A reassessment of Antarctic plateau reactive nitrogen based on ANTCI 2003 airborne and ground based measurements

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Abstract

The first airborne measurements of nitric oxide (NO) on the Antarctic plateau have demonstrated that the previously reported elevated levels of this species extend well beyond the immediate vicinity of South Pole. Although the current database is still relatively weak and critical laboratory experiments are still needed, the findings here suggest that the chemical uniqueness of the plateau may be substantially greater than first reported. For example, South Pole ground-based findings have provided new evidence showing that the dominant process driving the release of nitrogen from the snowpack during the spring/summer season (post-depositional loss) is photochemical in nature with evaporative processes playing a lesser role. There is also new evidence suggesting that nitrogen, in the form of nitrate, may undergo multiple recycling within a given photochemical season. Speculation here is that this may be a unique property of the plateau and much related to its having persistent cold temperatures even during summer. These conditions promote the efficient adsorption of molecules like HNO_3 (and very likely HO_2NO_2) onto snow-pack surface ice where we have hypothesized enhanced photochemical processing can occur, leading to the efficient release of NO_x to the atmosphere. In addition, to these process-oriented tentative conclusions, the findings from the airborne studies, in conjunction with modeling exercises suggest a new paradigm for the plateau atmosphere. The near-surface atmosphere over this massive region can be viewed as serving as much more than a temporary reservoir or holding tank for imported chemical species. It defines an immense atmospheric chemical reactor which is capable of modifying the chemical characteristics of select atmospheric constituents. This reactor has most likely been in place over geological time, and may have led to the chemical modulation of some trace

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species now found in ice cores. Reactive nitrogen has played a critical role in both establishing and in maintaining this reactor.

1. Introduction

During the last decade there has been a growing interest in the atmospheric chemistry of polar regions (Domine' and Shepson, 2002 and references therein). Among the reasons for this increased interest is the relevance of this chemistry to the interpretation of chemical signatures in polar ice cores. The latter can provide insights about major geophysical events in the earth's past history as well as point to changes that have occurred in the planet's climate (Legrand and Delmas,1987; Legrand and Feniet-Saigne, 1991). An understanding of atmospheric chemistry is relevant because it provides one of the critical inputs for evaluating the air-to-snow "transfer function" for a chemical proxy species. An evaluation of this transfer function requires that all of the processes that modulate the concentration of a chemical species be known from its point of origin to the point of deposition. As applied to the generic species "reactive nitrogen," earlier efforts to interpret ice cores have resulted in minimal success (Legrand and Kirchner, 1990; Legrand and Mayewski, 1997; Wolff, 1995). Having the ability to interpret the levels of nitrogen in ice cores potentially could provide important insights about the planet's past atmospheric chemical fluctuations, particularly as related to its oxidizing capacity. The significance of "reactive nitrogen" lies in the fact that in the chemical form of NO it has a major impact on the levels of both OH and O_3, the two most important oxidizing agents in the earth's atmosphere (Finlayson-Pitts and Pitts, 2000 and references therein).

Reflecting the uncertainties that still exist in interpreting ice-core nitrate levels are several recent studies showing that polar snow fields can release significant emissions of NO_x (Honrath et al., 1999, 2000; Jones et al., 2000; Ridley et al., 2000; Davis et al., 2001; Beine et al., 2002a, b). One of the major mechanisms identified as being responsible for these emissions is the UV photolysis of nitrate ions in firn (Honrath et al., 1999, 2000). Possibly even more complex processes may generate still other nitrogen species such as HONO (Zhou et al., 2001; Beine et al., 2002a, b). Collectively, these field observations have led to a flurry of laboratory studies designed to better understand the detailed photochemical and physical processes operating within polar firn (Dubowski et al., 2001, 2002; Boxe et al., 2003; Cotter et al., 2003).

Nowhere has this newly identified polar-atmospheric source of NO_x resulted in larger perturbations to the background levels of this species than observed at South Pole (SP), Antarctica (Davis et al., 2001, 2004a, b). In two of the earliest field studies carried out in 1998 and 2000 (e.g., Investigation of Sulfur Chemistry in Antarctica (ISCAT), observed NO levels were found to range from a low of 10 pptv to a high of ~600 pptv, with median levels estimated at 223 and 86 pptv, respectively. As previously found in the Arctic (Honrath et al., 1999, 2000), shading experiments at SP, along with measurements of snow surface nitrate levels (Dibb et al., 2004), have all pointed to the importance of nitrate photolysis as the dominant source of NO. Reflecting these enhancements in NO, 24h averaged atmospheric hydroxyl radical (OH) concentrations have been measured at 2×10^6 molecules cm^{-3}, rivaling in magnitude time averaged values found in the tropical marine boundary layer (Mauldin et al., 2001, 2004). Not surprisingly, the near surface atmosphere at SP has also been found to be a net-photochemical source of ozone (Crawford et al., 2001; Chen et al., 2004; Helmig et al., 2007a).

Davis et al., in their 2004 paper, undertook a detailed examination of the possible causes for the highly elevated levels of NO at SP. Specifically, they explored the possible reasons why the SP environment might support higher NO levels than observed at other polar sites (e.g., Summit, Alert, Neumayer, and Halley Bay) where median values are typically an order of magnitude lower. Using data from the 1998 and 2000 ISCAT studies, Davis et al. (2004a) concluded that among the important factors favoring SP were: (1) 24h of continuous sunlight during summer; (2) a strong tendency for shallow planetary

boundary layers (PBL) to occur during the summer season; (3) a geographical location that places SP near the base of a large air drainage field; and (4) extremely low temperatures throughout the summer season resulting in very low primary production rates for HO_x radicals. The latter two factors are of central importance in that the presence of a drainage basin provides an excellent opportunity for the accumulation of NO_x. Very low rates for primary production, of HO_x, on the other hand, can lead to the creation of a HO_x–NO_x chemical system that is highly non-linear. In this system, because NO_x can act as a sink for HO_x radicals, the NO_x lifetime can increase with increasing concentrations of NO_x. This, in turn, can lead to rapid increases in NO_x when the latter reaches levels of ~ 250 pptv or higher.

An issue not clearly resolved by the Davis et al. analysis was whether NO_x surface emissions at SP might be substantially larger than those at other polar sites. Based on the limited flux studies at each site, it might be concluded that emissions at SP are as much as three times larger than those at Neumayer, Antarctica (Jones et al., 2001); whereas, for Summit (Honrath et al., 2002) it could be argued that they are perhaps a factor of 1.5 larger. Considering, however, that quite different techniques were used in each of these studies, it is still questionable whether the above comparison is meaningful. Among the concerns is the fact that very little effort appears to have been made to obtain high-resolution vertical distribution data on nitrate in firn at each site. As discussed later in the text, this could be a critical factor. Yet another concern is the strong possibility that there might be considerable variability in the NO_x emission rate on the plateau and at other sites, both temporally and spatially. More specifically, flux measurements of NO_x have only been recorded at the SP's Atmospheric Research Observatory (ARO) and then only over a two week period. Thus, questions have persisted about the station somehow influencing the surrounding environment.

This paper expands on what was learned from the two previous field studies at SP using the results from the ANTCI 2003 field study. In particular, it expands the geographical area over which NO and NO_y observations will have been recorded. This was achieved using an airborne sampling platform. The results from this airborne study together with the SP observations have made possible an examination of the following topics: (1) contrasting plateau levels of

reactive nitrogen with those measured at coastal sites; (2) examining new photochemical evidence to determine its role in post-depositional losses of nitrate; (3) examining possible species and processes that might provide a basis for reactive nitrogen undergoing multi-recycling events within a given season; and (4) exploring the large scale influence of plateau NO_x emissions on the oxidizing properties of this unique environment.

2. Sampling platforms, measurement techniques and model description

Three independent sampling efforts took place during the ANTCI 2003 field study. The Twin Otter aircraft sampled from 27 November to 6 December 2003 (see Fig. 1 for flight tracks and area of investigation); at SP, ground-based sampling was carried out from 22 November to 31 December; and also at SP, tethered balloon sampling was implemented over the time period of 13 December to 31 December. Airborne chemical measurements included the trace gases NO, NO_y, and dimethyl sulfide (DMS). The measurements at the SP ground site were far more extensive and a detailed list of the species and parameters measured can be found in the ANTCI 2003 overview paper (Eisele et al., 2007). The observations recorded on the tethered balloon were also quite extensive and have been reported on by Helmig et al. (2007a,b).

2.1. Airborne Measurements

NO and NO_y were measured using a custom built chemiluminescence instrument. In this system, NO_y (e.g., the sum of NO, NO_2, HNO_3, HO_2NO_2, and organic nitrates) is detected after first being converted into NO using a heated molybdenum catalytic converter. The chemiluminescence NO measurement technique is one that has been well characterized as reflected in several instrument intercomparison studies involving both airborne and ground-based sampling platforms (Hoell et al., 1987, Gregory et al., 1990). During the ANTCI 2003 field study, the instrument was switched between the NO and NO_y modes of measurement every 5 min. The duty cycle consisted of: NO measurement, 3 min; NO zero, 1 min; NO_y zero, 1 min; NO_y measurement, 3 min. Calibrating the NO system involved the use of standard addition methodology, and this was performed at least twice per flight. Artifact tests using zero air were carried out twice each day, once before
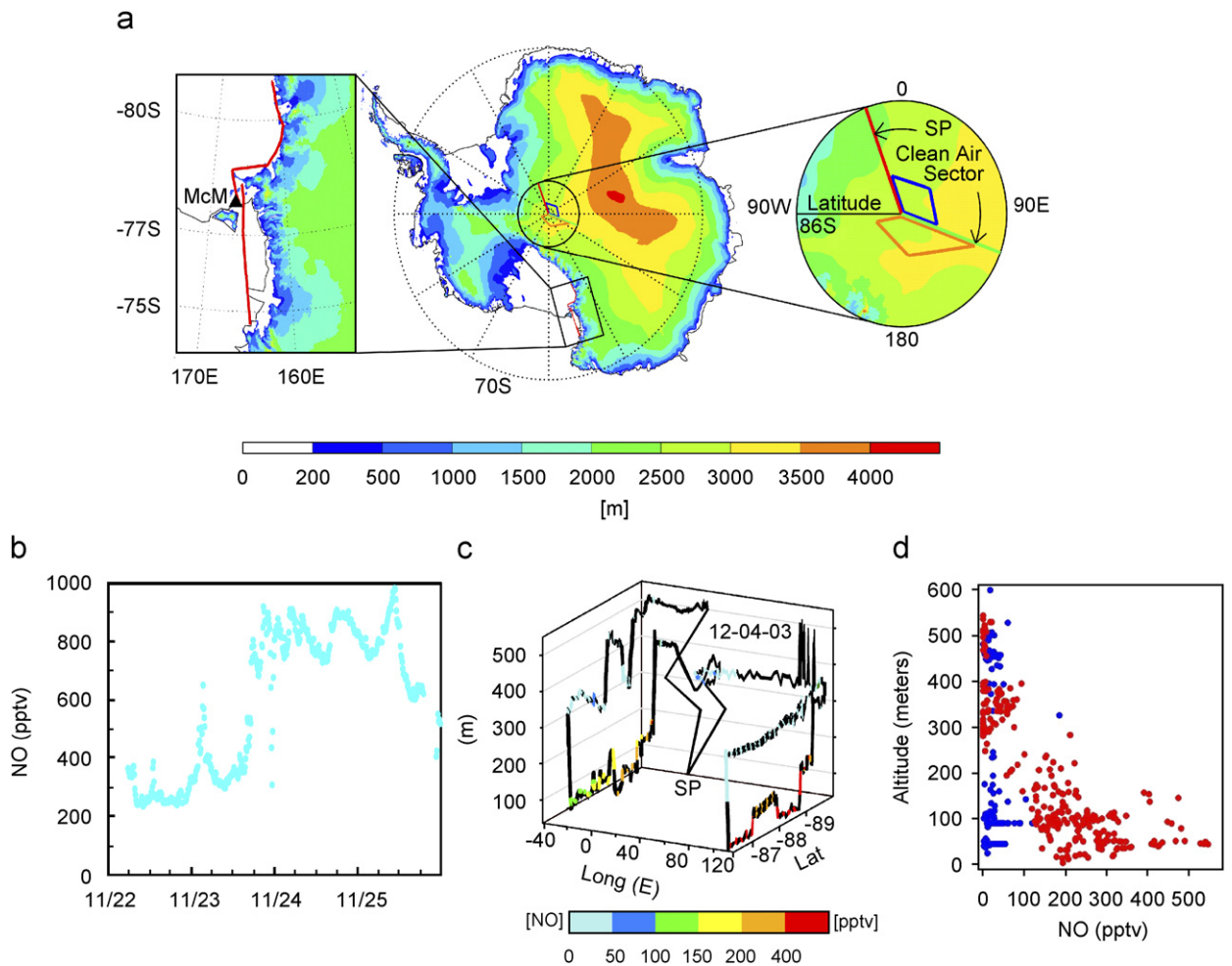
Fig. 1. (a) Topographical map of Antarctica (center panel) with approximated Twin Otter sampling flight tracks as flown during the ANTCI 2003 field study. The latter were focused on the coastal area surrounding McMurdo Station (left panel) and on a plateau region having the South Pole as the epicenter (right panel). (b) Time series plot showing the recorded variation in the concentration of NO over a 4-day period at South Pole's Atmospheric Research Observatory (ARO) during the ANTCI 2003 intensive field campaign. (c) Twin Otter sampling flight tracks depicting the variation in NO concentration (color coded) and aircraft altitude above ground level (AGL) along the clean air sector longitudinal vectors 340° (−20°E) and 110°E. (d) Altitude (AGL) versus NO concentration plot over plateau terrain (red dots) and coastal areas (blue dots). Note, each concentration/altitude data point represents the average value of 20 individual 5 s observations.

a flight and after landing. The 2σ detection limit for NO was 5 pptv. Because of its conversion to NO, the NO_y measurement required a determination of the NO conversion efficiency for each nitrogen species to ensure that the converter was working according to specifications. This was achieved using known amounts of NO_2, HNO_3, and propyl nitrate at three different times during the flight program. These tests revealed that throughout the time period of airborne sampling the conversion efficiency for NO_2 was typically 95–98%; whereas, for propyl nitrate and HNO_3 it was closer to 92–95%. However, since there was no a priori way of knowing the chemical mix of

the gas being sampled, no correction was made to the recorded NO_y value. The NO_y values reported, therefore, always represent a slight underestimate of the true value of NO_y. The limit of detection for NO_y for a 1-min sampling period was 25 pptv. (Note, the higher LOD for NO_y reflects the uncertainty in the artifact signal for this species in the field (for details see Fahey et al., 1986; Luke et al., 1998)).

2.2. Model Description

The time-dependent photochemical box-model used in this study is the same one previously used

by the Georgia Tech and NASA Langley research groups. It encompasses full HO_x/NO_x/CH_4/NMHC (non-methane hydrocarbon) chemistry and contains ~250 reactions. A complete listing of the most important features of this model can be found in Crawford et al. (1999). Gas kinetic rate coefficients in the model were those taken from Sander et al. (2003) and Atkinson et al. (1992) with updated values being used when available. Photochemical J values were calculated for plateau altitudes and latitudes under summertime clear-sky conditions. In general, the clear-sky model calculated values were found to be in reasonable agreement (90%) with those based on spectral irradiance flux measurements recorded at SP by the Biospherical Instrument Inc. company.

3. Observations

3.1. Plateau

Although a major focus of this paper is on NO data generated from Twin Otter sampling, the SP ground-based NO observations have also provided an important nitrogen data base. For example, as shown in Fig. 1(b) some of the highest NO values ever measured at the ARO facility were those recorded in late November 2003 (i.e., consistently in excess of 600 pptv (parts per trillion by volume)). The maximum level of ~1000 pptv (i.e., reached on 25 November) represents the single highest value of NO ever measured at SP. The median for the entire ANTCI 2003 ground-based sampling period was 231 pptv, ranking it as one of the highest overall values of the three studies conducted at SP. Equally interesting, when the 22–26 November data block is examined in greater detail, a common characteristic is that the wind direction is easterly oriented (see also Neff et al., 2007). A similar trend was also found for the 1998 and 2000 ISCAT studies. (Davis et al., 2001, 2004a). One exception to this general trend occurred when wind speeds dropped below $2–2.5\,m\,s^{-1}$. Under these rare conditions, very shallow PBLs formed quickly with resulting rapid rises in NO. In some of these cases, evidence was found indicating that the SP power station could also act as a modest source of NO due to the variable direction of the wind at these low speeds. Statistically, the dominant winds at SP range 340–0–110°, i.e., a sector known as "the clean air sector" (CAS). For the data shown in Fig. 1(b), 75% of the observations fall within the smaller

wedge of 45° to 110°. The fetch associated with this wedge potentially extends outward to distances of 1600 km or more, and encompasses terrain that typically has an elevation significantly higher than SP.

As seen in Fig. 1, the Twin Otter observations were predominantly recorded either over a geographical area just upwind of CAS or along its borders. This sampling scenario was specifically designed to address the question: do NO concentrations drop off with increasing distance from SP? Evidence indicating that this does not typically happen is shown in Fig. 1(c). In this case the Twin Otter flights are shown ranging out to distances of ~400 km from SP. When assembled and converted into a single vertical distribution, these data appear as shown in Fig. 1(d). Here the highest concentrations are clearly seen at the lowest above-ground altitudes (hereafter labeled as altitude above ground level, AGL). This finding is again consistent with the idea that snow emissions of NO_x are the dominant source of this species. But, it is also noteworthy that some of the highest measured airborne values of NO were recorded on flight tracks whose geographical orientation was along the eastern edge of CAS, i.e., along a longitudinal flight heading of 110° (see Fig. 1(c)). These observations support the high values seen at the ARO facility, and are consistent with the idea that one of the factors leading to elevated levels of NO at SP is its being geographically located near a convergence point for air drainage from the plateau. In particular, since much of this drainage comes from higher elevations on the plateau, these air parcels are frequently associated with flow from an easterly direction.

3.2. Coast

As shown in Fig. 1(d), the NO observations recorded along the coast were in most cases substantially lower in concentration than those recorded on the plateau. Most of these coastal flights were within 400 km of McMurdo with flight tracks oriented along the Ross Ice Shelf (see Fig. 1a). When at altitudes below 250 m AGL, values are seen ranging from a low of 3 pptv to highs of 35 pptv. The median value of 28 pptv is shifted somewhat toward the higher end of the distribution, partially reflecting abrupt perturbations observed in NO which reached levels of ~100 pptv. Some of these can be attributed to times when the aircraft encountered the McMurdo Station plume.

Most though were due to flight tracks that crossed glacial outflows at low AGLs. One of these led to highly elevated levels of NO and NO_y and will be discussed in still a later paper.

NO_y concentrations along the Ross Ice Shelf, were typically more than three times the value observed for NO at low to intermediate AGL levels. This is consistent with model predictions which suggest that at the warmer temperatures and lower O_3 levels characteristic of the coast, the ratio of NO to NO_2 should be closer to 1:1.5 rather than 2.3:1 estimated for the colder plateau. It also reflects, however, additional contributions from alkylnitrates and HNO_3. The ratio of NO_y to NO observed on the plateau at low AGL levels was also higher than that estimated from the combined NO and NO_2 concentrations. In this case we estimate that significant contributions come from both HNO_3 and HO_2NO_2 (Sjostedt et al., 2004).

The relatively low concentrations of NO observed along the Ross Ice Shelf are consistent with the observations previously reported at two ground-based coastal sites, Palmer Station (Jefferson et al., 1998) and Neumayer (Jones et al., 2001). Both of these stations have reported NO at levels typically <10 pptv. Neither of these sites now appears to be close to an area that might have been influenced by the previously noted glacial outflow phenomenon.

At altitudes above 250 m, Fig. 1d shows low but persistent coastal concentrations of NO up to 500 m, with values ranging from 5–25 pptv. The source of the elevated NO is unknown at this time, but one can surmise that the removal of plateau NO_x, due to a combination of vertical mixing and advection (e.g., see Wang et al., 2007), might be involved.

4. Results and Discussion

4.1. The Nitrogen Cycle

As presented in the "Introduction" section, the photochemically driven release of reactive nitrogen in polar environments is currently an area of major scientific interest. Much of this interest is focused on the well known chemical impact that NO_x has on the critical atmospheric oxidant, OH. Not as well documented but of great interest to glacio-chemists is the potential importance of this process in understanding post-depositional losses of nitrogen from ice fields (De Angelis and Legrand, 1995; Rothlisberger et al., 2000, 2002; Wagnon et al.,

1999; Mulvaney et al., 1998). Most prevalent on the Antarctic plateau, the post-depositional loss process seems to depend on the fact that some acidic species have the ability to migrate within the firn. In the case of reactive nitrogen, it is nitrate in the form of HNO_3 that exhibits this behavior (Mulvaney et al., 1998; Rothlisberger et al., 2000, 2002; Wagnon et al., 1999; Legrand et al., 1996; and De Angelis and Legrand, 1995) although as will be discussed latter in the text, pernitric acid (HO_2NO_2) may also play a role.

In Fig. 2 the post-depositional loss process is shown along with several other processes now thought to be important in the recycling of plateau nitrogen. Also highlighted in this diagram is the fact that the primary source(s) of plateau reactive nitrogen still remain as "speculative". Possibilities range from stratospheric inputs to sources that dependent on long range transport, e.g., biomass burning, lightning, etc. (Wolff, 1995). (Note, more recently McCabe et al., 2007, using an isotopic signature analysis of nitrate, have reported that the stratosphere may well provide upwards of 25% of the total nitrogen source.) Once deposited, however, indications are that this primary nitrogen is strongly influenced by the process known as "snow metamorphosis", during which time considerable migration of HNO_3 occurs. This migration within the firn layer appears to be at least partially responsible for some of the highest concentrations for acidic species being found near the snow's surface (Rothlisberger et al., 2000; Wolff, 1995). With the onset of spring, two different mechanisms can then potentially lead to the release of this reactive nitrogen to the atmosphere. The first of these is shown in Fig. 2 as "evaporative loss". This is a thermodynamically driven process that should lead to the release of HNO_3 with the warming of the snow-pack surface layer. The second form of nitrogen loss, also shown in Fig. 2, is photochemical in nature and unlike the evaporation process leads to the production of NO_x. The chemical/physical processes outlined in Fig. 2, starting with nitrate photolysis and/or evaporation and ending with atmosphere-to-snow deposition of HNO_3/HO_2NO_2, define "nitrogen recycling" on the plateau.

In the text below, we explore both the photochemical and the evaporative mechanisms in somewhat greater detail in an effort to further explore the relative importance of each process as related to the post-depositional loss of reactive nitrogen. This discussion is then followed by a
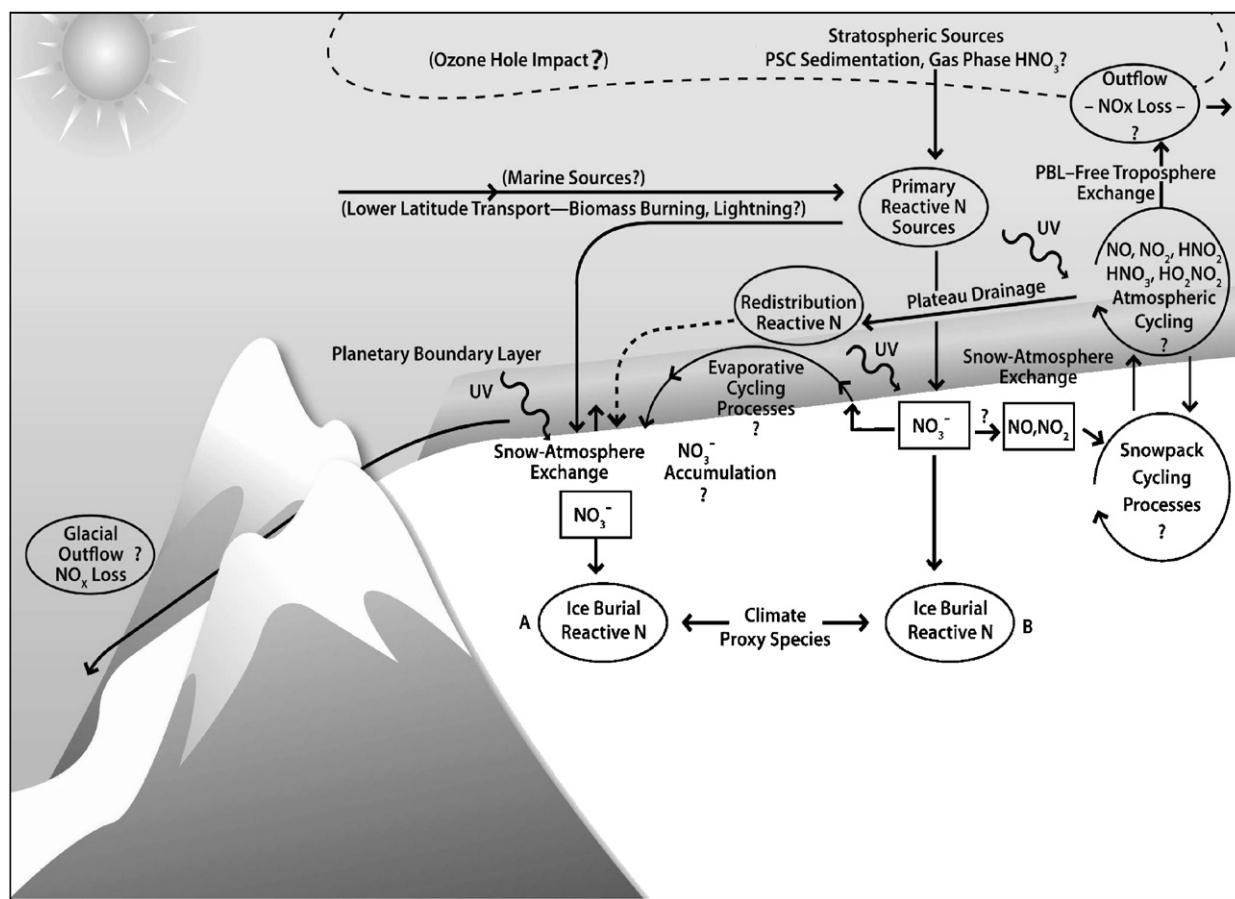
Fig. 2. Schematic diagram illustrating the critical processes encompassing the reactive nitrogen budget for the Antarctic plateau. These include: primary sources, post-depositional loss mechanisms, and atmospheric/snow recycling. The symbol "?" displayed throughout the diagram suggests that currently there is only a qualitative understanding of many processes.

more quantitative examination of nitrogen recycling, based on three newly recorded NO vertical distributions.

4.1.1. Evaporative versus photochemical release of nitrogen

As stated previously, numerous studies have now reported evidence of post-depositional losses of nitrate in polar environments. Most, but not all, of these have involved the Antarctica continent (Burkhart and Hutterli, 2004, and Rothlisberger et al., 2002). Factors now believed to influence the degree to which this process occurs at any given site include snow accumulation rate, the firn temperature gradient, elevation, and snow acidity (Rothlisberger et al., 2000). For locations involving very low accumulation rates (Wagnon et al., 1999, and Rothlisberger et al., 2000), nitrate levels are frequently highly elevated near the surface of the snow-pack, with decreases in

concentration being an order of magnitude or more within the first meter. The temperature gradient within the firn layer can play a significant role in the redistribution process in that for much of the year the surface snow tends to be colder than the ice below due to surface radiative cooling (Brandt and Warren, 1997). Since each year new nitrate is added to that already present, it is apparent that some nitrate must also be lost to the atmosphere. As outlined above, the two mechanisms believed to be most responsible for this loss are evaporation and photochemistry. Pointing to the possible importance of the evaporation process, Beine et al.(2002a) in a study at Alert, Nunavut, Canada found that in comparing the flux associated with photochemically released nitrogen (e.g., both in the form of NO_x and HONO) with the corresponding measured nitrate loss, only half of the latter loss could be accounted for. Thus, these authors have suggested that there is a high likelihood that

some snow nitrate may have found an alternative path of escape from the sampling area. One possibility is that HNO_3 was evaporating from the site since this loss would not have been measured with the instrumentation available.

More germane to the focus of this work (e.g., Antarctic plateau), Blunier et al. (2005) have recently reported an interesting isotopic study involving ^{15}N in conjunction with snow samples taken from Dome C, a low accumulation area of the plateau. Investigators in this study examined the nitrogen isotopic signature on two Dome C surface cores and found an increase in the fractional isotope signature with depth along with decreasing nitrate concentration levels. In an independent laboratory photochemical study, they then used artificial snow to determine the fractionation factor for the photolysis of nitrate. By comparing this fractionation value with the results from the surface ice cores, the conclusion was reached that the photolysis of nitrate in snow was most likely not the major process leading to the loss of nitrate in the top centimeters of firn at Dome C. It was further noted that these results appeared to be consistent with the recent photochemical modeling predictions for Dome C carried out by Wolff et al. (2002). The latter study reported that photolysis could account for no more than 40% of the surface nitrate removal at the Dome C site. In a closing remark, however, Blunier did point out that if nitrate in the Dome C area were undergoing "multiple cycling" due to photolysis it could compromise the interpretation he was giving to his experimental results.

In still a more recent study Savarino et al. (2006), from an examination of year long sampling of aerosols at Durmont d'Urville in which nitrogen and oxygen isotopic ratios in particulate nitrate were examined, found that during the winter months the largest nitrogen source at this coastal station was that resulting from the denitrification of the stratosphere, e.g., polar stratospheric cloud sedimentation. During the late spring/early summer time period, however, the source was determined to be coming from the plateau due to re-emissions of HNO_3 and the photochemical release of NO_x. These authors further stated that their results were most consistent when nearly equal amounts of HNO_3 were assumed from evaporation and from photochemistry.

Based on the previous ISCAT results and the newer findings coming out of ANTCI 2003, two points appear relevant. First, the cited Wolff et al. (2002) modeling estimate for the photochemical release of NO_x at Dome C appears to be at odds with recent field studies on the plateau. For example, the NO_x flux measurements reported by Oncley et al. (2004) reveal that when compared to the modeling results of Wolff et al., but for SP rather than Dome C, they are four times larger than those estimated by Wolff et al. (2002). Equally troublesome is the high degree of chemical coupling that seems to exist among the many different measured forms of nitrogen at SP (e.g., NO, HNO_3, HO_2NO_2, NO_y, and "filterable nitrate"). If evaporation were dominant, one might expect the resulting HNO_3 to have a rather weak correlation with the levels of other nitrogen oxide species, particularly NO. On the other hand, if photochemistry dominates post-depositional loss, the initial formation of NO_x should lead to a significant correlation between nitrogen species. In the latter regard, it is interesting that the model calculated kinetic rates of formation for both HNO_3 and HO_2NO_2 from NO_2 are found to be highly correlated with their respective measured concentrations (e.g., both r^2 values ~ 0.7 (Sjostedt et al., 2004)). Equally significant is the high degree of correspondence shown in the time series plot of several nitrogen species as shown in Fig. 3. The key components of this plot are NO, "filterable nitrate", HNO_3, and HO_2NO_2. Although a visual inspection of this plot suggests a relatively high degree of correlation, a regression analysis of these data reveals that all r^2 values for species versus NO are $\geqslant 0.60$, with the value for HNO_3 versus HO_2NO_2 being 0.72. Even though some degree of correlation might be expected between these species, due to the influence of the boundary layer depth, it seems unlikely that these results could be explained if each species had a different source.

That photochemistry is driving a very large fraction of the SP nitrogen budget during the summer can be further appreciated by comparing the level of NO generated from the photolysis of gas phase HNO_3 with actual NO observations themselves. (Note, in this modeling exercise it is assumed that all of the observed HNO_3 came from evaporation.) In this case, the results reveal that the ambient NO level generated from HNO_3 photolysis is nearly 30 times lower than that typically observed. Yet a final piece of evidence showing the absence of major direct emissions of HNO_3 are the efforts made at SP during ISCAT 2000. In this case the nitric acid gradient was measured over the snow-pack (Dibb et al., 2004). The results indicated nearly always lower levels in the firn air than immediately above it in the atmosphere.
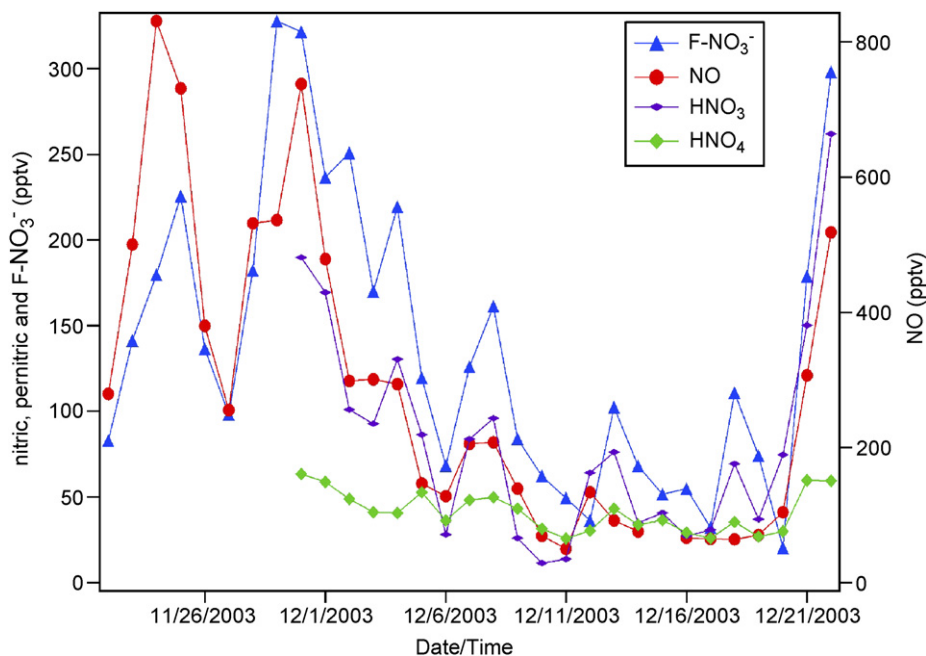
Fig. 3. Time series plot of NO, HNO_3, HO_2NO_2, and filterable nitrate as recorded at the ARO facility at South Pole over the time period of 21 November–22 December 2003 as part of the ANTCI 2003 field campaign. The data for the chemical species labeled here as "filterable nitrate" was collected using a high-vol sampler. Laboratory tests have shown that this system collected both nitrate particles as well as gas phase acidic species such as HNO_3. Further details can be found in the companion paper by Arimoto et al. (2007).

In spite of these compelling collective results, it is apparent that there is still much that we do not understand about plateau atmospheric chemistry. As such, we would not argue at this time that one can exclude the evaporation process as having some importance in the post-depositional loss of nitrate. It is quite possible, for example, that at other sites (especially those having low accumulation rates) or at other times of the year evaporative losses may be far more important. Further studies to explore these possibilities are needed.

4.1.2. Photochemical Nitrogen Recycling Factor

Although a general overview of nitrogen recycling was given above, the concept of recycling as related to plateau reactive nitrogen can most easily be defined at the microscale. Here the overall process can be viewed as occurring in three steps. In the first of these, a nitrate ion in surface snow is photochemically energized, resulting in a NO_x species being successfully emitted into the atmosphere. Once in the atmosphere, NO_x is then rapidly converted into either HNO_3 or HO_2NO_2. In the final step, the latter species are redeposited to the snow's surface, thus regenerating the original nitrate

ion. Numerous research groups have made a convincing case for the process defined as "nitrate recycling" (e.g., Honrath et al., 1999; Jones et al., 2000; Ridley et al., 2000; Davis et al., 2001; Beine et al., 2002b; and Savarino et al., 2006).

Here, we explore the reactive nitrogen recycling process quite independently using recently generated Antarctic NO field data. For this purpose it has been convenient to define a new quantity labeled here, "nitrogen recycling factor" (NRF). Using the above micro scale definition, NRF may be viewed as simply the average number of times that a given nitrogen species undergoes a recycling event within a photochemical season on the plateau. In this context, the modeling results by Wolff et al. (2002) suggest that its value is significantly less than 1.0, meaning that in one season most surface nitrate never undergoes the release of NO_x. Shifting the definition from the micro to the macro-level, the latter may be expressed simply as the ratio of the total yearly mass of nitrogen emitted into the plateau's atmosphere (e.g., as kg (N) in the form of NO_x) to the yearly mass of "primary nitrogen" (kg (N) deposited to the plateau's surface. (Note, primary nitrogen as shown in Fig. 2 is external/imported reactive nitrogen). In more practical

terms, the latter quantities can be scaled down, resulting in the new ratio: Areal Mass of Nitrogen (i.e., kg (N)) in the form of NO_x emitted into the plateau atmosphere each Year (AMNY) to Areal Mass of Primary Nitrogen deposited to the plateau each Year (AMPNY). However, what is immediately apparent in the latter definition is that AMNY, which represents the column mass of nitrogen released per unit area per year, to be of any real significance in evaluating NRF, needs to be "representative" of the entire plateau. Thus, considering the limited areas of the plateau that now have been sampled, and these for only very limited time periods, it is apparent that the estimated value for AMNY is by far the largest uncertainty in the current effort to evaluate NRF.

Retuning to our final working definition for NRF, it can be seen that in the form cited above it simply represents the ratio of two fluxes, one for nitrogen emission, the other for deposition. (Note, current observational data indicate that most nitrogen emissions on the plateau occur during a 4-month period centered around summer, thus the yearly value can be taken as defined by the spring/summer photochemical season. By contrast, it is still unclear what the exact time period is for "primary" nitrogen deposition, although it is suspected to occur predominantly during the Austral winter and perhaps very early spring months (Legrand and Kirchner, 1990; Wolff, 1995; Rothlisberger et al., 2000)). Fractional values for NRF (e.g., significantly lesser than unity) could be interpreted as indicating that the data base used is indeed too limited to be meaningful or that multiple nitrogen-recycling events simply do not occur. On the other hand, values $\geqslant 1.0$ could be interpreted as an indication that such events are quite common; or, alternatively, that the results are fortuitous and simply reflect the fact that we are again working with a very limited data base.

In our evaluation of AMNY two steps are involved: first, there is an estimate made of the Instantaneous Overhead-Column Burden of NO_x (IOCBN, e.g., column mass (N) per unit area, kg (N) km^{-2}); and second, this quantity is multiplied by a time factor given by the number of NO_x lifetimes (days) that could occur within the total number of days defining a "plateau photochemical season". Since the latter is a yearly occurrence, the numerical value for AMNY is in units of mass of N (kg), per area (km^2), per unit time (yr). To arrive at the number of NO_x lifetimes, the number of active

solar days (e.g., 110 days with solar zenith angles $\leqslant 77°$) was divided by a weighed average value for the NO_x lifetime. This term was estimated for conditions defined by the atmospheric column in which NO measurements were recorded. For example, for the data shown in Fig. 1(d), its value ranged from 8 to 14 h depending on elevation, leading to a final weighted average of 11 h. However, upon folding in the seasonal effects on the NO_x lifetime (e.g., spanning the time period of 20/10–23/02), its average value increased to 15 h or 0.63 days.

To evaluate the IOCBN term in AMNY, the NO vertical distribution was first displayed as shown in Fig. 1(d) (e.g., 2003 airborne data). This distribution was then converted into a column burden expressed in NO molecular units by fitting a curve to the median values estimated from the NO data contained within each 25 m altitude interval from 0 to 500 m. The corresponding value for NO_x was then calculated based on box model estimates of the ratio for NO/NO_x, again reflecting kinetic/photochemical "k" and "J" values characteristic of SP temperatures. Ozone concentrations used in this calculation were those given by the median values defined by the SP balloon experiments conducted during the summer of 2003 (e.g., see Helmig et al., 2007a). Finally, the column burden, expressed in terms of mass rather than molecular units was obtained using the appropriate atomic weights of each species.

As discussed earlier in the text, the NO data bases from which we estimated IOCBN values came from three independent sources: the airborne data recorded during the last week of November and the first week of December of 2003; the SP balloon data recorded during the last 2 weeks of December 2003; and the airborne data recorded during the first 2 weeks of December in the sampling year 2005. Quite significant is the fact that minimal geographical overlap occurred between these three data sets.

Based on the above evaluations, the airborne ANTCI 2003 NO distribution resulted in a final estimated AMNY value of 6.2 kg N km^{-2} yr^{-1}. The independent balloon derived NO distribution (Helmig et al., 2007b) provided a second estimate of 1.4 kg N km^{-2} yr^{-1}, and the third independent data set, based on ANTCI 2005 airborne measurements, resulted in an estimated AMNY value of 3.9 kg N km^{-2} yr^{-1}. As previously discussed, our estimated value for IOCBN defines the single largest source of uncertainty in the evaluation of AMNY,

and hence, in NRF. The next largest uncertainty involves the estimate given for the average NO_x lifetime, $\pm$ a factor 1.3. Still smaller are the uncertainties associated with the conversion of NO to NO_x, $\pm$ 10–15%, and the number of active solar days, $\pm$10%. Given these uncertainties and the fact that the extreme values of AMNY, estimated from three independent data sets, are within a factor of 5 of each other, the current results can be viewed either as quite reassuring or just blind luck!

We have chosen here to interpret these results as encouraging and therefore have proceeded to convert the above estimates into NRF values. As discussed previously, this last step requires yet another independently evaluated quantity, AMPNY. Unfortunately, the average deposition of primary nitrogen to the plateau is not a well-documented quantity either. One of best estimates is that reported by Legrand and Kirchner (1990). However, their value is limited to deposition of primary nitrogen at SP. Even so, it is based on 100 years of nitrate ice-core records. This assessment leads to an estimated value for AMPNY of 2.1 kg N km^{-2} yr^{-1}. Although it represents the "net" deposition of primary nitrogen and thus does not reflect the NO_x that is lost each year from the plateau due to advection (i.e., see Wang et al., 2007), we estimate that it is unlikely that it is too low by more than a factor of 1.5. The above value is most likely on the high side relative to the rest of the plateau since it is known that surface nitrate levels at SP tend to be nearly 5 times higher than those for low accmulation regions at higher elevations on the plateau (Wolff, 1995, Rothlisberger et al., 2000). Davis et al. (2004a,b) have suggested that due to major photochemical emissions of NO_x on the plateau during the spring/summer season, much of the surface nitrogen at SP might simply be nitrogen that has been advected from higher plateau elevations.

Taking the higher value for AMPNY based on the Legrand/Kirchner's deposition flux and using the average value for AMNY (estimated from three NO data bases), the NRF value estimated here is 1.8. Thus, this NRF value suggests that there is a high likelihood that on average near surface nitrogen recycles more than once during a photochemical season. Quite noteworthy, however, is the point made above that the average "primary nitrogen" flux to the plateau could be factors of three to five times lower than that used, thus increasing our estimate of NRF by a similar amount.

Among the possible impacts resulting from the multiple recycling of reactive nitrogen would be the intense focusing of nitrate onto the upper most layers of the snow pack each year, a trend that appears to be quite common on the plateau, especially for low accumulation regions (Rothlissberger et al., 2000). Perhaps equally dramatic are the consequences of this recycling phenomenon on average levels of NO in the near surface atmosphere on the plateau. The impact in this case would involve the coupling of the recycling process with the highly non-linear HO_x–NO_x chemistry previously discussed by Davis et al. (2004a,b) in which increasing concentrations of NO_x lead to an increase in the lifetime of NO_x, thus promoting still larger increases. This combination might be a possible explanation for some of the very large and abrupt increases seen in NO levels at SP during recent SP field studies. In some cases, NO levels of $\leqslant$20 pptv have been observed spiraling upwards to concentrations of over 600 pptv in less than 15 h (Davis et al., 2001, 2004a,b). Although the onset of shallow PBL is an important component of these events, they alone do not appear to be capable of explaining this type of observation. Modeling of these super-events using PBL depths measured at the time typically requires nitrogen emission fluxes which are 2–4 times larger than the highest flux estimates at SP by Oncley et al. (2004, see also Wang et al., 2007). For comparison, these fluxes would be 8–16 times higher than those estimated by Wolff et al. (2002).

4.1.3. Snow photochemical NO_x release mechanisms

Accepting the results from the recycling factor calculations as meaningful, two questions surface: what photochemical source on the plateau can explain these results and why might this source be unique to the plateau? As a starting point, at present there appears to be no basis for seriously questioning the overall reliability of previously reported ice/nitrate studies (Dubowski et al., 2001, 2002; Boxe et al., 2003, 2006; Chu and Anastasio, 2003, Jacobi and Hilker, 2007, Cotter et al., 2003, Zellner et al., 1990, and Mack and Bolton, 1999). Although differences between them exist, these tend to be modest. The one significant issue that seems to still be under debate is whether photochemical snow models take into consideration the possible temperature dependence for transporting photochemical products, generated within an ice matrix and/or QLL, into interstial firn air and to the atmosphere. The latter factor has recently been the focus of

several interesting experiments reported by Boxe et al., (2003, 2006).

For purposes of this discussion, we will assume that most of what has previously been reported in the literature represents a good approximation of what we will label here as "conventional ice-nitrate photochemistry". Thus, whatever new source or sources identified here should be viewed as operating in parallel with those that have already been documented in the literature.

Given this as a starting point, it would seem that any new photochemical source of NO_x would have to possess one or both of the following characteristics: (1) involve a species not previously considered as a source of NO_x but having a much higher efficiency for NO_x production; or (2) involve a previously unknown reaction channel having a highly efficient pathway for producing NO_x but involving a previously considered source species. In the case of option (1), the task of identifying a new species is rather straight forward in that previous measurements at SP have shown very elevated levels of the species pernitric acid. This species is currently not included in conventional photochemical snow models. What makes this an interesting possibility is that the integrated absorption cross-section is ~40 times larger than that for HNO_3 (Sander et al., 2003). Although this means that its photochemical lifetime is less than a day in the atmosphere, deposition to the surface is also less than a day. Equally significant is the fact that box model calculations indicate that the formation of HO_2NO_2 is one of the dominant pathways for the conversion of NO_x into fully oxidized nitrogen.

The reasons for pernitric acid not being cited in previous modeling efforts include the fact that no measurements of this species have been reported at polar sites other than at SP. For example, it is thermally unstable in the atmosphere, and is cited as having a high probability of hydrolyzing in the presence of water. Although these characteristics have discouraged its use in models focused on polar sites such as Alert, Summit, Neumayer, Hally Bay, etc., they do not remove it from serious consideration on the much colder plateau. As first suggested by Slusher et al. (2002), it is quite possible that this species alone may account for much of the recycling phenomenon. Much encouraging in this regard our relatively recent laboratory results showing that HO_2NO_2 is quite stable over the temperature range of 200–246 when on an ice surface (Zhuangiie et al., 1996). Equally interesting our still other laboratory

results that indicate that in solution it can have a lifetime of 30 min when H_2O_2 is present in slight excess (Appelman and Gosztola, 1995).

Focusing on option (2), one of the clear trends that emerge from previous ice-nitrate laboratory studies is the extremely low efficiency measured for the photochemical production of NO_x. This is due primarily to the photochemical quantum yield being quite low (note, the quantum yield, Φ, expresses the probability that a specific chemical process will occur when a photon of radiation is absorbed). Typical Φ values reported in laboratory studies at temperatures corresponding to those found on the plateau can be as low as 0.002 to 0.0004, depending on pH (Chu and Anastasio, 2003, Dubowski et al., 2001, Jacobi and Hilker, 2007). The major reason for these low Φ values, in both liquids and ice, is the inability of the initially formed primary photochemical products to escape the cage of water molecules surrounding them when they are born. First studied by Noyes in the early 1950's (Noyes, 1954, 1956), this "cage effect" is well recognized by radiation and photochemists that carry out studies in liquids and solids. The primary photo-fragments undergo collisions with the surrounding H_2O molecules until they dissipate their excess kinetic energy and then recombine. When they recombine, they typically, but not always, reform the original molecular species which absorbed the incident radiation. This geminate recombination process is the crux of the very low Φ values measured in the laboratory involving nitrate-ice mixtures, i.e., very few primary photo-products escape into the bulk liquid or ice matrix. Thus, in exploring possible more efficient photochemical channels for producing NO_x, the value of Φ is critical. In this context, a unique characteristic of the plateau relative to other polar sites is the persistent cold temperatures in both winter and summer.

The significance of very low temperatures lies in the fact that under these conditions ice surfaces readily adsorb molecular species like HNO_3 and very likely HO_2NO_2. For example, in recent laboratory experiments by Abbatt (1997) and later by Ullerstam et al. (2005), adsorption studies were carried out using HNO_3 at partial pressures corresponding to those observed on the plateau. The ice coating the flow tube in these experiments was held at temperatures ranging from 214 to 239 K. Interestingly, the results showed that the lower the temperature the greater the adsorption on the ice surface. It was further determined that

HNO$_3$ uptake followed a non-dissociative Langmuire adsorption-isotherm. The latter suggests that either the HNO$_3$ was not dissociating upon bonding to the surface or that it was simply forming an ion pair that was occupying only one active site on the surface (Ullerstam et al., 2005, Cox et al., 2005). Under low partial pressure conditions (e.g., <150 pptv), these investigators also found that the ice surface was always under saturated (e.g., $<1 \times 10^{14}$ molecules cm^{-2}); and the lower the partial pressure the greater the degree of under-saturation. Yet another revealing observation was that HNO$_3$ appeared to occupy two different types of sites on the ice surface. The first type site involved weakly bonded HNO$_3$ (e.g., possibly an H-bonded molecule or ion pair site) which when the HNO$_3$ pressure was reduced came back off the ice surface. In contrast, the second type site exhibited much stronger bonding, and this HNO$_3$ could not be easily removed (i.e., irreversible). Speculation is that HNO$_3$ molecules at the second site were fully dissociated and that the nitrate ion had migrated into the liquid film on individual ice crystals (i.e., QLL) or into the bulk ice. The latter results suggest that at polar sites having much warmer temperatures than the plateau, it is unlikely that any significant population of surface weakly adsorbed HNO$_3$ would be found. Furthermore, if temperatures reach the melting point of ice, it is likely that all nitrate becomes incorporated into the ice matrix and/or QLL.

Based on the above findings, one can argue that an important characteristic for any species that might contribute to the rapid recycling of nitrogen would be its ability to be successfully adsorbed onto the surface of ice crystals. In the case of HNO$_3$, this process has a strong dependence on temperature, with lower temperatures promoting greater adsorption. Overall, four different ice sites can be identified that could serve as photochemical reaction-sites: bulk ice, the quasi-liquid layer (QLL) surrounding bulk ice, ice grain boundaries, and the outer surfaces of ice crystals. On the plateau, conditions are such that statistically some significant fraction of the population of HNO$_3$ (and likely HO$_2$NO$_2$) molecules, at any given time, should be on ice crystals that are physically located on the outer most ice surface of the snow-pack. This setting can clearly be distinguished from all previous laboratory experiments where an ice-nitrate medium in the form of bulk ice or a quasi-liquid layer surrounding bulk ice have defined the region undergoing photolysis. In the proposed new photochemistry, individual HNO$_3$ and/or HO$_2$NO$_2$ molecules (or ion pairs) are seen as being weakly bonded to an ice surface either via H-bonding or by strong dipole interactions (e.g., resulting from ion pair formation).

Under the above conditions, those nitrate species absorbing UV radiation would have a higher tendency to photofragment while relatively free of cage effects, and thus lead to a higher rate of
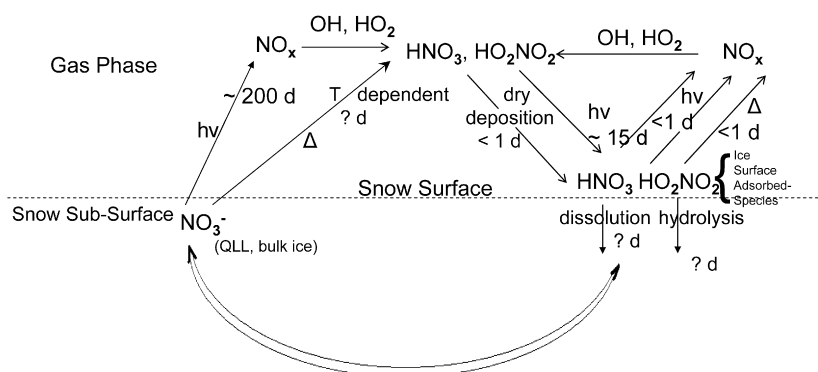

Fig. 4. Proposed Antarctic Plateau Nitrogen recycling chemistry. The chemical scheme shown depicts both conventional photochemical processes leading to the release of NO$_x$, evaporative processes leading to the release of HNO$_3$, and proposed new photochemical processes that might efficiently return nitrogen from the snowpack to the atmosphere. A critical requirement for the latter involves the adsorption of nitrogen species such as HNO$_3$ and HO$_2$NO$_2$ on the surface of ice crystals. The short time constants listed for these newly proposed processes assume that the quantum yields for these could approach unity. Thus, to the extent that there are other factors that might compromise the efficiency of these processes (e.g., burial processes), the time constants would have to be increased. (Note: an alternative to the one step direct photolysis of HO$_2$NO$_2$ to form NO$_x$ would be the formation of HONO on the surface via a heterogeneous reaction as reported earlier by Zhou et al., 1993).

production of NO_x. Until quite recently, however, there has never been an observation of this process under controlled low temperature laboratory conditions (see ''Note added in proof''). It can be argued that since water molecules are highly dynamic over ice, with many monolayers being exchanged between the atmosphere and ice surface, that over a rather short time interval these loosely bonded species would again be buried. Alternatively, riming could take place in which all HNO_3 species would be buried. If this were to happen one would expect that there would again be a drop in the value of Φ. However, HNO_3, once on the outer surface of ice, may have a high tendency to remain on the surface as H_2O molecules bond preferentially to other H_2O species already a part of the ice matrix. Interestingly, in the experiments carried out by Ullerstam et al. (2005), no evidence was found for the burial of HNO_3 molecules cited as being weakly bonded to the ice surface even though significant vapor phase H_2O was present. Only under super-saturation conditions were these weakly bonded species readily buried. Even so, it is recognized here that much uncertainty exist concerning the proposed surface photochemistry. For this reason, an intense round of laboratory studies is very much needed to more fully explore the proposed new domain of ice photochemistry.

In Fig. 4 the above cited process as well as those reflecting well established mechanisms are shown in schematic form. As indicated in the figure, the estimated time constant for initiating chemical bond rupture for surface adsorbed species is significantly shorter than that for photolysis of nitrate using conventional photochemistry (e.g., $\geqslant 150$ days). However the short times given for the new photolysis processes assume that the species photolyzed is near or at an ice surface and virtually free of cage effects. Thus, to the extent that some degree of burial takes place and cage effects are operating, the time constants cited in the figure would have to be substantially increased. An interesting side note on the proposed surface photolysis mechanism is that it fully enfolds the idea that there could be some degree of post-depositional loss of HNO_3 due to evaporation. If, for example, in early spring surface warming of the ice provided an evaporative source of this species, these initially released molecules could serve to activate the proposed surface driven photochemical mechanism.

4.2. Impact of Nitrogen on Plateau Oxidation Chemistry

In addition to the important issues of post-depositional losses of nitrate, and plateau recycling of nitrogen, the aircraft-generated NO data set (Fig. 1d) proved to be of considerable value in expanding on earlier assessments of the chemical consequences of plateau nitrogen (Chen et al., 2001, 2004; Crawford et al., 2001; Davis et al., 2001, 2004a and references therein). As shown in Fig. 5, this relates specifically to the levels of O_3 and OH radicals in the near surface atmosphere over the plateau. Observations documenting photochemical O_3 enhancements at SP were first reported by this research team following the 1998 ISCAT study (Crawford et al., 2001). These early results have been further amplified on during the ANTCI 2003 study based on a tethered balloon study at SP (Helmig et al., 2007a). Results from the latter study have shown O_3 enhancements of 10 ppbv and larger to be quite common, even at elevations of 300 m above the plateau's surface.

Regarding OH, extensive observations have been recorded of enhancements in this species during the field studies of 1998, 2000, and 2003. These, however, have all been limited to ground-level measurements at SP (Mauldin et al., 2001, 2004). The new airborne NO data set (Fig. 1d) has now
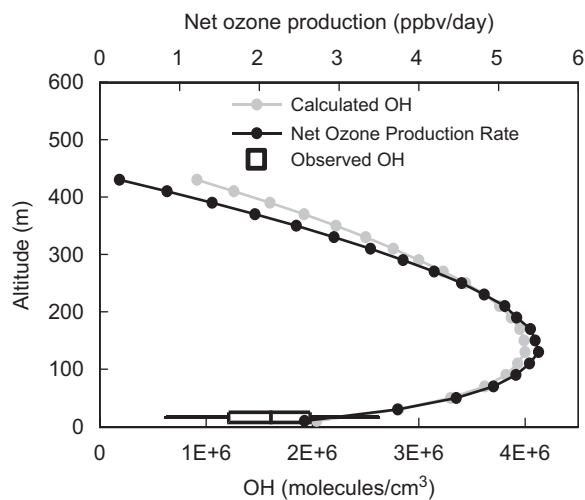

Fig. 5. Model calculated vertical profiles for OH (molecules cm^{-3}) and net photochemical production of O_3 in parts per billion by volume (ppbv) per day. Input to this model included the NO data shown in Fig. 1(d) and O_3 and H_2O data recorded from a tethered balloon (see Helmig et al., 2007a). (Note: the altitude at which the maximum in [OH] occurs reflects the high degree of non-linearity of the HO_x–NO_x chemical system.)

made possible model calculations of atmospheric vertical profiles of OH up to AGL altitudes of 500 m. As Fig. 5 reveals, OH levels are predicted to reach upwards of 4×10^6 molecules cm^{-3}. Interestingly, the highest OH concentrations do not correspond to the maximum value seen for NO in Fig. 1d. This apparent anomaly represents another clear example of the non-linear chemistry that can unfold in a HO_x–NO_x chemical system. In particular, reactive nitrogen in this system in the form of NO_x can serve both to promote OH production as well as act as a sink for this species, depending on its concentration level.

If one extends the OH profile shown in Fig. 5 to still other regions of the plateau, the larger impact of NO_x surface emissions becomes apparent. In this new paradigm for the plateau, nitrogen-driven photochemistry results in major OH enhancements that extend up to 150 to 300 m above the surface (see Neff et al., 2007). Horizontally, however, the enhancements extend across the entire plateau. In this enlarged chemical picture, continuously elevated levels of OH and O_3 are maintained throughout the spring/summer/early fall time periods by steady emissions of NO_x (see also Wang et al., 2007). As a result, the near surface plateau atmosphere is converted into a highly energized chemical reactor.

5. Summary and Conclusions

The findings reported here have provided major new insights on the chemical/physical processes controlling the composition of the Antarctic plateaus near surface atmosphere. The airborne measurements, in particular, have removed many of the reservations about the representativeness of the earlier NO observations recorded at SP. We now know that highly elevated NO concentrations can be found over significant areas of the plateau. Still larger regions need to be explored, but the current findings suggest that major surprises are unlikely to be found as related to emissions of NO_x.

A significant new topic explored in this work involves the question; does plateau reactive nitrogen undergo multiple recycling within the same season? The results here suggest that it is quite likely that it does. Although the database from which this tentative conclusion has been drawn can not at this time be labeled robust, the consistency of the results is highly encouraging. Among the remaining

important issues is that of identifying the specific photochemical process and/or species that may be responsible for this multi-recycling phenomenon. What has been hypothesized here, based on limited laboratory evidence, is that this form of recycling would be promoted through the adsorption of species such as HNO_3 and/or HO_2NO_2 onto the surfaces of polycrystalline ice. The latter configuration could potentially provide a photochemical pathway whereby cage effects were minimized, leading to elevated quantum yields for the production of NO_x. However, we also have noted that pernitric acid itself, could provide the answer. Photolysis of this species even within an ice matrix/QLL environment would be far more efficient in producing NO_x than nitrate due to its much higher UV absorption cross-section. The critical unknown here is what is the stability of pernitric on/in ice under plateau conditions? whether under plateau conditions pernitric acid readily hydrolyzes on contact with ice.

A final issue examined in this work involved an evaluation of the 2003 airborne NO data set in the context of what it can tell us about the oxidizing characteristics of the larger plateau region. In this case, the conclusion reached was that if elevated NO levels are common to the entire plateau, as suggested by the ANTCI 2003 airborne results, the enhancements in near surface concentrations of OH would turn the plateau into a large chemical reactor. This reactor, the size of continental USA, would promote the further oxidation of any chemical species entering it, if not already in its highest oxidation state. Current field measurements of reactive sulfur species like DMS strongly suggest that this is the most likely reason why only trace levels of this species have been observed during the spring/summer months at sites like the SP. On those occasions when marine air is transported to the pole, DMS is rapidly oxidized as it enters the plateau's lower atmosphere. How many other species may be routinely influenced by the presence of this oxidizing canopy is unknown at this time, but the post-depositional release of methane-sulfonic acid (MSA) and its subsequent oxidation by OH to form sulfate may be among these. What is reasonably apparent, is that the interaction between the NO_x–HO_x chemical systems on the plateau has most likely been on-going over geological time. Thus, it has undoubtedly led to some degree of modulation of reactive nitrogen levels now found in ice core samples.

The chemistry revealed here, as well as in many companion papers of this special issue, suggests that we just now may be turning the corner in our understanding of the bigger picture for plateau nitrogen. Even so, well-designed field studies that can record credible emission and/or deposition fluxes for NO_x, HNO_3, and HO_2NO_2 are very much needed. In addition, far more detailed surface snow experiments are required. As mentioned earlier in the text, there is also a very great need for sophisticated laboratory studies in which the adsorption of HNO_3 and HO_2NO_2 onto ice surfaces is examined at temperatures typical of the plateau. Most critical are laboratory photochemical experiments designed to measure the efficiency with which these adsorbed species might release NO_x to the atmosphere. There are also many levels of modeling that continue to be needed, ranging from snow-atmosphere 1-D models to box and 3-D models. The 3-D models, in particular, must be able to simulate in a realistic fashion NO_x fluxes from the snow's surface as a function of plateau environmental conditions. Finally, there must be a continuing effort to identify the centrally important primary sources of plateau nitrogen.

Note added in proof: Very recently it has been reported in the Journal of Physical Chemistry [DOI:10.1021/jp072596j(2007)] that HNO_3 vapor adsorbed onto the surface of polycrystalline ice at 100 K releases to the atmosphere atomic oxygen atoms with very high transitional energies when photolyzed with a UV laser. The species NO was also observed as a secondary product.

Acknowledgments

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