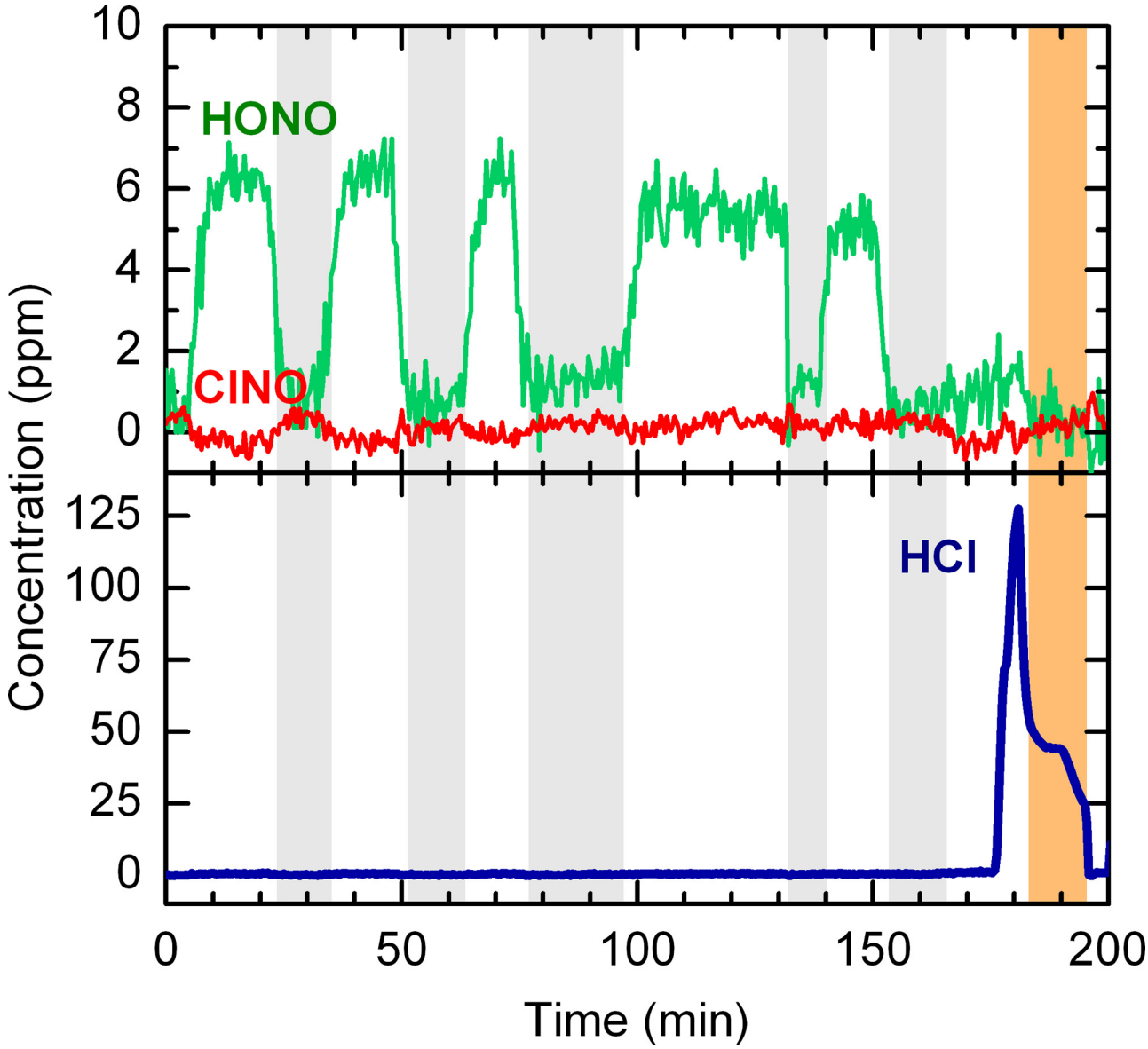

Fig. S1. Control experiment showing that nitrous acid (HONO) is effectively removed from a gaseous mixture of HONO and H_2O in nitrogen when passed over fumed SiO_2 pellets (gray shaded regions), but not when the mixture is bypassed through an empty chamber (clear regions). Subsequent addition of gaseous HCl to the SiO_2 reactor (orange shaded region) does not lead to formation of gaseous ClNO.

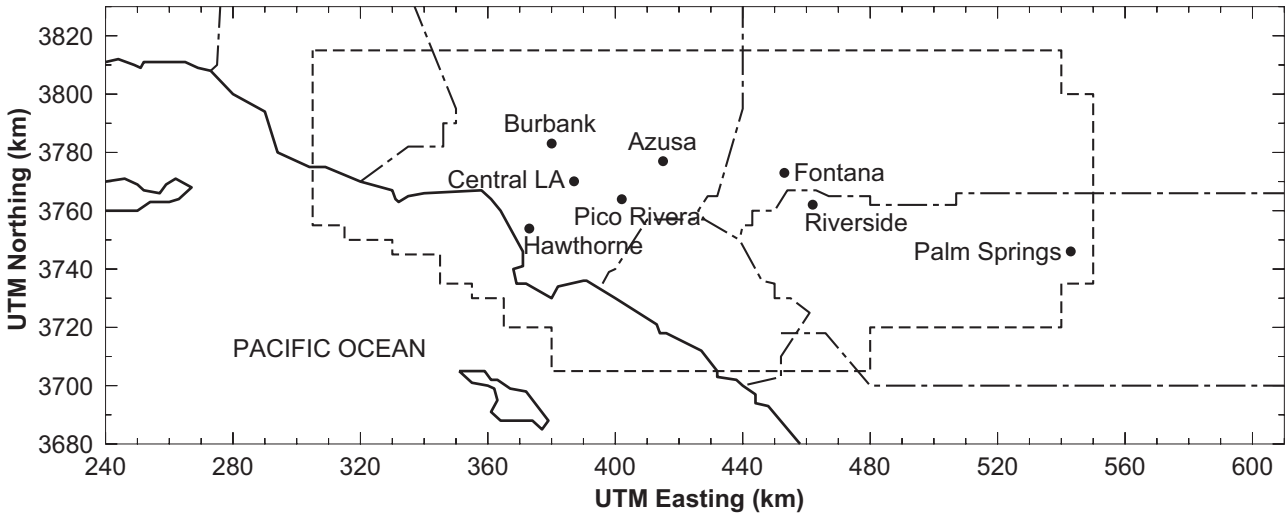

Fig. S2. Ambient air quality simulations using the University of California Irvine-California Institute of Technology (UCI-CIT) airshed model were carried out for the South Coast Air Basin (SoCAB) of California (region enclosed by the dashed line).