**Atmospheric
Chemistry
and Physics**

Deposition of dinitrogen pentoxide, N_2O_5, to the snowpack at high latitudes

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Abstract. Dinitrogen pentoxide, N_2O_5, is an important nighttime intermediate in the oxidation of NO_x that is hydrolysed on surfaces. We conducted a field campaign in Fairbanks, Alaska during November 2009 to measure the gradient and derive a flux (and deposition velocity) of N_2O_5 depositing to snowpack using the aerodynamic gradient method. The deposition velocity of N_2O_5 under Arctic winter conditions was found to be $0.59 \pm 0.47\,\mathrm{cm\,s^{-1}}$, which is the first measurement of this parameter to our knowledge. Based on the measured deposition velocity, we compared the chemical loss rate of N_2O_5 via snowpack deposition to the total steady state loss rate and found that deposition to snowpack is at least 1/8th of the total chemical removal of N_2O_5 that is located within the first few meters above the ground surface.

1 Introduction

High-latitude nighttime nitrogen oxide chemistry is dominated by the oxidation of NO_2 by ozone to form nitrate radical, NO_3 Reaction (R1). NO_3 and NO_2 combine to form N_2O_5, (R2) in a temperature dependent equilibrium that is favored under cold and dark conditions that exist in winter at high latitudes. The major chemical loss process for N_2O_5 is heterogeneous hydrolysis Reaction (R3) on aerosol particles or possibly snow surfaces. The following reactions are the nighttime pathway for N_2O_5 chemical removal.

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \tag{R1}$$

$$NO_2 + NO_3 \leftrightarrows N_2O_5 \tag{R2}$$

$$N_2O_5 + H_2O \xrightarrow{\text{Surface}} 2HNO_3 \tag{R3}$$

The production of nitric acid Reaction (R3) contributes to acid rain, adds fixed nitrogen to the ecosystem, and removes NO_x. Acid rain is known to have many damaging effects on the environment. The effects of nitrification have been documented in mid latitudes (Andersen and Hovmand, 1995; Bytnerowicz et al., 1998; McNeill et al., 2006; Fenn et al., 2003), and removal of NO_x affects the possibility of downwind ozone production.

The heterogeneous reaction of N_2O_5 Reaction (R3) is an important reaction for NO_x loss. In a modeling study, Dentener and Crutzen (1993) found that during the winter 80 % of high latitude NO_x is lost by Reaction (3), which is the dominant dark pathway to nitric acid. Since the Dentener and Crutzen (1993) modeling study, many laboratory experiments have been completed investigating N_2O_5 heterogeneous hydrolysis and the dependence on aerosol particle chemical composition (Mozurkewich and Calvert, 1988; Kirchner et al., 1990; Hanson and Ravishankara, 1991; van Doren et al., 1991). The N_2O_5 uptake coefficient, or surface reaction probability, γ, describes the probability of chemical reaction of N_2O_5 on an aerosol surface. In more recent models, different parameterizations of γ have been used that identify the dependence on aerosol composition and temperature (Riemer et al., 2003; Evans and Jacob, 2005). Riemer et al. (2003) included two lower values of γ based more recent laboratory studies, 0.02 for sulfate aerosol particles and 0.002 for nitrate aerosol particles in their model. Evans and Jacob (2005) not only varied the composition of the aerosol, but also included relative humidity and temperature dependences in their model. This model showed increasing uptake coefficients the farther north in latitude and as the temperature decreased. Bertram and Thornton (2009) parameterized N_2O_5 based on γ's dependence on H_2O(l), Cl^- and NO_3^- for organic and inorganic mixed aerosols.

Most measurements of ambient N_2O_5 have been performed under summer mid-latitude conditions (Brown et al., 2001, 2006; Matsumoto et al., 2005; Wood et al., 2005;
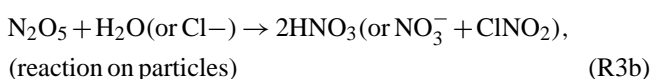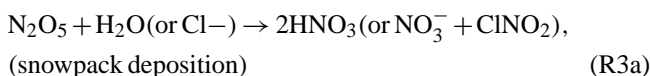
Bertram et al., 2009), which would be the less representative of high latitude winter measurements. Brown et al. (2006) was the first field study to show a dependence of the heterogeneous hydrolysis on aerosol particle composition in a large aircraft field study over Eastern North America. Brown et al. (2006) related N_2O_5 chemistry to sulfate aerosol particle content and observed faster uptake of N_2O_5 to the aerosol particles when the aerosol particles had high sulfate content. Most recently, mid-latitude field studies found N_2O_5 in both coastal (Roberts et al., 2008) and inland (Thornton et al., 2009) regions reacts with chloride and forms nitryl chloride. Nitryl chloride is a photolabile nighttime reservoir that can produce reactive chlorine radicals when photolysed at sunrise (Thornton et al., 2009). Bertram et al. (2009) employed a new technique measuring the uptake coefficient of N_2O_5 on ambient aerosols directly by using chemical ionization mass spectroscopy (CIMS) to measure reactive loss of N_2O_5 when added to a flow tube reactor containing ambient aerosols.

Our research group has previously performed high latitude field studies and have reported aerosol surfaces densities were insufficient to account for the chemical loss of N_2O_5 at high latitudes (Ayers and Simpson, 2006; Apodaca et al., 2008). We implicated other reactive surfaces for N_2O_5 chemical loss, such as ice, either on atmospheric particles or in the snowpack. Ayers and Simpson (2006) measured N_2O_5 on the top of a building, 85 m above the ground and found higher mixing ratios aloft, which is consistent with some of the N_2O_5 removal being by deposition to Earth's snow-covered surface. Calculated steady-state lifetimes aloft ranged from minutes to several hours. Higher N_2O_5 mixing ratios further from Earth's surface is in agreement with others who have studied the vertical profile of N_2O_5 (Brown et al., 2003, 2007a, b; Geyer and Stutz 2004; Stutz et al., 2004). Apodaca et al. (2008) observed the mixing ratios of N_2O_5 to be much lower and the average lifetime was 6 min under nighttime high relative humidity conditions, which is common in the wintertime Arctic near the surface. In these past studies, there was not a sufficient amount of meteorological data recorded to separate snowpack deposition from reaction on particles.

Here, we report upon a field campaign quantifying the loss of N_2O_5 by snowpack deposition. The deposition velocity of N_2O_5 helps to improve process-based models aimed at understanding the vertical profile of N_2O_5 at high latitudes and the fate of NO_x via the nighttime chemical pathway. Measuring a flux during nighttime in the Arctic is difficult due to extreme atmospheric stability. In a very stable atmosphere the vertical mixing is hindered and turbulence is sporadic and upper layers may become decoupled from the ground (Anderson and Neff, 2008). The experimental design to measure a flux required sufficient instrumentation and calculations to have an adequate fetch and neutral atmospheric conditions appropriate to satisfy the Monin-Obukhov similarity theory. Although the deposition velocity of N_2O_5 has not been measured, its value is thought to be similar to that of nitric acid

(Cadle et al., 1985; Lovett, 1994; Wesely and Hicks, 2000). Sommariva et al. (2009) conducted a large scale modeling study on marine boundary layer deposition and used a value for N_2O_5 of $1\,\mathrm{cm\,s^{-1}}$ based on Brown et al. (2004) reported deposition velocity of nitric acid.

In this study, we measure the N_2O_5 deposition flux using the aerodynamic gradient method. From the flux we can calculate the deposition velocity of N_2O_5. In addition to deposition of N_2O_5 to the surface, N_2O_5 is also lost by reaction on atmospheric particles. It is likely that heterogeneous hydrolysis (reaction with water) is dominant, but reaction could also occur with chloride to give nitryl chloride. Therefore, we can divide all losses of N_2O_5 into two sub-processes based upon where the reaction occurs (snowpack or aloft).

$$N_2O_5 + H_2O(\text{or Cl}-) \rightarrow 2HNO_3(\text{or }NO_3^- + ClNO_2),$$
$$\text{(snowpack deposition)} \qquad\qquad\qquad\qquad \text{(R3a)}$$

$$N_2O_5 + H_2O(\text{or Cl}-) \rightarrow 2HNO_3(\text{or }NO_3^- + ClNO_2),$$
$$\text{(reaction on particles)} \qquad\qquad\qquad\qquad \text{(R3b)}$$

The measured deposition velocity of N_2O_5 is combined with atmospheric assumptions to estimate the effective snowpack deposition rate k_{3a} Reaction (R3a). We also measured the total chemical removal rate of N_2O_5 via a steady-state analysis, which determines the sum of the loss rates k_{3a} and k_{3b}. Therefore, the relative role of the two sub-processes, snowpack deposition and atmospheric reactions, is determined. We conclude by discussing implications of these results for the deposition of nitric acid, NO_x losses, and N_2O_5 vertical profiles at high latitudes.

2 Experimental design

The field site for the study was located in a snow-covered agricultural field 20 km southwest of the city of Fairbanks (the site coordinates are $64.75929°$ N, $148.10618°$ W, 161 m a.s.l.). An insulated hut on skis housed the instruments at this remote field site. The field study operated continuously from 5 November 2009 until 18 November 2009. Mildly polluted air originating from Fairbanks is carried from the northeast direction by a down-slope drainage flow towards the field site. The local drainage flow is guided by a U-shaped ridge that forms a bowl around the field site as seen in the contour map in Fig. 1a.

Using the contour lines in Fig. 1a, we can estimate the slope of the field site. The bowl loses 6 m of elevation in 400 m of fetch, a change of 1.5 % or a 0.8° slope. The fetch is a uniform flat upwind distance from the measurement towers. Oke (1987) estimates that the fetch should be at least 100 times the maximum measurement height, which, in our case, is 2.4 m, indicating a 240 m fetch is required. Our site satisfies the minimum requirement with a 400 m fetch. Under
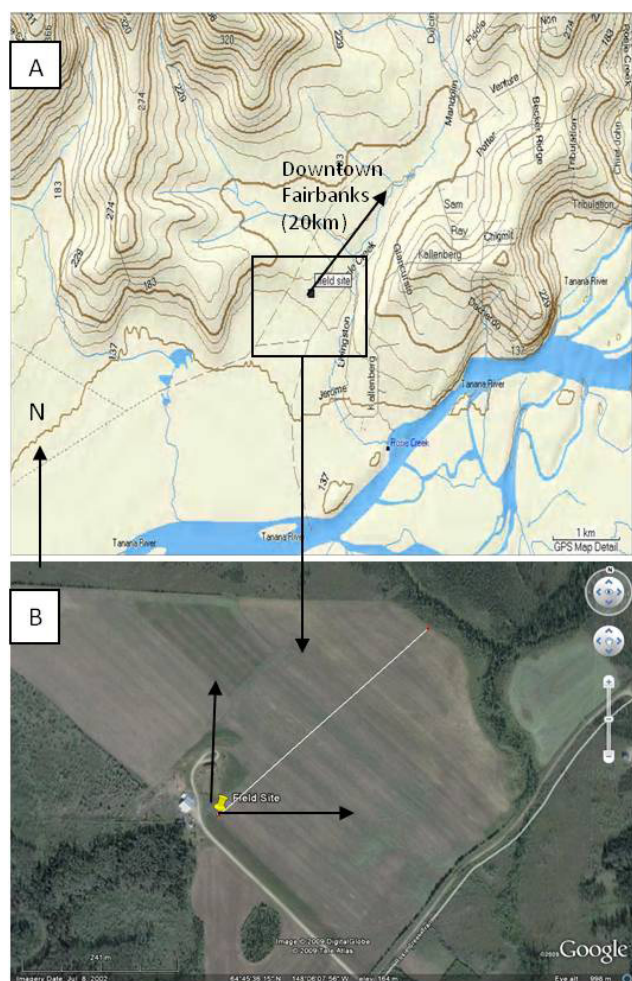
Fig. 1. Field site location: **(A)** contour map of field site with a black outline of the field site area. **(B)** Expanded satellite image of the inside of the black box area on map **(A)** (Google, Inc. 2009). The black arrows in map **(B)** represent the wind direction selection criteria. The white line is the dominant wind direction with a maximum distance to the trees of 400 m (fetch). The yellow marker is location of field site. During the field campaign, the field was covered with snow.

the common nighttime cold and stable air flow in the Arctic, we recognize the possibility of needing longer fetch, which will be discussed below and in the supplement.

3 Methods

3.1 Chemical measurements

A field portable instrument using cavity ring down spectroscopy (CRDS) was developed in our laboratory to measure N$_2$O$_5$ at remote sites (Simpson, 2003; Ayers et al., 2005). We have used this CRDS instrument during past field studies (Ayers and Simpson, 2006; Apodaca et al., 2008) and the major modification we made for the present field study was

adding a 10 m Teflon inlet. The 3/8" (9.5 mm) inner diameter PFA Teflon inlet was configured with a 100 slpm bypass flow to minimize the contact time of the sampled air with the inlet. The total residence time in the fast-flow inlet is 0.4 s. Flow-changing studies were carried out to determine inlet loss of N$_2$O$_5$ on the tubing resulting in a transmission of 76 %. The transmission of N$_2$O$_5$ on the inlet and instrumental surfaces were taken into account in the analysis resulting in corrected ambient mixing ratios, as has been done in past studies (Ayers and Simpson, 2006; Apodaca et al., 2008). The new inlet conditions in the main bypass flow line are turbulent with a Reynolds number of 14 400. The flow in the measurement cell is laminar with a Reynolds number of 690. In addition to the N$_2$O$_5$ instrument, the same high-flow inlet provided air to ancillary instruments that measure NO$_x$ (Thermo Environmental 42c) and ozone (Dasibi 1008 RS). The intake of the inlet was held on the chemical measurement tower and moved between two heights to quantify gradients in each chemical species being measured (Fig. 2, Part II). Because the same inlet was used for both sampling heights, the 76 % fast flow inlet transmission does not affect the measurement of the deposition velocity.

3.2 Steady state analysis of N$_2$O$_5$ measurements

We use the steady state approximation to calculate a lifetime of N$_2$O$_5$ from the concentration of N$_2$O$_5$ divided by the source rate of N$_2$O$_5$ (Apodaca et al., 2008),

$$\tau_{N_2O_5ss} = \frac{[N_2O_5]}{k_1[NO_2][O_3]}. \tag{1}$$

The source rate of N$_2$O$_5$ is the rate coefficient for Reaction (1), k_1, multiplied by the concentration of NO$_2$ and ozone. We assume we achieve steady state rapidly (Apodaca et al., 2008), although this assumption is discussed later. The steady-state lifetime of N$_2$O$_5$ is used to determine the total loss rate of N$_2$O$_5$, the sum of Reactions (R3a) and (R3b).

3.3 Near surface gradient measurements

Figure 2 shows the field configuration of the chemical inlet and meteorological measurement towers designed for near-surface gradient measurements. Two separate towers, one with a moving inlet for chemical measurements and one for meteorological measurements, were used so the vibration of the moving inlet did not affect the meteorological measurements. The measurement towers were located 2 m upwind from the instrument-housing insulated hut.

The moveable-inlet tower alternated position every 150 s between "up" and "down" heights, 2.35 m and 0.95 m, respectively. The moveable inlet sampled the gases, N$_2$O$_5$, NO$_x$ and ozone, at the two levels. The up/down state of the inlet was recorded in data files and used in post-processing to calculate gradients in each chemical. The moveable inlet was mounted on a separate tower horizontally displaced 0.5 m from the meteorological tower.
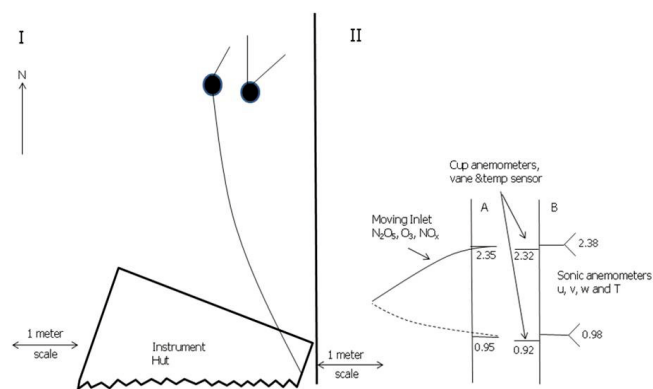
Fig. 2. (I) The plan view and orientation of the two measurement towers and instrument hut. **(II)** Elevation view of the moving inlet tower (A) and the meteorological tower (B). All distances are in meters.

The meteorological tower supported both slow- and fast-response instrumentation. The slow-response system consisted of two RM Young cup anemometer and wind vanes to measure wind speed and direction (model 03001-5) and two temperature sensors (RM Young 41342) at the same heights as the moveable inlet (within a few cm, as noted on Fig. 2) and logged as one minute averages on a Campbell Scientific CR10x data logger. The meteorological tower and sampling inlet both faced into the prevailing wind direction at approximately the same length from the towers (within a few cm) so they were horizontally aligned.

The meteorological measurement tower also supported two sonic anemometers (RM Young model 84 000) producing 10 Hz data on a separate data logger (Chaparral Physics). The purpose of the sonic anemometers at the same height as the low frequency meteorological tower instruments is twofold. First, the redundant measurements verify the temperature, wind speed and direction data and gradients. Second, the high frequency data from the sonic anemometers allow validation of our flux measurements by calculating the heat flux by both the aerodynamic gradient method and eddy covariance. The details of the heat flux comparison by the aerodynamic and eddy covariance methods can be found in the Supplement.

3.4 Aerodynamic gradient flux analysis

There are three main flux measurement techniques: the aerodynamic method, the Bowen ratio method, and the eddy covariance method (Oke, 1987; Monteith and Unsworth, 1990; Bocquet, 2007). The aerodynamic method uses a two (or more) point profile system to measure the chemicals near surface gradient and anemometers to measure the wind speed and direction and gradients. Using the aerodynamic method, we rely on the Monin-Obukhov similarity theory to derive a flux equation for N$_2$O$_5$. The similarity theory states that

under neutral atmospheric stability the surface layer is homogenous and the eddy diffusivity transfer coefficient of momentum, K_m, is equal to the gas's transfer coefficient, $K_{N_2O_5}$ (Oke, 1987; Monteith and Unsworth, 1990; Arya, 2001). The two transfer coefficients can be set equal and the unknown flux can be solved for using the aerodynamic approach found in Oke (1987). A negative flux of N$_2$O$_5$ results from a higher concentration of N$_2$O$_5$ at the higher measurement level than near the surface, which is a downward-directed flux. To obtain the deposition velocity, we divide the opposite of the flux by the average concentration of N$_2$O$_5$,

$$v_{dep} = -\frac{F_{N_2O_5}}{C_{N_2O_5}} = -k^2 \frac{\frac{\Delta \overline{u} \Delta \overline{C_{N_2O_5}}}{[\ln(z_1/z_2)]^2}}{C_{N_2O_5}} (\Phi_M \Phi_{N_2O_5})^{-1}. \quad (2)$$

In this equation, $\Delta \overline{u}$ is the average difference in wind speed between the two heights, z_1 and z_2, $\Delta \overline{C_{N_2O_5}}$ is the average difference in mixing ratio of N$_2$O$_5$ between the two heights, k is the Von Karman constant, which equals 0.4. The average N$_2$O$_5$ mixing ratio is $\overline{C_{N_2O_5}}$. The deposition velocity (v_{dep}) is independent of the amount of pollution (the amount of N$_2$O$_5$) and is therefore more useful for modeling of snowpack deposition. When the deposition velocity is positive, N$_2$O$_5$ is directed downward toward the surface.

The generalized stability factor, $(\Phi_M \Phi_{N_2O_5})^{-1}$, allows us to correct the flux ($F_{N_2O_5}$) for atmospheric conditions that are near neutral (Oke, 1987). The generalized stability factor has different equations under different atmospheric stabilities and we used the generalized stability factors and R_i range found in Oke (1987) and these factors are the same as Monteith and Unsworth (1990), but the R_i range application is different. The gradient Richardson number, R_i, is used to indentify appropriate atmospheric stability conditions and to correct the flux for a slightly stable or unstable atmosphere. The dimensionless Richardson number relates the vertical gradients of wind and temperature by taking the ratio of the buoyancy to shear stress, (Stull, 1988)

$$R_i = \frac{g}{T} \frac{\left(\frac{\Delta \overline{T}}{\Delta z}\right)}{\left(\frac{\Delta \overline{u}}{\Delta z}\right)^2}. \quad (3)$$

The linear approximation for Richardson number Eq. (3) is more accurate than the logarithmic approximation (Arya, 2001) under stable atmospheric conditions. Under nighttime Arctic conditions, we are more commonly under stable atmospheric conditions, so we used the linear approximation for the Richardson number. On the other hand, when the Richardson number is above 0.25, turbulence decays and the atmosphere is very stable, and laminar flow, once established, is stable. When the Richardson number is less than -1, the atmosphere is dominated by free convection (Monteith and Unsworth, 1990; Stull, 1988).

The aerodynamic method for calculating the flux of N$_2$O$_5$, $F_{\mathrm{N_2O_5}}$ only applies under a very narrow window of atmospheric stability under a nearly neutral atmosphere. A neutral atmosphere is defined by having negligible buoyancy effects.

Outside of the gradient Richardson index range -1 to 0.25, the general stability factors, $(\Phi_M \Phi_{\mathrm{N_2O_5}})^{-1}$ are unusually large or small and cannot correct the flux to account for divergence from near neutral atmospheric conditions. As the Richardson number approaches 0.25, this is considered the critical Richardson number beyond which turbulent exchange is completely dissipated. The value of 0.25, where all turbulent exchange is absent, is only an approximation to the limit of turbulent exchange. Some turbulence exchange has been reported with a gradient Richardson number as high as 1 (Pardyjak et al., 2002). We use general stability factors and acceptable R_i ranges from Oke (1987). Two different general stability factor correction functions are used, one for positive R_i values, and one for negative R_i values. Because these general stability factors become large towards limits, we only analyzed data in the range $-0.1 < R_i < 0.12$. We used a narrow range of R_i values to ensure we not reaching our fetch limitations, and based on a method described in Horst and Weil (1994), we are measuring $>90\%$ of the true flux.

4 Results

Chemical species (N$_2$O$_5$, NO$_2$, and O$_3$) were averaged over 30 min intervals. Within each half-hour data-averaging period, there are 15 min of "up" and 15 min of "down" data, which were averages of up/down periods of 150 s at each state. The two individual state averages were differenced and divided by the height difference to get the chemical gradients. Steady-state chemical lifetimes were calculated using temperature-dependent formation kinetics. Wind speed and temperature differences were calculated from the two intercalibrated instrument sets. The gradient Richardson number, R_i, was calculated to determine periods where the stability was appropriate for the calculation of fluxes.

First, a filter was applied for the wind direction and a solar flag for nighttime data to find appropriate nights for analysis. The data were then selected by calculating the Richardson number in Eq. (3) and using the narrow range of $0.12 > R_i > -0.1$. From the results of the gradient Richardson number calculation, wind direction, and instrument calibrations we focused our analysis on three nights of the campaign. The three nights were 5, 10 and 11 November 2009. On these three nights the parameters were met for calculating a deposition velocity except for one half hour period on 5 November 2009 where the Richardson number was 0.16, and was slightly out of range; however, this point was included in the analysis for completeness.

In Fig. 3, all three nights had neutral to near neutral atmospheric conditions. The temperature averages on the 5,

10, and 11 November 2009 were $-4°$, $-18°$, $-14°$C, respectively. The highest temperature gradient was seen on 5 November with a 1 °C difference in the two heights and a stable atmosphere. In this case, the upper level was warmer indicating an inversion, which is typical of cold, stable Arctic nights. Most of the data had small to no inversions, which was appropriate of measuring a flux. The average wind speeds were 2.3, 2.7 and 2.5 m s^{-1}, respectively. The difference in wind speeds and the difference in N$_2$O$_5$ mixing ratios were used to calculate the flux, the numerator in the deposition velocity Eq. (2). Figure 4 shows a histogram of the measurements of the deposition velocity. More than 90 % of the deposition velocities are positive or directed downward toward the snowpack. The average deposition velocity is 0.59 ± 0.47 cm s^{-1}, where the standard deviation describes the variability of the measurements. An alternative calculation of the deposition velocity that uses both turbulence measurements from the sonic anemometer and the observed chemical gradient agrees with the gradient method, as described in the Supplement.

In addition to measuring chemical gradients and comparing the gradient data to the meteorology, we also used chemical measurements to calculate the steady state lifetime of N$_2$O$_5$ using Eq. (1). The steady state lifetime represents total chemical loss of N$_2$O$_5$, including snowpack deposition and atmospheric reactions. The time series of the average NO$_2$, O$_3$, source rate, N$_2$O$_5$ and steady state lifetime of N$_2$O$_5$ are displayed in Fig. 5.

The mixing ratio of NO$_2$ ranges from a few to 20 ppbv at night. Although we found large differences in N$_2$O$_5$ between heights (15 % on average and up to 50 %), the difference between NO$_2$ and ozone between the heights was small. The average difference in NO$_2$ between the two measurement heights varied by less than 2.6 ± 3 % and the ozone varied by 1 ± 2 %. Because the gradients in all chemicals other than N$_2$O$_5$ were small, Fig. 5 shows half-hour averages independent of the up/down state of the sampler.

The average steady state lifetime of N$_2$O$_5$ is 6 min. The transport timescale of polluted air to reach the site from Fairbanks given an average measured speed of 2.3 m s^{-1} and 20 km distance and assuming direct transport is around 2 h. The transport timescale is longer than the maximum calculated lifetime of N$_2$O$_5$ of 10 min, reinforcing the picture that the steady-state approximation is decent in this application.

5 Discussion

5.1 Deposition velocity of N$_2$O$_5$

A number of studies have used micrometeorology methods to measure trace gas dry deposition velocities (Lovett, 1994; Wesely and Hicks, 2000; Watt et al., 2004; Muller et al., 2009). Deposition velocities above a snow pack have been measured for ozone and are summarized in, Helmig et
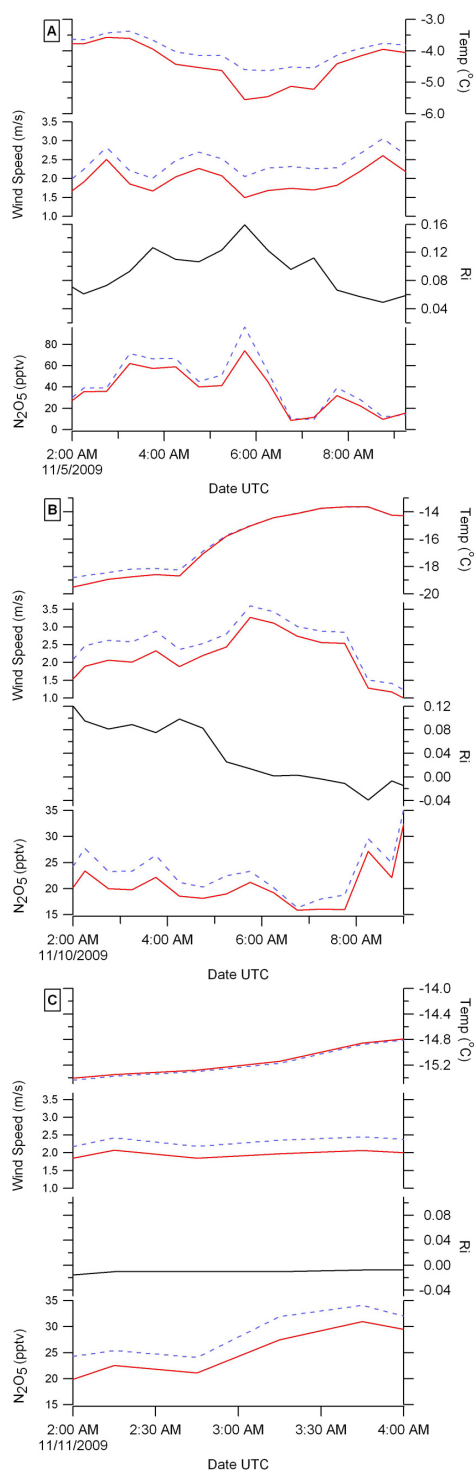
Fig. 3. Temperature (°C), wind speed (m s^{-1}), Richardson number and mixing ratio of N_2O_5 in pptv for **(A)** 5 November 2009, **(B)** 10 November 2009 and **(C)** 11 November 2009. The red solid trace is always the lower height and the blue dashed trace is the higher measurement height. The black solid line, 3rd axis from the top is the Richardson number.
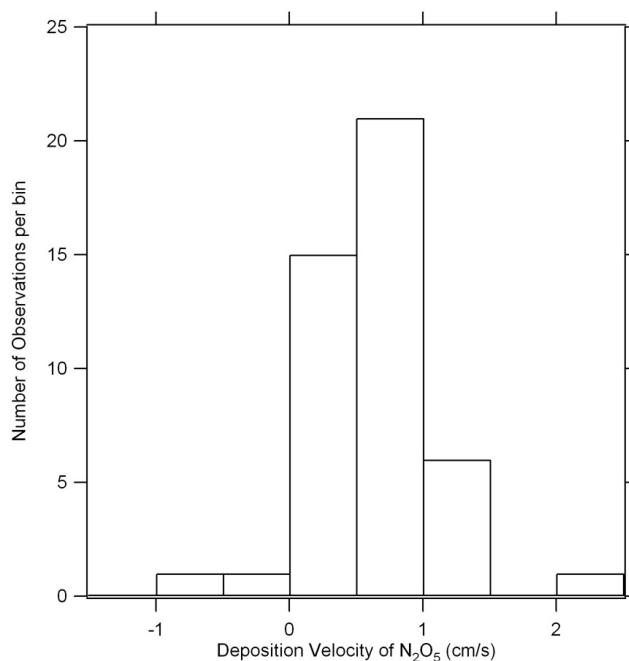

Fig. 4. Histogram showing the distribution of deposition velocities of N_2O_5 on the selected data analysis nights 5, 10 and 11 November 2009.

al. (2007) and Wesley and Hicks (2000). Arctic studies of the deposition velocities to snow pack have been measured for ozone and found to be less than or equal to 0.01 cm s^{-1} (Helmig et al., 2009). Wesley and Hicks (2000) summarized NO and NO$_2$ deposition velocities and found they are generally negligible and this is consistent with our findings of small ozone and NO$_2$ gradients There are several studies quantifying the emission of NO$_x$ from the snowpack and though NO$_x$ emission from the snowpack can be significant, it is driven by photochemistry (Honrath et al., 2002; Jones et al., 2001), which is not relevant in the present nocturnal study. Jones et al. (2001) studied NO$_x$ emission from the Arctic snowpack by measuring NO$_2$ at two different heights and found a diurnal cycling of NO$_x$ with deposition velocities near zero at night. To our knowledge, there are no reported deposition velocities for N_2O_5. A positive deposition velocity means N_2O_5 is reacting to other species on snowpack surfaces. At high latitude in winter, snow pack covers almost the entire ground surface. The snowpack deposition is a reactive loss of N_2O_5 and it is therefore important to quantify the deposition velocity for understanding the fate of nitrogen oxides in the high latitude environments.

Our measured downward directed deposition velocity of N_2O_5 to the snowpack is on the order of 1 cm s^{-1} and is in the same range as previously reported values for nitric acid over snow ($0.5 - 1.4$ cm s^{-1}) (Cadle et al., 1985). In Fig. 4, the average deposition velocity for all three focus nights is 0.59 ± 0.47 cm s^{-1}. The similarity of our observed
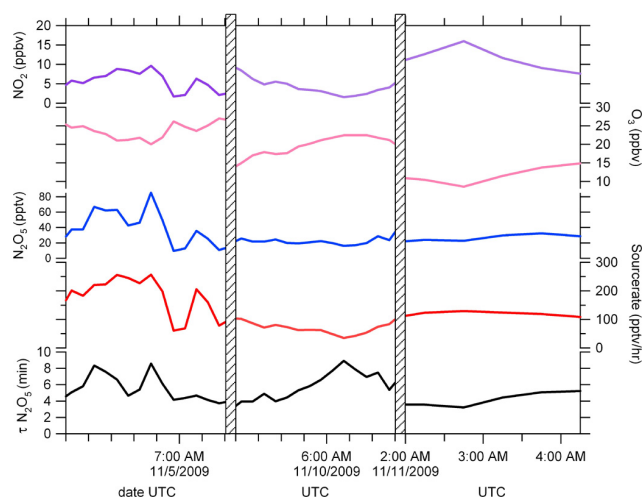
Fig. 5. From top to bottom are the mixing ratios of NO$_2$ (ppbv), O$_3$ (ppbv) and N$_2$O$_5$ (pptv), source rate of N$_2$O$_5$ (pptv h^{-1}) and the steady state lifetime of N$_2$O$_5$ as $\tau_{N_2O_5ss}$ (min) on three nights 5, 10 and 11 November 2009.

deposition velocity to that of nitric acid indicates that turbulent transport to the snowpack is likely a large contributor to the resistance to deposition of N$_2$O$_5$, and that chemical limitation in reaction at the ice surface is probably of secondary importance.

5.2 Comparisons of N$_2$O$_5$ chemical removal rates

To compare the atmospheric N$_2$O$_5$ chemical removal rate arising from snowpack deposition to the total steady state chemical removal rate, we need to estimate an effective deposition layer height. The profile of the N$_2$O$_5$ deposition flux through the boundary layer is unknown, but decays to zero at the boundary layer height by the definition that the boundary layer is the region influenced by surface chemical processes. Because the flux decreases with height, the effective layer height, z_{eff}, over which N$_2$O$_5$ is deposited, is less than the boundary layer height under moderately stable conditions. The profile of the momentum flux is represented by the shear stress equation for a moderately stable boundary layer and decays toward zero as a power law, as shown in Arya (2001). The local scaling law that applies to the power law in Arya (2001) was originally proposed by Nieuwstadt (1984) showing that local friction velocity parameters and temperature scales are similar to the Monin-Obukhov similarity theory parameters under slightly stable boundary layer conditions. The vertical profile of the N$_2$O$_5$ deposition flux has the same shape as the momentum flux profile based the Monin-Obukov similarity theory, which assumes that all the fluxes are the same in the surface layer, typically the lower 10 % of the boundary layer (Oke, 1987; Monteith and Unsworth, 1990; Arya, 2001). Using this flux profile, we show in the supplemental material that z_{eff} is ap-

proximately 15 m. The N$_2$O$_5$ chemical removal rate arising from snowpack deposition Reaction (R3a) is then given by

$$k_{3a} = \frac{v_{dep}}{z_{eff}}. \tag{4}$$

For these three nights, the average chemical removal rate is 0.024 min^{-1} for snowpack deposition (k_{3a}). This chemical removal can be compared to the total removal rate that is estimated from the steady-state lifetime of N$_2$O$_5$ by

$$k_3 = 1/\tau_{N_2O_5ss}. \tag{5}$$

During these three nights, we find that the total chemical removal rate, k_3, of N$_2$O$_5$ is 0.18 min^{-1}.

From these results, we find that, on average, about 1/8 of the chemical removal of N$_2$O$_5$ arises from deposition of N$_2$O$_5$ to the surface. The range of k_{3a} is 0.042 to 0.005 min^{-1} based on the standard deviation of the average deposition velocity. The chemical removal rate, k_{3a}, ranges from none to $^1/_4$ of the chemical removal rate of N$_2$O$_5$, k_3. However, there are a number of reasons that this estimate of the fraction of N$_2$O$_5$ depositional loss might be larger. First, the calculation of the effective surface layer relies upon an unknown flux profile for N$_2$O$_5$ and similarity theory. Because boundary layer height is difficult to determine under stable Arctic conditions, (Anderson and Neff, 2008) an error in the estimation of z_{eff} from the boundary layer height would directly impact the fraction of chemical removal that is due to surface deposition. Second, although the fetch in our experiment satisfies the Oke (1987) criteria, other authors (Horst and Weil, 1994; Horst, 1999) indicate that during stable atmospheric conditions, more fetch is required. If the fetch were not sufficient, then the gradient in N$_2$O$_5$ would have not fully developed at the point of measurement and the deposition velocity would be underestimated. A larger value of deposition velocity would increase the fraction of the chemical removal that is due to the surface deposition. Lastly, it is possible that the system does not completely achieve steady state, in which case the total chemical removal of N$_2$O$_5$ would be overestimated. The majority of these factors would raise the fraction of chemical removal that is due to deposition to the snowpack, possibly even making it the dominant process for air masses sampled within a few meters of the snowpack.

The other possible chemical removal of N$_2$O$_5$ is reaction on aerosol particles. Apodaca et al. (2008) found that measured aerosol particle loadings along with reasonable assumptions for reactive uptake of N$_2$O$_5$ ($\gamma_{N_2O_5}$) were insufficiently fast to explain the total steady-state removal of N$_2$O$_5$ measured earlier at this same field site. The possible loss to aerosol particles could be as high as three quarters of the total loss of N$_2$O$_5$, depending on the effect of relative humidity and snowpack deposition loss. Apodaca et al. (2008) also found chemical removal of N$_2$O$_5$ is faster in the presence of ice saturation conditions, which was interpreted as possibly due to reactions on ice particles in the atmosphere or reactions on the snowpack. Reactions on the snowpack would

give the signature of increased chemical removal of N_2O_5 for ice-saturated airmasses because air that comes in contact with snowpack will become saturated with respect to ice by either sublimation of the snowpack ice or condensation of super-saturated water vapor onto the snowpack. Therefore, the current measurements, which indicate a significant role for snowpack deposition combined with the result that aerosol processes are probably too slow to be a major sink of N_2O_5 and the correlation with ice saturation all appear to point to a significant role for deposition of N_2O_5 to snowpack as a major process for air sampled within meters of the snowpack surface. This finding in combination with the fact that the Arctic wintertime conditions are very often stable with hindered vertical mixing indicates that removal process of N_2O_5 even just tens of meters from the Earth's surface are likely to be quite different and probably significantly slower. If the chemical removal of N_2O_5 is significantly slower at higher altitudes, N_2O_5 may act as a reservoir and transport farther than would be indicated by ground-based studies alone. Aircraft, or possibly tethered balloon studies would be able to assess the question of the fate of N_2O_5 aloft and possible role for frozen or unfrozen aerosol particles in that atmospheric layer.

6   Conclusions

The average deposition velocity towards the snowpack surface of N_2O_5 is $0.59 \pm 0.47 \, \mathrm{cm\,s^{-1}}$. The calculation of this deposition velocity is dependent upon the fetch being sufficient for complete development of the near-surface gradient as well as general stability factor corrections, which may act to underestimate the actual deposition velocity. This deposition velocity parameter can be used in models to help understand the fate of NO_x pollution at high latitudes. The deposition velocities along with an assumed flux profile were used to approximate the chemical removal rate arising from deposition and to compare this rate to the total steady state chemical removal rate. In this comparison, we find that deposition to snowpack is responsible for 1/8 of the total removal, and also that the actual fraction of N_2O_5 deposition to snowpack may be more than this estimate. Therefore, we conclude that deposition of N_2O_5 to the snowpack is a significant and possibly the dominant process for air sampled with a few meters above snowpack. Airmasses aloft may experience slower losses, which would lead to enhanced transport of N_2O_5 aloft as well as an important role for vertical mixing in the fate of N_2O_5 emitted at high latitudes.

Supplementary material related to this article is available online at:
**http://www.atmos-chem-phys.net/11/4929/2011/
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