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N₂O₅ uptake coefficients and nocturnal NO₂ removal rates determined from ambient wintertime measurements

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[1] Heterogeneous N₂O₅ uptake onto aerosol is the primary nocturnal path for removal of NO_x (= NO + NO₂) from the atmosphere and can also result in halogen activation through production of ClNO₂. The N₂O₅ uptake coefficient has been the subject of numerous laboratory studies; however, only a few studies have determined the uptake coefficient from ambient measurements, and none has been focused on winter conditions, when the portion of NO_x removed by N₂O₅ uptake is the largest. In this work, N₂O₅ uptake coefficients are determined from ambient wintertime measurements of N₂O₅ and related species at the Boulder Atmospheric Observatory in Weld County, CO, a location that is highly impacted by urban pollution from Denver, as well as emissions from agricultural activities and oil and gas extraction. A box model is used to analyze the nocturnal nitrate radical chemistry and predict the N₂O₅ concentration. The uptake coefficient in the model is iterated until the predicted N₂O₅ concentration matches the measured concentration. The results suggest that during winter, the most important influence that might suppress N₂O₅ uptake is aerosol nitrate but that this effect does not suppress uptake coefficients enough to limit the rate of NO_x loss through N₂O₅ hydrolysis. N₂O₅ hydrolysis was found to dominate the nocturnal chemistry during this study consuming ~80% of nocturnal gas phase nitrate radical production. Typically, less than 15% of the total nitrate radical production remained in the form of nocturnal species at sunrise when they are photolyzed and reform NO₂.

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1. Introduction

[2] The nitrate radical (NO₃) and its reservoir partner dinitrogen pentoxide (N₂O₅) are nocturnal trace gases present at large concentrations in polluted air masses. N₂O₅ is lost to heterogeneous uptake by aerosol. This heterogeneous uptake is responsible for the nocturnal removal of nitrogen oxides (NO_x = NO + NO₂), which can be a significant portion of the overall NO_x removal budget [Brown *et al.*, 2004; Dentener and Crutzen, 1993]. Heterogeneous N₂O₅ uptake can also result in halogen activation through production of nitryl chloride (ClNO₂) which is photolyzed into atomic

chlorine in the morning [Finlayson-Pitts *et al.*, 1989; Osthoff *et al.*, 2008; Thornton *et al.*, 2010].

[3] The rate coefficient of the N₂O₅ heterogeneous loss ($k_{\text{N}_2\text{O}_5}$) is proportional to the aerosol surface area density (A), the mean molecular speed of N₂O₅ (\bar{v}), and the N₂O₅ uptake coefficient ($\gamma(\text{N}_2\text{O}_5)$) as shown in equation (1), which is valid for small uptake coefficients such that gas phase diffusion to the particle surface does not limit the uptake [Fuchs and Sutugin, 1970].

$$k_{\text{N}_2\text{O}_5} \approx \frac{1}{4} \bar{v} A \gamma(\text{N}_2\text{O}_5) \quad (1)$$

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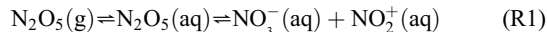
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[4] The uptake coefficient represents a reaction probability (i.e., the fraction of molecules which do not return to the gas phase after a collision with the surface).

[5] The N₂O₅ uptake coefficient typically depends on the aerosol composition and relative humidity and has been the subject of multiple laboratory studies and two recent reviews [Brown and Stutz, 2012; Chang et al., 2011]. The measured uptake coefficients on water droplets range from 0.01 to 0.06. On tropospheric aerosol which is not strongly acidic, N₂O₅ is ionized into aqueous nitrate (NO₃⁻) and the cation NO₂⁺. The competition between components of the aerosol that react with NO₂⁺ determines the aqueous concentration of molecular N₂O₅ in the aerosol and subsequently, the portion of N₂O₅ which returns to the gas phase after accommodation. Any N₂O₅ which returns to the gas phase effectively reduces the uptake coefficient.

[6] Laboratory experiments have identified four mechanisms which affect the N₂O₅ uptake coefficient on tropospheric aerosol. First, numerous studies on inorganic salts and some organic substrates have found reduced uptake at low relative humidity and for solid particles [Hallquist et al., 2003; Hu and Abbatt, 1997; Thornton et al., 2003]. In these studies, the lower concentration of condensed water reduces the rate at which N₂O₅ ionizes. Second, Wahner et al. [1998b] have found that presence of nitrate (NO₃⁻) in the aerosol reduces the uptake by an order of magnitude, and this result has been confirmed by Mentel et al. [1999], Hallquist et al. [2003], and Bertram and Thornton [2009]. Upon accommodation into the aerosol, N₂O₅ is ionized into NO₃⁻ and NO₂⁺ as shown in reaction (R1).



[7] The accommodation and ionization set up an equilibrium between gas phase N₂O₅ and aqueous NO₂⁺. Aerosol enhanced in nitrate will shift the equilibrium toward gas phase N₂O₅ and effectively reduce uptake coefficient. The suppression of the uptake coefficient by nitrate is called the “nitrate effect.” Third, Bertram and Thornton [2009] have shown that aerosol chloride (Cl⁻) can reduce the suppression of uptake by nitrate. The nitrate suppression is reduced because the reaction of NO₂⁺ with Cl⁻ is favored over the reaction with NO₃⁻. Fourth, several studies have shown reduced uptake of N₂O₅ on organic aerosol relative to aqueous aerosol [Badger et al., 2006; Cosman and Bertram, 2008; McNeill et al., 2006; Park et al., 2007]. Anttila et al. [2006] have parameterized this effect in terms of an aerosol particle with an organic shell and an inorganic core. These organic coatings may reduce the availability of water on the aerosol surface and decrease the ionization rate of molecular N₂O₅.

[8] These laboratory results have rarely been tested against uptake coefficients determined from field measurements. There have been only four studies where uptake coefficients have been determined from ambient in situ measurements. Bertram et al. [2009] directly measured the N₂O₅ loss rate coefficient in a flow tube reactor with ambient aerosol and in combination with aerosol surface area density measurements determined the uptake coefficient. These measurements in Seattle, Washington and Boulder, Colorado show a decrease in the uptake coefficient as the aerosol organic to sulfate ratio increased. Riedel et al. [2012a] have also

measured ambient N₂O₅ uptake coefficients using a flow tube reactor and observed suppression of the uptake coefficient correlated with aerosol nitrate in La Jolla, California. Two aircraft studies have been used to determine N₂O₅ uptake coefficients in isolated plumes. Over New England and the Ohio River valley, Brown et al. [2006] found the uptake coefficient to be variable; high on sulfate particles (~0.02) but an order of magnitude lower otherwise. A similar aircraft study in Texas found uptake coefficients to be low (average value of 0.003) but with too few determinations to parameterize a dependence on aerosol composition or relative humidity (RH) [Brown et al., 2009].

[9] All of the prior field determinations of $\gamma(\text{N}_2\text{O}_5)$ have been for summertime or warm conditions. There are several important differences between winter and summer with respect to N₂O₅ uptake. First, longer nights during the winter allow for increased nocturnal NO_x removal through the N₂O₅ pathway. Second, in summer, N₂O₅ chemistry represents a smaller fraction of total nitrogen oxide loss because it competes with nighttime NO₃ chemistry during warm conditions as well as daytime photochemical reactions of NO_x. In winter, by contrast, a much larger fraction of the reactive nitrogen loss proceeds through N₂O₅ [Davis et al., 2008; Dentener and Crutzen, 1993; Evans and Jacob, 2005; Macintyre and Evans, 2010]. Third, N₂O₅ heterogeneous uptake may differ substantially in winter due to a change in aerosol composition. Winter aerosols tend to have higher concentrations of nitrate and lower concentrations of organics, due to shifts in thermodynamic equilibrium of ammonium nitrate and reduced oxidation of volatile organic compounds, respectively [Zhang et al., 2007; F. Öztürk et al., Vertically resolved chemical characteristics and sources of submicron aerosols in a suburban area near Denver, Colorado, submitted to *Journal of Geophysical Research: Atmospheres*, 2013, hereinafter referred to as Öztürk et al., submitted manuscript, 2013]. Field investigations have not explored the influence of these factors on N₂O₅ uptake and reactive nitrogen loss. Here we present ambient, vertically resolved measurements of key nitrogen oxide species, including N₂O₅ and ClNO₂, along with aerosol composition and relative humidity which are integrated into an iterative box model to determine the efficiency of winter N₂O₅ uptake at a polluted, midcontinental location. The influence of N₂O₅ hydrolysis on the overall nocturnal loss of nitrogen dioxide (NO₂) is explored and compared with the daytime loss of NO₂.

2. The Nitrogen, Aerosol Composition, and Halogens on a Tall Tower (NACHTT) Field Study

[10] The Nitrogen, Aerosol Composition, and Halogens on a Tall Tower (NACHTT) field study took place in the wintertime from 17 February through 14 March 2011. S. S. Brown et al. (The nitrogen, aerosol composition and halogens on a tall tower experiment, submitted to *Journal of Geophysical Research: Atmospheres*, 2013, hereinafter referred to as Brown et al., submitted manuscript, 2013) have provided an overview of the NACHTT field study including a description of all of the measurements, the climatology, and the scientific goals. Here we describe the instruments and measurements critical to this analysis and the measurement site.

Table 1. Critical Measurements Used in This Analysis

Location	Species	Detection Limit	Method ^a	Accuracy	Reference
Aboard the Elevator Carriage	NO ₃	3 pptv (2σ, 1 s)	CRDS (660 nm)	± 20% (1σ)	[Wagner et al., 2011]
	N ₂ O ₅	3 pptv (2σ, 1 s)	CRDS (660 nm)	± 11% (1σ)	[Wagner et al., 2011]
	NO ₂	90 pptv (2σ, 1 s)	CRDS (405 nm)	± 3% (1σ)	[Wagner et al., 2011]
	NO	140 pptv (2σ, 1 s)	CRDS (405 nm)	± 5% (1σ)	[Wagner et al., 2011]
	O ₃	120 pptv (2σ, 1 s)	CRDS (405 nm)	± 5% (1σ)	[Wagner et al., 2011]
	CINO ₂	5 pptv	CIMS (I ⁻)	± 20%	[Kercher et al., 2009]
	Dry surface area density		UHSAS	± 33%	[Cai et al., 2008]
	Sulfate	9 ng m ⁻³ (3σ, 10 s)	AMS	± 35%	[Bahreini et al., 2009]
	Nitrate	9 ng m ⁻³ (3σ, 10 s)	AMS	± 33%	[Bahreini et al., 2009]
	Ammonium	5 ng m ⁻³ (3σ, 10 s)	AMS	± 33%	[Bahreini et al., 2009]
	Chloride	1 ng m ⁻³ (3σ, 10 s)	AMS	± 35%	[Bahreini et al., 2009]
	Organics	7 ng m ⁻³ (3σ, 10 s)	AMS	± 37%	[Bahreini et al., 2009]
On the 22 m Platform	VOCs	< 3 pptv	Whole Air Samples/GC-MS	± 1%–15%	[Russo et al., 2010]
On 9 m Tower	Photolysis rates	Varies With Species	Filter Radiometer	± 14%	[Stark et al., 2007]
In Trailer (2 m High Inlet)	OH	10 ⁵ molecules cm ⁻³	CIMS (H ₂ SO ₄)	± 35%	[Tanner et al., 1997]

^aCRDS, Cavity Ringdown Spectrometer; CIMS, Chemical Ionization Mass Spectrometer; UHSAS, Ultra High Sensitivity Aerosol Spectrometer; AMS, Aerodyne Aerosol Mass Spectrometer; GC-MS, gas chromatography mass spectrometer.

[11] The study was located at the Boulder Atmospheric Observatory (BAO) in Weld County, Colorado. The BAO has a 300 m tower with an external elevator carriage capable of lifting ~1400 kg. Several instruments were placed in a temperature-controlled (nominally 25°C) enclosure mounted on the elevator for vertical profiling. The elevator ascended and descended at ~0.5 m/s and produced a vertical profile approximately every 10 min during continuous profiling. The height of the elevator was measured by counting the teeth of the elevator gear and was consistent with the measured global positioning system altitude. During the field study, profiling was done continuously, only limited by the weather and maintenance of the instruments and elevator. The elevator was not operated when the wind speed exceeded 12 m/s or ice was present on the elevator rails. The instruments were maintained daily, which typically resulted in an interruption of profiling that lasted 1–4 h.

[12] Five instruments were installed aboard the carriage elevator, and the measured species used in this analysis along with detection limits and accuracies are listed in Table 1. First, a cavity ringdown spectrometer measured nitrogen oxides and ozone [Wagner et al., 2011]. A 662 nm diode laser was used to measure the absorption from NO₃, and a 405 nm diode laser was used to measure absorption from NO₂. In separate channels, N₂O₅ was measured by thermal conversion to NO₃, and NO and O₃ were measured by chemical conversion to NO₂. The inlet for the NO₃ and N₂O₅ measurements consisted of 45 cm of 0.25 in. OD Teflon perfluoroalkoxy (PFA) tubing. A Teflon membrane (Pall Corp. R2PJ047, 2 μm pore size, 25 μm thickness) was used to remove aerosol from the sample stream and was replaced every 2 h by an automatic filter changer. Daily measurements of the N₂O₅ inlet transmission [Fuchs et al., 2008; Wagner et al., 2011] did not show a loss of N₂O₅ on the inlet surface. The transmission of NO₃ through the inlet was not measured but was estimated to be 85% based on previous measurements of the loss of NO₃ on Teflon tubing [Dubé et al., 2006]

and validation experiments in an environmental simulation chamber [Dorn et al., 2013]. The inlet tubing and fittings were replaced daily. A separate inlet tube (45 cm of 0.25 in. OD Teflon PFA tubing) was used for the sampling of NO, NO₂, and O₃.

[13] Second, CINO₂ was measured using a chemical ionization mass spectrometer (CIMS) with the iodine anion as a reagent [Kercher et al., 2009]. The CIMS shared an inlet with the NO₃ and N₂O₅ measurement which allowed the CINO₂ measurement to be calibrated relative to the N₂O₅ cavity ringdown measurement. N₂O₅ was added to the tip of the inlet daily. During calibrations, a NaCl salt bed was inserted into the sample stream, the N₂O₅ that was added to the inlet was converted to CINO₂ with unit yield [Riedel et al., 2012b], and the resulting CINO₂ mixing ratio was calibrated with the N₂O₅ measurement. When the salt bed was removed from the sample stream, the production of CINO₂ on the inlet surface was measured. The CINO₂ production on the inlet surface was always less than 5% of the N₂O₅ addition. The third instrument was another chemical ionization mass spectrometer that used acetate as the reagent ion and measured gas phase acids [Veres et al., 2008]. These measurements were not used in this analysis but are described in detail by T. C. VandenBoer et al. (Understanding the role of the ground surface in HONO vertical structure: High resolution vertical profiles during NACHTT, submitted to *Journal of Geophysical Research: Atmospheres*, 2013, hereinafter referred to as VandenBoer et al., submitted manuscript, 2013).

[14] Fourth, a compact time of flight aerosol mass spectrometer (C-ToF-AMS, termed “AMS” hereafter) was used to measure the nonrefractory composition of particles with physical diameters between 100 and 700 μm [Bahreini et al., 2009]. The AMS was calibrated with NH₄NO₃ before the field campaign and 5 times during the campaign. The aerosol encountered during the NACHTT campaign is described in detail by F. Öztürk et al. (submitted manuscript, 2013). Fifth, an optical particle counter (Ultra High Sensitivity Aerosol Spectrometer (UHSAS)—Droplet

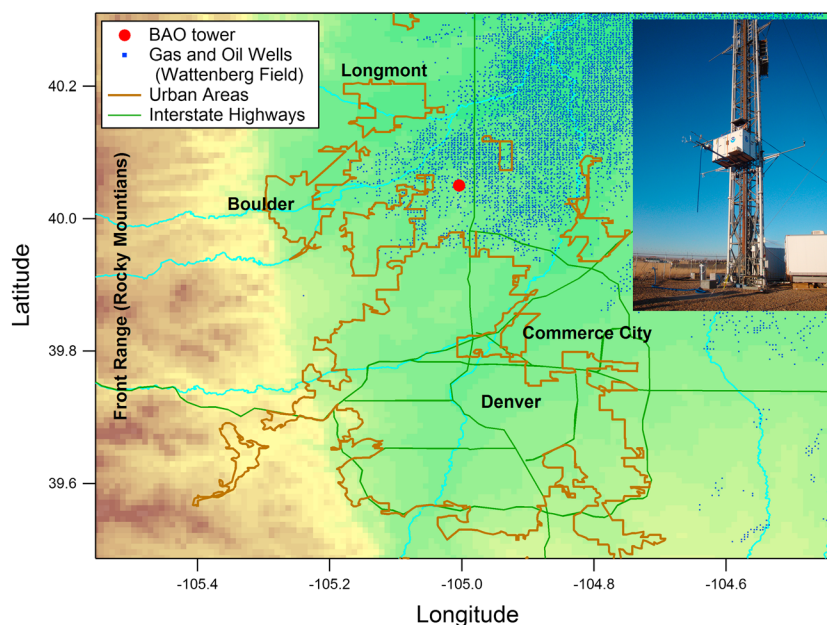


Figure 1. The BAO tower is located north of Denver and is surrounded by urban areas, including Boulder and Longmont, and wells for gas and oil production. There is a large coal-fired power plant and a refinery in Commerce City. The insert shows a photograph of the base of the tower and the moveable instrument enclosure.

Measurement Technologies) shared an inlet with the AMS and was used to measure particle size distributions for particles with physical diameters between 70 nm and 0.8 μm [Cai *et al.*, 2008].

[15] Both the AMS and the optical particle counter sampled from a common inlet behind a cyclone impactor that removed particles larger than 2.5 μm . The aerosol was heated and dried as it entered the instrument enclosure. The instrument enclosure was between 10°C and 30°C warmer than the ambient temperature, and the relative humidity in the aerosol inlet was typically less than 20%.

[16] In addition to instruments mounted on the elevator, several measurements were made from a fixed platform mounted on the main tower at a height of 22 m. From this platform, whole air samples were collected and were subsequently analyzed by a gas chromatography mass spectrometer (GC-MS) for speciated volatile organic compound (VOC) concentrations. Soluble trace gases were also measured from the platform by a tandem mist chamber. A cascade impactor was used to collect filter samples of aerosol that were analyzed by ion chromatography and neutron activation.

[17] Filter-based radiometers (used to measure photolysis rates of O₃, NO₂, and NO₃) were mounted at the top of a second scaffolding tower; 9 m tall and 15 m south of the main tower [Stark *et al.*, 2007]. The hydroxyl radical (OH) was measured by conversion to isotopically labeled sulfuric acid and detection using a chemical ionization mass spectrometer [Tanner *et al.*, 1997]. The OH measurement was housed in a trail near the base of the main tower and sampled directly through the trailer wall at a height of 2 m. Meteorological measurements (ambient temperature, wind speed and direction, relative humidity) were made aboard the movable

elevator carriage as well as at fixed-height stations on the tower located 10, 100, and 300 m above ground.

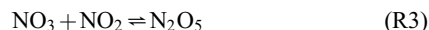
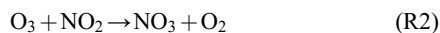
[18] A map of the area surrounding the BAO tower is shown in Figure 1. The measurement site is surrounded by urban areas, most significantly the Denver metro area to the south. There are several large point sources of pollution emissions such as the Cherokee station power plant and Suncor refinery in Commerce City, an industrial area 28 km south of the measurement site. The Wattenberg gas and oil field surrounds the measurement site and extends to the northeast. Typically, air masses observed at the BAO tower are strongly influenced by the Front Range urban area and have been shown to be affected by oil and gas production [Gilman *et al.*, 2012]. Urban aerosol haze, known as the Denver brown cloud, is common at this site in winter time [Groblicki *et al.*, 1981]. Periodic strong downslope winds from the west along the Rocky Mountain Foothills bring relatively clean continental background air to the site.

3. Iterative Box Model

[19] The N₂O₅ loss rate coefficient is determined using an iterative box model constrained by ambient vertically resolved measurements of N₂O₅, NO₂, and O₃ from the NACHTT field study. Simultaneous measurements of the submicron particle distribution and relative humidity are used to estimate the ambient aerosol surface area density and subsequently the N₂O₅ uptake coefficient.

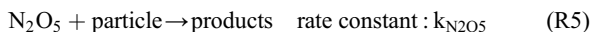
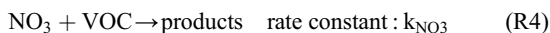
[20] The source of ambient N₂O₅ is the reaction of ozone (O₃) and nitrogen dioxide (NO₂) that forms the gaseous nitrate radical (NO₃) (R2). (Here we use the term “nitrate radical” to refer to neutral, gas phase NO₃, and “nitrate” alone to refer to the aqueous anion NO₃⁻.) NO₃ then reacts with NO₂ again to form N₂O₅ (R3). N₂O₅ is thermally

unstable and decomposes, setting up an equilibrium between NO₃ and N₂O₅.



[21] During the daytime, NO₃ and N₂O₅ are present in small concentrations due to removal of NO₃ by photolysis and reaction with NO. The mixing ratios are typically not more than a few parts per thousand by volume (pptv) and then only under certain conditions [Brown *et al.*, 2005]. However, during the night, the concentrations of NO₃ and N₂O₅ can be significant. During NACHTT, the average nocturnal mixing ratios for NO₃ and N₂O₅ were 5 and 140 pptv, respectively. The equilibrium partitioning between NO₃ and N₂O₅ is determined by the NO₂ concentration and the ambient temperature. N₂O₅ is favored by higher NO₂ concentrations and lower temperatures. The average NO₂ mixing ratio was 5.6 parts per billion by volume (ppbv), and a typical nighttime temperature was 0°C. For these conditions, the equilibrium ratio of N₂O₅ to NO₃ is 102:1, using the equilibrium constant recommend by Sander *et al.* [2011].

[22] NO₃ is the primary atmospheric oxidant in urban influenced air during night and reacts (R4) with biogenic volatile organic compounds (VOCs) and sulfur compounds and some classes of highly reactive anthropogenic VOCs [Atkinson, 1991]. N₂O₅ is lost through heterogeneous reactions (R5) with aerosol with a loss rate coefficient described by equation (1).



[23] An additional loss pathway for N₂O₅ is the possible homogeneous hydrolysis of N₂O₅ studied by Wahner *et al.* [1998a] which is neglected in this analysis because there is little absolute humidity during the winter time. Additionally, Brown *et al.* [2009] found that observed N₂O₅ lifetimes and water vapor concentrations were consistent with a lower rate constant than recommended for the homogeneous hydrolysis reaction. This analysis assumes that all losses of N₂O₅ can be attributed to heterogeneous loss on aerosol surfaces.

[24] The equilibrium between NO₃ and N₂O₅ (R3) is established relatively quickly at ambient tropospheric temperatures and typical urban NO₂ mixing ratios [Brown *et al.*, 2003]. However, the loss rates of NO₃ due to reactions with VOCs and the uptake of N₂O₅ by aerosol can be significantly slower than the forward and reverse reactions in (R3). The NO₃ and N₂O₅ concentrations do not achieve steady state until there is balance between the nitrate radical production and losses of both NO₃ and N₂O₅. In such cases the steady state analysis used by Brown *et al.* [2006, 2009] cannot be applied. Additionally, the NACHTT data set had vertical transects but not horizontal transects. Vertical transects at night include considerable meteorological variability that covaries with the NO₂ levels, making the steady state analysis used by Brown *et al.* [2006, 2009] far more difficult even when the steady state approximation is valid. An alternate method of determining the N₂O₅ loss rate coefficient is to use an iterative

box model that does not assume steady state but that requires knowledge of time zero (i.e., the time since emission of NO_x into an air mass or the time since sunset). One analysis strategy would be to determine periods when the steady state approximation is valid and apply a steady state analysis to those times and the box model for all other cases. However, to determine when the steady state approximation is valid, it is necessary to run a box model and assume a reaction duration. For this analysis, we simply applied the box model to all cases including those for which the steady state approximation is valid. The reaction duration is assumed to be the time since sunset, which is appropriate for air masses unaffected by nocturnal emissions. The iterative box model used here is described briefly below and in more detail in Appendix A.

[25] The iterative box model begins with an air mass containing only O₃ and NO₂ which then react to form NO₃ and N₂O₅ as described by reactions (R2) and (R3). The equilibrium cycling between NO₃ and N₂O₅ is fast when NO₂ concentrations are large (> 1 ppbv), reaction durations are long (> 1 h), and the temperature is low. The lifetime of NO₃ with respect to N₂O₅ formation is 30 s at 0°C and 1 ppbv of NO₂, and the lifetime of N₂O₅ with respect to thermal decomposition is 10 min at 0°C. In this box model, it is computationally advantageous to eliminate these fast reactions, allowing the time step in the box model to be larger. Specifically, the differential equation for NO₂ contains two terms from the forward and reverse of reaction (R3) which describe the equilibrium cycling between NO₃ and N₂O₅. When NO₃ and N₂O₅ are in equilibrium, these two terms have nearly the same magnitude, and in the box model, they are replaced by an approximation which depends on only the O₃ and NO₂ concentration instead of the NO₃ and N₂O₅ concentration (discussed in Appendix A). Without these equilibrium cycling terms and their dependence on NO₃ and N₂O₅, the differential equations for O₃ and NO₂ can be numerically solved without knowledge of NO₃ or N₂O₅ concentrations. Because the final (or measured) values of O₃ and NO₂ are known, the differential equations for O₃ and NO₂ can then be integrated backward in time starting with the measured concentrations of NO₂ and O₃.

[26] Once the initial O₃ and NO₃ mixing ratios are determined, the differential equations for N₂O₅ and NO₃ (reactions (R4) and (R5)) are integrated forward in time to determine the final concentration of N₂O₅. An initial guess of 10⁻⁵ s⁻¹ is used for the N₂O₅ loss rate coefficient. The box model concentration of N₂O₅ is then compared to the measured N₂O₅ concentration, and the N₂O₅ loss rate coefficient is iteratively adjusted using the secant method until the N₂O₅ concentration predicted by the box model agrees with the measured N₂O₅ concentration. Once the N₂O₅ loss rate coefficient is known, the uptake coefficient can be determined using equation (1).

[27] When applying the iterative box model to ambient data, additional chemistry not included in the iterative box model could affect the observed N₂O₅ concentration and bias the retrieved uptake coefficient. NO, the principal component of emitted NO_x, reacts efficiently with NO₃ and quickly converts the NO₃/N₂O₅ reservoir into NO₂, effectively resetting the zero time for the iterative box model. The uncertainty from NO emissions after sunset is minimized by excluding data when NO is observed above the detection limit and limiting the analysis to times when the nocturnal atmosphere

is stable such that fresh NO emissions are confined to the surface layer.

[28] The potential temperature difference between the top (300 m) and bottom (10 m) of the tower is used to exclude air masses in which NO was not observed but was possibly affected by nocturnal emissions. When the potential temperature difference is large, the nocturnal atmosphere is stable and layered, the upward mixing from the surface is minimized, and air masses above the surface are less affected by nocturnal emissions. The iterative box model is only applied to data collected when the potential temperature difference is greater than 8°C and the elevator is at least 20 m above ground. The potential temperature difference of 8°C was chosen to eliminate retrieved uptake coefficients that were unphysical (> 1). This filtering by potential temperature does not eliminate all air masses affected by nocturnal emissions; in particular, emissions from warm combustion sources that are buoyant and rise through the nocturnal layers. These air masses would best be modeled using a reaction duration that is the transport time from the emission point to the measurement site. However, because the emission locations and emission times are not known (with the exception of two plumes), this uncertainty is accounted for by estimating the sensitivity of the retrieved uptake coefficient to the reaction duration and including that in the total uncertainty.

[29] The reaction duration (or zero time) used in the iterative box model is the time since sunset. Using sunset as the zero time can be inaccurate if there are nocturnal emissions as described above (a shorter reaction duration than the time since sunset) or if the photolysis of NO₃ has slowed enough to let N₂O₅ accumulate before sunset [Geyer *et al.*, 2003] (a longer reaction duration than the time since sunset). The median mixing ratio of N₂O₅ at sunset during NACHTT was 16 pptv and ranged from 60 to < 3 pptv (detection limit). Most nights, the integrated nitrate radical production was several parts per billion and the N₂O₅ produced before sunset was a small fraction of that total. To account for the uncertainty of the reaction duration, the iterative box model was also applied with a longer reaction duration of 125% and with a shorter reaction duration of 75%. If the N₂O₅ concentration has achieved steady state, the reaction duration has little effect on the retrieved uptake coefficient. However, this uncertainty can be significant when the N₂O₅ loss rate is slow and steady state has not been achieved. The amount of change in the retrieved uptake coefficient is used as the uncertainty from the reaction duration and added in quadrature to the uncertainty from NO₃ reactivity that is discussed in the next section.

[30] The nocturnal production of nitrous acid, HONO, is also not included in the iterative box model. Unlike nocturnal NO emissions, HONO production is unlikely to affect the retrieved uptake coefficients. Nitrous acid is produced by a heterogeneous process that consumes NO₂ throughout the course of the night [Kleffmann, 2007]. Several studies have found that the most significant surface for HONO production is the ground [Wong *et al.*, 2011; Young *et al.*, 2012], and because data used in this analysis do not include measurements below 20 m, HONO production on the ground surface should not affect the retrieved uptake coefficients significantly. If HONO production on aerosol surfaces were significant, the calculated concentration of NO₂ used in the

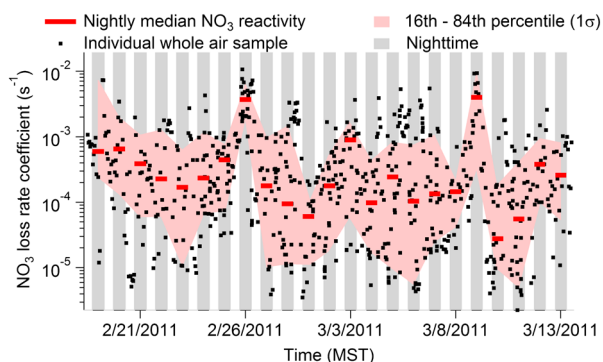


Figure 2. NO₃ reactivity calculated from the VOCs measured in whole air samples. Black dots indicate each whole air sample. The dark red lines show the median reactivity for each night and the light red shade area shows the 16th through 84th percentiles (i.e., 68% of the data or $\pm 1\sigma$) for each night. Shaded bars indicate each night.

box model would be inaccurate. However, the analysis of T. C. VandenBoer *et al.* (submitted manuscript, 2013) found that during NACHTT aerosol uptake of NO₂ is a very slow process, and HONO production can be neglected relative to reaction of NO₂ with O₃ for air masses above surface level.

3.1. NO₃ Reactivity

[31] The measured concentrations of O₃, NO₂, and N₂O₅ can be used directly in this iterative box model; however, the NO₃ reactivity or NO₃ loss rate coefficient is estimated based on the VOC concentrations measured in the whole air samples. The NO₃ loss rate coefficient is calculated using whole air samples, which were collected hourly at height of 22 m on the tower, together with laboratory-measured rate constants. When a species' concentration was below the instrumental detection limit, its concentration was assumed to be zero for the purposes of the NO₃ reactivity calculation. The results of this calculation are shown in Figure 2. In each whole air sample, the concentrations of 82 species were measured, although only 42 with known rate constants were used to estimate the NO₃ reactivity [Atkinson, 1991; Atkinson and Arey, 2003]. Among these, four species contributed most significantly to the NO₃ reactivity (median mixing ratio and 90th percentile): 2 methyl 2 butene (6 and 16 pptv), styrene (3 and 10 pptv), delta limonene (1.5 and 6 pptv), and alpha pinene (1 and 4 pptv). Delta limonene and alpha pinene are biogenic VOCs and are typically observed at higher concentration during the summer, but even the small concentrations observed during NACHTT can affect the NO₃ reactivity. Because the NO₃ reactivity of the whole air samples typically varied by at least a factor of 10 over each night and their collection point was not colocated with the elevator-based measurements, the median NO₃ reactivity from each night was applied to the entire night and 16th and 84th percentiles were used as the lower and upper uncertainties. The 16th and 84th percentiles were chosen because they correspond to ± 1 standard deviation of a normal distribution.

[32] When NO₃ reactivity is low ($\sim 1 \times 10^{-4} \text{ s}^{-1}$) and the NO₃ lifetime is in the range of a few hours, it is likely that species not measured during NACHTT, such as peroxy radicals (RO₂), contribute significantly to the NO₃ reactivity.

For example, at a mixing ratio of 1 pptv, HO₂ would consume NO₃ with a first-order rate coefficient of $\sim 1 \times 10^{-4} \text{ s}^{-1}$ [Hall *et al.*, 1988], similar to the entire NO₃-VOC reactivity on lower reactivity nights. Peroxy radical measurements during winter are sparse, although Fleming *et al.* [2006] reported average total nighttime peroxy radical mixing ratios of 8–10 pptv at a coastal location in the UK during winter. Reactions of NO₃ with RO₂ are likely a small influence in this analysis since the equilibrium between NO₃ and N₂O₅ strongly favors the latter. However, if N₂O₅ uptake were also very small due to low aerosol surface or small uptake coefficient, the NO₃-RO₂ reactions would be more significant.

[33] An additional loss pathway for NO₃ is heterogeneous uptake on aerosol. Because the reported NO₃ uptake coefficients are an order of magnitude smaller than those for N₂O₅ on most inorganic aerosols [Brown and Stutz, 2012] and the typical NO₃ mixing ratio is also smaller, this pathway is estimated in previous studies to account for a very small fraction of the nitrate radical chemistry [Aldener *et al.*, 2006; Wong and Stutz, 2010] and is neglected in this analysis. We note that NO₃ heterogeneous uptake could be important if aerosol species such as polycyclic aromatic hydrocarbons were abundant [Gross and Bertram, 2008].

[34] The uncertainty in the uptake coefficient due to NO₃ reactivity can vary greatly depending on conditions such as equilibrium ratio of NO₃ and N₂O₅ and the approach to steady state. If the nitrate radical production rate and the N₂O₅ loss rate are sufficiently fast, even large changes in the NO₃ reactivity have little effect on the retrieved uptake coefficient. However, when the nitrate radical production rate is slower, the uncertainty in the NO₃ reactivity can have a larger effect. To account for this uncertainty, the box model was applied using three different NO₃ reactivities at each data point; the median reactivity, 84th percentile reactivity, and the 16th percentile reactivity. In this data set, the equilibrium ratio of N₂O₅ and NO₃ and the loss rates of N₂O₅ and NO₃ strongly favor N₂O₅. Consequently, the lower limit of NO₃ reactivity typically results in nearly the same uptake coefficient as the median value. However, the upper limit of NO₃ reactivity at times makes the NO₃ loss rate competitive with the N₂O₅ loss rate and reduces the retrieved uptake coefficient. The resulting uncertainty is skewed toward lower values of the uptake coefficient. In some cases the NO₃ loss rate is greater than the nitrate radical production rate in which case the uncertainty includes zero, leading some data to provide only an upper limit to the uptake coefficient. Inclusion of peroxy radical reactions with NO₃ (see above) would also skew the retrieved uptake coefficients lower and be of particular significance when the nitrate radical chemistry is proceeding slowly (low NO₂ mixing ratio or low surface area density). The uncertainties due to the NO₃ reactivity are added in quadrature to the uncertainty from the reaction duration and are displayed along with the retrieved uptake coefficient throughout this analysis.

3.2. Ambient Surface Area Density

[35] The ambient aerosol surface area density is also needed to convert the N₂O₅ loss rate coefficient to an uptake coefficient using equation (1). The optical particle counter aboard the elevator measured dry particle distributions for particles with diameters between 60 nm and 0.8 μm. The ambient surface area density is estimated by applying a

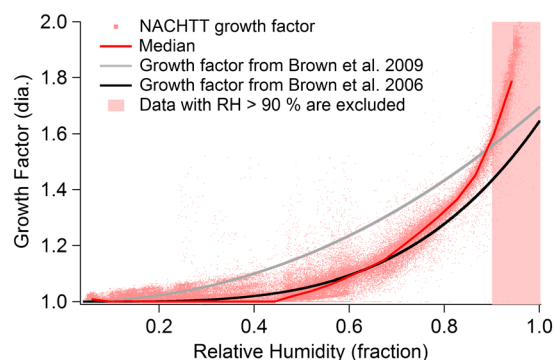


Figure 3. The diameter growth factor calculated using the measured aerosol composition, the ambient relative humidity, and an aerosol thermodynamic model (ISORROPIA II). The red points indicate individual data points. The gray and black lines show growth factor parameterizations used in two previous studies which reported N₂O₅ uptake coefficients. The pink-shaded area indicated data that were excluded from the analysis due to uncertainty in the aerosol thermodynamic model at high relative humidity. Note that the surface area correction factor is the square of the diameter growth correction factor.

calculated growth factor to the particle distribution measured at low relative humidity by the optical particle counter.

[36] The growth factor is estimated using the ISORROPIA II aerosol thermodynamics model [Fountoukis and Nenes, 2007] and the aerosol composition measured by the AMS aboard the elevator. The AMS reported the total nonrefractory mass of the dried aerosol and the mass of five components: sulfate, nitrate, ammonium, organics, and chloride. During NACHTT, the average aerosol mass loading was 4.6 μg/m³ and the average composition by mass was 19% sulfate, 39% nitrate, 14% ammonium, 27% organics, and < 1% chloride. The aerosol thermodynamics model only considers the inorganic components of the aerosol, so any contribution to the hygroscopicity from the organic portion was neglected. The model was set up to allow the aerosol to effloresce. For each datum reported by the AMS, the model calculated the mass of condensed water on the aerosol. The diameter growth factor was determined by taking the cube root of the ratio of wet aerosol mass to the dry aerosol mass. The estimated diameter growth factor is shown in Figure 3. For comparison, two growth factor parameterizations used in previous studies that reported N₂O₅ uptake coefficient are shown as well. Data with relative humidity greater than 90% have been excluded because of difficulty quantifying the growth factor and uncertainty in the relative humidity measurement. These data are shaded pink in Figure 3. Because the AMS reported aerosol composition data every 10 s, the growth factors calculated from these data were interpolated and applied to the particle size distributions which were measured every second.

[37] Both the measurement uncertainty from the optical particle counter and the uncertainty in the aerosol hygroscopicity contribute to the uncertainty in the ambient surface area density. For the dry particle size distributions measured by the optical particle counter, the number of particles and the particle diameters are both uncertain by ±10%. This leads to ±33% uncertainty in the dry surface area density. Any additional contribution to ambient surface area density from

super-micron particles is not included in this estimate, and if the super-micron contribution is significant, then the retrieved uptake coefficients would be an upper limit for the actual uptake coefficient.

[38] The growth factor used here is based on the nonrefractory inorganic portion of the aerosol measured by the AMS and is 1.6 at 90% RH. Synthetic ammonium nitrate and ammonium sulfate (the majority of aerosol mass during NACHTT) have diameter growth factors of 1.75 and 1.7 at 90% RH, respectively [Hu *et al.*, 2011], and are comparable to the growth factor calculated here. Some refractory aerosols such as NaCl (not detected by the AMS) have larger growth factors > 2.0 at 90% RH [Swietlicki *et al.*, 2008]. Organic aerosol is typically less hygroscopic than ammonium nitrate and sulfate. Duplissy *et al.* [2011] found that the growth factor at 90% RH on secondary organic aerosol increased from 1.25 to 1.6 as the aerosol aged. Fresh soot is hydrophobic and has a growth factor < 1.1 [Swietlicki *et al.*, 2008]. Based on the aerosol composition during NACHTT (72% ammonium nitrate and sulfate and 28% organics), a conservative estimate of the uncertainty in the growth factor at 90% RH is $\pm 20\%$ and ranges from 1.3 to 1.9. The uncertainty in the growth factor is reduced at lower relative humidity.

[39] When the uncertainty in the diameter growth factor is squared and added in quadrature with the measurement uncertainty from the optical particle counter, the combined uncertainty in the ambient surface area is approximately a factor of 2 (i.e., -50% and $+200\%$) at 90% RH and is reduced to the measurement uncertainty from the optical particle counter ($\pm 33\%$) at 0% RH. The uncertainty in the ambient surface area density leads directly to a proportional uncertainty in the N₂O₅ uptake coefficient, through equation (1). Because this uncertainty is simply related to the surface area density and relative humidity, it is not shown in the figures and only stated in the text.

3.3. Filtering

[40] The exclusion of data based on observed NO, potential temperature differences less than 8°C, RH greater than 90%, and periods when critical data were not reported (i.e., instrument zeroing, calibration, and maintenance) significantly reduce the amount of data available for use in this analysis. Data were collected for 25 days, yielding 323 h of data during the night. Filtering the data based on potential temperature difference was most restrictive and reduced the available data set to 14% of the total nighttime data. The potential temperature difference was only greater than 8°C on 9 out of 25 nights and then typically only for a few hours before sunrise. Subsequent filtering by NO mixing ratio, relative humidity, and missing data further reduce the amount of data analyzed to 7% of the total nighttime data or 85,440 one second data points.

3.4. Aerosol Nitrate Fraction

[41] One of the goals of this analysis is to correlate the N₂O₅ uptake coefficient with aerosol composition. At high relative humidity, water condensed on aerosol can be the majority of the aerosol mass and will strongly influence the concentration of other aerosol species, such as nitrate. When estimating the aerosol growth factor, the mass of water condensed on the aerosol is an intermediate product. This condensed water mass was added to the total dry mass

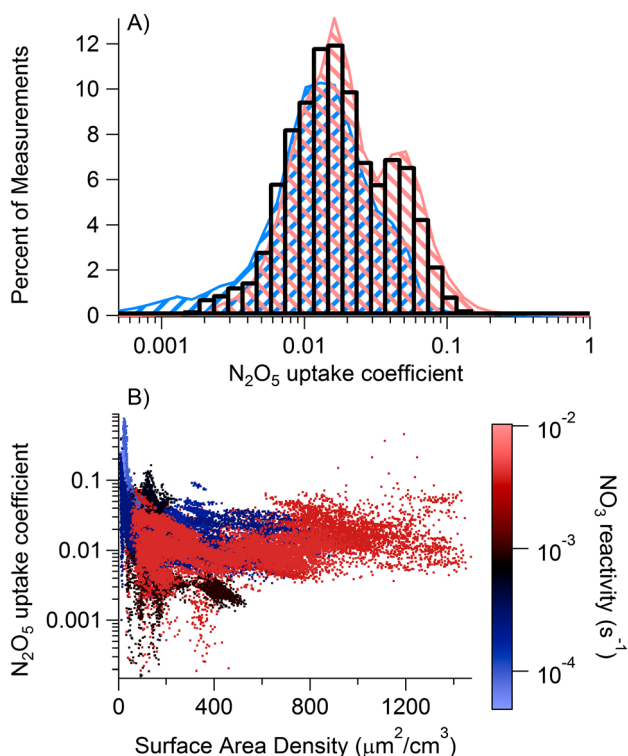


Figure 4. (a) A histogram of N₂O₅ uptake coefficients retrieved from the iterative box model described in Appendix A. The distribution of N₂O₅ uptake coefficients peaks below 0.02 with a secondary peak at 0.04. The red and the blue traces show histograms of the lower and upper uncertainty due to NO₃ reactivity and reaction duration. (b) The N₂O₅ uptake coefficient scattered against the surface area density and colored by the NO₃ reactivity.

measured by the AMS and used to determine the aerosol nitrate and sulfate mass fractions. If it is assumed that the aerosol is internally mixed and all the constituents are in the liquid phase, it would be possible to estimate the nitrate or sulfate concentration. However, because of the significant uncertainty in applying these assumptions uniformly across the entire data set, our alternate approach to avoid such uncertainties is to compare the N₂O₅ uptake coefficient with the nitrate and sulfate mass fraction, which are closer to the directly measured parameters.

4. Results

[42] A histogram of all of the uptake coefficients determined using the iterative box model is shown in Figure 4a plotted on a logarithmic scale. The red and the blue traces show histograms of the upper and lower uncertainty due to the NO₃ reactivity and reaction duration. The distribution of uptake coefficients peaks at 0.015, and there is secondary peak at 0.04. The distribution ranges from 0.002 to 0.1. The peak of the distribution agrees with previous ambient determinations and laboratory experiments. However, the upper end of the distribution in Figure 4 does not agree with laboratory experiments such as Van Doren *et al.* [1990] and Bertram and Thornton [2009] in which the largest measured uptake coefficient was 0.06 and 0.035, respectively. In the

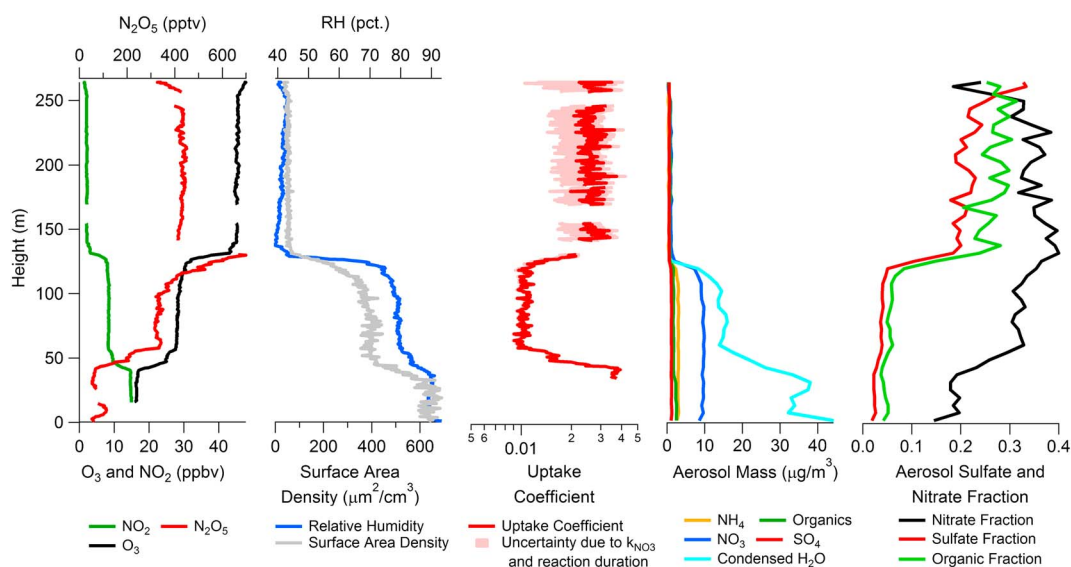


Figure 5. An example profile collected a between 12:47 and 12:55 A.M. on 5 March shows anticorrelation between the N₂O₅ uptake coefficient (third and fifth panels) and aerosol nitrate fraction. The first panel shows measured mixing ratios of O₃, NO₂, and N₂O₅. The second panel shows the relative humidity and the RH-corrected surface area density. The N₂O₅ uptake coefficient retrieved from the iterative box model is shown in the third panel and pink shading indicated the uncertainty in the retrieval due to the uncertainty of NO₃ reactivity and reaction duration. The fourth panel shows the aerosol composition measured by an aerosol mass spectrometer and the condensed water calculated by ISORROPIA II. The fifth panel shows the fraction of aerosol mass which is nitrate, sulfate, and organics including the calculated condensed water in the total mass.

NACHTT data set, the higher values of the uptake coefficient are correlated with low surface area densities and low NO₃ reactivities as shown in Figure 4b. This disagreement at the upper end of the distribution may be due to missing contributions to the surface area density from super-micron particles or to the NO₃ reactivity by peroxy radicals.

[43] A single profile of the N₂O₅ uptake coefficient is shown in Figure 5 along with measurements used to calculate it. This profile was collected on 5 March 2011 between 12:47 and 12:55 A.M. The profile is characterized by three distinct layers. The highest layer above 130 m is dry (RH = 40%) and has little aerosol mass or surface area density. The lower two layers (0–40 and 40–130 m) are much more humid, 80% and 90% RH, respectively. The aerosol composition in the two lower layers is also very similar and dominated by ammonium nitrate. The main difference in the aerosol between these two layers is the relative humidity and consequently the fraction of aerosol mass that is nitrate. In the lowest layer, the nitrate fraction is 18% and is diluted compared with the middle layer where the nitrate fraction is 32%. The two lower layers also have the same nitrate radical production rate of ~0.3 ppbv/h; however, the N₂O₅ concentration in the lowest layer is ~60 pptv and in the middle layer is greater than 300 pptv. As expected, the retrieved N₂O₅ uptake coefficient reflects this trend in the N₂O₅ concentration. In the lowest layer, the N₂O₅ uptake coefficient is near 0.04; however, in the middle layer, uptake coefficient drops below 0.01. The correlation between the uptake coefficient and the aerosol nitrate fraction suggests that in the middle layer, the N₂O₅ uptake is suppressed by nitrate.

[44] The upper layer in Figure 5 is very different from the lower layers, and the N₂O₅ chemistry is much slower. The

nitrate radical production rate is ~0.12 ppbv/h and the surface area density is ~60 µm²/cm³. Because the reaction rates are much slower, the N₂O₅ concentration in the upper layer has not yet reached its steady state value and the iterative box model is much more sensitive to the uncertainty in NO₃ reactivity and reaction duration. In the upper layer, the retrieved uptake coefficient is ~0.03, but the uncertainty includes values as low as 0.015. Because the nitrate fraction is similar in the upper and middle layer, it might be expected that the uptake coefficient would be suppressed similar to the middle layer. However, the aerosol in the upper layer has a different dry composition compared to the lower layers. Both sulfate and organic fraction of the aerosol is much larger than in the lower layers. High aerosol sulfate concentrations have been correlated with larger N₂O₅ uptake coefficients [Brown *et al.*, 2006; Hu and Abbatt, 1997] while organics coatings can suppress the N₂O₅ uptake coefficient [Anttila *et al.*, 2006].

[45] The anticorrelation between the N₂O₅ uptake coefficient and aerosol nitrate fraction is also clear in the 2 h before sunrise on 2 March as shown in Figure 6. The upper panel of Figure 6 shows the time series of the aerosol nitrate mass fraction and the time series of the N₂O₅ uptake coefficient (logarithmic scale). The gray-shaded background shows the height of elevator. The lower panel of Figure 6 shows the same data as in the upper panel, except here, the uptake coefficient is scattered against the nitrate fraction. Again, the uptake coefficient is anticorrelated with the nitrate fraction, indicating the role of nitrate in suppressing the uptake of N₂O₅.

[46] In the same manner as the 5 March profile, relative humidity controls the amount of condensed water on the aerosol

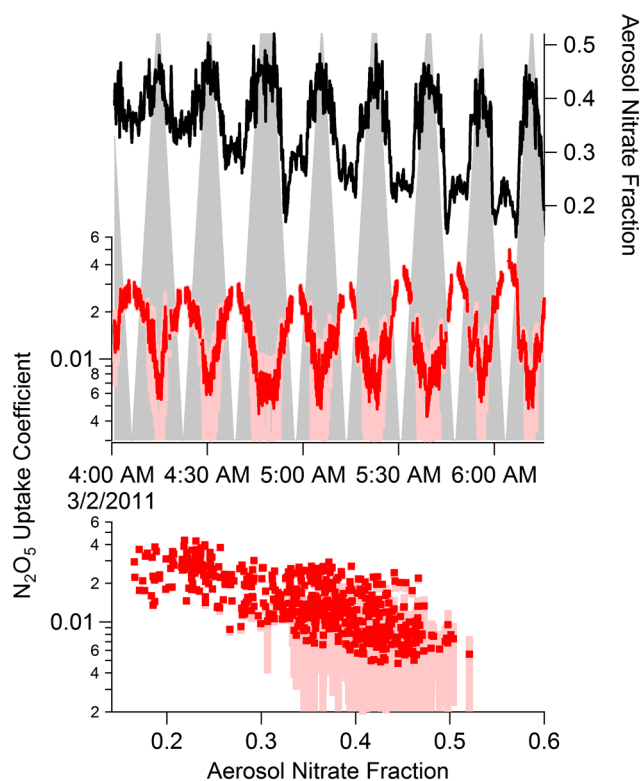


Figure 6. (top) The time series of aerosol nitrate fraction (black) and N₂O₅ uptake coefficient (red) for approximately 2 h of data before sunrise on 2 March. The gray background indicated the height of the elevator on the tower at the time of measurement. (bottom) A scatterplot of the N₂O₅ uptake coefficient and aerosol nitrate fraction. The pink bars indicate the uncertainty in the uptake coefficient due to uncertainty in NO₃ reactivity and reaction duration.

and consequently the nitrate fraction during the 2 March time period shown in Figure 6. This is clearly seen in the profile shown in Figure 7 between 4:58 and 5:06 A.M. on 2 March. At 50 m, the uptake coefficient is 0.026 and the nitrate fraction is 0.3. The uptake coefficient decreases as the height increases (0.005 at 250 m), and the nitrate fraction rises to 0.45 at the top of the profile. The nitrate fraction of the dry aerosol is lower at the top of the profile than at the bottom. However, the condensed water fraction changes more dramatically, accounting for 40% of the aerosol mass at the bottom of the profile and near 0% at the top. The net result is a nitrate fraction that increases with height. The dependence of the retrieved N₂O₅ uptake coefficient with height is qualitatively consistent with suppression of this uptake by aerosol nitrate.

[47] Suppression of N₂O₅ uptake by nitrate can be seen throughout the entire data set in addition to the individual profiles described above. Figure 8 shows N₂O₅ uptake coefficient from all of the data used in this analysis scattered against the aerosol nitrate fraction. The data have been binned according to the nitrate fraction, and in each bin, the median, 5th, 16th, 84th, and 95th percentiles were calculated and displayed as boxes and whiskers. The uncertainty due to NO₃ reactivity and duration for each individual data point is shown as pink bars. When the aerosol nitrate fraction is below 0.1, the median uptake coefficient was 0.04. However, when the nitrate fraction is greater than 0.25, the median uptake coefficient is reduced by at least a factor of 2.

[48] For comparison, the *Bertram and Thornton* [2009] parameterization is also shown in Figure 8 along with its uncertainty. The parameterization requires the molarity of water and the molar ratio of nitrate to water. The water molarity used here was 30 mol/L, and a model aerosol consisting of only ammonium nitrate and water was used to convert the nitrate mass fraction to the molar ratio of nitrate to water. Neither of these assumptions has a strong effect on the

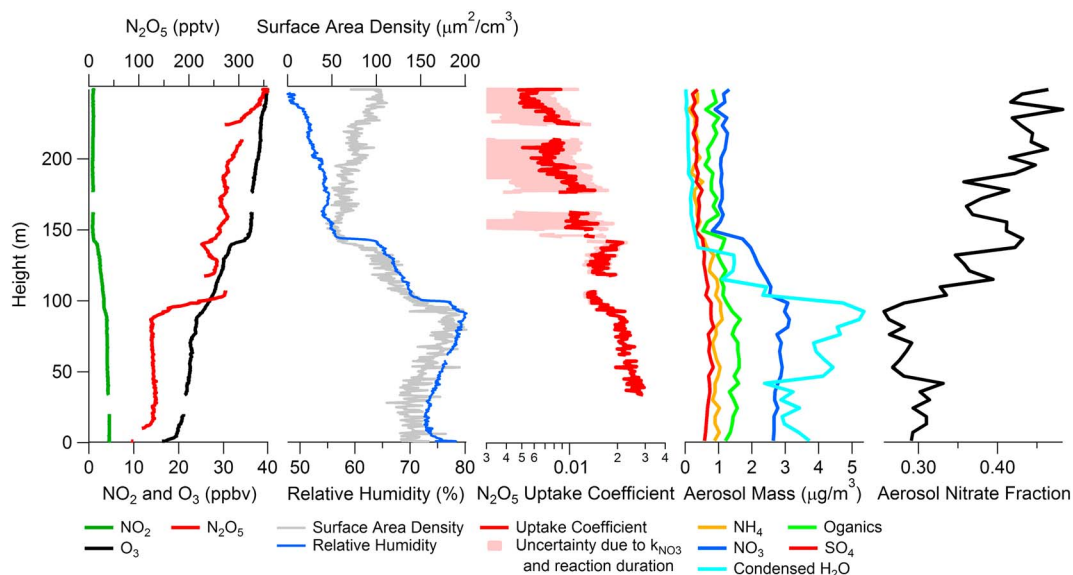


Figure 7. A profile collected in the morning of 2 March between 4:58 and 5:06 A.M. The panels are the same format as Figure 5.

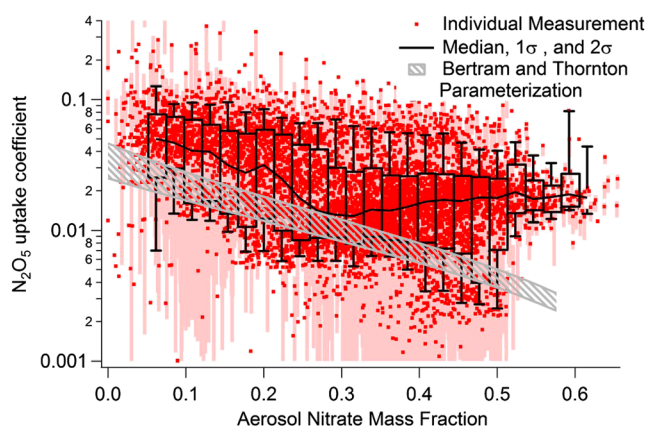


Figure 8. A plot of N₂O₅ uptake coefficients, determined using an iterative box model, scattered against the aerosol nitrate fraction. The uptake coefficients were binned according to the aerosol nitrate fraction. The median, the 84th to 16th percentiles ($\pm 1\sigma$), and 95th to 5th percentiles ($\pm 2\sigma$) are shown as overlaid boxes and whiskers. The uncertainty of individual measurements is shown in pink. For comparison, the Bertram and Thornton [2009] parameterization of the N₂O₅ uptake coefficient based on laboratory measurement is shown in gray.

magnitude of the uptake coefficient for conditions shown in Figure 8. Because this analysis is focusing on the nitrate effect, the chloride concentration in the parameterization was set to zero. Chloride was a minor component of submicron aerosol during NACHTT and was often below the AMS detection limit. Its influence, if present at higher concentrations, would be to reduce any suppression due to nitrate.

[49] The Bertram and Thornton parameterization predicts smaller uptake coefficients than the uptake coefficients retrieved by the box model. This could be due to either the errors in applying the iterative box model to the analyzed air masses (such as incorrect NO₃ reactivity or nocturnal NO_x emissions) or differences between the ambient aerosol and the synthetic aerosol used by Bertram and Thornton to develop the parameterization. One possible difference between the laboratory and ambient conditions is the temperature. Several laboratory studies have measured larger uptake coefficients at low temperatures [Griffiths and Cox, 2009; Hallquist et al., 2003; Van Doren et al., 1990]. The Bertram and Thornton parameterization was based on room temperature measurements at 25°C, whereas the average nocturnal temperature for the NACHTT data set is 1°C and a range of -6°C to 7.5°C included 90% of the analyzed data.

[50] In a complementary analysis, T. P. Riedel et al. (Vertically resolved ClNO₂ and Cl₂ measurements from a tall tower in a polluted continental setting: Insights into chlorine activation within urban or power plant plumes, submitted to *Journal of Geophysical Research*, 2013, hereinafter referred to as Riedel et al., submitted manuscript, 2013) have identified two power plant plumes in the NACHTT data set and studied ClNO₂ production in these plumes. The N₂O₅ uptake coefficient was also estimated in each of these plumes and agreed with the uptake coefficient retrieved from the iterative box model.

[51] Correlations of derived uptake coefficients with aerosol nitrate were the most obvious feature of the

NACHTT data set. Other correlations with, for example, the sulfate content, were not robust, in part because other components of the aerosol were smaller and tended to vary less than the nitrate content, which is the dominant component in the Denver urban area in winter. This work can also be contrasted with uptake coefficients determined from ambient aircraft measurements during summer conditions [Brown et al., 2006; Brown et al., 2009]. Both of these studies were based on the variation of NO₃ and N₂O₅ steady state lifetimes with NO₂ across discrete pollution plumes transected by the aircraft and resulted in a limited number of determinations. In the northeast U.S. in August 2004, uptake coefficients were shown to vary over the range 0.002–0.02, with the larger uptake coefficients associated with sulfate rich aerosol, and the smaller ones associated with mixed organic and sulfate aerosol. In Texas during October 2006, uptake coefficients were not clearly correlated with aerosol composition but had an average value of 0.003 with considerable scatter in the data that ranged from 4×10^{-4} to 0.019. Neither of these aircraft studies during the summer encountered large amounts of nitrate in the aerosol.

5. Nocturnal NO_x Loss

[52] Nocturnal loss of NO₂ accounts for a significant portion of the total conversion of NO₂ to HNO₃ and the subsequent removal of emitted nitrogen oxides from the atmosphere. Nighttime NO_x removal is especially important in the winter when the temperature is cooler (favoring N₂O₅ formation relative to NO₃) and the nights are longer (favoring dark chemistry over photochemistry). The NACHTT data set and retrieved uptake coefficients represent an opportunity to quantify the total amount of NO₂ removed during the night and to determine the amount of NO₂ which is reformed at sunrise by photolysis of nocturnal species (NO₃, N₂O₅, and ClNO₂).

[53] Nocturnal removal of NO_x proceeds primarily by nitrate radical production, N₂O₅ hydrolysis, and subsequent wet deposition. The nocturnal NO_x removal rate can be quantified by considering the fraction of NO₂ consumed by nitrate radical chemistry in each of four possible pathways. First, NO₃ can be lost through reactions with VOCs. The second pathway is loss through N₂O₅ heterogeneous hydrolysis. When N₂O₅ is taken up on the aerosol, it typically reacts with water and forms two molecules of nitric acid. The third pathway is uptake to chloride-containing particles. Instead of forming nitric acid alone, one nitric acid and one nitryl chloride (ClNO₂) molecule are formed. Because it is insoluble, the ClNO₂ is repartitioned back into the gas phase, where it builds up in the atmosphere throughout the night and undergoes morning photolysis to atomic chlorine and NO₂. The fourth pathway is for NO₃ to undergo no further reactions except for cycling between NO₃ and N₂O₅. At sunrise, this NO₃ is photolyzed and the entire N₂O₅ reservoir thermally decomposes to reform NO_x.

[54] Each of these pathways can be assigned a number representing the NO₂ molecules removed from the atmosphere by each nitrate radical. The potential for removing NO₂ is shown in Table 2. The reactions of NO₃ with VOCs proceed by a variety of mechanisms, but for alkene reactions with NO₃, they proceed via addition of NO₃ to a carbon-carbon double bond, resulting predominantly in an organic nitrate product. A typically small fraction of the nitrogen is regenerated as NO₂ in these reactions, though the organic

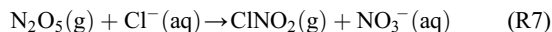
Table 2. NO₂ Removal Potential

Nitrate Radical Pathway	NO ₂ Removal Potential
NO ₃ reactions	1 ^a
N ₂ O ₅ hydrolysis	2
ClNO ₂ formation	1
NO ₃ /N ₂ O ₅ recycling	0

^a Assuming unity yield of organic nitrates in NO₃-alkene reactions that leads to complete removal of the reactive nitrogen and omitting reaction of NO₃ with peroxy radicals that recycle NO₂ with unit yield.

nitrate versus NO₂ yield depends strongly on the particular VOC. Some reactions, such as those of NO₃ with aldehydes, lead to HNO₃ production. For simplicity, reactions of NO₃ with VOCs are assumed to lead to complete removal of reactive nitrogen. A more complete treatment of NO₃ chemistry would not significantly alter the conclusions of this wintertime analysis, since NO₃ reactions were the minor path for nighttime NO_x loss.

[55] Using the results of the iterative box model, it is possible to quantify the fraction of the nitrate radical production consumed by each of the four possible pathways. Once the N₂O₅ loss rate coefficient has been determined by the iterative box model, the reaction duration is extended from sunset to sunrise. The concentrations at sunrise along with the integrated losses of NO₃ and N₂O₅ can be used to determine the partitioning between each of the possible pathways. To account for ClNO₂ formation, reaction (R4) must split into two reactions (R6 and R7).



[56] The summed rate for these reactions is the N₂O₅ loss rate determined using the iterative box model. The ratio of the rates of reactions (R6) and (R7) is the ClNO₂ yield. Because ClNO₂ simply builds up throughout the night and undergoes no further reactions, the ClNO₂ yield can be determined by comparing ClNO₂ concentration with the integrated amount of N₂O₅ loss to aerosol uptake, as shown in equation (2). The integral is performed over the duration of the box model, which in this case is the time from sunset until the time when the concentration of ClNO₂ is measured, yielding

$$\Phi = \frac{[\text{ClNO}_2]}{\int k_{\text{N}_2\text{O}_5} [\text{N}_2\text{O}_5] dt} \quad (2)$$

[57] The ClNO₂ yield calculated using equation (2) is more sensitive to the reaction duration than the N₂O₅ uptake coefficient. In the case where steady state is achieved, the uptake coefficient is insensitive to reaction duration; however, the integrated amount of N₂O₅ loss is directly proportional to the reaction duration. For air masses influenced by nocturnal emissions (such as a buoyant power plant plume), the ClNO₂ yield would be underestimated and should be considered a lower limit. Figure 9 shows a histogram of the ClNO₂ yields calculated using equation (2) and only includes the filtered data set to which the box model was applied. The majority of the ClNO₂ yields are less than 10%. Because the ClNO₂ concentrations were reported every 10 s, the calculated

ClNO₂ yield was interpolated to 1 s to match the other measurements (O₃, NO₂, N₂O₅, etc.).

[58] The ClNO₂ yield has been estimated in two other analyses of the NACHTT data set. T. P. Riedel et al. (submitted manuscript, 2013) used a similar box model and measured ClNO₂ concentration to describe ClNO₂ production in two power plant plumes and found that yields of 40% and 80% fit each plume. Aside from these plumes, T. P. Riedel et al. (submitted manuscript, 2013) found that an average yield of 5% fits the remainder of the nocturnal data which is consistent with this analysis. A. H. Young et al. (Phase partitioning of soluble trace gases with size-resolved aerosols in near-surface continental air over northern Colorado, USA during winter, submitted to *Journal of Geophysical Research*, 2013, hereinafter referred to as Young et al., submitted manuscript, 2013) estimated the yield using the size-resolved aerosol composition and a ClNO₂ yield parameterization. This method found the median yield was over 90% for all particle sizes. The discrepancy between the bottom-up (using aerosol composition) and top-down (using ClNO₂ concentration) methods of estimating the ClNO₂ yield have not been resolved.

[59] Calculated using the iterative box model, the fractions of the nitrate radical chemistry in each pathway as a function of the measured NO₂ mixing ratio are shown in Figure 10. For the purpose of calculating the nitrate radical production and its loss pathways, the box model duration has been extended such that it runs from sunrise to sunset. In each panel of Figure 10, the red points indicate individual box model calculations. The black line shows the median value when binned according to NO₂ mixing ratio. In Figure 10a, the integrated nocturnal nitrate radical production is displayed along with a histogram of NO₂ mixing ratios. The integrated nitrate radical production depends strongly on the NO₂ mixing ratio and reaches a maximum of ~6 ppbv when the NO₂ mixing ratio is 25 ppbv. However, typical nitrate radical production is 1–2 ppbv at NO₂ concentrations of 4 ppbv. The variation around the median nitrate radical production is due to variation in the ozone concentration. Figures 10b–10d show the fraction of nitrate chemistry in

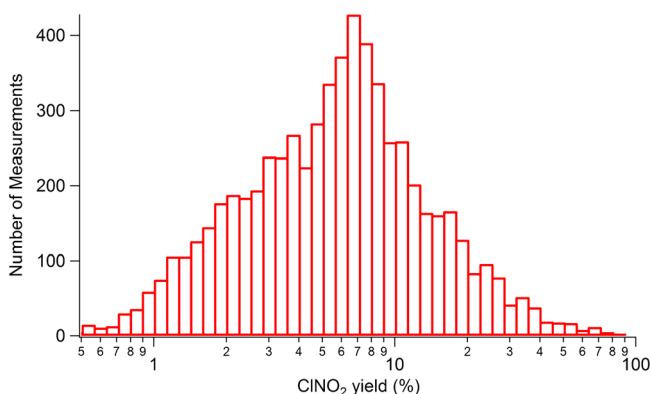


Figure 9. ClNO₂ yield is shown in histogram form. The yields are determined from ClNO₂ measurements and the integrated N₂O₅ uptake on aerosol. The integrated N₂O₅ uptake was determined using the iterative box model; hence, this histogram only includes data to which the iterative box model was applied and is subject to uncertainties in the NO₃ reactivity and the reaction duration.

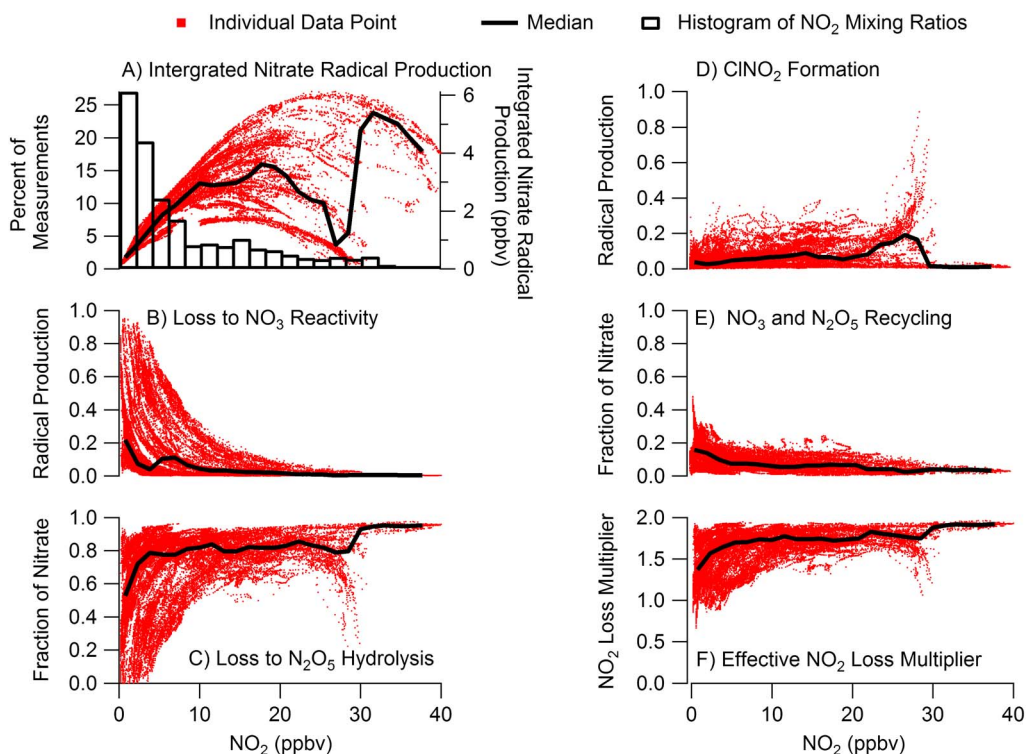


Figure 10. Nitrate radical chemistry in unperturbed nocturnal air masses can proceed along four possible pathways. Based on a box model calculation running from sunset to sunrise, the fraction of nitrate radical production going to each pathway is shown as red dots. The fraction in each pathway is binned according to the measured NO₂ mixing ratio, and median in each bin is shown as a black line. (a) The integrated nitrate radical production and a histogram showing the frequency of measured NO₂ mixing ratios. (b) The fraction of nitrate radical production lost to reactions between NO₃ and VOCs. (c) The loss to N₂O₅ hydrolysis. (d) The fraction associated with ClNO₂ formation. (e) The fraction which remains as NO₃ and N₂O₅ at sunrise. (f) The NO₂ loss multiplier (defined in the text).

each of the four possible pathways. The largest portion of the nitrate radical chemistry is N₂O₅ hydrolysis shown in Figure 10c. It typically accounts for 80% of the nitrate radical production at NO₂ mixing ratios between 4 and 30 ppbv. At NO₂ mixing ratios less than 4 ppbv, the N₂O₅ hydrolysis fraction drops to 60%. The losses to NO₃-VOC reactions (Figure 10b) are typically less than 10% but can be large when the NO₂ concentration is low. The fraction of nitrate radical production which results in ClNO₂ formation is shown in Figure 10d and is typically less than 10%, although there were a few data points associated with a direct emission of chloride when the ClNO₂ yield was larger than 50%. The portion of the NO₃ and N₂O₅ which did not react any further and was photolyzed at sunrise is shown in Figure 10e. This fraction was typically less than 10% at moderate NO₂ levels.

[60] The nocturnal lifetime of NO₂ with respect to nitrate radical production depends on the fraction of nitrate radical chemistry proceeding by each pathway, and some of the NO₂ loss is returned when nocturnal species are photolyzed at sunrise. The net nocturnal NO₂ loss can be quantified by the integrated nitrate radical production and an NO₂ loss multiplier, η , defined in equations (3) and (4) using the NO₂ removal potential of each pathway in Table 2. In equation (4), the fraction of nitrate radical chemistry in each pathway is represented as F .

$$\Delta\text{NO}_2 = \eta \times \int_{\text{sunset}}^{\text{sunrise}} k_1[\text{O}_3][\text{NO}_2]dt \quad (3)$$

$$\eta = 1 \times F(\text{NO}_3 \text{ reactivity}) + 2 \times F(\text{N}_2\text{O}_5 \text{ hydrolysis}) + 1 \times F(\text{ClNO}_2 \text{ formation}) \quad (4)$$

[61] The NO₂ loss multiplier has been calculated for each run of the box model calculation and is displayed in Figure 10f. The median is typically greater than 1.7 but drops to 1.4 at low levels of NO₂. Some data points are dominated by NO₃ reactivity at low levels of NO₂ and the NO₂ loss multiplier is close to one. If NO₂ is recycled via NO₃ reaction, either with peroxy radicals or with alkenes, the NO₂ loss multiplier could be lower.

6. The Impact of the Nitrate Effect on Nocturnal NO₂ Removal

[62] When the N₂O₅ uptake coefficient is suppressed by high aerosol nitrate, the effect on the NO₂ loss multiplier can be categorized into three cases. First, we consider the case where all of the nocturnal nitrate radical production is consumed by N₂O₅ hydrolysis and the N₂O₅ concentration has risen to its steady state level. In this case, the N₂O₅ loss

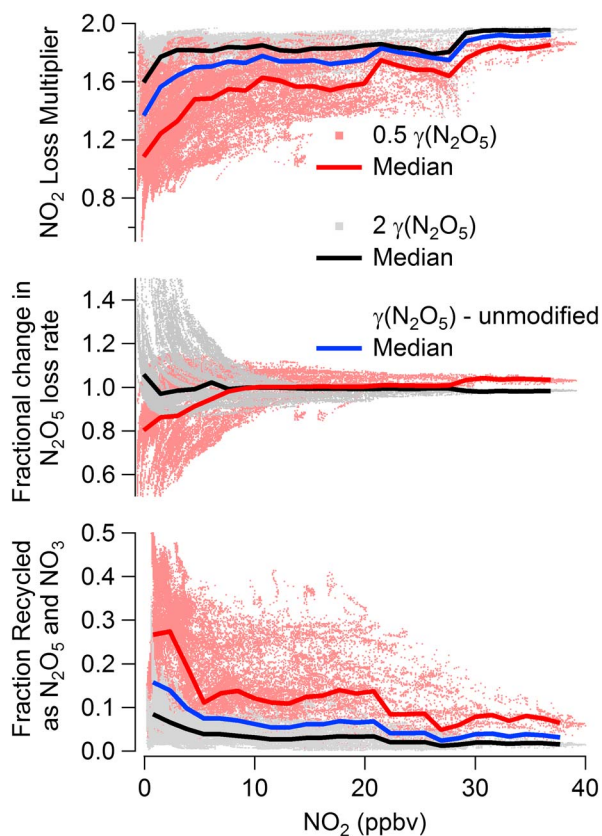


Figure 11. Box model calculation showing the sensitivity of nighttime NO_x loss to changes in the N₂O₅ uptake coefficient. Doubling and halving of the $\gamma(\text{N}_2\text{O}_5)$ are considered, consistent with the observed nitrate effect from the preceding analysis. (top) The effect on the NO₂ loss multiplier, (middle) the N₂O₅ loss rate, and (bottom) fraction of NO₃ and N₂O₅ remaining at sunrise.

rate is the same as the nitrate radical production rate ($\text{O}_3 + \text{NO}_2$) and any changes in the N₂O₅ uptake coefficient are buffered by an increase or decrease in the N₂O₅ concentration. Reducing the loss rate coefficient (uptake coefficient) will not change the loss rate. Because the steady state N₂O₅ concentration will be larger, the amount of N₂O₅ and NO₃ photolyzed at sunrise will be similarly larger. The increase in the amount of N₂O₅ recycled will reduce the NO₂ loss multiplier; however, the change in uptake coefficient is buffered by changes in the N₂O₅ concentration.

[63] The second case occurs when the NO₃ and N₂O₅ loss rates are competitive and steady state is achieved. When the N₂O₅ concentration rises due to the decreased uptake coefficient, the NO₃ concentration also rises and the fraction of nitrate radical production that is lost through the NO₃ reactivity pathway increases. Because NO₃ reactivity removes less NO₂ than does N₂O₅ hydrolysis, the NO₂ loss multiplier is reduced.

[64] The third way that a reduced uptake coefficient can affect the NO₂ loss rate is by increasing the time taken for the N₂O₅ and NO₃ concentrations to achieve steady state, which reduces the fraction of nitrate radical production going through both the NO₃ reactivity and the N₂O₅

hydrolysis pathways. This effect can be important when the N₂O₅ lifetime is a few hours but not if it is only a few minutes.

[65] The box model was used to investigate the impact of the nitrate effect on nocturnal NO₂ loss by artificially turning the nitrate effect off and on. This is done by doubling and halving the uptake coefficient in the box model corresponding to the magnitude of the median nitrate effect observed in this analysis.

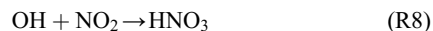
[66] The first regime described above is most representative of the NACHTT data set where most of the nitrate radical production is consumed by N₂O₅ hydrolysis. However, at low NO₂ mixing ratios, there are data points where the NO₃ reactivity is important or steady state is not achieved. In these cases the nitrate effect can be important.

[67] The upper panel of Figure 11 shows the NO₂ loss multiplier for the cases where the uptake coefficient is increased (red) and decreased (black). The median from the unmodified case is shown in blue. At an NO₂ mixing ratio of 5 ppbv, the unmodified NO₂ loss multiplier is 1.7. Doubling the uptake coefficient increases the NO₂ loss multiplier to 1.8 (i.e., a 6% increase) and halving the uptake coefficient reduces the NO₂ loss multiplier to 1.5 (12% decrease). For lower (higher) NO₂ mixing ratios, the effect is larger (smaller).

[68] The middle panel of Figure 11 shows the fractional change in the N₂O₅ loss rate. When the uptake coefficient is increased/decreased, the loss rate normalized by the unmodified loss rate is shown in black/red. Because changes in the uptake coefficient are buffered by the N₂O₅ concentration, the median N₂O₅ loss rate does not change dramatically. The median loss rate is within 10% of the unmodified loss rate except at low NO₂ mixing ratios. However, there are data points at low NO₂ mixing ratios where the N₂O₅ loss rate is either halved or doubled. The lower panel of Figure 11 shows the fraction of nitrate radical production which remains as N₂O₅ and NO₃ at sunrise. When NO₂ is 5 ppbv, the median recycled fraction is 11%, 7.5%, and 5% for the halved, unmodified, and doubled uptake coefficient, respectively. This calculation would be much more sensitive to a large reduction in $\gamma(\text{N}_2\text{O}_5)$, such as the order of magnitude decreases attributed to organic aerosol during summertime.

7. Daytime NO₂ Loss

[69] The primary daytime sink of NO_x is the conversion of NO₂ to HNO₃ by the reaction of NO₂ with the hydroxyl radical (OH), which is photochemically generated.



[70] Photochemical formation of peroxyacyl nitrates (PAN) [Roberts, 2007] and organic nitrates [Day et al., 2003] also create long-lived nitrogen species and are local or permanent sinks for NO_x, especially during winter when thermal dissociation of PAN is slow. Here we only consider the primary daytime pathway and compare with the nighttime loss of NO_x that proceeds mainly through NO₂ oxidation by O₃ and subsequent N₂O₅ hydrolysis.

[71] The relative importance of daytime and nighttime mechanisms varies with season. During winter, the short days and cooler temperatures favor nocturnal loss via

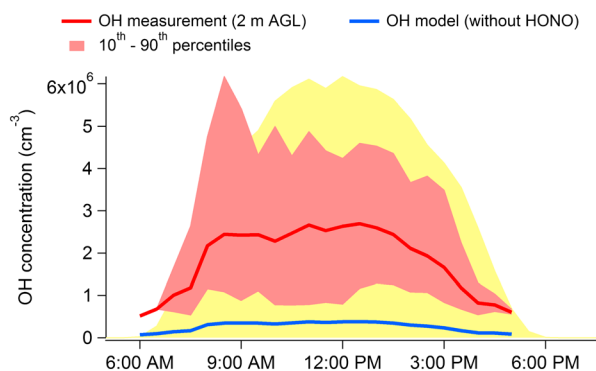


Figure 12. The measured OH concentration (at 2 m above ground level) is shown as a diurnal average (red) along with the 10th through 90th percentiles (pink). The yellow background shows the photolysis rate of NO₂ to indicate the time of day. The model OH concentration in the absence of HONO is shown in blue.

N₂O₅ hydrolysis, while longer summer days and higher OH concentrations favor daytime oxidation by OH. Using the retrieved N₂O₅ uptake coefficients and the daytime hydroxyl radical concentration, the importance of each NO₂ removal process can be estimated and compared during the NACHTT study.

[72] The hydroxyl radical (OH) concentration was measured near the base of the BAO tower 2 m above the ground. The OH measurements were available only during the first half of the field study from 17 February 2011 to 27 February 2011. A diurnal average of OH measurements is shown in Figure 12, where the average daily peak concentration was 2×10^6 molecules/cm³, and the typical daily peak was between 1 and 6×10^6 molecules/cm³. These concentrations are consistent with other midlatitude wintertime measurements in urban environments [Heard *et al.*, 2004; Kanaya *et al.*, 2007; Ren *et al.*, 2006]. In a separate analysis of the OH measurements from the NACHTT field study, S. Kim *et al.* (The primary and recycling sources of OH during the NACHTT-2011 campaign, submitted to *Journal of Geophysical Research: Atmospheres*, 2013) found the OH concentration near the ground was influenced by photolysis of HONO near the surface, and in the absence of HONO, the modeled OH concentration would be a factor of 7 lower. HONO has a strong vertical gradient near the ground and could affect the OH concentration up to a height of 50 m (T. C. VandenBoer *et al.*, submitted manuscript, 2013). In the absence of HONO above the surface layer, the OH concentration is likely to have been lower. However, because there is considerable uncertainty in OH concentration above the surface layer where the measurement was made, a range of concentrations is used to calculate the daytime NO₂ loss. The average measured concentration at 2 m height (2×10^6 molecules/cm³) is used as the upper end of the range and the modeled OH concentration in the absence of HONO (3×10^5 molecules/cm³) is used as the lower end of the range.

[73] To estimate the daytime loss of NO₂, it is also necessary to consider the influence of NO_x on the OH concentration. Our approach is to use the NO_x dependence

from the *Ehhalt and Rohrer* [2000] parameterization shown in equation (5). *Ehhalt and Rohrer* [2000] have parameterized the OH concentration as a function of NO₂ mixing ratio, and the photolysis rates of O₃ and NO₂. Because the parameterization was developed for summertime conditions in Germany with high solar insolation, biogenic VOC emissions, and relative humidity, its absolute value is not applicable to the conditions of NACHTT. However, the parameterization does provide a simplified dependence of both NO₂ and photolysis rates, which we take advantage of here by scaling it to match the upper and lower limits of the OH concentration.

$$[\text{OH}] = 4.1 \times 10^9 \times (J_{\text{O}^1\text{D}})^{0.83} (J_{\text{NO}_2})^{0.19} \frac{140\text{NO}_2 + 1}{0.41(\text{NO}_2)^2 + 1.7\text{NO}_2 + 1} \quad (5)$$

[74] The daytime conversion of NO₂ to HNO₃ can then be determined by integration over the course of the day and then compared to the nighttime loss of NO₂. The nighttime loss of NO₂ is shown in Figure 13 as a function of NO₂ concentration and colored by the observed O₃ mixing ratio. This nighttime loss was calculated using the iterative box model and is the product of the integrated nitrate radical production (Figure 10a) and the NO₂ loss multiplier (Figure 10e). The spread in the nocturnal data is primarily due to the variation of the O₃ concentration and the subsequent variation in the nitrate radical production rate. The daytime NO₂ loss is calculated by integrating the rate of reaction (R8) using the upper and lower limits for the OH concentration. The average NO₂ mixing ratio during

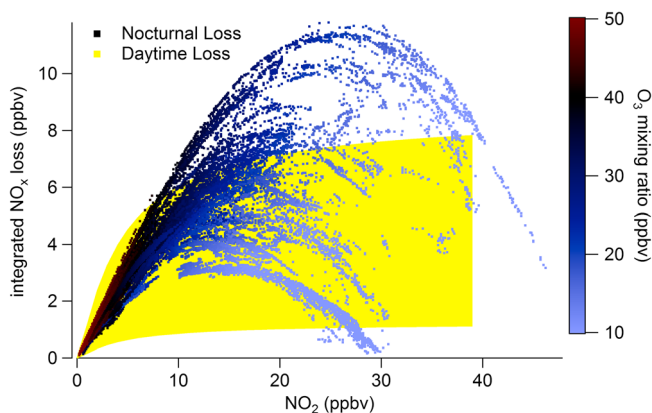


Figure 13. The estimated loss of NO₂ during the night and day is shown as function of NO₂. The losses have been integrated over the course of the night or day. The nocturnal loss (blue-black) was calculated using a box model and the retrieved N₂O₅ uptake coefficient. The spread in the nocturnal data is due to varying levels of O₃ and subsequently varying nitrate radical production rates. The daytime loss (yellow) was estimated using measured and modeled OH concentrations and NO_x dependence from the *Ehhalt and Rohrer* [2000] parameterization. The range results from the uncertainty in the OH concentration. The upper limit uses measured OH at the surface level and the lower limit uses a modeled OH concentration.

NACHTT was 5.6 ppbv, and at this NO₂ mixing ratio, the lower daytime NO₂ loss was 0.6 ppbv while the upper end of the range was 4.5 ppbv. The nocturnal loss ranged from 2.2 to 4.4 ppbv.

[75] Oxidation of NO_x is the main source of nitrate that forms ammonium nitrate aerosol, the primary aerosol component of wintertime urban haze known as the Denver Brown Cloud in this location (*Neff* [1997]; (F. Öztürk et al., submitted manuscript, 2013); (A. H. Young et al., submitted manuscript, 2013)). If the OH concentration is lower above the surface layer, this analysis suggests nighttime oxidation through N₂O₅, rather than photochemical conversion through OH, is the primary mechanism for wintertime NO₂ oxidation and the subsequent aerosol production.

8. Conclusions

[76] During wintertime in a polluted environment, the N₂O₅ uptake coefficient was determined from ambient measurements using an iterative box model. The retrieval of the uptake coefficient was possible in the wintertime conditions because N₂O₅ hydrolysis dominated the nitrate radical chemistry and because the strong nocturnal layering isolated the analyzed air masses from nocturnal NO emissions. To perform a similar analysis in the summer, direct measurements of NO₃ reactivity and more precise NO measurements would be necessary.

[77] The range of retrieved uptake coefficients was broadly in agreement with laboratory measurements on synthetic aerosol. However, under conditions of low surface area density and low NO₃ reactivity, the retrieved uptake coefficients were significantly larger than laboratory measurements. The discrepancy is possibly due to unmeasured VOC species that would contribute to the NO₃ reactivity or contributions by super-micron particles to the surface area density.

[78] The analysis is consistent with suppression of N₂O₅ uptake by aerosol nitrate. Vertically resolved measurements sampled several nocturnal layers that had a range of relative humidity, which played a crucial role controlling the amount of water condensed on the aerosol and hence, the aerosol nitrate fraction that determines the magnitude of the uptake coefficient suppression. Aerosol nitrate mass fractions of 30% were observed to suppress the uptake coefficient by a factor of two. The magnitude of the suppression was smaller than that observed on synthetic aerosol by *Wahner et al.* [1998b] and *Bertram and Thornton* [2009]. The quantitative disagreement between laboratory measurements of the nitrate effect and ambient data could be due to a temperature difference but also reflects the need for more detailed understanding of ambient aerosol composition coincident with the suppressed N₂O₅ uptake.

[79] Using the retrieved uptake coefficient, the box model duration was extended to sunrise to examine the nocturnal NO₂ loss. During NACHTT, the average NO₂ mixing ratio was 5.6 ppbv. At this level, N₂O₅ hydrolysis typically accounted for 77% of nitrate radical chemistry and for each nitrate radical produced 1.7 NO₂ molecules were removed from the atmosphere. At sunrise, ~13% of the nitrate radical production was in the form of NO₃, N₂O₅, or ClNO₂, and reformed NO₂ as the nocturnal species was photolyzed during the morning.

Appendix A: Iterative Box Model

[80] The measured concentration of N₂O₅ can be directly predicted using a box model only if the N₂O₅ loss rate coefficient is known. However, if the box model is sufficiently constrained such that the N₂O₅ loss rate coefficient is the only adjustable parameter, then the value of the loss rate coefficient can be adjusted iteratively until the N₂O₅ concentrations matches the measured concentration.

[81] The box model used above includes five reactions describing the production and loss of NO₃ and N₂O₅ (R9–R13). The rate constants for the first three reactions (R9–R11) are known, and the recommended rate constants from National Aeronautics and Space Administration-Jet Propulsion Laboratory are used here [*Sander et al.*, 2011]. The loss rate coefficient for NO₃ reactions with VOCs (R12) is determined from ambient measurements of VOC and laboratory-measured rate coefficients. The N₂O₅ loss rate coefficient (R13) is determined by iterating the box model.



[82] A coupled set of four differential equations (A5–A6) describes the time evolution of each of the four species in reactions (R9)–(R13).

$$\frac{d[\text{O}_3]}{dt} = -k_1[\text{O}_3][\text{NO}_2] \quad (\text{A1})$$

$$\frac{d[\text{NO}_2]}{dt} = -k_1[\text{O}_3][\text{NO}_2] - k_{2f}[\text{NO}_3][\text{NO}_2] + k_{2r}[\text{N}_2\text{O}_5] \quad (\text{A2})$$

$$\frac{d[\text{NO}_3]}{dt} = +k_1[\text{O}_3][\text{NO}_2] - k_{2f}[\text{NO}_3][\text{NO}_2] + k_{2r}[\text{N}_2\text{O}_5] - k_{\text{NO}_3}[\text{NO}_3] \quad (\text{A3})$$

$$\frac{d[\text{N}_2\text{O}_5]}{dt} = +k_{2f}[\text{NO}_3][\text{NO}_2] - k_{2r}[\text{N}_2\text{O}_5] - k_{\text{N}_2\text{O}_5}[\text{N}_2\text{O}_5] \quad (\text{A4})$$

[83] Because cycling between NO₃ and N₂O₅ is fast and is established quickly in high NO_x conditions, one differential equation can be eliminated by assuming NO₃ and N₂O₅ are in equilibrium [*Brown et al.*, 2003]. This also allows for a larger time step to be used in the box model. With the assumption of equilibrium, NO₃ and N₂O₅ can be represented by a single variable, nocturnal nitrogen, NN, such that [NN] = [N₂O₅] + [NO₃]. The equilibrium constant (K_{eq}) can then be used to calculate the concentrations of each species (A5–A6).

$$[\text{N}_2\text{O}_5] = \left(\frac{1}{1 + \frac{1}{K_{\text{eq}}[\text{NO}_2]}} \right) [\text{NN}] \quad (\text{A5})$$

$$[\text{NO}_3] = \left(1 - \frac{1}{1 + \frac{1}{K_{\text{eq}}[\text{NO}_2]}} \right) [\text{NN}] \quad (\text{A6})$$

[84] The differential equations for NO₃ and N₂O₅ are then combined into a single cycling equation (A7) and the terms describing the equilibrium cycling cancel.

$$\frac{d[\text{NN}]}{dt} = +k_1[\text{O}_3][\text{NO}_2] - k_{\text{N}_2\text{O}_5}[\text{N}_2\text{O}_5] - k_{\text{NO}_3}[\text{NO}_3] \quad (\text{A7})$$

[85] Nominally, the assumption of equilibrium between NO₃ and N₂O₅ also simplifies the differential equation for NO₂ (A2), where the second and third terms cancel. However, here the assumption of equilibrium leads to an error which accumulates as the equations are integrated. For each molecule of NO₃ that is produced and lost through NO₃ reactions with VOCs, one molecule of NO₂ is lost. However, for each molecule of N₂O₅ lost through heterogeneous chemistry, two molecules of NO₂ are lost. The loss of an additional molecule of NO₂ is accounted for by a small difference in the second and third terms of equation (A3). This difference can be accounted for by assuming the difference between the terms is proportional to the nitrate radical production and that proportionality constant s is constant in time (A8).

$$k_{2f}[\text{NO}_3][\text{NO}_2] - k_{2r}[\text{N}_2\text{O}_5] = s \times k_1[\text{O}_3][\text{NO}_2] \quad (\text{A8})$$

[86] This physical meaning of s is the ratio of nitrate radical production which goes through N₂O₅ (either as N₂O₅ or lost through uptake) to the total nitrate radical production. Using equation (A4), the difference can be expressed in terms of N₂O₅.

$$k_{2f}[\text{NO}_3][\text{NO}_2] - k_{2r}[\text{N}_2\text{O}_5] = \frac{d[\text{N}_2\text{O}_5]}{dt} - k_{\text{N}_2\text{O}_5}[\text{N}_2\text{O}_5] = s \times k_1[\text{O}_3][\text{NO}_2] \quad (\text{A9})$$

[87] To determine the value of the proportionality constant s , equation (A9) is integrated from start of the box model to an arbitrary time t_2 .

$$\int_0^{t_2} dt \times s \times k_1[\text{O}_3][\text{NO}_2] = \int_0^{t_2} dt \times \frac{d[\text{N}_2\text{O}_5]}{dt} - \int_0^{t_2} dt \times k_{\text{N}_2\text{O}_5}[\text{N}_2\text{O}_5] \quad (\text{A10})$$

[88] Because s is constant with respect to time, it can be pulled out of the integral. Then, equation (A10) can be solved for s and the cumulative nitrate radical production in the denominator can be replaced by the cumulative loss of O₃.

$$s(t_2) = \frac{\int_0^{t_2} k_{\text{N}_2\text{O}_5}[\text{N}_2\text{O}_5]dt + [\text{N}_2\text{O}_5](t_2)}{\int_0^{t_2} k_1[\text{O}_3][\text{NO}_2]dt} = \frac{\int_0^{t_2} k_{\text{N}_2\text{O}_5}[\text{N}_2\text{O}_5]dt + [\text{N}_2\text{O}_5](t_2)}{[\text{O}_3](0) - [\text{O}_3](t_2)} \quad (\text{A11})$$

[89] This definition of s intuitively makes sense as the ratio of the N₂O₅ concentration plus cumulative N₂O₅ lost to the cumulative nitrate radical production. It varies between 0 and 1 according to the amount of NO₃ or N₂O₅ chemistry. Even though it has explicit time dependence stated in equation (A11), it is averaged over from the start of the box model to time t_2 . After making these

simplifications, the box model consists of three differential equations (A12, A13, A14).

$$\frac{d[\text{O}_3]}{dt} = -k_1[\text{O}_3][\text{NO}_2] \quad (\text{A12})$$

$$\frac{d[\text{NO}_2]}{dt} = -(1 + s(t_2)) \times k_1[\text{O}_3][\text{NO}_2] \quad (\text{A13})$$

$$\frac{d[\text{NN}]}{dt} = +k_1[\text{O}_3][\text{NO}_2] - k_{\text{N}_2\text{O}_5}[\text{N}_2\text{O}_5] - k_{\text{NO}_3}[\text{NO}_3] \quad (\text{A14})$$

[90] Because the final concentrations are known it would be convenient to integrate these equations backward in time and iterate the N₂O₅ loss rate coefficient until the N₂O₅ concentration was zero at sunset. However, because the ambient N₂O₅ concentration could be in steady state, several different start times would yield the same final N₂O₅ concentration and it is unlikely the iterations would converge.

[91] An alternate method of integrating these equations is to do it in two steps. First, the equations for O₃ and NO₂ are integrated backward in time to sunset. Then, the equation for nocturnal nitrogen can be integrated forward from sunset until the time of the measurements starting with an N₂O₅ concentration of zero at sunset. The box model will then predict a final N₂O₅ concentration. The N₂O₅ loss rate coefficient can then be iterated until the predicted N₂O₅ concentration matches the measured concentration.

[92] The model depends on the N₂O₅ loss rate coefficient in two places: in the equations for nocturnal nitrogen (A14) and a weaker dependence in $s(t)$ (A11). To help the model

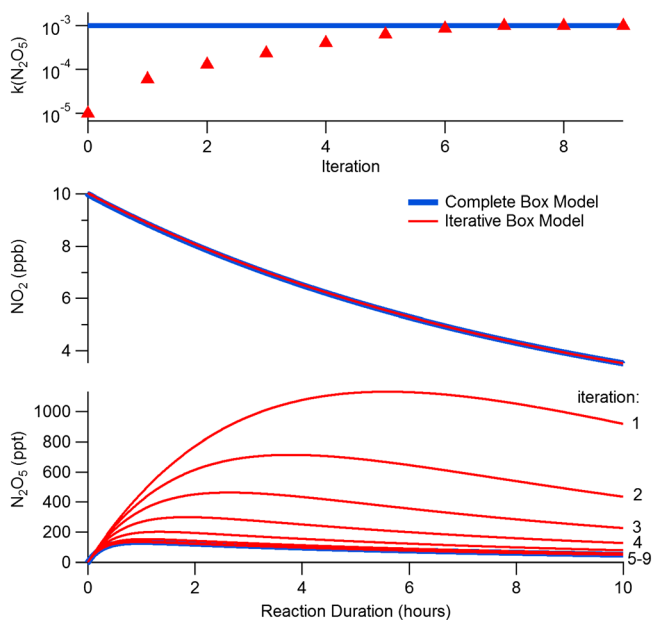


Figure A1. An example of the iterative box model calculations and a comparison to the full box model using equations (A1)–(A4). (top) The N₂O₅ loss rate coefficient used in each iteration and the target value (0.001) used to generate the data. (middle and bottom) The NO₂ and N₂O₅ mixing ratios as a function of reaction time for each iteration. Conditions: Temperature = 0°C, $k_{\text{NO}_3} = 0.001 \text{ s}^{-1}$, Pressure = 840 hPa, $\text{O}_3(t = 0) = 40 \text{ ppbv}$, $\text{NO}_2(t = 0) = 10 \text{ ppbv}$.

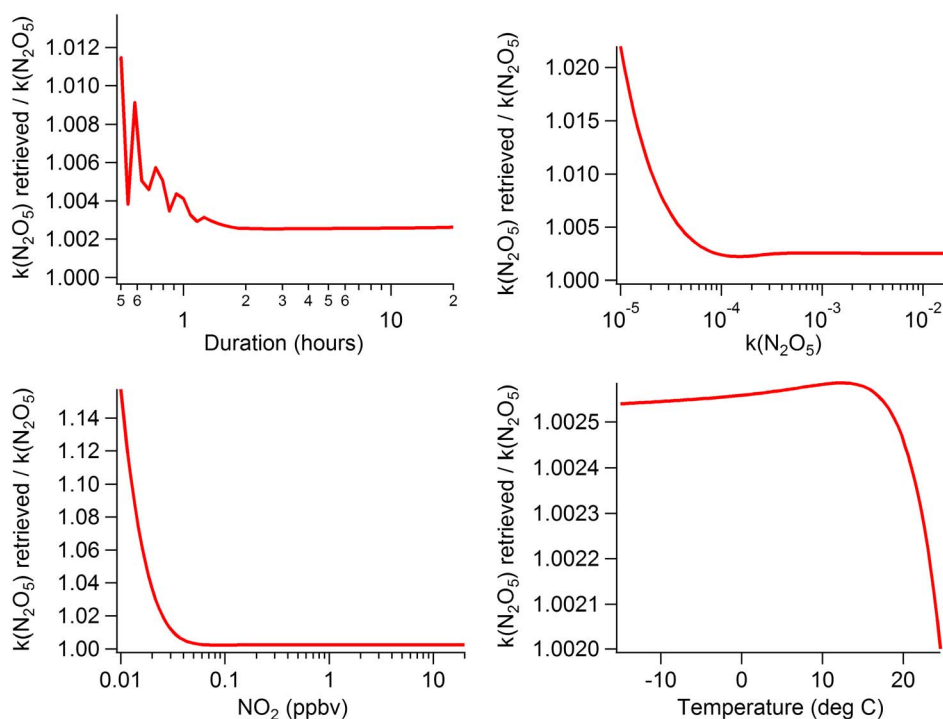


Figure A2. A box model using equations (A1)–(A4) and a range of loss rate coefficients and initial conditions were used to calculate O₃, NO₂, NO₃, and N₂O₅ concentrations. The iterative box model described in Appendix A was used to retrieve the N₂O₅ loss rate coefficient. A comparison of the retrieved loss rate coefficients and those used initially is shown here. The retrieved N₂O₅ loss rate coefficient normalized to the initial loss rate coefficient is shown as a function of duration, initial loss rate coefficient, initial NO₂, and temperature. In all cases, the error in the retrieved loss rate coefficient is less than 2% except when NO₂ mixing ratios are < 0.03 ppbv.

converge to a solution, the loss rate coefficient is varied in two steps. Initially, $s(t)$ is taken to be 1, and the O₃(t) and NO₂(t) are calculated backward in time. Then, the nocturnal nitrogen is calculated and loss rate coefficient is adjusted until the final N₂O₅ concentration is matched. Then, a new $s(t)$, O₃(t), and NO₂(t) are calculated using equation (A11) and N₂O₅ concentrations from the previous iteration. The process is continued until loss rate coefficient changes less than 1%. If the number of iterations of the first step exceeds 30 or the second step exceeds 10, the calculation is stopped and the datum is marked as nonconvergent. Typically, the calculation converges in with 5 iterations in the first step and 3 in the second step. The average time taken depends on the initial guess, the duration of the calculation, and the time step used. For the NACHTT data set, this calculation was implemented using the Igor Pro data analysis software package. The calculation took ~5 ms for each hour of duration on a notebook computer using a time step of 30 s and an initial guess of 10^{-5} for the N₂O₅ loss rate. The script used for this calculation is included in the supporting information.

[93] One complication of using the iterative box model is the possibility that there are multiple solutions or more than one loss rate coefficient that produces the same final N₂O₅ concentration. This possibility was investigated numerically for loss rate coefficients between 10^{-7} s^{-1} and 1 s^{-1} , and multiple roots were not found.

[94] For some input conditions, the iterative box model will return a negative N₂O₅ loss rate coefficient. This nonphysical result means the nitrate radical production rate

and/or reaction time is not large enough to produce the final N₂O₅ concentration. This situation frequency occurs when calculating uncertainties. Either the lower limit of the reaction duration or the upper limit NO₃ reactivity is used, and a negative N₂O₅ loss rate is required to produce the final N₂O₅ concentration. In this case, the iterative box model is considered to have not converged, or if the error bars are being calculated, a value of zero is used for the lower limit of the loss rate coefficient.

[95] This method of retrieving the N₂O₅ loss rate coefficient was checked by using the full differential equations for the box model (A1–A4). The final concentrations were then fed into the iterative box model and N₂O₅ loss rate coefficient retrieved. An example of the iterative box model is shown in Figure A1. The upper panel shows the value of the loss rate coefficient for each iteration. The middle and lower panels show the NO₂ and N₂O₅ mixing ratios as a function of reaction duration for each iteration and for the box model using the full differential equations. In this case the losses are dominated by N₂O₅, and $s(t)$ (A11) is nearly equal to one, which is close to the initial guess. Because $s(t)$ does not change much between the initial guess and the final iteration, the NO₂ mixing ratios do not change much with each iteration. However, the N₂O₅ mixing ratio does change significantly as the model converges. For these conditions, the box model converged in 9 iterations.

[96] The accuracy of the iterative box model was tested over a range of initial conditions. The reaction duration, N₂O₅ loss rate coefficient, initial NO₂, and temperature were

varied. Then, loss rate coefficient was retrieved using the iterative box model. A comparison of the results is shown in Figure A2. Except for initial NO₂ mixing ratios less than 100 ppt, the retrieval was accurate to better than 1%. Because the change in the loss rate coefficient must only be less than 1% for the retrieval to stop iterating, this level of agreement is expected. For small mixing ratios of NO₂, cycling between NO₃ and N₂O₅ takes a long time to establish equilibrium and the assumption of equilibrium used in the retrieval is not valid. Therefore, the disagreement at low NO₂ mixing ratio is expected.

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References

- Aldener, M., et al. (2006), 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, *J. Geophys. Res.*, *111*, D23S73, doi:10.1029/2006JD007252.
- Anttila, T., A. Kiendler-Scharr, R. Tillmann, and T. F. Mentel (2006), On the reactive uptake of gaseous compounds by organic-coated aqueous aerosols: Theoretical analysis and application to the heterogeneous hydrolysis of N₂O₅, *J. Phys. Chem. A*, *110*(35), 10,435–10,443, doi:10.1021/jp062403c.
- Atkinson, R. (1991), Kinetics and mechanisms of the gas-phase reactions of the NO₃ radical with organic compounds, *J. Phys. Chem. Ref. Data*, *20*(3), 459–507, doi:10.1063/1.555887.
- Atkinson, R., and J. Arey (2003), Gas-phase tropospheric chemistry of biogenic volatile organic compounds: A review, *Atmos. Environ.*, *37*, S197–S219, doi:10.1016/s1352-2310(03)00391-1.
- Badger, C. L., P. T. Griffiths, I. George, J. P. D. Abbatt, and R. A. Cox (2006), Reactive uptake of N₂O₅ by aerosol particles containing mixtures of humic acid and ammonium sulfate, *J. Phys. Chem. A*, *110*(21), 6986–6994, doi:10.1021/jp0562678.
- Bahreini, R., et al. (2009), Organic aerosol formation in urban and industrial plumes near Houston and Dallas, Texas, *J. Geophys. Res.*, *114*, D00F16, doi:10.1029/2008JD011493.
- Bertram, T. H., and J. A. Thornton (2009), Toward a general parameterization of N₂O₅ reactivity on aqueous particles: The competing effects of particle liquid water, nitrate and chloride, *Atmos. Chem. Phys.*, *9*(21), 8351–8363, doi:10.5194/acp-9-8351-2009.
- Bertram, T. H., J. A. Thornton, T. P. Riedel, A. M. Middlebrook, R. Bahreini, T. S. Bates, P. K. Quinn, and D. J. Coffman (2009), Direct observations of N₂O₅ reactivity on ambient aerosol particles, *Geophys. Res. Lett.*, *36*, L19803, doi:10.1029/2009GL040248.
- Brown, S. S., and J. Stutz (2012), Nighttime radical observations and chemistry, *Chem. Soc. Rev.*, *41*(19), 6405–6447, doi:10.1039/c2cs35181a.
- Brown, S. S., H. Stark, and A. R. Ravishankara (2003), Applicability of the steady state approximation to the interpretation of atmospheric observations of NO₃ and N₂O₅, *J. Geophys. Res.*, *108*(D17), 4539, doi:10.1029/2003JD003407.
- Brown, S. S., et al. (2004), Nighttime removal of NO₃ in the summer marine boundary layer, *Geophys. Res. Lett.*, *31*, L07108, doi:10.1029/2004GL019412.
- Brown, S. S., et al. (2005), Aircraft observations of daytime NO₃ and N₂O₅ and their implications for tropospheric chemistry, *J. Photochem. Photobiol. A*, *176*, 270–278.
- Brown, S. S., et al. (2006), Variability in nocturnal nitrogen oxide processing and its role in regional air quality, *Science*, *311*(5757), 67–70, doi:10.1126/science.1120120.
- Brown, S. S., et al. (2009), Reactive uptake coefficients for N₂O₅ determined from aircraft measurements during the Second Texas Air Quality Study: Comparison to current model parameterizations, *J. Geophys. Res.*, *114*, D00F10, doi:10.1029/2008JD011679.
- Cai, Y., D. C. Montague, W. Mooiweer-Bryan, and T. Deshler (2008), Performance characteristics of the ultra high sensitivity aerosol spectrometer for particles between 55 and 800 nm: Laboratory and field studies, *J. Aerosol. Sci.*, *39*(9), 759–769, doi:10.1016/j.jaerosci.2008.04.007.
- Chang, W. L., P. V. Bhave, S. S. Brown, N. Riemer, J. Stutz, and D. Dabdub (2011), Heterogeneous atmospheric chemistry, ambient measurements, and model calculations of N₂O₅: A review, *Aerosol Sci. Technol.*, *45*(6), 665–695, doi:10.1080/02786826.2010.551672.
- Cosman, L. M., and A. K. Bertram (2008), Reactive uptake of N₂O₅ on aqueous H₂SO₄ solutions coated with 1-component and 2-component monolayers, *J. Phys. Chem. A*, *112*(20), 4625–4635, doi:10.1021/jp8005469.
- Davis, J. M., P. V. Bhave, and K. M. Foley (2008), Parameterization of N₂O₅ reaction probabilities on the surface of particles containing ammonium, sulfate, and nitrate, *Atmos. Chem. Phys.*, *8*(17), 5295–5311, doi:10.5194/acp-8-5295-2008.
- Day, D. A., M. B. Dillon, P. J. Wooldridge, J. A. Thornton, R. S. Rosen, E. C. Wood, and R. C. Cohen (2003), On alkyl nitrates, O₃, and the “missing NO_y”, *J. Geophys. Res.*, *108*(D16), 4501, doi:10.1029/2003JD003685.
- Dentener, F. J., and P. J. Crutzen (1993), Reaction of N₂O₅ on tropospheric aerosols: Impact on the global distributions of NO_x, O₃, and OH, *J. Geophys. Res.*, *98*(D4), 7149–7163, doi:10.1029/92JD02979.
- Dorn, H. P., et al. (2013), Intercomparison of NO₃ radical detection instruments in the atmosphere simulation chamber SAPHIR, *Atmos. Meas. Tech.*, *6*(5), 1111–1140, doi:10.5194/amt-6-1111-2013.
- Dubé, W. P., S. S. Brown, H. D. Osthoff, M. R. Nunley, S. J. Ciciora, M. W. Paris, R. J. McLaughlin, and A. R. Ravishankara (2006), Aircraft instrument for simultaneous, in situ measurement of NO₃ and N₂O₅ via pulsed cavity ring-down spectroscopy, *Rev. Sci. Instrum.*, *77*(3), doi:10.1063/1.2176058.
- Duplissy, J., et al. (2011), Relating hygroscopicity and composition of organic aerosol particulate matter, *Atmos. Chem. Phys.*, *11*(3), 1155–1165, doi:10.5194/acp-11-1155-2011.
- Ehhalt, D. H., and F. Rohrer (2000), Dependence of the OH concentration on solar UV, *J. Geophys. Res.*, *105*(D3), 3565–3571, doi:10.1029/1999JD901070.
- Evans, M. J., and D. J. Jacob (2005), Impact of new laboratory studies of N₂O₅ hydrolysis on global model budgets of tropospheric nitrogen oxides, ozone, and OH, *Geophys. Res. Lett.*, *32*, L09813, doi:10.1029/2005GL022469.
- Finlayson-Pitts, B. J., M. J. Ezell, and J. N. Pitts (1989), Formation of chemically active chlorine compounds by reactions of atmospheric NaCl particles with gaseous N₂O₅ and ClONO₂, *Nature*, *337*(6204), 241–244, doi:10.1038/337241a0.
- Fleming, Z. L., P. S. Monks, A. R. Rickard, B. J. Bandy, N. Brough, T. J. Green, C. E. Reeves, and S. A. Penkett (2006), Seasonal dependence of peroxy radical concentrations at a Northern hemisphere marine boundary layer site during summer and winter: Evidence for radical activity in winter, *Atmos. Chem. Phys.*, *6*, 5415–5433, doi:10.5194/acp-6-5415-2006.
- Fountoukis, C., and A. Nenes (2007), ISORROPIA II: A computationally efficient thermodynamic equilibrium model for K⁺-Ca²⁺-Mg²⁺-NH₄⁺-Na⁺-SO₄²⁻-NO₃⁻-Cl⁻-H₂O aerosols, *Atmos. Chem. Phys.*, *7*(17), 4639–4659, doi:10.5194/acp-7-4639-2007.
- Fuchs, N. A., and A. G. Sutugin (1970), *Highly Dispersed Aerosol*, Ann Arbor Science, Ann Arbor, MI.
- Fuchs, H., W. P. Dube, S. J. Ciciora, and S. S. Brown (2008), Determination of inlet transmission and conversion efficiencies for in situ measurements of the nocturnal nitrogen oxides, NO₃, N₂O₅ and NO₂, via pulsed cavity ring-down spectroscopy, *Anal. Chem.*, *80*(15), 6010–6017, doi:10.1021/ac8007253.
- Geyer, A., et al. (2003), Direct observations of daytime NO₃: Implications for urban boundary layer chemistry, *J. Geophys. Res.*, *108*(D12), 4346, doi:10.1029/2002JD002967.
- Gilman, J. B., B. M. Lerner, W. C. Kuster, and J. A. de Gouw (2012), Source signature of volatile organic compounds (VOCs) from oil and natural gas operations in northeastern Colorado, *Environ. Sci. Technol.*, doi:10.1021/es304119a.
- Griffiths, P. T., and R. A. Cox (2009), Temperature dependence of heterogeneous uptake of N₂O₅ by ammonium sulfate aerosol, *Atmos. Sci. Lett.*, *10*(3), 159–163, doi:10.1002/asl.225.
- Groblicki, P. J., G. T. Wolff, and R. J. Countess (1981), Visibility-reducing species in the Denver “Brown Cloud”: Relationships between extinction and chemical composition, *Atmos. Environ.*, *15*(12), 2473–2484, doi:10.1016/0004-6981(81)90063-9.
- Gross, S., and A. K. Bertram (2008), Reactive uptake of NO₃, N₂O₅, NO₂, HNO₃, and O₃ on three types of polycyclic aromatic hydrocarbon surfaces, *J. Phys. Chem. A*, *112*(14), 3104–3113, doi:10.1021/jp7107544.
- Hall, I. W., R. P. Wayne, R. A. Cox, M. E. Jenkin, and G. D. Hayman (1988), Kinetics of the reaction of NO₃ with HO₂, *J. Phys. Chem.*, *92*(17), 5049–5054, doi:10.1021/j100328a043.
- Hallquist, M., D. J. Stewart, S. K. Stephenson, and R. A. Cox (2003), Hydrolysis of N₂O₅ on sub-micron sulfate aerosols, *Phys. Chem. Chem. Phys.*, *5*(16), 3453–3463, doi:10.1039/b301827j.
- Heard, D. E., L. J. Carpenter, D. J. Creasey, J. R. Hopkins, J. D. Lee, A. C. Lewis, M. J. Pilling, P. W. Seakins, N. Carslaw, and K. M. Emmerson (2004), High levels of the hydroxyl radical in the winter urban troposphere, *Geophys. Res. Lett.*, *31*, L18112, doi:10.1029/2004GL020544.

- Hu, J. H., and J. P. D. Abbatt (1997), Reaction probabilities for N₂O₅ hydrolysis on sulfuric acid and ammonium sulfate aerosols at room temperature, *J. Phys. Chem. A*, *101*(5), 871–878, doi:10.1021/jp9627436.
- Hu, D., J. Chen, X. Ye, L. Li, and X. Yang (2011), Hygroscopicity and evaporation of ammonium chloride and ammonium nitrate: Relative humidity and size effects on the growth factor, *Atmos. Environ.*, *45*(14), 2349–2355, doi:10.1016/j.atmosenv.2011.02.024.
- Kanaya, Y., R. Cao, H. Akimoto, M. Fukuda, Y. Komazaki, Y. Yokouchi, M. Koike, H. Tanimoto, N. Takegawa, and Y. Kondo (2007), Urban photochemistry in central Tokyo: 1. Observed and modeled OH and HO₂ radical concentrations during the winter and summer of 2004, *J. Geophys. Res.*, *112*, D21312, doi:10.1029/2007JD008670.
- Kercher, J. P., T. P. Riedel, and J. A. Thornton (2009), Chlorine activation by N₂O₅: Simultaneous, in situ detection of ClNO₂ and N₂O₅ by chemical ionization mass spectrometry, *Atmos. Meas. Tech.*, *2*(1), 193–204, doi:10.5194/amt-2-193-2009.
- Kleffmann, J. (2007), Daytime sources of nitrous acid (HONO) in the atmospheric boundary layer, *Chemphyschem*, *8*(8), 1137–1144, doi:10.1002/cphc.200700016.
- Macintyre, H. L., and M. J. Evans (2010), Sensitivity of a global model to the uptake of N₂O₅ by tropospheric aerosol, *Atmos. Chem. Phys.*, *10*(15), 7409–7414, doi:10.5194/acp-10-7409-2010.
- McNeill, V. F., J. Patterson, G. M. Wolfe, and J. A. Thornton (2006), The effect of varying levels of surfactant on the reactive uptake of N₂O₅ to aqueous aerosol, *Atmos. Chem. Phys.*, *6*, 1635–1644, doi:10.5194/acp-6-1635-2006.
- Mentel, T. F., M. Sohn, and A. Wahner (1999), Nitrate effect in the heterogeneous hydrolysis of dinitrogen pentoxide on aqueous aerosols, *Phys. Chem. Chem. Phys.*, *1*(24), 5451–5457, doi:10.1039/a905338g.
- Neff, W. D. (1997), The Denver Brown Cloud studies from the perspective of model assessment needs and the role of meteorology, *J. Air Waste Manage. Assoc.*, *47*(3), 269–285, doi:10.1080/10473289.1997.10464447.
- Osthoff, H. D., et al. (2008), High levels of nitryl chloride in the polluted subtropical marine boundary layer, *Nat. Geosci.*, *1*(5), 324–328, doi:10.1038/ngeo177.
- Park, S.-C., D. K. Burden, and G. M. Nathanson (2007), The inhibition of N₂O₅ hydrolysis in sulfuric acid by 1-butanol and 1-hexanol surfactant coatings, *J. Phys. Chem. A*, *111*(15), 2921–2929, doi:10.1021/jp068228h.
- Ren, X., et al. (2006), Behavior of OH and HO₂ in the winter atmosphere in New York City, *Atmos. Environ.*, *40*, S252–S263, doi:10.1016/j.atmosenv.2005.11.073.
- Riedel, T. P., T. H. Bertram, O. S. Ryder, S. Liu, D. A. Day, L. M. Russell, C. J. Gaston, K. A. Prather, and J. A. Thornton (2012a), Direct N₂O₅ reactivity measurements at a polluted coastal site, *Atmos. Chem. Phys.*, *12*(6), 2959–2968, doi:10.5194/acp-12-2959-2012.
- Riedel, T. P., et al. (2012b), Nitryl chloride and molecular chlorine in the coastal marine boundary layer, *Environ. Sci. Technol.*, *46*(19), 10,463–10,470, doi:10.1021/es204632r.
- Roberts, J. M. (2007), Peroxyacetic nitric anhydride (PAN) and related compounds, in *Volatile Organic Compounds in the Atmosphere*, edited by R. Koppmann, pp. 221–268, Blackwell, London.
- Russo, R. S., Y. Zhou, K. B. Haase, O. W. Wingenter, E. K. Frinak, H. Mao, R. W. Talbot, and B. C. Sive (2010), Temporal variability, sources, and sinks of C1–C5 alkyl nitrates in coastal New England, *Atmos. Chem. Phys.*, *10*(4), 1865–1883, doi:10.5194/acp-10-1865-2010.
- Sander, S. P., et al. (2011), Chemical kinetics and photochemical data for use in atmospheric studies, Evaluation No. 17, *JPL Publication 10-6*.
- Stark, H., B. M. Lerner, R. Schmitt, R. Jakoubek, E. J. Williams, T. B. Ryerson, D. T. Sueper, D. D. Parrish, and F. C. Fehsenfeld (2007), Atmospheric in situ measurement of nitrate radical (NO₃) and other photolysis rates using spectroradiometry and filter radiometry, *J. Geophys. Res.*, *112*, D10S04, doi:10.1029/2006JD007578.
- Swietlicki, E., et al. (2008), Hygroscopic properties of submicrometer atmospheric aerosol particles measured with H-TDMA instruments in various environments—A review, *Tellus Series B-Chemical and Physical Meteorology*, *60*(3), 432–469, doi:10.1111/j.1600-0889.2008.00350.x.
- Tanner, D. J., A. Jefferson, and F. L. Eisele (1997), Selected ion chemical ionization mass spectrometric measurement of OH, *J. Geophys. Res.*, *102*(D5), 6415–6425, doi:10.1029/96JD03919.
- Thornton, J. A., C. F. Braban, and J. P. D. Abbatt (2003), N₂O₅ Hydrolysis on sub-micron organic aerosols: The effect of relative humidity, particle phase, and particle size, *Phys. Chem. Chem. Phys.*, *5*(20), 4593–4603, doi:10.1039/b307498f.
- Thornton, J. A., et al. (2010), A large atomic chlorine source inferred from mid-continental reactive nitrogen chemistry, *Nature*, *464*(7286), 271–274, doi:10.1038/nature08905.
- Van Doren, J. M., L. R. Watson, P. Davidovits, D. R. Worsnop, M. S. Zahniser, and C. E. Kolb (1990), Temperature dependence of the uptake coefficients of HNO₃, HCl, and N₂O₅ by water droplets, *J. Phys. Chem.*, *94*(8), 3265–3269, doi:10.1021/j100371a009.
- Veres, P., J. M. Roberts, C. Warneke, D. Welsh-Bon, M. Zahniser, S. Herndon, R. Fall, and J. de Gouw (2008), Development of negative-ion proton-transfer chemical-ionization mass spectrometry (NI-PT-CIMS) for the measurement of gas-phase organic acids in the atmosphere, *Int. J. Mass Spectrom.*, *274*(1–3), 48–55.
- Wagner, N. L., W. P. Dube, R. A. Washenfelder, C. J. Young, I. B. Pollack, T. B. Ryerson, and S. S. Brown (2011), Diode laser-based cavity ring-down instrument for NO₃, N₂O₅, NO, NO₂ and O₃ from aircraft, *Atmos. Meas. Tech.*, *4*, 1227–1240, doi:10.5194/amt-4-1227-2011.
- Wahner, A., T. F. Mentel, and M. Sohn (1998a), Gas-phase reaction of N₂O₅ with water vapor: Importance of heterogeneous hydrolysis of N₂O₅ and surface desorption of HNO₃ in a large teflon chamber, *Geophys. Res. Lett.*, *25*(12), 2169–2172, doi:10.1029/98GL51596.
- Wahner, A., T. F. Mentel, M. Sohn, and J. Stier (1998b), Heterogeneous reaction of N₂O₅ on sodium nitrate aerosol, *J. Geophys. Res.*, *103*(D23), 31,103–31,112, doi:10.1029/1998JD100022.
- Wong, K. W., and J. Stutz (2010), Influence of nocturnal vertical stability on daytime chemistry: A one-dimensional model study, *Atmos. Environ.*, *44*(31), 3753–3760, doi:10.1016/j.atmosenv.2010.06.057.
- Wong, K. W., H. J. Oh, B. L. Lefer, B. Rappenglueck, and J. Stutz (2011), Vertical profiles of nitrous acid in the nocturnal urban atmosphere of Houston, TX, *Atmos. Chem. Phys.*, *11*(8), 3595–3609, doi:10.5194/acp-11-3595-2011.
- Young, C. J., et al. (2012), Vertically resolved measurements of nighttime radical reservoirs in Los Angeles and their contribution to the urban radical budget, *Environ. Sci. Technol.*, *46*(20), 10,965–10,973, doi:10.1021/es302206a.
- Zhang, Q., et al. (2007), Ubiquity and dominance of oxygenated species in organic aerosols in anthropogenically-influenced Northern Hemisphere midlatitudes, *Geophys. Res. Lett.*, *34*, L13801, doi:10.1029/2007GL029979.