

10.8 NITRIC ACID FORMATION IN URBAN, POWER PLANT, AND INDUSTRIAL PLUMES DURING THE TEXAS AIR QUALITY STUDY

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1. INTRODUCTION

Nitric acid (HNO_3) was measured from an aircraft in the planetary boundary layer and free troposphere up to 7 km on 14 flights during the Texas Air Quality Study. The fast-response measurements of HNO_3 reported here were obtained between August 16, 2000 and September 13, 2000 aboard the NCAR Electra aircraft, which was based at Ellington Field, Texas.

By characterizing HNO_3 formation and loss in the troposphere, the fate of NO_x emissions and the rate and yield of O_3 production can be better understood. HNO_3 measured here is formed from the oxidation of NO_x and lost by wet and dry deposition.

Flight plans were designed to investigate the evolution of emissions from point sources (primarily power plants and refineries) and urban areas. The aircraft interrogated air masses both upwind and at various distances downwind from regions with high NO_x or VOC emissions. When the aircraft intersected plumes from point sources, plume widths were typically on the order of a km when the aircraft was less than approximately 20 km from the point source. Since the aircraft speed was 110 m/s, the aircraft crossed these recently emitted plumes in several seconds. Hence, instruments with a rapid time response (approximately 1 s) are essential for capturing these rapid transients in the atmosphere.

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2. MEASUREMENTS

Using a chemical ionization mass spectrometer (CIMS) with SiF_5^- reagent ions, HNO_3 mixing ratios were measured at a 1 Hz sample rate. HNO_3 measurement using this highly selective ion chemistry is not degraded by large water vapor concentrations or interferences from other species. Rapid time response (1 s) is achieved using a heated Teflon inlet. In-flight standard addition calibrations from a HNO_3 permeation source were used to determine the instrument sensitivity of 1.1 ± 0.1 Hz/pptv. Contributions to the HNO_3 signal from instrument artifacts were accounted for by regularly performing in-flight instrument background checks, where HNO_3 was removed from the ambient air sample by diverting the sampled air through a nylon wool filter located near the inlet tip, shown in Figure 1.

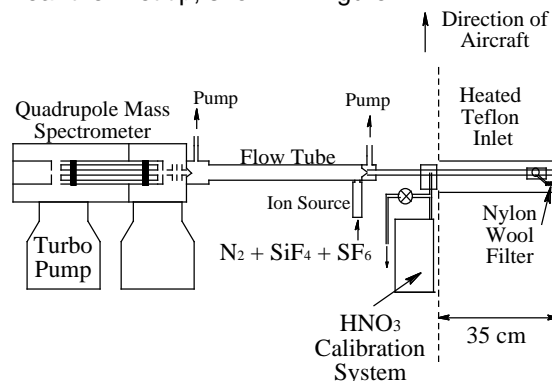


Figure 1. HNO_3 CIMS instrument diagram. The dashed line represents the wall of the aircraft, and the inlet is housed in a pylon so that the sampled air is not influenced by the aircraft boundary layer.

Measurement accuracy, which is determined from uncertainties in the standard addition calibrations and background measurements, is the sum of $\pm 10\%$ and ± 130 pptv.

3. RESULTS

HNO_3 mixing ratios ranged from less than 100 pptv in the free troposphere to over 15 ppbv in the boundary layer downwind from Houston. Coincident in-situ measurements of other reactive nitrogen species are used to examine NO_y partitioning and HNO_3 formation during this month-long measurement campaign. Rapid HNO_3 formation is frequently observed in pollution plumes from power plants, urban areas, and refineries. An example of these measurements (Figure 2) and the correlations between the measured reactive nitrogen species (Figure 3) are shown for a transect of a power plant plume.

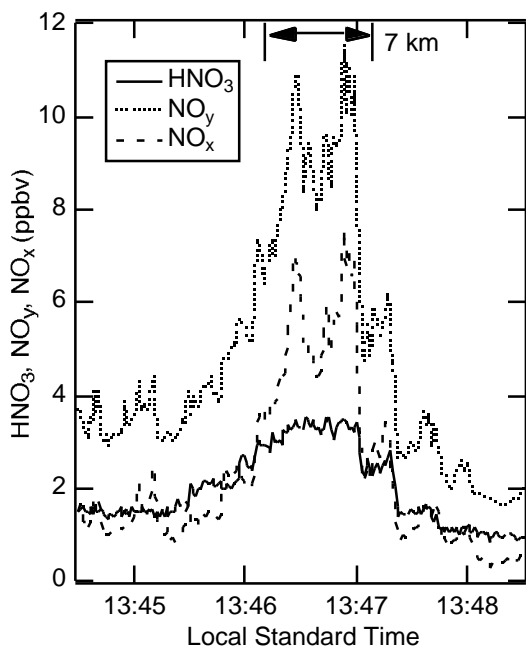


Figure 2. Measurements recorded during a flight transect approximately 36 km downwind from the Parish power plant on August 28, 2000, at an altitude of 650 m.

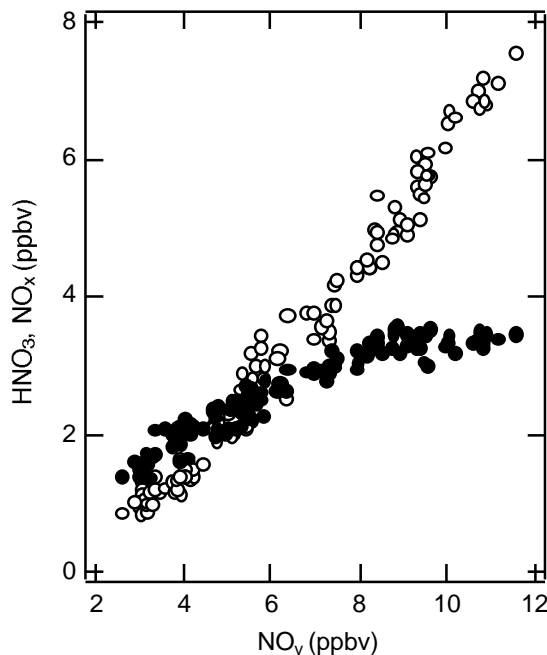


Figure 3. 1 second measurements of HNO_3 (solid circles) and NO_x (open circles) as a function of NO_y for the flight transect shown in Figure 2. Correlation slopes determined from linear least squares fits of this data give $\text{NO}_x/\text{NO}_y = 0.75$ and $\text{HNO}_3/\text{NO}_y = 0.25$. In these plumes, a compact correlation between the reactive nitrogen species is typically observed, indicating a similarly rapid time response for each of the measurements.

Efficient HNO_3 formation from a power plant plume shown here is contrasted with the HNO_3 formation observed in plumes from urban and refinery sources. In photochemically aged power plant, urban, and refinery plumes, HNO_3 production is most favored in power plant plumes and least favored in refinery plumes.