Chapter 10
Heterogeneous Atmospheric Chemistry of Nitrogen Oxides: New Insights from Recent Field Measurements

Steven S. Brown, Nicholas L. Wagner, William P. Dubé, and James M. Roberts

Abstract The heterogeneous chemistry of nitrogen oxides that occurs in the dark is important to both the overall budgets of reactive nitrogen in the atmosphere, as well as the formation of oxidants. Two of the most relevant processes include the conversion of NO_2 to HONO on ground surfaces and the uptake of N_2O_5 to produce either HNO_3 or $ClNO_2$ on aerosol surfaces. Results from recent field measurements that have investigated the latter process have demonstrated several important findings. First, the uptake of N_2O_5 is highly variable, and the uptake coefficient, $\gamma(N_2O_5)$, is often smaller than model parameterizations based on laboratory studies would suggest. Second, production of $ClNO_2$ is much more efficient than previously thought, and is formed in relatively high yields even at interior continental sites that are well removed from direct sources of sea spray. Finally, N_2O_5 uptake and $ClNO_2$ production both vary strongly with height in the nocturnal boundary layer, leading to significant complexity in this nighttime chemistry.

10.1 Introduction

The chemistry of nitrogen oxides is central to the understanding of atmospheric oxidants. The photochemical cycling between NO and NO_2 (commonly referred to as NO_x) is the chemical source for ozone in the troposphere [11]. Oxidation of NO to NO_2 by O_3 and the subsequent photolysis of NO_2 back to NO and atomic oxygen produces a net null cycle. Reaction of NO with peroxy radicals (RO_2), derived
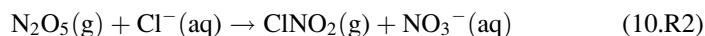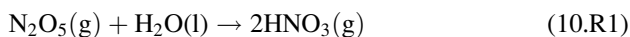
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mainly from the photochemical oxidation of volatile organic compounds, perturbs this cycle and leads to net ozone production. This mechanism influences both air quality and climate. It is responsible for the production of large excess ozone in urban areas that is linked to health impacts [25]. Anthropogenic NO_x emission during the industrial era are also responsible for the increase in tropospheric ozone [22], the third most important greenhouse gas after carbon dioxide and methane [34].

Heterogeneous reactions of nitrogen oxides, such as the surface or aerosol uptake of NO_2 or N_2O_5, have also been understood for several decades as an important part of the overall nitrogen oxide budget [21]. As discussed below, they also exert a strong influence on tropospheric oxidants. Several of these processes occur during darkness – that is, they do not proceed to a significant extent in the presence of sunlight because of the photochemical instability of either the reaction products or their precursors. Two nighttime heterogeneous reactions discussed in this manuscript include nitrous acid production and dinitrogen pentoxide uptake. The latter is the major emphasis of this paper.

The nighttime conversion of NO_2 to nitrous acid (HONO) and can be an important radical source in urban areas [35]. Daytime production of HONO may also be an important radical source, but it remains poorly quantified due to uncertainty in the mechanism for sunlight-driven production (see, for example, George et al. [20]). Conversion of NO_2 to HONO is thought to occur primarily on the ground or other surface rather than in the aerosol phase, since the laboratory-measured uptake coefficients to aerosol are too small to explain observed nighttime HONO levels [6]. Vertically resolved HONO measurements typically show that it has a strong nighttime vertical gradient due to its source at ground level and its production in a stable nocturnal boundary layer [43]. Although HONO production is an important component of nighttime heterogeneous nitrogen oxide reactions, this paper does not discuss the topic in detail due in part to the many contributions dealing with this topic within the context of this workshop. Its description here does provide an important point of comparison to the nighttime heterogeneous reactions of NO_3 and N_2O_5, described below.

The second nighttime heterogeneous process is aerosol uptake of dinitrogen pentoxide, N_2O_5. This compound forms principally at night from the reversible addition of NO_3 with NO_2. Although homogeneous hydrolysis of N_2O_5 to nitric acid, HNO_3, is strongly favored thermodynamically, it is kinetically limited and is very slow as a gas phase reaction [41, 42]. The hydrolysis occurs readily in the aerosol phase, however, by the mechanism described in Sect. 10.2. Nitryl chloride arises from the heterogeneous reaction of N_2O_5 with aerosol phase chloride (Cl^-), a reaction that competes with N_2O_5 hydrolysis to produces nitric acid (or aerosol phase nitrate) [3, 18]. A key finding from recent field measurements is that nitryl chloride, $ClNO_2$, is present in surprisingly large concentrations in urban air masses across a wide range of environments [31, 37].

$$N_2O_5(g) + H_2O(l) \rightarrow 2HNO_3(g) \qquad (10.R1)$$

$$N_2O_5(g) + Cl^-(aq) \rightarrow ClNO_2(g) + NO_3^-(aq) \qquad (10.R2)$$

Because $ClNO_2$ does not have rapid sinks in the dark, it builds up overnight as reaction (10.R2) proceeds. It undergoes photolytic degradation after sunrise to produce atomic chlorine radicals and to regenerate NO_2.

$$ClNO_2 + h\nu \rightarrow NO_2 + Cl \qquad (10.R3)$$

Production and loss of $ClNO_2$ is thus analogous to that of HONO in that it is a radical reservoir species that forms through nighttime heterogeneous nitrogen oxide reactions, and in that it influences next-day photochemistry through morning photolysis to produce both radicals and NO_x. Nighttime $ClNO_2$ formation differs substantially from that of HONO in that it proceeds mainly on the aerosol phase rather than on the ground surface. Because it also occurs at night when the atmosphere is poorly mixed, the nighttime distribution of both N_2O_5 and $ClNO_2$ are likely to differ from that of HONO. The vertical distributions of N_2O_5, $ClNO_2$ and HONO are important to understanding the influence nitrogen oxide heterogeneous chemistry over urban areas.

The remainder of this manuscript focuses primarily on recent advances in the understanding of N_2O_5 and $ClNO_2$, with comparisons to HONO formation where appropriate.

10.2 Tropospheric Chemistry of N_2O_5

Heterogeneous hydrolysis of N_2O_5 via reaction (10.1) has a large impact on both regional and global budgets for tropospheric NO_x. On the regional scale, the rate of overnight NO_x loss through this reaction influences next-day ozone formation as well as the formation of nitrate aerosol [13, 32], especially in winter [28]. The landmark study of Dentener and Crutzen [14] demonstrated the importance of N_2O_5 hydrolysis in regulating both the global burden of nitrogen oxides and oxidants. Their study showed a 50% reduction in global NO_x as a result of reaction (10.1), with an 80% reduction in the northern hemisphere during winter. The reaction decreased global modeled O_3 and OH by 9% each, with a 25% reduction in O_3 in the springtime northern mid-latitudes and subtropics. Subsequent studies have largely confirmed the importance of this reaction for NO_x and oxidants, although estimates for the impact have varied with assumptions about the efficiency of the reaction [1, 16, 17, 24, 27, 38, 39]. The impact of $ClNO_2$ formation has not been considered in regional or global models to date.

The earlier model studies on N_2O_5 hydrolysis [14, 24, 39] relied on the relatively simple assumption that the reaction proceeds with a constant aerosol uptake coefficient, $\gamma(N_2O_5) = 0.1$ [30]. In the limit where gas phase diffusion to the particle surface is negligible (valid for small particle sizes and small uptake coefficients), the first order loss rate coefficient for N_2O_5, k_{N2O5}, is proportional to the uptake coefficient.

$$k_{N_2O_5} = \frac{1}{4} c_{mean} S_A \gamma(N_2O_5) \qquad (10.1)$$

Fig. 10.1 Mechanism for the
uptake of gas phase N_2O_5 to
aerosol and its subsequent
reaction. The figure shows
N_2O_5 ionization and reaction
with liquid water, solution
phase NO_3^- and Cl^-, as well
as the potential role of
organics. See text for detailed
description
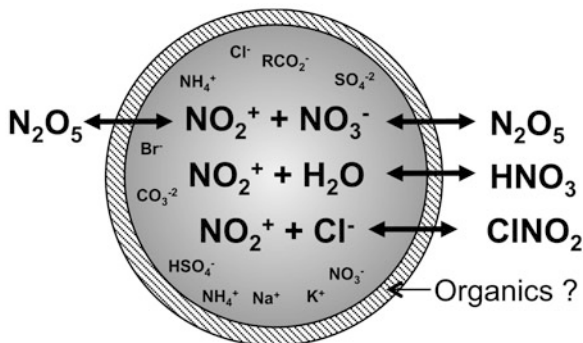
Here c_{mean} is the gas-kinetic mean molecular speed of N_2O_5, and S_A is the aerosol
surface area density (surface area per unit volume). As more recent laboratory data has
become available (see, for example the review of [12] and references therein), models
have incorporated the variability of $\gamma(N_2O_5)$ as a function of aerosol composition and
relative humidity (RH). The task is difficult, however, since recent laboratory-derived
$\gamma(N_2O_5)$ studies span a range of more than two orders of magnitude, from less than
10^{-4} on organic substrates to 0.04 on pure water droplets.

Figure 10.1 shows a simple mechanism for the heterogeneous uptake of N_2O_5 to
the aerosol phase and illustrates some of the factors that regulate its efficiency and
the branching between HNO_3 and $ClNO_2$. The initial step is solvation of N_2O_5
followed by ionization to NO_2^+ (aq) and NO_3^- (aq). While NO_3^- is a common
anion that is stable in solution, NO_2^+ is reactive, and its fate determines both the
reaction efficiency and the branching to different products. Indeed, NO_2^+ may not
exist as a bare cation, but rather as a hydrate (i.e., $H_2O•NO_2^+$) [4]. Thus the first step
in the mechanism involving both N_2O_5 solvation and ionization is highly dependent
on the availability of liquid water, which is the first and likely most important
parameter determining the efficiency of N_2O_5 uptake. Liquid water also reacts
directly with NO_2^+, leading to the irreversible production of aerosol phase nitrate
or gas phase nitric acid.

A second parameter that influences the uptake efficiency is the presence of excess
aerosol phase nitrate. The presence of this anion, derived either from N_2O_5 hydrolysis
itself, or from daytime oxidation of nitrogen oxides, reverses the ionization process
to regenerate gas phase N_2O_5 and effectively suppresses the uptake coefficient.
Uptake coefficients on pure nitrate aerosol are approximately 1 order of magnitude
smaller than on other inorganic salts at moderate RH, for example [41, 42]. A third
parameter is the presence of aerosol phase chloride, which also competes with
both NO_3^- and liquid water for reaction with NO_2^+. Competition between Cl^- and
H_2O is the primary factor that influences the branching between HNO_3 and $ClNO_2$.
Laboratory studies have shown that Cl^- reacts approximately 450 times more rapidly
with NO_2^+ than H_2O [33], such that only a small amount of aerosol phase chloride is
required to substantially increase the production of $ClNO_2$. Competition between Cl^-
and NO_3^- for reaction with NO_2^+ can reverse the nitrate effect in aerosol that are rich
in both chloride and nitrate, with Cl^- reacting approximately 30 times more rapidly
than NO_3^- [4].

Finally, N_2O_5 uptake coefficients are strongly influenced by the presence of aerosol phase organics. Organics generally lead to suppression of N_2O_5 uptake, though the mechanism for this suppression remains unclear and likely depends on the type of organic. For example, organics may form coatings on inorganic particles that present a hydrophobic barrier through which N_2O_5 must diffuse in order to solvate and react with liquid water or other inorganic ions, as represented in Fig. 10.1 [19]. The organic component may also simply act to reduce the liquid water content of the aerosol phase, suppressing $\gamma(N_2O_5)$. While recent parameterizations for use in atmospheric models have successfully treated the laboratory data related to the inorganic composition and its relative humidity dependence [4, 13], the dependence of $\gamma(N_2O_5)$ on organic content is a somewhat more difficult problem (e.g., [5, 17]) that has not led to reproducible agreement between parameterizations and field observations of N_2O_5. The next sections describe some of the efforts toward characterization of N_2O_5 uptake coefficients and branching to HNO_3 and $ClNO_2$ from field measurements.

10.3 Uptake Coefficients of N_2O_5 from Aircraft Measurements

Recent measurements of N_2O_5 in ambient air during field intensives have allowed for the direct characterization of its heterogeneous chemistry and have provided tests for parameterizations used to represent this reaction in atmospheric models. There are now several methods for detection of NO_3 and N_2O_5 at part per trillion levels using *in-situ* instruments [12]. Our research group has developed instruments based on cavity ring-down spectroscopy, a high sensitivity optical detection method, using either pulsed or continuous-wave lasers at 662 nm, where NO_3 has a strong maximum in its absorption spectrum [15, 40]. The instruments detect NO_3 directly using a combination of optical absorption at 662 nm and zeroing via chemical titration with NO. Thermal dissociation of N_2O_5 in a second channel with a heated inlet provides a measurement of the sum of NO_3 and N_2O_5, with N_2O_5 determined by difference. This instrument has flown on the NOAA P-3 aircraft during three separate field campaigns in North America, as Fig. 10.2 shows. These include a 2004 study in New England, a 2006 study in Texas a 2010 study in California. Each included a series of nighttime flights that characterize the regional and vertical distribution of NO_3 and N_2O_5, their precursors and their major sinks. Data from these research flights have also provided quantitative determinations of N_2O_5 uptake coefficients.

The 2004 study in New England was the first airborne measurement of N_2O_5. Analysis of these data identified a large regional variability in the N_2O_5 uptake coefficient [8], as shown in Fig. 10.2b. Quantitative determinations of $\gamma(N_2O_5)$ were based on observations of NO_3, N_2O_5, their production rate from NO_2 and O_3, and aerosol surface area measured by a particle-counting instrument. The NO_3 production rate is simply the product of the rate coefficient, k, for the reaction of NO_2 with O_3 with the concentrations of these two species. The N_2O_5 lifetime is
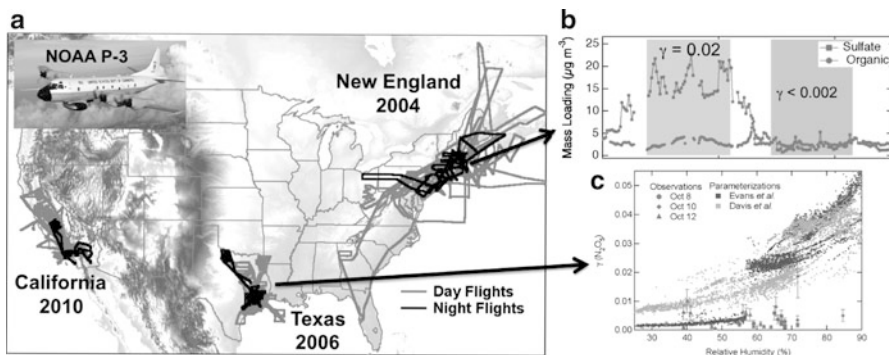
Fig. 10.2 (**a**) Map of aircraft campaigns of the NOAA P-3 that have included night flights and measurements of NO_3 and N_2O_5. (**b**) Variation in sulfate and organic aerosol from August 9–10, 2004 during the New England study. (**c**) Dependence of observed and parameterized N_2O_5 uptake coefficients on relative humidity during the Texas 2006 study

defined as the ratio of the N_2O_5 mixing ratio to this production rate and is a common measure of N_2O_5 reactivity [7].

$$P(NO_3) = k[O_3][NO_2] \tag{10.2}$$

$$\tau(N_2O_5) = N_2O_5/P(NO_3) \tag{10.3}$$

On the August 9–10 flight, nighttime levels of N_2O_5 over Ohio and Pennsylvania (the Ohio River Valley Area) were small even in the presence of large levels of NO_x and O_3, indicating that N_2O_5 had a steady-state lifetime of approximately 13 min. Downwind of New York City, by contrast, levels of N_2O_5 ranged to greater than 3 parts per billion, with a lifetime in excess of 6 h. Sulfate aerosol levels on were larger over the Ohio River Valley, which has large sulfur emission from coal-fired electric power generating plants in that region. Uptake coefficients for N_2O_5 on this highly acidic, sulfate-dominated aerosol were similar to those derived from laboratory studies on sulfate salts over moderate to high RH, with $\gamma(N_2O_5) = 0.02$. The area downwind of New York had a more neutral, mixed sulfate/organic aerosol, with $\gamma(N_2O_5) < 0.002$, more than an order of magnitude smaller. The suppression in $\gamma(N_2O_5)$ may have been related to reduced aerosol acidity (e.g., more neutralized aerosol containing a larger nitrate content), increased organic content relative to sulfate, RH (60–80% over the Ohio River Valley, 40–65% downwind of New York) or a combination of these factors. The principal conclusion related to N_2O_5 uptake coefficients from the 2004 study was that they are variable, and that the variability was linked to sulfate aerosol derived from coal sulfur emissions and its ratio to other aerosol components, such as organics.

Night flights during the 2006 Texas study provided determinations of $\gamma(N_2O_5)$ in the region around the urban area of Houston, Texas as well as a rural area of north Texas [10]. Comparison of the $\gamma(N_2O_5)$ derived from the aircraft observations to parameterizations for use in atmospheric models showed that the

parameterizations systematically over-estimated the observations, even though they explicitly included the effects of aerosol composition and RH. The parameterizations included Evans and Jacob [17], currently used in the GEOS-Chem global atmospheric chemical model, and Davis et al., [13], developed at the U.S. Environmental Protection Agency for use in regional air quality models. While the Evans parameterization explicitly included organic aerosol, it showed a steeper RH dependence than the observations, producing large over-estimates of $\gamma(N_2O_5)$ above 50% RH. The Davis parameterization did not include organic aerosol, and overestimated the observations over the entire RH range. Aerosols in Texas were composed of mixed sulfate/organic in which the sulfate was fully neutralized by ammonium. This aerosol type resembled that observed downwind of New York from the 2004 New England study.

Data from the 2010 study in California are still undergoing analysis to quantitatively determine the N_2O_5 uptake coefficients. The following section on $ClNO_2$ production will briefly discuss findings from that study, which identified a large variation in N_2O_5 reactivity with height above ground level within the nighttime boundary layer structure of the Los Angeles basin.

10.4   Wintertime N_2O_5 Measurements

Heterogeneous N_2O_5 uptake has a greater impact on NO_x and oxidant levels in winter than in summer. Colder temperature shift the equilibrium between NO_3 and N_2O_5 in favor of the latter, reduced wintertime biogenic emissions lead to smaller reactivity for NO_3, and reduced solar actinic flux and longer nights increase the importance of N_2O_5 reactions relative to photochemistry in the oxidation and removal of NO_x. Despite the importance of N_2O_5 in the wintertime, the database for characterization of its heterogeneous chemistry from ambient measurements is smaller in the winter season than in the summer. Simpson and coworkers have characterized N_2O_5 production and loss in the Arctic [2, 23], but there are few measurements at mid-latitudes. All of the aircraft measurements described in Sect. 10.3 occurred during warm season months, for example.

Figure 10.3 shows an example wintertime measurement from a recent study near Denver, CO, USA. Data are from a 300 m tower located approximately 30 km north of the urban center. The tower has a movable carriage on the outside that allows vertical profiling over the entire height of the tower approximately once every 10 min. A previous publication describes the measurement site and its use for nighttime vertical profiling [9]. Instruments for measurements of nitrogen oxides, halogen species, organic and inorganic acids and aerosol size distributions and composition were installed on the tower during a field intensive in February and March, 2011. Figure 10.3 shows a single vertical profile of O_3, NO_2, NO_3 production rate, $P(NO_3)$, N_2O_5, N_2O_5 lifetime and $\gamma(N_2O_5)$ derived from these measurements and the aerosol surface area density (not shown).
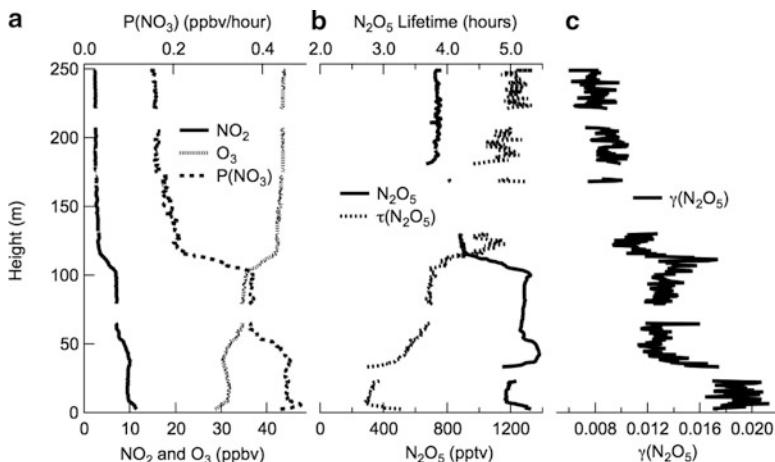
Fig. 10.3 The altitude (*left axis*) dependence of (**a**) NO_2, O_3 (*bottom axis*) and nitrate radical production rate, (P(NO_3), *top axis*); (**b**) N_2O_5 (*bottom axis*) and N_2O_5 lifetime (*top axis*); and (**c**) N_2O_5 uptake coefficient derived from the measurements in the first two panels

Figure 10.3 shows large variations in the nighttime concentrations of N_2O_5 and its precursors over a small altitude range near the surface. This observation is consistent with previous understanding of the mixing of urban pollutants in a stable nocturnal boundary layer [36]. Figure 10.3 shows enhanced mixing ratios of NO_2 (~10 ppbv) below approximately 100 m, along with decreased mixing ratios of O_3, below 110 m, which is likely the top of the nocturnal boundary layer in this example. (Note that there is another slight increase in NO_2 near the bottom of the profile at approximately 10 m that likely represents a shallow surface layer [9].) The NO_3 production rate is high throughout the nocturnal boundary layer. The lifetime of N_2O_5 shows the opposite trend, varying from 2 h near the surface to 5 h at the top of the profile. Although the N_2O_5 lifetime is a common measure of reactivity, it is often only an upper limit to the reactivity (i.e., the lifetime from Eq. (10.3) is a lower limit to the actual lifetime of N_2O_5), especially under cold conditions [7]. The uptake coefficients shown in panel C are derived from Eq. (10.1), where $k(N_2O_5)$ is taken as the inverse of $\tau(N_2O_5)$; the calculation is verified by a box model analysis that considers the reaction time and the approach to steady state. The derived uptake coefficients have considerable uncertainty (more than a factor of 2 in this case), but the variation with height is likely to be at least qualitatively correct. In this example, near-surface $\gamma(N_2O_5)$ is large, near the value of 0.02 typical for organic salts. The value of $\gamma(N_2O_5)$ at the top of the profile is approximate a factor of two smaller. The aerosol composition for this profile (not shown) was mixed organic/inorganic, with the inorganic component dominated by ammonium nitrate. Further analysis on the entire data set from this campaign will examine the role of nitrate aerosol in suppression of $\gamma(N_2O_5)$ in wintertime. The example in Fig. 10.3 demonstrates that N_2O_5, its lifetime, and its uptake coefficient are variable as a function of height above surface level.

10.5 Nitryl Chloride Production

The recent discovery of unexpectedly large amounts of nitryl chloride in urban air at night has added a new dimension to the complexity of N_2O_5 heterogeneous chemistry. The demonstration of sensitive $ClNO_2$ detection in ambient air by chemical ionization mass spectrometry (CIMS) has enabled field investigations of this compound [26]. During a ship-based campaign along the U.S. Gulf Coast and the area near Houston, TX, Osthoff et al. [31] showed that $ClNO_2$ mixing ratios reached part per billion levels and that the yield of $ClNO_2$ from uptake of N_2O_5 was in the range 10–65% for the coastal environment in which the study took place. The study also demonstrated that the mass of $ClNO_2$ produced was much larger than the chloride mass present in the submicron aerosol, which accounts for the majority of the surface area on which N_2O_5 uptake occurs. The observation implied that a gas phase reservoir of HCl, in equilibrium with the aerosol phase, was required to sustain $ClNO_2$ production. The ultimate source of this chloride was thought to be acid displacement from supermicron sea salt, which contains a large chloride mass but presents a smaller surface area for heterogeneous reaction, at least relative to urban, submicron aerosol. Thornton et al. [37] demonstrated that $ClNO_2$ is also consistently present at hundreds of parts per trillion in the Denver urban plume in wintertime. Yields of $ClNO_2$ from that study ranged from 7 to 36%, indicating substantial $ClNO_2$ production even at an inland location, nearly 1,600 km from the nearest coastline. The source of this inland chloride was not clear from that study, although a similar requirement for a gas phase HCl reservoir was inferred from the relationship between gas phase $ClNO_2$ and aerosol phase chloride. A model estimate derived from a NO_x emission inventory, the fraction of this NO_x oxidized through N_2O_5, and the yield of $ClNO_2$ estimated from long-term monitoring network data of aerosol chloride, suggested that the atomic chlorine production from nighttime $ClNO_2$ production is 1.4–3.6 Tg y^{-1} in the continental U.S. and 8–22 Tg y^{-1} globally. Observations of $ClNO_2$ at a separate, mid-continental site in Calgary, Canada [29], are consistent with these conclusions and corroborate the widespread production of $ClNO_2$ in inland urban areas.

A prime uncertainty in the estimates of $ClNO_2$ production and its impacts is its vertical distribution. The initial field work on $ClNO_2$ was based on nighttime surface-level measurements, which are not necessarily representative of the entire vertical distribution of NO_x pollution within an urban-influenced, nighttime boundary layer. Figure 10.4 shows one example of vertically resolved measurements of both N_2O_5 and $ClNO_2$ from aircraft during the 2010 field study in California (see Fig. 10.2). The profile is from a missed approach of the P-3 to an airfield in the Los Angeles basin on May 31, 2010. The aircraft reached a minimum altitude of approximately 100 m above ground level, sufficient to probe the residual daytime boundary layer and part, but probably not all, of the nocturnal boundary layer. The maximum altitude on this profile extended above the residual layer and into the cleaner, free troposphere above it. The steep increases in potential temperature,
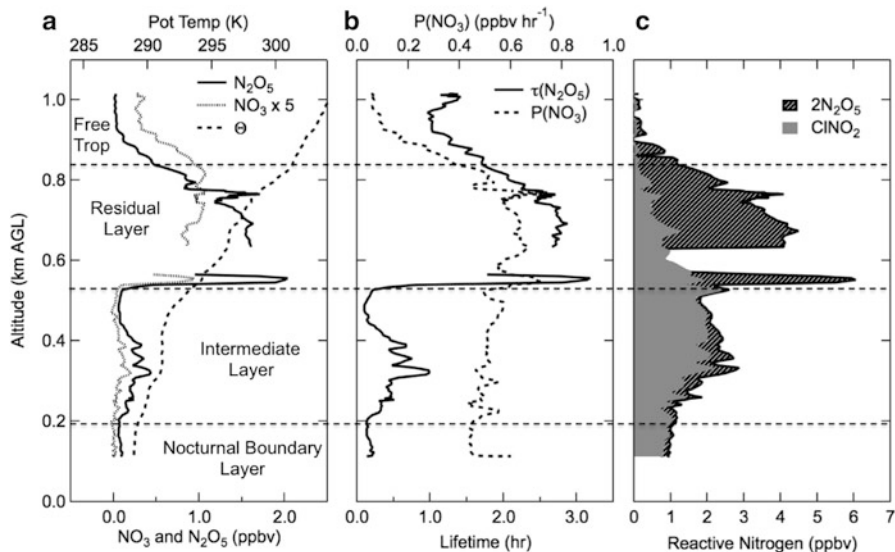
Fig. 10.4 Vertical profile from the NOAA P-3 aircraft over an airfield in the Los Angeles basin at 2:30 AM local time on May 31, 2010. (**a**) NO_3, N_2O_5 (*bottom axis*) and potential temperature, Θ (*top axis*). (**b**) NO_3 production rate, $P(NO_3)$ (*top axis*) and N_2O_5 lifetime, $\tau(N_2O_5)$ (*bottom axis*), as in Eqs. 10.2 and 10.3. (**c**) Mixing ratios of $ClNO_2$ and $2 \times N_2O_5$. The N_2O_5 is stacked on the $ClNO_2$ to show the sum of the nitrogen in the two species

Θ in panel A, with height define the multiple layer structures on this profile. These include the nocturnal boundary layer to approximately 100 m, an intermediate layer above it to approximately 500 m, the a residual daytime boundary layer to slightly above 800 m, and the cleaner free troposphere above. The NO_3 production rate in panel B is moderately large and relatively constant with height to the top of the residual layer. The NO_3 and N_2O_5 mixing ratios (Panel A) increase sharply at the interface to the residual layer, however, as does the N_2O_5 lifetime (Panel B). These observations indicate more efficient N_2O_5 uptake in the lower layers and a smaller uptake coefficient in the residual layer. Panel C shows the reactive nitrogen present as $ClNO_2$ and N_2O_5, where N_2O_5 has been multiplied by a factor of 2 since it contains two nitrogen atoms. In the lower layers, there is little N_2O_5 relative to $ClNO_2$, indicating both a high $ClNO_2$ yield and efficient N_2O_5 uptake. The residual layer, by contrast, has N_2O_5 in excess over $ClNO_2$, consistent with lower yields and slower uptake.

Like Houston, where the first ship-based $ClNO_2$ measurements took place, Los Angeles is a coastal city with a ready source of aerosol chloride from sea salt and a large source of urban NO_x. The Los Angeles basin also has frequent exceedences of U.S. national air quality standards for ozone pollution. Regeneration of NO_x and production of Cl radicals may be a contributing factor in this ozone production. Accurate models of the role of nighttime chemistry in next-day ozone in Los-Angeles

will require an understanding of the vertical distribution of both N_2O_5 and $ClNO_2$ to constrain the magnitude of the Cl and NO_x source as well as its distribution. The vertical variability in Fig. 10.4 illustrates the complexity of this problem, which will be the subject of ongoing analysis of data from the 2010 night flights in California.

10.6   Conclusions and Recommendations for Future Work

Recent field measurements of N_2O_5 and $ClNO_2$ have provided new insights into the nighttime heterogeneous chemistry of nitrogen oxides and its impact on reactive nitrogen and oxidants on both regional and global scales. Advances in analytical instrumentation for sensitive and accurate *in-situ* detection of these species have enabled these studies, which have led to several important conclusions. First, the efficiency of N_2O_5 uptake is highly variable, and the uptake coefficient to aerosol, $\gamma(N_2O_5)$ is frequently, though not exclusively, smaller than parameterizations designed for use in atmospheric models. The uptake coefficient is large on aerosol that is dominated by inorganic sulfate, and smaller on mixed organic/sulfate aerosol. Inorganic nitrate likely also serves to suppress N_2O_5 uptake, while chloride tends to counteract the nitrate effect and enhance uptake. Second, production of $ClNO_2$ from N_2O_5 heterogeneous uptake is surprisingly efficient, even in continental locations that are well removed from continental chloride sources. The reaction proceeds rapidly on the large aerosol surface area presented by submicron aerosol of urban origin containing only modest chloride content. The observations are consistent with a gas phase chloride reservoir in the form of HCl. Finally, vertically resolved measurements from aircraft and a tall tower have demonstrated that N_2O_5 uptake and $ClNO_2$ production may vary as a function of height above ground level within a stable nighttime boundary layer structure.

Field studies to date have only partially addressed the uncertainties in nighttime nitrogen oxide chemistry, and there are several outstanding issues for future work. First, these efforts should seek to expand the database for *in-situ* measurements of N_2O_5 and the dependence of its uptake on aerosol composition and relative humidity. Where possible, such studies should include vertical resolution to understand the variability throughout the boundary layer structure. Second, there is relatively little data available in the winter season, when N_2O_5 uptake is most important to nitrogen oxide and oxidant budgets, and when $ClNO_2$ production may provide a large source of atomic Cl radicals. Third, the database for $ClNO_2$ measurements remains quite sparse. A larger number of measurements across a wider range of environments and seasons is required to fully understand the influence of this compound in the recycling of NO_x and as a source of chlorine radicals. Finally, field studies should seek to understand the relative importance of nighttime radical reservoirs, such as $ClNO_2$ and HONO, which have similar characteristics but which likely have very different spatial distributions and production efficiencies in different environments. Their relative and absolute contributions to regional oxidation budgets remain uncertain.

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