GEOPHYSICAL RESEARCH LETTERS, VOL. 20, NO. 22, PAGES 2531-2534, NOVEMBER 19, 1993

NEW OBSERVATIONS OF THE NO_y/N_2O CORRELATION IN THE LOWER STRATOSPHERE

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Abstract. During the Airborne Arctic Stratospheric Expedition II (AASE II), September 1991 through March 1992, *in situ* measurements of reactive nitrogen (NO_y) and N_2O were made in the Northern Hemisphere lower stratosphere. We present an analysis of this new data and compare it with results from similar data taken during AASE in the winter of 1989. In the Northern Hemisphere there is a consistent linear correlation of N_2O and NO_y which shows no interannual variation. Cases of departure from a linear correlation are examined and classified as being due to denitrification (NO_y loss) or sampling air from a region where the photochemical lifetime of NO_y is decreased. The latter case was observed for the first time in the winter of 1992.

Introduction

Measurements of long lived tracers in the stratosphere provide a useful framework within which to interpret concurrently measured mixing ratios of photochemically active molecules [*Schoeberl et al.*, 1989, *Yatteau et al.*, 1990, *Kawa et al.*, 1992a]. These tracer measurements also provide data for comparison with 2D and 3D stratospheric models. *Plumb and Ko* [1992] have recently presented a general discussion of the character of the tracer correlations that are expected in the stratosphere. For tracers that are long lived relative to vertical transport times, linear tracer correlations are expected. This is the case frequently observed for the tracer pair N_2O and NO_y [*Fahey et al.*, 1990, *Kawa et al.*, 1990]. When tracer lifetimes are shorter, but are still long compared with horizontal transport times, correlations are still compact, but depart from linearity.

Previous *in situ* observations of N_2O and NO_y below 20 km show a linear correlation for values of N_2O above 100 ppb except where denitrification through PSC formation and particle sedimentation has occurred, or in cases where a PSC is actually present in the sampled air mass [*Fahey et al.*, 1990; *Kawa et al.*, 1992b]. At lower values of N_2O (higher altitudes) the lifetime of NO_y becomes shorter due to its photochemical destruction, and the correlation departs from linearity. Based upon ATMOS observations [*Gunson et al.*, 1990, *Russell et al.*, 1988] this departure occurs at N_2O below about 50 ppb at mid-latitudes [see *Fahey et al.*, 1990, Figure 2].

Paper number 93GL03004
0094-8534/93/93GL-03004$03.00

Experiment

The AASE II campaign and its general motivation are described in this issue [*Anderson and Toon*, 1993]. The N_2O instrument used for the AASE II campaign, the Airborne Tunable Laser Absorption Spectrometer (ATLAS) is described in detail in *Podolske and Loewenstein* [1993] and more briefly in *Loewenstein et al.* [1989, 1990]. The N_2O data has a 2-sigma uncertainty of ±10%.

The NOy instrument ($NO_y = NO + NO_2 + ClONO_2 + 2N_2O_5 + HNO_3$ + particulate nitrogen) used in this campaign is described in *Fahey et al.* [1989a]. The estimated 1-sigma uncertainty of the NO_y data is ±15 to 20%. The *in situ* N_2O and NO_y data are simultaneous measurements taken from the NASA ER-2 aircraft. Both instruments provide measurements at a rate of 1 hz. The results used in our analyses have been averaged over five second intervals (horizontal resolution 1 km).

Results and Discussion

During the AASE II field campaign the correlation of NO_y and N_2O was sampled on 18 flights, as well as 2 pre-campaign test flights, at latitudes from 22 to 90 degrees North (See Table 1 for flight parameters). The flights spanned latitudes inside and outside the North Polar vortex and provide a more extensive picture of the correlation of these tracers than obtained previously. However, the lower values of N_2O and correspondingly higher values of NO_y are observed only at the highest latitudes in winter because of the limited vertical sampling range available. Thus the largest dynamic range of this tracer correlation so far observed is at high latitudes during winter. Polar stratospheric temperatures during the winter of 1991-92 fell below the nitric acid tri-hydrate (NAT) saturation temperature at 50 mb for 40 days with the cold temperatures lasting into late January. By contrast in winter 1988-89 during AASE the number of days below the NAT limit was 69 and cold temperatures persisted into mid-February.

We have analyzed 20 flights of AASE II for which both N_2O and NO_y data are available (Table 1) and for most of them we observed a linear NO_y/N_2O correlation. For a subset of 17 flights for which N_2O values were all greater than 100 ppb we derived an average regression line for NO_y/N_2O. This is shown in Figure 1 along with the range of the regression fits for individual flights indicated by the hatched region. The NO_y/N_2O data from AASE in 1989 were analyzed by *Kawa et al.* [1990] and *Fahey et al.* [1990] who presented an average regression line for the data from that campaign. A comparison of the average NO_y/N_2O

Table 1: Minmum observed N_2O, Maximum observed ClO, and latitude range for 20 flights of AASE II used in the present analysis.

Date	Max. N_2O ppb	Min. ClO ppb	Latitude
910917	185	0.04	37.5-51
910919	180	0.02	37.5-22
911004	185	0.12	37.5-65
911006	140	0.07	65-85
911008	135	---	65-87.5
911010	135	0.07	65-71
911012	130	0.07	65-90
911014	170	0.05	65-37.5
911208	174	0.15	45-52
911214	175	0.12	45-68
920108	150	0.55	45-63
920112	170	0.12	45-22
920116	100	1.1	45-69
920120 *	65	1.5	45-68 (50)
920213 *	60	0.70	45-69 (56)
920217 *	46	1.0	45-69 (55)
920222	170	0.10	45-23
920315	170	0.12	45-67
920318	114	0.17	45-70
920322	175	0.12	45-24

* Flights not included in NO_y/N_2O regression average. Numbers in parentheses under latitude range are approximate latitudes at which the ER 2 crossed the the vortex wind speed maximum.

correlations computed for the two Arctic campaigns is shown in Figure 2. From these 2 data sets the average relationship for the Northern Hemisphere winter is:

$$[NO_y] = 20.7 - 0.0644\,[N_2O] \quad ; \quad 22 \text{ to } 90\ N$$

where N_2O and NO_y are in ppb. This is in general agreement with our theoretical understanding of the transport and photochemistry of these molecules [*Fahey et al.*, 1990, *Plumb and Ko*, 1992].

The data for the 17 flights in AASE II included in this average have been examined for correlations with sulfate particle surface area and concentrations of the radical ClO.

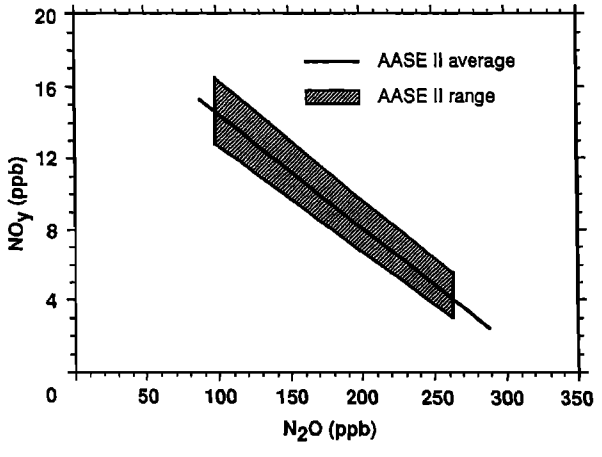

Fig. 1. The observed NO_y/N_2O correlation for the period September 1991 through March 1992: The solid line is the average of 17 flights (Table 1). The hatched region shows the range of observed NO_y/N_2O correlations.

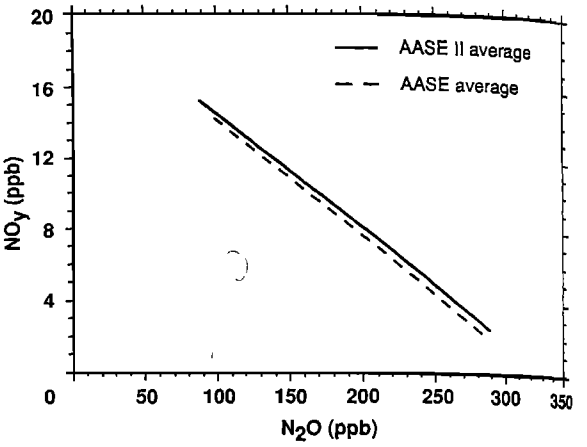

Fig. 2. The average NO_y/N_2O correlation observed during AASE and AASE II. AASE curve from *Kawa et al.* [1990].

The presence of enhanced radicals indicates chemical processing of the air and enhanced aerosol surface area is indicative of the presence of air containing Pinatubo volcanic aerosols. The NO_y/N_2O linear correlation is found to be unperturbed by abrupt increases of ClO by a factor of 10 or greater. These changes generally occur over a few degrees of latitude across the polar vortex edge, a region where abrupt changes of N_2O and NO_y are also observed [*Kawa et al*, 1990]. Similarly, no influence of enhanced particle surface area due to Pinatubo aerosols is observed in the NO_y/N_2O correlation data.

During the course of 3 flights which were directed into the vortex during AASE II we observed values of N_2O of 65 ppb or less (Table 1). The question arises whether these low values might have originated at altitudes approaching the peak of the NO_y vertical distribution. At altitudes above 25 to 30 km the NO_y distribution will be influenced by the loss reaction NO + N, and NO_y will, therefore, cease to be a very long lived tracer. We can thus expect that as N_2O values decrease below 100 ppb the gradient equilibrium condition will gradually cease to be valid. In gradient equilibrium the tracer lifetimes are long relative to the vertical transport time scale and the resultant tracer correlation is linear [*Plumb and Ko*, 1992]. Thus a linear correlation of N_2O and NO_y will no longer be observed in the data.

The linear correlation of N_2O and NO_y may also break down via denitrification as was observed in 1987 in the Airborne Antarctic Ozone Experiment (AAOE) and on some flights in AASE [*Fahey et al., 1989, Kawa et al.*, 1990]. In these cases it was demonstrated that the breakdown of the linear correlation reflects actual removal of NO_y through the sedimentation of polar stratospheric cloud (PSC) particles containing HNO_3. The signature of this deviation from a linear correlation is a sudden departure from the correlation line below some value of N_2O. In all AAOE flights into the vortex this value was about 140 ppb, a value consistently observed at about the location where temperatures fell below the nitric acid tri-hydrate (NAT) condensation temperature [*Fahey et al.*, 1989b]. In AASE on several occasions a similar sudden breakdown of the NO_y/N_2O correlation was observed.

Figure 3 shows examples of observed NO_y/N_2O correlations: 3a) a linear pre-vortex case from AASE II; 3b) a "variant" case from AASE II; and 3c) a PSC denitrification

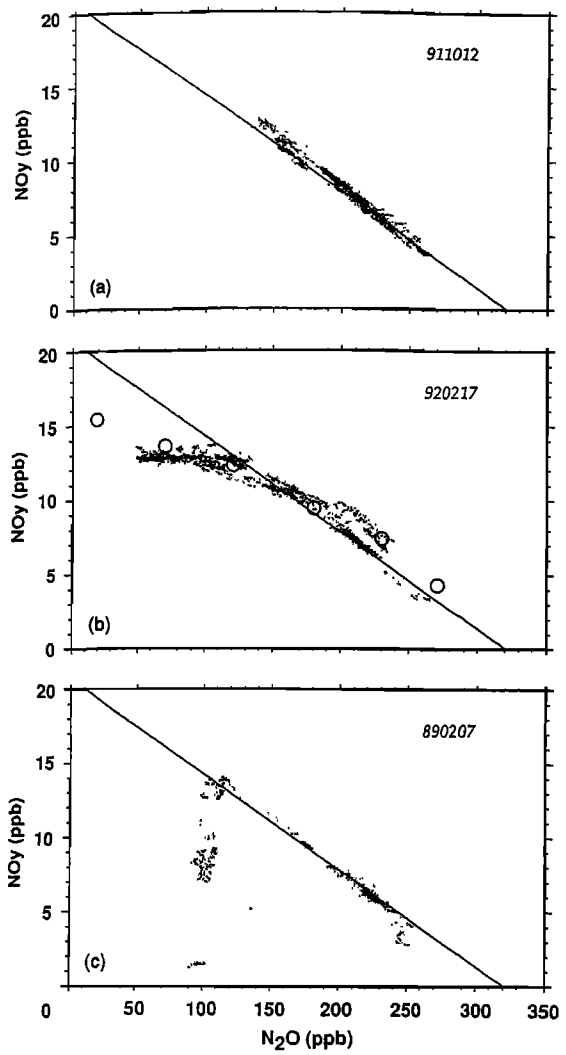

Fig. 3. Three cases of observed NO_y/N_2O correlations: a) linear correlation from AASE II; b) non-linear correlation from AASE II; open circles are from the Goddard mechanistic model discussed in the text; c) non-linear correlation from AASE illustrating denitrification. Solid lines show the average correlation given in the text.

case from AASE. Based on all the NO_y data it appears that in AASE II there were no observed cases of recently denitrified air. The 3 "variant" flights in AASE II (see Table 1) display departures from a linear NO_y/N_2O correlation at low N_2O values. The departure, illustrated in Figure 3b for one of these flights, is not characteristic of denitrification observed previously (Figure 3c), but appears more like behavior expected from sampling near the NO_y distribution peak.

Model Comparison

To gain insight into the expected NO_y distribution in winter at high latitudes we look at a model run for these conditions. Figure 4 shows N_2O and NO_y calculated for early winter 1989-90 using the Goddard Space Flight Center 3D chemistry and transport model [*Jackman et al.*, 1993]. A global, spectral, mechanistic model whose 100 mb lower boundary is continuously forced by daily NMC height analyses is used to produce winds and temperatures that

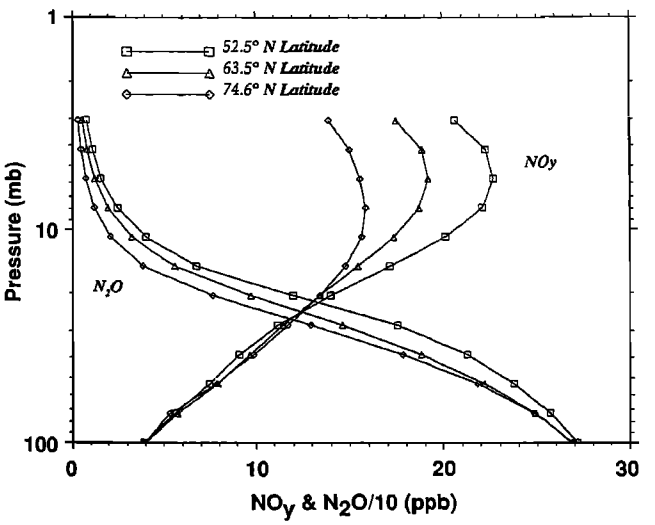

Fig. 4. Zonally averaged NO_y and N_2O profiles for three latitudes on January 3, 1990 from the GSFC mechanistic model [*Jackman et al.*, 1993]

drive the off-line 3D chemistry and transport model. The latter is initialized in late October 1989 with results from a 2D model. The results in Figure 4 are for Jan 3, 1990. They show that the altitude of the NO_y maximum as well as its magnitude decrease with increasing latitude. In the model the NO_y maximum at high latitudes descends with time through fall and early winter. Because strong descent in the polar vortex is observed to continue in January and February we might expect that the NO_y maximum would descend further by mid-February when the data in Figure 3b were taken. Open circles in Figure 3b are from the 75 N model run.

The model maximum NO_y at 75 N is 16 ppb, close to the maximum 13 ppb of NO_y observed on February 17, 1992, the flight shown in Figure 3b. The observed 50 ppb minimum N_2O on February 17 occurs slightly below the NO_y peak at about 20 mb in the model. The required 6 to 8 km descent to reconcile the model and measurements remains difficult to explain. The known cold pole problem in the mechanistic model makes it likely, however, that the model tracers will not show sufficient descent in the vortex. These model results make it plausible that the data of February 17 can be explained by dynamics. To test this idea and make detailed data and model comparisons, runs of the mechanistic model carried out for the AASE II time period are required.

Denitrification cannot be ruled out as a contribution to the observed NO_y/N_2O nonlinearity. However, back-trajectories of observed parcels with the lowest N_2O values for the 3 days showing non-linear NO_y/N_2O indicate almost no cases of temperatures low enough to form PSCs for the 10 days prior to the sampling of the relevant parcels. These regions also happen to correspond to the highest ClO values observed during the campaign ($ClO \geq 0.70$ ppb) indicating that heterogeneous processes must have occurred within the several weeks just prior to the observations. There is the possibility that denitrification occurred more than 10 days before the observation and that the NO_y/N_2O departure from linearity is a remnant of this earlier denitrification. In this case, however, mixing would tend to destroy the compact correlation observed in Figure 3b.

Summary

In a series of aircraft flights in the northern hemisphere (1989, AASE and 1991-92, AASE II) we have observed a consistent linear correlation between the tracers N_2O and NO_y. These data span a large latitude range (22 to 90 N), but are limited in the range of altitude, season, and of NO_y and N_2O values. The correlation is described theoretically in terms of the relationship of two very long lived tracers which are in gradient equilibrium, i.e. their lifetimes are long compared with vertical transport time scales [*Plumb and Ko,* 1992]. At higher altitudes or in PSC formation regions this linear relation is expected to fail. Such behavior due to PSCs has been observed in a number of cases in the Arctic vortex in 1989 as well as on all flights into the Antarctic vortex in 1987.

Deviations from a linear correlation were observed on 3 AASE II flights for $N_2O < 100$ppb. The most likely cause is interpreted here as dynamical rather than heterogeneous NO_y removal.

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(Received: March 12, 1993;
Revised: September 8, 1993;
Accepted: October 15, 1993)