Observations of stratospheric NO_x using MIPAS-ENVISAT

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Abstract

The global view offered by satellite observations is essential for monitoring behaviour and trends of the Earth's atmosphere. NO_x gases are involved in the principal natural pathway for ozone destruction and yet their global distribution is still not well understood. MIPAS is a limb viewing fourier transform spectrometer launched aboard ESA's ENVISAT in March 2002. It operates in the infra-red, covering the altitude range 6-68 km at a vertical resolution of around 3km. Reactive nitrogen species observable by the MIPAS instrument include NO, $\mathrm{NO_2}$, $\mathrm{N_2O_5}$ and $\mathrm{HNO_3}$ although here we infer NO and $\mathrm{N_2O_5}$ amounts using a simple photochemical model. These gases all play an important role in stratospheric ozone chemistry. We also observe $\mathrm{N_2O}$ which is a tropospheric source gas from which the reactive nitrogen species are derived. Using MIPAS observations we are able observe the global distribution of these species in the stratosphere during the period July 2002 - March 2004. Descent is seen in the southern polar vortex. We are also able to discern global qualitative correlations between NO_y and $\mathrm{N_2O}$, which give an indication of the origin and chemical history of air [2].

Odd nitrogen chemistry

We observe zonal mean NO_x which here includes nighttime $\mathrm{NO_2}$ and $\mathrm{N_2O_5}$. Nighttime $\mathrm{N_2O_5}$ is derived from a simple photochemical model based on the following equations. These equations summarise the main reactions controlling the distribution of observable reactive nitrogen in the stratosphere.

Reactive nitrogen originates from the oxidation of $\mathrm{N_2O}$;

$$\mathbf{N_2O + O(^1D) \rightarrow 2NO} \quad (1)$$

At sunset NO is quickly converted into $\mathrm{NO_2}$;

$$\mathbf{NO + O_3 \rightarrow NO_2 + O_2} \quad (2)$$

There is then a slower conversion of $\mathrm{NO_2}$ into $\mathrm{N_2O_5}$ during the night;

$$\mathbf{NO_2 + NO_3 + M \rightarrow N_2O_5 + M} \quad (3)$$

NO is rapidly reformed at sunrise;

$$\mathbf{NO_2} + h\nu \rightarrow \mathbf{NO + O(^3P)} \quad (4)$$
$$\mathbf{NO_2 + O \rightarrow NO + O_2} \quad (5)$$
$$(6)$$

$\mathrm{N_2O_5}$ is also photolysed during the day, more slowly;

$$\mathbf{N_2O_5} + h\nu \rightarrow \mathbf{NO_2 + NO_3} \quad (7)$$

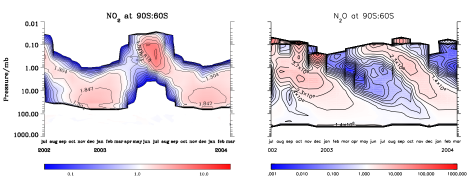
$\mathrm{N_2O_5}$ may be lost via acid deposition onto aerosol surfaces as $\mathrm{HNO_3}$. This is slow and especially important in the lower stratosphere.

$$\mathbf{N_2O_5 + H_2O/aerosol \rightarrow 2HNO_3} \quad (8)$$

The definition of NO_y includes NO_x and $\mathrm{HNO_3}$.

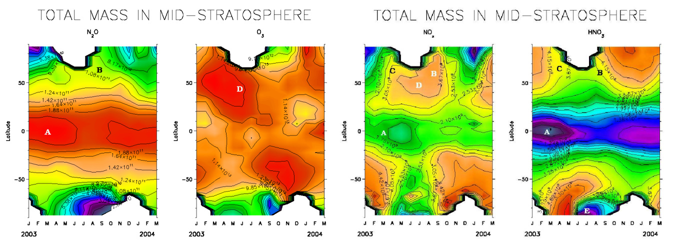
Downward transport in the polar vortex

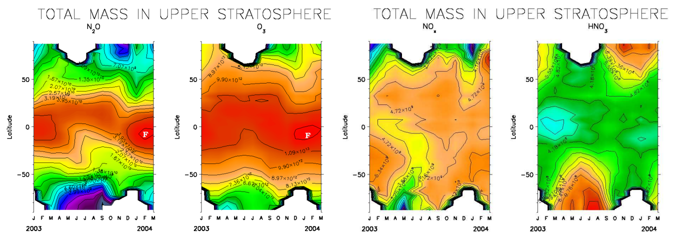
The plots below show fractional enhancements of $\mathrm{NO_2}$ and $\mathrm{N_2O}$ relative to the yearly mean calculated at a given altitude. Descent of air in the southern hemisphere polar vortex is clearly visible in the months June–September.



Stratospheric distributions of nitrogen species

Monthly averaged total mass in 5 degree latitude bands was calculated in the mid-stratosphere (25–35 km), upper-stratosphere (35–50 km) and stratopause region (50–60 km) for the period January 2003 – March 2004.





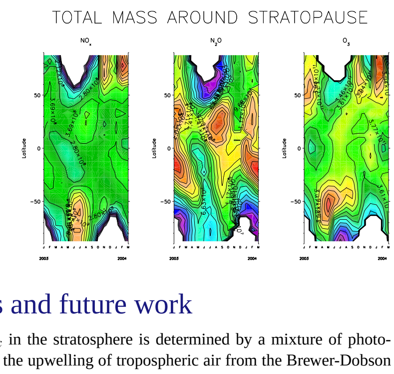
It has been reported that at altitudes below 30 km there is an anti-correlation between NO_y and $\mathrm{N_2O}$ [1]. In the above plots low NO_x and $\mathrm{HNO_3}$ and high $\mathrm{N_2O}$ is seen around the equator in the mid-stratosphere associated with the upwelling of tropospheric air, (see A). Conversely, towards the poles, lower $\mathrm{N_2O}$ corresponds with higher $\mathrm{HNO_3}$ and NO_x, (see B). Interconversion between NO_x and $\mathrm{HNO_3}$ is visible at mid-latitudes. An increase in NO_x associated with a decrease in $\mathrm{HNO_3}$ is observed as daylight hours increase, (see C). As NO_x increases, $\mathrm{O_3}$ is seen to decrease, (see D). Denitrification in the in the southern polar winter is visible in $\mathrm{HNO_3}$ from June–September 2003, (see E).

In the upper-stratosphere high $\mathrm{N_2O}$ around the equator indicates air originates from lower altitudes. This corresponds to high $\mathrm{O_3}$ amounts since here we are above the peak in ozone concentrations, (see F). It is reported that the anti-correlation between $\mathrm{N_2O}$ and NO_y is not compact at these altitudes [1], as may be evident from these figures.

Behaviour in the stratopause region

Above the stratosphere observed NO_x (here $\mathrm{NO_2}$ only) in mid-latitudes follows the distribution of $\mathrm{N_2O}$. At these altitudes rapid loss of NO_x dominates resulting in a positive correlation between $\mathrm{N_2O}$ and NO_x [1];

$$\mathbf{NO + N \rightarrow N_2 + O} \quad (9)$$
$$\mathbf{NO_2 + N \rightarrow N_2 + O + O} \quad (10)$$



Conclusions and future work

These results suggest that the distribution of NO_x in the stratosphere is determined by a mixture of photochemical and transport effects. In tropical regions, the upwelling of tropospheric air from the Brewer-Dobson circulation is the predominant factor. At mid-latitudes photochemical effects dominate. There is a qualitative anti-correlation between $\mathrm{N_2O}$ and NO_y in the mid-stratosphere. However, there is no clear correlation between the species in the upper stratosphere. Above the stratosphere, the correlation between these gases is reversed and becomes positive. A more quantitative look at the correlations between stratospheric NO_x, $\mathrm{N_2O}$, $\mathrm{HNO_3}$ and $\mathrm{O_3}$ and what this means in terms of transport and chemistry will be undertaken as future work.

References

[1] H. A. Michelson, G. L. Manney, M. R. Gunson, and R. Zander. Correlations of stratospheric abundances of NO_y, $\mathrm{O_3}$, $\mathrm{N_2O}$, and $\mathrm{CH_4}$ derived from ATMOS measurements. *Journal of Geophysical Reasearch*, 103:28347–28359, 1998.

[2] R. A. Plumb and M. K. W. Ko. Interrelationships between mixing ratios of long-lived stratospheric constituents. *Journal of Geophysical Reasearch*, 97:10145–10156, 1992.

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