Subsidence, Mixing and Denitrification of Polar Vortex Air Measured During POLARIS

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1 ER-2 flight on April 26, 1997

1.1 Descent and Mixing

We use the correlation between CH_4 and N_2O as measured during the POLARIS campaign in spring 1997 to estimate the degree of mixing between descended air masses from the vortex and air masses from mid-latitudes. As the outside vortex reference correlation between CH_4 and N_2O we use a profile measured by the MkIV instrument on May 8 during a flight from Fairbanks (65 N, 148 W). PV maps and the measured N_2O profile clearly indicate that this profile was measured in air masses which are not influenced by polar vortex air. The measured CH_4/N_2O correlation agrees well with those measured in November 1994 between 40 and 50 north during the ATMOS/ATLAS-3 mission. The CH_4/N_2O mixing ratios measured during the MkIV flight are plotted as red circles in Figure 4.

A pronounced curvature is visible in the extra-vortex CH_4/N_2O correlation at N_2O levels below 250 ppbv. In contrast to that the ER-2 found a nearly linear correlation between both gases on its flight from Fairbanks on April 26. The low N_2O levels measured by the ER-2 between 500 and 510 K potential temperature indicate that remanents of polar vortex air masses have been sampled during this flight.

The CH_4/N_2O vmrs measured by the ER-2 are shown as green crosses in Figure 4. The CH_4 measurements at N_2O levels below 175 ppbv deviate significantly from the extra-vortex reference. Since the ratio between both long-lived tracers cannot be changed by reversible transport or chemistry the obvious change in the correlation can be explained only by irreversible mixing of extra-vortex air with subsided air from the polar vortex. We call the air masses whose mixing resulted in the observed CH_4/N_2O relationship 'the inner-vortex end-member' and 'the extra-vortex end-member'.

The mixing can occur only between air masses on the same isentropic surface. It is reasonable to suggest that the bulk of the mixing took place late in spring, after most of the descent. Therefore the extra-vortex air involved in the mixing process is the ambient outside vortex air at the flight level of the ER-2. At that level (500-510 K) the extra-vortex N_2O and CH_4 vmrs have been about 200 and 1360 ppbv respectively. In fact, the green mixing line in Figure 4 meets the extra-vortex reference correlation at approximately these values. This point defines the properties of the extra-vortex end-member and is marked in Figure 4.

The pre-mixing CH_4/N_2O relation of the inner-vortex end-member can be found by extrapolating the green mixing line to the point where it intersects with the reference correlation. This is illustrated by the dotted line in Figure 4 and the approximate CH_4/N_2O vmrs of the inner-vortex end-member are indicated in the figure.

A certain amount of curvature in the green mixing line indicates that the inner-vortex end-members for the various probed air masses had slightly different properties. Inhomogenous subsidence inside the polar vortex tends to cause inhomogenous properties of the vortex air masses on one isentropic level. Subsequent isentropic mixing within the vortex tend to homogenize these differences. The observed curvature in the vortex CH_4/N_2O mixing line might indicate that this homogenization was not complete before the mixing with extra-vortex air started.

The respective CH_4 and N_2O mixing ratios of the various inner-vortex end-members have been calculated for all measurements along the ER-2 flight track. This has been done by calculating the intersections of the reference correlation with straight lines through the respective CH_4/N_2O measurements and the extra-vortex end-member, assuming that the reference correlation reflects the situation during the formation of the vortex in fall reasonably well. This assumption is justified by the fact that the correlations measured by the MkIV agree well with the correlations measure in November 1994 during ATMOS/ATLAS-3. Figure 5b shows the N_2O vmr of the calculated intersections which are interpreted as the pre-mixing N_2O vmrs of the inner-vortex end-members. The uncertainties of these values have been estimated based on the uncertainties in the definition of the properties of the extra-vortex end-member and the precision of the MkIV measurements.

The approximate altitudes from which the inner-vortex end-members subsided through the winter are shown in Figure 5c. The altitudes have been estimated using the calculated pre-mixing inner-vortex N_2O vmr and the MKIV extra-vortex N_2O profile.

The ratio between inner-vortex air and extra-vortex air in the sampled air masses has been calculated from the N_2O vmr of the extra-vortex end-member, the measured N_2O vmrs and the N_2O vmrs of the respective inner-vortex end-members. The results are given in Figure 5d.

1.2 Denitrification

The pre-mixing NO_y vmrs of the inner-vortex end-members can be estimated from the calculated pre-mixing N_2O vmrs of these air masses and the NO_y/N_2O correlation measured by the MkIV instrument for extra-vortex conditions. Again we assume that the extra-vortex conditions reflect the situation during the formation of the vortex reasonably well, which is justified by the good agreement with the correlations measured by ATMOS/ATLAS-3 NO_y/N_2O during November 1994.

The uncertainties of the calculated pre-mixing N_2O vmrs and the precision of the MKIV NO_y and N_2O measurements have been used to estimate the uncertainties of the pre-mixing NO_y vmrs in the inner-vortex mixing-members. Comparisons of the MkIV NO_y / N_2O correlation with the ATMOS/ATLAS-3 measurements in fall 1994 suggest that at the relavant N_2O levels around 30 ppbv the natural variability of the correlation is rather small, i.e. within the error bars of the MkIV instrument.

The pre-mixing NO_y vmrs of the extra-vortex end-member have been estimated from the MkIV NO_y measurements at the flight level of the ER-2 and the extra-vortex (i.e. N_2O vmr > 200 ppb) measurements of the ER-2. The estimated pre-mixing NO_y vmrs of the inner-vortex and extra-vortex air masses together with the fraction of inner-vortex vs. extra-vortex air has been used to predict the NO_y mixing ratio which should have been present for each N_2O measurement along the flight path of the ER-2 in absence of denitrification. Figure 5e shows the calculated NO_y*, the NO_y* which have been estimated from the N_2O vmrs without considering subsidence and mixing and the measured NO_y along the flight path of ER-2.

Figure 6 shows the extra-vortex reference NO_y, the NO_y* calculated for subsidence and end-member mixing derived from the CH_4/N_2O correlation and the measured NO_y against N_2O. The NO_y* agrees well with the measured NO_y for N_2O mixing ratios larger than 125 ppbv. This shows that in this region the observed deficit in NO_y can be explained by subsidence and end-member mixing alone. However, at N_2O level below 100 ppbv, a deficit of measured NO_y compared with NO_y* is visible. The 1-2 ppbv deficit in NO_y is interpreted as the result of mild irreversible denitrification earlier in the winter. Since the denitrification took place before the bulk of the mixing, it is already diluted by the mixing effect. The average pre-mixing inner-vortex denitrification for those air masses should have been around 2-3 ppbv to cause the observed deficit in NO_y. Most likely the denitrification inside the polar vortex caused a patchy picture of higher denitrified areas and areas without denitrification. In the following weeks the comparable fast mixing inside the vortex caused a certain amount of averaging over the different air masses inside the vortex yielding the 2-3 ppbv denitrification reported above. This process took place before the mixing with outside vortex air masses.

2 ER-2 flight on June 30, 1997

The same analysis have been made with measurements of the ER-2 flight on June 30, 1997. The results are shown in Figures 7-8.

During this flight the ER-2 found remnants of polar vortex air at 510-530 K potential temperature, i.e. slightly higher altitudes compared with the flight of April 26. The inner vortex end-members probed during the flight descendet from about 37 km during the winter (Figure 7b). The calculated NO_y* and the NO_y measurements agree very well throughout the flight (Figure 8). The large deficits of NO_y compared with the extra-vortex reference can be explained by descent and mixing alone. No indication for denitrification was found.

3 OMS flight on June 30, 1997

On the same day as the latter ER-2 flight, the OMS balloon borne instrument payload measured a profile of several trace species and found polar vortex air in two altitude regions around 500-520 K and 615-637 K potential temperature. The measured CH_4/N_2O mixing ratios obtained during the descent are plotted in Figure 9 together with the extra-vortex reference measured by the MkIV instrument.

The vortex air masses found around 500-520 K had similar properties as those probed by the ER-2 on the same day and in the same altitude region. The measurements in air masses which have not been influenced by the polar vortex (black crosses in Figure 9) agree remarkably well with the measurements of the MkIV instrument in May.

Now we focus on the air masses probed between 615 and 637 K potential temperature. The CH_4/N_2O relation of these air masses reveal a mixing line with a steeper slope than those indicated by the ER-2 measurements at lower altitudes. The mixing line meets the reference correlation at CH_4/N_2O mixing ratios of 1130 ppbv and 140 ppbv respectively. The MkIV measurement at this point was taken at 615 K potential temperature which coincides well with the range of levels of the OMS measurements forming the mixing line. The slope of the mixing line indicates that the inner-vortex end-member originated from well above the altitude reached by the MkIV instrument (37 km). We used data from ATMOS/ATLAS-3 to identify the intersection of the extended mixing line with the reference correlation of CH_4/N_2O (Figure 10). The intersection of the dashed mixing line in Figure 10 with the extra-vortex reference indicates that the inner vortex mixing member originated at an extremely low N_2O level and at a CH_4 level of about 200 ppbv. Figure 11 shows that such low CH_4 levels are normally found above 50 km altitude. This result indicates that the air masses probed by the OMS platform between 615 and 637 K are the result of mixing of extra-vortex air with mesospheric air, wich descended inside the polar vortex.

The NO_y/CH_4 correlation measured by ATMOS/ATLAS-3 between 40 and 50° N (Figure 12) has been used to calculate NO_y* from the estimated pre-mixing inner-vortex CH_4 vmrs for the air masses probed by the OMS platform between 615 and 637 K potential temperatures (Figure 13). This Figure shows that above 600 K quite low NO_y/N_2O ratios can be produced purely by mixing processes between subsided mesospheric air masses with extra-vortex air.

4 Conclusions

ER-2 flight on April 26, 1997: The vortex air found at 500-510 K descended from an early winter altitude of about 33 km. Slightly denitrified air was found only for N2O levels below 100 ppbv. The apparent 1-2 ppbv deficit in NOy at these N2O levels can be explained by a pre-mixing denitrification of about 2-3 ppbv.

ER-2 flight on June 30, 1997: The inside vortex air found at 520-530 K descended from an early winter altitude of about 37 km. NOy* and NOy agree very well throughout the flight. No indication for denitrification was found. The measured low NOy values are the result of descent and mixing.

OMS profile on June 30, 1997: The air masses measured at around 620 K potential temperature level have been the result of mixing of extra-vortex air from that level with mesospheric air, which previously subsided in the vortex. The NOy vmrs estimated for those air masses from subsidence and mixing are as low as 7 ppbv at N2O levels between 50 and 75 ppbv.

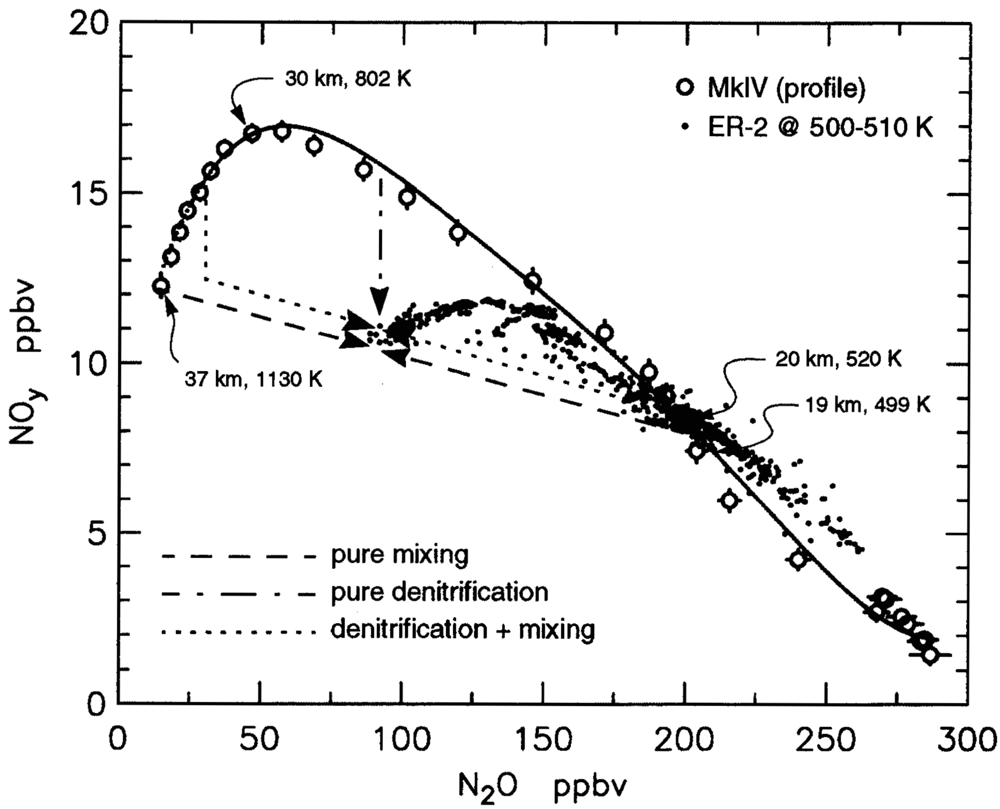

Figure 1: NO_y/N_2O correlations measured during the MkIV flight on May 8, 1997 and during the ER-2 flight on April 26, 1997. The MkIV data represent a vertical profile between 8 and 37 km altitude. The potential temperatures of some data points are indicated in the plot. The error bars denote the 1σ precision of the MkIV measurements. All ER-2 data points have been measured between potential temperatures of 500 and 510 K. The ER-2 NO_y measurements were obtained by the NOAA chemilumescence instrument with a 1 σ total uncertainty of better than 10 % (? precision); the ER-2 N_2O measurements were made by the ALIAS diode laser instrument with a 1σ total uncertainty of 5% (1% precision). The dashed, dotted and dash-dotted lines illustrate scenarios with different degrees of denitrification and descent that could explain the low NO_y vmrs observed by the ER-2 at N_2O values below 100 ppbv.

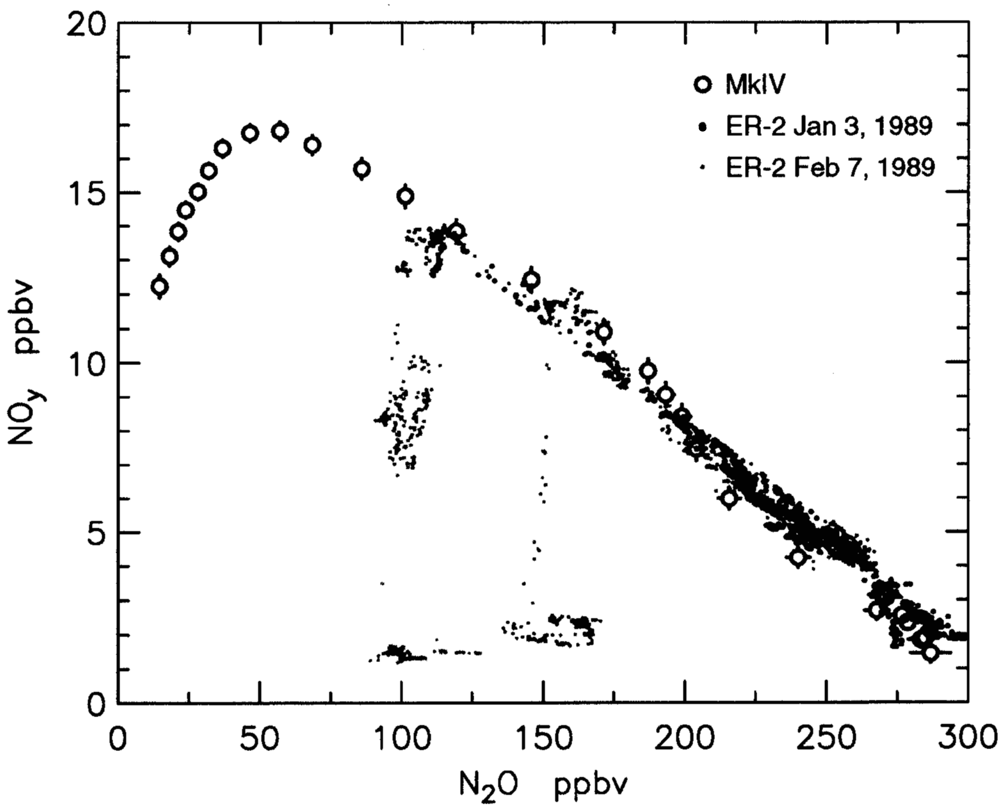

Figure 2: As in Figure 1, but for ER-2 data measured during an early winter and a mid-winter flight during AASE in 1989. The ER-2 data has not been filtered by Θ. The ER-2 observations of N_2O were obtained by the ATLAS instrument with a 1 σ total uncertainty of 3%.

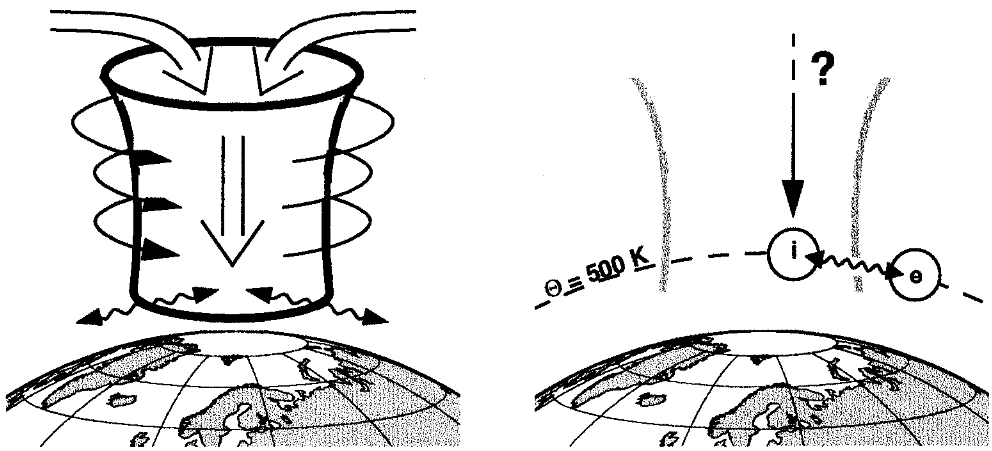

Figure 3: Illustration of the large scale descent in the polar vortex, which brings air masses from high altitudes to low potential temperature levels where they can mix with outside vortex air mainly during the late vortex and vortex break up period. In the right hand panel the descended inner-vortex mixing member is marked by an 'i' and the extra-vortex mixing member is marked by an 'e'. To predict the properties of the mixed air masses, the original level of the air mass 'i' has to be estimated.

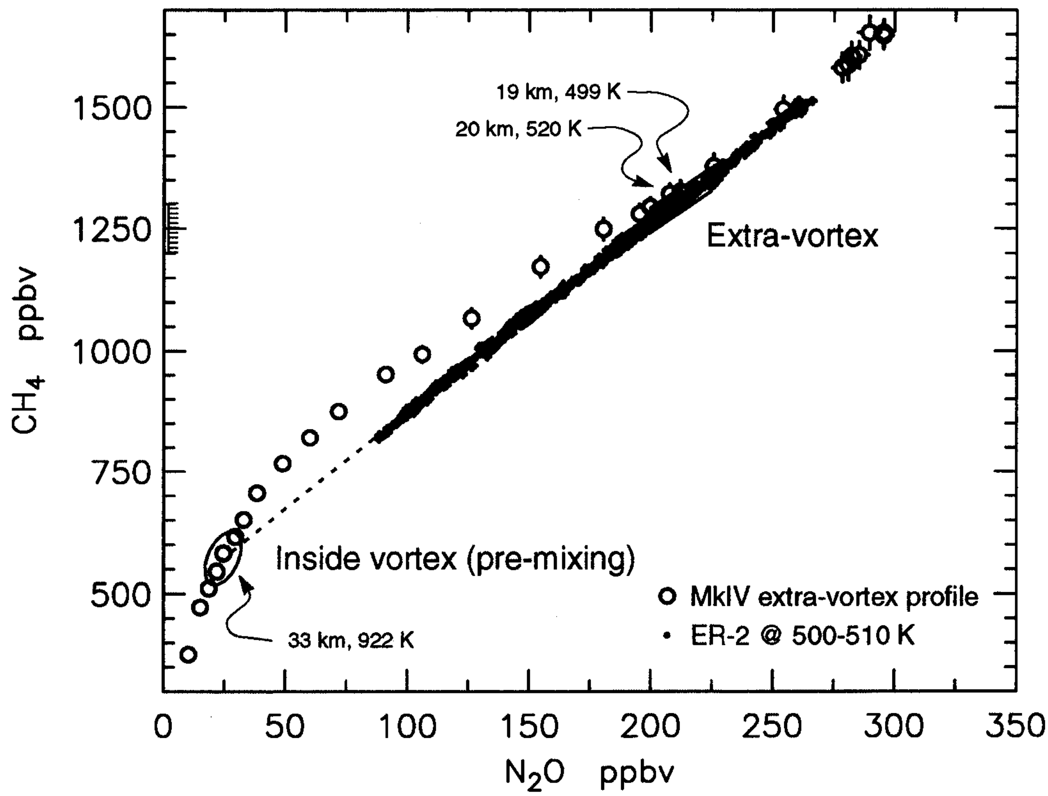

Figure 4: CH_4 / N_2O correltaion measured by the MkIV and the ER-2 ALIAS instrument on the same flight as in Figure 1. The 1 σ total uncertainty of both the ALIAS CH_4 and N_2O measurements is 5% (1% precision). The error bars for the MkIV measurement denote the 1σ precision. The mixing line for the ER-2 measurements is indicated by the dotted line. The regions where the mixing line intersects the extra-vortex reference correlation denote the air masses that have mixed to produce the properties observed by the ER-2 along the mixing line. The inside and outside vortex mixing end-members are indicated. The altitudes and potential temperatures of the MkIV measurements in these regions are shown.

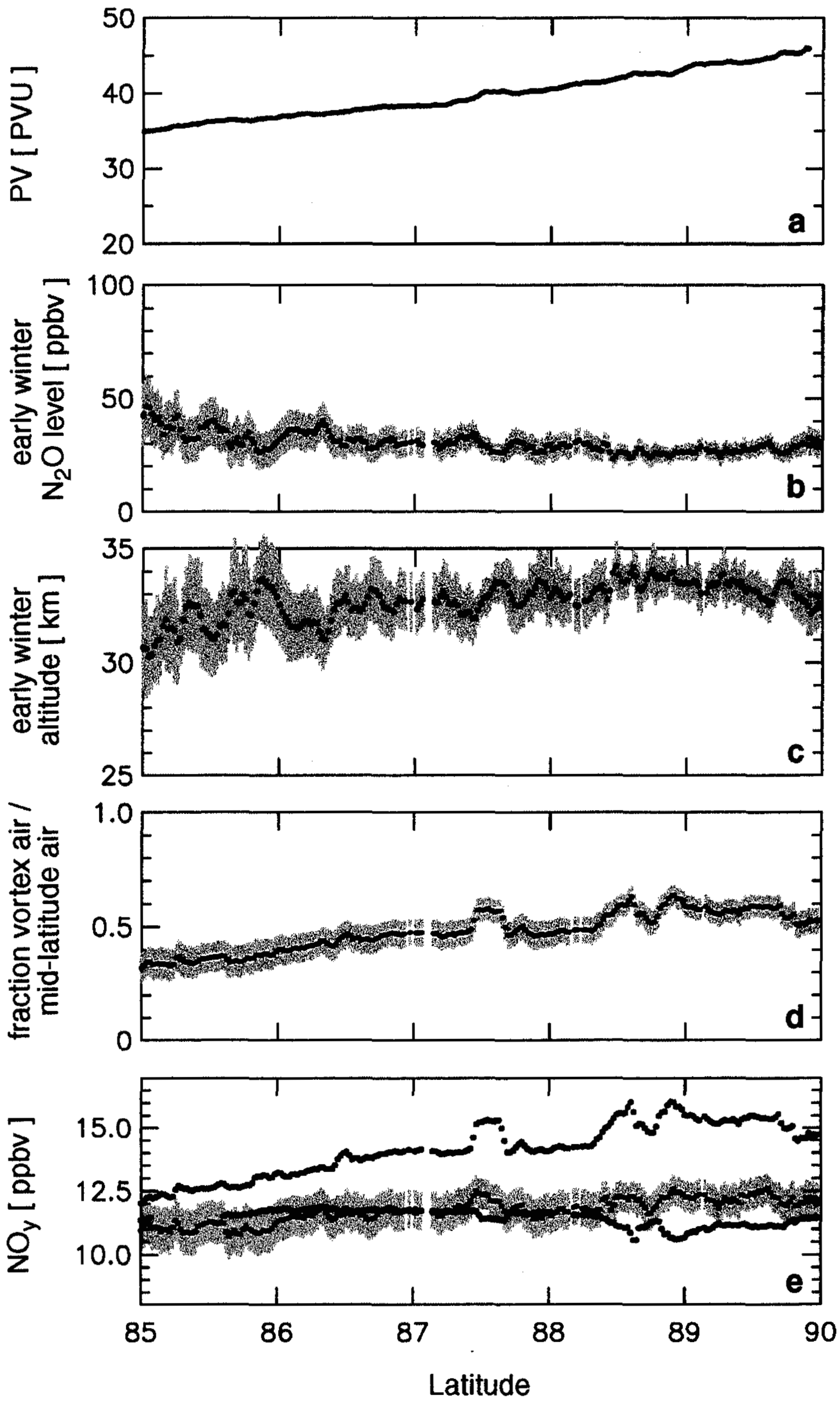

Figure 5: Measured and calculated quantities along the northbound track of the ER-2 flight on April 26, 1997. The gray shaded areas give an estimate of the uncertainty based on the errors in the measurements and the uncertainty in defining the properties of the extr-vortex mixing end-member. (a) Potential vorticity (1 PVU = 10^{-6} K $\cdot$ m^2 $\cdot$ s^{-1} $\cdot$ kg^{-1}), (b) Calculated pre-mixing N_2O level of the inner-vortex mixing end-member, (c) corresponding approximate early winter altitude of the inner vortex air, (d) fraction of inner-vortex air vs. extra-vortex air in the mixed sample, (e) NO_y* which would have been predicted from the N_2O vmrs without considering mixing (blue), NO_y* predicted with consideration of mixing (red), and NO_y measured by the NOAA chemiluminescence instrument aboard the ER-2 (green).

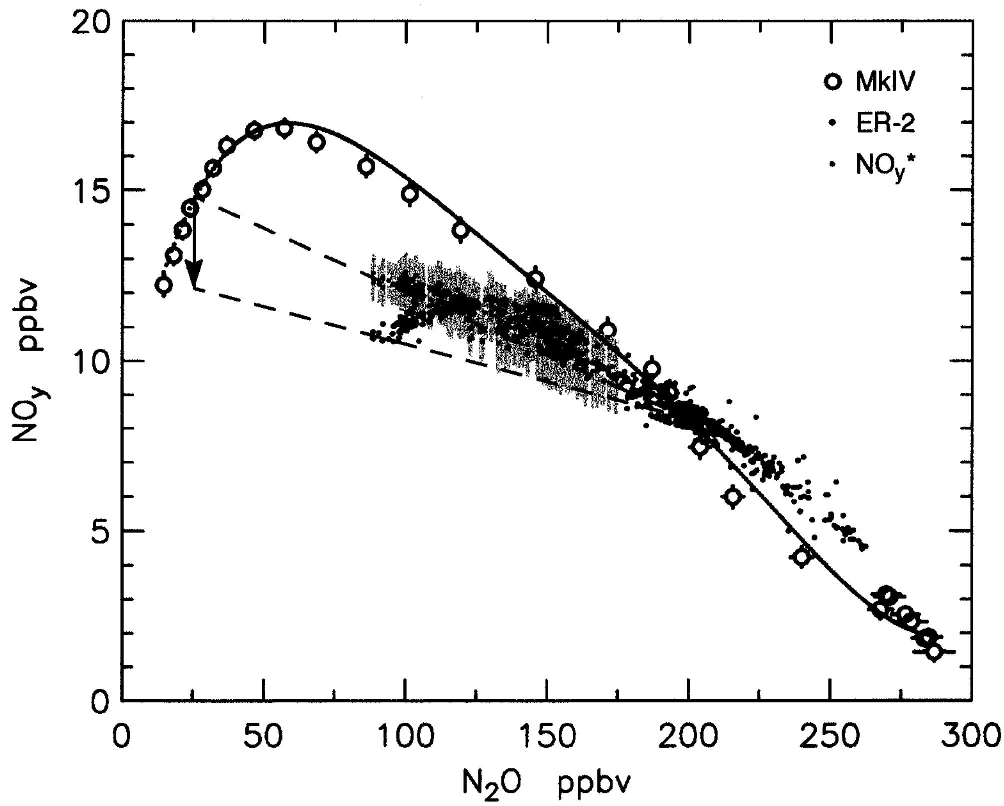

Figure 6: MkIV and ER-2 measurements as in Figure 1. The NO_y predicted for the air masses sampled by the ER-2 (defined as NO_y*, red) and its uncertainty (gray, c.f. Figure 5) are compared with the measured NO_y. NOy* was calculated from the degree of descent and mixing derived from the CH_4/N_2O correlation. The NO_y vs. NO_y* deficit at low N_2O levels is interpreted as a signature of irreversible denitrification. The pre-mixing degree of denitrification in the air masses is estimated by a back-projection of the measured properties of the mixed sample to the inner-vortex mixing end-member properties (dashed lines). The estimated average pre-mixing degree of denitrification in the sampled air masses is indicated by the arrow. Since the air masses inside the vortex are rapidly mixed and the denitrification typically occurs inhomogenously, this degree of denitrification is likely the result of the mixing of more heavily denitrified air masses with less or non-denitrified inner vortex air.

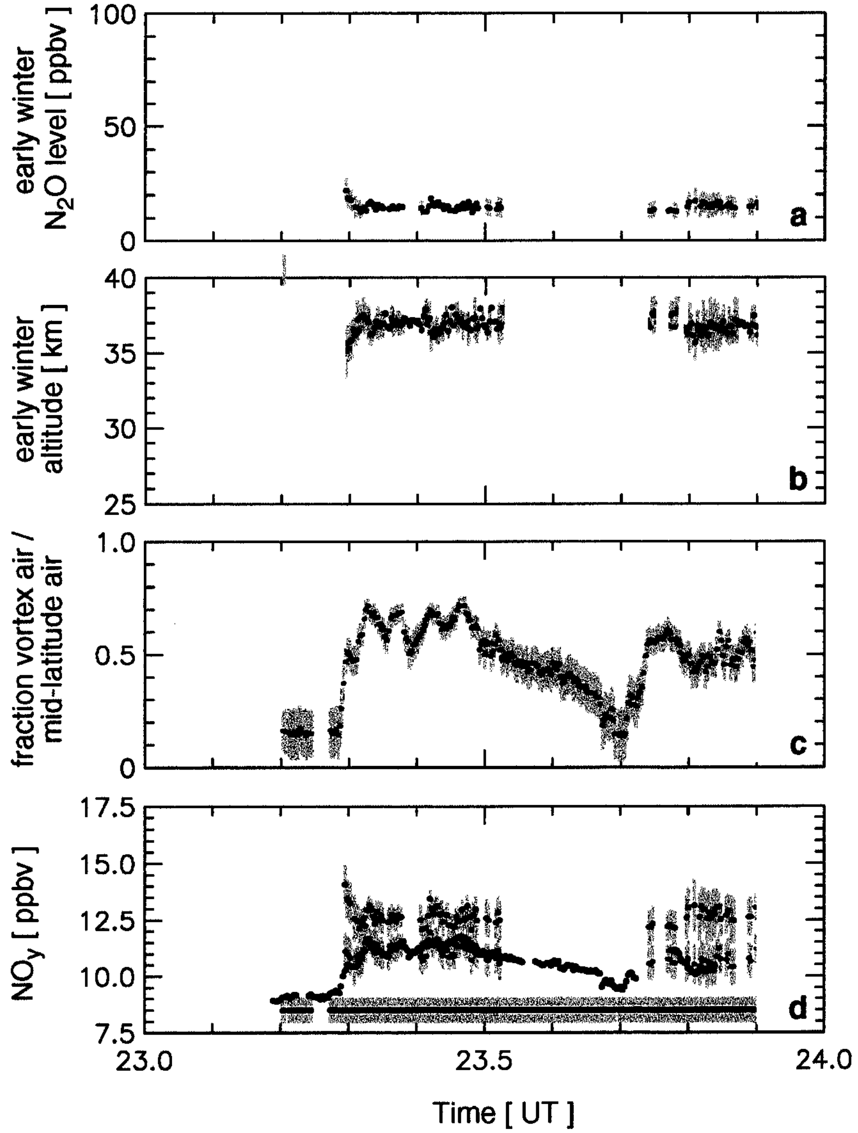

Figure 7: As Figure 5, but for the westbound portion of the ER-2 flight at potential temperatures of 510-530 K near 65° N on June 30. -> *Note: We will use longitude for the x-axis in the next version of the figure ! Panel d will be changed (black will be removed, blue is wrong in this version)*

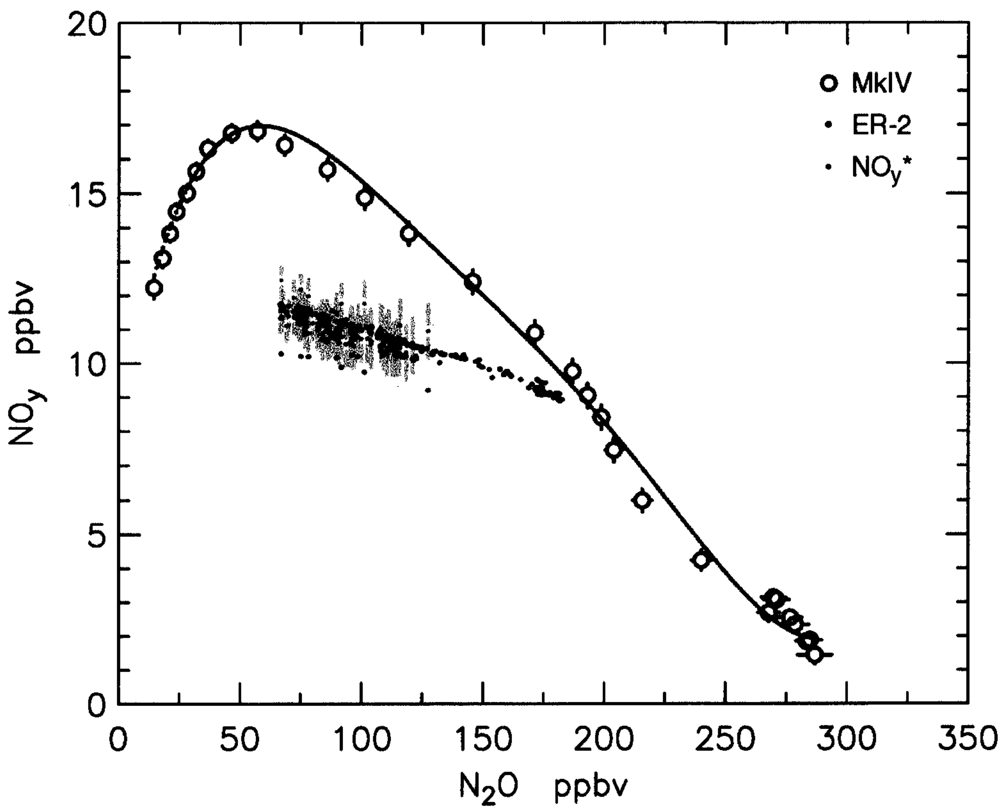

Figure 8: As in Figure 6, but for the ER-2 flight on June 30, 1997. The vortex remnants were encountered while the ER-2 was between potential temperatures of 510 and 530 K; only ER-2 measurements between these levels have been plotted. No indication for denitrification is apparent.

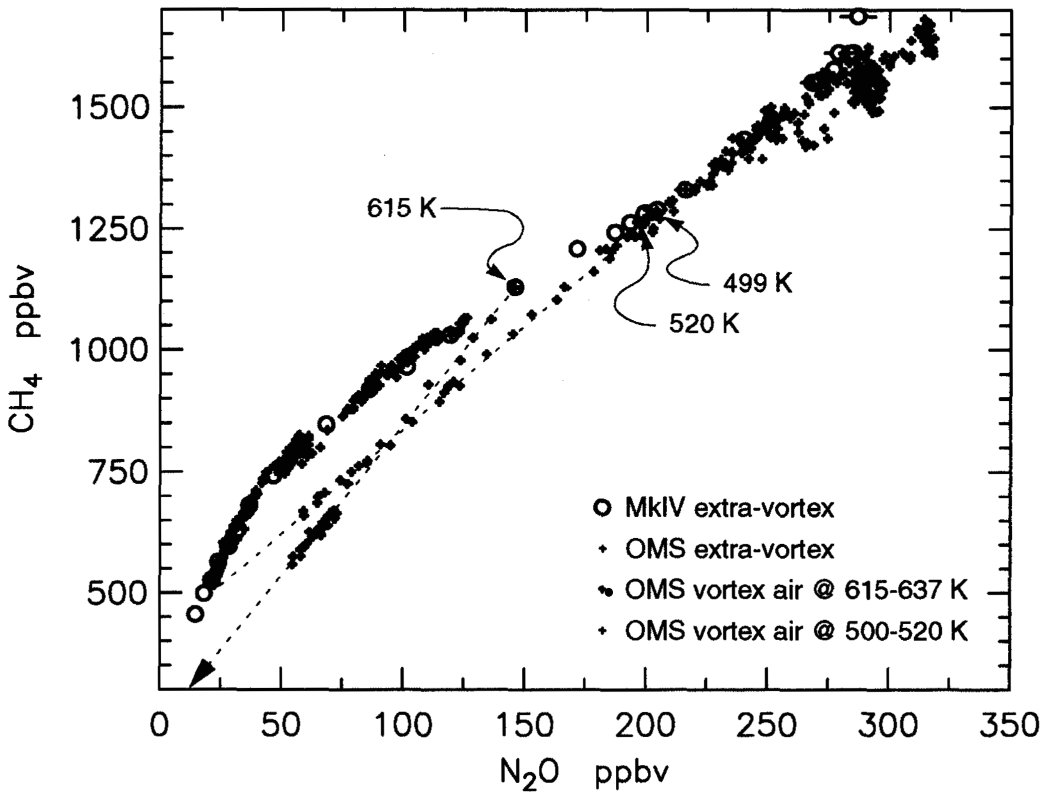

Figure 9: CH_4 / N_2O correlation observed by the ALIAS II instrument during the OMS balloon flight on June 30, 1997, compared to the same MkIV measurements shown in Figure 4. The ALIAS II OMS data has been grouped into extra-vortex samples (black) and measurements obtained during the penetration of two distinct layers of vortex air remnants (green: 615-637 K, blue: 500-520 K). The observations within the vortex remnants reveal distinct mixing lines (dashed) for each potential temperature surface. Measurements from the MkIV instrument on May 8 are given in red. The potential temperatures of the MkIV data points at the intersections with the OMS mixing lines are indicated.

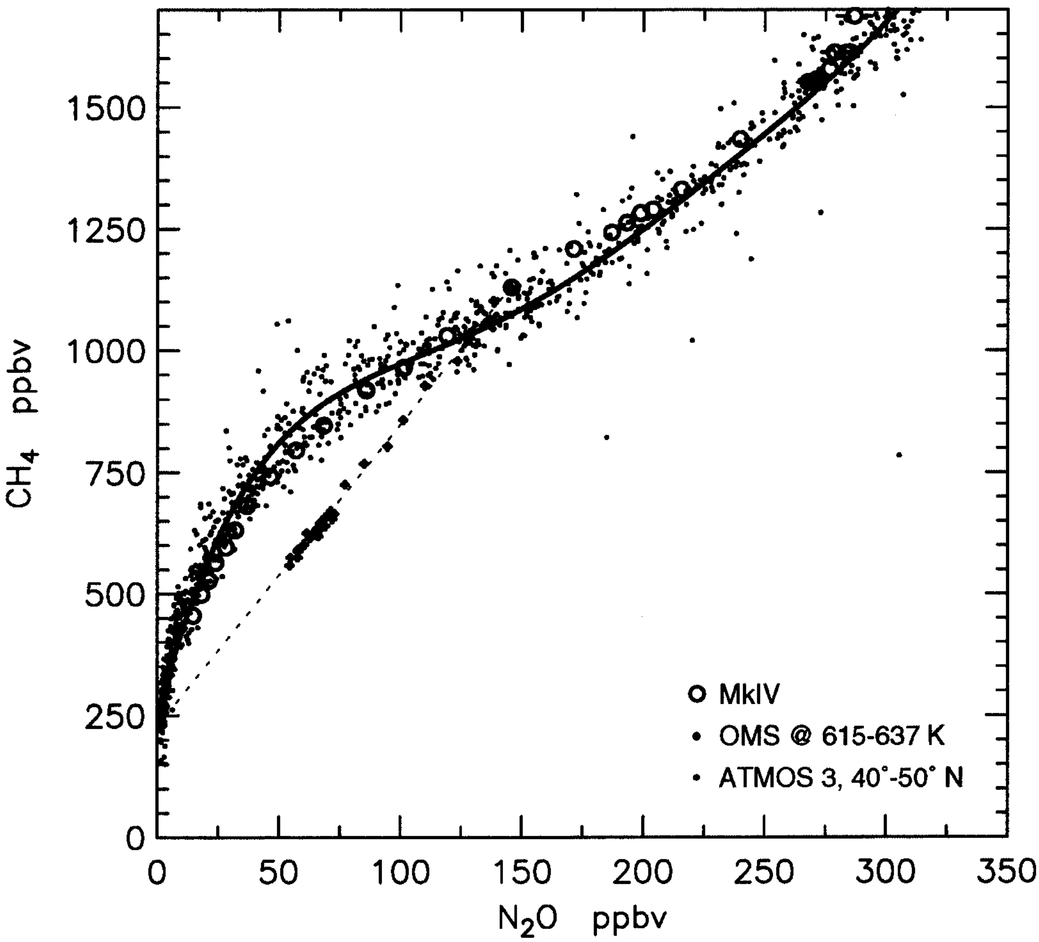

Figure 10: CH_4/N_2O correlation for the OMS encounter of vortex remnants at 615 - 637 K potential temperature (green) compared with an extra-vortex reference correlation established by ATMOS/ATLAS-3 measurements obtained between 40 and 50° N in early November 1994 (blue dots, a fit to the data is plotted as blue line). The MkIV reference correlation from May 1997 is shown in red.

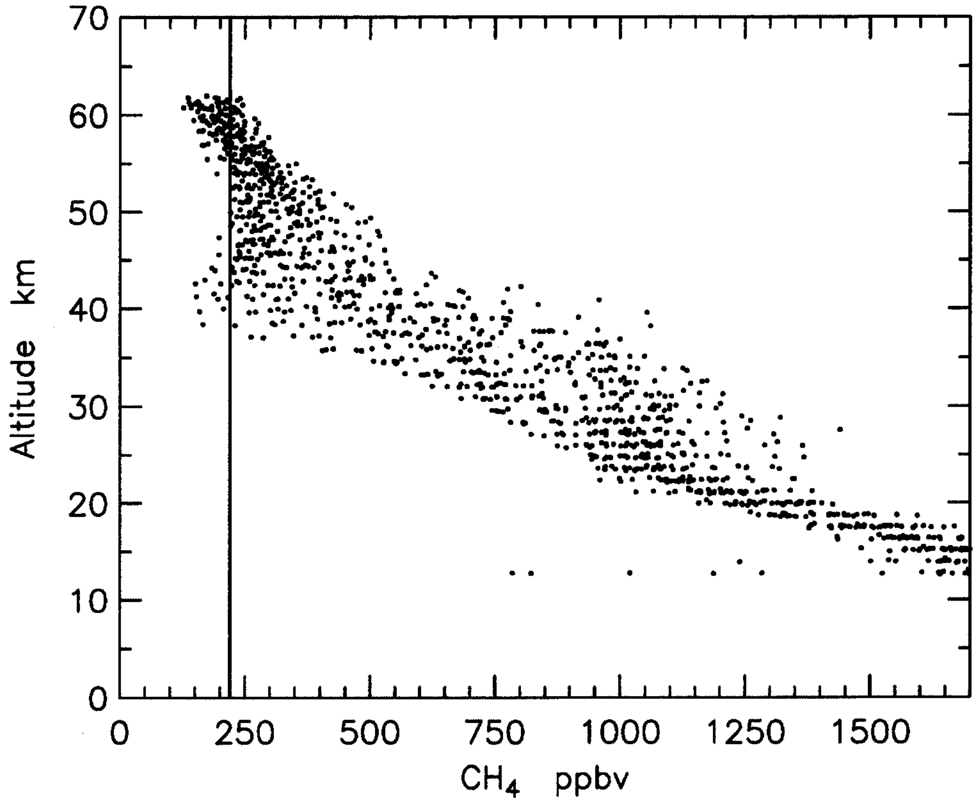

Figure 11: CH_4 profile measured by ATMOS/ATLAS-3 between 40 and 50° N in early November 1994. The vertical line denotes the CH_4 vmr of the pre-mixing inner-vortex end-member of the OMS mixing line observed at 615-637 K potential temperature.

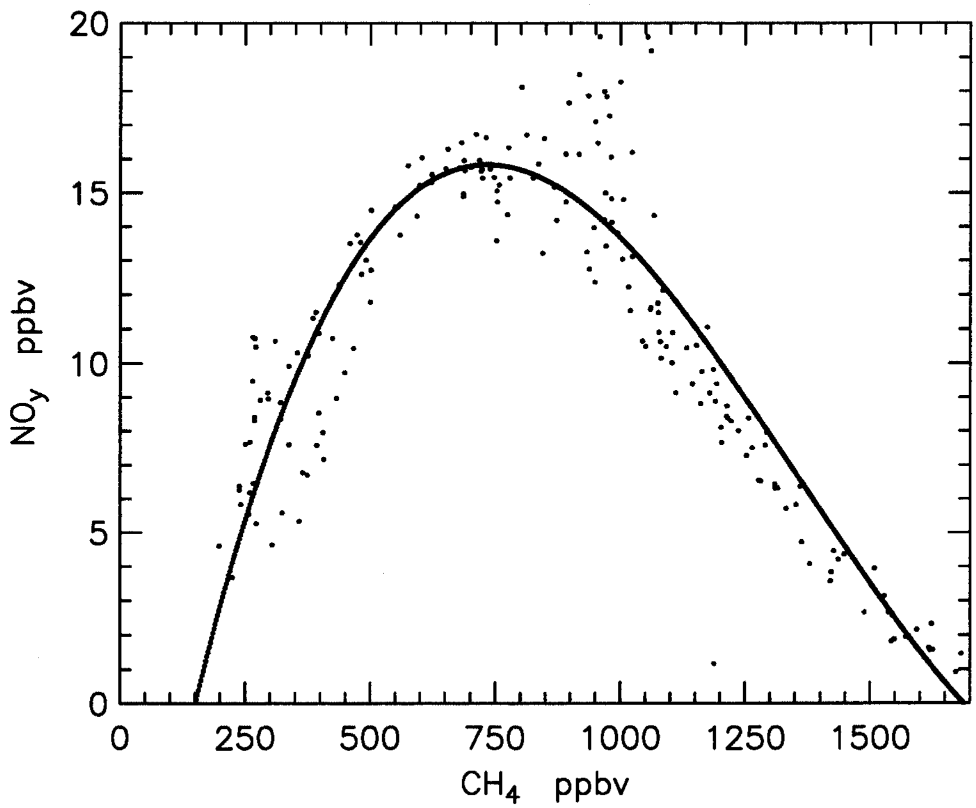

Figure 12: NO_y/CH_4 reference correlation measured by ATMOS/ATLAS-3 between 40 and 50° N in early November 1994. The fit to the data has been used to estimate the pre-mixing NO_y vmr based on the estimated pre-mixing CH_4 vmr (c.f. Figure 10).

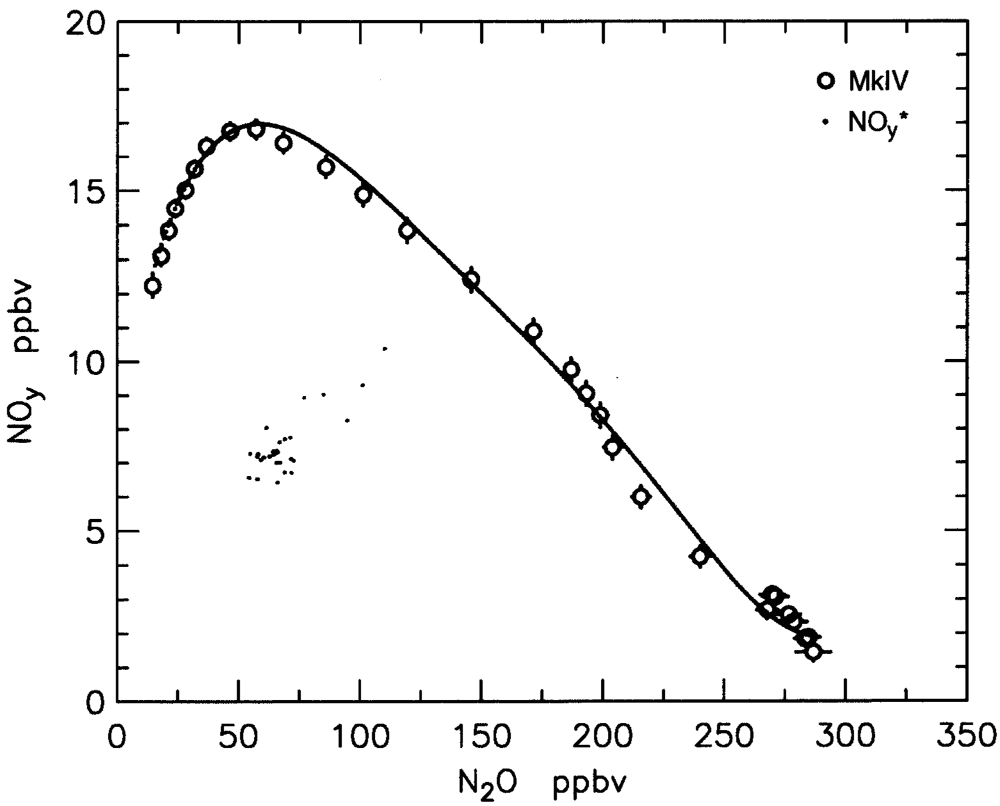

Figure 13: The NO_y*/N_2O correlation predicted for the air masses measured by OMS between 615 and 637 K on June 30 based on the degree of subsidence and mixing inferred from the CH_4 vs. N_2O correlation. No denitrification has been assumed. MkIV data as in Figure 1.