

Aircraft measurements of O₃, HNO₃, and N₂O in the winter Arctic lower stratosphere during the Stratosphere-Troposphere Experiment by Aircraft Measurements (STREAM) 1

A. Bregman,^{1,2} P. F. J. van Velthoven,³ F. G. Wienhold,⁴ H. Fischer,⁴
T. Zenker,⁴ A. Waibel,^{5,6} A. Frenzel,⁵ F. Arnold,⁵ G. W. Harris,⁷
M. J. A. Bolder,² and J. Lelieveld²

Abstract. Simultaneous in situ measurements of O₃, HNO₃, and N₂O were performed in the Arctic (68°–74°N) lower stratosphere during February 1993 on board a Cessna Citation aircraft up to 12.5 km altitude, during the first Stratosphere-Troposphere Experiment by Aircraft Measurements (STREAM) campaign. Strong variations in the concentrations, distributions, and ratios of these trace gases were found from the maximum altitude down to the tropopause. Close to the tropopause, vortex air was present with relatively low N₂O concentrations. The observed N₂O-HNO₃ relation agrees with earlier measurements of total nitrogen and N₂O inside the vortex, suggesting subsidence of vortex air across the bottom of the vortex. This air also contained low O₃ concentrations relative to N₂O, indicating enhanced O₃ loss by chemical reactions involving stratospheric particles. Based on trajectory calculations and assuming a potential temperature cooling rate of 0.6 K d⁻¹, we estimate an O₃ loss of 4–7 ppbv d⁻¹ (0.9–1.2% d⁻¹), in the Arctic lower stratosphere for the period January–February 1993. Air parcels originating from middle latitudes, containing relatively low O₃ and N₂O concentrations, may have originated from the vortex earlier in the winter. In addition, the results also show high HNO₃ concentrations relative to O₃ and N₂O. Air parcels originating from high latitudes may have been enriched in HNO₃ by sedimentation and evaporation of nitric acid containing particles, which would explain the relatively high HNO₃ concentrations and HNO₃/O₃ ratios measured. Heterogeneous chemistry on sulfuric acid particles, probably enhanced in concentration by gravitational settling of the Pinatubo aerosol, is the most plausible explanation for the observed high HNO₃ concentrations relative to N₂O in air parcels originating from midlatitudes.

Introduction

Recent measurements have shown that O₃ is significantly depleted in the lowest parts of the winter polar and midlatitude stratosphere both in the northern and in the southern hemispheres [e.g., McCormick *et al.*, 1992; Wege and Claude, 1994]. The midlatitude O₃ decrease may be explained by (1) local chemical O₃ loss enhanced through heterogeneous reactions on sulfate aerosols [Brasseur and Granier, 1992], by (2) transport of air from the polar vortex, which is depleted in O₃ by heterogeneous chemistry involv-

ing polar stratospheric clouds (PSCs) and transported to lower latitudes across the vortex edge [Tuck *et al.*, 1992; Proffitt *et al.*, 1989], and by (3) meridional transport of vortex air, containing low-O₃ concentrations, below the bottom of the vortex (below potential temperature levels of 410 K in the Arctic, the so called “outflow region”), which has descended through radiative cooling. This assertion is supported by observations of layers with low O₃ concentrations below the bottom of the vortex [Reid *et al.*, 1993; Proffitt *et al.*, 1993]. Because of heterogeneous reactions on polar stratospheric clouds (PSCs) and sulfate aerosols within the vortex, NO_x can be significantly reduced in the descending vortex air. In addition, this air is characterized by enhanced chlorine reservoir species, e.g., ClONO₂, releasing active chlorine when exposed to sunlight. The effects of these chemical transformations on O₃ in the lower stratosphere have been studied in several modeling studies [e.g., Rodriguez *et al.*, 1991; Solomon *et al.*, 1993; Brasseur and Granier, 1992; Cox *et al.*, 1993; Turco and Hamill, 1992; Müller *et al.*, 1994; Toumi *et al.*, 1993]. Also, measurements have been performed to investigate the implications of enhanced sulfate aerosol abundance by the eruption of Mount Pinatubo and consequences for O₃ loss at midlatitudes [e.g., Fahey *et al.*, 1993; Weaver *et al.*, 1993; Hofmann *et al.*, 1993, 1994a] and high latitudes [e.g., Toohey *et al.*,

¹Institute for Marine and Atmospheric Sciences, Utrecht, Netherlands.

²Department of Air Quality, Wageningen University, Wageningen, Netherlands.

³Royal Netherlands Meteorological Institute, De Bilt.

⁴Air Chemistry Department, Max Planck Institute for Chemistry, Mainz, Germany.

⁵Max Planck Institute for Nuclear Physics, Heidelberg, Germany.

⁶Now at Max Planck Institute for Chemistry, Mainz, Germany.

⁷Center for Atmospheric Chemistry, Department of Chemistry, York University, North York, Ontario, Canada.

1993; Avallone *et al.*, 1993; Hofmann and Oltmans, 1993]. Since HNO_3 is a main product of NO_x conversion, it can be used as a tracer for heterogeneous reactions on sulfuric aerosols. Also, PSCs contain HNO_3 which can be released by evaporation in the lowest parts of the stratosphere after sedimentation of these particles [Arnold and Knopp, 1989; Arnold *et al.*, 1992; Hübler *et al.*, 1990]. From the theory of gas phase chemistry and transport processes in the middle atmosphere it is expected that concentrations of O_3 and HNO_3 are highly correlated and that those of N_2O and HNO_3 are anticorrelated [Brasseur and Solomon, 1986]. N_2O reacts with $\text{O}(^1D)$ in the lower stratosphere yielding NO , and in this region O_3 can be formed photochemically. N_2O has a long chemical lifetime in the lower stratosphere and can thus be regarded as a conservative quantity, yielding information about the history of air parcels [Loewenstein *et al.*, 1990; Lait *et al.*, 1990]. Enhanced O_3 loss and heterogeneous processing affect O_3 and HNO_3 differently and change the ratio between HNO_3 and O_3 . Therefore measured ratios of $\text{O}_3/\text{N}_2\text{O}$ and $\text{HNO}_3/\text{N}_2\text{O}$ yield information about O_3 and HNO_3 perturbations. In wintertime the chemical lifetime of HNO_3 and O_3 in the lower stratosphere is longer than the characteristic timescale of vertical advection, which is about 3 months [Solomon *et al.*, 1985]. Hence the distributions of these trace gases in this region are determined by atmospheric dynamics rather than photochemistry. Since O_3 and HNO_3 have the same source region, the correlation between HNO_3 and O_3 is maintained during transport in the lower stratosphere. The correlation between the three species will also be maintained after upward transport from the troposphere, where N_2O concentrations are relatively high and the O_3 and HNO_3 concentrations are much lower. Deviations of these relations occur when the lifetime of one of the tracers is reduced due to enhanced photochemical breakdown or by rapid transport from source regions, with different concentrations. For example, the $\text{O}_3\text{-N}_2\text{O}$ relation at low latitudes clearly deviates from that in high latitudes due to the relatively short lifetime of O_3 by photochemistry in the tropical region [Plumb and Ko, 1992]. In addition, Proffitt *et al.* [1992] show a breakdown of the $\text{O}_2\text{-N}_2\text{O}$ relation by enhanced photochemical O_3 loss during summertime. Hence latitudinal and seasonal dependences of these relationships introduce uncertainties in the determination of "reference" relationships, and their interpretation thus needs to be carried out with caution.

In several previous studies, NO_y ($\text{NO} + \text{NO}_2 + 2\text{N}_2\text{O}_5 + \text{HNO}_3 + \text{ClONO}_2 + \text{minor species}$) was used as a tracer instead of HNO_3 , as used here. Proffitt *et al.* [1989] provide a method to calculate inner vortex O_3 loss in the Antarctic winter. By using in situ measurements and two-dimensional model results, they determined empirical relations among NO_y , O_3 , and N_2O outside the vortex, which were used as reference relations, representative for a "chemically unperturbed region." Their study and others have confirmed that O_3 and NO_y are strongly anticorrelated with N_2O in the lower stratosphere in the Antarctic [Strahan *et al.*, 1989] and in the Arctic [Proffitt *et al.*, 1990; Kawa *et al.*, 1990; Fahey *et al.*, 1990; Hübler *et al.*, 1990; Kondo *et al.*, 1992; Weinheimer *et al.*, 1993; Collins *et al.*, 1993] and that the ratio NO_y/O_3 may be almost constant in the lower stratosphere [Proffitt *et al.*, 1989; Murphy *et al.*, 1993]. However, these measurements in the Antarctic and Arctic also show

that O_3 loss and heterogeneous processing can significantly change these ratios. In addition, it may be expected that the relative contribution of HNO_3 to NO_y varies significantly, depending on the importance of heterogeneous processing. NO_y may contain 50–90% HNO_3 during wintertime in the lower stratosphere at high latitudes [Fahey *et al.*, 1989; Kondo *et al.*, 1992] and 60–85% close to the polar vortex boundary [Kawa *et al.*, 1992]. In the lower stratosphere, HNO_3 is thus a more sensitive indicator of the influence of heterogeneous reactions on stratospheric chemistry than NO_y . In this paper, simultaneous in situ measurements of gaseous HNO_3 , O_3 , and N_2O are presented, which were carried out in the Arctic winter lower stratosphere, below the bottom of the vortex. The measurements were performed on board an aircraft as part of the first Stratosphere-Troposphere Experiment by Aircraft Measurements (STREAM I) project. The measurements have been carried out between 68° and 74°N during February 1993. We report $\text{HNO}_3\text{-N}_2\text{O}$, $\text{O}_3\text{-N}_2\text{O}$, and $\text{HNO}_3\text{-O}_3$ relations, in search of evidence for photochemical O_3 loss and enhanced HNO_3 formation through heterogeneous reactions on sulfuric aerosols. The results are compared to earlier measurements, in particular from the Airborne Arctic Stratospheric Experiment (AASE) I and II campaigns.

Description of the Campaign

Three flights were carried out February 16, 17, and 18, 1993, with a Dutch Cessna Citation II aircraft, which operated from Kiruna Airport in northern Sweden. The measurements were performed in the afternoon at different levels between 6 and 12.5 km altitude: one flight level in the troposphere and three in the stratosphere. The aircraft remained for about 10 min at each flight level and stayed for 45 min at the maximum flight altitude. The flights were carried out north and northeast of Kiruna. Local weather forecast and radiosonde data of the nearest meteorological stations were provided by the Swedish Meteorological Service. Further, synoptic weather information, e.g., geopotential heights, potential temperatures, wind speed and wind direction, potential vorticity (PV), and relative humidity at different pressure levels were derived from the European Centre for Medium-Range Weather Forecast (ECMWF) analyses by the Royal Netherlands Meteorological Institute (KNMI). The KNMI also calculated tropopause heights from the PV distribution and 10 day back trajectories from the ECMWF three-dimensional wind fields. The Free University of Berlin provided temperatures at 100- and 200-mbar pressure levels from meteorological stations at high northern latitudes.

Instrumentation

Ozone was measured by a chemiluminescence monitor, with ethylene as reaction gas. Optimization of the technique, including pressure independence between 600 and 1100 mbar, has been described by Gregory *et al.* [1983]. The monitor pressure was maintained between 600 and 1100 mbar and the reaction chamber flow was decreased to 300 mL min^{-1} [Mehrabzadeh *et al.*, 1983; O'Brien *et al.*, 1983]. The instrument response time is 5 s and the precision 0.5 parts per billion by volume (ppbv). The total inaccuracy was mainly determined by the internal calibration source and was

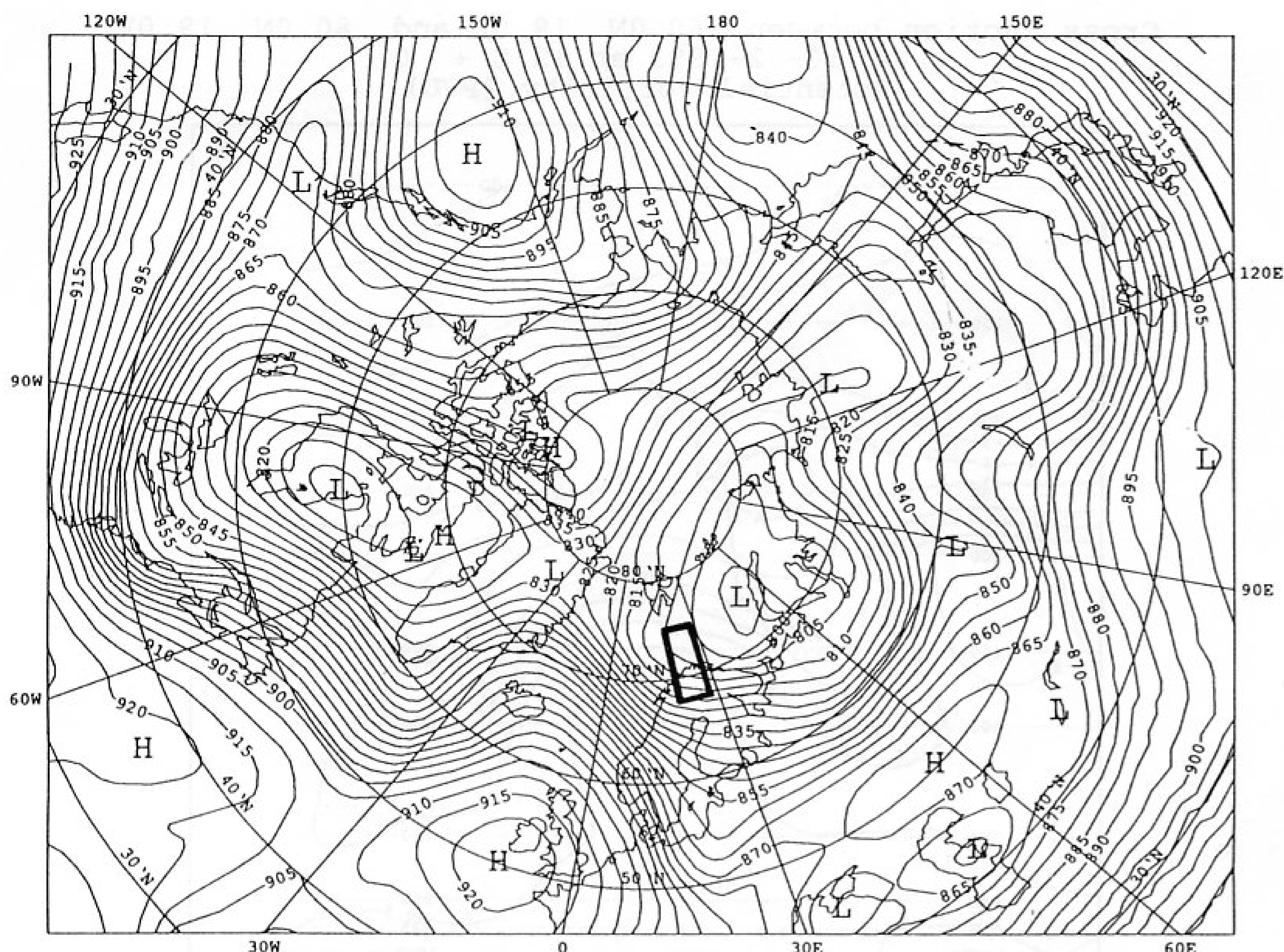


Figure 1. The European Centre for Medium-Range Weather Forecasts (ECMWF) analysis (geopotential heights in $10^2 \text{ m}^2 \text{ s}^{-2}$) of 1200 UT at the 300-mbar level is shown for February 17, 1993. The solid lines indicate the flight area.

6–7% for the flight on February 17, 1993, and 3–4% on the other flights.

N_2O was measured using a tunable diode laser (TDLAS) spectrometer, built and operated by the Max Planck Institute for Chemistry in Mainz. The monochromatic output from a lead-salt diode laser is rapidly scanned [1 kHz] across a single rotational-vibrational absorption line of N_2O centered at $4.47 \mu\text{m}$. Ambient air is pumped at a stabilized pressure of 45 mbar through a multiple reflection cell (White cell), which provides an optical absorption pathlength of 45.9 m. A high-frequency modulation scheme is applied to quantify the absorption from N_2O in the sampled air. A calibration spectrum was regularly recorded during the flights and compared with the ambient spectrum, while purging the White cell with standard gas. A precision of 1% could be reached, limited by the stability of the laser operation point and calibration uncertainties. Total inaccuracy of 5% was mainly determined by the standard calibration gas. The technique is described in more detail by *Wienhold et al.* [1994].

HNO_3 and several other trace gases were measured with an automated liquid neon cooled quadrupole mass spectrometer, built and operated by the Max Planck Institute for Nuclear Physics, Heidelberg. The air is sampled through a 4-cm-diameter flow tube, and the sampled HNO_3 reacts with CO_3^{2-} ions, injected by an ion source, which was mounted in the tube. The product ions are transported into the mass spectrometer in which a pressure $< 10^{-4}$ mbar is maintained. The HNO_3 concentrations are determined by measuring the reactant and product ions, the residence time of the ions, and

the rate coefficients of the ion molecule reactions. The latter is known within 40% uncertainty [*Möhler and Arnold, 1991*]. The ions are counted by a multichannel analyzer with a detection limit of a few tens of parts per trillion by volume. Instrument precision is about 10%. The technique was originally employed by *Arnold and Knopp* [1987] and described in more detail by *Möhler and Arnold* [1991] and *Arnold et al.* [1992].

Meteorological Conditions

Figure 1 shows the flight area during the STREAM campaign, superposed on the geopotential height map of the 300-mbar pressure level on February 17, 1993. There were low-pressure areas located at Siberia and the United States and a high-pressure area west of the United Kingdom, which was associated with the jet stream over northern Scandinavia with occasionally strong winds, varying from west to north. The low-pressure area above Siberia moved southwestward to eastern Scandinavia. Prevailing northerly winds, maintained by the jet stream, transported stratospheric air southward. At this location, there was a relatively sharp transition between the high-pressure and the low-pressure areas. This can be seen in Figures 2a–2c, where the vertical cross sections of the potential vorticity are shown. The bold lines show the flight tracks and the dashed area indicates the region with PV units between 1 and 2, where the dynamical tropopause was located. South of the area studied, the tropopause was lifted by the high-pressure system. The tropopause heights varied significantly due to the occurrence of frontal activity.

Cross section between 60.0N 19.0E and 80.0N 19.0E
on 16-2-1993 at 12 Z + 0
Potential vorticity (PVU)

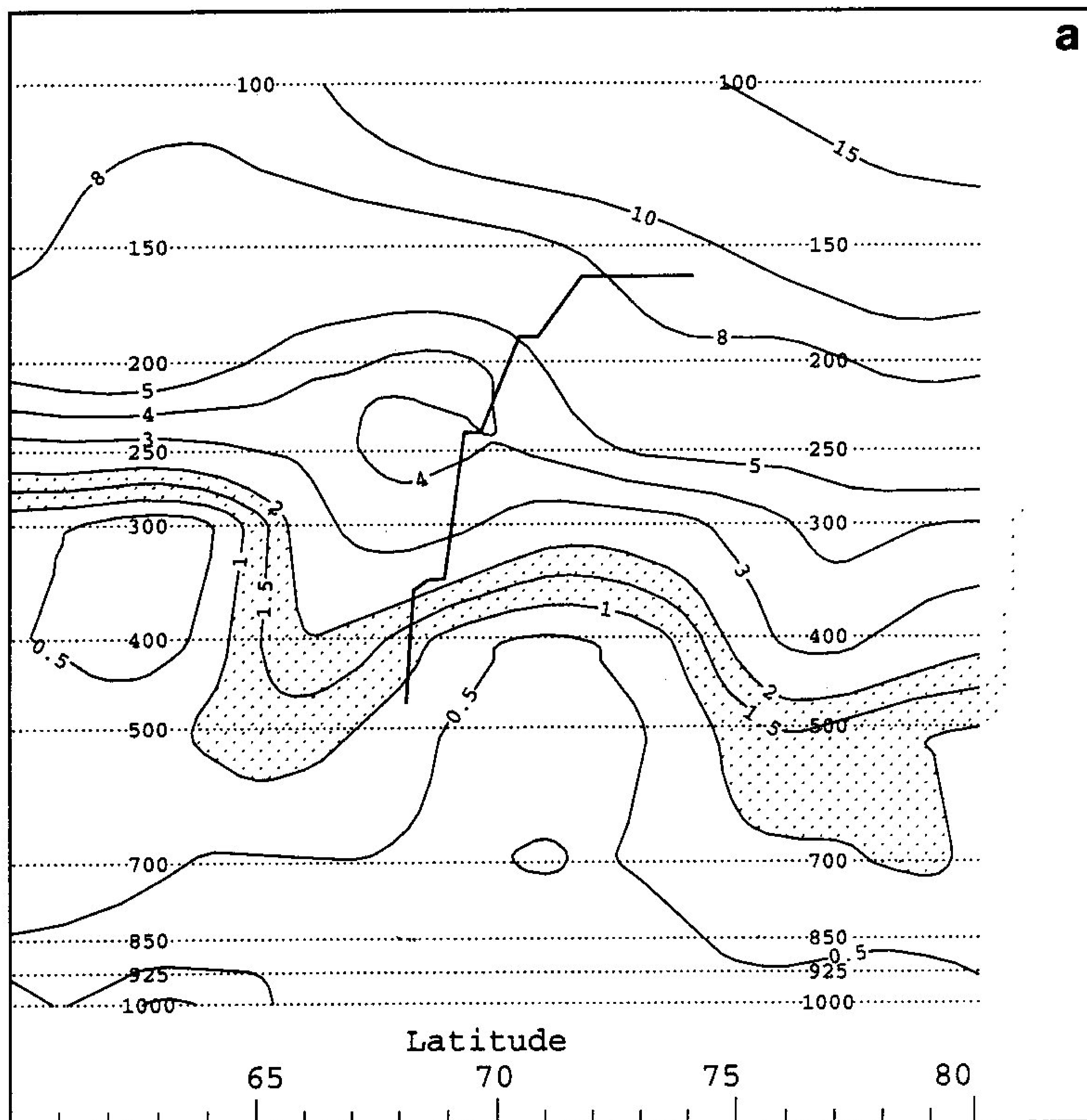


Figure 2. (a)–(c) Potential vorticity (PV) cross sections, calculated from ECMWF 1200 UT analyses. PV is shown (solid lines) in PVU units ($\text{PVU} = \text{K kg}^{-1} \text{m}^2 \text{s}^{-1}$). The vertical ordinate is the pressure altitude in millibars (dashed lines). The bold lines represent the flight tracks with the ascents and descents. The dotted area is the area with PVU between 1 and 2, where the dynamical tropopause is located.

Results

The HNO_3 data presented are 128-s averaged data from 10 mass spectra. The mean mixing ratio of N_2O was determined in 6-s intervals using a real-time multiple linear regression algorithm that compared the ambient spectrum to a calibration spectrum. The O_3 data were archived with a frequency of 1 Hz. The O_3 and N_2O data were filtered (1/128 Hz) for comparison with the HNO_3 data. The HNO_3 measurements were carried out at ambient pressures lower than 350 mbar to avoid pressure-induced ion defragmentation of the product ions.

Vertical Distributions and Air Parcel History

The time series of O_3 , HNO_3 , and N_2O of the three flights are depicted in Figures 3a and 3b. The correlation between the species can clearly be seen in the small-scale fluctuations. In Figures 4a–4c the vertical distributions of O_3 , HNO_3 , and N_2O are shown as a function of potential temperature (θ) and pressure altitude, measured during the ascents and descents. The altitudes of the tropopause are indicated by the solid lines. The O_3 concentrations ranged from 60 ppbv in the free troposphere to 700 ppbv in the stratosphere at maximum altitude. The HNO_3 concentrations were 5–6 ppbv at the maximum flight level, decreasing with altitude to less than 100 pptv at the tropopause level. The N_2O concentrations varied between 240 and 290 ppbv in

the stratosphere and were occasionally less than 240 ppbv. Tropospheric concentrations were approximately 310 ppbv. The maximum HNO_3 and O_3 concentrations measured are comparable for all three days; however, the N_2O concentrations on February 17 are significantly lower than on the other days. During all flights we observe significant layering in the vertical profiles and large horizontal variation at altitudes where the potential temperature remained approximately constant, indicating that the aircraft flew through air masses with different origins.

To investigate the meteorological history of the air parcels, 10-day back trajectories were calculated from the analyzed three-dimensional wind fields from the ECMWF. The trajectories are depicted in Figure 5 (horizontal distributions) and Figure 6 (vertical distributions). Figure 7 shows the geopotential heights on the 50-mbar level for February 17, in which the structures of the polar vortex can be seen. Parts of the vertical profiles in Figures 4a–4c have been labeled, indicating correspondence to the trajectory source regions in Figures 5 and 6. It is remarkable that on February 16, 17, and 18, many air parcels have followed the vortex geopotentials below the bottom of the vortex. These air parcels are characterized by relatively low N_2O and high O_3 concentrations, and thus may indicate the presence of vortex air. On the other hand, the HNO_3 concentrations are highly variable, especially on February 16 and 18. Transport of

Cross section between 60.0N 26.0E and 80.0N 26.0E
on 17-2-1993 at 12 Z + 0
Potential vorticity (PVU)

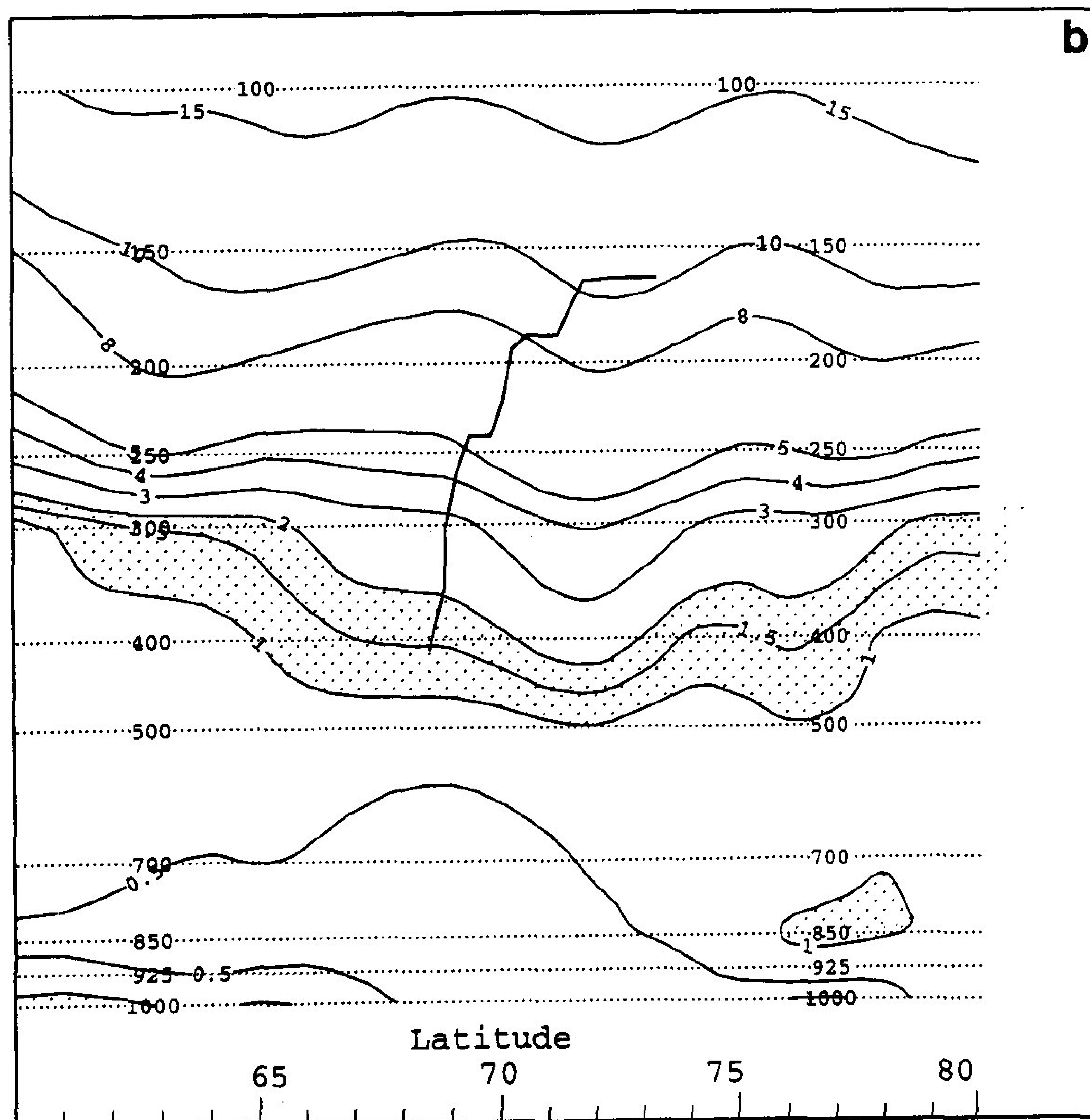


Figure 2. (continued)

midlatitude air to high latitudes is characterized by relatively high N_2O concentrations; but also, in these air parcels the HNO_3 concentrations are variable.

On February 17, most stratospheric air parcels observed, originating from both middle and high latitudes, contained relatively low N_2O concentrations; but an interesting distinction is found for HNO_3 : all air parcels originating from midlatitudes (A in Figure 4b) contained relatively high HNO_3 concentrations and the air parcels originating from high latitudes (B) contained relatively low HNO_3 concentrations. These variable HNO_3 concentrations will be discussed in more detail in the following sections.

On February 16, 17, and 18, relatively high N_2O and low HNO_3 concentrations were found just above the tropopause. The back trajectories of these air parcels suggest that they originate from the troposphere (see Figures 6a, 6b, and 6c), indicating organized upward motion in the warm sector of a frontal system previous to the flights.

Data Comparison

Because previous experiments, as used for comparison here, yielded simultaneously measured N_2O , O_3 , and NO_y , our HNO_3 data are compared with estimated HNO_3 , assuming that the NO_y measured contain 80% HNO_3 [Fahey et al., 1989; Kondo et al., 1992; Kawa et al., 1992]. The HNO_3 thus derived is referred to as HNO_3^* . During the AASE I campaign in February 1989, measurements showed typical HNO_3^* concentrations between 0.5 and 3 ppbv throughout

the winter at high northern latitudes [Hübler et al., 1990], significantly lower than the HNO_3 concentrations measured during STREAM. In situ measurements of NO_y , O_3 , and N_2O have also been carried out in AASE II, during the winter of 1992 at high northern latitudes. HNO_3^* concentrations increased with altitude to approximately 3 ppbv in the lower stratosphere at 12 km altitude, while the ozone concentrations increased from 40 to 800 ppbv [Weinheimer et al., 1993]. Our observations of stratospheric HNO_3 concentrations are significantly higher. Further, HNO_3 concentrations in the lower stratosphere during STREAM I are also higher than indicated by balloon-borne measurements of HNO_3 in the Arctic [Fast et al., 1993]. However, our relatively high HNO_3 concentrations agree with earlier balloon and aircraft measurements of enhanced HNO_3 concentrations ascribed to sedimentation and evaporation of stratospheric particles [Arnold and Knopp, 1989; Schlager and Arnold, 1990a, b; Arnold et al. 1992; Hübler et al., 1990]. During the European Arctic Stratospheric Ozone Experiment (EASOE) campaign during the winter of 1991/1992, HNO_3 has been measured in the lower stratosphere [von Clarmann et al., 1993; Oelhaf et al., 1994; Spreng and Arnold, 1994; Murcray et al., 1994]. Maximum concentrations were lower than indicated by our results, but some EASOE profiles obtained in February 1992, using aircraft- and balloon-borne mass spectrometers, show relatively high HNO_3 concentrations, at an altitude just above the maximum STREAM flight level, thus comparable to our results

Cross section between 60.0N 21.0E and 80.0N 21.0E
on 18-2-1993 at 12 Z + 0
Potential vorticity (PVU)

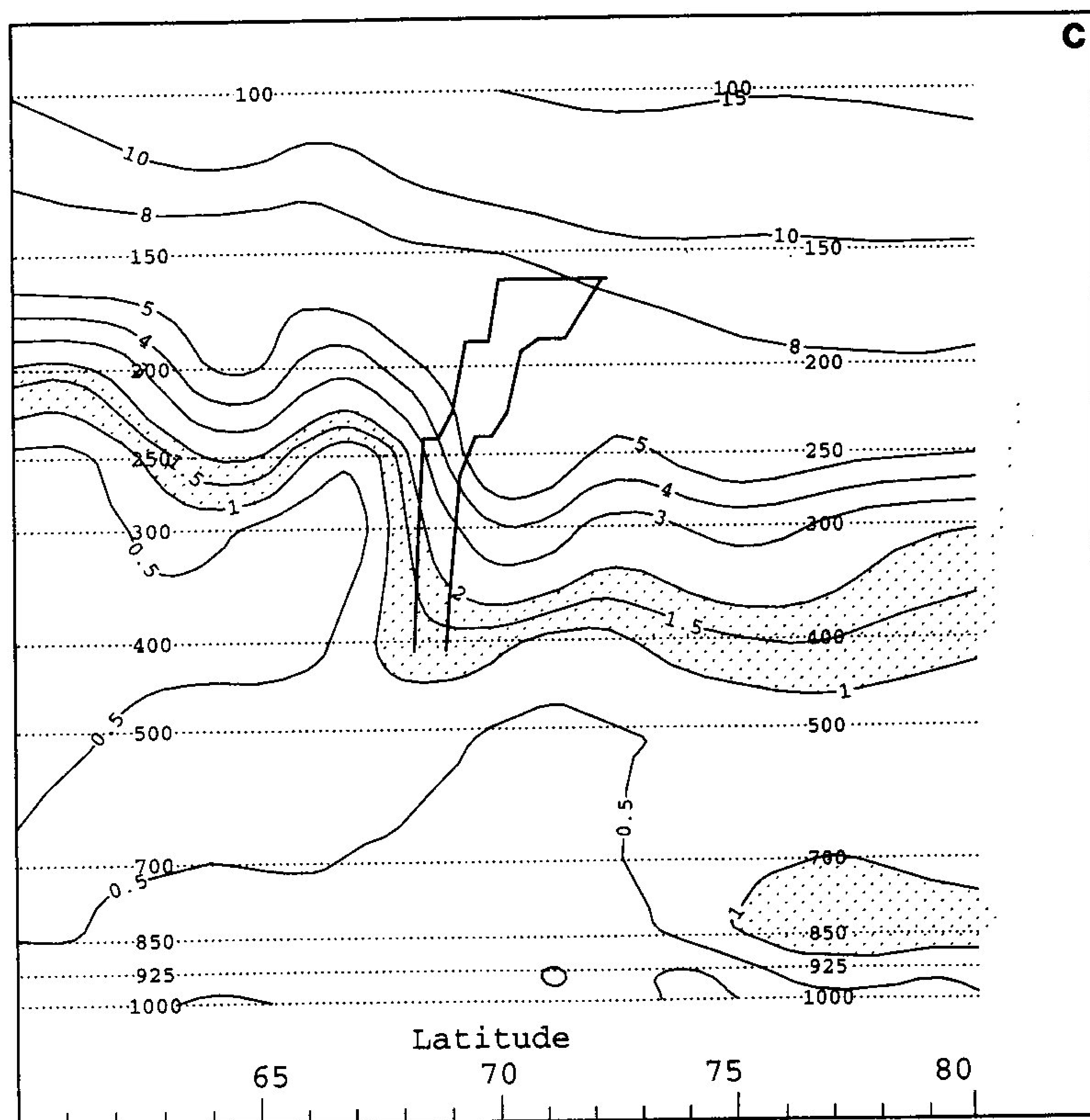


Figure 2. (continued)

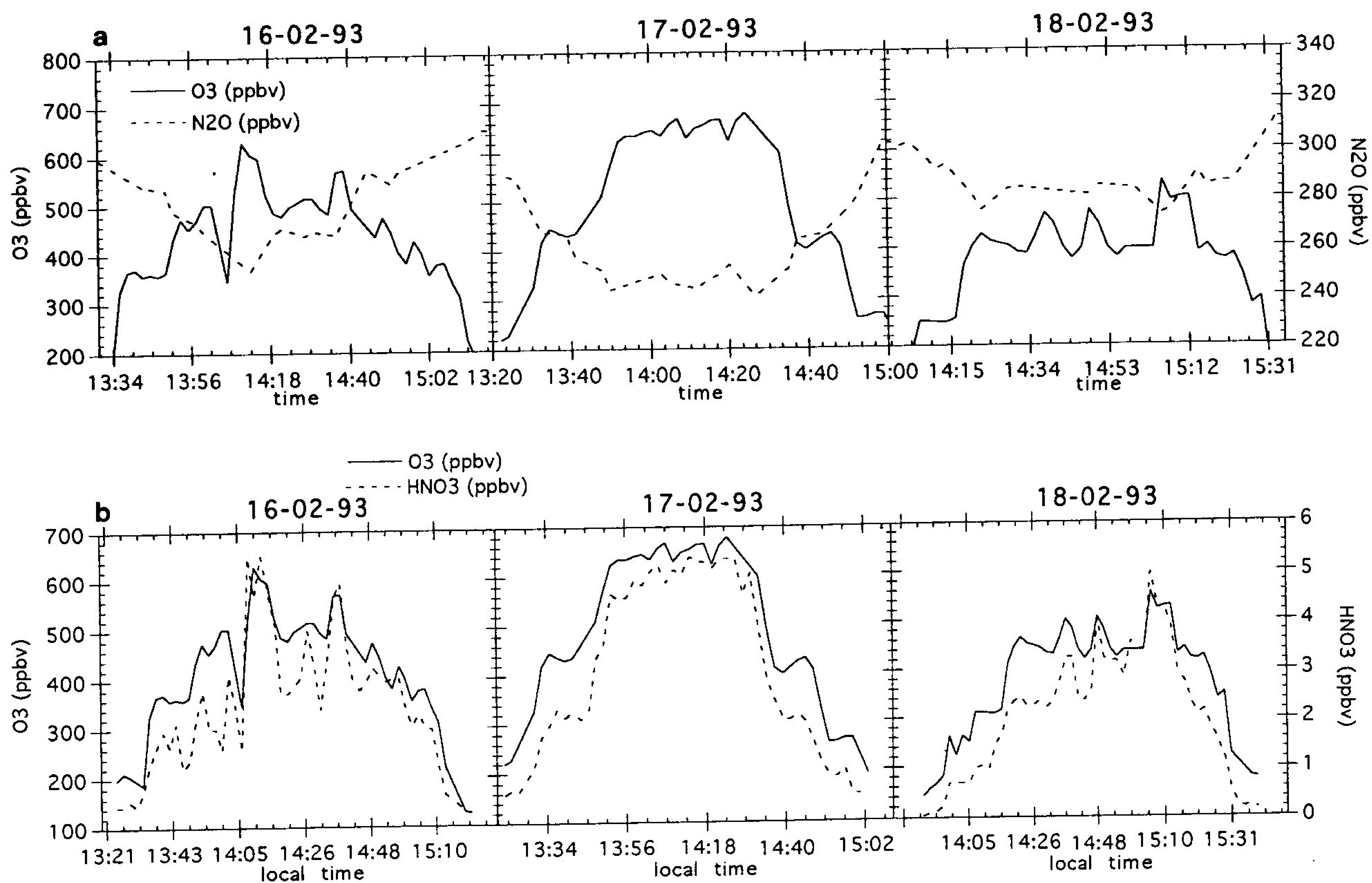


Figure 3. Time series (local time) of O_3 (solid lines), (a) N_2O and (b) HNO_3 (both dashed lines) for the flights on February 16, 17, and 18, 1993.

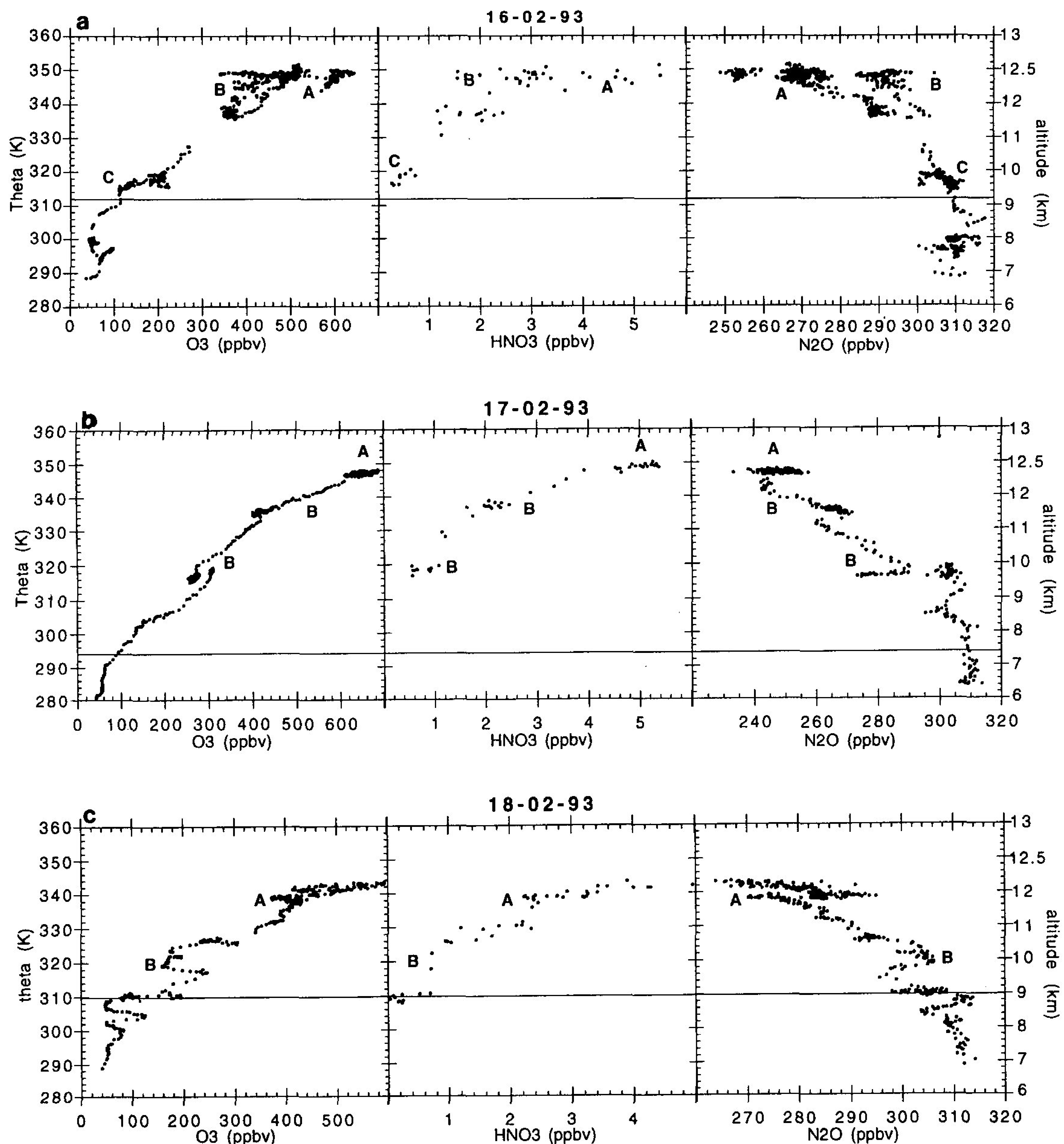


Figure 4. (a)–(c) Vertical distributions of O_3 , N_2O , and HNO_3 parts per billion by volume (ppbv) during ascent and descent for the flights on February 16, 17, and 18, 1993. The tropopause heights are indicated with the solid lines. A, B, and C correspond to A, B, and C in Figures 5 and 6 from which an indication about the origin of the air parcels can be obtained. The A labels indicate the highest flight level. Labels B, on February 16 and 17, correspond to air parcels between 10 and 12 km altitude, and on February 18, B labels correspond to air parcels at 10 km altitude. Labels C correspond to air parcels at 9–10 km altitude.

[Spreng and Arnold, 1994]. On the other hand, HNO_3^* measured by Kondo *et al.* [1994] at Kiruna, on March 31, 1992, was significantly lower than the HNO_3 concentrations from STREAM.

The upper tropospheric N_2O measurements during STREAM agree well with N_2O concentrations measured during AASE II [Collins *et al.*, 1993] and EASOE [Kondo *et al.*, 1994]. The N_2O concentrations in the lower stratosphere during STREAM on February 16 and 18 agree with the results of AASE II [Proffitt *et al.*, 1993]. However, significantly lower N_2O concentrations were found on February 17 when we measured concentrations down to 235 ppbv.

HNO_3 and O_3

The correlations between HNO_3 and O_3 for all flights are shown in Figure 8, indicating the results of the DC-8 flights in February 1992, carried out during the AASE II campaign (37° to $75^\circ N$ latitude) [Weinheimer *et al.*, 1993]. The STREAM data show significantly higher concentrations of HNO_3 relative to O_3 . The discrepancies remain even if we assume NO_y to be entirely composed of HNO_3 , instead of the above mentioned fraction of 80%. Figures 9a–9c show the altitude dependence of the ratio HNO_3/O_3 . The dashed lines indicate the results from the AASE I campaign [Mur-

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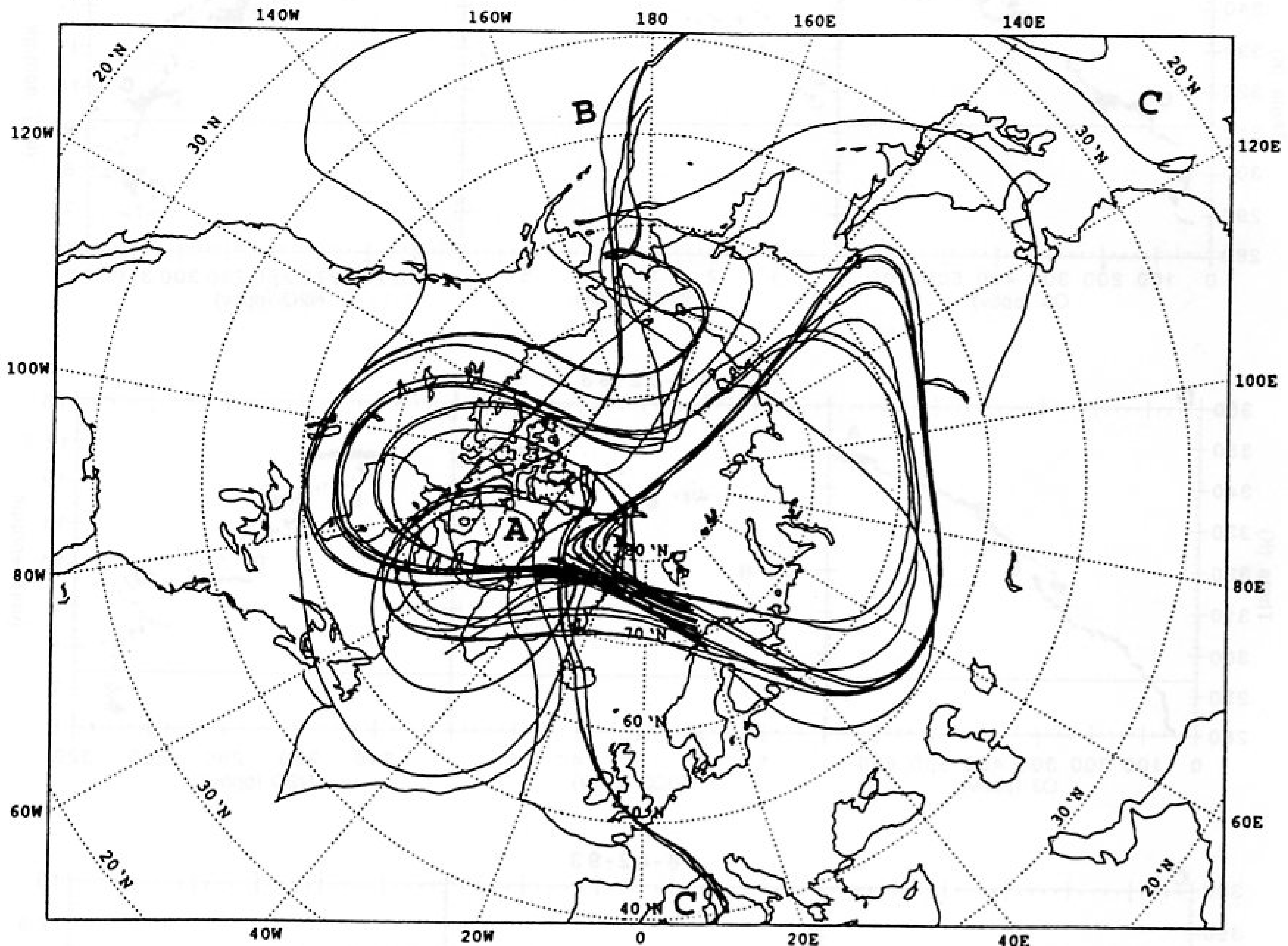


Figure 5. (a)–(c) Ten-day back trajectories, based on the ECMWF three-dimensional wind fields for February 16, 17, and 18, 1993. The trajectories were calculated every 2 hours. Every trajectory ends at the flight track. Marked trajectories correspond to air parcels marked in the vertical distributions (see Figures 2a–2c).

phy et al., 1993]. The STREAM data exhibit an increase of the HNO_3/O_3 ratio with altitude, whereas the AASE I data show a nearly constant ratio in the lower stratosphere. The HNO_3/O_3 ratio is plotted against N_2O in Figure 10, showing also the results of the AASE II flights in February 1992 [Weinheimer *et al.*, 1993]. These ratios of AASE II converge to $3\text{--}4 \times 10^{-3}$ for relatively low concentrations of N_2O , whereas the STREAM data indicate ratios between 4 and 10×10^{-3} . This shows that the partitioning of nitrogen species within NO_y , i.e., the fraction of HNO_3 , is much more variable than NO_y itself. As we will see later, the HNO_3 concentration and, in particular, the partitioning of NO_y species yields much information about the chemical history of the air parcels studied.

O_3 and N_2O

Scatterplots of N_2O and O_3 from all three flights are presented in Figure 11. There is a clear anticorrelation discernable between the depicted species for all flights. The different origins of the air parcels, as described earlier, determine the different ratios; air parcels originating from midlatitudes are characterized by higher ratios than air parcels originating from high latitudes. This is clearly shown by the differences in the ratios of February 17 as compared to February 16 and 18. The solid circles show the results of

the DC-8 February flights of AASE II [Collins *et al.*, 1993]. The ER-2 data [Proffitt *et al.*, 1993] fall within the range between the line and the DC-8 data (Figure 11). We obtain significantly lower N_2O concentrations and lower O_3 concentrations relative to N_2O compared to the DC-8 data. The O_3 - N_2O relation from the AASE II DC-8 data are similar to “extra vortex air” relations [Collins *et al.*, 1993] and is thus not influenced by O_3 depletion, as observed in the vortex air. The deviating O_3 - N_2O relation measured during STREAM thus may indicate descent of vortex air. In fact, the lower limits of the O_3 - N_2O relation in the AASE II ER-2 data at high latitudes, below the vortex bottom, are within the range of the STREAM results [Proffitt *et al.*, 1993], except those obtained February 17, when O_3 concentrations were significantly lower relative to N_2O . Since the ER-2 flew at higher potential temperature levels when the N_2O concentrations in Figure 11 were measured than during STREAM, this may indicate stronger subsidence during the winter of 1992/1993 than during the previous winter.

N_2O and HNO_3

In Figure 12, the scatterplots of HNO_3 and N_2O for the three flights show a clear anticorrelation of these species. The dashed line represents the empirical relation between HNO_3^* and N_2O obtained from the February DC-8 flights

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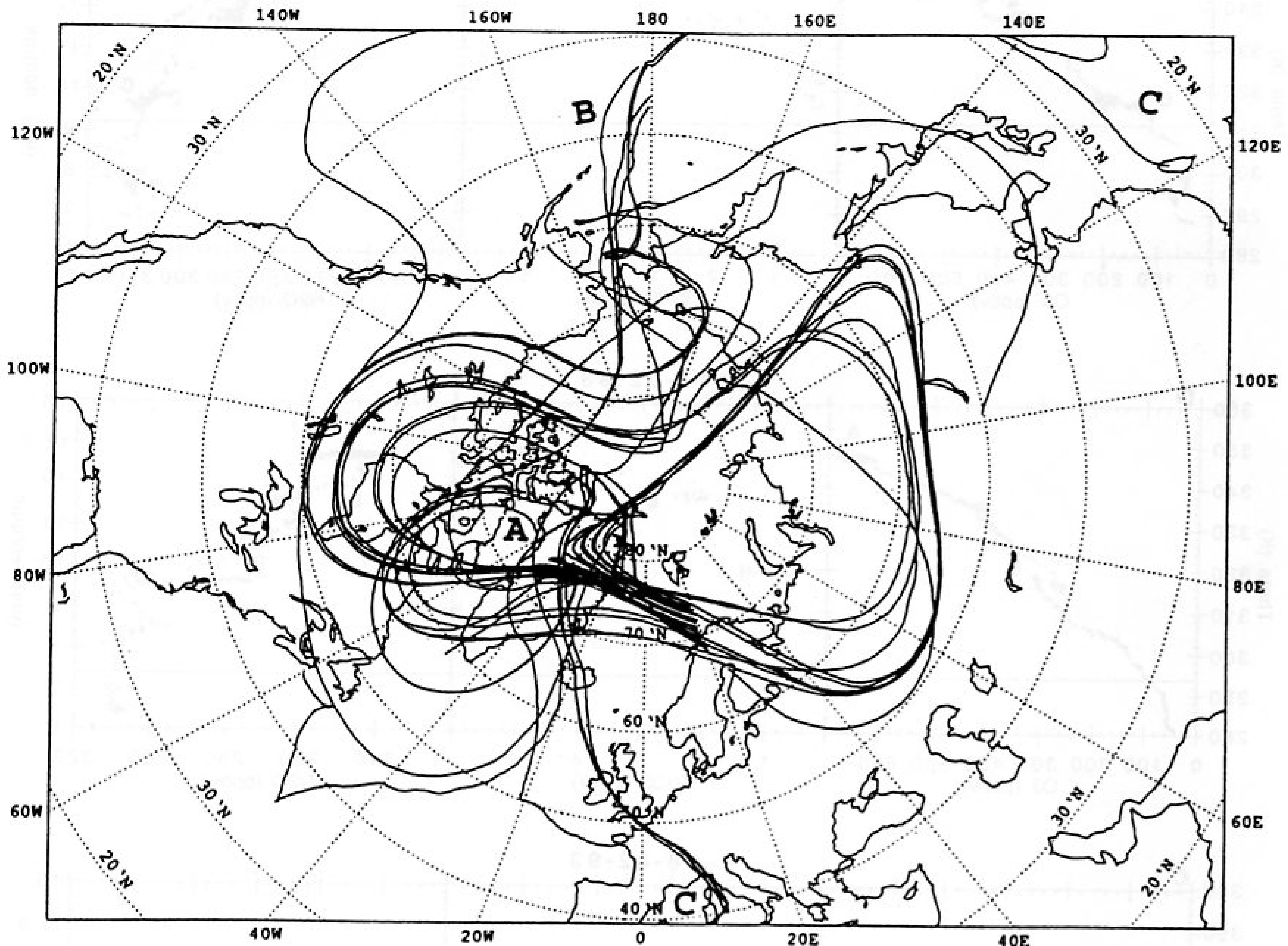


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In Figure 12, the scatterplots of HNO_3 and N_2O for the three flights show a clear anticorrelation of these species. The dashed line represents the empirical relation between HNO_3^* and N_2O obtained from the February DC-8 flights

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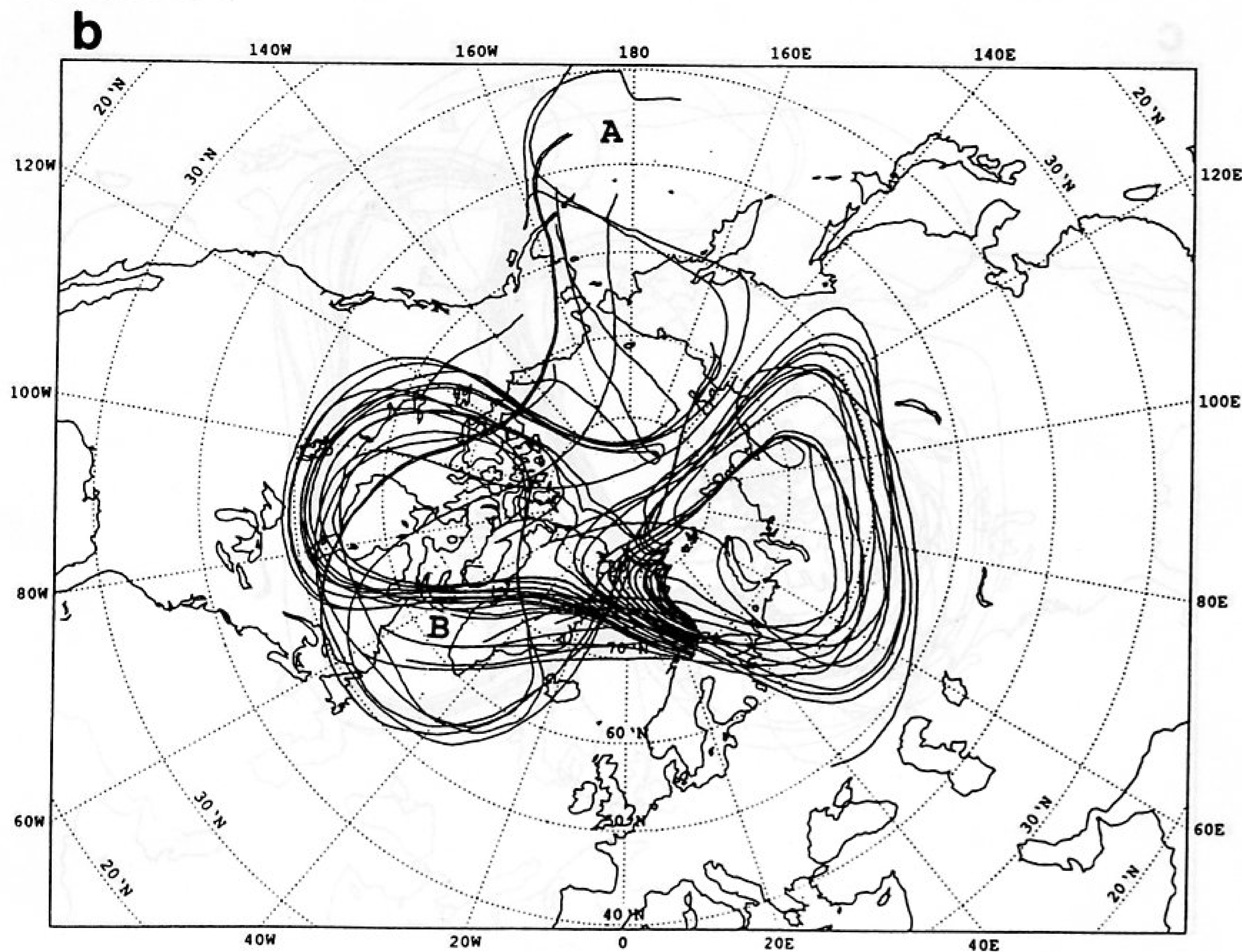


Figure 5. (continued)

during AASE II [Weinheimer *et al.*, 1993; Loewenstein *et al.*, 1993]. For February 16 and 18, 1993, the relation between HNO_3 and N_2O approximately agrees with the HNO_3^* - N_2O relations from Weinheimer *et al.* [1993], although substantial variability is apparent in the STREAM data, occasionally showing a significantly higher $\text{HNO}_3/\text{N}_2\text{O}$ ratio compared to AASE II. These air parcels originate both from middle and from high latitudes.

The empirical relation derived by Kawa *et al.* [1990] (solid line in Figure 12) represents the $\text{N}_2\text{O}/\text{HNO}_3^*$ relation higher up in the stratosphere. The $\text{HNO}_3/\text{N}_2\text{O}$ ratio we measured on February 17 agrees with Kawa *et al.* [1990], except for the highest HNO_3 concentrations, measured at the maximum flight level (12.3 km altitude). The air parcels on this level all originate from lower latitudes, whereas the back trajectories of all other stratospheric air parcels remain within the vortex during the period considered (Figure 5).

Implications for O_3 Loss and Heterogeneous Chemistry

The relations between O_3 and HNO_3 from our data show significant differences compared to the AASE I and AASE II results for air parcels from both middle and high latitudes. Also, the O_3 - N_2O relation on February 17 for air parcels originating from high latitudes shows differences with the AASE II results. These discrepancies may have been caused by differences in meteorological conditions, influencing the ratios between the trace gases, e.g., through stronger subsi-

dence and mixing. On the other hand, heterogeneous processes may have occurred during and previous to STREAM, leading to vertical redistribution of nitrogen species. In addition, enhanced O_3 loss may have occurred; both processes affect the relations between the trace gases.

O_3 Loss

There may be several causes for the low O_3 concentrations relative to those of N_2O on February 17, 1993, in comparison to the other two flights and the AASE II results: (1) our measurements may have been carried out deeper in the stratosphere (relatively low tropopause); relatively "old" vortex air with lower O_3 concentrations relative to N_2O may have been encountered; (2) mixing with air from lower latitudes with lower O_3 concentrations relative to N_2O ; (3) decreased concentrations of O_3 by enhanced chemical destruction. To discern between these possibilities, the relation between O_3 and N_2O in other regions, e.g., in the inner vortex at higher altitudes and in outer vortex air but also during prewinter conditions, must be known. There are no measurements to fulfill these requirements for the 1993 winter. However, such data are available for the 1992 winter. On the basis of the AASE II measurements, Proffitt *et al.* [1993] inferred that descending air inside the vortex may be enriched in O_3 relative to N_2O in the absence of heterogeneous O_3 loss. They also showed that the ratio between N_2O and O_3 for air with $\theta < 420$ K is about the same inside and outside the polar vortex. On the other hand, Browell *et al.* [1993] suggest that transport of outer vortex air

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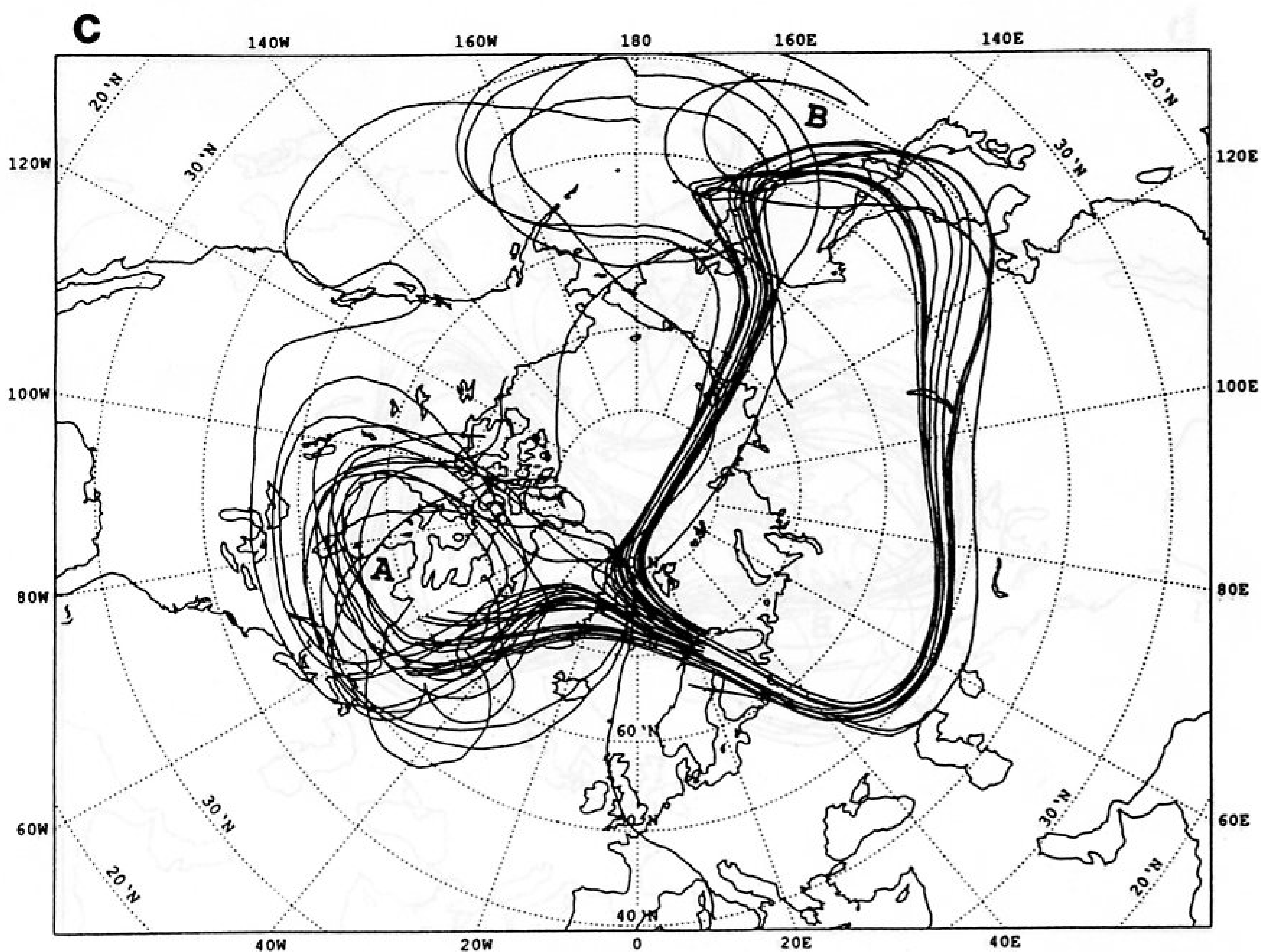


Figure 5. (continued)

into the vortex area, with $380\text{ K} < \theta < 420\text{ K}$ and relatively low O_3 concentrations, can indeed account for relatively low O_3 concentrations in that region. In addition, midlatitude air may have originated in part from the vortex, which is reduced in O_3 through heterogeneous processing by PSCs and transported across the vortex earlier in the winter [Tuck *et al.*, 1992]. The stratospheric air parcels on February 17 that were characterized by low O_3 concentrations relative to N_2O all originate from high latitudes, thus possibilities 1 and 2 do not appear to be applicable. However, for air parcels originating from middle latitudes, containing relatively low N_2O and O_3 concentrations, southward transport of vortex air earlier in the winter may be considered, which is also consistent with the relatively high HNO_3/O_3 ratios measured during STREAM.

The air parcel trajectories preceding February 17 with relatively low O_3 and N_2O concentrations and a $\text{HNO}_3\text{-N}_2\text{O}$ relation typical for vortex air appear to have followed the inner vortex structure for at least 10 days. The vortex remained stable during the winter time previous to the STREAM flights. Thus enhanced photochemical loss of O_3 during diabatic descent inside the vortex may be considered as an explanation for the low O_3 concentrations relative to N_2O on February 17. From linear regression analysis we infer that the potential temperatures of these air parcels are 15 K (at $\text{N}_2\text{O} = 280\text{ ppbv}$) to 20 K (at $\text{N}_2\text{O} = 240\text{ ppbv}$) lower than those encountered on February 18. Assuming a potential temperature cooling rate of 0.6 K d^{-1} [Larsen *et*

al., 1994], this difference in potential temperature is equivalent to a 25–33 days descent in the vortex. The O_3 concentrations in these air parcels are 30–32 ppbv lower on February 17 compared to February 18; thus we deduce an O_3 decrease of $4\text{--}7\text{ ppbv d}^{-1}$, corresponding to $0.9\text{--}1.2\% \text{ d}^{-1}$. This agrees with the estimated O_3 destruction rates for the 1993 early winter [Larsen *et al.*, 1994]. These results also agree with O_3 depletion in the lower part of the stratosphere between mid-January and mid-February 1992 [Proffitt *et al.*, 1993].

Heterogeneous Chemistry

About 1.5 year after the eruption of Mount Pinatubo, enhanced concentrations of sulfate aerosols still persisted in the lower stratosphere [Deshler *et al.*, 1993; Beyerle *et al.*, 1994; Rosen *et al.*, 1994]. The residence (*e* folding) time of volcanic aerosols in the stratosphere was estimated at 1.14 years, based on measurements after the eruption of El Chichon [Snetsinger *et al.*, 1992]. Recent measurements by Stone *et al.* [1993] suggest that the *e*-folding time for the Pinatubo particles is 1.13 years, thus comparable to the estimate of Snetsinger *et al.* [1992]. In line with the estimations of the Pinatubo aerosol *e*-folding time, enhanced column amounts of HNO_3 at 45°S were found until May 1993 [Koike *et al.*, 1994].

Heterogeneous processing involving sulfate aerosols enhance the gaseous HNO_3 concentration relative to O_3 and N_2O , through reaction (1) at midlatitudes and through reac-

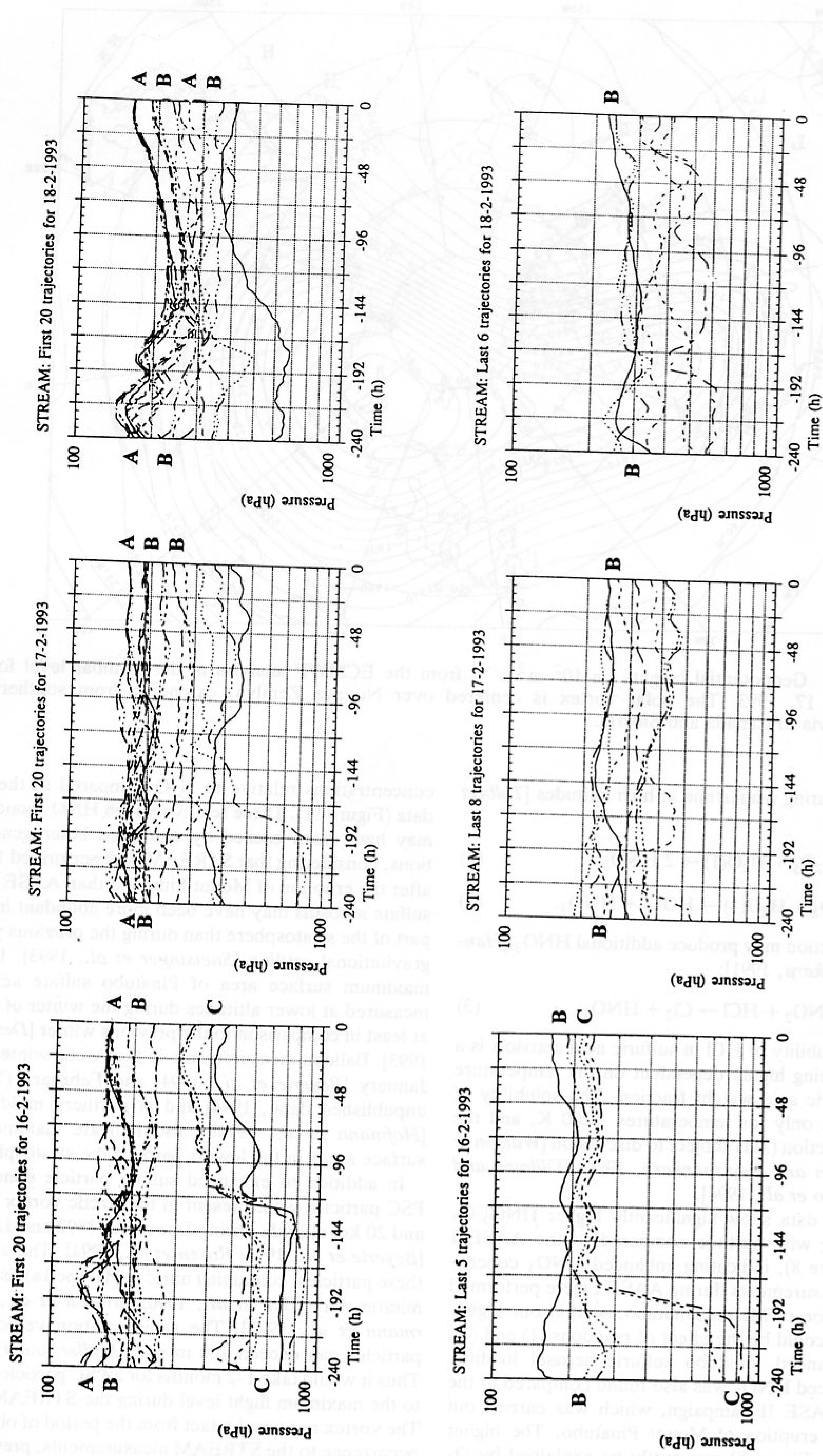


Figure 6. Time series (hours) and vertical distribution (pressure coordinates in millibars) of the trajectories on February 16, 17, and 18, 1993. Marked trajectories correspond to air parcels marked in the vertical distributions (see Figures 2a-2c).

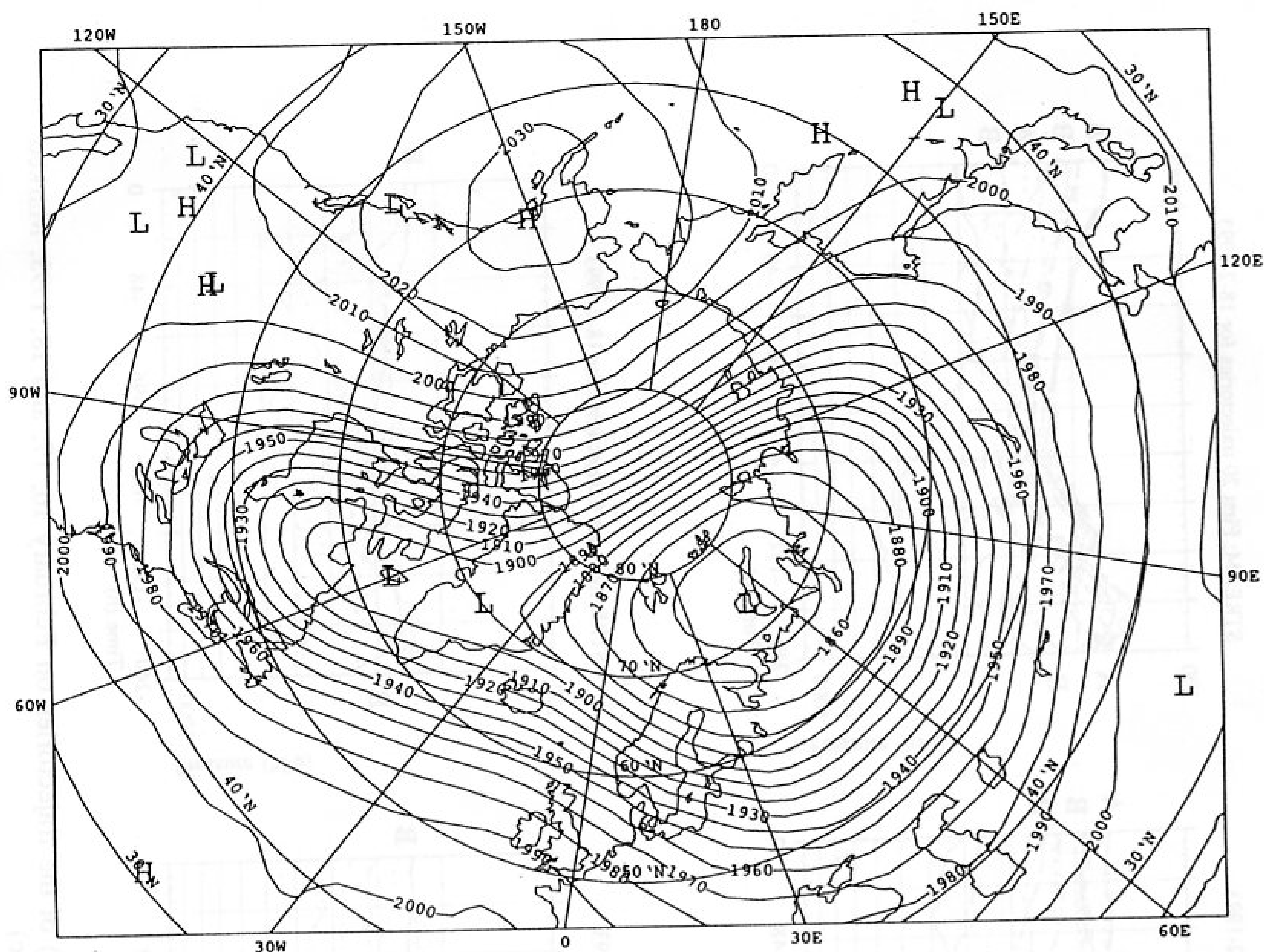
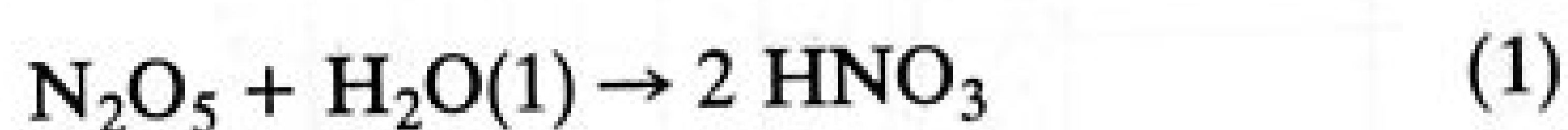
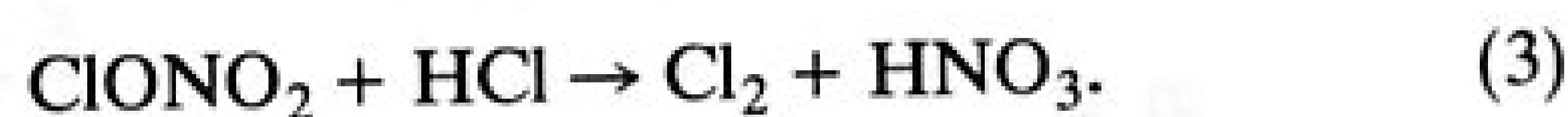


Figure 7. Geopotential heights (in $10^2 \text{ m}^2 \text{ s}^{-2}$) from the ECMWF analysis at the 50-mbar level for February 17, 1993. The polar vortex is centered over Novaya Zemlya, extending from southern Scandinavia to Canada and Siberia.

tions (1) and (2) during wintertime at high latitudes [Tolbert *et al.*, 1988]:



The following reaction may produce additional HNO_3 [Hanson and Ravishankara, 1991]:



However, the solubility of HCl in sulfuric acid aerosols is a limiting factor, being highly dependent on the temperature and on the sulfuric acid weight fraction. The solubility of HCl is significant only for temperatures $< 200 \text{ K}$, and the importance of reaction (3) is subject to discussion [Watson *et al.*, 1990; Hanson and Ravishankara, 1994; Williams and Golden, 1993; Luo *et al.*, 1994].

The STREAM data show significantly higher HNO_3/O_3 ratios, increasing with altitude compared to the AASE I results (see Figure 8), indicating enhanced HNO_3 concentrations. The measurements during AASE I were performed before the eruption of Mount Pinatubo, so that our higher HNO_3/O_3 ratios could be the effect of reactions (1) and (2), due to the enhanced Pinatubo sulfuric aerosol loading. However, enhanced HNO_3 was also found compared to the results of the AASE II campaign, which was carried out earlier after the eruption of Mount Pinatubo. The higher HNO_3/O_3 ratios (Figure 8) can partly be explained by O_3 depletion, as described in the previous section. Also, air parcels which originate from midlatitudes had higher HNO_3

concentrations relative to N_2O compared to the AASE II data (Figure 11). These relatively high HNO_3 concentrations may have been caused by enhanced heterogeneous reactions, considering that STREAM was performed 1 year later after the eruption of Mount Pinatubo than AASE II and that sulfate aerosols may have been more abundant in the lower part of the stratosphere than during the previous year due to gravitational settling [Snetsinger *et al.*, 1993]. In fact, the maximum surface area of Pinatubo sulfate aerosols was measured at lower altitudes during the winter of 1992–1993, at least in comparison to the previous winter [Deshler *et al.*, 1993]. Balloon measurements in the Arctic winter of 1993 in January [Beyerle *et al.*, 1994] and February (T. Deshler, unpublished data., 1994) and at northern middle latitudes [Hofmann *et al.*, 1994b] also indicate maximum aerosol surface areas in the lowest parts of the stratosphere.

In addition to enhanced sulfate particle concentrations, PSC particles were present in the Arctic vortex between 16 and 20 km altitude during December 1992 and January 1993 [Beyerle *et al.*, 1994; Rosen *et al.*, 1994]. The size range of these particles, containing nitric acid (type 1a), is 0.5 to a few micrometers [Dye *et al.*, 1990; Browell *et al.*, 1990; Borrmann *et al.*, 1993]. The sedimentation velocity of such particles can exceed 100 m d^{-1} [Müller and Peter, 1992]. Thus it would take 1–2 months for a PSC particle to sediment to the maximum flight level during the STREAM campaign. The vortex remained intact from the period of observed PSC occurrence to the STREAM measurements, preventing mixing with warmer air. Moreover, the stratospheric temperatures in the northern hemisphere winter were unusually low

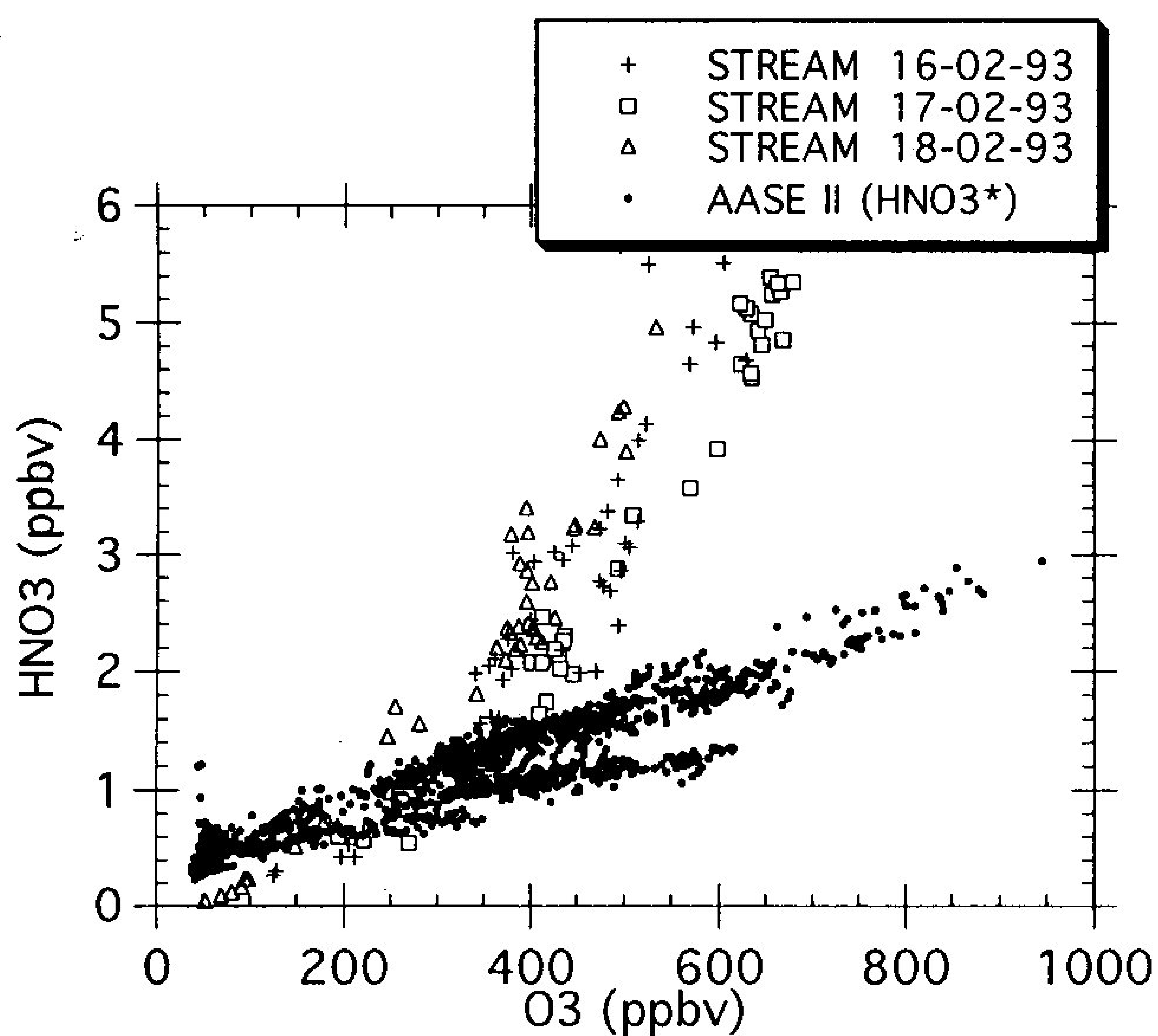


Figure 8. HNO_3 versus O_3 (ppbv) of the three Stratosphere-Troposphere Experiment by Aircraft Measurement (STREAM) flights compared to the results of the Airborne Arctic Stratospheric Experiment (AASE) II DC-8 flights in February 1992. It is assumed that NO_y contains 80% HNO_3 (see text). The solid circle represents the AASE II data.

[National Oceanic and Atmospheric Administration (NOAA), 1993] and conditions favorable for PSC type 1 formation at potential temperature levels between 380 and 550 K and, occasionally, even below 380 K occurred up to early March 1993, hence 1 month later than during the previous winter [Larsen *et al.*, 1994; Waters *et al.*, 1993]. The PSC particles thus may have remained (partly) intact during descent, causing denitrification of the upper air and subsequent evaporation and nitrification of the lower stratosphere. A clear signature of sedimentation and consequent redistribution of HNO_3 was observed by Arnold and Knopp [1989], Schlager and Arnold, [1990a, b], and Arnold *et al.* [1992]. Enhancement of NO_y concentrations in the lower stratosphere, as a result of sedimentation of PSCs, has also been measured by Hübler *et al.* [1990], Fahey *et al.* [1990], and Kawa *et al.* [1990]. This also seems the most likely explanation for both the high HNO_3 concentrations relative

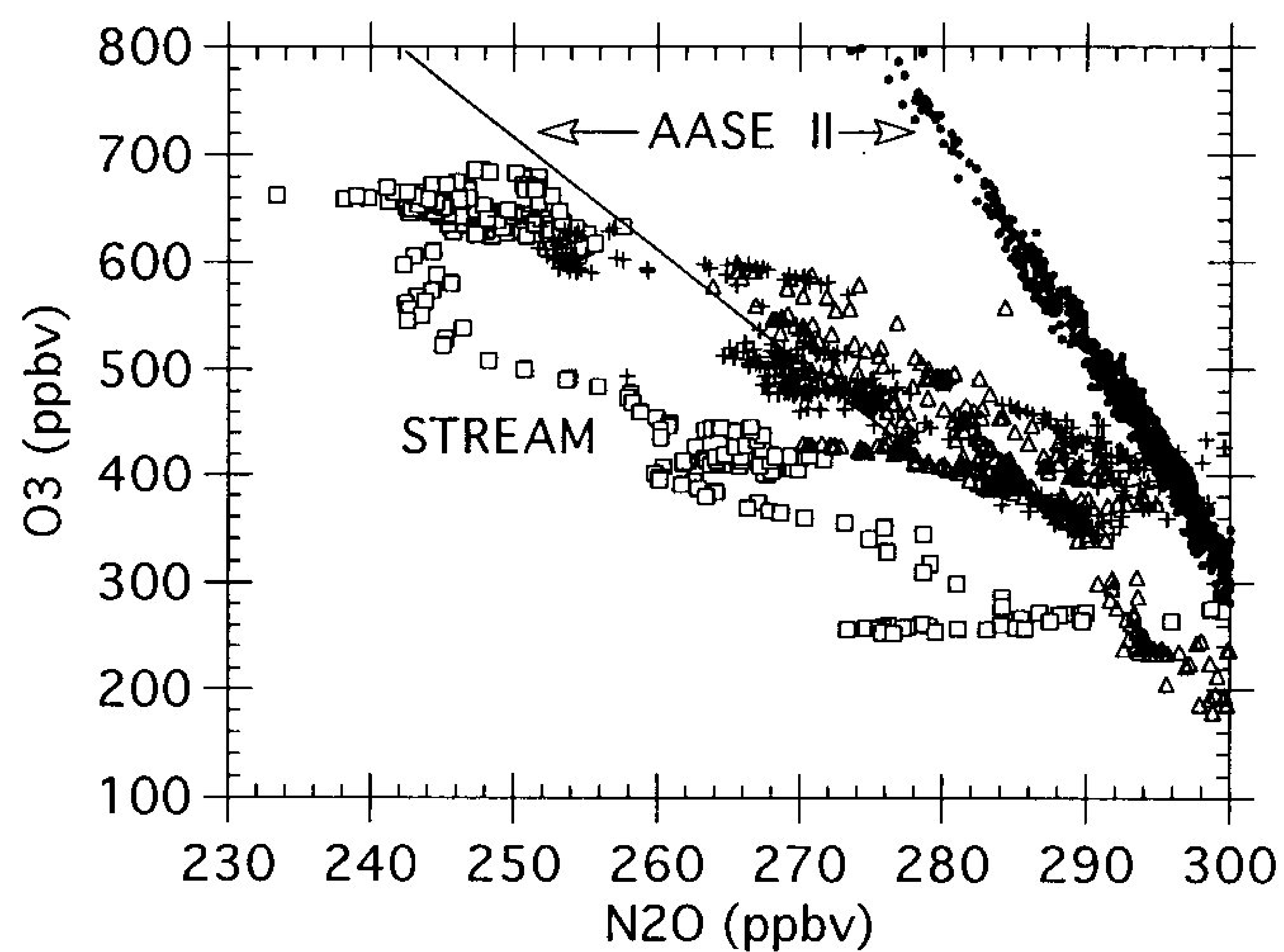


Figure 10. Comparison of the HNO_3/O_3 ratio relative to the N_2O concentration (ppbv) for February 16, 17, and 18, 1993, with the results of AASE II DC-8 (February 1992) flights (solid circles).

to N_2O in air parcels originating in the vortex area during STREAM. On the other hand, Notholt *et al.* [1994] proposed that denitrification of the stratosphere by PSC formation and sedimentation was not significant during the 1992/1993 winter, based on their measurements of HNO_3 column measurements. However, denitrification by PSCs and subsequent evaporation carries HNO_3 to lower altitudes, so that the column densities may not change. In fact, their HNO_3 column densities measured in February 1993 show strong variation, which may indicate temporary HNO_3 perturbations by its trapping into PSCs.

Finally, it is important to stress that the high variability of the HNO_3 concentrations relative to N_2O measured during STREAM are also related to a variable contribution of HNO_3 to NO_y . For example, during wintertime in the high-latitude lower stratosphere the contribution of HNO_3 to NO_y decreases in favor of ClONO_2 after exposure to sunlight in combination with heterogeneous chemistry involving stratospheric particles [Kawa *et al.*, 1992; Müller *et al.*, 1994]. This is confirmed by high concentrations of ClONO_2 , measured in the Arctic lower stratosphere in the winter [von Clarmann *et al.*, 1993; Oelhaf *et al.*, 1994]. Air parcels which

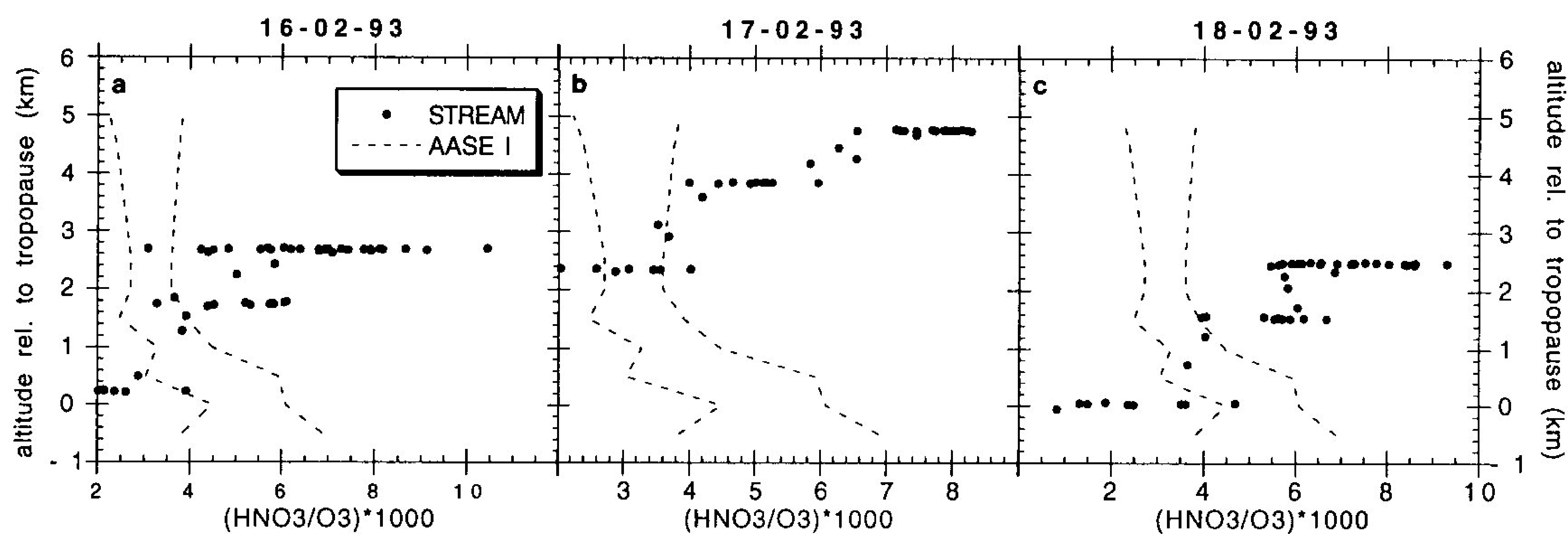


Figure 9. Vertical distribution of the HNO_3/O_3 ratios for the three STREAM flights compared to the HNO_3/O_3 ratio measured during AASE I, February 1989. The dashed lines indicate the range of the AASE I ratios.

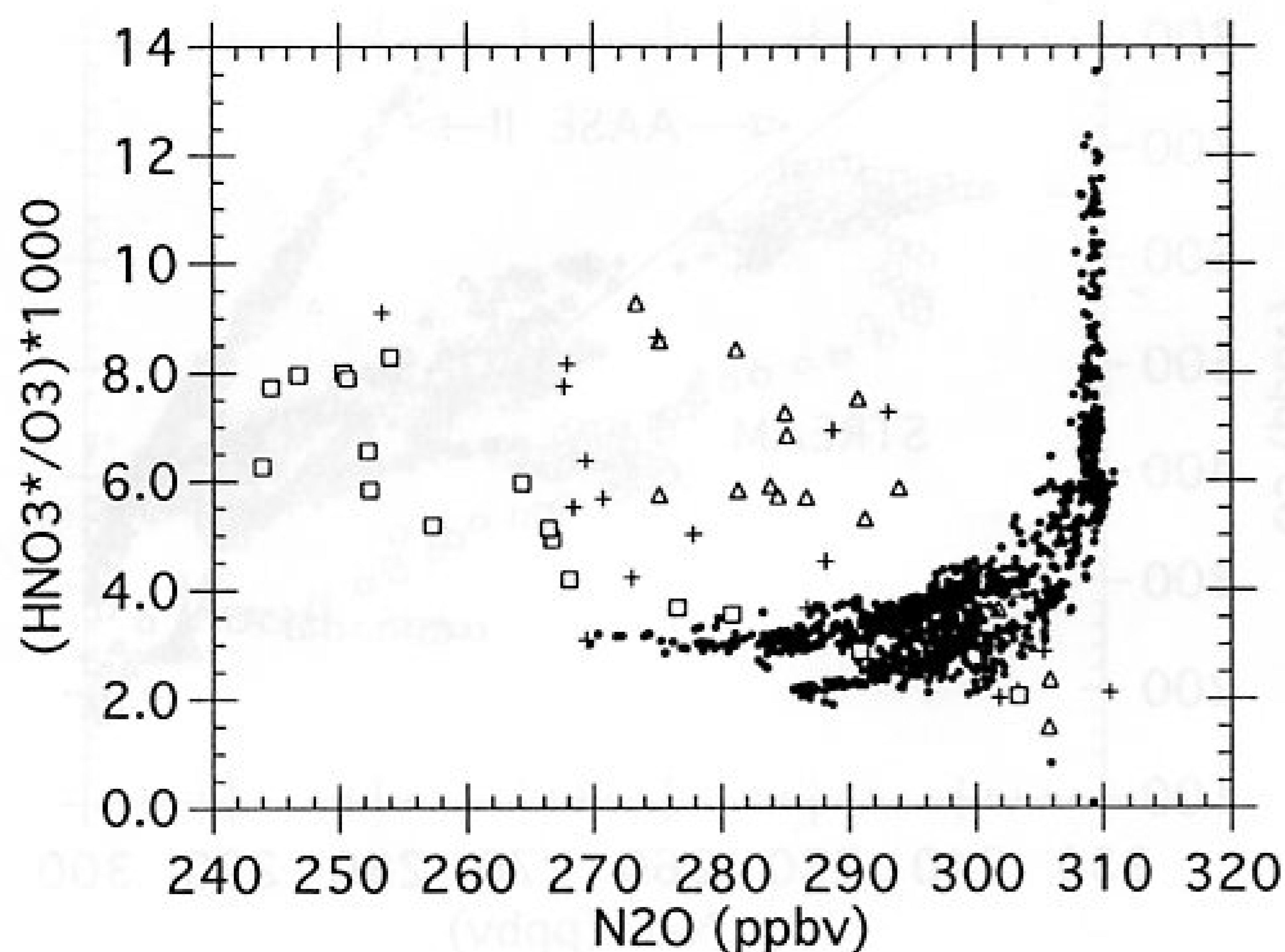


Figure 11. Comparison of the relation between O_3 and N_2O (ppbv) of all three STREAM flights with the results of the AASE II DC-8 February flights (solid circles) and the lower limit of the AASE II ER-2 measurements (solid line). The symbols correspond to the different STREAM and AASE II DC-8 flights, as indicated in Figure 8.

followed the vortex area during 10 days previous to the flights may have been exposed to sunlight, so that the assumption of 80% HNO_3 in NO_y may not be valid, and HNO_3^* may have been overestimated.

Summary and Conclusions

We have presented the results of in situ measurements of HNO_3 , O_3 , and N_2O performed in the lower stratosphere at high northern latitudes during the first STREAM campaign in February 1993. The results show highly variable distribu-

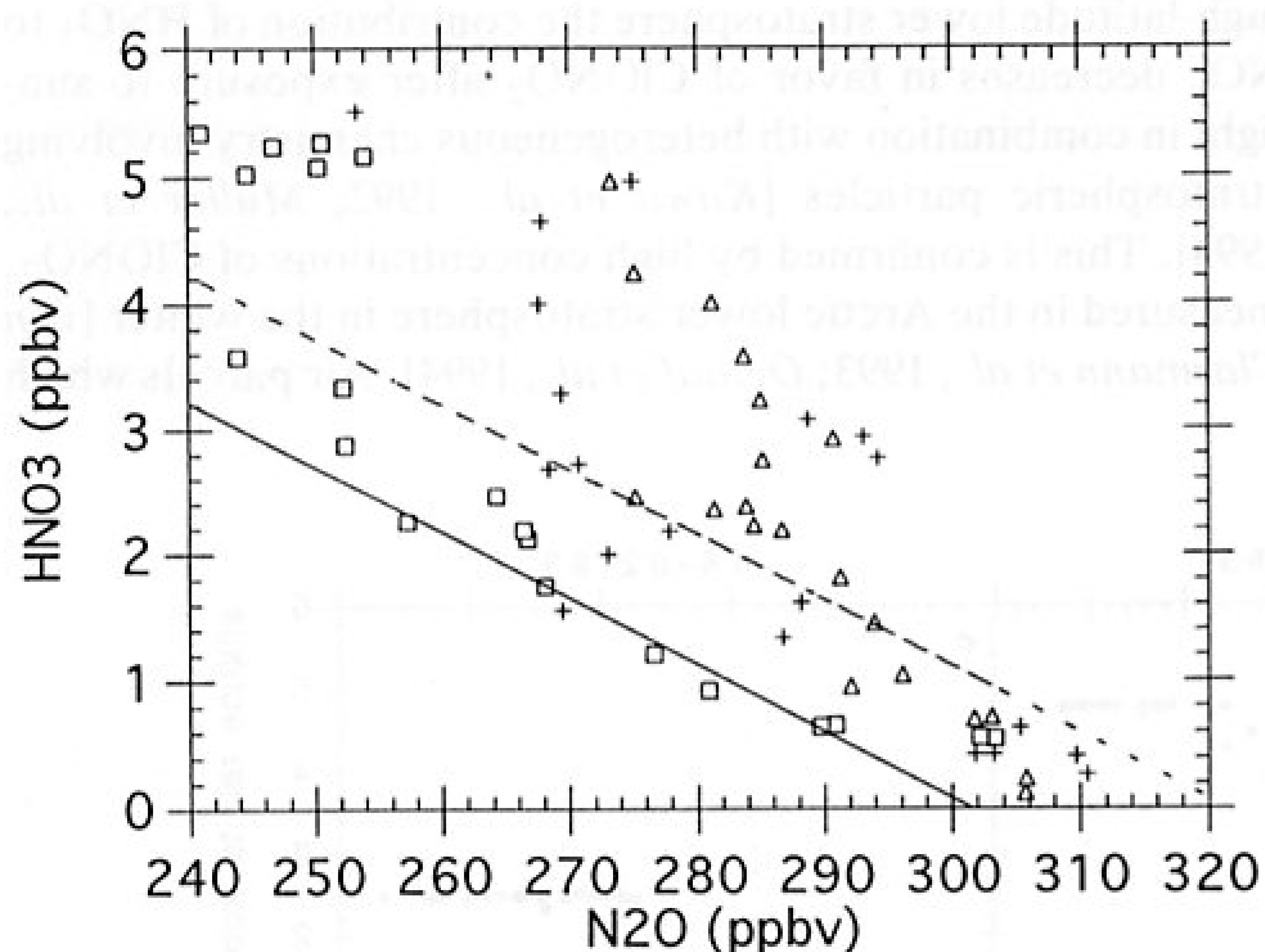


Figure 12. The relation between HNO_3 and N_2O (ppbv) for all three flights compared to the empirical relations derived from HNO_3^* and N_2O data measured during AASE I and AASE II (see text). The solid line represents Arctic polar vortex air (calculated from data measured by the ER-2, February 1989). The dashed line represents the AASE II DC-8 data of the February 1992 flights. The symbols correspond to the different STREAM flights, as indicated in Figure 8.

tions and ratios of these trace gases in the lower part of the Arctic stratosphere, indicating chemically perturbed vortex air below the bottom of the vortex and the presence of tropospheric air in the lower stratosphere by upward transport. Low O_3 concentrations relative to N_2O were measured for N_2O concentrations down to 235 ppbv. The air parcels with the lowest O_3 and N_2O concentrations were observed during a flight on February 17, 1993. The calculated 10-day back trajectories indicate that these air parcels have remained within the vortex, implying that the air has descended by diabatic cooling. These air parcels were characterized by HNO_3 - N_2O relations typical for vortex air. The low O_3 concentrations relative to N_2O on February 17 are explained by enhanced O_3 loss. Based on the comparison of the O_3 - N_2O relations of February 16, 17, and 18, we estimate an O_3 loss of 4–7 ppbv d^{-1} (0.9–1.2% d^{-1}) in the lower stratosphere during mid-January to mid-February 1993. The STREAM data are compared with previous measurements of NO_y , O_3 , and N_2O during the AASE I (February 1989) and AASE II (February 1992) campaigns, assuming that NO_y contains 80% HNO_3 . The NO_y/O_3 ratios measured during AASE I are constant with altitude in the stratosphere, while our HNO_3/O_3 ratios show much more variability in the stratosphere and they increase with altitude. As a result of heterogeneous chemistry involving sulfuric acid particles, repartitioning between $ClONO_2$ and HNO_3 within NO_y may have occurred, so that the contribution of HNO_3 to NO_y was not constant. The measurements of AASE I were performed before the eruption of Mount Pinatubo in 1991. The higher O_3/HNO_3 ratios measured during STREAM may have been caused by Pinatubo aerosol in the lower stratosphere, leading to higher HNO_3 concentrations through heterogeneous reactions. The STREAM data also show significantly higher HNO_3 concentrations relative to N_2O and to O_3 compared to the results of AASE II, which was performed after the eruption of Mount Pinatubo. These differences can partly be explained by assuming heterogeneous O_3 loss in the vortex. The vortex air may have descended through the bottom of the vortex, or may have crossed the vortex edge earlier in the winter and transported into the region of the measurements. The high HNO_3 concentrations relative to N_2O suggest a stronger influence of heterogeneous chemistry on Pinatubo aerosols in the lower stratosphere, compared to 1992, due to enhanced sulfuric aerosol abundance by gravitational settling of the particles. In addition to heterogeneous processing by sulfate aerosols these ratios may also have been affected by the presence of PSC particles. The air parcels originating from the vortex area may have been denitrified through preceding PSC formation, enriching the lower stratosphere in HNO_3 by sedimentation and subsequent evaporation of the particles, which we consider the most likely explanation of the measured relatively high HNO_3/N_2O ratios. Because of the prevailing low temperatures in the vortex, PSCs occurred more frequently during the 1992/1993 winter compared to the previous winter. Thus we infer important perturbations of Arctic lower stratospheric chemistry by PSCs and volcanic aerosols 20 months after the eruption of Mount Pinatubo.

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F. Arnold, A. Frenzel, and A. Waibel, Max Planck Institute for Nuclear Physics, Heidelberg, Germany.

M. J. A. Bolder, A. Bregman (corresponding author), and J. Lelieveld, Department of Air Quality, P. O. Box 8129, Wageningen University, 6700 EV, Wageningen, Netherlands.

H. Fischer, F. G. Wienhold, and T. Zenker, Air Chemistry Department, Max Planck Institute for Chemistry, Mainz, Germany.

G. W. Harris, Center for Atmospheric Chemistry, Dep. of Chemistry, York University, North York, Ontario, Canada.

P. F. J. van Velthoven, Royal Netherlands Meteorological Institute, P. O. Box 201, De Bilt, Netherlands.

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