# WATER VAPOUR ISOTOPE MEASUREMENTS: COMPARISONS BETWEEN RESULTS FROM MIPAS AND THE ODIN SUB-MILLIMETRE RADIOMETER

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## **ABSTRACT**

The isotopic composition of stratospheric water vapour depends on the sources of water vapour and the temperature and precipitation history of the stratospheric air. Isotopic measurements therefore have potential to aid invesigation of dehydration in the polar vortex, of stratospheric/tropospheric exchange, of upward transport in the tropics and of subsidence at polar latitudes.

Here we compare measurements of  $\mathrm{H}_2^{16}\mathrm{O}$ , HDO and  $\mathrm{H}_2^{18}\mathrm{O}$  from two satellite limb-sounding instruments: the Michelson Interferometer for Passive Atmospheric Sounding (MIPAS), an infra-red limb sounder on Envisat, and the Sub-Millimetre Radiometer (SMR), a microwave limb sounder on board the Odin satellite.

Key words: MIPAS; ODIN; water vapour; isotope.

## 1. INTRODUCTION

#### 1.1 Isotope fractionation

When water evaporates from the oceans, the lighter isotopes are more likely to evaporate than the heavier ones, leading to tropospheric water vapour being depleted in heavy isotopes relative to the ocean water. Also, when condensation occurs, the heavier water isotopes condense more readily than the lighter ones, so that air entering the stratosphere from the troposphere is strongly depleted in heavy isotopes. This is known as the "vapour pressure isotope effect". The effect is more pronounced for substitution of light atoms, so we expect to see a greater effect for HDO than for  $\mathrm{H}_2^{18}\mathrm{O}$ . The biggest depletions are expected in the tropical lower stratosphere.

In the stratosphere, water vapour is produced by the oxidation of methane. Methane is less depleted in deuterium than tropospheric water vapour, so we would expect to the D/H ratio of water vapour to increase with height in the stratosphere.  $\rm H_2O$  formed by the stratospheric oxidation of methane uses atoms from atmospheric oxygen, which is expected to have a higher  $^{18}\rm O/^{16}\rm O$  ratio than water vapour from the troposphere, so we might also expect the  $^{18}\rm O/^{16}\rm O$  ratio of water vapour to increase with height in the stratosphere.

## 1.2 MIPAS

The MIPAS spectra contain enough information to distinguish minor isotopes of many gases, including H<sub>2</sub><sup>18</sup>O and HDO. Microwindows for these isotopes were selected using the Oxford microwindow selection software (1), and the retrievals performed using the MORSE (MIPAS Orbital Retrieval using Sequential Estimation) retrieval code (2), also developed at Oxford.

#### 1.3 The ODIN Sub-Millimetre Radiometer

The Sub-Millimetre Radiometer (SMR) is a limb sounding instrument on board the Swedish-led Odin satellite, which was launched in February 2001. Like Envisat, it flies in a polar sun-synchronous orbit. Atmospheric measurements are performed in a time-sharing mode with astronomical observations. The water vapour isotope mode is specifically designed for observations of stratospheric H<sub>2</sub>O, H<sub>2</sub><sup>18</sup>O and HDO using two 800 MHz wide bands centred at 488.9 and 490.4 GHz. Observations are made in water vapour isotope mode approximately 4 days per month. A retrieval algorithm based on optimal estimation has been adopted for the ground segments of Odin-SMR in Sweden and in France. The Odin retrieval results presented here were produced using the Bordeaux CTSO-v223 algorithm. It should be pointed out that these results are preliminary, and yet to be validated.

# 1.4 Comparisons

Here we compare MIPAS and ODIN zonal mean fields of  $\mathrm{H}_2^{16}\mathrm{O}$ ,  $\mathrm{H}_2^{18}\mathrm{O}$  and HDO for  $22^{nd}$  November 2002. The figures presented show only the altitude ranges where the MIPAS and Odin altitude ranges for each of the isotopes overlap. Zonal means were calculated for  $10^{\,o}$  latitude bins. Since isotopic retrievals from both instruments are preliminary, it was hoped that these comparisons would be useful in the validation process.

## 2. $H_2O$

Fig. 1 shows zonally averaged water vapour fields as observed by MIPAS and the Odin SMR, while Fig. 2 shows the percentage difference between the two instruments. (There was no MIPAS data available in the latitude range 90S–80S for this particular day). The

MIPAS retrieval covers the altitude range 12-60 km (although it should be possible to retrieve down to 6 km in cloud-free cases), while the Odin-SMR retrieval covers the range 20-70 km. Fig. 1 shows an approximate altitude range of 20-60 km. Random errors on single profile retrievals of H<sub>2</sub>O from both MIPAS and Odin are expected to be of the order of 10%. It can be seen that the fields are qualititavely similar. However, there are noticeable differences. The fields would not be expected to be exactly the same, since the MIPAS and Odin limb scans would not have been in exactly the same locations. However, Fig. 2 shows consistent biases across all latitude bands. At 50 mbar, Odin-SMR values are lower than MIPAS values by around 50%. Odin–SMR values in this region are around 1.5 ppmv. This is probably unrealistically low. In the region 10-20 mbar, agreement is good, but Odin-SMR values are generally slightly higher than MIPAS values across most latitude bands. At higher altitudes, Odin-SMR values are lower than MIPAS values. This is probably due to a high bias in the MIPAS  $H_2O$  at these altitudes.

#### 3. HDO

## 3.1 Volume mixing ratios

For the Odin–SMR, HDO is measured in a time–shared mode during roughly half of the 15 orbits per "water vapour isotope mode" measurement day, each orbit corresponding to about 60 individual limb scans. The measurement precision (random error) for a single profile retrieval of HDO is about 20–30%, and information is obtained between 18–55 km. Further work is required to characterise various instrumental and spectroscopic uncertainties before the accuracy of the Odin-SMR profiles can be determined.

For MIPAS, HDO can be retrieved wherever there is Level 1B data available. Typical random errors on a single profile are also of the order of 20-30%. There is sufficient information to retrieve HDO over the altitude range 6–42 km.

Fig. 3 shows zonally averaged HDO fields as observed by MIPAS and the Odin SMR. Fig. 4 shows the percentage difference between the zonal means from the two instruments. As with  $\rm H_2O$ , the fields are qualitatively similar. Odin–SMR HDO values are noticeably higher than MIPAS values at around 100 mbar, at the lower edge of the Odin–SMR measurement range. At higher altitudes, the differences are not consistent across all latitude bands. This is encouraging. Differences are generally within  $\pm 30\%$ .

# 3.2 $\delta \mathbf{D}$

Isotopic compositions are usually expressed using delta notation, in which the isotopic ratios (for example deuterium to hydrogen) of the sample of interest and a reference sample are related by

$$\delta D = \left(\frac{\left(\frac{D}{H}\right)_{sample} - \left(\frac{D}{H}\right)_{reference}}{\left(\frac{D}{H}\right)_{reference}}\right) \times 1000 \quad (1)$$

The units are per mil, and the reference ratio is taken from the accepted standard for that particular species. In the case of water, the standard is taken from *Standard Mean Ocean Water* (SMOW). The ratio D/H in SMOW is taken to be  $1.55 \times 10^{-4}$ . The  $\left(\frac{D}{H}\right)_{sample}$  is the isotopic ratio of the measured water vapour and is calculated as

$$\left(\frac{D}{H_{sample}}\right) = \frac{VMR(HDO)}{2 \times VMR(H_2O)}$$
 (2)

where VMR(HDO) and  $VMR(H_2O)$  are the measured mixing ratios. (The factor of 2 in the denominator originates from the way that the reference D/H ratio in SMOW is defined. This factor is not required for the definition of  $\delta^{18}$ O in water vapour.)

Fig. 5 shows zonal means of  $\delta D$  as measured by MIPAS and the Odin–SMR. The  $\delta$ –value plots are quite different. We would expect to see a maximum depletion in the tropical lower stratosphere, with the depletion diminishing with height due to the water vapour produced by methane oxidation (see Section 1.1). The maximum depletion in the Odin–SMR  $\delta D$  field seems to be higher in altitude than we might expect. This area of maximum depletion in the Odin–SMR field also coincides with the region where the Odin–SMR H<sub>2</sub>O is higher than the MIPAS H<sub>2</sub>O. Small differences in the volume mixing ratio of either the major or the minor isotope can lead to large differences in the  $\delta$ –values. Some further work is required to characterise the errors on these  $\delta D$  fields.

# 4. $H_2^{18}O$

# 4.1 Volume mixing ratios

Fig. 6 shows zonally averaged H<sub>2</sub><sup>18</sup>O fields as observed by MIPAS and the Odin–SMR. Fig. 7 shows the difference between the zonal means from the two instruments.

Single–profile precision is of the order of 20–30% for both the MIPAS and the Odin profiles. Again, the plots are qualitatively similar, but there are noticeable differences. The zonal mean profile at 20S–10S is an example of where the differences are particularly noticeable. In general, differences are within  $\pm 30\%$ .

Fig. 8 shows zonally averaged  $\delta^{18}$ O fields as observed by MIPAS and the Odin–SMR. The reference <sup>18</sup>O/<sup>16</sup>O ratio in SMOW is taken to be  $2.00 \times 10^{-3}$ . We might expect to see a maximum depletion in the tropical lower stratosphere, with the depletion diminishing with increasing height. However, this is not seen here in the fields from either of the instruments. The MIPAS field shows a small area of enrichment in the lower stratosphere in the 10S-20S latitude band, and the greatest depletions at about 1 mbar over the equator and in the northern polar region. The  $\delta^{18}$ O field from the Odin–SMR shows maximum depletions at around 10 mbar, in the region where the Odin  $H_2O$  is greater than the MIPAS  $H_2O$ . The  $\delta^{18}O$ fields from the two instruments do not match expectations, or each other, which is worrying. As with the  $\delta D$ values, further work is needed on the error analysis.

## 5. $CH_3D + HDO$

One source of HDO in the stratosphere is the oxidation of  $CH_3D$ . It is expected (3) that HDO production should be in near balance with  $CH_3D$  destruction. We therefore expect the quantity  $CH_3D + HDO$  to be approximately constant with altitude in the lower stratosphere. With MIPAS, it is possible to obtain simultaneous measurements of  $CH_3D$  (from 12–30 km) and HDO, providing a useful internal validation of MIPAS HDO profiles.

Fig. 9 shows zonal mean CH<sub>3</sub>D + HDO as measured by MIPAS. It can be seen that the quantity is approximately constant with altitude in the lower stratosphere.

#### 6. SUMMARY

The zonal mean fields of volume mixing ratio of  $\rm H_2O$ , HDO and  $\rm H_2^{18}O$  from MIPAS and the Odin–SMR look qualitatively similar. However, the zonal mean fields of  $\delta \rm D$  and  $\delta^{18}O$  as measured by the two instruments look quite different. This is due not only to the differences in the measurements of the minor isotopes from the two instruments, but also largely to the differences between the measurements of the main isotope. Further validation work will be required on both the MIPAS and the Odin–SMR water vapour isotope measurements.

## REFERENCES

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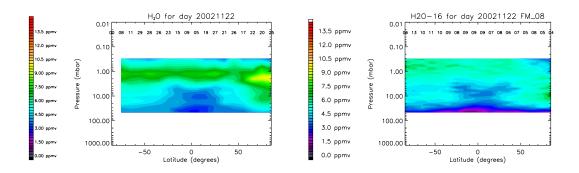


Figure 1.  $H_2O$  zonal mean distribution from MIPAS (left) and the Odin–SMR (right). The numbers at the top of the plots show the number of profiles averaged in each of the  $10^{\circ}$  latitude bins.

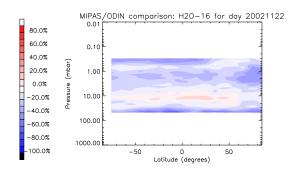


Figure 2. H<sub>2</sub>O percentage difference: (Odin–SMR - MIPAS)/MIPAS

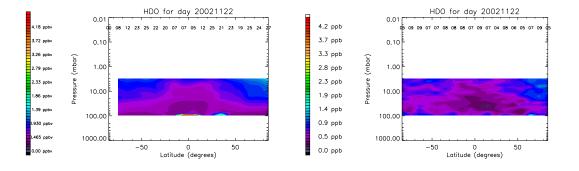


Figure 3. HDO zonal mean distribution from MIPAS (left) and the Odin–SMR (right). The numbers at the top of the plots show the number of profiles averaged in each of the  $10^{\circ}$  latitude bins.

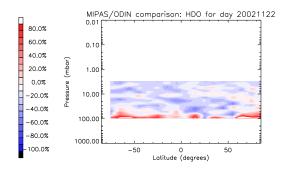


Figure 4. HDO percentage difference: (Odin–SMR - MIPAS)/MIPAS

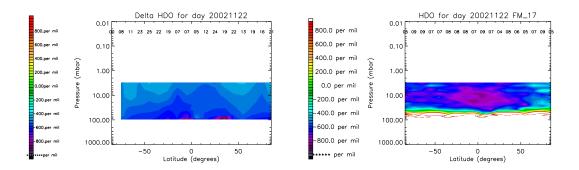


Figure 5.  $\delta D$  zonal mean distribution from MIPAS (left) and the Odin–SMR (right). The numbers at the top of the plots show the number of profiles averaged in each of the  $10^{\circ}$  latitude bins.

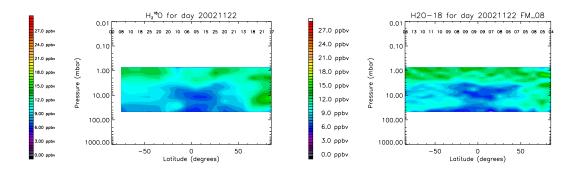


Figure 6.  $H_2^{18}O$  zonal mean distribution from MIPAS (left) and the Odin–SMR (right). The numbers at the top of these plots show the number of profiles averaged in each of the  $10^{\circ}$  latitude bins.

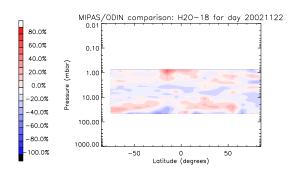


Figure 7.  $H_2^{18}O$  percentage difference: (Odin–SMR - MIPAS)/MIPAS

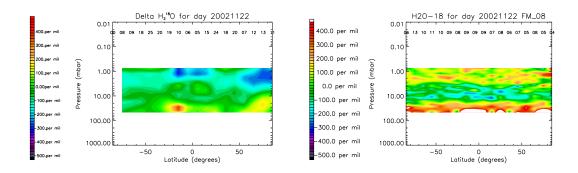


Figure 8.  $\delta^{18}O$  zonal mean distribution from MIPAS (left) and the Odin–SMR (right). The numbers at the top of the plots show the number of profiles averaged in each of the  $10^{\circ}$  latitude bins.

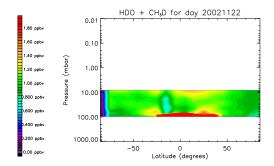


Figure 9.  $HDO + CH_3D$  zonal mean distribution from MIPAS