



# Measurement of NOx gases using MIPAS-ENVISAT

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## ABSTRACT

NO, NO<sub>2</sub> and N<sub>2</sub>O<sub>5</sub> play a central role in stratospheric chemistry. We use MORSE, (MIPAS Orbital Retrieval using Sequential Estimation), to retrieve NO<sub>2</sub> and N<sub>2</sub>O<sub>5</sub>. Significant improvements are made to the N<sub>2</sub>O<sub>5</sub> retrieval by retrieving a single value for the aerosol continuum across the N<sub>2</sub>O<sub>5</sub> emission feature.

Performing a retrieval of NO is complicated by Non-LTE effects. Instead, we infer NO concentrations using diurnal NOx conservation and compare NO estimates with the IMK-IAA Non-LTE retrieval. Through consideration of time since sunrise/set, rate constants for diurnal NOx interconversion are determined.

## MIPAS

The Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) is a limb viewing Fourier transform spectrometer aboard ENVISAT. It operates in the near to mid infra-red where many important species affecting the chemical and radiative properties of the atmosphere have characteristic emission features.

The MORSE retrieval algorithm uses an optimal estimation approach, (Rodgers, 2000). The forward model used is the RFM, (Reference Forward Model), which is a line by line radiative transfer code.

## MICROWINDOWS

Retrievals are performed using small sections of the spectrum, known as microwindows, which maximise information content and minimise systematic and random errors to the target molecule.

## IMPROVEMENTS TO N<sub>2</sub>O<sub>5</sub> RETRIEVAL

The spectral signature of N<sub>2</sub>O<sub>5</sub> resembles that of the aerosol continuum. For an accurate retrieval, N<sub>2</sub>O<sub>5</sub> needs to be retrieved jointly with aerosol. Simulated joint retrievals showed precision was significantly improved by retrieving a single value for aerosol across the entire spectral region, rather than retrieving a different value for aerosol in each microwindow.

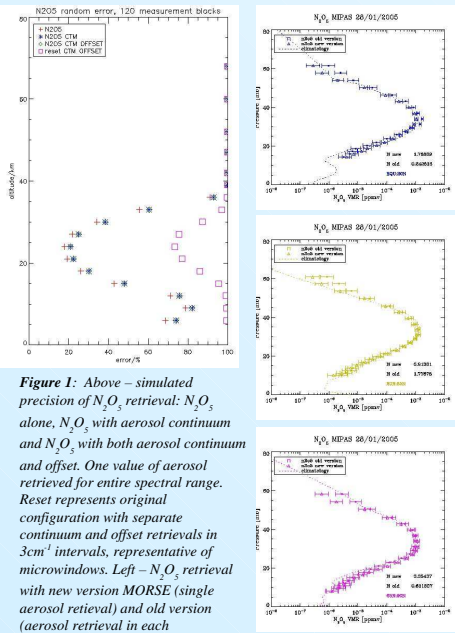


Figure 1: Above - simulated precision of N<sub>2</sub>O<sub>5</sub> retrieval: N<sub>2</sub>O<sub>5</sub> alone, N<sub>2</sub>O<sub>5</sub> with aerosol continuum and N<sub>2</sub>O<sub>5</sub> with both aerosol continuum and offset. One value of aerosol retrieved for entire spectral range. Reset represents original configuration with separate continuum and offset retrievals in 3cm<sup>-1</sup> intervals, representative of microwindows. Left - N<sub>2</sub>O<sub>5</sub> retrieval with new version MORSE (single aerosol retrieval) and old version (aerosol retrieval in each microwindow).

Retrievals were performed using microwindows in both the A-band and B-band. However, retrieving just one value for aerosol across the entire spectral region means we should restrict our spectral range for performing the retrieval to either the A-band feature or the B-band feature. Retrievals showed insignificant differences between the two. Retrievals in future work will be performed using B-band microwindows.

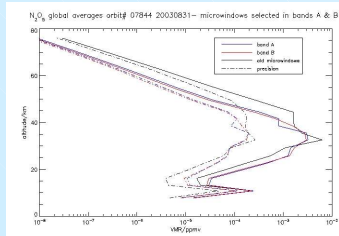
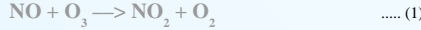


Figure 2: N<sub>2</sub>O<sub>5</sub> retrieval and precision for single orbit on 31-08-2003, using A-band only and B-band only microwindows.

## NOx CHEMISTRY

NO and NO<sub>2</sub> are the dominant catalysts of ozone destruction in the stratosphere. At sunset, NO is rapidly converted to NO<sub>2</sub> (1) which is gradually incorporated into N<sub>2</sub>O<sub>5</sub> (2-3), slowing NOx-catalysed ozone destruction at night. NO and NO<sub>2</sub> are liberated again during the day, mainly by photolysis (4,6).

### Nighttime



### Daytime



## ESTIMATING NO CONCENTRATIONS

Performing a retrieval of NO is difficult due to complicating effects of Non-LTE. However, from the above chemical scheme it is possible to infer daytime NO concentrations from the diurnal conservation of NO, NO<sub>2</sub> and N<sub>2</sub>O<sub>5</sub>. NO<sub>3</sub> may be neglected in the balance, as its concentration is always at least an order of magnitude smaller than the other components. Some comparisons of NO estimates with IMK-IAA Non-LTE retrievals are shown in figure 4.

$$(\text{NO}_2 + 2\text{N}_2\text{O}_5)_{\text{night}} \sim (\text{NO}_2 + 2\text{N}_2\text{O}_5 + \text{NO})_{\text{day}}$$

## RESULTS OF NO ESTIMATES

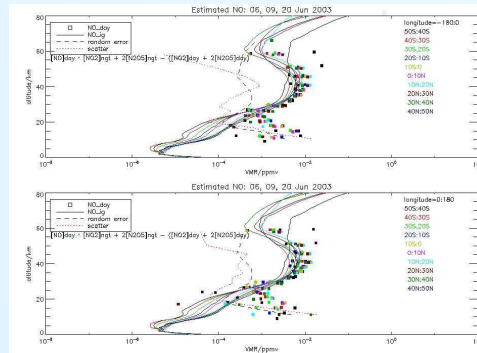


Figure 3: Results of NO estimation split by latitude band and E and W hemisphere for dates in June 2003.

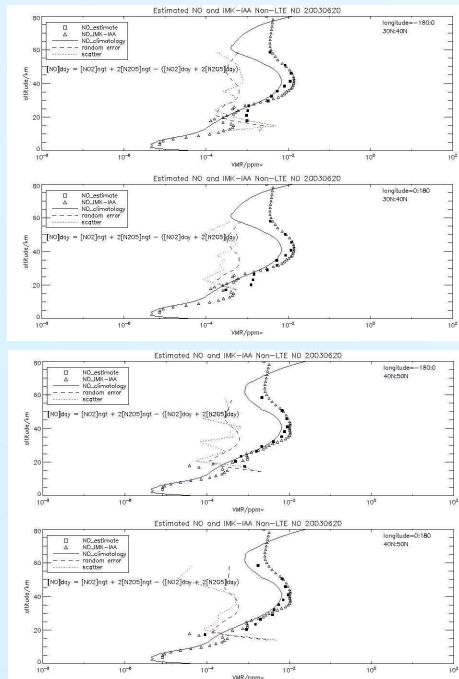


Figure 4: Comparison of IMK-IAA Non-LTE NO retrievals with NO estimates on 20-06-2003 at 30N:40N and 40N:50N. Split into E and W hemispheres.

## CALCULATING RATE CONSTANTS

Rate constants k, reaction (2), and J, reaction (6), are calculated considering the diurnal variation in NO<sub>2</sub> and N<sub>2</sub>O<sub>5</sub>. Considering reactions (2) and (3) and assuming steady state NO<sub>3</sub>, expected concentrations of N<sub>2</sub>O<sub>5</sub> and NO<sub>2</sub> at night are given by:

$$[\text{N}_2\text{O}_5]_{\text{night}} = 0.5[\text{NO}_2]_{\text{set}} (1 - \exp(-2k[\text{O}_3](t - t_{\text{set}}))) + [\text{N}_2\text{O}_5]_{\text{set}}$$
$$[\text{NO}_2]_{\text{night}} = [\text{NO}_2]_{\text{set}} \exp(-2k[\text{O}_3](t - t_{\text{set}}))$$

Concentrations of N<sub>2</sub>O<sub>5</sub> during the day decay exponentially, mainly through photolysis:

$$[\text{N}_2\text{O}_5]_{\text{day}} = [\text{N}_2\text{O}_5]_{\text{rise}} \exp(-J(t - t_{\text{rise}}))$$

MIPAS sits in a sun-synchronous orbit. So to obtain variation in time since sunrise/set, data is gathered over a 6 month period from June-December 2003. Time since sunrise/set is calculated to consider effects of elevation, which can be significant in the stratosphere. To allow for the determination of the residual N<sub>2</sub>O<sub>5</sub> at sunset, an iterative calculation was performed to determine k, J, [NO<sub>3</sub>]<sub>set</sub> and residual [N<sub>2</sub>O<sub>5</sub>]<sub>set</sub> using retrieved values of NO<sub>2</sub>, N<sub>2</sub>O<sub>5</sub> and O<sub>3</sub>. The residual is found to be negligible in most cases.

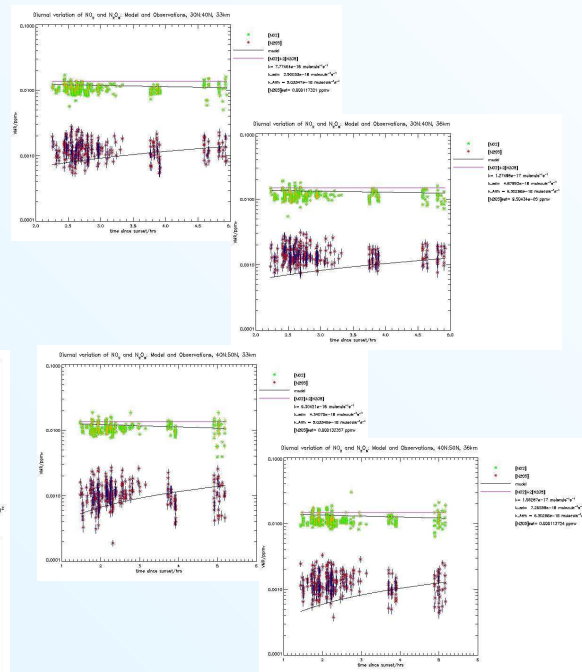


Figure 5: Results of determination of rate constant, k. Dates from June to December 2003. Top - 30N:40N at 33 and 36km. Bottom - 40:50N at 33 and 36km. Values of k are determined using retrievals in given latitude band on a single day. k given above is then an average of all these results. Model lines are calculated using the Arrhenius rate constant, which has experimentally determined parameters and depends only upon temperature. Line in pink represents assumption of constant total NOx in the model. However, changing total NOx is the source of most of the scatter seen in the observations.

Results are shown in the mid-stratosphere at 33 and 36km, where the model is most applicable. Below this height, hydrolysis of N<sub>2</sub>O<sub>5</sub> onto aerosol surfaces becomes important. Above this height, thermal decomposition of N<sub>2</sub>O<sub>5</sub> becomes significant as stratospheric temperatures increase. The best agreement is seen around 35km although N<sub>2</sub>O<sub>5</sub> values have a high bias with respect to the model values. Estimates of J show that N<sub>2</sub>O<sub>5</sub> has a photochemical lifetime of less than half a day at these altitudes, corresponding to negligible residual N<sub>2</sub>O<sub>5</sub> at sunset.

## CONCLUSIONS AND FUTURE WORK

Improvements to the N<sub>2</sub>O<sub>5</sub> retrieval have allowed us to perform some indirect measurements of NO and estimate rate constants associated with NOx chemistry in the stratosphere.

NO estimates show first order agreement with IMK-IAA NO profiles although discrepancies need to be investigated. The seasonal and latitudinal agreement should also be examined.

Estimates of the time constant, k, in the mid-stratosphere are often in agreement with laboratory values. However, the source of the high bias in N<sub>2</sub>O<sub>5</sub> needs to be determined. N<sub>2</sub>O<sub>5</sub> data is currently being reprocessed using new B-band microwindows. An improved estimation of J, accounting for solar zenith angle dependence is under investigation.

## References

1. Chemical Kinetics and Photochemical Data for Use in Stratospheric Modelling. JPL publication 97-4
2. G. Brasseur and S. Solomon. Aeronomy of the Middle Atmosphere. D. Reidel Publishing Company, 1986.
3. R. Toumi, J. A. Pyle, C. R. Webster, R. D. May. Theoretical Interpretation of N2O5 Measurements. Geophys. Res. Lett., Vol. 18, No. 7, pages 1213-1216. July 1991.