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An investigation into the chemistry of HONO in the marine boundary layer at Tudor Hill Marine Atmospheric Observatory in Bermuda

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S1 Photolysis rate constant calculation

The photolysis rate constants (J_i) for NO_2, HONO, HNO_3 and O_3 was calculated combining measured ultra-violet ($UV_{measured}$) light intensity (Eppley TUV radiometer, 295–385 nm) with the tropospheric ultraviolet and visible radiative transfer model (https://www2.acom.ucar.edu/modeling/tropospheric-ultraviolet-and-visible-tuv-radiation-model). The radiative transfer model calculated the gas-phase photolysis rate constants J_i^{model} and light intensity between 295–385 nm (UV_{model}) under clear-sky conditions. The location (32.2647° N, 64.8788° W), height (53 m above the sea level), sampling time, total ozone column, and aerosol optical depth at 550 nm were used as model inputs. The total ozone column and aerosol optical depth data were satellite retrieved daily averages that were obtained from the Ozone Monitoring Instrument (Aura satellite) and the Moderate Resolution Imaging Spectroradiometer (Aqua satellite), respectively. Satellite retrieved data were downloaded using NASA's GIOVANNI tool (https://giovanni.gsfc.nasa.gov/giovanni/). The following equation was used to correct for cloud coverage:

$$J_i = J_i^{model} \times \frac{UV_{measured}}{UV_{model}} \times \frac{UV_{model}^*}{UV_{measured}^*} \quad \text{(S1)}$$

where UV_{model}^* and $UV_{measured}^*$ are the solar noon modeled and measured UV intensities under clear-sky conditions. The difference between UV_{model}^* and $UV_{measured}^*$ is less than 3%.

S2 Aerosol nitrate photolysis rate constant

Aerosol samples collected from Bermuda were used in photochemistry experiments (section 2.2, main text) that determined the production rate constant of HONO from particulate nitrate that is normalized by solar irradiation during tropical noontime ($J_{pNO_3\rightarrow HONO}^N$, s^{-1}):

$$J_{pNO_3\rightarrow HONO}^N = \frac{P_{HONO}}{N_{nitrate}} \times \frac{3.0\times10^{-7}}{J_{actn}} \quad \text{(S2)}$$

where P_{HONO} (mol s^{-1}) is the rate of HONO produced through the photolysis of nitrate on the aerosol filter during the short-period (5 min) light exposure, $N_{nitrate}$ (mol) is the amount of total nitrate in the aerosol sample, and J_{actn} (s^{-1}) is the photolysis rate constant of nitrate in an actinometer solution. Equation S2 normalized the particulate nitrate photolysis rate constant to tropical noontime conditions (ground level, solar zenith angel = 0°) where the photolysis rate constant is ~3×10^{-7} s^{-1} for aqueous nitrate and ~7×10^{-7} s^{-1} for gaseous nitric acid.

Nitrate actinometers were prepared following Jankowski et al. (1999, 2000) in order to monitor the effective UV intensity of the light source employed in the photochemistry experiments. Each chemical actinometer was a 5 ml solution containing 1 mM sodium benzoate and 1 mM sodium nitrate that was added to a quartz cuvette (1 cm pathlength). Upon UV exposure, the photolysis of aqueous nitrate produces OH radicals and the reaction between OH radical and benzoic acid yields salicylic acid. During our experiment, the actinometer was placed under the solar simulator for 5 min, and the produced salicylic acid was quantified by a fluorescence spectrometer (Hitachi L-7480) with an excitation wavelength of 305 nm and an emission wavelength of 410 nm. J_{actn} was calculated using:

$$J_{actn} = \frac{[Salicylic\ acid]}{[\mathrm{Nitrate}]\times 0.2\times \mathrm{t}} \quad \text{(S3)}$$

where [Salicylic acid] is the concentration of salicylic acid produced during the irradiation (mol L^{-1}), [Nitrate] is the concentration of nitrate in the actinometer solution (0.001 mol L^{-1}), 0.2 is the production yield of salicylic acid from the reaction of OH radical and sodium benzoate, and t (s) is the irradiation time.

Figure S1: A map of Bermuda Island. The star symbol represents the location of the Tudor Hill Marine Atmospheric Observatory.

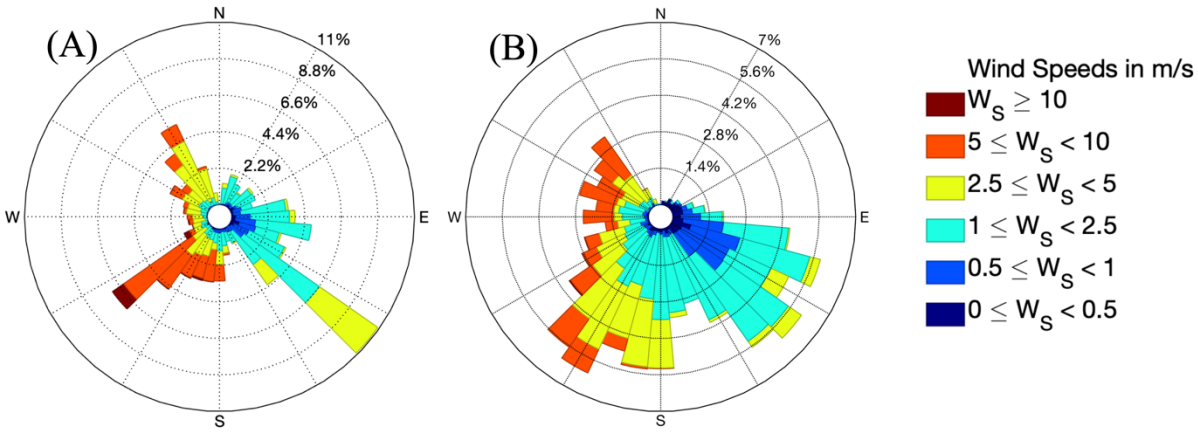

Figure S2: Polar wind plots for the (A) spring and (B) summer field campaigns in 2019.

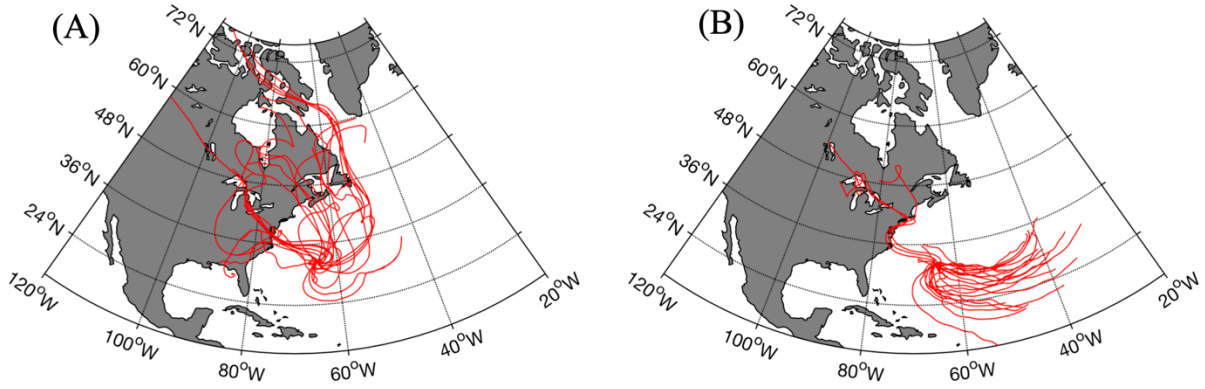

Figure S3: 7-day air mass backward trajectories calculated daily starting at local noontime for the (A) spring and (B) summer field campaigns in 2019. The backward trajectories were calculated with NOAA'S HYSPLIT model (https://www.ready.noaa.gov).

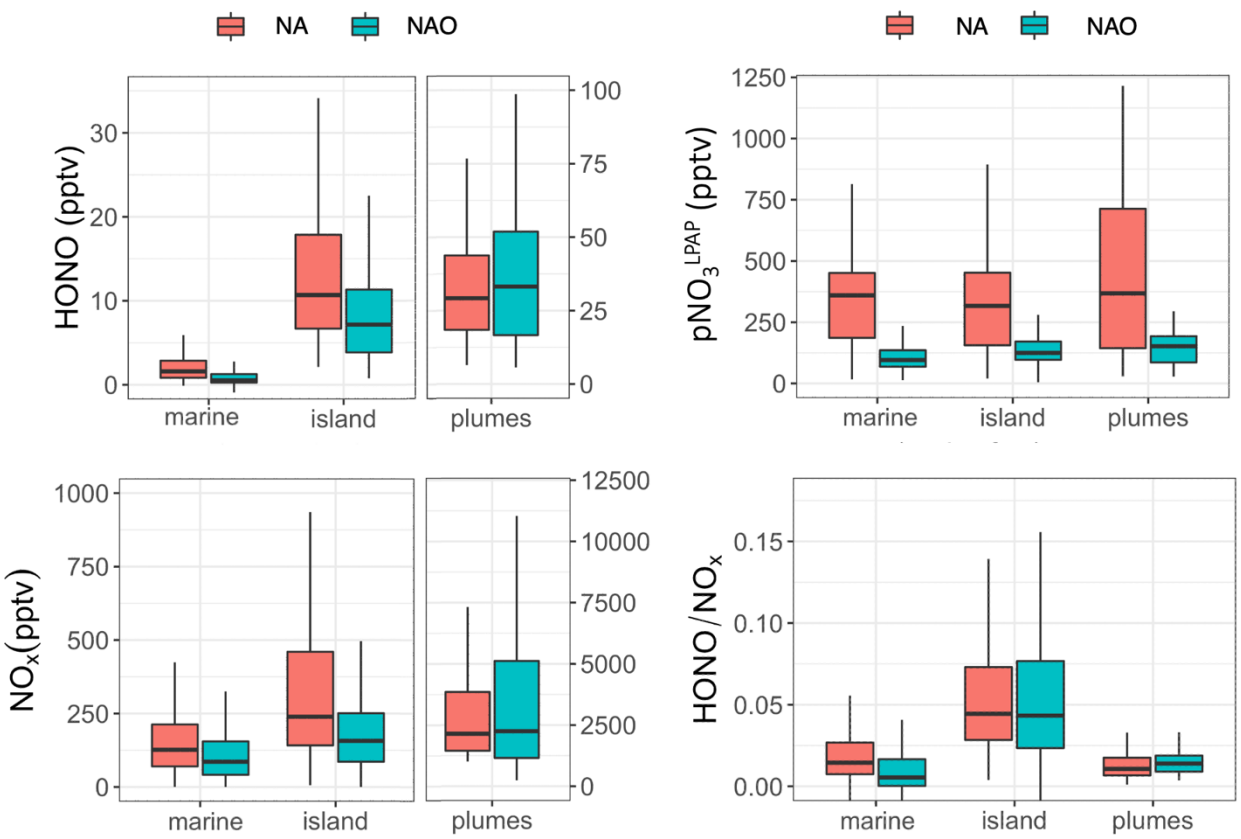

Figure S4: Whisker plots comparing HONO, NO_x, pNO_3^{LPAP} concentrations and HONO/NO_x ratios in clean marine air, island-influenced air, and polluted plumes in the North American (NA) air during spring and the North Atlantic Ocean (NAO) air during the summer. The thick lines represent median values, the boxes the 25th and 75th percentiles, and the whiskers the largest value within 1.5 times interquartile range above 75th percentile and the smallest value within 1.5 times interquartile range below 25th percentile.

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