

## Nighttime removal of NO<sub>x</sub> in the summer marine boundary layer

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Received 2 January 2004; revised 13 February 2004; accepted 3 March 2004; published 10 April 2004.

[1] The nitrate radical, NO<sub>3</sub>, and dinitrogen pentoxide, N<sub>2</sub>O<sub>5</sub>, are two important components of nitrogen oxides that occur predominantly at night in the lower troposphere. Because a large fraction of NO<sub>2</sub> reacts to form NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> during the course of a night, their fate is an important determining factor to the overall fate of NO<sub>x</sub> (=NO and NO<sub>2</sub>). As a comprehensive test of nocturnal nitrogen oxide chemistry, concentrations of O<sub>3</sub>, NO, NO<sub>2</sub>, NO<sub>3</sub>, N<sub>2</sub>O<sub>5</sub>, HNO<sub>3</sub> and a host of other relevant compounds, aerosol abundance and composition, and meteorological conditions were measured in the marine boundary layer from the NOAA research vessel *Ronald H. Brown* off the East Coast of the United States as part of the New England Air Quality Study (NEAQS) during the summer of 2002. The results confirm the prominent role of NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> in converting NO<sub>x</sub> to HNO<sub>3</sub> at night with an efficiency on par with daytime photochemical conversion. The findings demonstrate the large role of nighttime chemistry in determining the NO<sub>x</sub> budget and consequent production of ozone. **INDEX TERMS:** 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry. **Citation:** Brown, S. S., et al. (2004), Nighttime removal of NO<sub>x</sub> in the summer marine boundary layer, *Geophys. Res. Lett.*, 31, L07108, doi:10.1029/2004GL019412.

### 1. Introduction

[2] Photochemical ozone production in the troposphere depends critically on NO<sub>x</sub> (=NO + NO<sub>2</sub>). The budget for the emissions of NO<sub>x</sub> and its rate of removal from the atmosphere are therefore of substantial current interest. The chief NO<sub>x</sub> removal mechanism is the conversion of NO<sub>2</sub> to nitric acid (HNO<sub>3</sub>), a soluble compound whose primary fate in the troposphere is deposition to the surface or rain-out. Figure 1 summarizes the two most important pathways by which this

conversion may occur. One is the daytime reaction of NO<sub>2</sub> with hydroxyl radical (OH) [McConnell and McElroy, 1973]; the other is the formation of the nitrate radical, NO<sub>3</sub>, and dinitrogen pentoxide, N<sub>2</sub>O<sub>5</sub> [Platt et al., 1984], compounds that occur in appreciable concentration only at night in the lower troposphere.

[3] Dinitrogen pentoxide is a unique component of total reactive nitrogen (NO<sub>y</sub>) in the troposphere because it has a bond energy that allows for reversible, temperature-dependant storage and/or transport of NO<sub>x</sub> and because it contains two NO<sub>x</sub> moieties. As the acid anhydride of nitric acid, it hydrolyzes readily to HNO<sub>3</sub> via a heterogeneous reaction on the surface of aerosol particles, a potentially efficient NO<sub>x</sub> sink. Several global scale modeling studies have highlighted the importance of N<sub>2</sub>O<sub>5</sub> hydrolysis in regulating NO<sub>x</sub> [Dentener and Crutzen, 1993; Riemer et al., 2003]. The nitrate radical is a key nighttime oxidant [Platt and Heintz, 1994]; reaction of NO<sub>3</sub> with hydrocarbons and reduced sulfur compounds can produce a significant quantity of HNO<sub>3</sub>. Although the loss of NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> represents a potentially large contribution to the removal of NO<sub>x</sub> from the atmosphere, it has remained poorly quantified. Recent estimates for the nocturnal conversion rate of NO<sub>x</sub> to HNO<sub>3</sub> based on measurements of NO<sub>3</sub> via Differential Optical Absorption Spectroscopy (DOAS) have ranged from values roughly equal to the daytime conversion rate to significantly smaller conversion rates at night [Smith et al., 1995; Heintz et al., 1996; Allan et al., 2000; Geyer et al., 2001; Vrekoussis et al., 2003].

### 2. Measurements

[4] Recently, we have demonstrated a sensitive, in-situ method for detection of both NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> based on Cavity Ring-Down Spectroscopy (CaRDS) [Brown et al., 2002]. The CaRDS instrument detects NO<sub>3</sub> via its strong visible absorption band near 662 nm and simultaneously detects N<sub>2</sub>O<sub>5</sub> by thermal conversion to NO<sub>3</sub> in a separate absorption cell. During the summer of 2002, this instrument was deployed on the NOAA research vessel (R/V) *Ronald H. Brown* to measure NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> concentrations in the marine boundary layer as part of the New England Air Quality Study. The ship carried a suite of in-situ measurements of trace gases (O<sub>3</sub>, nitrogen oxides, speciated VOC, etc.), aerosol size and composition, and meteorological data. Of particular importance to this study was the measurement of HNO<sub>3</sub> via mist chamber sampling/ion chromatography with a time resolution of 5 min [Scheuer et al., 2003]. Figure 2 shows the cruise track of the R/V *Brown* along the East Coast of the United States. The continental outflow

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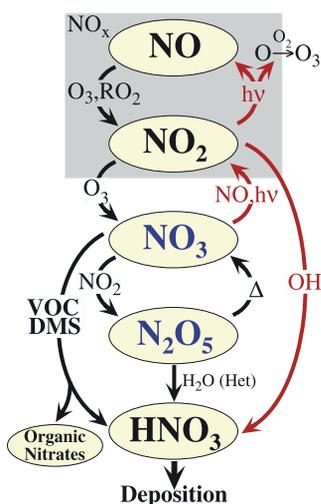
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**Figure 1.** Chemical cycling of nitrogen oxides. Red arrows indicate reactions that require sunlight, while black arrows indicate reactions that do not. Note that reaction of NO with NO<sub>3</sub> is shown in red because, in the absence of recent NO<sub>x</sub> emission, the presence of NO requires solar photolysis of NO<sub>2</sub>.

over the ocean surface in this region provides a unique opportunity for the study of the chemical transformations occurring within polluted air masses, both because of the lack of emissions from sources close to the detection region, and because the stability of the boundary layer over the ocean surface reduces the influence of meteorological effects on the abundances of trace compounds. The combination of in-situ observations of NO<sub>2</sub>, NO<sub>3</sub>, N<sub>2</sub>O<sub>5</sub> and HNO<sub>3</sub> in the polluted continental outflow over the ocean surface provides a direct, experimental quantification of the relative efficiencies of day and night conversion of NO<sub>x</sub> to HNO<sub>3</sub>.

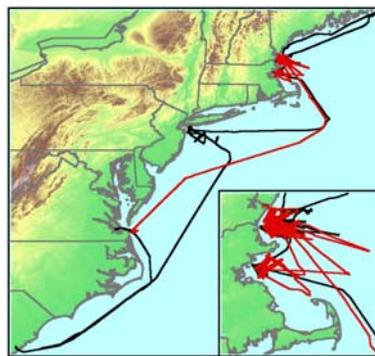
### 3. Results

[5] The upper panel of Figure 3 plots a diurnal average of the mixing ratio of HNO<sub>3</sub> from the NEAQS campaign, along with those of NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub>. Also shown is a spectral radiometer measurement of the photolysis rate coefficient of O<sub>3</sub> to produce O(<sup>1</sup>D), an important OH precursor. The average is for the final 11 days of the NEAQS data set (red portion of the cruise track in Figure 2). The diurnal pattern of NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> illustrates the efficient daytime destruction of NO<sub>3</sub> and the buildup of both compounds during the night. Daytime mixing ratios were typically below the instrumental detection limit (except in late afternoon on some occasions), whereas the nighttime mixing ratios reached averaged values of 17 and 84 pptv for NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub>, respectively. It is worth noting that these abundances are small compared to NO<sub>x</sub>, as shown in Figure 4. The latter had an average mixing ratio of 4.0 ppbv at night, when it was almost exclusively NO<sub>2</sub>, so that on average the sum, NO<sub>3</sub> + 2 × N<sub>2</sub>O<sub>5</sub> (since N<sub>2</sub>O<sub>5</sub> contains 2 NO<sub>x</sub>), was approximately 5% of NO<sub>2</sub>. The small abundances of NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> relative to NO<sub>2</sub> imply that the removal of NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub>, and therefore NO<sub>x</sub>, was efficient. Reaction of NO<sub>2</sub> with O<sub>3</sub> (rate limiting) and the subsequent reaction of

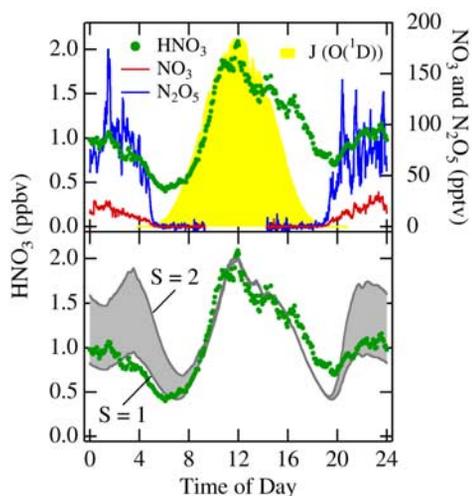
NO<sub>3</sub> with NO<sub>2</sub> may consume 60–90% of the NO<sub>2</sub> within a given air parcel in the course of a 10 hour night for the average conditions during NEAQS. The presence of only a small amount of NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> relative to NO<sub>x</sub> indicates rapid nocturnal sinks for NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub>.

[6] The diurnal pattern of nitric acid in Figure 3 is consistent with this observation. It displays a clear maximum in the middle of the day, peaking at approximately local noon, coincident with the peak in the O<sub>3</sub> photolysis rate. The daytime HNO<sub>3</sub> profile approximately follows its source from photochemical OH production. In addition to the noon maximum, the HNO<sub>3</sub> profile shows definite minima at dusk and dawn, periods when neither the night nor day production is active. The minima occur when there is insufficient sunlight to drive significant production of OH, but sufficient sunlight to produce enough NO from NO<sub>2</sub> photolysis to suppress NO<sub>3</sub>. Finally, the profile shows a relatively constant, large HNO<sub>3</sub> abundance throughout the night, providing clear evidence for a strong, nocturnal source. That the HNO<sub>3</sub> profile follows its sources throughout a diurnal cycle implies a sink that removes HNO<sub>3</sub> on a timescale comparable to diurnal variations. As discussed below, deposition to the ocean surface from the shallow marine boundary layer can plausibly account for the entire HNO<sub>3</sub> sink, although there may also have been a smaller contribution due to uptake by sea salt aerosol. (The loading of NO<sub>3</sub><sup>-</sup> in the supermicron aerosol, sampled through a 7 stage impactor and analyzed by ion chromatography, was equivalent to 17% of the gas-phase HNO<sub>3</sub> concentration.) Radiosondes launched from the R/V *Brown* showed the marine boundary layer to be roughly 100 m and showed that it did not have large day-to-night variations in either depth or stability (W. M. Angevine et al., Coastal boundary layer influence on pollutant transport in New England, submitted to *Journal of Applied Meteorology*, 2003).

[7] The lack of large variation in the marine boundary layer height, its stability or the temperature (with an average diurnal variation of 3.6°C) allows a direct comparison of the daytime and nighttime HNO<sub>3</sub> source in Figure 3. Since the HNO<sub>3</sub> loss is rapid, its concentration is proportional to its production rate in each period, and direct integration of the profile yields an estimate for the relative HNO<sub>3</sub> production during day and night. The area underneath the profile during



**Figure 2.** Map of the East Coast of the United States showing the cruise track of the R/V Ronald H. Brown during July–August, 2002. The red segment of the cruise track shows the ship position during the 11 day average of Figure 3.



**Figure 3.** *Upper panel:* Diurnally averaged mixing ratios of NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> (1 min average, 40% measurement uncertainty, 120% relative standard deviation during the averaging period) and HNO<sub>3</sub> (5 min average, 35% uncertainty, 80% relative standard deviation) for the final 11 days of the NEAQS campaign (July 29–August 9, 2002). Local noon on the x-axis is taken as the minimum in the solar zenith angle. The yellow background (no scale) shows J(O(<sup>1</sup>D)). (One three hour period, 11:45–14:45 on July 30, 2002, has been excluded from the HNO<sub>3</sub> average on the basis of large NO<sub>x</sub> mixing ratios, but this did not significantly affect any of the interpretation discussed in the text.) *Lower Panel:* Comparison of the diurnally average HNO<sub>3</sub> mixing ratio to a calculation (shaded area) based on integration of equations (1)–(3) plus a constant first-order loss term. The shaded region shows the possible range of nocturnal values for S between 1 and 2 (see text).

the nighttime hours (SZA  $\geq 90^\circ$ , or 9.8 hours) accounts for 35% of the total, indicating that roughly this fraction of HNO<sub>3</sub> arises from nocturnal sources. This time period accounts for 41% of a diurnal cycle, meaning that the averaged nocturnal production rate of HNO<sub>3</sub> was roughly 80% of the average daytime production rate. An additional HNO<sub>3</sub> measurement on the R/V *Brown* by a similar method [Russell *et al.*, 2003] but with lower time resolution (2 hours) suggested HNO<sub>3</sub> production at night accounted for approximately 30% of the total, in line with the conclusion from the higher time-resolution data.

#### 4. Analysis

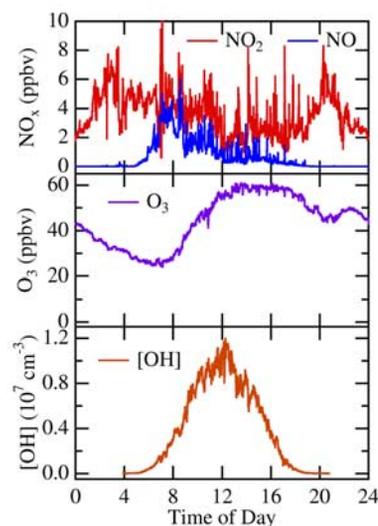
[8] Production of HNO<sub>3</sub> from the reaction of NO<sub>2</sub> with photochemically produced OH accounts for the majority of NO<sub>x</sub> loss during the day. Additional daytime NO<sub>x</sub> losses, such as organic nitrate formation [Day *et al.*, 2003], remain uncertain but are likely small in comparison. Formation of peroxyacetyl nitrates (PANs) is a significant instantaneous NO<sub>2</sub> loss but not a long-term NO<sub>x</sub> sink. At night, on the other hand, HNO<sub>3</sub> production represents a lower limit to the actual NO<sub>x</sub> loss since the major nocturnal sinks for NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> do not yield exclusively gas phase HNO<sub>3</sub>. For example, the primary sinks for NO<sub>3</sub> during NEAQS were reactions with biogenic hydrocarbons (e.g., isoprene and

terpenes) emitted from land-based sources and dimethyl sulfide (DMS) emitted from the ocean. While the reaction of NO<sub>3</sub> with DMS yields nitric acid with unit efficiency [Jensen *et al.*, 1992], the yields of gas phase nitric acid from the reactions of NO<sub>3</sub> with biogenic hydrocarbons (e.g., isoprene) are small, and the yields and fates of different products of the initial oxidation step are uncertain [Atkinson and Arey, 2003]. The primary sink for N<sub>2</sub>O<sub>5</sub> is hydrolysis (i.e., N<sub>2</sub>O<sub>5</sub> + H<sub>2</sub>O  $\rightarrow$  2HNO<sub>3</sub>), a process thought to occur mainly heterogeneously on the surface of aerosol. Because submicron aerosol accounted for a large fraction (>96%) of the total aerosol surface, heterogeneous loss of N<sub>2</sub>O<sub>5</sub> likely occurred mainly in this fraction of the aerosol (i.e., not on the larger sea salt particles). The resulting HNO<sub>3</sub> would not likely remain in the aerosol phase due to the high acidity of the submicron aerosol [Clegg *et al.*, 1998], which Aerosol Mass Spectrometry (AMS) measurements showed to have an ammonium to sulfate mole ratio less than two. The observed nitrate loading of 0.3  $\mu\text{g m}^{-3}$  (also from AMS data) was equivalent to 0.1 ppbv of gas phase HNO<sub>3</sub>, and showed no day to night variation. Submicron aerosol therefore sequestered at most 10% of gas phase HNO<sub>3</sub>.

[9] The lower panel of Figure 3 compares the observed HNO<sub>3</sub> mixing ratio to a calculation based on daytime and nighttime production and a sink that is constant during both periods. The daytime loss rate for NO<sub>x</sub> and the production rate for HNO<sub>3</sub> are nearly equivalent, governed primarily by the association of OH with NO<sub>2</sub> to form HNO<sub>3</sub> with rate coefficient  $k_{\text{day}}$ .

$$-\frac{d[\text{NO}_x]_{\text{day}}}{dt} \approx \frac{d[\text{HNO}_3]_{\text{day}}}{dt} = k_{\text{day}} \times [\text{OH}] \times [\text{NO}_2] \quad (1)$$

An expression for the nighttime NO<sub>x</sub> loss rate comes from the assumption of a steady state in the intermediates, NO<sub>3</sub>



**Figure 4.** Diurnal averaged mixing ratios of NO<sub>x</sub> (NO and NO<sub>2</sub>) (upper) and O<sub>3</sub> (middle). The spikes in NO<sub>x</sub> are due to ship plumes, which have been filtered from the data at night (60 data points removed out of more than 15,000 in the average). The lower panel shows the averaged calculated OH concentration.

and N<sub>2</sub>O<sub>5</sub> (reasonable for NEAQS conditions, with warm nocturnal temperatures and rapid sinks for these compounds [Brown *et al.*, 2003]), and the observation of near total losses for these compounds. The reaction of NO<sub>2</sub> with O<sub>3</sub> (rate coefficient  $k_{\text{night}}$ ) is then the limiting step that determines the nocturnal NO<sub>x</sub> loss rate.

$$\frac{d[\text{HNO}_3]_{\text{night}}}{dt} \leq \left| \frac{d[\text{NO}_x]_{\text{night}}}{dt} \right| \approx k_{\text{night}} \times S \times [\text{NO}_2] \times [\text{O}_3] \quad (2)$$

The factor S varies between one (loss dominated by NO<sub>3</sub> reactions) and two (loss dominated by N<sub>2</sub>O<sub>5</sub> reactions).

$$S = 1 + \frac{k_{\text{N}_2\text{O}_5} \times K_{\text{eq}} \times [\text{NO}_2]}{k_{\text{NO}_3} + k_{\text{N}_2\text{O}_5} \times K_{\text{eq}} \times [\text{NO}_2]} \quad (3)$$

Here  $k_{\text{NO}_3}$  and  $k_{\text{N}_2\text{O}_5}$  refer to the effective first-order loss rate coefficient for these compounds, and  $K_{\text{eq}}$  is the equilibrium constant for the reversible reaction of NO<sub>3</sub> with NO<sub>2</sub> to form N<sub>2</sub>O<sub>5</sub>. The calculation in the lower panel of Figure 3 is an integration of equations (1) and (2) plus an assumed, first-order loss term for HNO<sub>3</sub>. The integration assumes an equality in equation (2) and switches the nocturnal production on and off according to the observed rise and decay of NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub>. The shaded region encompasses values of S between one and two. The measured diurnal averages of NO<sub>2</sub> and O<sub>3</sub> shown in Figure 4 are inputs to the calculation. The NO<sub>2</sub> profile shows variability due to the inhomogeneous emissions of this primary pollutant, but no large difference in the average day/night concentrations. The diurnal average of the OH concentration, also shown in Figure 4, comes from an average of daily, calculated values [Derwent, 1999; Warneke *et al.*, 2004]. The HNO<sub>3</sub> sink rate coefficient ( $1/\tau_{\text{HNO}_3}$ ) is an adjustable parameter used to match the peak daytime values in the calculation to the observation. The procedure yields an HNO<sub>3</sub> lifetime,  $\tau_{\text{HNO}_3} = 2.3$  hours, a value that is consistent with the observed time constant for changes in the nitric acid concentration in Figure 3. This lifetime gives a deposition velocity from a 100 m boundary layer of 1.2 cm s<sup>-1</sup>, consistent with previously reported values for HNO<sub>3</sub> [Hanson and Lindberg, 1991]. The calculation reproduces the broad features of the observed diurnal variation in HNO<sub>3</sub>, although there are small differences with the minima in the HNO<sub>3</sub> profile near dawn and dusk. The observed values generally fall toward the lower end of the calculated range, indicating either that the loss of NO<sub>3</sub> was larger than that of N<sub>2</sub>O<sub>5</sub>, or that the observation is in fact a lower limit to the actual loss of NO<sub>x</sub>. As we will show in a forthcoming publication (M. Aldener *et al.*, In situ measurements of NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> during NEAQS: Reactivity and loss mechanisms, manuscript in preparation, 2004), losses of NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> were roughly equivalent during NEAQS (i.e., S near 1.5), suggesting the latter interpretation is correct. Thus, although the integration of the nitric acid profile suggested roughly 1/3 of the HNO<sub>3</sub> production occurred at night, the actual nocturnal loss of NO<sub>x</sub> may have been a larger fraction of the total.

[10] The chemistry that gives rise to NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> is a determining factor in the loss of NO<sub>x</sub> from the atmosphere. The foregoing discussion has shown that nighttime processes destroy a comparable quantity of NO<sub>x</sub> pollution as do daytime processes over the ocean surface off the New

England coast, and that they must therefore have a significant influence on the air quality of the region. From a more general perspective, the role of NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub>, i.e., their ability to serve as either a reservoir or a sink for NO<sub>x</sub>, may vary strongly with both season and location. The abundance of N<sub>2</sub>O<sub>5</sub> is a key in this regard since it varies up to part per billion mixing ratios and may account for significant fraction of NO<sub>y</sub>, and since the variability in N<sub>2</sub>O<sub>5</sub> chemistry can lead to either strong or weak sinks for NO<sub>x</sub>. Characterization of these nocturnal processes is therefore critical to understanding the cycling of atmospheric NO<sub>x</sub>.

[11] **Acknowledgments.** The authors thank Michael Trainer, Andrew Newman, James Roberts, Doug Worsnop and Ronald Cohen for useful discussions. This work was funded by the New England Air Quality Study and by NOAA's Health of the Atmosphere Program.

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