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N_2O and O_3 relationship in the lowermost stratosphere: A diagnostic for mixing processes as represented by a three-dimensional chemistry-transport model

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Abstract. A three-dimensional chemistry-transport model has been used to investigate N_2O and O_3 distributions in the lowermost stratosphere at middle and high latitudes in the Northern Hemisphere. The model results are compared with detailed in situ aircraft observations, performed in the winters of 1994–1995 and 1996–1997 and spring 1996, as part of the Stratosphere Troposphere Experiment by Aircraft Measurements (STREAM) II and III. In addition, observations performed earlier in the winter of 1997 during the Polar Stratospheric Aerosol Experiment (POLSTAR) I mission have been included. It is shown that slopes from the observed N_2O-O_3 relationships can be used to characterize air masses in the lowermost stratosphere and to test a global tropospheric-stratospheric chemistry-transport model. The calculated slopes are consistent with the general view of the N_2O-O_3 distribution in the lower stratosphere. However, examining the lowermost stratosphere in detail, the model occasionally calculates significantly steeper slopes than observed. The observed shallower slopes reflect the presence of polar vortex air. Depending on the strength and the persistence of the polar vortex during winter, confined polar stratospheric air masses reach the tropopause, even during late spring at midlatitudes. This is consistent with the view that stratosphere-troposphere exchange and vortex erosion take place along isentropic surfaces from the polar reservoir.

1. Introduction

Global chemistry-transport models (CTMs), used to assess the tropospheric O_3 budget, need to simulate the lower part of the stratosphere correctly. One validation method is based on relationships of long-lived species. Thus the N_2O-O_3 relationship has previously been used to diagnose ozone depletion in the lower stratosphere [*Proffitt et al.*, 1990, 1993; *Bregman et al.*, 1995, 1997; *Grewe et al.*, 1998]. Owing to their long lifetimes in the lowermost stratosphere the slopes derived from the N_2O-O_3 relationship are assumed to obey the "slope-equilibrium" concept, representing a balance between transport and chemical processes [*Mahlman et al.*, 1986]. A significant change of the slopes on timescales shorter than the dynamic timescales can only be caused by relatively fast chemistry, for example, by photochemical O_3 production in the tropical stratosphere or by enhanced chemical O_3 loss in the polar vortex on aerosols or ice particles. Nevertheless, a model study by *Hall and Prather* [1995] illustrated that the latitudinal variation of the N_2O-O_3 slopes can be explained by standard gas phase chemistry in combination with transport. This means that the slopes reflect the "photochemical aging" of the air along its transit from the tropics to higher latitudes in the large-scale meridional circulation.

However, if mixing processes are dominant, the change in the N_2O-O_3 slopes may disappear when the air is mixed with air from chemically less active areas. Hence the existence of a slope gradient depends on the intensity of mixing between regions with different chemically active regimes, which, in turn, depends on the strength of potential transport barriers. In the lowermost stratosphere the most important regions in this respect are the polar vortex, the (sub)tropical stratosphere, and the troposphere. The N_2O-O_3 slopes can thus be used as a diagnostic tool to assess whether the CTM correctly describes tracer transport in the lower stratosphere.

Airborne in situ measurements and satellite observations confirm the latitudinal variation of the slopes, with decreasing values from the tropical region toward high latitudes and with less steep slopes inside than outside the polar vortex during wintertime [*Proffitt et al.*, 1990, 1993; *Michelsen et al.*, 1998, 1999].

The above mentioned previous observational and model studies mainly focused on the lower stratosphere. Little attention has been given to the lowermost stratosphere, that is, that part of the stratosphere where the potential temperature (θ) levels intersect the troposphere (below 380 K) [see *Holton et al.*, 1995]. It is generally assumed that the "equilibrium concept" of the N_2O-O_3 relationship is valid especially in this part of the stratosphere, because of the relatively short meridional mixing timescales. However, detailed in situ observations in the lowermost stratosphere have thus far been too sparse to confirm this. Measurements have been carried out on board the NASA DC-8 aircraft during the AASE II mission from January to March 1992 at middle and high latitudes in the

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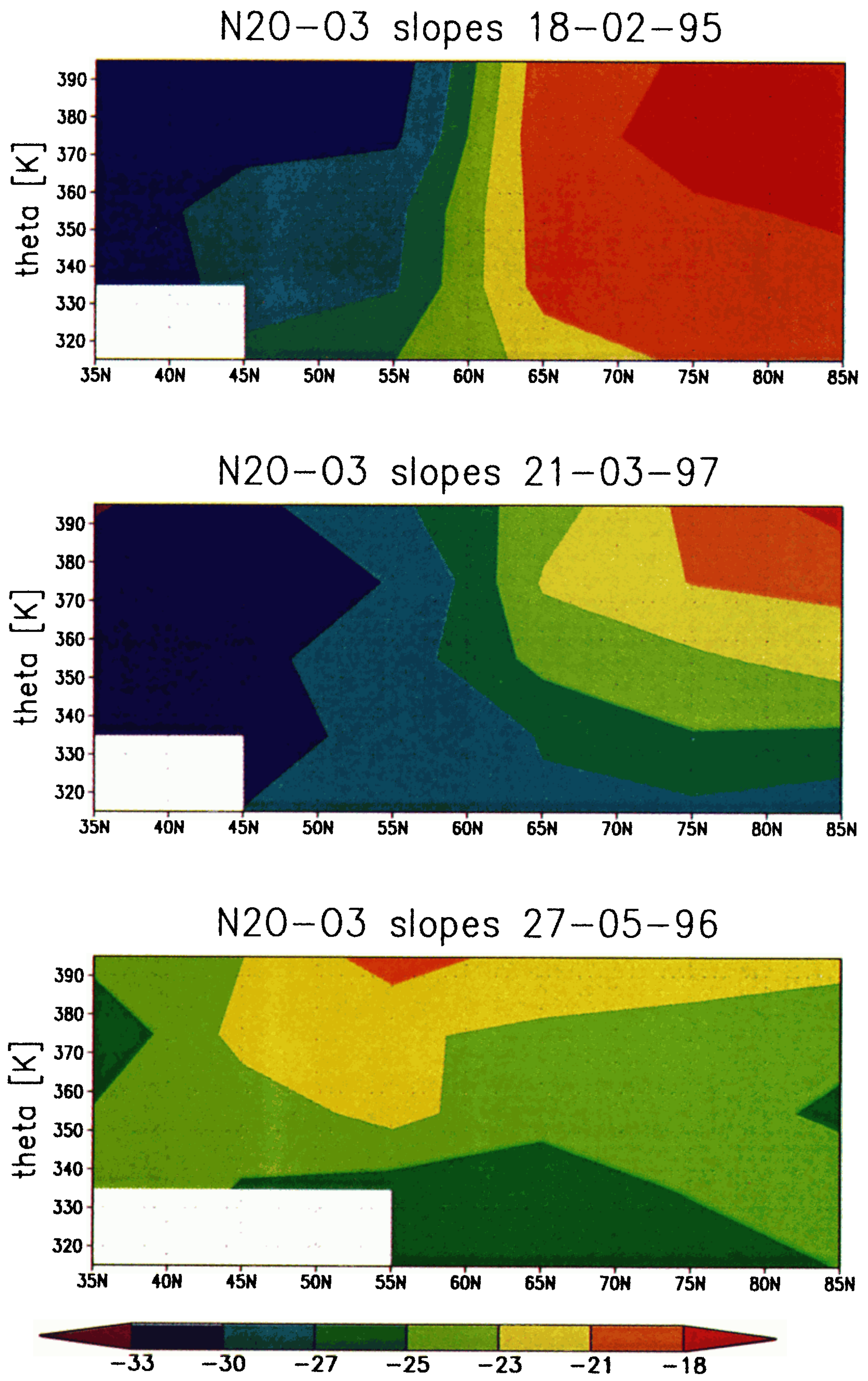

Plate 1. The N_2O-O_3 slope distribution as a function of potential temperature (K) and latitude, calculated by the Tracer Model version 3 (TM3) model for (a) February 18, 1995, (b) March 21, 1996, and (c) May 27.

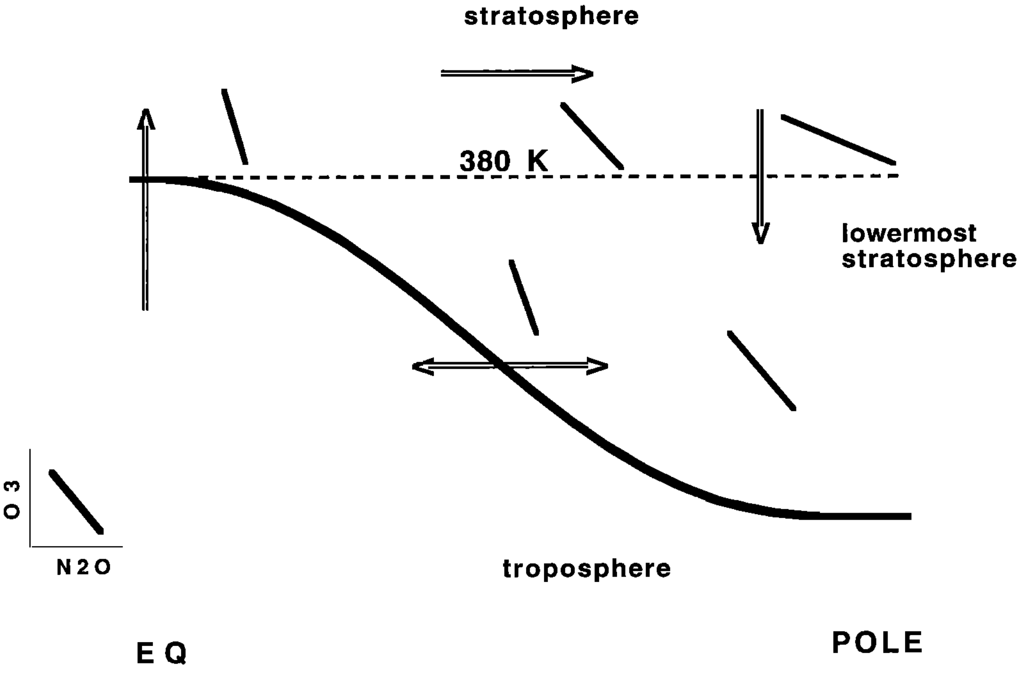

Figure 1. Schematic overview of the distribution of N_2O-O_3 slopes (single solid lines) in the lowermost stratosphere. The arrows denote the prevailing transport, and the bold solid line represents the tropopause (see text for details).

Northern Hemisphere [*Collins et al.*, 1993]. These data show relatively compact relationships and steeper slopes in January and February than in March. During the Pacific Exploratory Mission (PEM)-West B mission, N_2O and O_3 were measured at midlatitudes during March 1994, and these slopes were comparable to the March slopes discussed by Collins et al. [*Singh et al.*, 1997]. The reasons for these deviating slopes in March were not clear, and Singh et al. mention both the presence of polar vortex air and mixing of tropospheric with stratospheric air as possible causes.

The present study extends previous work by comparing detailed in situ observations in the lowermost stratosphere with the results of a three-dimensional CTM pertaining to different winters and spring in the 1995–1997 period. We illustrate that in combination with the analysis of time series, the slope diagnosis is a useful validation method for global three-dimensional CTMs. On the basis of the N_2O-O_3 relationship we characterize the air in the lowermost stratosphere and discuss the effect of chemical ozone loss and mixing processes on the slope distribution. In section 2 a description of the model is given. Section 3 outlines the general view of the N_2O-O_3 relationship in the lowermost stratosphere and describes the meridional and seasonal variation calculated by the model. A comparison between the model results and in situ observations is presented in section 4. Section 5 discusses the role of different mechanisms, which may cause a change of the N_2O-O_3 slopes. The conclusions follow in section 6.

2. Model Description

The chemistry-transport model Tracer Model version 3 (TM3) used describes tracer transport and chemistry in the troposphere and lower stratosphere up to 10 hPa. TM3 is an improved version from the original TM2 model, developed by *Heimann* [1993]. The model distinguishes 19 vertical layers, defined according to terrain following coordinates near the surface, pressure levels in the lower stratosphere, and a combination of the two in between. The vertical spacing in the area of interest in this study is approximately 1 km. The horizontal resolution of the model is 3.75° × 5° (latitude/longitude).

The horizontal and vertical tracer transports are derived from 6 hourly mean meteorological fields of the European Centre for Medium-Range Weather Forecasts (ECMWF). Advection is calculated with the first-order slopes scheme from *Russell and Lerner* [1981]. The cloud scheme of *Tiedke* [1989] is applied to calculate the subgrid-scale convective fluxes.

The total number of chemical species is 70, of which 30 are transported. The chemistry scheme contains 118 gas phase, 37 photolysis, and 30 heterogeneous reactions. The photolysis rates in the troposphere are calculated according to *Krol and van Weele* [1997] and *Landgraf and Crutzen* [1998]. The photolysis rates in the stratosphere are calculated from a radiation code originally developed by *Lary and Pyle* [1991]. Calculation of the absorption cross sections and quantum yields has recently been updated (G. Becker, private communication, 1998). The chemistry is solved with an implicit Eulerian backward iterative approximation [*Hertel et al.*, 1993] with an integration time step of 40 min. A more detailed description and validation of the model chemistry scheme is given by *van den Broek et al.* [2000].

Most of the tropospheric chemistry is adopted from *Houweling et al.* [1998], including the emissions of several trace species. The model further consists of an updated algorithm [*Carslaw et al.*, 1995a, b] to calculate heterogeneous reaction rates on supercooled liquid and solid particles of soluble species in the stratosphere. The sulfuric acid fields are calculated iteratively using SAGE II aerosol surface area density fields [*Thomason and Poole*, 1997], updated for 1995, 1996, and 1997 (L. W. Thomason, personal communication, 1999), and the analytic expressions from *Carslaw et al.* [1995a, b].

Surface level N_2O, CH_4, CFC 11, and CFC 12 concentrations and atmospheric growth rates are taken from the *World Meteorological Organization (WMO)* [1998] estimates.

In the top three layers of the model (10–50 hPa), total inorganic chlorine, bromine, and nitrogen (Cl_y, Br_y, and NO_y) are constrained using observed correlations with N_2O [*Daniel et al.*, 1996; *Keim et al.*, 1997]. In addition, O_3 is constrained in the same layers by a zonal mean O_3 climatology [*Fortuin and Kelder*, 1998] using a relaxation time of 3 days to take into account the longitudinal O_3 variations, associated with synoptical disturbances in the troposphere [*Lelieveld and Dentener*, 2000]. Since the O_3 climatology does not include the years studied in this paper, we scaled the stratospheric levels using the Global Monitoring Experiment (GOME) on board the ERS-2 satellite. We have used GOME level 2 monthly mean total O_3 column observations of 1996 (M. Bittner, personal communication, 1998), which show good agreement with ground-based total ozone observations [*Lambert et al.*, 1999]. F11, F12, CH_4, and N_2O concentrations are constrained only at the top (10 hPa) based on cryogenic limb array etalon spectrometer (CLAES) observations, performed on the UARS satellite [*Roche et al.*, 1996; *Nightingale et al.*, 1996]. We have used 1992 and 1993 CLAES observations version 7 and created zonal and monthly mean 10 hPa fields for every month between 76°S and 76°N and extrapolated these to the poles. We further applied the same relaxation method as for the O_3 climatology. The model was initialized with the O_3 climatology of *Fortuin and Kelder* [1998] between 1000 and 10 hPa and two-dimensional model results [*Law and Pyle*, 1993] for the long-lived trace species at January 1, 1994. We ran the model from this date to the time of the in situ observations described in section 4.

3. N_2O-O_3 Relationship

3.1. Latitude and Altitude Dependence

N_2O is emitted in the troposphere by biogenic and antropogenic processes. Its major sink is photolysis in the middle and upper stratosphere and oxidation by $O(^1D)$ in the lower stratosphere [*Intergovernmental Panel on Climate Change*, 1990; *WMO*, 1998]. As a consequence, its local chemical lifetime in the troposphere is very long (thousands of years), decreasing to weeks or less in the middle stratosphere, and it is of the order of 100 years in the lowermost stratosphere [*Prather and Remsberg*, 1992]. In contrast, O_3 production occurs primarily in the (sub)tropical stratosphere, driven by the photolysis of O_2 (Chapman cycle). Its chemical breakdown occurs mainly through the catalytic HO_x(=OH + HO_2), NO_x(=NO + NO_2), ClO_x(=Cl + ClO), and BrO_x(=Br + BrO) cycles [e.g., *Wayne*, 1994]. The chemical lifetime of O_3 is therefore much shorter than of N_2O, varying from several weeks in the tropical lower stratosphere [*Ko et al.*, 1989] to more than a year at middle and high latitudes in the lowermost stratosphere [*Solomon et al.*, 1985]. Since the N_2O source and destruction region is opposite to that of O_3, these species are anticorrelated, so that the slopes are negative. Even in the tropical lower stratosphere, the chemical lifetime of O_3 is sufficiently long to maintain a significant anticorrelation with N_2O. Since the O_3 relative to N_2O levels are higher than at high latitudes, the N_2O-O_3 slopes decrease from the tropics towards higher latitudes. Figure 1 illustrates the latitudinal and altitude dependence of the N_2O-O_3 slopes in the lowermost stratosphere. Through the Brewer-Dobson circulation the uplifted tropical air is transported to higher latitudes [*Haynes et al.*, 1991]. During this transport the slopes decrease as a result of chemical O_3 loss. At higher latitudes the air is transported to the lowermost stratosphere in the downward branch of the Brewer-Dobson circulation. As mentioned in section 1, the existence of a meridional slope gradient in the lowermost stratosphere depends on the balance between meridional mixing and chemistry. This implies that the strength of the polar front and diabatic descent in the polar regions [*Manney et al.*, 1994] and the intensity of mixing from the (sub)tropics [*Appenzeller et al.*, 1996] play an important role. Hence, if this meridional gradient exists, it is expected to be present mainly during winter and early spring. Farther down, the lowermost stratosphere is affected by transport from the troposphere [e.g., *Holton et al.*, 1995; *Chen*, 1995] and its influence on the N_2O-O_3 slope will be discussed in section 5.2.

3.2. Model N_2O-O_3 Slope Distribution

The N_2O-O_3 slope distribution is calculated with the TM3 model for the northern winter 1994–1995 and for the period March 1996 to March 1997. It is particularly interesting to compare the 1994–1995 and 1996–1997 winters, because the meteorological situation in the lower stratosphere was quite different during those winters. During the 1994–1995 winter the vortex was strongly developed with relatively low temperatures already in December 1994, which continued for at least 2 months. The 1996–1997 winter was relatively warm with a weakly developed vortex until the end of January, after which the vortex became very strong and isolated [*Coy et al.*, 1997]. Plate 1 illustrates the general distribution of the N_2O-O_3 slopes (ppbv $ppbv^{-1}$) in the lowermost stratosphere, as calculated by the model. It shows the calculated latitudinal cross sections of the N_2O and O_3 slopes as a function of θ in the northern hemispheric lowermost stratosphere up to 400 K for February 18, 1995, March 21, 1997, and May 27, 1996. These dates were chosen on the basis of available in situ observations, as will be described later. The slopes were calculated in bins of 10° latitude and 15 K, and for all longitudes within these bins, except for tropospheric air (where $O_3 > 100$ ppbv). The white areas indicate that all longitudes contained tropospheric air. For both winter days the minimum slopes vary from -30 to -35 in the tropical region to -15 at high latitudes. A similar pattern was calculated by *Hall and Prather* [1995] for θ levels exceeding 360 K. In the lowermost stratosphere the latitudinal gradient decreases but is still discernable at midlatitudes on February 18, 1995, and March 21, 1997. On February 18, 1995, the calculated slopes agree with those observed by *Collins et al.* [1993], but they are somewhat steeper on March 21, 1997.

However, between both winters, significant differences are apparent (Plates 1a and 1b). On March 21, 1997, the slopes at high latitudes are much steeper than on February 18, 1995. The air is "photochemically older" in February 1995 compared to March 1997. This is consistent with the difference in duration and strength of the polar vortex between both winters, as mentioned earlier. Later we will illustrate the minor role of heterogeneous chemistry in the polar vortex on the N_2O-O_3 slope distribution in the lowermost stratosphere. The much steeper slopes in March 1997 north of 65°N between θ levels of 340–370 K indicate a higher degree of mixing with air from midlatitudes, whereas the less steep slopes in February 1995 indicate a stronger influence of polar vortex air. A more strongly developed polar vortex allows the air parcels, being O_3 depleted, to reach the lowermost stratosphere by diabatic descent across the bottom of the vortex, which is generally found at θ levels of 380–400 K. In 1996–1997 the polar vortex started to cool down much later in the winter, and therefore the slopes are steeper in March 1997 compared with February 1995, despite the observed record low column O_3 densities in March 1997 [*Coy et al.*, 1997]. It is important to realize that these low total column O_3 densities reflect O_3 loss within the vortex and that this O_3 depleted air has not yet reached the lowermost stratosphere in March.

The occurrence of very low temperatures in the polar vortex air in December 1994 and January 1995, and the differences with March 1997, are corroborated by HNO_3 and NO_y observations during the same missions. In February 1995, indications of denitrification were found by HNO_3-H_2O cloud particle sedimentation from ~20 km altitude and subsequent evaporation of the particles at ~12 km altitude [*Sugita et al.*, 1998; *Waibel et al.*, 1999; *Fischer et al.*, 1997], whereas the March 1997 data did not show any sign of denitrification [*Fischer et al.*, 2000]. It is not likely that such strong denitrification signals would have been observed in 1995 if the polar vortex was warmer and less isolated.

In contrast with the wintertime slope distribution the slopes on May 27, 1996, show no meridional gradient and are relatively constant in altitude, reflecting well-mixed conditions throughout the lowermost stratosphere after the vortex aloft has disappeared. The levels vary between −25 and −21 in agreement with the observed slopes at midlatitudes in March 1992 [*Collins et al.*, 1993]. Note that the slopes at midlatitudes are steeper in winter than in May, indicating a stronger influence from the (sub)tropical stratosphere in winter containing steeper slopes. This agrees with *Appenzeller et al.* [1996], who found that downward transport by the meridional circulation from the tropics, across the 380 K potential temperature level, into the lowermost stratosphere at midlatitudes reaches a maximum during winter and reaches its minimum during late spring and early summer.

The seasonal variation of the N_2O-O_3 slopes is illustrated in Figure 2 which shows the calculated slopes for every first day of the month from March 1996 to March 1997 at three different isentropic levels, averaged between 65° and 75°N (Figure 2a) and 45° and 55°N (Figure 2b). During winter at high latitudes the slopes are less steep than during late spring after the vortex has disappeared, and the air is mixed with air from midlatitudes. The slopes flatten in late winter when polar vortex air, containing less O_3 relative to N_2O, is transported into the lowermost stratosphere by diabatic descent. At midlatitudes the seasonal dependence of the slopes shows a somewhat different pattern. Also, the vertical gradient is significantly less during most of the year than it is at high latitudes. During winter the slopes are steeper than at high latitudes. In late winter and spring the slopes flatten because of mixing with high-latitude air, which is transported downward by diabatic descent from the polar vortex in agreement with the diagnosis of SAGE II observations by *Wang et al.* [1998]. The steepest slopes are found in early winter, when downward transport into the lowermost stratosphere from the global-scale meridional circulation is at maximum [*Appenzeller et al.*, 1996].

Although very little observational evidence is available from the lowermost stratosphere to illustrate the seasonal and latitudinal variation of the slopes, these findings appear consistent with the general understanding of the N_2O-O_3 relationship in this part of the atmosphere. However, the results also illustrate the presence of polar vortex air in the lowermost stratosphere, transported by diabatic descent during wintertime and early spring across the bottom of the vortex. Depending on the strength of the polar vortex and the subsequent downward transport prior to the dates in Figure 2, a weak meridional gradient may appear, indicating a strong influence of polar vortex air down to θ levels of approximately 350 K. Evidently, this air was not yet mixed effectively with (sub)tropical air. As will be discussed in section 4, observations, indeed, provide evidence of polar vortex air in the lowermost stratosphere.

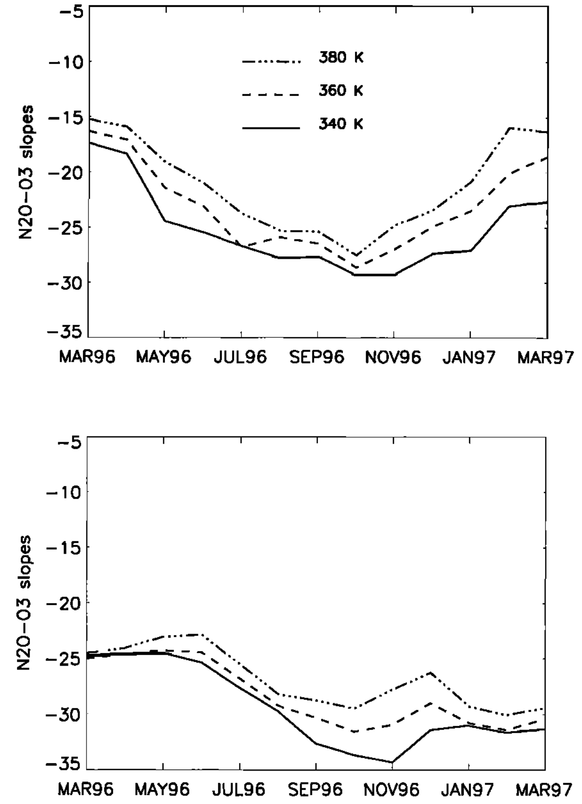

Figure 2. The calculated N_2O-O_3 slopes at the first day of every month between March 1996 and March 1997, calculated by linear interpolation for three different potential temperature surfaces at (a) high latitudes 65°–75°N and (b) midlatitudes 45°–55°N.

4. Model Results and Aircraft Observations

4.1. Observations

The observations were made near the Arctic Circle during February 1995 and March 1997 and in midlatitudes during May–June 1996 in the framework of the Stratosphere Troposphere Experiment by Aircraft Measurements (STREAM) project. In this project, in situ measurements of a variety of trace gases and particles have been carried out in the tropopause region on board a Cessna Citation twin-engine jet aircraft. In 1995 and 1997 the flights were performed from Kiruna airport (67.9°N) in north Sweden, and during 1996 the flights were from Shannon airport (52.4°N) in Ireland. We discuss eight high-latitude flights, performed on February 9, 18, 21, and 24 (1995) and March 9, 14, 21, and 23 (1997) and three midlatitude flights, performed on May 22, 23, and 27 (1996). The 1995 and 1997 N_2O data were measured with a Tunable Diode Laser Absorption Spectroscopy (TDLAS), developed at the Max-Planck-Institute for Chemistry, Mainz, Germany. The technique is described in more detail by *Wienhold et al.* [1994, 1998]. The overall measurement accuracy during both missions was 2.8%. The 1996 N_2O measurements were performed with a novel in situ gas chromatograph, called Gas Chromatograph for the Observation of Stratospheric Tracers (GHOST), developed at the Forschungszentrum, Jülich, Germany. This technique is described in detail by *Bujok* [1998] and O. Bujok et al. (GHOST-A novel airborne gas chromatograph for in situ measurements of long-lived tracers in the lower stratosphere, submitted to *Journal of Atmospheric Chemistry*, 2000) (hereinafter referred to as Bujok et al., submitted manuscript, 2000). The precision and accuracy were better than 0.8% and 2%, respectively. For two flights of the STREAM 1997 campaign the TDLAS N_2O measurements were compared with the GHOST measurements. The data from both instruments agreed within their combined uncertainty (Bujok et al., submitted manuscript, 2000). During all three STREAM missions, O_3 was measured with a Bendix 2002 chemiluminescence monitor, described by *Bregman et al.* [1995]. The average precision was 2%; the accuracy was 10% during STREAM 1995 and was 5% during STREAM 1996 and 1997.

The O_3 and N_2O data from the STREAM 1995 and 1997 missions have been described and discussed in other studies. The observations from the high-latitude mission during STREAM 1995 are described by *Fischer et al.* [1997] and *Lelieveld et al.* [1999]. The March 1997 O_3 and N_2O measurements are discussed by *Fischer et al.* [2000], *Lelieveld et al.* [1999], and *Schneider et al.* [1999].

In addition to the STREAM missions, during January 1997 in situ measurements of O_3 and N_2O in the lowermost stratosphere in the same flight area were performed on board the German Falcon aircraft during the Polar Stratospheric Aerosol Experiment (POLSTAR) I project (H. Ziereis et al., Aircraft measurements of NO_y, O_3, and tracer correlations in the Arctic subvortex region during POLSTAR, manuscript in preparation, 2000). The flights were carried out on January 24, 28, and 30 and February 1, 4, and 6, 1997.

Since the POLSTAR I measurements were performed 1–2 months prior to the STREAM observations, we have the opportunity to compare the O_3-N_2O slopes in "well-mixed" conditions with those when the vortex aloft was established a month before the observations were performed, whereas it remained strongly isolated at least until the end of the measurement campaign.

4.2. N_2O-O_3 Time Series

In Figure 3 the time series of the observed and the modeled O_3 and N_2O mixing ratios are shown for the three STREAM missions. Both N_2O and O_3 were sampled at a frequency of 1 Hz, and the data shown represent 1 min average data, except N_2O during 1996, which was sampled once every 2 min (shown with squares). Two flights of each mission have been chosen, illustrating features typical for the particular mission. The model-calculated tracer fields were interpolated to flight locations and pressure levels. Only the data at pressure levels below 700 hPa are presented.

The model-calculated O_3 concentrations are overestimated relative to both flights' measurements in 1995 and on the highest flight level during May 23, 1996; they are underestimated on the first part of the flight on March 23, 1997. The calculated N_2O mixing ratios show good agreement, except at the highest flight levels in 1996 and on March 14, 1997. During the flight on May 23, 1996, one would expect the observed decrease in N_2O to coincide with an increase in O_3, as calculated by the model. Remarkably, however, the observed increase at the highest flight levels is almost negligible, and the model consequently overestimates O_3.

There is considerable small-scale variability discernable from the observations, which is obviously not followed by the model. For example, the significant O_3 decrease observed at the highest flight level on February 21, 1995, coinciding with an increase in N_2O, is caused by an intrusion of subtropical air at spatial scales not resolved by the model.

Considering the relatively coarse horizontal and vertical resolution and the fact that the horizontal flight area covers only a few grid boxes, the model is able to simulate the trace gas distributions for many flight levels relatively well. However, there are also significant deviations between observations and model calculations, which cannot easily be explained. Therefore another useful way to compare the model results with the observations is to investigate the tracer correlations.

4.3. Correlations

By comparing the modeled and observed N_2O-O_3 relationship, we obtain a consistent picture. Plate 2 shows the observed (dots) and modeled (squares) N_2O-O_3 relationships for all flights of the 1995 and 1997 STREAM winter missions and the POLSTAR I mission. It is interesting to see the clear differences in the structure of the observed relationship during both STREAM missions. The 1995 measurements show much more scatter than in 1997 and contain three data clusters with significantly less steep slopes. This is consistent with the fact that the lowermost stratosphere in 1995 contained more polar vortex air than in 1997. Additional indicators of enhanced polar vortex air presence in 1995 are given by the lower N_2O concentrations in 1995 compared with 1997 and by the potential vorticity (PV) of the sampled air parcels. ECWMF analyses indicate (not shown) that the PV along the flight tracks were approximately 2 PV units higher in 1995 than in 1997 for the same pressure levels relative to the tropopause. Note further that the observed slopes in February 1995 are comparable to what has been observed previously within the polar vortex at pressure levels below 100 hPa [*Proffitt et al.*, 1993], and very similar slopes are calculated by the model for the same pressure levels, being 1–2 grid boxes higher than the locations of the interpolated model results. Recent observations illustrate the decrease of the N_2O-O_3 slopes in the lower stratosphere through mixing of vortex with extravortex air [*Michelsen et al.*, 1998, 1999]. The ER-2 measurement data of *Michelsen et al.* [1998, 1999] demonstrate that these "mixed" slopes decrease further to typical polar vortex slopes down to altitudes where N_2O mixing ratios are about 220–230 ppbv. Here we show that in 1994–1995 slopes occurred that are typical of the polar vortex.

A linear fit of the POLSTAR I N_2O-O_3 relationship is shown by the solid blue line in Plate 2, with the vertical lines indicating the scatter. Since the POLSTAR I mission took place 1–2 months prior to STREAM, the slopes are slightly steeper than the STREAM 1997 slopes, indicating a higher degree of mixing with midlatitude air in January than in March 1997. The period between establishment of the vortex (mid-January) and the POLSTAR I flights was too short to transport polar vortex air into the lowermost stratosphere. About 1–2 months later, a weak influence of polar vortex air shifted the STREAM N_2O-O_3 slopes slightly downward.

The interpolated model results show steeper slopes than

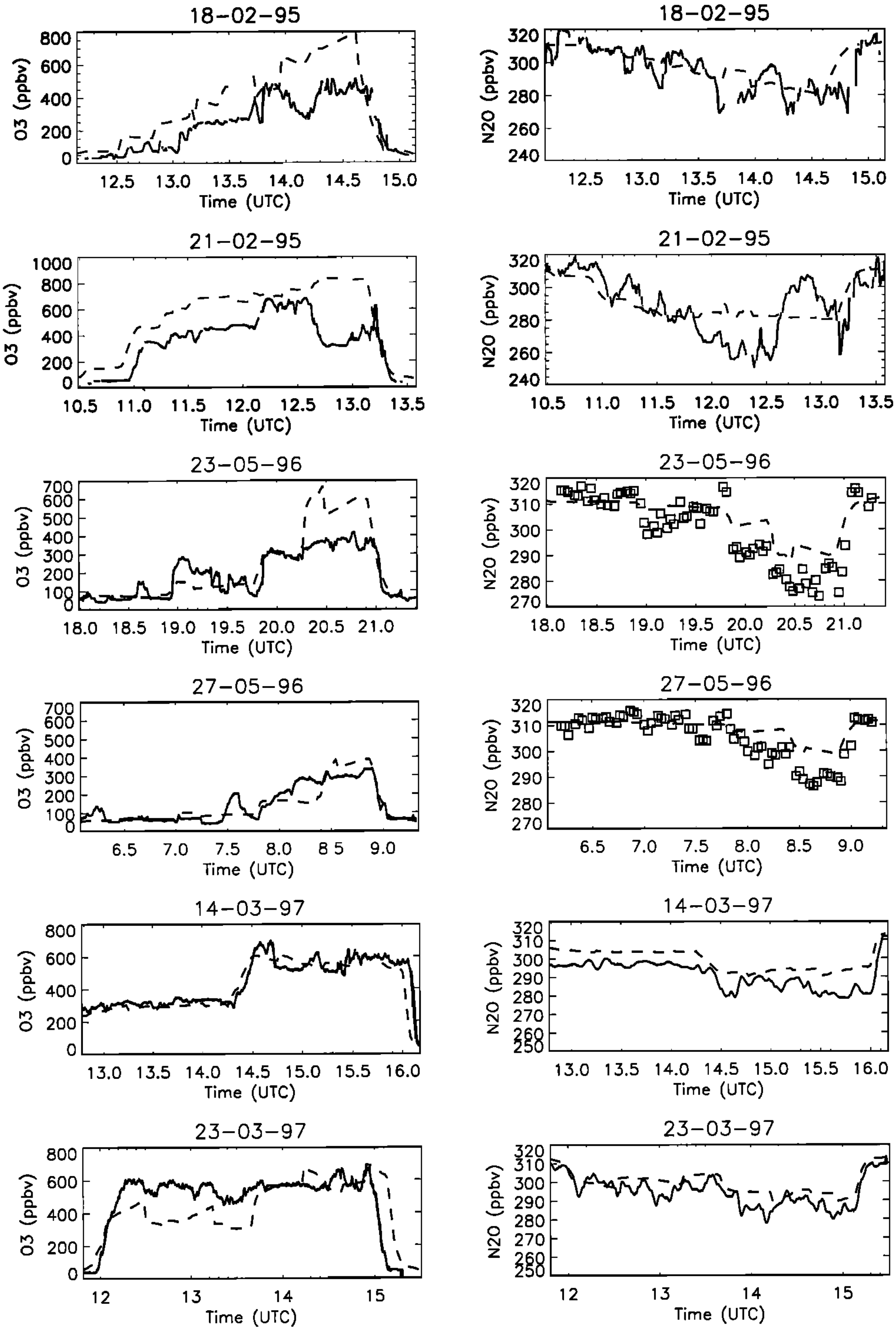

Figure 3. Time series of N_2O and O_3 mixing ratios (ppbv) measured during Stratosphere Troposphere Experiment by Aircraft Measurements (STREAM) in February 1995, May 1996, and March 1997. Dashed lines show the interpolated model results.

observed. However, the calculated slopes show better agreement when the observed slopes represent well-mixed conditions. The largest differences are found for STREAM 1995, whereas the calculated slopes on January 2, 1997 are close to the POLSTAR I data.

Figure 4 show the results from three flights during STREAM 1996, as well as the interpolated model results. The agreement between the observations and model is good at N_2O mixing ratios exceeding 300 ppbv, although at lower N_2O levels the calculated slopes are much steeper. A number of observations at middle and high latitudes indicate that these observed deviating slopes are typical for the polar region during wintertime [*Collins et al.*, 1993; *Proffitt et al.*, 1990, 1993; *Michelsen et al.*, 1998]. We have investigated at which time and location the model calculates slopes comparable to those observed. The steep solid line in Figure 4 illustrates the calculated midlati-

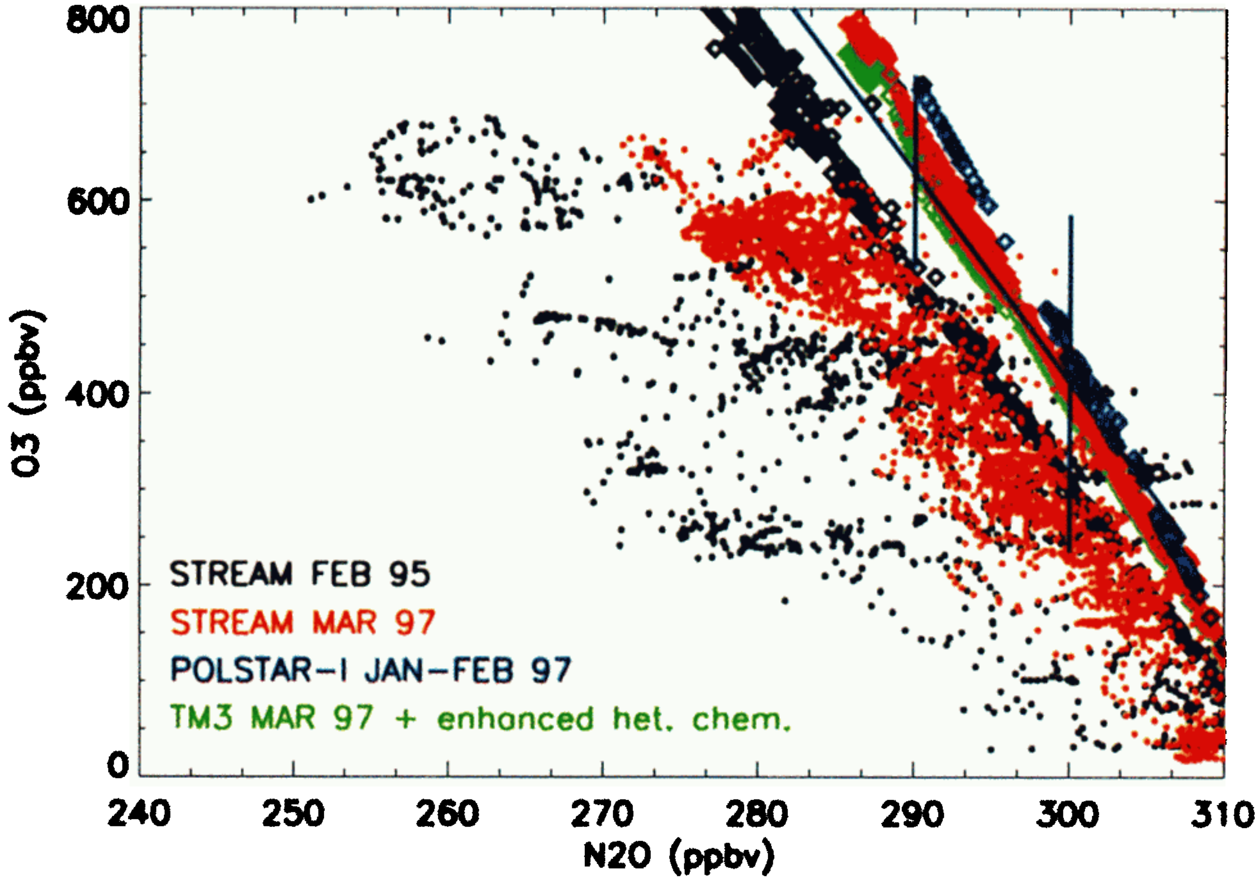

Plate 2. N_2O versus O_3 mixing ratios (ppbv) as observed in January and February 1997 during POLSTAR-I (blue solid line), February 1995 (black dots) and March 1997 (red dots) during STREAM. The diamonds show the model results pertaining to each mission. The green squares represent model results for all STREAM flights during March 1997 including enhanced heterogeneous chemistry. See text for details.

tude slopes at a θ level of 380 K for May 1996. Although this slope is slightly smaller than the interpolated slopes at lower θ levels, it is still significantly steeper than observed, so that it is unlikely that downward transport at midlatitudes caused the observed deviating slopes. The lower solid line represents the calculated slopes at a θ level of approximately 425 K in February 1996 at 70°N, being comparable with the observed slopes, suggesting that the air originates directly from the polar vortex. Note that the polar vortex during the 1995–1996 winter was extremely long-lived, until at least mid-April 1996, while severe chemical O_3 loss took place [e.g., *Müller et al.*, 1997; *Hansen et al.*, 1997], in line with the possibility that remnants of the polar vortex can be observed even during late May. However, it remains remarkable that these confined polar air masses occur so close to the midlatitude tropopause, at least on several days in the May 22–27 period, as observed in different flight directions.

It is interesting to note that previous studies suggested the presence of polar vortex air at midlatitudes during springtime in the lowermost stratosphere. For example, *Reid and Vaughan* [1991] observed O_3 depleted laminae at midlatitudes, based on O_3 sonde and lidar measurements, with peak frequencies between 13 and 15 km altitude during April and May. They suggested that the air originated from the polar vortex, which, after having descended to the base of the vortex by diabatic cooling, was transported to midlatitudes. Another study showed N_2O-O_3 slopes in the lowermost stratosphere, based on observations during PEM-West [*Singh et al.*, 1997] at midlatitudes during March 1994, which were only slightly steeper than the depressed slopes discussed here. Although *Singh et al.* [1997] also mention mixing with tropospheric air as a possible cause, it is more likely that they sampled air masses that originated from the polar region.

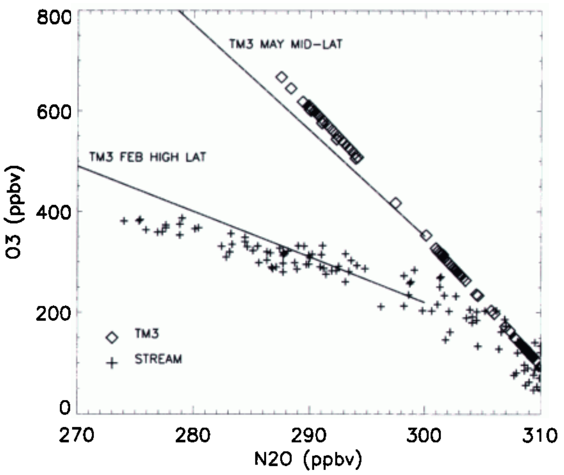

Figure 4. N_2O versus O_3 mixing ratios (ppbv) of all STREAM III observations in May 1996 (crosses) and the interpolated model results (diamonds). The solid lines represent (upper solid line) model calculations for midlatitude conditions during May and (lower solid line) polar conditions during February 1996 (see text for details).

5. Discussion

5.1. Model Uncertainties

The model is able to reproduce differences in the N_2O-O_3 slopes between the winters of 1994–1995 and 1996–1997, but the differences are too small, and the calculated slopes are overestimated when the influence of the polar vortex becomes discernable in the observations. This is either due to an overestimation of the O_3 (1995) or the N_2O mixing ratios (1996 and 1997), as can be seen in the time series comparisons (Figure 3). Since the slopes reflect "photochemical aging," the air in the lower stratosphere in the model has not resided in the stratosphere long enough, that is, the tropospheric influence is too recent. The top of the model at 10 hPa may affect the representation of the meridional transport, such that transport from the (sub)tropics to midlatitudes is too rapid. Consequently, enhanced mixing between the lowermost stratosphere and polar vortex air does not lead to a sufficiently large change in the model-calculated N_2O-O_3 slopes at middle and high latitudes.

Before discussing the different causes for these discrepancies, we need to investigate the effect of uncertainties in the O_3 climatology, which is used to constrain the model between 10 and 50 hPa. We therefore changed the O_3 climatology according to the standard deviations which vary up to 5% [*Fortuin and Kelder*, 1998]. The effect on the O_3 concentration and subsequently the O_3-N_2O slopes in the lowermost stratosphere are, however, negligible.

One could argue that the deviating slopes in the observations reflect the presence of polar vortex filaments, which were not captured by the model. This may be due to its relatively course spatial resolution or because the filaments were calculated in the wrong location and hence disregarded when interpolating the model on the flight coordinates. However, the observed deviating slopes were found during every flight, covering an area of more than 10^6 km^2, which makes it unlikely that only polar vortex filaments were sampled. In addition, the calculated longitudinal variability of the N_2O-O_3 slopes is small, and no filamentary structures could be distinguished.

Another possible cause of the model overestimation of the slopes may be numerical diffusion, so that influences from the troposphere or from lower latitudes, where the slopes are steeper, are too strong. Although this possibility needs future investigation, preliminary results from an O_3 tracer study with a less diffusive second-order advection scheme gives rise to even more O_3 in the lowermost stratosphere thus increasing the discrepancies (A. Bregman et al., manuscript in preparation, 2000).

In addition, enhanced chemical O_3 loss through heterogeneous chemistry on liquid or ice particles might also influence the slope distribution. Although the model includes heterogeneous chemistry on ice and liquid particles, the chemical ozone loss during the wintertime is somewhat underestimated (van den Broek et al., submitted manuscript, 2000). By correcting the temperature according to recent observations and adjusting the nitric acid trihydrate formation threshold temperatures, the calculated O_3 loss was in much better agreement with the observations (van den Broek et al., submitted manuscript, 2000). We used the same corrections and calculated the N_2O-O_3 distribution for January to April 1997. In Plate 2 the interpolated model results for all 1997 flights are shown by the green squares. The differences appear to be small and cannot explain the discrepancies between the calculated and observed slopes. This is consistent with the findings of *Hall and Prather* [1995], who were able to calculate the observed N_2O-O_3 slope distribution without accounting for heterogeneous chemistry.

5.2. Mixing of Tropospheric Air Into the Lowermost Stratosphere

An important question is whether mixing of tropospheric air into the lowermost stratosphere could have caused the deviating slopes in May 1996. This may occur either by isentropic transport caused by wave breaking [*Holton et al.*, 1995; *Chen*, 1995] or by diabatic cross-isentropic transport associated with synoptic baroclinic disturbances in the subtropical region [*Rood et al.*, 1997]. On the basis of calculated slopes in the subtropical troposphere and stratosphere we infer that these mixing processes have not caused the observed slopes.

Assuming an isentropic surface that connects the troposphere in the (sub)tropics and the stratosphere at midlatitudes, the regular anticorrelation between N_2O and O_3 in the midlatitude stratosphere changes to an almost vertical relationship in the troposphere (i.e., varying O_3 mixing ratios and relatively constant N_2O mixing ratios of 310–315 ppbv). Thus isentropic mixing of tropospheric with stratospheric air parcels results in a linear anomalous mixing line intermediate between these relationships. This mixing concept is described by *Waugh et al.* [1997]. Figure 5a shows the calculated N_2O-O_3 tropospheric (asterisks) and stratospheric (triangles) relation on May 27, 1996, for θ levels between 355 and 365 K. The overall relationship only curves slightly and downward. Thus the anomalous mixing line hardly deviates from the original slopes, and it is also steeper. The solid line represents the observed slope in 1996, and the dashed line shows that a tropospheric O_3 mixing ratio of approximately 300 ppbv is needed to explain the observed slopes, which is not realistic.

Next, we address diabatic cross-isentropic mixing of tropospheric air into the lowermost stratosphere. For this transport mechanism the above mixing concept cannot be applied, since it takes place across θ levels. Figure 5b shows two distinct slopes in the (sub)tropical region and at midlatitudes for different θ levels, calculated for May 27, 1996. The (sub)tropical slope is steeper than that at midlatitudes for reasons described in section 2. In this situation, mixing would result in an increase of the midlatitude slopes, rather than a decrease.

Hence troposphere-stratosphere transport cannot have caused the observed deviating slopes, so that the only plausible explanation is diabatic descent from the polar vortex into the lowermost stratosphere, after which the air was transported to midlatitudes without effectively being mixed with air from lower latitudes.

6. Conclusions

We have compared detailed in situ N_2O and O_3 observations in the lowermost stratosphere during winter and spring with the results of a three-dimensional CTM. Considering the relatively course grid of the model, we obtain good agreement between model results and observations for many parts of the measurement flights. However, the model sometimes overestimates both O_3 and N_2O, especially at the highest flight levels. It is further shown that the N_2O-O_3 slope diagnosis is a useful validation method, since the slopes represent a quasi-conserved quantity. The model results are consistent with the general understanding of the N_2O-O_3 relationship in the lowermost stratosphere. They show a latitudinal slope gradient during wintertime, which diminishes during summer. This in-

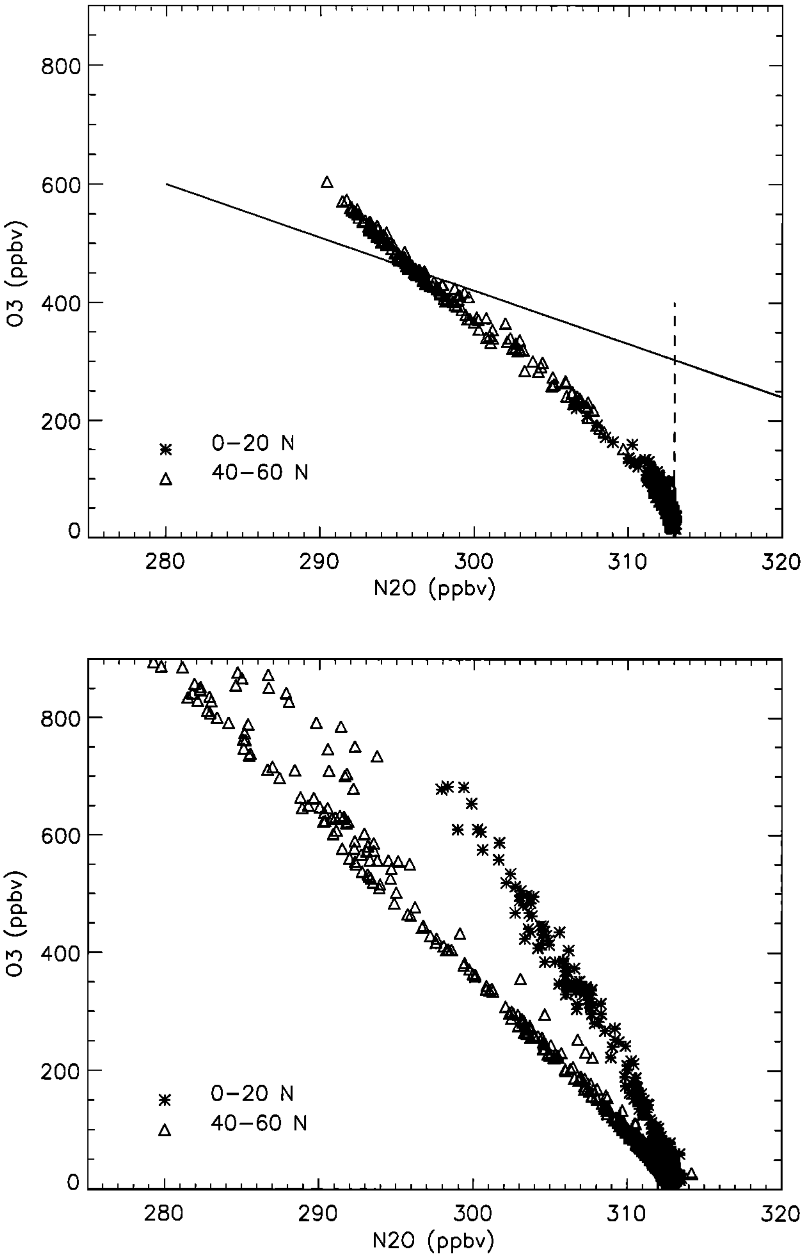

Figure 5. Calculated N_2O versus O_3 mixing ratios (ppbv) on May 27, 1996, at an isentropic level of 360 K for midlatitudes (triangles) and the tropical region (asterisks). (a) The solid line represents the anomalous mixing line needed to explain the observed N_2O-O_3 slopes. (b) Calculated N_2O versus O_3 mixing ratios (ppbv) on May 27, 1996, at all altitudes in the lowermost stratosphere for midlatitudes (triangles) and the tropical region (asterisks).

dicates the presence of polar vortex air, transported across the vortex bottom by diabatic descent, which has not mixed completely with air from lower latitudes.

On basis of the slope diagnosis the observations indicate that the direct influence of the polar vortex extends to the lowermost stratosphere, even close to the tropopause down to θ levels of 340 K. The vertical extent of this influence depends on the strength and the lifetime of the polar vortex during the winter. The model is able to represent differences in the slope distribution between the late winters of 1995 and 1997, consistent with the differences in strength between the polar vortices in these winters, but it underestimates the absolute difference. The calculated N_2O-O_3 slopes in the lowermost stratosphere agree with the observations in well-mixed conditions but are too steep when the influence of polar vortex air is noticeable in the observations. Since the slopes represent the age of air, the most plausible explanation for these discrepancies is that the air in the lower stratosphere in the model has not remained in the stratosphere long enough. The model top at 10 hPa may lead to an enhanced transport from the tropics to higher latitudes and to weak downward transport at middle and high latitudes. Therefore a model top at 10 hPa limits the possibilities of studying the lower stratosphere. The recent refinements of the ECWMF analyses, extending up to 0.1 hPa and resolving

50 vertical layers, will likely improve the representation of the stratospheric meteorology, which may help in resolving this issue in the near future.

According to the model results, and based on previous observations in the polar vortex, the observed slopes during late spring 1996 at midlatitudes appear to be strongly influenced by polar vortex air. These air masses have descended by diabatic cooling to the base of the polar vortex and were transported into the midlatitude lowermost stratosphere. It is interesting that such vortex remnants are found in late spring, close to the midlatitude tropopause, as observed on several days in different directions, suggesting that they may cover a relatively large area. We have further illustrated that the deviating slopes at midlatitudes cannot have been caused by mixing of (sub)tropical air into the lowermost stratosphere. This confirms that high-latitude stratospheric air is transported to lower latitudes and into the lowermost stratosphere, likely along isentropic surfaces, after which it is mixed into the troposphere.

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