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Meridional distributions of NOx, NOy, and other species in the lower stratosphere and upper troposphere during AASE II

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Abstract. The meridional distribution of NOx in the lower stratosphere and upper troposphere is inferred from 10 flights of the NASA DC-8 in the northern winter of 1992, along with like distributions of NOy, NO2(NOy), CO, and C2Cl4. In the lowest few km of the stratosphere there is little vertical gradient in NOx over the range of latitudes measured (40°-90°N). There is a substantial latitudinal gradient, with 50 pptv above the pole and 120 pptv near 40°N. In the uppermost few km of the troposphere, background values range from 30 pptv above the pole to 90 pptv near 40°N. On two occasions higher values, up to 140 pptv in the mean, were seen 2-3 km below the tropopause in association with frontal systems. The meridional distributions of CO and C2Cl4 show the same feature, suggesting that the source of the elevated NOx is near the earth's surface.

Introduction

In the upper troposphere and lower stratosphere, NO and NO2 (NOx) play important roles in the production and destruction of O3. The region near the tropopause is one where O3 has its greatest effect as a greenhouse gas and where the lifetime of NOx is relatively long, so a given emission can have a larger impact. The global distribution of NOx in this region is only poorly known, however. Ehhalt et al. [1992] show the meridional distribution of NO derived from measurements taken in June, 1984; Wahner et al. [in preparation] show the same for January, 1991. Carroll et al. [1990] show NOx measurements from early 1989. In this paper we complement those measurements with meridional distributions derived from measurements taken in the winter of 1992 during the Airborne Arctic Stratospheric Expedition II (AASE II). In conjunction we show the distributions of NOy, NO2(NOy), CO, and C2Cl4.

The Measurements

AASE II is summarized by Anderson and Toon [1993]. The measurements reported here were obtained during the 10 flights of the NASA DC-8 during February and March. Figure 1 shows the latitudes and longitudes of the 1-min measurement intervals used in the present analysis. Altitudes range from 30°N to the North Pole, and from 150°W to 20°E (aside from more complete longitudinal coverage in the immediate vicinity of the pole).

For NOx, NOy, and CO, averages are computed for those 1-min intervals that are completely filled with higher resolution samples (2 s for NOx and NOy, 5 s for CO). For the carbon species, grab samples, the integration times are dependent on altitude, but typically in the range 20-120 s. The chemical measurement techniques are described elsewhere (in Walega et al. [1991] and Weinheimer et al. [1993] for NOx and NOy, in Anderson et al. [1993] and references therein for the reactive carbon species). At low mixing ratios of NO and NO2 the overall uncertainty in 1-min NOx values is 20 pptv (including bias and precision errors). The percentage error decreases with increasing NOx, and it is ~35% for the highest values shown. The measurement of NOy (NO, NO2, HNO3, ClONO2, 2N2O5, H2O2NO2, etc.) shows a significant lag in air with large gradients in HNO3 (an inlet problem), as when crossing the tropopause. The resulting errors can be rather large (~35%), but underestimates on ascent tend to cancel overestimates on descent so the effect is reduced for the averages shown here. Altitudes are computed relative to the altitude of the tropopause, the height of which is determined at 14-s intervals along the flight track using remotely sensed temperature profiles, as described by Gary [1989]. Data from this instrument are not available for the January flights, so those flights are excluded from the present analysis.

The Meridional Distribution of NOx

Figure 2a shows the meridional distribution of NOx as a histogram, explicitly illustrating the binning used and also the number of 1-min NOx samples in each bin. In order to have an adequate number of samples in each bin, and at the same time preserve altitude resolution, the bin dimensions are 15° in latitude by 1 km in altitude. The midpoints of the bins are given on the horizontal axes of the histogram. For the 30°-45°N latitude bin, most of the samples are closer to 45°N than 30°N.

As the numbers of samples on the individual columns indicate, the sampling is extensive above the tropopause (except for the lowest latitude bin), but limited below. Nonetheless there is consistency among the altitude profiles for the different latitude bins. In descending from the stratosphere to the troposphere, there is a decrease in NOx in all four latitude bins immediately below the tropopause. With further descent there is a marked increase in the middle two latitude bins, spanning 45°-75°N, with a slight increase for the 30°-45°N range, and little change with altitude for the 75°-90°N range. For the two latitude ranges with data in the lowest altitude range, there is a marked decrease in NOx at the lowest level. This suggests the presence of a layer of NOx peaking at 2-3 km below the tropopause (see Figure 1 for the latitudes sampled). However, an examination of the individual flight profiles reveals that this is not a consistent feature and is primarily due to two events (discussed later) during the 10 flights. Thus the appearance of a layer at 2-3 km below the tropopause should be viewed as reflecting the occasional occurrence of relatively high values there, but no significance is attached to the exact shape, position, and latitudinal dimension of the apparent layer. Although the elevated NOx may be intermittent, it occurs frequently enough and with high enough values (at least in this sample) to have an impact on the means.
Fig. 1. Combined flight track of the DC-8 for the 10 flights in February and March 1992. Points plotted with an 'x' are those at altitudes between 2 and 3 km below the tropopause, the level of the elevated mixing ratios.

Figure 2b shows these binned mixing ratios as a contour plot. The principal features of the histogram of course remain: In the lower stratosphere, (1) there is little vertical gradient in NOx, and (2) there is a marked latitudinal gradient, with values of 50 pptv above the pole, increasing to 120 pptv toward 40°N. In the troposphere, (3) there is a relative minimum 0-1 km below the tropopause with values of 40 pptv north of 45°N, and (4) there are higher values of NOx present within a few km of the tropopause, with averages peaking at 130 pptv for this particular sample. When the medians are contoured instead of the means, these same basic features are present and with about the same magnitudes (not shown).

Figure 2c is the same as Figure 2b, except it excludes data during the two events principally responsible for the apparent layer 2-3 km below the tropopause. Those high values were obtained during the final descent into Stavanger (Norway, 59°N, 6°E) on 920214 and during the final descent into Bangor (Maine, USA, 45°N, 69°W) on 920217. Winds from a mesoscale model (J.-F. Lamarque, personal communication) for 920214 demonstrate two potential sources of polluted surface air to account for the high values measured: (1) Back trajectories show transport of surface air from southern England to aircraft altitudes (~6 km) near Stavanger in approximately 48 hours. (2) There is also, at the time of measurement and slightly before, convergence in the vicinity of Stavanger, indicating the possibility of local convection. Thus the high values are possibly due to either advective/convective transport from England or convective transport over Norway. On 920217 there was a front oriented east-west near the U.S.-Canada border [NOAA, 1992] as the southbound DC-8 approached Bangor through this area at an altitude of 6 km. This, combined with the presence of precipitation in the region [NOAA, 1992], suggests that the source of the elevated species abundance was convection of polluted boundary layer air. Exclusion of these two periods gives a representation (Figure 2c) of winter background conditions (not strongly influenced by recent pollution-laden convection) at the latitudes and longitudes flown. After exclusion the standard deviations of the 1-min values in the grid boxes range from 3% to 92% of the respective means; the mean is 47%. Prior to exclusion of the high values, the maximum was greater than 200%.

Figure 3 shows the 1-min NOx measurements of Figures 2a,b (high values not excluded) binned and contoured in a similar manner, except using altitude relative to sea level. This facilitates comparison with the NO distributions in Ehhalt et al. [1992] and Wahner et al. [in preparation], and with the NOx profile in Carroll et al. [1990]. The NOx inferred from the measured NO is expected to have a distribution similar to that for NO, as demonstrated for the summertime measurements [Ehhalt and Drummond, 1988], so it is meaningful to compare the NO from those studies with the NOx from AASE II.

The dominant feature in the January TROPOZ II measurements of Wahner et al. [in preparation] is a strong latitude gradient with much higher NO at 50°-60°N, 100-500 pptv for 5-11 km altitude, than at lower latitudes, where values are generally 100 pptv and less. This latitude gradient is in the opposite direction from that for background conditions in AASE II (Figure 2c), but it is in the same direction as that for many hydrocarbons in winter [Anderson et al., 1993]. Another difference is that the mean mixing ratios for 30°-60°N were generally higher for NO alone in TROPOZ II (100-500
NOx (pptv) NOx/NOy

Fig. 3. Contour plot of NOx as a function of altitude above the ground.

These differences are very striking, but it is not clear why they arise. One factor may be the difficulty in obtaining representative measurements for a species such as NOx which is relatively short-lived and has variable, localized sources. Also there is the possibility of systematic differences due to sampling different longitudes.

In contrast with this, the AASE II measurements are very similar in overall magnitude with those from AASE I [Carroll et al., 1990], where the high latitude (>59°N) median NOx was 40 pptv in the stratosphere, and 59 pptv in the troposphere. The midlatitude (near 40°N) median NOx was 102 pptv in the stratosphere, and 56 pptv in the troposphere.

Unlike the maximum at 6-7 km, the transition in NOx at the tropopause (Figure 2) is "smeared out" and is not readily apparent when altitude relative to the ground is used (Figure 3). There is enough variation in the height of the tropopause that the low values just below the tropopause are distributed over several bins of altitude above the ground, causing the transition to be lost in that representation.

Meridional Distributions of NOy and NOx/NOy

Figure 4 shows the meridional distribution of NOy relative to the height of the tropopause. There is little variation with latitude, and from 1 km below the tropopause to 3 km above, there is a uniform altitude gradient of ~600 pptv/km. In the troposphere, there is a layer 2-3 km below the tropopause, similar to the apparent layer in NOx. Interestingly, the NOy layer does not completely disappear when the two high-NOx periods are excluded (not shown). The greater persistence of this feature for NOy may reflect its longer lifetime. The region of high NOy extends to lower altitudes over the pole which is due to the polluted air seen in a profile measured at the pole on 920314.

Fig. 4. NOy contour plot, as in Fig. 2b.

Fig. 5 shows the meridional distribution of the NOx/NOy ratio (high values not excluded). In the stratosphere, NOx/NOy increases in going from high to low latitudes, similar to NOx. Since there is little latitudinal gradient in NOy, the increase in NOx is due to a change in the NOy partitioning, one factor being the increased photolysis of HNO3 at lower latitudes.

In the stratosphere at higher latitudes (50°-90°N), the NOx/NOy ratio increases from ~3% to ~8% as the tropopause is approached from above. NOx is relatively constant at ~70 pptv in the middle of this range of latitudes. One cause for the increase in the NOx/NOy ratio may be a slowing of the conversion of NOx to NOy as the tropopause is approached. As the tropopause is approached, O3 and temperature decrease, and both of these trends are likely to slow the conversion of NOx to NOy, whether via gas phase conversion of NO2 to HNO3 by reaction with OH, or via heterogeneous conversion of N2O5 to HNO3 after the reaction of NO2 with O3. If such a
mechanism controls the NO\textsubscript{x}/NO\textsubscript{y} ratio, then the relative constancy of NO\textsubscript{x} follows coincidentally from the opposing gradients in NO\textsubscript{y} and NO\textsubscript{x}/NO\textsubscript{y}. On the other hand, a NO\textsubscript{x} source, such as aircraft, could also be a factor. In the troposphere, NO\textsubscript{y}/NO\textsubscript{x} mirrors closely the distribution of NO\textsubscript{x} (Figure 2b). Peak averages are 14-18\%; against a background with average values of 4-10\%.

Meridional Distributions of Carbon Species

The high levels of NO\textsubscript{x} and NO\textsubscript{y} in the troposphere are correlated with high levels of CO (Figure 6) and C\textsubscript{2}Cl\textsubscript{4} (Figure 7). Similar layers appear for each of these species, as well as for a number of other reactive carbon species (not shown), including C\textsubscript{2}H\textsubscript{4}. The presence of C\textsubscript{2}Cl\textsubscript{4} indicates an industrial origin, and CO a combustive origin, of the elevated NO\textsubscript{x} and NO\textsubscript{y} in the troposphere. Moreover the relatively short lifetime of C\textsubscript{2}H\textsubscript{4} (perhaps 2-4 days for these conditions) indicates the freshness of the emission. While CO and NO\textsubscript{x} are known to be emitted by aircraft, C\textsubscript{2}Cl\textsubscript{4} is unlikely to be, so the earth's surface is the likely source of the emissions. This is corroborated by the meteorology discussed earlier for the two days that contribute most to the elevated NO\textsubscript{x}.

Summary

Meridional distributions of NO\textsubscript{x} in the lower stratosphere and upper troposphere are presented within the context provided by distributions of other species. In the lower stratosphere, there is no significant altitude gradient but a substantial latitude gradient (Figure 2b). In the upper troposphere, variability complicates the picture. For background conditions, that is, in the absence of recent pollution-laden convection (though not necessarily without such impact in the longer term), the pattern is similar to that in the lower stratosphere with little systematic variation with height, but a latitude gradient from 30\textdegree N to 90\textdegree N (Figure 2c).

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