

On the cryogenic removal of NO_y from the Antarctic polar stratosphere

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Abstract

We review current knowledge about the annual cycle of transport of nitrogen oxides to, and removal from, the polar stratosphere, with particular attention to Antarctica where the annual winter denitrification process is both regular in occurrence and severe in effect. Evidence for a large downward flux of NO_y from the mesosphere to the stratosphere, first seen briefly in the Limb Infrared Monitor of the Stratosphere (LIMS) data from the Arctic winter of 1978-1979, has been found during the 1990s in both satellite and ground-based observations, though this still seems to be omitted from many atmospheric models. When incorporated in the Stony Brook - St. Petersburg two dimensional (2D) transport and chemistry model, more realistic treatment of the NO_y flux, along with sulfate transport from the mesosphere, sulfate aerosol formation where temperature is favorable, and the inclusion of a simple ion-cluster reaction, leads to good agreement with observed HNO_3 formation in the mid-winter middle to upper stratosphere. To further emphasize the importance of large fluxes of thermospheric and mesospheric NO_y into the polar stratosphere, we have used observations, supplemented with model calculations, to define new altitude dependent correlation curves between N_2O and NO_y . These are more suitable than those previously used in the literature to represent conditions within the Antarctic vortex region prior to and during denitrification by Polar Stratospheric Cloud (PSC) particles. Our NO_y - N_2O curves lead to a 40% increase in the average amount of NO_y removed during the Antarctic winter with respect to estimates calculated using NO_y - N_2O curves from the Atmospheric Trace Molecule Spectroscopy (ATMOS)/ATLAS-3 data set.

Key words *polar stratosphere – reactive nitrogen – heterogeneous chemistry – tracer-tracer correlations*

1. Introduction

The production and transport of oxides of nitrogen in the atmosphere and their subsequent cryogenic removal by Polar Stratospheric Clouds (PSCs) (denitrification) over polar regions constitutes one of the most fascinating atmospheric cycles traced out in recent years. The influx of large quantities of nitrogen oxides from the winter polar mesosphere into the stratosphere,

and the formation of HNO_3 in the mid-to-upper stratosphere, was first implied by observations of anomalously large amounts of NO_2 and HNO_3 by the Limb Infrared Monitor of the Stratosphere (LIMS) during the Arctic winter of 1978-1979 (Russell *et al.*, 1984; also see WMO, 1985, vol. II, for a summary of LIMS measurements). There was no further direct confirmation of these observations, however, until the launching of Upper Atmospheric Research Satellite (UARS) late in 1991. Although transport from the winter mesosphere into the stratosphere is now well established over both polar regions, denitrification of the lower stratosphere is quite variable from year to year in the Arctic under current climatic conditions, and we concentrate here on the more regular and severe denitrification process of the Antarctic. In this paper we review some recent work helping to establish the large flux of

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NO₂ into the Antarctic winter stratosphere, the chemical routes by which a significant fraction is transformed into HNO₃ above 30 km altitude, the condensation of HNO₃ into PSCs at lower altitudes, and their removal from the stratosphere by gravitational fallout.

Measurements made with the Stony Brook Ground-Based Millimeter-wave Spectrometer (GBMS) during the decade of the 1990s, along with measurements by the Cryogenic Limb Array Etalon Spectrometer (CLAES) and the Microwave Limb Sounder (MLS) onboard the UARS, have revealed much more detail about the formation of HNO₃ in fall and winter over a large vertical range of the southern polar stratosphere, its descent as part of winter vortex dynamics, and its freeze-out in PSC particles (Kawa *et al.*, 1995; de Zafra *et al.*, 1997; Santee *et al.*, 1998, 1999; McDonald *et al.*, 2000).

There has been considerable effort to explain how HNO₃ can form in the mid-to-upper stratosphere in winter (*e.g.*, Kawa *et al.*, 1995, and references therein). Chemical conversion from NO₃ + NO₂ → N₂O₅, followed by N₂O₅ + H₂O → 2 × HNO₃ has been generally assumed, but the latter reaction is far too slow in the gas-phase, and some sort of heterogeneous (*i.e.*, surface or condensed-state) chemical reaction has been sought. The altitude range where HNO₃ is formed (30–50 km) in polar winter is much too warm for the formation of polar stratospheric clouds, and sulfate aerosols (which could take the place of PSCs) have often been considered non-existent above ~ 30 km (see Garcia and Solomon, 1994, for an early refutation of this prejudice, and Mills *et al.*, 1999, for a more thorough analysis). In Section 3 we will discuss recent work (de Zafra and Smyshlyaev, 2001) in which earlier suggestions for the formation of HNO₃ have been revisited, with new results which, despite initial doubts, seem to confirm the viability of these formation mechanisms.

Regardless of the partitioning of NO_y in the stratosphere (where NO_y ≈ HNO₃ + NO + NO₂ + 2 × N₂O₅ + ClONO₂), descent of NO_y from the mesosphere during polar winters is of great importance for the nitrogen budget in polar stratospheres. Since the late 1980's, correlations between the two long-lived species N₂O and NO_y have been used to estimate denitrification in polar

stratospheres, which is of great importance in determining the severity and duration of spring-time ozone loss. More recent studies show that seasonally dependent mixing across the vortex boundary can alter such correlations dramatically, so that mid-latitude NO_y-N₂O correlation curves are not representative of the correlation present at high southern latitudes prior to denitrification. Transport of large concentrations of NO_y from the upper atmosphere to the lower stratosphere inside the vortex adds to this discrepancy, increasing the error when computing Antarctic winter denitrification using NO_y-N₂O curves obtained outside the southern vortex as a reference. Our current work on the NO_y-N₂O correlation is an attempt to remedy this situation through seasonal estimates of NO_y versus N₂O at the southernmost latitudes, and will be discussed in Section 4.

2. Transport of NO_y into the polar stratosphere

Observations with the LIMS instrument in the Arctic winter of 1978–1979 indicated NO₂ mixing ratios on the order of 100 ppbv in the upper Arctic stratosphere and lower mesosphere, as well as anomalously large amounts of HNO₃, as referenced in Section 1. Despite these findings, and their confirmation in the early 1990s by additional ground-based measurements and measurements from instruments onboard UARS, many atmospheric chemical and transport models in use through the 1990s have failed to incorporate these findings of a large winter NO_y flux over polar regions: see for instance figs. 3.5.1a through 3.5.1c of Park *et al.* (1999), where 11 out of 13 models tested show NO_y deficiencies by one or two orders of magnitude above ~ 50 km relative to LIMS observations. NO_y enters the polar mesosphere both by transport from lower latitudes and by *in situ* production in the mesosphere and thermosphere in the auroral regions near the magnetic poles (*e.g.*, Siskind *et al.*, 1997 and references therein; Randall *et al.*, 1998, 2001). Callis (2001) has also recently emphasized the inadequacy of most atmospheric models in either realistically parameterizing or dealing directly with creation and downward transport of NO_y in polar regions.

It is not our intention to deal further with the question of production or transport in the upper polar atmosphere in this paper, but merely to point out that efforts intended to model chemical processes in the polar stratosphere are certain to lead to inaccuracies unless and until realistic parameterizations of downward stratospheric NO_y fluxes through the fall and winter seasons are used.

3. The production of HNO_3 in the winter mid-stratosphere

The most complete record of the behavior HNO_3 in the Antarctic stratosphere as a function of both time and altitude comes from the GBMS

observations taken at the South Pole during 1993, 1995, and 1999 (de Zafra *et al.*, 1997; McDonald *et al.*, 2000; de Zafra and Smyshlyaev, 2001; Muscari *et al.*, 2002). Figure 1 shows a composite average of these observations: the evolution of gas-phase HNO_3 follows very nearly the same pattern for each individual year, with minor variations driven mainly by lateral transport. Two features are very evident from fig. 1. First, HNO_3 increases significantly after sunset in the lower stratosphere, due to the cessation of direct photolysis of HNO_3 and to the conversion of other nitrogen oxides to nitric acid. Second, shortly after day 160 (early to mid-June), significant new HNO_3 begins to form as high as ~ 50 km, and is carried downward in the general rapid descent of air towards the lower stratosphere,

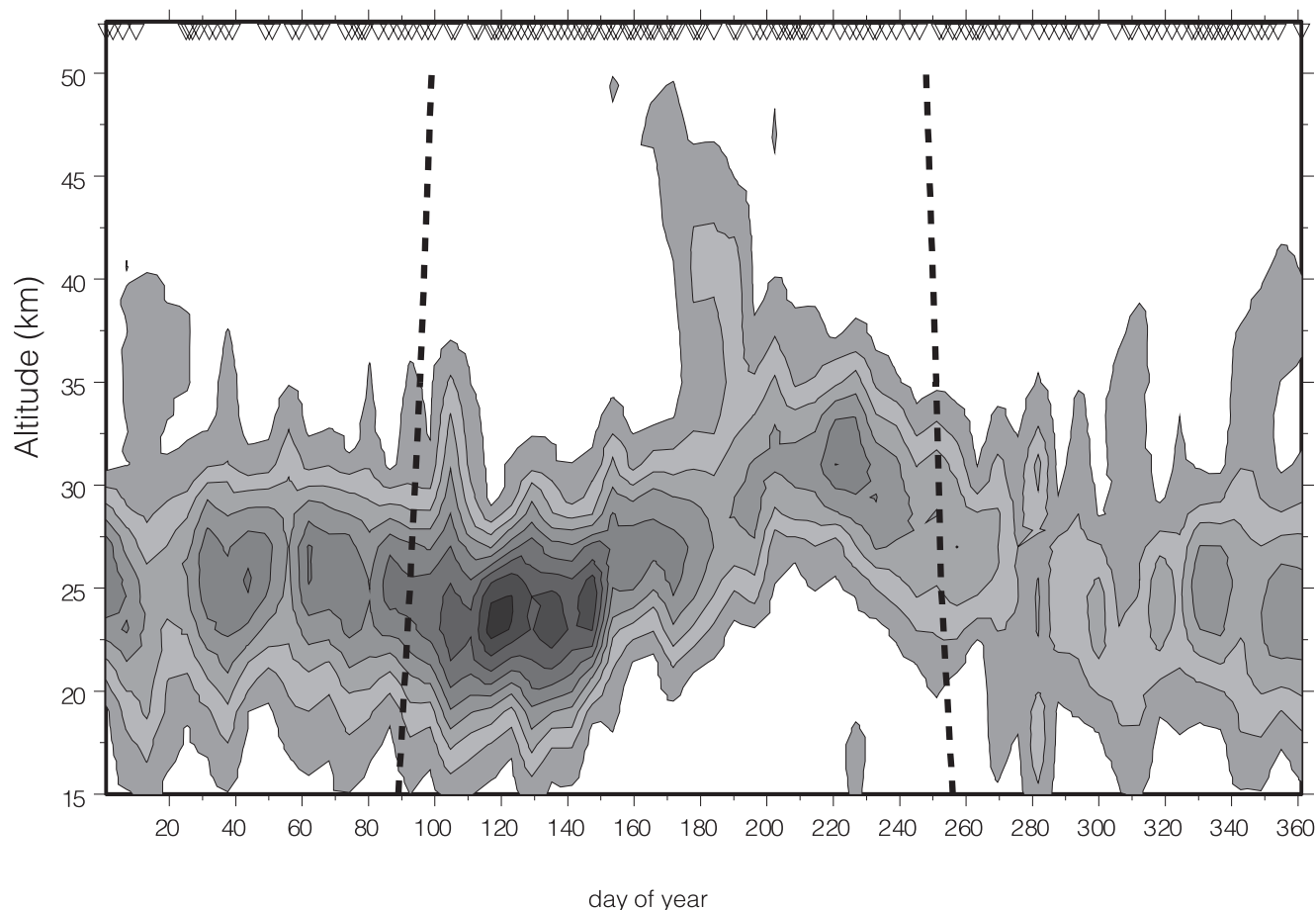


Fig. 1. Three-year average of HNO_3 measurements over the South Pole (1993, 1995, and 1999). Triangles along the upper boundary indicate days when measurements were taken over the three years. The lightest gray contour filling indicates mixing ratios between 1 and 3.5 ppbv. Contours increase in increments of 2.5 ppbv to a maximum of 21-23.5 ppbv. Heavy dashed lines mark sunset and sunrise as a function of altitude.

while increasing its mixing ratio along the way. The first of these processes poses no problems in stratospheric chemistry, but the second has been a persistent puzzle since the early LIMS measurements first suggested anomalously large amounts of HNO₃ high in the polar winter stratosphere.

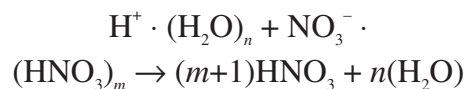
The most plausible route for formation of HNO₃ in the upper nighttime stratosphere is by the gas-phase transformation NO₂ + NO₃ → N₂O₅, followed by reaction with water: N₂O₅ + H₂O → 2(HNO₃). It is known from laboratory rate studies that the latter reaction is far too slow in the gas-phase to account for the rapid formation of observed amounts of HNO₃, and a heterogeneous (surface) reaction seems to be required. The Antarctic stratospheric temperature is surprisingly warm at this time and altitude, however, ranging from ~ 225 to 250 K, which is much too warm for the condensation of PSCs. The problem, therefore, has been to find a plausible chemical mechanism for rapidly making HNO₃ under conditions found in the polar winter stratosphere at 35-45 km.

In some recent work (de Zafra and Smyshlyaev, 2001) we have considered earlier suggestions (Garcia and Solomon, 1994; Mills *et al.*, 1999) that extend sulfate aerosol production above the previously accepted cut-off of ~ 30 km over the poles. In common with these earlier studies, microphysical modeling of sulfate aerosol condensation in the Stony Brook-St. Petersburg 3D chemical and transport model did not extend the condensation of sulfate aerosols significantly above 36-37 km for the temperature field of the 1993 Antarctic stratosphere, even when coupled with enhanced sulfate transport from the mesosphere, as in Mills *et al.* (1999). This mechanism therefore cannot provide heterogeneous conversion of N₂O₅ to nitric acid in the critical region above ~ 37 km. We also reconsidered earlier investigations involving ion-cluster reactions in place of standard heterogeneous chemistry, to carry the burden of N₂O₅ conversion above ~ 35-40 km. Kawa *et al.* (1995) had considered the ion-cluster reaction



first considered by Böhringer *et al.* (1983) in

relation to a different problem in stratospheric NO_y chemistry. Similar to standard heterogeneous reactions, ion-cluster reactions are orders of magnitude faster than gas-phase reactions (Böhringer *et al.*, 1983). Additional, more complex reactions such as



were considered by Aikin (1997), and any of these could serve to create HNO₃ at altitudes above ~ 35 km, although not all result in the non-clustered gas phase HNO₃ which is detected by the GBMS or CLAES instruments. In the model studies cited above, it appeared that a large ion-cluster density, such as those associated with unusually large solar flares, would be necessary to rapidly generate enough HNO₃ in the relatively short time-span required by observations. We believe these studies used models which did not incorporate a sufficiently large flux of NO_y (mostly NO₂) coming from the polar winter mesosphere, however, as discussed in Section 2.

When these combined mechanisms (sulfate aerosol formation, occurring when and where temperatures are cold enough below ~ 37 km, supplemented by ion-cluster reactions extending to ~ 45-50 km), are used along with an increase in the downward NO_y flux to realistic values, we have obtained calculated production of HNO₃ in quite good qualitative agreement with our GBMS observations from the South Pole (de Zafra and Smyshlyaev, 2001). We have gotten this agreement by assuming ion-cluster production only from the relatively constant galactic cosmic ray flux, as calculated by Beig *et al.* (1993), without adding input from solar events, or the supplementary ion reactions considered by Aikin. We also note that the global calculations of Beig *et al.* (1993) could only be verified against mid-latitude measurements, and may be uncertain by a factor of ~ 2 in polar regions (G. Brasseur, private communication). Given the relatively conservative assumptions we have made about total ion-cluster production, the use of only a single ion-cluster reaction, and the supplemental production by sulfate aerosols at altitudes above ~ 30 km where they can form, we believe the

question of how HNO₃ is generated throughout the polar winter stratosphere is probably no longer a mystery.

NO₂ can be converted to HNO₃ throughout most of its journey from the mesosphere through the polar stratosphere in winter. Because this process is undoubtedly variable, depending on changes in ion-cluster and sulfate aerosol density as well as on temperature, we believe that care must be exercised when interpreting amounts of NO₂ that reach the mid-to-lower stratosphere in one year relative to another (*e.g.*, Randall *et al.*, 1998 and 2001). These varying amounts may not accurately indicate variable rates of downward transport, or alternatively, variable production rates at high altitudes, until one factors in the role played by conversion to HNO₃ and the variation of that process over time, altitude, and seasons.

4. Annual variations of NO_y within the Antarctic vortex region

Although descent of NO_y from the upper atmosphere takes place during fall and winter, its effects on the polar stratosphere are not limited to those seasons. To study such effects, we have recently estimated the variations of the correlation curve between N₂O and NO_y, as a function of time and altitude in the Antarctic stratosphere (Muscari, 2001). Until now, many studies have used measurements of the NO_y-N₂O correlation curve taken outside the Antarctic vortex to represent pre-denitrification conditions (*i.e.* during fall) inside the vortex region. From this standard or reference relationship, the severity of denitrification within the winter or spring vortex has been inferred. If the vortex region hosts unusually large downward NO_y fluxes, however, or is characterized by a small but frequent mixing with regions at the edge of the vortex, the use of correlations from outside the vortex as reference for vortex conditions will lead to false conclusions (see, *e.g.*, Plumb *et al.*, 2000); in this case an under-estimation of the amount of NO_y removed annually from the polar stratosphere.

Our determinations of NO_y mixing ratio profiles cover the potential temperature range 465-960 K (~ 18-30 km), and have been ob-

tained for the spring and summer of 1993 and throughout the year 1995, when the largest overlap of data sets is available from both MLS and GBMS instruments. The estimation of NO_y involves the use of several sources of data: HNO₃ measurements by the GBMS (in good agreement with HNO₃ version 5 retrievals of the Microwave Limb Sounder onboard UARS, as shown by Muscari *et al.*, 2002); NO and NO₂ by the Halogen Occultation Experiment (HALOE) aboard UARS (Russell *et al.*, 1993), and NO₂ by the Polar Ozone and Aerosol Measurements II (POAM II) instrument aboard SPOT-3 (Glaccum *et al.*, 1996). Calculations of the minor NO_y constituents N₂O₅, ClONO₂, and HO₂NO₂, which are not readily available from measurements over the periods in question, are made from a photochemical box model. Since GBMS and satellite measurements are not co-located, we have used only satellite data that can be connected to GBMS measurements by air parcel trajectory tracing, and the box model takes into account any change in species concentrations that may occur along the trajectories. Local solar exposure and meteorological conditions along trajectories are taken from UKMO gridded reanalysis data for specific dates involved.

The NO_y values obtained, as well as the measured N₂O profiles, were binned in 6 pseudo-seasons defined as: Summer (Su), Fall (F), Early Winter (EW), Late Winter (LW), Early Spring (ES), and Late Spring (LS). Results for the year 1995 are shown in fig. 2a-c, where numbers next to data points indicate various potential temperature levels. In summer and fall (fig. 2a), before and during the formation of the polar vortex, with temperatures still above the HNO₃ condensation threshold, the correlation profile appears similar in shape to those observed in previous studies (*e.g.*, Fahey *et al.*, 1989): that is, the correlation shows linearity for N₂O values larger than 100 ppbv, with NO_y reaching its maximum for N₂O around 100 ppbv and then decreasing rapidly for smaller N₂O values. Data points from both seasons were fitted with a 4th order polynomial, shown as a black solid curve in fig. 2a. This fit suggests that the NO_y mixing ratio at the fall theta levels 585 K (n. 3) and 620 K (n. 4) may be biased high by ~ 10% with respect to the polynomial curve.

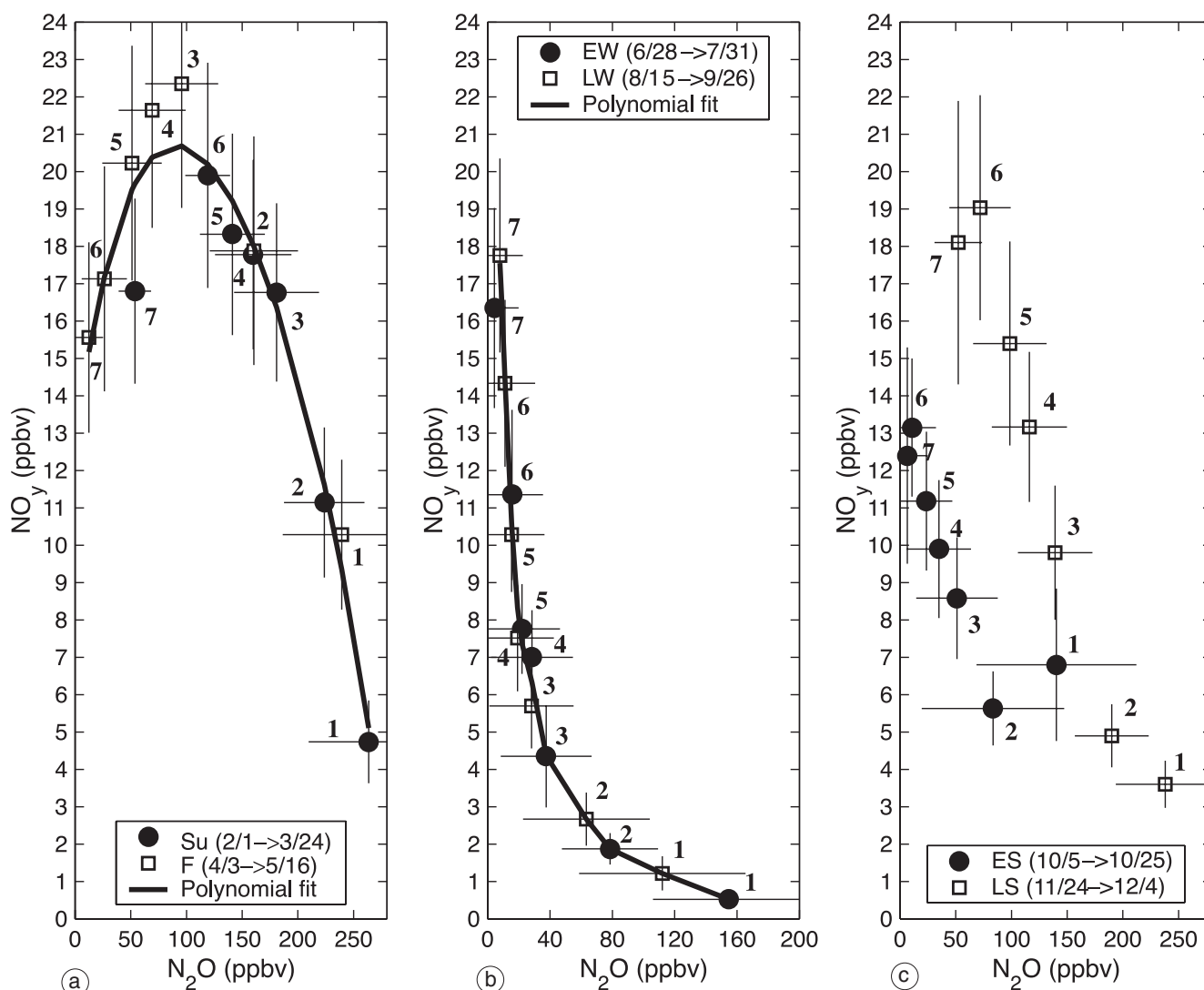


Fig. 2a-c. Correlation plots for NO_y versus NO_2 at various seasons within the region of the Antarctic vortex. a) Su = Summer, F = Fall; b) EW and LW = Early and Late Winter; c) ES and LS = Early and Late Spring. The black curves are 4th order polynomial fits to all data points in (a) and (b). Numbers from 1 to 7 designate increasing altitudes, at potential temperatures of 465, 520, 585, 620, 655, 740, and 960 K, respectively.

Between May 16 (last day of data averaged in the austral fall period) and June 28 (first day included in the early winter) temperatures in the vortex drop below 195 K at most altitudes considered here, and HNO_3 gas-phase depletion takes place through condensation on PSCs. Figure 2b shows a correlation clearly affected by NO_y depletion, and N_2O values that have decreased at all levels from fall to early winter, due to descent of N_2O -deficient air from the mid and upper stratosphere. (Notice the different X-axis scale between fig. 2b and fig. 2a,c). Both

early winter and late winter data points depict the same relationship between NO_y and N_2O , one sign of a vortex well isolated from the non-denitrified regions outside. The consistency between the NO_y - N_2O correlations obtained in early and late winter, together with that observed between summer and fall for N_2O mixing ratios larger than 100 ppbv, implies that these estimates have a greater precision than suggested by the formal error estimates indicated by error bars in the figure.

Downward transport inside the vortex is illustrated by the displacement along the winter

correlation that characterizes each theta level. The LW polar stratosphere is characterized by small concentrations of NO_y at lower theta levels, due to denitrification, and large concentrations of NO_y at the upper theta levels due to descent of air rich in NO_y but poor in N_2O . A 4th order polynomial fit to these winter curves is also displayed in fig. 2b (solid black curve).

Averaging meteorological data for fall and winter 1995, we calculated approximate NO_y column densities corresponding to the summer/fall and winter polynomial fits, over the range 10-300 ppbv of N_2O (~ 14-33 km for April 1995 over the South Pole). We obtained $\sim 2.5 \times 10^{26}$ molecules of NO_y/km^2 (or 5.8 kg/km^2 of nitrogen) for the 1995 summer/fall polynomial fit, and 1.42×10^{25} molecules of NO_y/km^2 (or 0.33 kg/km^2 of nitrogen) for the 1995 winter polynomial fit. If we approximate the mean size of the polar vortex with the size of the Antarctic continent, the total loss of nitrogen in the Antarctic stratosphere is about 7.6×10^7 kg. This estimate of the winter nitrogen loss is however a lower limit, because downward transport brings NO_y -enriched air from above 960 K, while NO_y depletion takes place in the lower stratosphere. Thus more nitrogen is removed from the lower stratosphere by the end of the winter/spring period than that which is initially present in the fall.

Figure 2c shows results for early and late spring, when the Antarctic polar vortex starts to weaken, and mixing across its edge leads to renitrification of the lower stratosphere. From LW to ES, the lower theta levels show an increase in both NO_y and N_2O . NO_y increases because outside the vortex the lower stratosphere experienced only a minor nitrogen loss (if any at all), while N_2O increases because the air outside the vortex did not experience the strong descent that took place inside the vortex, and N_2O concentrations are therefore larger. With the end of winter the downward motion inside the vortex decreases gradually and eventually comes to an end (Crewell *et al.*, 1995), cutting off the input of NO_y from the mesosphere. Level 960 K (black circle n. 7) shows the effect of such a cut off, exhibiting a lower NO_y mixing ratio with respect to winter values, while level 740 K (black circle n. 6) clearly shows the beginning of the effects of denitrification over the NO_y - N_2O

correlation curve. The comparison of LW with ES results underlines how the nitrogen lost by the stratosphere is not limited to the nitrogen present in the stratosphere at the beginning of the winter, but extends to the reactive nitrogen brought down by winter descent of mesospheric air.

The late spring period shows a partial return of the Antarctic stratosphere to pre-winter conditions, with an increase of both NO_y and N_2O at most levels. Such a recovery is particularly advanced at 740 and 960 K where, in late November, potential vorticity maps show that the vortex has ceased to exist.

Comparing our results for the austral summer and fall of 1995 with Atmospheric Trace Molecule Spectroscopy (ATMOS)/ATLAS-3 results obtained during November 1994 at high latitudes outside the southern polar vortex (see fig. 3), we find that the NO_y mixing ratio is 18% larger within the vortex at the NO_y peak. The result is in very good agreement with model estimates of the increase in NO_y mixing ratio in the Antarctic lower stratosphere due to upper atmospheric sources of NO_y (Callis *et al.*, 2001). If the ATMOS/ATLAS-3 curve shown in fig. 3 were used as a reference for vortex conditions prior to the reactive nitrogen loss during winter 1995, instead of our 1995 summer/fall polynomial fit, the total nitrogen present in the Antarctic lower stratosphere before denitrification (and therefore denitrification itself) would be underestimated by about 20%, or a total of 1.63×10^7 kg, if we again approximate the size of the polar vortex by the size of the Antarctic continent.

A difference between our NO_y - N_2O estimates and the ATMOS/ATLAS-3 data from November 1994 is also found when comparing the degree of denitrification reached at the lower levels of the NO_y - N_2O curve (see fig. 3). The consistency in our results between winter 1995 and early spring 1993 (not shown) suggests that the degree of denitrification in the Antarctic lower stratosphere does not have a large variability. (This is also suggested by the large, long-lasting volume of the lower stratosphere where temperatures fall well below the PSC-formation value of ~ 195 K every winter). Early and late winter of 1995 and early spring of 1993 show smaller values of NO_y with respect to ATMOS/

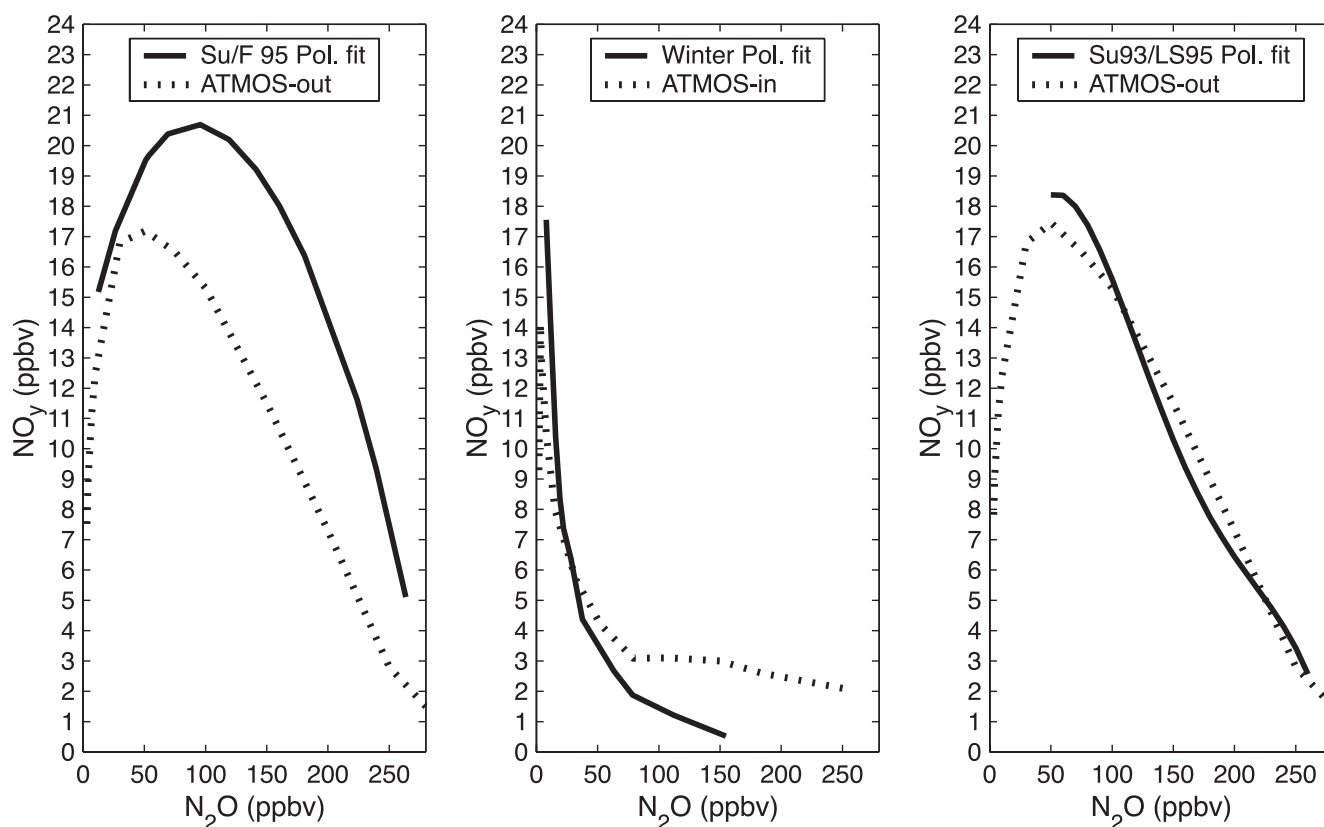


Fig. 3. Comparison of NO_y - N_2O correlations determined here, and those from the ATMOS/ATLAS-3 campaign of November 1994, obtained both outside (ATMOS-out) and inside (ATMOS-in) the Antarctic vortex. *Left panel:* the solid curve is the same as in fig. 2a, while dashed curve is ATMOS/ATLAS-3 data measured outside the Antarctic vortex boundary. *Middle panel:* solid curve is the same as in fig. 2b, while the dashed curve is ATMOS/ATLAS-3 data observed within the vortex. *Right panel:* the solid curve is the average of summer 1993 and late spring 1995 correlations, while the dashed curve represents ATMOS-out.

ATLAS-3 data for 1994 from inside the vortex. Although we cannot exclude interannual differences between 1993, 1994, and 1995, this discrepancy is more probably due to some mixing of air from the vortex edge with the denitrified air sampled by ATMOS in November, 1994, when vortex breakdown was well underway. Since this discrepancy is in the lower stratosphere, it does have a large impact on the underestimation of winter nitrogen loss discussed above. The effect is to add another 1.60×10^7 kg of nitrogen to the 1.63×10^7 kg computed earlier, making a total underestimate of $\sim 40\%$ from use of the ATMOS/ATLAS-3 extra-vortex reference curve.

The NO_y - N_2O correlation curves obtained in this recent analysis contribute to improving our knowledge about the transport of NO_y to the Antarctic lower stratosphere, and about winter

loss of nitrogen through HNO_3 condensation on PSC particles. Both phenomena are closely related to ozone loss and to climate-driving parameters such as temperature and aerosols concentration.

5. Summary

Following a considerable amount of research in polar regions by a large international effort, under the impetus of understanding seasonal polar ozone loss, we now know a great deal more about the annual cycle of oxides of nitrogen in the polar stratosphere. In this paper, we have concentrated on the cycle in Antarctica, since it currently results in considerably greater, as well as more regular, denitrification of the lower

stratosphere during winter. This occurs through the widespread and prolonged formation of polar stratospheric clouds, most likely a tripartite composite of HNO₃, H₂O and H₂SO₄ (*e.g.*, Santee *et al.*, 1998, and references therein), and their subsequent gravitational removal from the stratosphere. Poleward transport of NO₂ in the mesosphere and lower thermosphere is supplemented through formation by charged particles penetrating near the magnetic poles. Downward transport into the polar stratosphere creates a considerable flux of NO_y (mainly NO₂) during the winter. This NO₂ 'feed-stock', combined with efficient conversion to HNO₃ in the upper and middle stratosphere by ion-cluster reactions and heterogeneous reactions on sulfate aerosols, continually supplements the HNO₃ available to enter into PSCs in the lower stratosphere, where it is delivered by the steady subsidence of stratospheric air throughout the fall and winter.

Despite the new knowledge gained during the past 10-20 years, it appears that many, if not most, stratospheric chemical models still fail to properly account for the downward flux of NO_y in the polar winter stratosphere, often failing by one or more orders of magnitude (*e.g.*, see Park *et al.*, 1999). The larger winter flux of NO_y into the Antarctic vortex region, and perhaps other transport anomalies, moreover leads to a different 'pre-denitrification' relationship between N₂O and NO_y than the ones found experimentally at lower latitudes that have been used to represent this relationship within the vortex before denitrification occurs. This can lead to underestimates of the true removal of NO_y by as much as 40%.

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