NO_x derived from MIPAS/ENVISAT in the Southern Hemisphere vortex split-up event in Sep./Oct.2002

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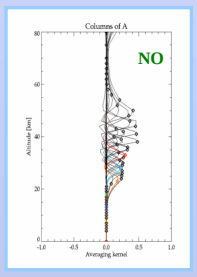
Introduction

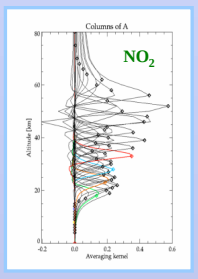
The split-up of the Southern polar vortex in September/October 2002 offers a valuable opportunity to study dynamical and chemical processes in the polar winter stratosphere. The active nitrogen compounds NO and NO_2, usually referred as NO_x, play a crucial role in the stratospheric ozone chemistry and the quantification of their concentrations will allow us to improve knowledge of important chemical processes in the stratosphere.

Vertical profiles of NO and NO_2 have been derived from high resolution atmospheric limb emission spectra in the mid-infrared measured by the Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) on ENVISAT during and after the vortex split-up (September 20th to October 13th) in the Southern hemisphere. In order to account for strong non-local thermodynamic equilibrium (non-LTE) emissions, particularly of NO, a dedicated non-LTE retrieval scheme [1] has been applied which is incorporated in the joint IMK/IAA MIPAS data processing facility [2].

NO and NO_2 retrieval

Non-LTE retrieval of NO and NO_2 have been performed with IMK/IAA data processor. Since chemical non-LTE excitation of NO in the stratosphere depends on NO_2 concentrations, NO_2 was retrieved first and the results were used in the successive NO retrieval.



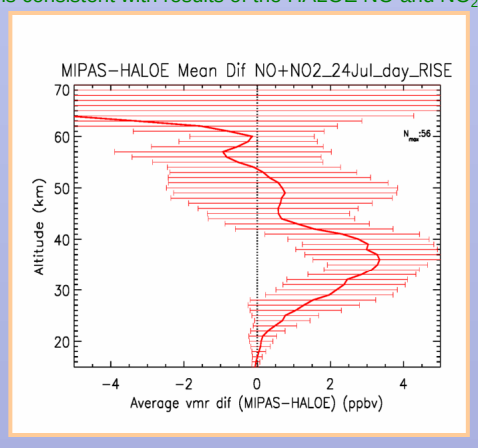


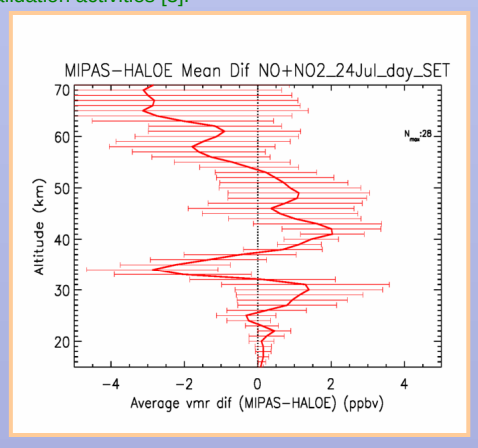
Columns of typical averaging kernels for NO and NO_2 retrievals

	NO	NO_2
tangent heights	20 -70 km	15-70 km
microwindows	1840 -1920 cm^{-1}	1580 – 1630 cm^{-1}
retrieval grid	0-120 km	0-200 km
regularisation	Tikhonov 1st order	Tikhonov 1st order
vertical resolution	10km @ 20-30 km 5 km @ 30-50km	7 km @ 20-30 km 4 km @ 30-50 km
noise error	1-3 ppb	0.2-0.8 ppb
non-LTE	included	included

MIPAS - HALOE intercomparison of NO_x

In order to validate the data products, MIPAS NO_x has been compared to HALOE measurements for data from July 24th, 2003 (orbits 2081 – 2083). Generally good agreement (< 2ppb) is reached in the stratosphere except for the 30-40 km region. At these altitudes MIPAS NO_x is 3ppb higher than HALOE sunrise NO_x and 3ppb lower than HALOE sunset NO_x. This can be explained by diurnal NO_x variations due to $NO_x \leftrightarrow N_2O_5$ conversion with amplitude of 5-6 ppb (maximum at sunrise, minimum at sunset) and is consistent with results of the HALOE NO and NO_2 validation activities [3].

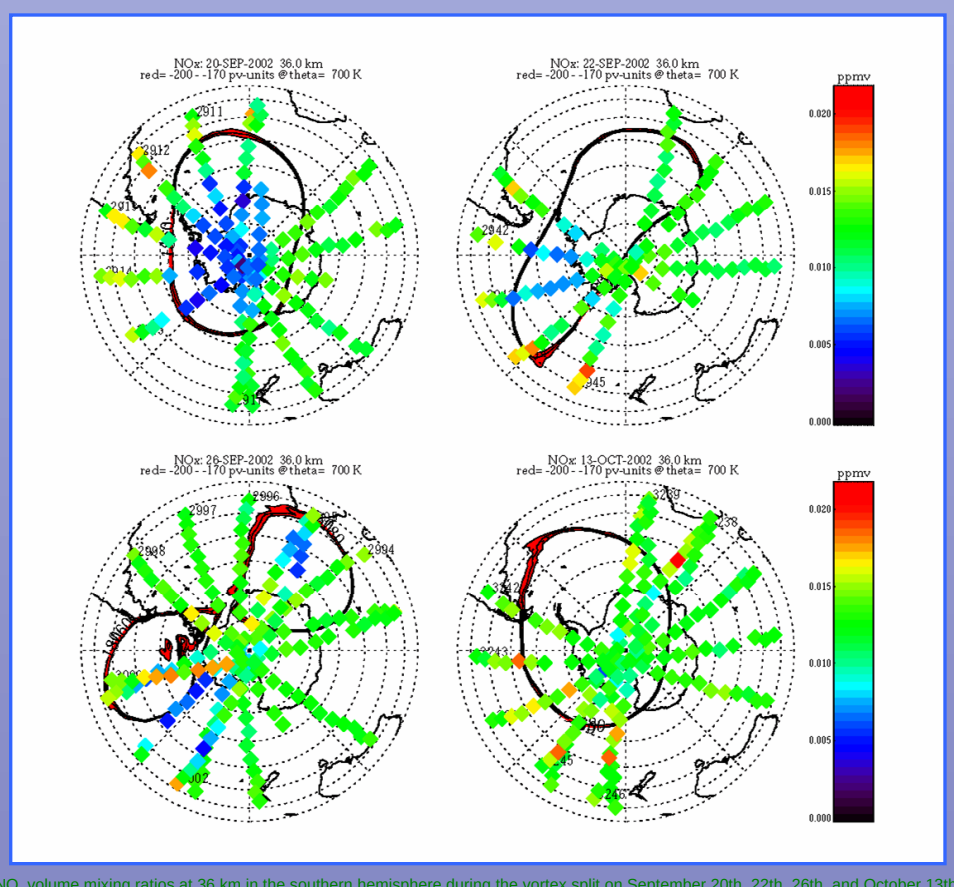




Mean differences between MIPAS and HALOE sunrise (left) and sunset (right) NO_x measurements. 1-_ variances of the differences are shown by the error bars.

Spatial NO_x distribution during the vortex split-up

Stratospheric NO_x volume mixing ratios generally show 2 to 3 times lower values within the polar vortex than outside before and during the split-up event (September 20th to 26th) indicating a high degree of denoxification. However, during the vortex split-up midlatidtude airmasses rich on NO_x are transported into the South polar region. In this period, NO_x amounts may change very fast driven by dynamical processes. For example, measurements at a given geolocation show first minimum and 6 hours later maximum NO_x volume mixing ratios. Unexpected peak values of NO_x are found at the vortex edge. In the late Antarctic winter situation on October 13th stratospheric NO_x is nearly recovered.



NO_x volume mixing ratios at 36 km in the southern hemisphere during the vortex split on September 20th, 22th, 26th, and October 13th.

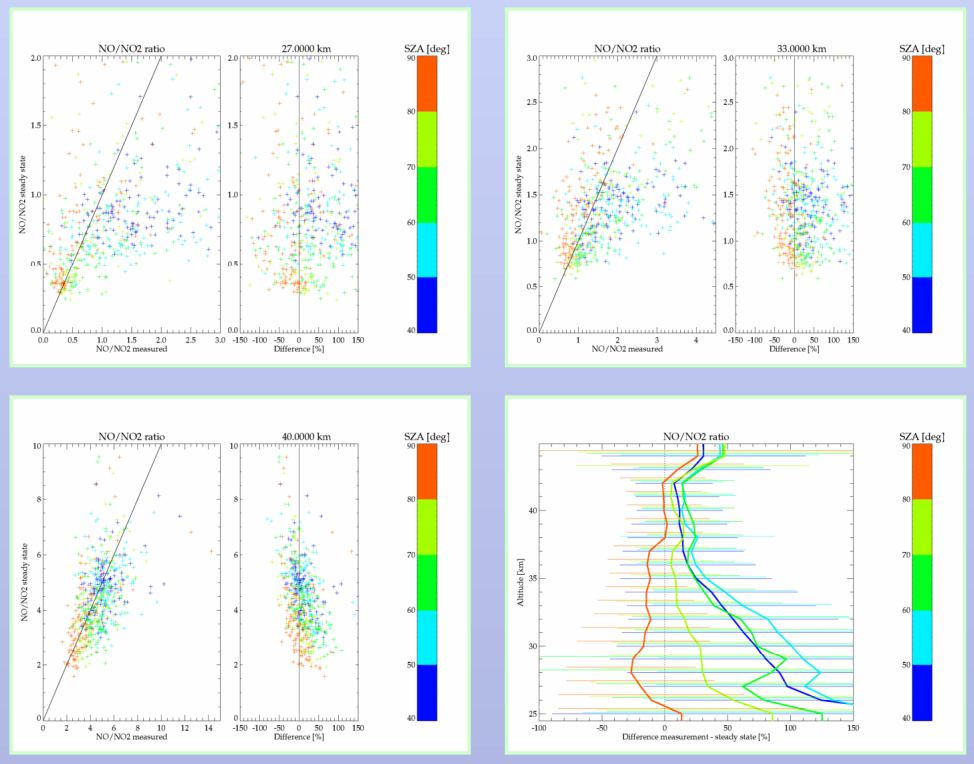
Partitioning between NO and NO_2 at daytime

In order to proof the self consistency of NO and NO_2 data products, the measured partitioning of NO and NO_2 has been compared to simple photochemical model calculations. Since photochemistry of NO_x is very fast, a steady state assumption for the NOx partitioning is valid. The NO/NO_2 ratio can then be expressed by:

$$\frac{[NO]}{[NO_2]} = \frac{J_{NO_2} + k_{NO_2+O}[O]}{k_{NO+O_3}[O_3] + k_{NO+ClO}[ClO]} \quad \text{with } [O] = \frac{J_{O_3}[O_3]}{k_{O+O_2+M}[O_2][M]}$$

The photolysis rates J_{NO2} and J_{O3} are calculated by the IAA photochemical model. A correction for albedo and multiple scattering has been applied to J_{NO2}. The kinetic rates for NO_2+O, NO+O_3, NO+ClO, and O+O_2+M have been taken from DeMore et al. [4]. Volume mixing ratios of O_3 and ClO, as well as p and T for calculation of the total number density, have been retrieved from the same MIPAS data sets.

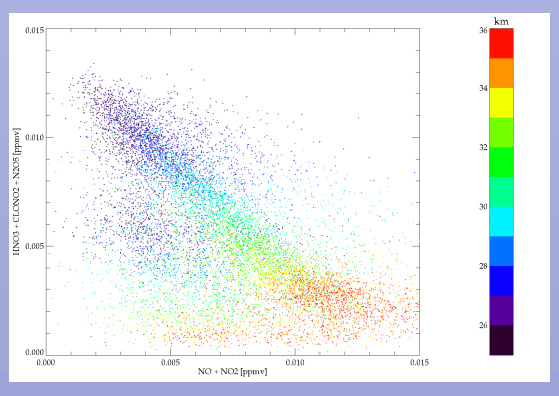
While for altitudes above 30 km generally good agreement between measurement and model is found, below this altitude the measurements overestimate the NO/NO_x ratio except for low solar zenith angles (SZA). Possible reasons are systematic or smoothing errors in the retrieved quantities, in particular NO (low vertical resolution below 30 km) or wrong temperature dependence of kinetic rates. Wrong modeling of photolysis rates could explain the spread of NO/NO_2 for different SZA, but not the enhanced ratio for high SZA in the lower stratosphere.



NO/NO_2 ratio calculated by a steady state photochemical model vs. measured NO/NO_2 for different altitudes. Data is taken from all measurements between Sept. 20th and Oct. 13th. Ratios for different solar zenith angles are indicated by colors. The lower right panel shows relative differences between modeled and measured NO/NO_2. 1-_ variances of the differences are shown by the error bars.

Correlation of NO_x with other NO_y compounds

Due to the photochemical conversion of active NO_x and the NO_y reservoir gases (HNO_3, N_2O_5, and $ClONO_2$), these quantities should be highly anticorrelated. This, in fact, is observed in the data between 25 and 34 km. Measured NO_x vmr is increasing with altitude while measured reservoir gas amounts decrease. NO_y reservoir gas vmr's plotted over NO_x vmr follow a 'straight line' indicating a nearly constant NO_y amount in the middle stratosphere. However, a bulk of measurements are concentrated left of the 'straight line', thus belonging to airmasses with low NO_y concentrations. These measurements can be assigned to locations inside the polar vortex.



Volume mixing ratio of NO_y reservoir gases versus NO_x. Data is taken from all measurements between September 20th and October 13th. Retrieved vmr's of different altitudes are indicated by colors.

Summary & Conclusions

- Retrieved stratospheric NO and NO_2 is in good agreement with HALOE data.
- Measured NO_x inside the polar vortex is considerably decreased wrt air outside vortex indicating denoxification.
- Airmasses rich on NO_x of probably midlatitude origin have been detected over the South pole during the split-up event.
- Peak values of NO_x have been measured at the vortex edge.
- Measured partitioning between NO and NO_2 agree with steady state chemical model above 30 km and for low SZA.
- Mismatch of measured and modeled NO/NO_2 ratios for high SZA below 30 km has to be investigated.
- Measured NO_x and NO_y reservoir gases vmr's show pronounced anticorrelation outside the vortex.
- Inside the vortex, measured NOx and NOy reservoir gases have lower vmr's and anticorrelation is less pronounced.

References

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Acknowledgements

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