RETRIEVAL OF $H^{15}NO_3/H^{14}NO_3$ VERTICAL ATMOSPHERIC DISTRIBUTION FROM MIPAS/ENVISAT LIMB-EMISSION MEASUREMENTS

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INTRODUCTION

Atmospheric infrared remote-sensing has the potential to provide accurate information on the isotopic composition of several molecular constituents. Since new precise spectroscopic parameters of isotopically substituted molecules are becoming available, further advances in the understanding of the mechanisms leading to **atmospheric isotope fractionation** are possible.

MIPAS (Michelson Interferometer for Passive Atmospheric Sounding), on-board the European satellite ENVISAT, is a mid-infrared emission FT interferometer probing the Earth's atmosphere with limb-scanning observations. The detected spectral radiances are routinely inverted to vertical distributions of pressure, temperature, and Volume Mixing Ratio (VMR) of H_2O, O_3, CH_4, N_2O, HNO_3, and NO_2. Non-operational scientific codes have proven that MIPAS spectra can also provide information on minor atmospheric trace constituents as well as on the distribution of the main isotopes in these gases [1].

The inclusion of **$H^{15}NO_3$ spectral line parameters** (relative to the fundamental ν_5 band) into MIPAS-dedicated spectroscopic database provided the possibility to identify, for the first time, $H^{15}NO_3$ in the atmosphere (near 871 cm^{-1}) [2], and to investigate the behaviour of ^{15}N in atmospheric nitric acid.

Never before has the heavy-to-light nitrogen isotopic ratio profile been retrieved from HNO_3 spectral signatures.

RETRIEVAL STRATEGY

The weak intensity of the $H^{15}NO_3$ ν_5 Q-branch prevents the retrieval of VMR profiles from individual MIPAS limb-scans.

A dedicated inversion algorithm, based on the Geofit Multi-Target Retrieval (GMTR) code [3], has been developed to carry out the one-dimensional **joint retrieval of $H^{14}NO_3$ and $H^{15}NO_3/H^{14}NO_3$ VMR profiles** by sequential analysis of subsequent MIPAS individual limb-scans.

Applying a regularized **sequential Kalman filter** approach, the $^{15}N/^{14}N$ isotopic ratio profile retrieved from one scan provides the a-priori estimate for the subsequent retrieval step, so that enough information is accumulated while sequentially processing the measurements.

The retrieval of $H^{14}NO_3$ VMR and $H^{15}NO_3/H^{14}NO_3$ (R) profiles is performed as follow:

$H^{14}NO_3$ retrieval

Optimal estimation with a-priori from ESA L2 data and 100% uncertainty. A mild Tikhonov regularization is applied to constrain the shape of the retrieved profile.

$H^{15}NO_3/H^{14}NO_3$ retrieval

Optimal estimation with a-priori from the analysis of the previous limb-scan (Kalman filter) using the full covariance matrix. At each step, the natural abundance of ^{15}N ($0.00365^\flat$) is assumed as initial-guess over the entire retrieval altitude range. The first scan is processed with a-priori estimate as the ^{15}N natural abundance with 100% uncertainty. A mild Tikhonov regularization is also applied to avoid the presence of oscillations that would be retained by the optimal estimation process and transmitted to the subsequent steps.

The retrieval is operated on 3 MicroWindows: two of them are the same adopted by ESA to routinely retrieve $H^{14}NO_3$ VMR profiles, while the third one contains the Q branch of the $H^{15}NO_3$ fundamental ν_5 band.

The $H^{15}NO_3$ line strengths take into account the natural isotopic abundance of ^{15}N, so the $H^{15}NO_3$ VMR profile is assumed equal to the $H^{14}NO_3$ one multiplied by $\overline{R}$ which is the retrieved profile and represents the deviations of the actual value of $^{15}N/^{14}N$ from the natural isotopic ratio.

$$\overline{VMR}_{H^{15}NO_3} = \overline{VMR}_{H^{14}NO_3} \cdot \alpha \cdot \overline{R}$$

$^\flat$ As reported by the IUPAC Commission of Atomic and Weights and Isotopic Abundances, 1983.

AVERAGING PROCESS

MIPAS nominal mode full resolution measurements at equinoxes and solstices for the period from July 2002 until March 2004 were processed.

Isotopic ratio profiles (R) were derived averaging limb-scans over different latitude bands - North Pole (NP: 60°N–90°N), South Pole (SP: 60°S–90°S), mid-latitudes (MID: 20°N–60°N and 20°S–60°S), equatorial (EQU: 20°N–20°S) - in the altitude range between 15 and 42 km (18 km for the equatorial belt).

The R profiles obtained, indicated in the rows of Table 1, showed good consistency (differences less than 2σ) within the same latitude band, thus permitting to calculate **isotopic ratio weighted mean profiles** for equinoxes and solstices as presented in Figure 1.

Codes		Profiles:
EQU-e	a	Sep02 (20-24) 358; Sep03 (20-24) 425; Mar03 (19-23) 430; Mar04 (09-13) 406
EQU-s	b	Dec02 (19-26) 430; Dec03 (19-26) 430; Jul02 (17-24) 430; Jun03 (16-24) 430
MID-e	c	Sep02 (20-22) 430; Sep03 (22-23) 430; Mar03 (20-22) 430; Mar04 (21-22) 430
MID-s	d	Dec02 (20-22) 430; Dec03 (20-22) 430; Jul02 (17-18) 430; Jun03 (16-18) 430
NP-e	e	Sep02 (20-24) 430; Sep03 (20-24) 305; Mar03 (18-27) 314; Mar04 (07-18) 350
NP-s	f	Dec02 (20-24) 430; Dec03 (20-25) 406; Jul02 (17-21) 430; Jun03 (16-21) 430
SP-e	g	Sep02 (20-24) 350; Sep03 (20-24) 306; Mar03 (18-27) 430; Mar04 (07-18) 430
SP-s	h	Dec02 (20-25) 345; Dec03 (20-25) 200; Jul02 (17-21) 430; Jun03 (16-23) 398

TABLE 1: MIPAS datasets used for R retrievals. First column: latitude band and equinox (**-e**) or solstice (**-s**) condition of the mean profile. Second column: panel of Figure 1 reporting the mean profile. Third column: month, year, days' range of measurements, and number of scans sequentially processed for each profile.

R PROFILES ($H^{15}NO_3/H^{14}NO_3$)

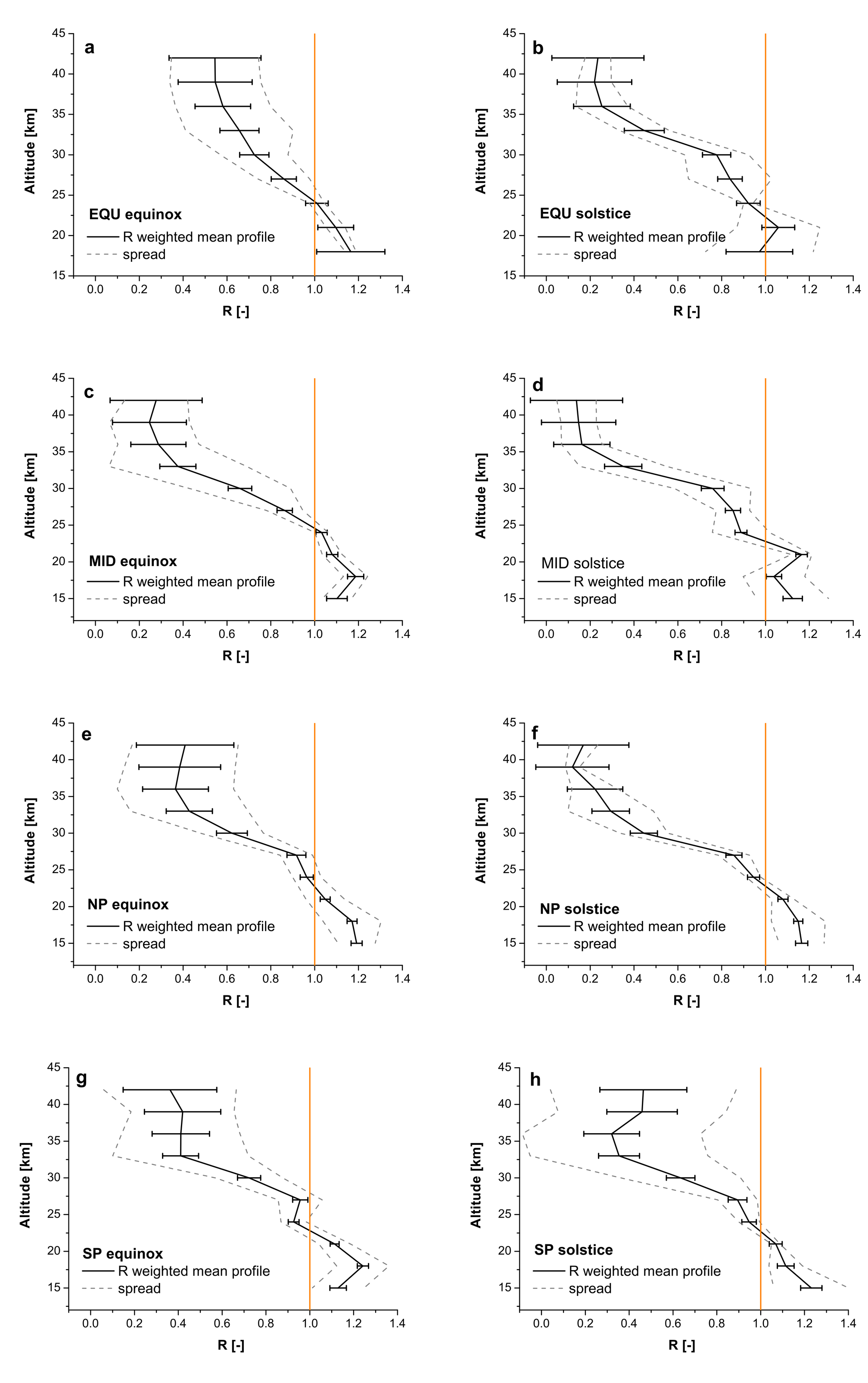

FIGURE 1: Isotopic ratio mean profiles for equinox (left) and solstice (right) conditions for equatorial (panels a-b), mid-latitudes (c-d), North Pole (e-f) and South Pole (g-h) latitude bands. Each profile is the weighted mean of 4 retrieved profiles. Error bars represent the 1σ standard error of the mean, while the spread of the 4 profiles used in the average is plotted with dash lines. The orange vertical line indicates the initial-guess profile assumed.

ERROR ANALYSIS

The use of a Kalman filter approach over sets of MIPAS measurements acquired on subsequent days strongly reduces the contribution of the random error on the retrieved isotopic ratio profile. As indicated in Figure 2, by sequentially processing 400 individual MIPAS limb-scans, the amplitude of the random error is of the same order of magnitude of the total systematic contribution, which becomes the error limiting the retrieval accuracy.

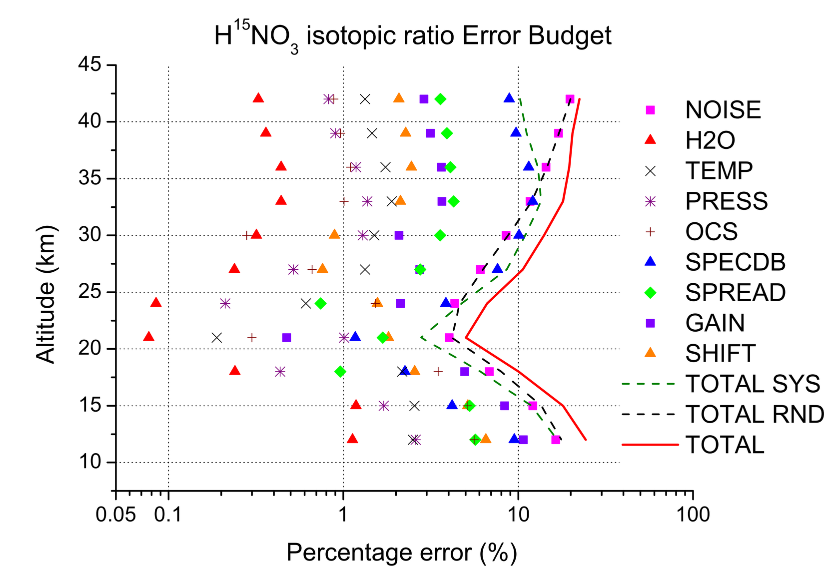

FIGURE 2: Relative error budget (in percent) for the isotopic ratio profile sequentially retrieved from MIPAS limb-scans. The main systematic contributions are reported.

SENSITIVITY ASSESSMENT

As reported in Figure 3, the isotopic ratio profiles retrieved possess generally from 4 to 6 degrees of freedom (DOF), and present a vertical resolutions between 3 and 8 km.

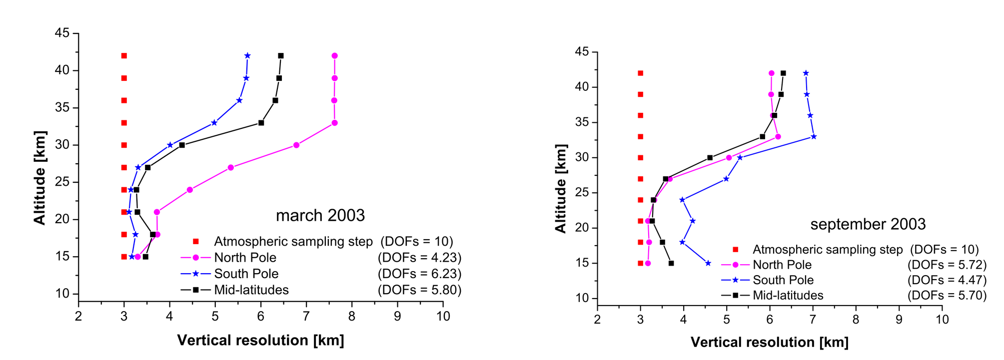

FIGURE 3: Vertical resolution as function of altitude, as represented by the full width at half maximum of the averaging kernels, for the months March 2003 and September 2003, for different latitude bands. The MIPAS measurement vertical grid step is also indicated.

RESULTS AND CONCLUSIONS

We have used atmospheric IR limb-emission spectra measured by the MIPAS satellite instrument to investigate the isotopic composition of atmospheric nitric acid.

The algorithm developed is able to retrieve smooth profiles with reasonable accuracy: about 10% from 20 to 25 km.

The $^{15}N/^{14}N$ isotopic ratio profiles derived from atmospheric nitric acid signature deviate from the standard isotopic abundance with strong **evidence of isotope fractionation**.

The retrieved isotopic ratio profiles systematically show a clear **depletion of $H^{15}NO_3$ above 25 km** altitude.

Latitudinal and temporal variations for the altitude range 15–42 km have been explored. Within each latitude band, no statistically significant temporal variations have been revealed among corresponding equinoxes and solstices, within observational and model uncertainties.

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