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

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Abstract. The meridional distribution of NO_x 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 NO_y , NO_x/NO_y , CO, and C_2Cl_4 . In the lowest few km of the stratosphere there is little vertical gradient in NO_x 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 over 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 C_2Cl_4 show the same feature, suggesting that the source of the elevated NO_x is near the earth's surface.

Introduction

In the upper troposphere and lower stratosphere, NO and NO_2 (NO_x) play important roles in the production and destruction of O_3 . The region near the tropopause is one where O_3 has its greatest effect as a greenhouse gas and where the lifetime of NO_x is relatively long, so a given emission can have a larger impact. The global distribution of NO_x 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 NO_x 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 NO_y , NO_x/NO_y , CO, and C_2Cl_4 .

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. Latitudes 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 NO_x , NO_y , and CO, averages are computed for those 1-min intervals that are completely filled with higher resolution

samples (2 s for NO_x and NO_y , 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 NO_x and NO_y , in Anderson et al. [1993] and references therein for the reactive carbon species). At low mixing ratios of NO and NO_2 the overall uncertainty in 1-min NO_x values is 20 pptv (including bias and precision errors). The percentage error decreases with increasing NO_x , and it is ~35% for the highest values shown. The measurement of NO_y (NO, NO_2 , HNO_3 , ClONO_2 , $2\text{N}_2\text{O}_5$, HO_2NO_2 , etc.) shows a significant lag in air with large gradients in HNO_3 (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 NO_x

Figure 2a shows the meridional distribution of NO_x as a histogram, explicitly illustrating the binning used and also the number of 1-min NO_x 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 NO_x 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 NO_x at the lowest level. This suggests the presence of a layer of NO_x peaking at 2-3 km below the tropopause (see Figure 1 for the longitudes 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 NO_x may be intermittent, it occurs frequently enough and with high enough values (at least in this sample) to have an impact on the means.

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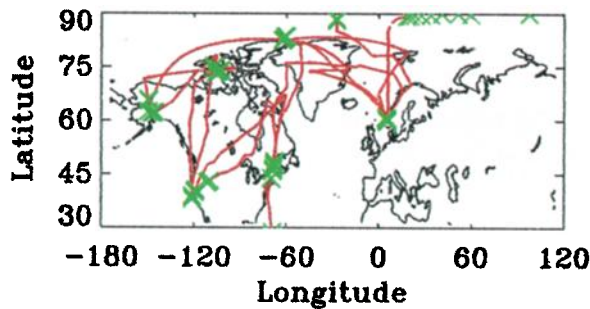


Fig. 1. Combined flight track of the DC-8 for the 10 flights in February and March 1992. Points plotted with an 'x' are those at altitudes between 2 and 3 km below the tropopause, the level of the elevated mixing ratios.

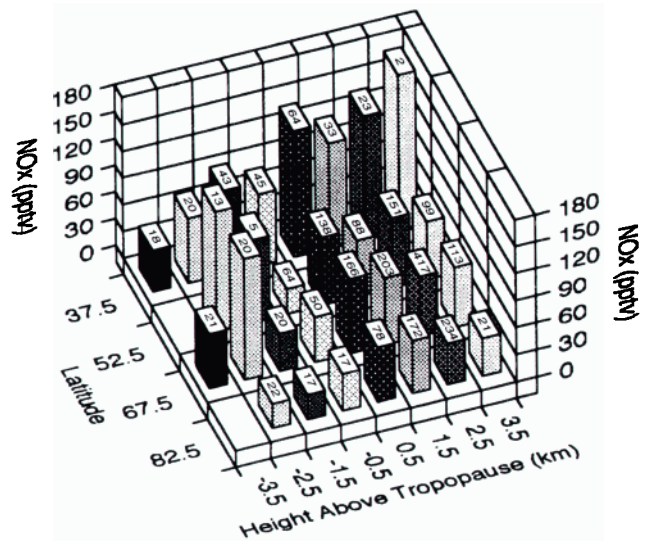


Figure 2b shows these binned mixing ratios as a contour plot. The principal features of the histogram of course remain: In the lower stratosphere, (1) there is little vertical gradient in NO_x, and (2) there is a marked latitudinal gradient, with values of 50 pptv above the pole, increasing to 120 pptv 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 NO_x 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 NO_x 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 NO_x profile in Carroll et al. [1990]. The NO_x 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 NO_x from AASE II.

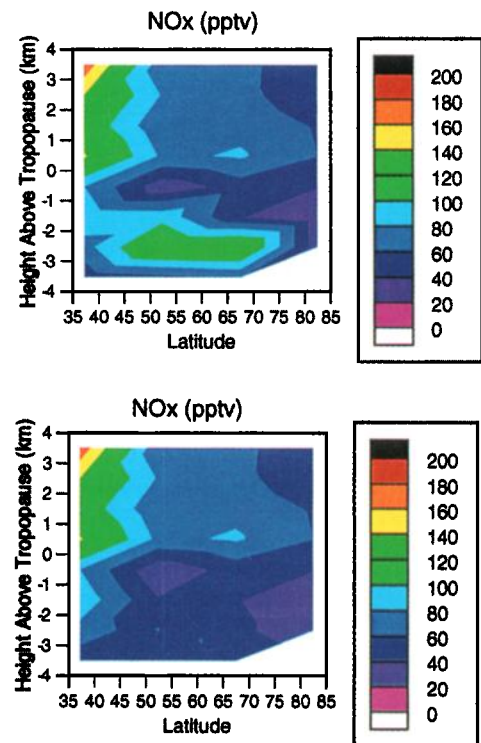


Fig. 2. (a) NO_x as a function of latitude and height above the tropopause, plotted as a histogram of the mean of all 1-min NO_x measurements within the bins indicated. The bins span 15° in latitude by 1 km in height with respect to the tropopause (TP). The number on each column is the number of 1-min samples in the bin. (b) Same means as in (a), except shown as a contour plot. (c) Same as (b), except excluding two periods of high NO_x, as described in the text.

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

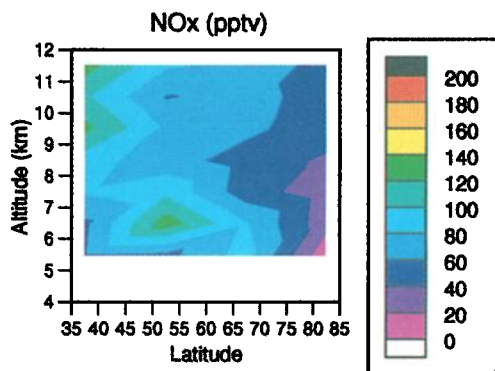


Fig. 3. Contour plot of NO_x as a function of altitude above the ground.

pptv) than for total NO_x in AASE II (40–140 pptv). 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 NO_x 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 NO_x was 40 pptv in the stratosphere, and 59 pptv in the troposphere. The midlatitude (near 40°N) median NO_x was 102 pptv in the stratosphere, and 56 pptv in the troposphere.

Unlike the maximum at 6–7 km, the transition in NO_x 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 NO_y and NO_x/NO_y

Figure 4 shows the meridional distribution of NO_y 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 NO_x. Interestingly, the NO_y layer does not completely disappear when the two high-NO_x periods are excluded (not shown). The greater persistence of this feature for NO_y may reflect its longer lifetime. The region of high NO_y extends to lower altitudes over the pole which is due to the polluted air seen in a profile measured at the pole on 920314.

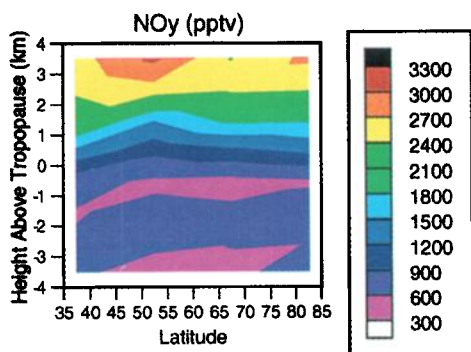


Fig. 4. NO_y contour plot, as in Fig. 2b.

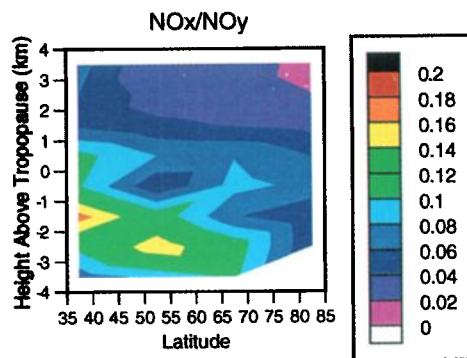


Fig. 5. NO_x/NO_y contour plot, as in Fig. 2b.

Figure 5 shows the meridional distribution of the NO_x/NO_y ratio (high values not excluded). In the stratosphere, NO_x/NO_y increases in going from high to low latitudes, similar to NO_x. Since there is little latitudinal gradient in NO_y, the increase in NO_x is due to a change in the NO_y partitioning, one factor being the increased photolysis of HNO₃ at lower latitudes. Over the pole at 2 km above the tropopause, NO_x is 50 pptv and NO_x/NO_y is 3%. Toward 40°N, values approach 120 pptv and 6%.

In the stratosphere at higher latitudes (50°–90°N), the NO_x/NO_y ratio increases from ~3% to ~8% as the tropopause is approached from above. NO_x is relatively constant at ~70 pptv in the middle of this range of latitudes. One cause for the increase in the NO_x/NO_y ratio may be a slowing of the conversion of NO_x to NO_y 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 NO_x to NO_y, 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

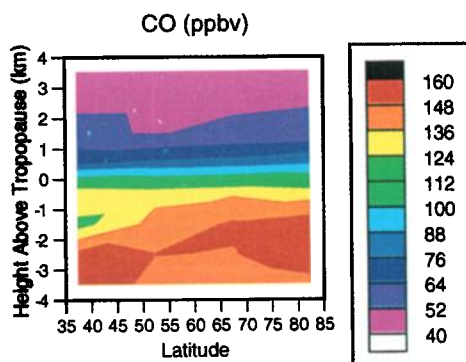


Fig. 6. CO contour plot, as in Fig. 2b.

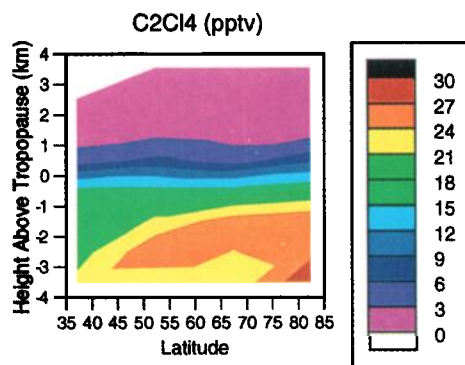


Fig. 7. C₂Cl₄ contour plot, as in Fig. 2b.

mechanism controls the NO_x/NO_y ratio, then the relative constancy of NO_x follows coincidentally from the opposing gradients in NO_y and NO_x/NO_y. On the other hand, a NO_x source, such as aircraft, could also be a factor. In the troposphere, NO_x/NO_y mirrors closely the distribution of NO_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_x and NO_y in the troposphere are correlated with high levels of CO (Figure 6) and C₂Cl₄ (Figure 7). Similar layers appear for each of these species, as well as for a number of other reactive carbon species (not shown), including C₂H₄. The presence of C₂Cl₄ indicates an industrial origin, and CO a combustive origin, of the elevated NO_x and NO_y in the troposphere. Moreover the relatively short lifetime of C₂H₄ (perhaps 2-4 days for these conditions) indicates the freshness of the emission. While CO and NO_x are known to be emitted by aircraft, C₂Cl₄ 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_x.

Summary

Meridional distributions of NO_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°N to 90°N (Figure 2c). One difference is that there is a modest gradient at the tropopause, leading to smaller mixing ratios in the troposphere at a given latitude. In frontal regions (two cases), convection leads to higher values within a few km of the tropopause. Although sporadic, these values occurred with sufficient frequency and magnitude to have a significant impact on the mean values in AASE II (Figure 2b vs. Figure 2c).

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