



Reactivity and loss mechanisms of NO₃ and N₂O₅ in a polluted marine environment: Results from in situ measurements during New England Air Quality Study 2002

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[1] Concentrations of NO₃ and N₂O₅ were measured using an in situ instrument aboard the NOAA research vessel *Ronald H. Brown* in the marine boundary layer along the United States east coast as part of the New England Air Quality Study (NEAQS) in the summer of 2002. We analyze the results in terms of the loss partitioning and sink budgets for both of these compounds. Analysis of the data on nights with large N₂O₅ losses allowed for a determination of its heterogeneous uptake coefficient and gave $\gamma(\text{N}_2\text{O}_5) = 0.03 \pm 0.02$. Reactions of NO₃ with terrestrially emitted biogenic volatile organic compounds (isoprene and monoterpenes), advected into the marine boundary layer, and with DMS emitted from the ocean surface were also important. In general, loss of NO₃ and N₂O₅ was rapid, and the partitioning between NO₃ and N₂O₅ losses was roughly equal. Because rapid N₂O₅ loss consumes NO_x at twice the rate of the reaction of NO₂ with O₃, whereas rapid NO₃ loss leads to NO_x removal at the same rate, the equal partitioning of losses indicates a nocturnal NO_x loss rate of approximately 1.5 times the rate of NO₂ + O₃. Activation of halogens from the uptake of NO₃ and N₂O₅ on sea salt was calculated to have produced substantial amounts of active Cl on some mornings through the nocturnal formation and sunrise photolysis of ClNO₂ if the process proceeded at the rate determined by laboratory studies. However, there was no direct observational evidence to test the magnitude of the predicted source.

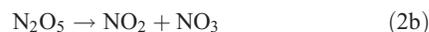
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1. Introduction

[2] The nitrate radical (NO₃) and dinitrogen pentoxide (N₂O₅) play a role in a number of important chemical processes within the troposphere, including the conversion of NO_x (= NO + NO₂) to nitric acid [Platt and Heintz, 1994; Richards, 1983; Smith et al., 1995], the nocturnal oxidation of volatile organic compounds (VOC) [Winer et al., 1984], the oxidation of dimethyl sulfide (DMS), emitted from the ocean surface, to sulfate aerosol [Allan et al., 1999; Lucas and Prinn, 2005; Yvon et al., 1996], and the growth of organic aerosol [Moldanova and Jungstrom, 2000]. Formation and reactions of NO₃ and N₂O₅ primarily provide a

nocturnal, non-photochemical pathway for these and other processes since photolysis and reaction with NO suppress formation of NO₃ in the presence of sunlight. Assessing and understanding the magnitude of these dark reactions in relation to their photochemical counterparts is an important, ongoing area of research.

[3] The formation and subsequent reactions of NO₃ and N₂O₅ in the atmosphere have been detailed previously [Wayne et al., 1991]. Briefly, nitrogen dioxide oxidizes slowly ($k \sim 3 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K [Sander et al., 2003]) in the presence of ozone to form NO₃, which enters into a thermal equilibrium with NO₂ to reversibly form N₂O₅.



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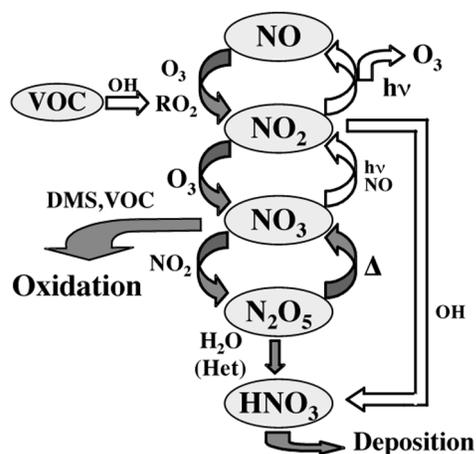
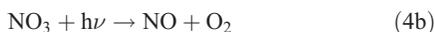


Figure 1. Schematic of nitrogen oxide chemistry showing photochemical ozone production from NO_x (= NO + NO₂) and VOC, conversion of NO_x to the nocturnal nitrogen oxides (= NO₃ + N₂O₅), and their subsequent losses by reactions with VOC and aerosol. Open arrows indicate reactions that take place mainly or exclusively in the presence of sunlight.

Rapid reaction of NO₃ with NO (itself produced photochemically from NO₂) and efficient photolysis of NO₃ by visible light (lifetime in direct sunlight estimated at 5 s) effectively reverse the formation of NO₃ during sunlit hours.



Nocturnal mixing ratios of NO₃ may range into the tens or even hundreds of pptv, while those of N₂O₅ may exceed 1 part per billion by volume (ppbv). At these levels, NO₃ becomes an important oxidant, particularly for unsaturated VOC (e.g., those of biogenic origin) and for dimethyl sulfide (DMS) over the oceans. The primary loss process for N₂O₅ is hydrolysis to form nitric acid; this reaction is a significant pathway for the conversion of NO_x (= NO and NO₂) to HNO₃, both regionally and globally [Dentener and Crutzen, 1993]. Figure 1 summarizes these reactions.

[4] Our recently developed, in situ instrument for the detection of both NO₃ and N₂O₅ [Brown *et al.*, 2002] was deployed for its first major field campaign during the New England Air Quality Study in 2002 (NEAQS 2002). The measurement platform was the NOAA research vessel *Ronald H. Brown* (R/V *Brown*), which sailed off the U.S. east coast, with a particular emphasis on the New England area, during a 4 week intensive measurement period in July and August 2002. In two previous manuscripts, we quantified the nocturnal oxidation of NO_x to HNO₃ in the marine environment [Brown *et al.*, 2004], and the daytime and nighttime oxidation of VOC [Warneke *et al.*, 2004]. A forthcoming manuscript will discuss the influence of NO₃ oxidation of DMS to the sulfur budget in a polluted marine

environment (H. Stark *et al.*, Influence of the nitrate radical on the oxidation of dimethyl sulfide in a polluted marine environment, submitted to *Journal of Geophysical Research*, 2006). The goal of this manuscript is to explore the reactions of NO₃ and N₂O₅ in more detail, with particular attention to the different loss mechanisms for these compounds and the influence of these reactions on nocturnal NO_x and VOC processing within polluted air masses.

2. Measurements of NO₃ and N₂O₅

[5] Concentrations of NO₃ and N₂O₅ were measured by cavity ring-down spectroscopy (CaRDS) using a previously described instrument [Brown *et al.*, 2002]. CaRDS is a high-sensitivity direct absorption technique based on the measurement of the time constant, τ , for single-exponential decay of light intensity from a high-finesse optical cavity [Busch and Busch, 1999]. Our instrument uses a pulsed laser system (Nd:YAG laser pumped dye laser) resonant with the peak of the NO₃ absorption spectrum near 662 nm to pump two separate optical cavities. One of these cavities is used to measure NO₃ via its 662-nm absorption from an inlet at ambient temperature, and the other is used to measure the sum of NO₃ + N₂O₅ from an inlet heated to 75 °C to induce thermal decomposition of N₂O₅ to NO₃. For the NEAQS 2002 sampling conditions, the instrument sensitivity was 0.5–2 pptv for NO₃ (5 s average) and 2–5 pptv for N₂O₅. The sensitivity range was limited by turbulent flow noise encountered under the conditions of this campaign and was somewhat larger than we have reported previously for this instrument.

[6] An important limitation to the accuracy of the NO₃ and N₂O₅ measurements during NEAQS 2002 was the inlet transmission efficiency, T_E. The CaRDS instrument, like many of the other gas-phase measurements, was housed in a sea container on an upper deck in the forward part of the ship. An air sample was drawn from a point above and immediately in front of the sea container (11 m above the sea surface) through a fast flow (300 standard liters per minute, SLPM) system consisting of 3 m of 3/4" OD PFA Teflon tubing. This inlet was exchanged regularly (every 2–3 days), and losses of NO₃ and N₂O₅, measured from the dependence of the signal on the flow rate through the system and on the length of the inlet tubing, were <10% (T_E estimated at 0.95 ± 0.05). Sample flows were drawn from the fast-flow manifold through 1" OD halocarbon wax-coated Pyrex tubing at 12 SLPM and 5–8 SLPM for the measurement of NO₃ (ambient temperature) and the sum, NO₃ + N₂O₅ (heated to 75°C), respectively. Unanticipated turbulent flow noise in the heated channel required reduction of this flow rate from its optimum of 12 SLPM. Laboratory characterization of the losses in this system prior to the campaign showed transmission efficiencies of 90 ± 5%; however, transmission tests carried out during and after the campaign showed that aging of the halocarbon wax surfaces led to a degradation of the T_E to 80 ± 15% for NO₃ and 60 ± 20% for NO₃ + N₂O₅. Each sample flow also passed through a Teflon membrane filter to suppress optical extinction at 662 nm from atmospheric aerosol. Filters were changed at regular, 1-hour intervals using a manual device. Field tests conducted during NEAQS 2002 confirmed

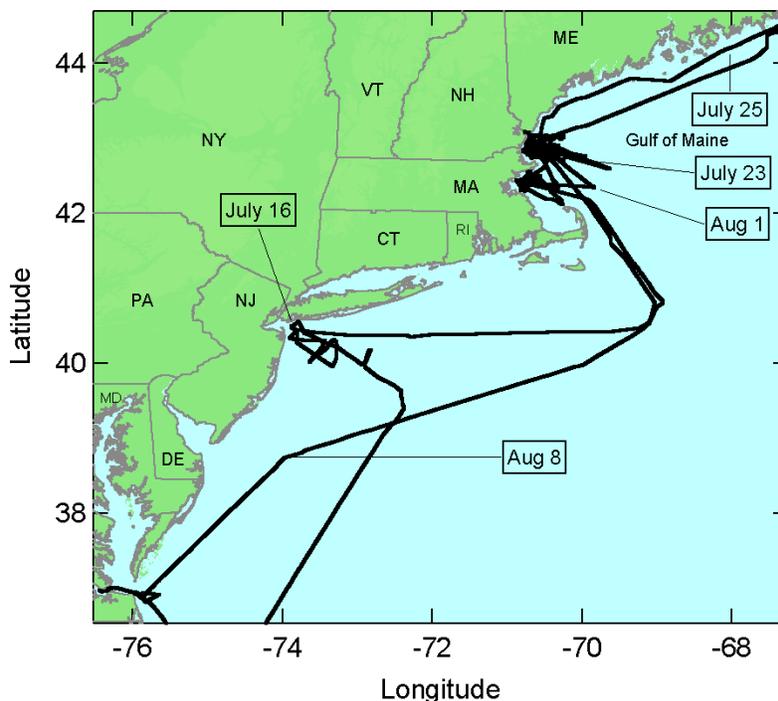


Figure 2. Map of the east coast of the United States showing the track of the R/V *Brown* and the intensive study area in the Gulf of Maine. Selected dates show the location of R/V *Brown* at different points during the campaign.

previously measured filter transmission efficiencies of $85 \pm 10\%$ for NO₃ and $>99\%$ for N₂O₅. The net transmission efficiency through the entire sampling system for NO₃ and N₂O₅ were 60% and 55%, respectively, and the corresponding uncertainties in the reported concentrations (based on propagation of the errors listed above) are 35% for NO₃ and 40% for N₂O₅. In the time since the 2002 campaign, the inlet system has been redesigned to increase the NO₃ and N₂O₅ inlet transmission efficiency (70% and 85%, respectively) and the measurement accuracy (25% and 20%, respectively) [Dubé *et al.*, 2006].

3. Data Overview

[7] The R/V *Brown* sailed from Charleston, South Carolina, on 12 July 2002, made a port call in Portsmouth, New Hampshire, from 26 to 29 July and returned to Charleston on 11 August. Excluding the period during the port call, the R/V *Brown* sampled in the area of the Massachusetts, New Hampshire and Maine coastlines from 17 July to 7 August, the area near New York City from 14 to 17 July and Norfolk, Virginia, from 9 to 10 August 2002. Figure 2 shows the ship track within the intensive study area. The suite of instruments on board the R/V *Brown* that were relevant to the analysis in this manuscript included in situ measurements of O₃, NO, NO₂ and NO_y (i.e., the sum of reactive nitrogen) by chemiluminescence at 1-min time resolution [Thornton *et al.*, 2003], HNO₃ by mist chamber at 5-min resolution [Dibb *et al.*, 2004], speciated VOC by GC-MS (5-min resolution each 30 min) [Goldan *et al.*, 2004], aerosol size distributions from a series of mobility analyzers and particle counters at 15-min time resolution,

and aerosol composition from a Particle into Liquid Sampler (PiLS) and an Aerosol Mass Spectrometer (AMS) [Bates *et al.*, 2005].

[8] Figure 3 shows an overview of the measured mixing ratios of NO₃ and N₂O₅ during the entire campaign. There are no data reported for the period from 19 to 26 July because of technical difficulties with the instrument. The mixing ratios of NO₃ and N₂O₅ ranged from the instrument detection limit up to 140 pptv and 1.6 ppbv, respectively. Concentrations of both species exhibited considerable variability due to the variety of different source regions sampled (e.g., urban outflow versus clean marine) and due to the variability of the chemical composition (i.e., NO_x, O₃, VOC, etc.) within each of the different air masses. The dominant flow in the New England region was offshore, impacted by emissions from the urban corridor between Washington, D. C., and Boston, Massachusetts, but air masses from Canada and from the Atlantic Ocean (as identified by back trajectory analysis) were also encountered.

4. Lifetimes and First-Order Loss Rate Coefficients for NO₃ and N₂O₅

[9] One of the most common and useful diagnostics in the analysis of atmospheric NO₃ and N₂O₅ is their steady state lifetime [Platt *et al.*, 1984], or the ratio of their concentrations to their source strength (molecules cm⁻³ s⁻¹) from the reaction of NO₂ with O₃ (reaction (1)). Because NO₃ and N₂O₅ are a closely coupled pair that interconvert rapidly, the lifetime of each depends on the loss rate for the other. At steady state, the loss frequency is equal to

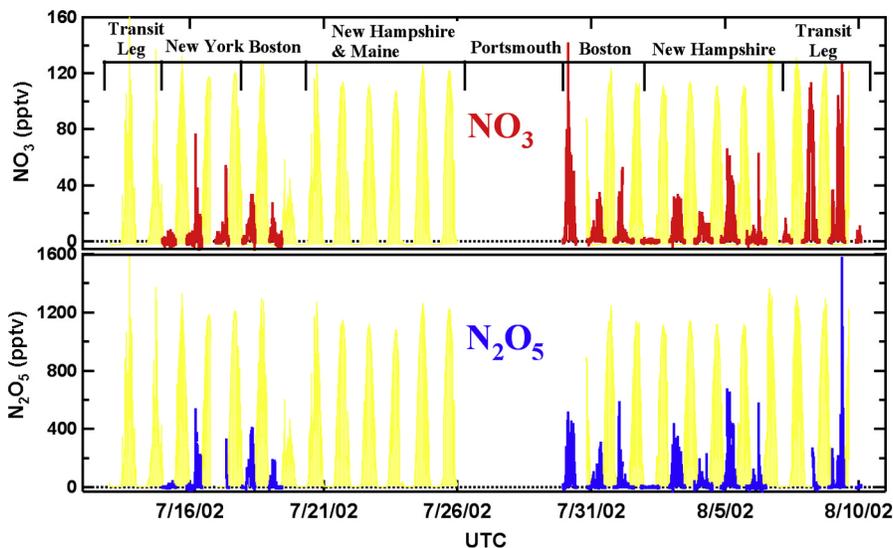


Figure 3. Overview of the measured mixing ratios of NO₃ and N₂O₅. The legend across the top indicates the sampling regions during each period. The shaded background shows the solar insolation measured at the ship to give a reference for day versus night in the time series.

the concentration over the production rate. Taking a single, first-order loss rate coefficient, k_{NO_3} , to describe the sum of all of the losses for NO₃, and a separate first-order loss rate coefficient, $k_{N_2O_5}$, to parameterize the losses for N₂O₅, the following two equations give an approximate relationship between the observed steady state lifetimes and the sinks for NO₃ and N₂O₅ [Brown *et al.*, 2003; Heintz *et al.*, 1996].

$$\tau_{NO_3} \equiv \frac{[NO_3]}{k_1[NO_2][O_3]} \approx (k_{NO_3} + k_{N_2O_5}K_{eq}[NO_2])^{-1} \quad (5)$$

$$\tau_{N_2O_5} \equiv \frac{[N_2O_5]}{k_1[NO_2][O_3]} \approx \left(k_{N_2O_5} + \frac{k_{NO_3}}{K_{eq}[NO_2]} \right)^{-1} \quad (6)$$

Here K_{eq} is the temperature-dependent equilibrium constant for the equilibrium between NO₂, NO₃ and N₂O₅ (reaction (2)). A derivation of these equations is given by Brown *et al.* [2003].

[10] Equations (5) and (6) show that, presuming NO₃ and N₂O₅ have achieved steady state, the individual loss rate coefficients, k_{NO_3} and $k_{N_2O_5}$, may be determined as the intercept and slope of a linear fit to a plot of $\tau_{NO_3}^{-1}$ against $K_{eq}[NO_2]$, or as the slope and intercept of a plot of $\tau_{N_2O_5}^{-1}$ against $(K_{eq} \times [NO_2])^{-1}$ [Brown *et al.*, 2006]. The steady state approximation was likely valid for most of the NEAQS 2002 data (average nocturnal temperature = 295 K, nocturnal NO₂ from 0.2 to 30 ppbv, average ~4 ppbv). A box model analysis showed that the time required to approach steady state for most conditions encountered during NEAQS 2002 was ≤ 1 hour, except for very weak sinks for NO₃ and N₂O₅, as described in section 5.3 below. Determination of average loss rate coefficients from the observed NO₂ dependence of the steady state lifetimes according to equations (5) and (6) was complicated by variability in the sinks for NO₃ and N₂O₅ relative to the

independent variable, $K_{eq}[NO_2]$, in equations (5) and (6). This effect was apparent from scatter in the observed steady state lifetimes that tended to obscure their NO_x scaling. Only a limited number of cases showed a clear dependence on NO_x outside of this scatter. For most cases, we have simply calculated the total losses for NO₃ and N₂O₅ from the right-hand side of equations (5) and (6) as described below and compared them to observed steady state lifetimes on the left-hand side of equations (5) and (6).

[11] The first-order loss rate coefficients can be calculated from measurements of the known sinks for NO₃ and N₂O₅ (i.e., VOC and aerosol). These calculated values will be referred to as $k_{NO_3}^{Calc}$ and $k_{N_2O_5}^{Calc}$. In the case of NO₃, the calculated loss rate coefficient is the sum of the measured hydrocarbons (including DMS) multiplied by their temperature-dependent rate coefficients for reaction with NO₃, $k_i(T)$ [Atkinson, 1991]. With the exception of ship plumes containing recently-emitted NO_x, NO was below its detection limit during nighttime hours, and reaction of NO₃ with NO (reaction (3)) has been neglected for the analysis of nighttime NO₃ measurements. Photolysis (reaction (4)) was also negligible at night. First-order heterogeneous loss for NO₃ on aerosol surface has been included using an assumed uptake coefficient for NO₃, $\gamma(NO_3) = 4 \times 10^{-3}$ [Allan *et al.*, 1999; Rudich *et al.*, 1996]. The aerosol surface area density, A ($\mu m^2 cm^{-3}$), was calculated from the measured, RH corrected, number and size distributions (up to 10 μm), assuming spherical particles.

$$k_{NO_3}^{Calc} = \sum_i k_i(T)[VOC_i] + \frac{1}{4}\bar{c}A\gamma(NO_3) \quad (7)$$

The first term is predicted to be by far the most important contribution at night, and is analyzed in detail in the following sections. Heterogeneous uptake of NO₃, calculated from the literature uptake coefficient given above, is small by comparison; however, relatively little is known about this uptake coefficient on real atmospheric aerosol; if

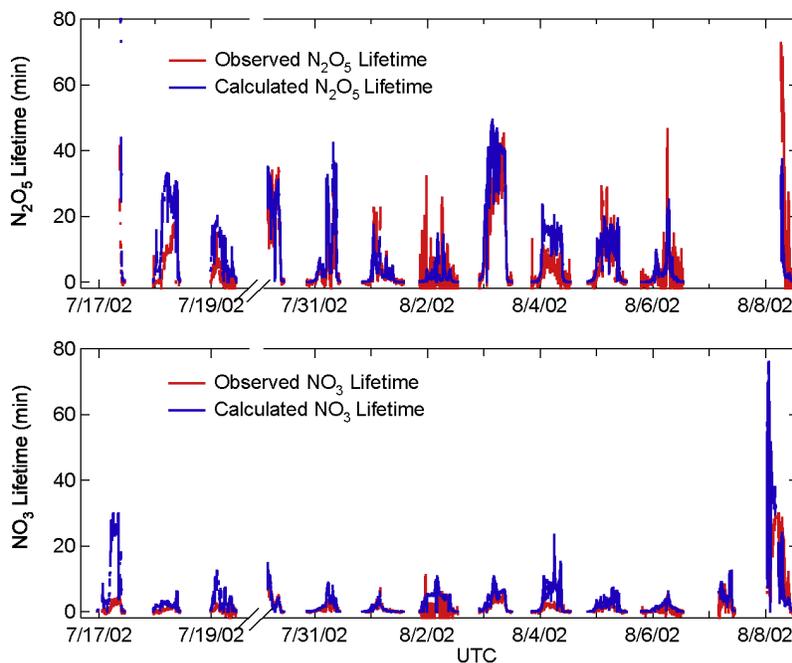


Figure 4. Observed (τ_{NO_3} , $\tau_{N_2O_5}$ from the left-hand side of equations (5) and (6) and calculated ($\tau_{NO_3}^{Calc}$, $\tau_{N_2O_5}^{Calc}$ from the right-hand side of equations (5) and (6) using $k_{NO_3}^{Calc}$, $k_{N_2O_5}^{Calc}$ from equations (7) and (8), respectively) steady state lifetimes for NO₃ and N₂O₅. Note that the gap in the data from Figure 3 is omitted from this time series (break in the x axis). Calculated values have been offset by +20 min for clarity (they are overlaid with no offset in the color version of the figure).

it were large (i.e., 0.04 rather than 0.004), heterogeneous uptake of NO₃ would be competitive with gas-phase reactions of NO₃ with VOC. The form of the NO₃ heterogeneous loss term is the same as that described below for N₂O₅ hydrolysis, except that it has not been corrected for gas-phase diffusion because the smaller uptake coefficient renders this correction negligible.

[12] The $k_{N_2O_5}^{Calc}$ include only the loss due to heterogeneous hydrolysis of N₂O₅ on aerosol, corrected for gas-phase diffusion to the particles [Fuchs and Stuginin, 1970].

$$k_{N_2O_5}^{Calc} = \bar{c}\gamma(N_2O_5) \times \sum_i N_i \pi r_i^2 \left\{ 1 + \gamma(N_2O_5) \frac{0.750 + 0.283K_n(r_i)}{K_n(r_i)[K_n(r_i) + 1]} \right\}^{-1} \quad (8)$$

$$K_n(r_i) = \frac{3D}{r_i \bar{c}} \quad (9)$$

Here N_i is the number density of particles (particles cm⁻³) in the size bin with average radius r_i , K_n is the Knudsen number, \bar{c} is the mean molecular speed and D is the gas phase diffusion coefficient for N₂O₅. Equation (8) reduces to a simpler form in the limit where gas phase diffusion to the particle can be neglected, valid for small particle diameter and small uptake coefficients.

$$k_{N_2O_5}^{calc} = \frac{1}{4} \bar{c} A \gamma(N_2O_5) \quad (10)$$

Although the differences between equations (8) and (10) were always less than 5%, N₂O₅ uptake was calculated using equation (8). Dry deposition (i.e., for uptake by the

ocean surface) for either NO₃ or N₂O₅ has not been included in the calculated loss rate coefficients. Assuming a 100 m depth for the marine boundary layer in the Gulf of Maine [Angevine *et al.*, 2004], and a deposition velocity for NO₃ and/or N₂O₅ of ~ 1 cm s⁻¹, similar to that for nitric acid in this region [Brown *et al.*, 2004], the predicted lifetime with respect to deposition is 2.5 hours [Wesely and Hicks, 2000]. This loss is 10–1000 times smaller than calculated losses due to VOC and aerosol. However, stratification and reduced mixing of marine air masses within the shallow boundary layer could lead to vertical gradients in NO₃, N₂O₅ and/or their sources and sinks that in turn could complicate the analysis of NO₃ and N₂O₅ sink budgets because of uncertainties in the rates of mixing processes between adjacent, inhomogeneous air masses [Geyer and Stutz, 2004]. These possible effects have not been included in this analysis.

[13] Observed lifetimes, τ_{NO_3} and $\tau_{N_2O_5}$, are defined as in equations (5) and (6) as the ratios of the observed concentrations to the source strengths. The calculated lifetimes, $\tau_{NO_3}^{Calc}$ and $\tau_{N_2O_5}^{Calc}$, are from the right-hand side of equations (5) and (6), using the calculated first-order loss rate coefficients, $k_{NO_3}^{Calc}$ and $k_{N_2O_5}^{Calc}$, temperature-dependent equilibrium constant, $K_{eq}(T)$, and the measured NO₂ concentrations. Figure 4 shows a comparison of the observed to the calculated lifetimes for the entire campaign. The calculated lifetimes have $\gamma(N_2O_5)$ held fixed at a value of 0.03 throughout (see section 5.1). Observed lifetimes were generally in a range of a few minutes, similar to previous measurements of NO₃ lifetimes by DOAS at surface sites [Allan *et al.*, 1999; Geyer *et al.*, 2001; Heintz *et al.*, 1996; Martinez *et al.*, 2000]. The observed lifetimes also generally agree with the calculations,

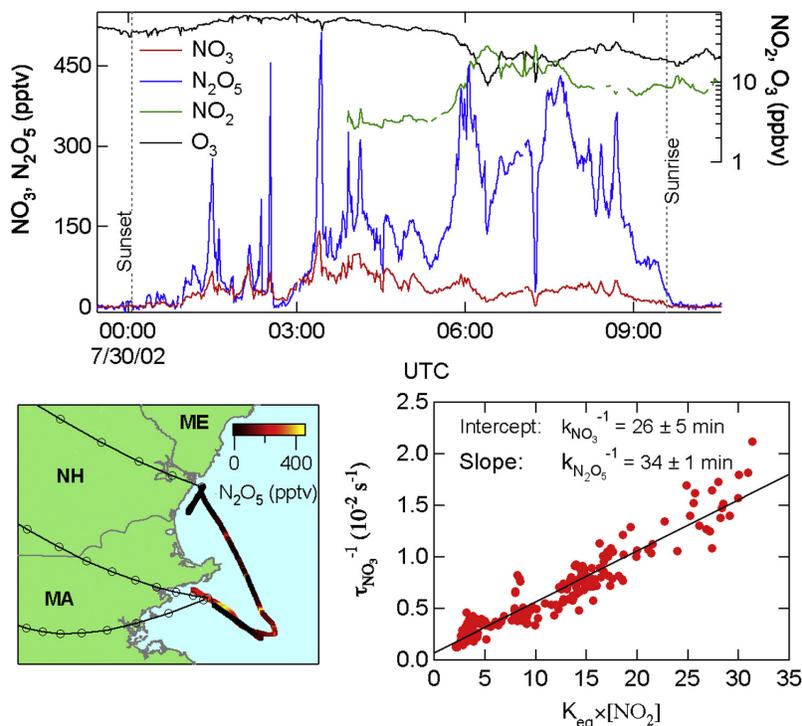


Figure 5. (top) Time series of NO₃, N₂O₅, NO₂, and O₃ mixing ratios. Time is in UTC, 4 hours offset from local time. Times of sunset and sunrise are marked. (bottom right) Plot of $\tau_{NO_3}^{-1}$ versus $K_{eq}[NO_2]$ as in equation (5) for the data from 0355 to 0930 UTC. The solid line is a linear fit ($r^2 = 0.82$) with the inverses of the slope and intercept shown in the legend. (bottom left) Map showing the R/V *Brown* track on 29–30 July 2002, shaded according to the mixing ratio of N₂O₅. Lines with circles are the calculated back trajectories for the sampled air masses, with each point representing one hour upwind.

although there are cases in which the observed lifetimes are either shorter than or longer than the calculations, as discussed below.

[14] The next section deals with the description and accounting of the known sinks and inferences about potential unknown sinks on a more detailed, night by night basis. Characterization of the relationship between the overall lifetimes of NO₃ and N₂O₅ and the specific sinks of either compound is important for several reasons. First, NO₃ is a strong nocturnal oxidant; comparison of observed and calculated losses of NO₃ due to reaction with VOC helps to assess the degree to which this nocturnal oxidation is understood. Second, the determination of N₂O₅ loss rates, in combination with the aerosol surface area, gives a measurement of the N₂O₅ uptake coefficient based solely on atmospheric observations. This reaction is important for the conversion of NO_x to HNO₃. Finally, the balance between NO₃ and N₂O₅ losses determines the efficiency of nocturnal NO_x removal. Under conditions where NO₃ and N₂O₅ react rapidly, this loss is rate limited by the reaction of NO₂ with O₃ [Brown *et al.*, 2004].

$$\frac{d[NO_x]}{dt} = -Sk_1[O_3][NO_2] \quad (11)$$

$$S = 1 + \frac{k_{N_2O_5}K_{eq}[NO_2]}{k_{NO_3} + k_{N_2O_5}K_{eq}[NO_2]} \quad (12)$$

Assuming that NO₃-VOC reactions irreversibly remove NO_x (i.e., that they do not regenerate NO₂), the factor *S* varies between 1 in the limit where NO₃ losses are rapid relative to those for N₂O₅ and 2 for the opposite case (i.e., hydrolysis of N₂O₅ removes 2 NO_x, whereas irreversible reaction of NO₃ consumes only one). Therefore the relative importance NO₃ and N₂O₅ sinks influences the nocturnal lifetime of NO_x by up to a factor of 2.

5. Case-by-Case Studies

5.1. Case 1: Losses Dominated by N₂O₅ Hydrolysis

[15] There were several nights on the 2002 campaign characterized by relatively slow loss of NO₃ in comparison to hydrolysis of N₂O₅. A sink budget analysis on these nights yields a determination of the heterogeneous uptake coefficients for N₂O₅, $\gamma(N_2O_5)$. Figure 5 shows an example from the time series of NO₃, N₂O₅, NO₂ and O₃ mixing ratios (averaged to 1-min resolution) on 29–30 July 2002. The bottom left graph shows a map of the ship track during this period, color coded according to N₂O₅. The air flow was mainly out of the W and NW, as calculated by the backward trajectories shown on the map (R. R. Draxler and G. D. Rolph, HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Tracker) Model, Air Resources Laboratory, NOAA, 2003, available at <http://www.arl.noaa.gov/ready/hysplit4.html>). The bottom right graph shows a plot of the inverse NO₃ lifetime, $\tau_{NO_3}^{-1}$, against the unitless quantity $K_{eq}[NO_2]$ according to equation (5) for the period of the

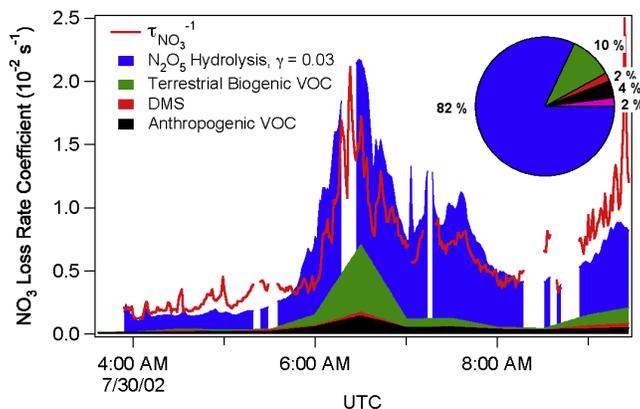


Figure 6. Comparison of observed and calculated values for the NO₃ first-order loss rate coefficient for the data in Figure 5. The calculated individual contributions from NO₃ reactions with anthropogenic VOC, terrestrially emitted biogenic VOC, dimethyl sulfide from equation (7), and the measured VOC concentrations are stacked together as shown in the legend. Also included in the stacked sum is the NO₃ loss from N₂O₅ hydrolysis, i.e., $k_{N_2O_5} K_{eq}[NO_2]$, with $\gamma(N_2O_5) = 0.03$ in equation (8). The inset pie chart gives the average contributions of these loss rate coefficients to the averaged, total loss over the course of the night using the same code as the legend. The additional 2% slice on the pie chart includes heterogeneous NO₃ loss with $\gamma(NO_3) = 4 \times 10^{-3}$.

night during which there were NO₂ data available (after 0400 UTC). The slope of the plot gives $k_{N_2O_5} = (5.0 \pm 0.1) \times 10^{-4} \text{ s}^{-1}$, and the intercept gives $k_{NO_3} = (6.4 \pm 1.2) \times 10^{-4} \text{ s}^{-1}$. The errors are from the fit alone and are underestimates of the true uncertainties in the derived rate coefficients. In particular, the value of k_{NO_3} obtained from the intercept is not well determined. It is comparable to the average, calculated value, $k_{NO_3}^{Calc}$, from the sum of the measured VOC data, $k_{NO_3}^{Calc} = 1 \times 10^{-3} \text{ s}^{-1}$ over the same time period. Changing the intercept to the value of $k_{NO_3}^{Calc}$ reduces the slope, i.e., the determined value of $k_{N_2O_5}$, by only 5%. Combined with the measured aerosol surface area of $260 \pm 140 \mu\text{m}^2 \text{ cm}^{-3}$ (where the error is from the variability rather than the measurement uncertainty), the value for $k_{N_2O_5}$ yields $\gamma(N_2O_5) = 0.03 \pm 0.02$.

[16] Figure 6 shows a breakdown of the individual contributions to the NO₃ and N₂O₅ sinks for the data in Figure 5 from 0400 to 0930 UTC from a plot of the calculated, inverse NO₃ lifetime, $(\tau_{NO_3}^{Calc})^{-1} = k_{NO_3}^{Calc} + k_{N_2O_5}^{Calc} K_{eq}[NO_2]$. There are four terms that encompass the majority of the NO₃ and N₂O₅ losses: N₂O₅ hydrolysis (weighted by $K_{eq}[NO_2]$ and with $\gamma(N_2O_5) = 0.03$), NO₃ reactions with terrestrially-emitted biogenic VOC, NO₃ reaction with DMS, and NO₃ reaction with anthropogenic VOC. The solid line shows the comparison to $\tau_{NO_3}^{-1} = k_1[NO_2][O_3]/[NO_3]$. The inset pie chart shows the average, relative contributions of each component of the NO₃ and N₂O₅ losses. Hydrolysis of N₂O₅ was the dominant loss pathway (82%) because of the relatively large mixing ratios of NO₂, which weights the loss in favor of N₂O₅, and because of the small loading of biogenic VOC, particularly DMS. Of the remaining 18% attributable to NO₃ reactions, the largest contribution was reaction with terrestrial biogenic VOC – i.e., biogenic VOC that was emitted from sources over land and advected into the marine boundary layer, primarily isoprene and monoterpenes (e.g., α -pinene). Anthropogenic

compounds, though they were abundant in this environment, are in general not particularly reactive with NO₃ and thus were calculated to have contributed only 4% to the loss. The calculated contribution of dimethyl sulfide to NO₃ and N₂O₅ loss on 29–30 July was anomalously low at only 2% because of small DMS concentrations, while heterogeneous loss of NO₃ would be predicted to contribute an additional 2% based on the assumed $\gamma(NO_3)$ given above. A larger $\gamma(NO_3)$ would obviously yield a larger contribution from heterogeneous loss; however, the small determined value of $k_{NO_3}^{Obs}$ for the single night shown in Figure 5 suggests that $\gamma(NO_3)$ was not likely to be much larger than its literature value on this night. This partitioning of losses yields a value of S in equations (11) and (12) of 1.82 averaged over the entire night. Therefore the total loss of NO_x should have proceeded at nearly twice the rate of the NO₂ + O₃ reaction.

[17] Figure 7 shows a similar set of data and analysis for 2–3 August 2002. The R/V *Brown* was just north of Cape Anne (northern Massachusetts coast) under conditions of SW to W flow. This night was similar to that in Figure 5 in that the NO₃ sinks were small and the observed and calculated lifetimes were in reasonable agreement. The plot of $\tau_{NO_3}^{-1}$ versus $K_{eq}[NO_2]$ shown in the bottom right graph also gives a similar result to the night of 29–30 July, although the scatter in these data make it more difficult to determine $k_{N_2O_5}$. A fit with the intercept constrained to the calculated value of $k_{NO_3}^{Calc} = 5.6 \times 10^{-4} \text{ s}^{-1}$ gives a slope of $k_{N_2O_5} = 6.1 \times 10^{-4} \text{ s}^{-1}$, while an unconstrained fit gives $k_{N_2O_5} = 4.7 \times 10^{-4} \text{ s}^{-1}$ and a larger intercept. Taking the average of the two fits gives $k_{N_2O_5} = (5.4 \pm 0.7) \times 10^{-4} \text{ s}^{-1}$. The solid line shows the constrained fit, and the text on the graph shows the inverse of the first-order N₂O₅ loss rate coefficient in minutes. Combined with the surface area value over this time period of $180 \pm 30 \mu\text{m}^2 \text{ cm}^{-3}$, the derived N₂O₅ uptake coefficient is $\gamma(N_2O_5) = 0.04 \pm 0.01$, consistent with the preceding example. Figure 8 shows the

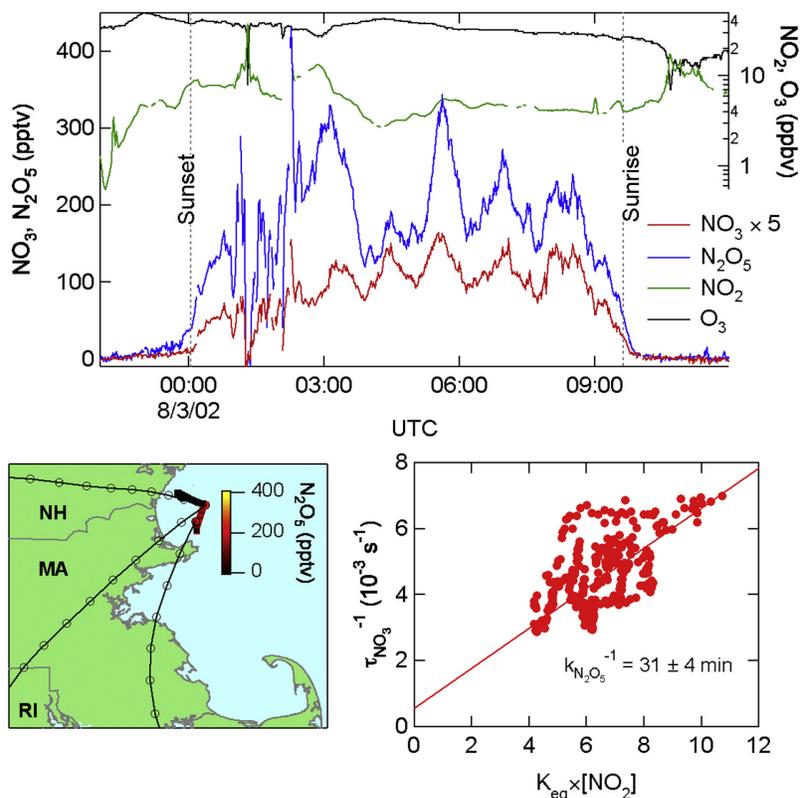


Figure 7. (top) Time series of NO₃, N₂O₅, NO₂, and O₃ for 2–3 August 2002, as in Figure 5, except with the NO₃ mixing ratio multiplied by a factor of 5 to make it visible on the scale of the left axis. Times of sunrise and sunset are marked. (bottom right) Plot of $\tau_{\text{NO}_3}^{-1}$ versus $K_{\text{eq}}[\text{NO}_2]$. The solid line is a linear fit, with the inverse of the slope and intercept shown on the graph. (bottom left) Map showing the R/V *Brown* track in the Gulf of Maine, shaded according to the N₂O₅ mixing ratio. Lines with circles are back trajectories as in Figure 5.

time series of the sum of the calculated losses and a pie chart of the averages for the entire night. Compared to 29–30 July, the reaction with DMS accounted for a larger fraction of the NO₃ loss (10%), while terrestrial biogenic VOC (isoprene and monoterpenes) reactions with NO₃ were negligible (2%). Similar to 30 July, however, loss of N₂O₅ accounted for 80% of the total, the value of *S* in equation (11) was 1.80, and the NO_x loss rate was nearly twice the rate of reaction (1).

[18] Table 1 summarizes the data for N₂O₅ first-order loss rate coefficients for the two nights discussed above. The first three columns show the first-order N₂O₅ loss rate coefficient, the aerosol surface area and the uptake coefficients, $\gamma(\text{N}_2\text{O}_5)$. The derived uptake coefficients are in the same range as literature values for N₂O₅ uptake on sulfate and ammonium sulfate aerosols from laboratory measurements [Hallquist *et al.*, 2003; Hu and Abbatt, 1997; Kane *et al.*, 2001; Mentel *et al.*, 1999]. The aerosol composition during NEAQS 2002 was dominated by organics (41–68%) and ammonium sulfate ((NH₄)_{*y*}H_{*x*}SO₄) (23–54%). The (NH₄)_{*y*}H_{*x*}SO₄ fraction tended to be acidic, with a mean ammonium to sulfate molar ratio of 1.7 [Bates *et al.*, 2005]. Laboratory studies with organic and/or mixed organic/inorganic aerosol have shown significantly smaller values of $\gamma(\text{N}_2\text{O}_5)$ in some cases relative to pure inorganic substrates [Thornton *et al.*, 2003; Folkers *et al.*, 2003]. A more

recent field study using aircraft data has shown strong suppression of $\gamma(\text{N}_2\text{O}_5)$ in some air masses that appeared to have been related to the aerosol organic fraction or to the aerosol acidity [Brown *et al.*, 2006]. In the NEAQS 2002 study, the data were not of sufficient quality for a systematic determination of the dependence of $\gamma(\text{N}_2\text{O}_5)$ on aerosol composition.

[19] The above analysis was based on the assumption that the hydrolysis of N₂O₅ proceeds exclusively via heterogeneous uptake on aerosol. Mentel *et al.* [1996] and Wahner *et al.* [1998] have measured rate coefficients for a homogeneous gas-phase component for N₂O₅ hydrolysis based on their data from large chamber studies. They found the proposed reaction to be the sum of a first- and second-order component in water vapor.

$$k_{\text{homogeneous}}(\text{N}_2\text{O}_5) = k_{\text{I}} \times [\text{H}_2\text{O}] + k_{\text{II}} \times [\text{H}_2\text{O}]^2$$

$$k_{\text{I}} = 2.5 \times 10^{-22} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (13)$$

$$k_{\text{II}} = 1.8 \times 10^{-39} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$$

Columns 5 and 6 in Table 1 give the N₂O₅ loss rate coefficients for each component of the homogeneous loss rate coefficient in equation (13). For 30 July and 3 August,

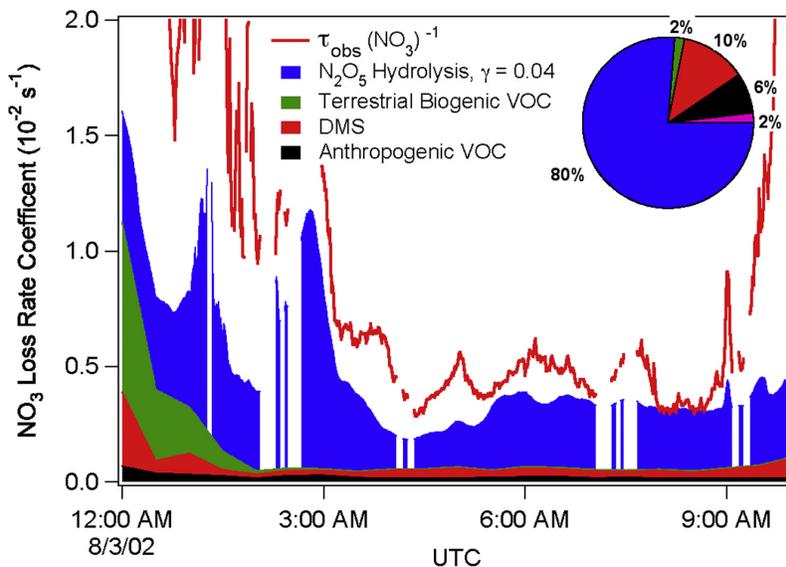


Figure 8. Comparison of observed and calculated NO₃ first-order loss rate coefficient for the data in Figure 7. The format of Figure 8 is analogous to that of Figure 6, except that $\gamma(\text{N}_2\text{O}_5) = 0.04$, as derived from Figure 7. Note that the contribution of NO to the NO₃ and N₂O₅ loss, which is significant before 1200 UTC, after 0930 UTC (i.e., during daylight), and for brief periods between 1240 and 0220 UTC, has been omitted. The inset pie chart shows the average of the calculated losses for the period between 0220 UTC and sunrise.

the first-order component would modestly reduce the uptake coefficients but would still allow for heterogeneous reaction to occur. Inclusion of the second-order component in equation (13) would require that essentially all of the N₂O₅ loss was due to the homogeneous reaction. Because of the considerable uncertainty in the field determinations of N₂O₅ first-order loss rate coefficients from the NEAQS 2002 data, it is not possible to rule out the parameterization of the homogeneous N₂O₅ hydrolysis shown above. However, given that heterogeneous hydrolysis is known to occur, the smog-chamber parameterization of the homogeneous hydrolysis is larger than this determination from ambient field data would support. This conclusion holds true for all of the NO₃ and N₂O₅ data from the NEAQS 2002 campaign and is also supported by an analysis of a more recent data set acquired from an aircraft [Brown *et al.*, 2006].

5.2. Case 2: Losses Dominated by NO₃ Reactions

[20] There were several nights during the 2002 campaign on which there were large mixing ratios of biogenic VOC, and, consequently, large losses of NO₃ in comparison to those for N₂O₅. Figure 9 illustrates such a case. The R/V *Brown* was again off of the northern Massachusetts coast under conditions of offshore flow (SW wind early in the night, NW flow later). The average of the total losses for NO₃ and N₂O₅ on this night were significantly larger than

those in Figures 6 and 8, mainly because of the presence of isoprene, monoterpenes (the terrestrially emitted biogenic VOC) and DMS. The aerosol surface, and therefore the predicted N₂O₅ heterogeneous loss rate constant, were similar to the previous two examples, but in this case were smaller than the calculated VOC loss rates. Because of the rapid loss rates, NO₃ and N₂O₅ were only observed during two distinct, large NO₂ plumes, one early and one late in the night, as marked in Figure 9.

[21] The decrease in the calculated loss rates for NO₃ that were associated with each plume were due to a drop in the mixing ratio of isoprene and monoterpenes within the NO_x-containing plumes. This observation implies that the increased source strength of NO₃ due to the presence of anthropogenic NO₂ increased the nocturnal oxidation rate of biogenic VOC relative to background air; that is, wherever there was sufficient NO_x to drive VOC oxidation during the transit time from the continent to the R/V *Brown*, the VOC concentrations were depleted. This spatial inhomogeneity in the nocturnal oxidation of VOC stands in contrast to daytime oxidation by OH, whose photochemical source from ozone photolysis in the presence of water vapor is more diffusely distributed. At night, nocturnal processing tends to occur most strongly within NO_x-containing plumes. Indeed, the second plume in Figure 9 was likely from a power plant source (NO₂ was correlated with ~15 ppbv of SO₂ in this plume) which emits a large amount of NO_x into

Table 1. Uptake Coefficients for N₂O₅ Determined From Analysis of Field Data

Date	$k_{\text{N}_2\text{O}_5}$, s ⁻¹	Surf Area, $\mu\text{m}^2 \text{cm}^{-3}$	$\gamma(\text{N}_2\text{O}_5)$	$k_{\text{I}}[\text{H}_2\text{O}]$, s ⁻¹	$k_{\text{II}}[\text{H}_2\text{O}]^2$, s ⁻¹	$\gamma(\text{N}_2\text{O}_5)$ Corrected for $k_{\text{I}} \times [\text{H}_2\text{O}]$
30 July	5.0×10^{-4}	260 ± 140	0.03	1.4×10^{-4}	5.5×10^{-4}	0.018
3 August	5.2×10^{-4}	180 ± 30	0.04	1.3×10^{-4}	5.2×10^{-4}	0.028

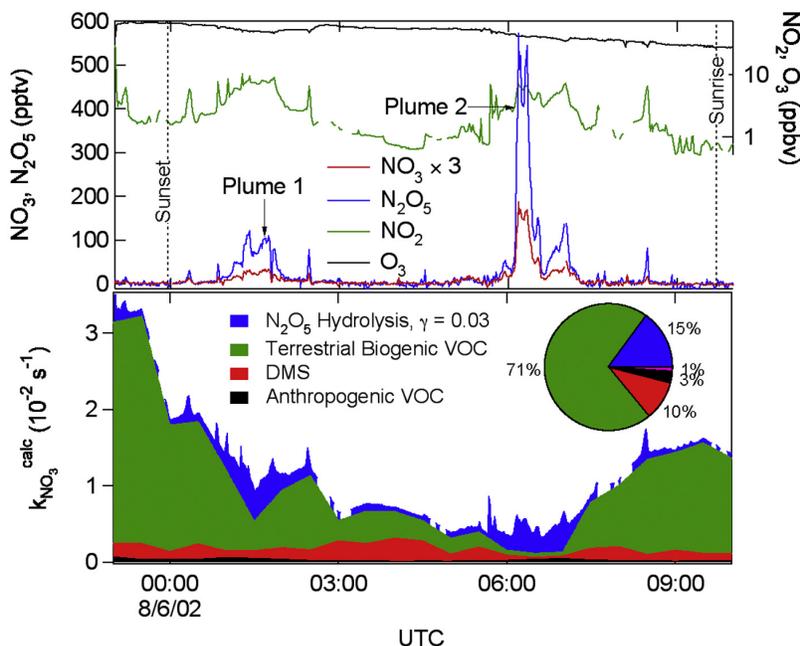


Figure 9. (top) Time series of NO₃, N₂O₅, NO₂, and O₃ for 5–6 August 2002, with NO₃ multiplied by a factor of 3. (bottom) Calculated NO₃ first-order loss rate coefficient, $k_{NO_3}^{calc}$, as in Figures 6 and 8. The contribution of NO, present before sunset and after sunrise, is not shown. The pie chart on the inset shows the average contributions of each loss pathway for the period between sunset and sunrise.

a relatively confined region, especially at night when mixing processes are slower.

[22] There was also a lack of agreement between the observed and calculated NO₃ loss rate coefficients for the data in Figure 9. This may be an indication of secondary chemistry occurring subsequent to the initial oxidation step for compounds such as isoprene and DMS, either as a result of peroxy radical reactions [Carshaw *et al.*, 1997; Geyer *et al.*, 2003; Jensen *et al.*, 1992; Platt *et al.*, 1990, 2002; Salisbury *et al.*, 2001] or reactions of NO₃ with secondary oxidation products (e.g., organic nitrates) [Atkinson and Arey, 2003], neither of which was measured during this campaign. Although it is not possible to quantify the potential contribution of these additional NO₃ reactions from the existing measurements, future modeling studies of this and other data sets will address these issues.

[23] A second example of large NO₃ losses due to the presence of biogenic VOC appears in Figure 10, which shows NO₃ and N₂O₅ mixing ratios for the night of 30–31 July 2002. On this night the R/V *Brown* was outside of Boston Harbor, south of Cape Anne and made SW-NE running transects perpendicular to a NW wind. Back trajectories showed relatively rapid transport (within a few hours) from central NH, an area with significant monoterpene emission [Geron *et al.*, 1994]. Figure 10 demonstrates the interaction that can occur between different VOC as a result of their common loss NO₃. The observed mixing ratio of the pinenes was anticorrelated with NO₃, as has been described previously by [Warneke *et al.*, 2004]. As described in the preceding example, the anticorrelation is presumably the result of loss of the reactive pinenes during transport to the R/V *Brown*

in air masses impacted by NO₂ emissions with increased source strength for NO₃ (observed on the SW end of each transect as the *Brown* sampled downwind of the Boston area). For example, the lifetime of α -pinene with respect to NO₃ oxidation averaged 8 min from 0500 to 0600 UTC when it was not observed, and >5 hours from 0300 to 0430 UTC, when it was present. During the latter part of the time series, the concentrations of pinenes and DMS were well correlated, even though DMS arises from an ocean source and the pinenes from a terrestrial one. In the air masses with lower NO₂ and measurable pinene mixing ratios, the increased concentrations of DMS were likely a result not only of decreased oxidation rate due to smaller NO₃ source strength (i.e., a smaller amount of available NO₃), but also of competition between the monoterpenes and DMS for the available NO₃. For example, α -pinene reacts with NO₃ approximately 6 times faster than does DMS [Atkinson, 1991], and so can effectively suppress nocturnal, NO₃-driven oxidation of DMS when it is present. The example demonstrates the interaction between the terrestrially emitted biogenic VOC and DMS in a polluted environment via their common sink to NO₃ reaction, and shows that DMS oxidation at night can be influenced not just by the presence of NO₃ derived from NO_x, but also by other VOC that act as sinks for NO₃.

5.3. Case 3: Weak Sinks for NO₃ and N₂O₅

[24] Although the observed lifetimes of NO₃ and N₂O₅ were quite short (i.e., on the order of a few minutes for NO₃) throughout the measurement period within the Gulf of Maine, the same was not true of other regions sampled during NEAQS 2002. Figure 11 shows the time series of NO₃, N₂O₅ and NO₂ from 7 to 8 August 2002, when the R/V *Brown* was well south of the New England study

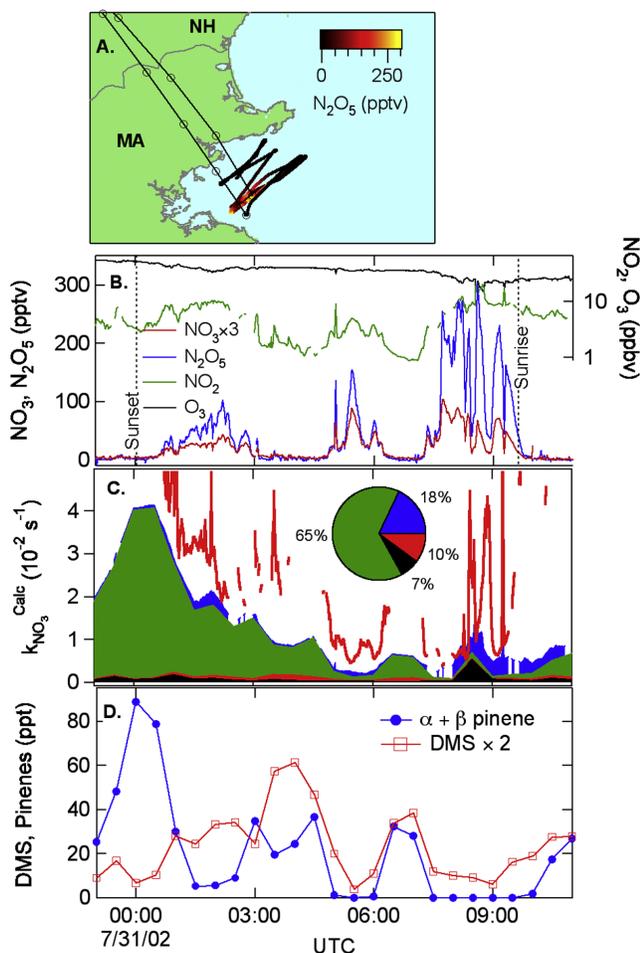


Figure 10. (a) Map of R/V *Brown* track, shaded by the N₂O₅ mixing ratios, and calculated back trajectories. (b) Time series from 30 to 31 July of NO₃, N₂O₅, NO₂, and O₃, with the NO₃ mixing ratio multiplied by a factor of 3. (c) Calculated first-order NO₃ loss rate coefficients, $k_{NO_3}^{Calc}$ showing the individual contributions. The pattern scheme is the same as in Figures 6, 8, and 9, and the solid line is $\tau_{NO_3}^{-1}$. The inset pie chart shows the average, relative contribution from each sink for the period between sunset and sunrise. (d) Time series of α -pinene and DMS. The correlation between these compounds is driven by their common sink via NO₃ reaction.

area on the transit back to its home port in Charleston, South Carolina. Observed lifetimes of NO₃ and N₂O₅ in this region were considerably longer (e.g., in excess of 30 min for NO₃). The map in the lower corner shows the R/V *Brown* position and back trajectories showing that the sampled air mass came from the north, passing over the New York City area roughly 12–14 hours upwind. There was somewhat lower NO_x (~1.5 ppbv NO₂) compared to most of the air sampled in the New England region that was of continental origin, yet the NO₃ mixing ratio reached its largest sustained values of the entire campaign (>100 pptv). Mixing ratios of N₂O₅ reached by far their largest observed values under similar conditions on the following night (see Figure 3) near Norfolk, Virginia. The inverse NO₃ lifetime, $\tau_{NO_3}^{-1}$, in the center panel shows reasonable agreement with the calculated loss rate coefficients, $k_{NO_3}^{Calc}$, although the value for $\gamma(N_2O_5) =$

0.03, determined under conditions of rapid N₂O₅ loss in the Gulf of Maine, may have been an overestimate in this region (see below). The apparent disagreement between the observed and calculated NO₃ lifetimes early in the night, until approximately 0330 UTC, is in fact not the result of a disagreement between the steady state model and the measurements. Rather, this is a case in which the approach to steady state was limited by the induction time (i.e., the time constant for loss of NO₃ and N₂O₅) [Allan *et al.*, 2000] because of the apparently weak sinks within this air mass. The disagreement late in the night, on the other hand, was likely due to a shift to a different air mass in which the sinks for NO₃ and N₂O₅ were not well accounted for. The slow losses for NO₃ and N₂O₅ may have been the result of a number of factors. First, the mixing ratios of biogenic VOC were small; terrestrially emitted biogenic VOC were all below their instrumental detection limits (<1 pptv), and DMS was observed at a maximum of 20 pptv prior to sunset. The aerosol surface area density was also relatively small, with an average value of 130 $\mu\text{m}^2 \text{cm}^{-3}$. Another factor that was distinct on the night of 7–8 August was the relative humidity of 55%, the smallest nocturnal average value of the campaign. Platt *et al.* [1984], for example, have reported large increases in NO₃ and N₂O₅ lifetimes at low RH over desert regions of southern California that they attributed to decreased aerosol particle growth. A final difference on 7–8 August was the depth of the mixed layer, which radiosonde data showed to be deeper on this leg of the R/V *Brown* cruise (~1 km) than in the Gulf of Maine (100 m) [Angevine *et al.*, 2004]. The deeper mixed layer may in turn have been related to warmer sea surface temperatures (25°C compared to 18°C in the Gulf of Maine) and may, among other things, have served to reduce the concentration of sinks for NO₃ and N₂O₅, such as DMS emitted from the ocean surface. In any case, Figure 11 shows that NO₃ and N₂O₅ losses were not observed to be universally rapid within the marine boundary layer during NEAQS 2002, and furthermore, that the variation in observed lifetimes may have been related to regional differences in factors such as DMS emissions, sea surface temperature, boundary layer mixing, etc.

5.4. Summary of Losses for the Entire Campaign

[25] Figure 12 shows a summary of the losses for NO₃ and N₂O₅ for the duration of the campaign. The averages in the chart are the calculated losses for nighttime hours only, and only for the time periods where NO₃ and N₂O₅ were reported. Direct losses for NO₃ were dominated by reactions with VOC, with heterogeneous uptake using the literature value of $\gamma(\text{NO}_3) = 4 \times 10^{-3}$ contributing only 2% to the total. Of the VOC losses, DMS was the most important, followed by terrestrially emitted biogenic hydrocarbons (mostly isoprene and monoterpenes). Only a small fraction of the total (7%) could be attributed to NO₃ reaction with anthropogenic VOC. The N₂O₅ loss is calculated using the measured aerosol surface area and a constant $\gamma(\text{N}_2\text{O}_5) = 0.03$, as determined from the analysis in section 5.1. Assuming this uptake coefficient is representative of the entire data set, the individual losses for NO₃ and N₂O₅, were, on average, approximately equal contributions to the total loss of the pair. Since the lifetime of these compounds in the New England region were short enough to make

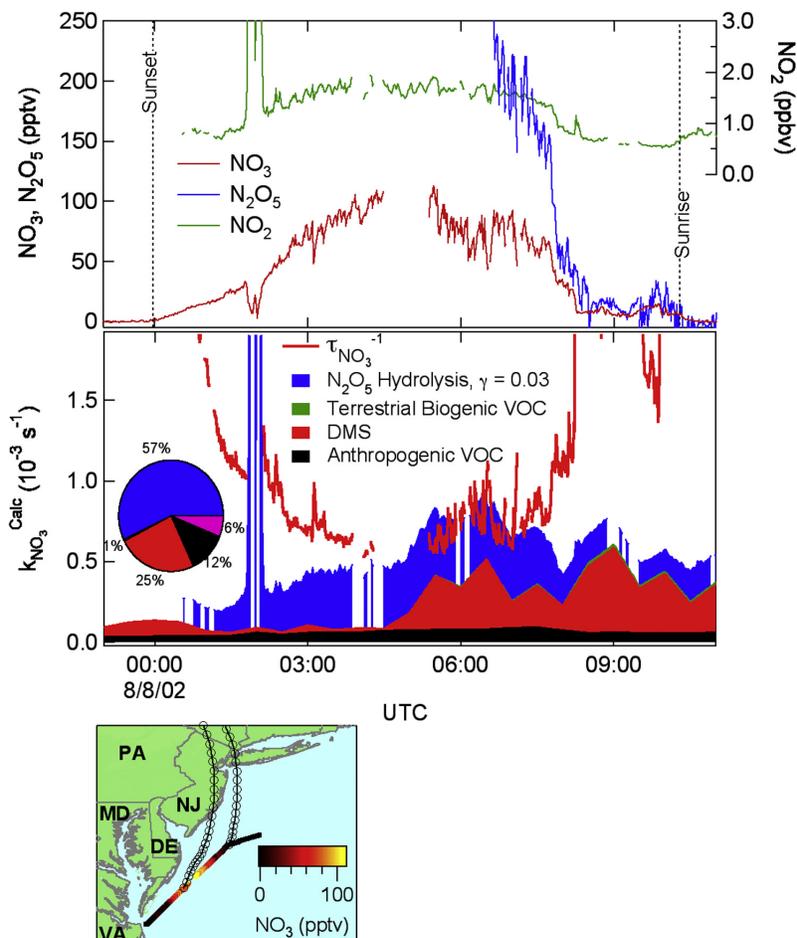


Figure 11. (top) Time series from 7 to 8 August of NO₃, N₂O₅, and NO₂. N₂O₅ was only available in the latter part of the night because of an instrumental difficulty. O₃ (not shown) was steady at 45 ppbv. (middle) Calculated first-order NO₃ loss rate coefficients, $k_{NO_3}^{Calc}$ showing the individual contributions. The solid line is $\tau_{NO_3}^{-1}$. The pie chart at the bottom shows the averaged contributions to this loss between sunset and sunrise. (bottom) Map of the R/V *Brown* track shaded by the NO₃ mixing ratio. Back trajectories are shown, as in Figures 5, 7, and 10.

reaction (1) the rate limiting step for loss of NO_x at night, the average value of S in equations (11) and (12) for this campaign should have been approximately 1.5 – i.e., the loss of NO_x at night occurred, on average, at 1.5 times the rate of the reaction of NO₂ with O₃. At the campaign average nocturnal O₃ concentration of 41 ppbv, the calculated nocturnal lifetime of NO_x (i.e., $(Sk_1[O_3])^{-1}$) was 6.0 hours, corresponding to greater than 80% loss of NO_x in a 10 hour night.

6. Nocturnal Halogen Activation

[26] Uptake of both NO₃ and N₂O₅ on sea salt aerosol can lead to the release of active halogens compounds to the gas phase according to the following reactions [Finlayson-Pitts *et al.*, 1989; Rossi, 2003].

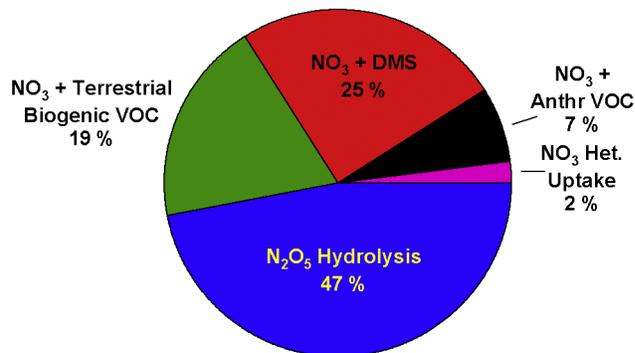
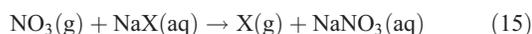


Figure 12. Fractional contributions to the reciprocal lifetime of NO₃ for the entire NEAQS 2002 campaign. Heterogeneous losses of NO₃ and N₂O₅ use constant values of 4×10^{-3} and 3×10^{-2} for the uptake coefficients, respectively. Variability in these uptake coefficients could change the partitioning of sinks considerably.

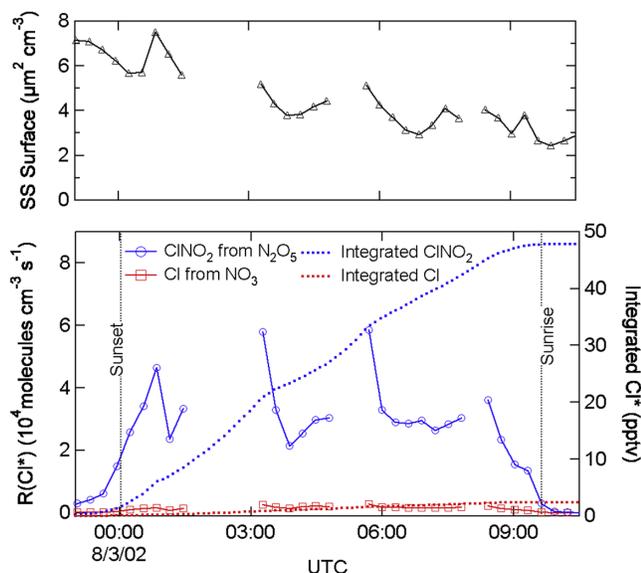


Figure 13. (top) Sea salt surface area calculated from the supermicron aerosol size distribution for 2–3 August 2002. (bottom) Calculated production rates for Cl containing compounds ($R(\text{Cl}^*)$, left axis) from NO₃ and N₂O₅ uptake on sea salt. The right axis shows the integrated Cl* yield in pptv assuming unit yield and zero loss.

Here X is primarily Cl but may include a small amount of Br [Behnke *et al.*, 1994]. This chemistry is potentially important in marine environments since halogen atoms are potent oxidants and since they can participate in cycles that catalytically remove ozone [Finlayson-Pitts *et al.*, 1989]. Aside from HCl, there were no measurements of gas phase halogens or halogen compounds as part of the R/V *Brown* measurement suite. The largest source of HCl in this polluted marine environment was most likely the uptake of nitric and/or sulfuric acid on sea salt. Thus there is no direct observational evidence for reactions (14) and (15) from the NEAQS 2002 campaign.

[27] The nocturnal reactive halogen source may nevertheless be estimated from the measured sea salt abundance, the concentrations of NO₃ and N₂O₅, and the uptake coefficients for these compounds on sea salt from laboratory studies. The aerosol surface area attributable to sea salt can be calculated from the aerosol size distributions in the supermicron range, which were dominated by sea salt and NO₃⁻. Submicron aerosol, by contrast, was dominated by NH₄⁺, non sea-salt sulfate and organics [Bates *et al.*, 2005]. The average calculated sea salt surface area density during NEAQS 2002 was small, at 5.5 μm² cm⁻³, or about 2% of the total aerosol surface, consistent with low wind speeds (avg. $\pm 1\sigma = 5 \pm 2$ m s⁻¹) in the Gulf of Maine in summer. A typical value for the uptake coefficient of N₂O₅ on aqueous salt solutions from lab studies is 0.03 [Behnke *et al.*, 1997; Stewart *et al.*, 2004], and the calculated N₂O₅ uptake rate on sea salt varied from zero up to 4×10^4 molecules cm⁻³ s⁻¹. The night of 2–3 August (see Figures 7 and 8) showed the strongest calculated ClNO₂ production rates, with an average value of 3×10^4 molecules cm⁻³ s⁻¹, as shown in Figure 13. The yield and the fate of the resulting ClNO₂ product is unknown. Under the assumption that it survives

until sunrise when it can be photolyzed to release Cl, the integrated halogen production on 2–3 August would have amounted to a 45 pptv halogen release, as shown against the right axis of Figure 13. Similarly, uptake coefficients for NO₃ on sea salt are in the range $\gamma(\text{NO}_3)_{\text{SS}} = 1\text{--}6 \times 10^{-3}$ [Rudich *et al.*, 1996]. Taking the 6×10^{-3} as an upper limit, the calculated uptake rates for NO₃ on sea salt varied between $0\text{--}6 \times 10^3$ molecules cm⁻³ s⁻¹. Figure 13 shows the Cl production rate and integrated Cl yield from NO₃ on 2–3 August assuming unit yield and no loss. It is important to stress that these estimates represent upper limits from the night with the strongest predicted source.

[28] There is insufficient evidence available from our analysis of this data set to date to test a halogen source of this magnitude at sunrise. Hydrocarbon oxidation, for example, was observed to proceed rapidly during the night and day, but much more slowly during the dawn and dusk periods [Warneke *et al.*, 2004]. The release of a halogen reservoir at dawn from photolysis of ClNO₂ with a lifetime of 1 hour [Behnke *et al.*, 1997], would tend to introduce faster VOC oxidation rates at this time of day, contrary to what was observed. Even though a dawn source rate for active Cl of the order of 3×10^5 atoms cm⁻³ s⁻¹ is substantial, the integrated effect on the oxidation of VOC would be modest. Thus the nocturnal halogen production cannot be easily quantified on the basis of the available data.

7. Summary and Conclusion

[29] Ship-based, in situ measurements of NO₃ and N₂O₅ in the polluted marine boundary layer off of the United States East Coast during the summer of 2002 from the NOAA research vessel *Ronald H. Brown* give a detailed picture of the nocturnal chemistry that governs both the rate of NO_x loss and the oxidation of VOC. Steady state lifetimes for NO₃ and N₂O₅ were comparable to those determined from previous surface-level DOAS measurements of NO₃. Analysis of the dependence of steady state lifetimes on NO_x, combined with calculated loss rate coefficients from measured aerosol loading and VOC concentrations allows for an accounting of the individual contributions to the losses of NO₃ and N₂O₅, and in some cases an estimate for the uptake coefficients for heterogeneous hydrolysis of N₂O₅, $\gamma(\text{N}_2\text{O}_5)$. Heterogeneous uptake coefficients determined from this data set were $\gamma(\text{N}_2\text{O}_5) = 0.03 \pm 0.02$ and compare well with values from laboratory measurements. The most obvious discrepancies between the observed and calculated NO₃ and N₂O₅ lifetimes occurred either on nights with large concentrations of biogenic VOC (isoprene, monoterpenes, DMS), possibly as a result of secondary chemistry between NO₃ and unmeasured second-generation reaction products. For the campaign as a whole, the loss partitioning between NO₃ and N₂O₅ was approximately equal; that is, about 50% of the loss of the NO₃ and N₂O₅ pair was due to reactions of each compound. Because NO₃ and N₂O₅ loss was rapid on most nights and because N₂O₅ hydrolysis was predicted to be responsible for roughly half of this loss, the removal of anthropogenic NO_x in this polluted marine environment was rate limited by the reaction of NO₂ with O₃ and proceeded at approximately 1.5 times the rate of this reaction. Finally, halogen

chemistry arising from the displacement of halides from sea salt aerosol by NO₃ and N₂O₅ may have provided a dawn Cl source during NEAQS 2002, but there are insufficient data available to test the magnitude of this source.

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