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# Deposition of dinitrogen pentoxide, N<sub>2</sub>O<sub>5</sub>, to the snowpack at high latitudes

D. M. Huff<sup>1,2</sup>, P. L. Joyce<sup>1,2</sup>, G. J. Fochesatto<sup>2,3</sup>, and W. R. Simpson<sup>1,2</sup>

<sup>1</sup>Department of Chemistry and Biochemistry, University of Alaska, Fairbanks, AK, USA

<sup>2</sup>Geophysical Institute, University of Alaska, Fairbanks, AK, USA

<sup>3</sup>Department of Atmospheric Science, University of Alaska, Fairbanks, AK, USA

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Correspondence to: W. R. Simpson (wrsimpson@alaska.edu)

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## Abstract

Dinitrogen pentoxide, N<sub>2</sub>O<sub>5</sub>, is an important nighttime intermediate in oxidation of NO<sub>x</sub> that is hydrolysed on surfaces. We conducted a field campaign in Fairbanks, Alaska during November, 2009 to measure the flux (and deposition velocity) of N<sub>2</sub>O<sub>5</sub> depositing to snowpack using the aerodynamic gradient method. The deposition velocity of N<sub>2</sub>O<sub>5</sub> under Arctic winter conditions was found to be 0.59 ± 0.47 cm/s, 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<sub>2</sub>O<sub>5</sub> via snowpack deposition to the total steady state loss rate and found that deposition to snowpack is a significant fraction of the total chemical removal of N<sub>2</sub>O<sub>5</sub> measured within a few meters of the ground surface.

## 1 Introduction

High-latitude nighttime nitrogen oxide chemistry is dominated by the oxidation of NO<sub>2</sub> by ozone to form nitrate radical, NO<sub>3</sub> (Reaction R1). NO<sub>3</sub> and NO<sub>2</sub> combine to form N<sub>2</sub>O<sub>5</sub>, (Reaction 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<sub>2</sub>O<sub>5</sub> is heterogeneous hydrolysis (Reaction R3). The following reactions are the nighttime pathway for N<sub>2</sub>O<sub>5</sub> chemical removal.



The production of nitric acid (Reaction R3) contributes to acid rain, adds fixed nitrogen to the ecosystem, and removes NO<sub>x</sub>. Acid rain is known to have many damaging effects on the environment. The effects of nitrification have been documented in mid

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latitudes (Andersen and Hovmand, 1995; Bytnerowicz et al., 1998; Fenn et al., 2003), and removal of  $\text{NO}_x$  affects the possibility of downwind ozone production.

The heterogeneous reaction of  $\text{N}_2\text{O}_5$  (Reaction R3) is an important reaction for  $\text{NO}_x$  loss. In a modeling study, Dentener and Crutzen (1993) found that during the winter 80% of high latitude  $\text{NO}_x$  is lost by Reaction (R3a), which is the dominant dark pathway to nitric acid. Since the Dentener and Crutzen (1993) modeling study, many laboratory experiments have been completed investigating  $\text{N}_2\text{O}_5$  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  $\text{N}_2\text{O}_5$  uptake coefficient, or surface reaction probability,  $\gamma$ , describes the probability of chemical reaction of  $\text{N}_2\text{O}_5$  on an aerosol surface. In more recent models, different parameterizations of  $\gamma$  have been used that identify the dependence on aerosol composition and temperature (Riemer et al., 2003; Evans and Jacob 2005). Bertram and Thornton (2009) parameterized  $\text{N}_2\text{O}_5$  based on  $\gamma$ 's dependence on  $\text{H}_2\text{O}(\text{l})$ ,  $\text{Cl}^-$  and  $\text{NO}_3^-$  for organic and inorganic mixed aerosols.

There have been several field measurements of  $\text{N}_2\text{O}_5$  at mid-latitudes (Brown et al., 2001; Matsumoto et al., 2005; Wood et al., 2005; Brown et al., 2006; Bertram et al., 2009). Brown et al. (2006) was the first field study to show a dependence on aerosol particle composition in a large aircraft field study over the Eastern US. Brown et al. (2006) related  $\text{N}_2\text{O}_5$  chemistry to sulfate aerosol particle content and observed faster uptake of  $\text{N}_2\text{O}_5$  to the aerosol particles when the aerosol particles had high sulfate content. Most recently, mid-latitude field studies found  $\text{N}_2\text{O}_5$  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  $\text{N}_2\text{O}_5$  on ambient aerosols directly by using chemical ionization mass spectroscopy (CIMS) to measure reactive loss of  $\text{N}_2\text{O}_5$  when added to a flow tube reactor containing ambient aerosols.

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Our research group has previously performed high latitude field studies and have reported aerosol surfaces densities were insufficient to account for all of the chemical loss of  $\text{N}_2\text{O}_5$  at high latitudes (Ayers and Simpson, 2006; Apodaca et al., 2008). We implicated other reactive surfaces for  $\text{N}_2\text{O}_5$  chemical loss, such as ice, either on atmospheric particles or in the snowpack. Ayers and Simpson (2006) measured  $\text{N}_2\text{O}_5$  on the top of a building, 85 m above the ground and found higher mixing ratios aloft, which is consistent with some of the  $\text{N}_2\text{O}_5$  removal being by deposition to Earth's snow-covered surface. Calculated lifetimes aloft ranged from minutes to several hours. Higher  $\text{N}_2\text{O}_5$  mixing ratios further from Earth's surface is in agreement with others who have studied the vertical profile of  $\text{N}_2\text{O}_5$  (Brown et al., 2003; Geyer and Stutz 2004; Stutz et al., 2004; Brown et al., 2007a, b). Apodaca et al. (2008) observed the mixing ratios of  $\text{N}_2\text{O}_5$  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 heterogeneous hydrolysis loss of  $\text{N}_2\text{O}_5$  by snowpack deposition. The deposition velocity of  $\text{N}_2\text{O}_5$  helps to improve process-based models aimed at understanding the vertical profile of  $\text{N}_2\text{O}_5$  at high latitudes and the fate of  $\text{NO}_x$  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  $\text{N}_2\text{O}_5$  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  $\text{N}_2\text{O}_5$  of 1 cm/s based on Brown et al. (2004) reported deposition velocity of nitric acid.

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### 3.2 Steady state analysis of N<sub>2</sub>O<sub>5</sub> measurements

We use the steady state approximation to calculate a lifetime of N<sub>2</sub>O<sub>5</sub> from the concentration of N<sub>2</sub>O<sub>5</sub> divided by the source rate of N<sub>2</sub>O<sub>5</sub> (Apodaca et al., 2008),

$$\tau_{\text{N}_2\text{O}_5\text{ss}} = \frac{[\text{N}_2\text{O}_5]}{k_1 [\text{NO}_2] [\text{O}_3]}. \quad (1)$$

- 5 The source rate of N<sub>2</sub>O<sub>5</sub> is the rate coefficient for Reaction (R1),  $k_1$ , multiplied by the concentration of NO<sub>2</sub> 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<sub>2</sub>O<sub>5</sub> is used to determine the total heterogeneous hydrolysis rate of N<sub>2</sub>O<sub>5</sub>, the sum of Reactions (R3a) and (R3b).

### 10 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.

15 The moveable-inlet tower alternated position between “up” and “down” heights, 2.35 m and 0.95 m, respectively. The moveable inlet sampled the gases, N<sub>2</sub>O<sub>5</sub>, NO<sub>x</sub> 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.

20 The meteorological tower supported both slow- and fast-response instrumentation. The slow-response system consisted of two RM Young cup anemometer and wind

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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.

5 The meteorological measurement tower also supported two sonic anemometers (RM Young model 84000) 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.

### 10 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<sub>2</sub>O<sub>5</sub>. 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,  $K_{\text{N}_2\text{O}_5}$  (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<sub>2</sub>O<sub>5</sub> results from a higher concentration of N<sub>2</sub>O<sub>5</sub> at the higher measurement level than

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data. 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 inter-calibrated 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  $-4^\circ$ ,  $-18^\circ$ ,  $-14^\circ$  C, respectively. The highest temperature gradient was seen on 5 November with a  $1^\circ$  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, respectively. The difference in wind speeds and the difference in  $\text{N}_2\text{O}_5$  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  $0.59 \pm 0.47$  cm/s.

In addition to measuring chemical gradients and comparing the gradient data to the meteorology, we also used chemical measurements to calculate the steady state

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lifetime of  $\text{N}_2\text{O}_5$  using Eq. (1). The steady state lifetime represents total chemical loss of  $\text{N}_2\text{O}_5$ , including snowpack deposition and atmospheric reactions. The time series of the average  $\text{NO}_2$ ,  $\text{O}_3$ , source rate,  $\text{N}_2\text{O}_5$  and steady state lifetime of  $\text{N}_2\text{O}_5$  are displayed in Fig. 5.

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

The average steady state lifetime of  $\text{N}_2\text{O}_5$  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 and 20 km distance and assuming direct transport is around 2 h. The transport timescale is longer than the maximum calculated lifetime of  $\text{N}_2\text{O}_5$  of 10 min, reinforcing the picture that the steady-state approximation is decent in this application.

## 5 Discussion

### 5.1 Deposition velocity of $\text{N}_2\text{O}_5$

Deposition velocities are parameters used to model the effects of nitrogen oxides on the environment. There are many studies using 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 our summarized in Helmig et 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 (Helmig et al., 2009). Wesley and Hicks (2000) summarized NO and  $\text{NO}_2$  deposition velocities and found

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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  $\text{N}_2\text{O}_5$  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  $\text{N}_2\text{O}_5$  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  $\text{N}_2\text{O}_5$  is heterogeneous hydrolysis on aerosol particles. Apodaca et al. (2008) found that measured aerosol particle loadings along with reasonable assumptions for reactive uptake of  $\text{N}_2\text{O}_5$  ( $\gamma_{\text{N}_2\text{O}_5}$ ) were insufficiently fast to explain the total steady-state removal of  $\text{N}_2\text{O}_5$  measured earlier at this same field site. Apodaca et al. (2008) also found chemical removal of  $\text{N}_2\text{O}_5$  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  $\text{N}_2\text{O}_5$  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  $\text{N}_2\text{O}_5$  and the correlation with ice saturation all appear to point to a significant role for deposition of  $\text{N}_2\text{O}_5$  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  $\text{N}_2\text{O}_5$  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  $\text{N}_2\text{O}_5$  is significantly slower at higher altitudes,  $\text{N}_2\text{O}_5$

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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  $\text{N}_2\text{O}_5$  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  $\text{N}_2\text{O}_5$  is  $0.59 \pm 0.47$  cm/s. 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  $\text{NO}_x$  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  $\text{N}_2\text{O}_5$  deposition to snowpack may be more than this estimate. Therefore, we conclude that deposition of  $\text{N}_2\text{O}_5$  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  $\text{N}_2\text{O}_5$  aloft as well as an important role for vertical mixing in the fate of  $\text{N}_2\text{O}_5$  emitted at high latitudes.

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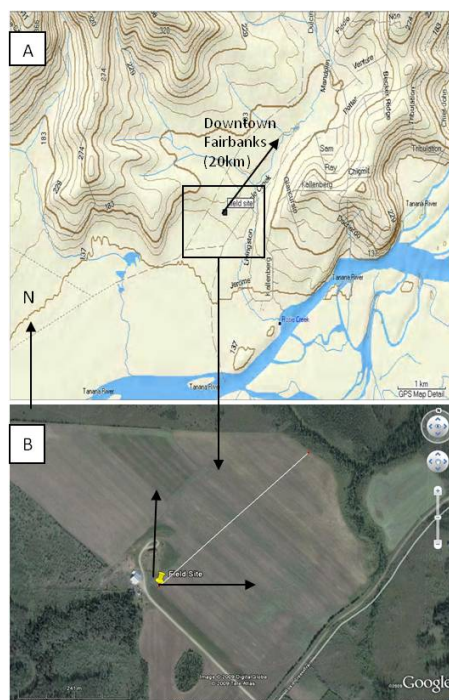
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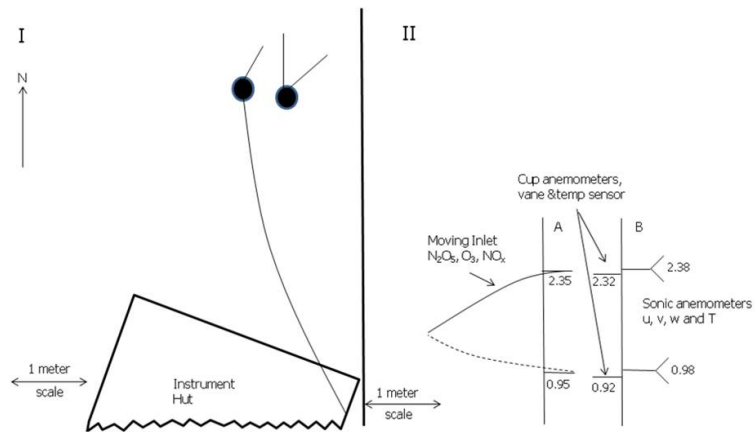
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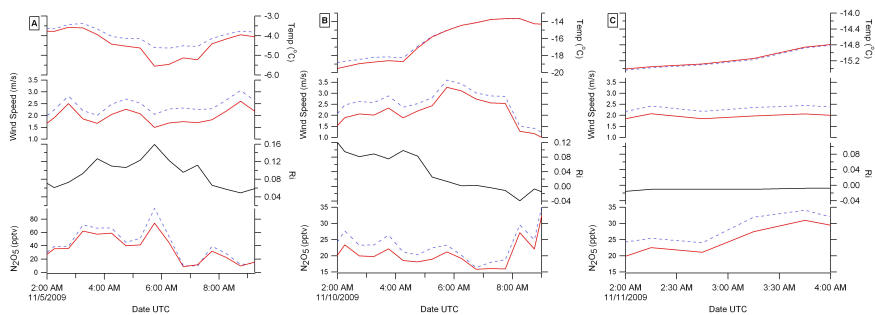
**Fig. 1.** Field site location: **(A)** contour map of field site with a black outline of the field site area. **(B)** Expanded satellite image of the inside of the black box area on map A. The black arrows in map B represent the wind direction selection criteria. The white line is the dominant wind 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.

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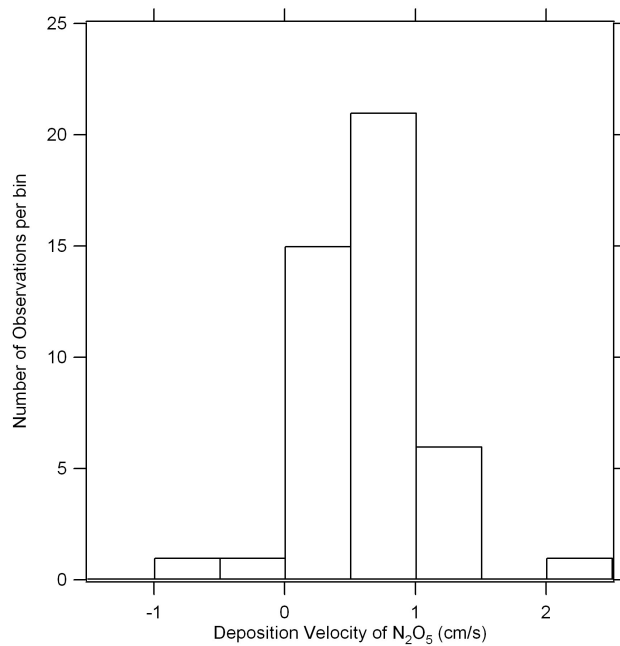
**Fig. 2.** (I) The plan view and orientation of the two measurement towers and instrument hut. (II) Elevation view of the moving inlet tower A and the meteorological tower B. All distances are in meters.

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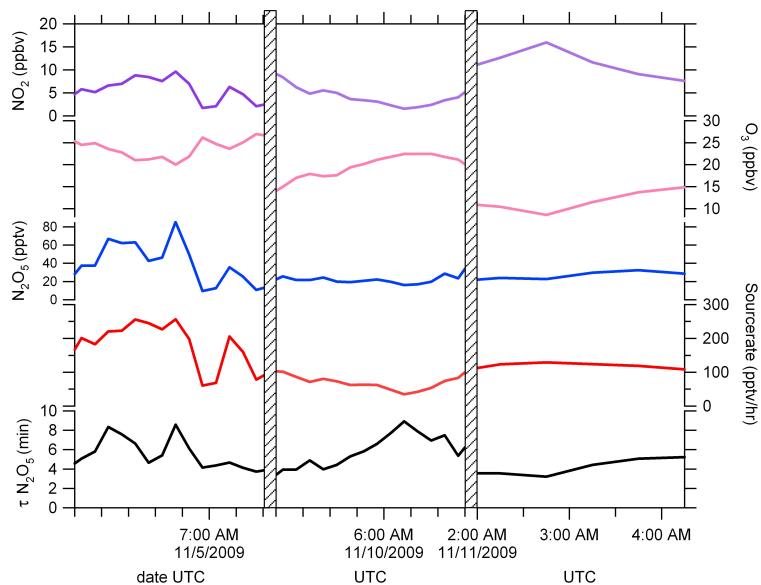
**Fig. 3.** Temperature (°C), wind speed (m/s), Richardson number and mixing ratio of N<sub>2</sub>O<sub>5</sub> in pptv for (A) 5 November 2009, (B) 10 November 2009 and (C) 11 November 2009. The red solid trace is always the lower height and the blue dashed trace is the higher measurement height. The black solid line, 3rd axis from the top is the Richardson number.

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**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.

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**Fig. 5.** From top to bottom are the mixing ratios of  $NO_2$  (ppbv),  $O_3$  (ppbv) and  $N_2O_5$  (pptv), source rate of  $N_2O_5$  (pptv/hr) and the steady state lifetime of  $N_2O_5$  as  $\tau_{N_2O_5}$ (min) on three nights 5, 10 and 11 November 2009.

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