

Analysis of new species retrieved from MIPAS

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Abstract

The Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) instrument which operated on the Envisat satellite from 2002-2012 is a Fourier transform spectrometer for the measurement of high-resolution gaseous emission spectra at the Earth's limb. It operates in the near- to mid-infrared, where many of the main atmospheric trace gases have important emission features. The initial operational products were profiles of Temperature, H₂O, O₃, CH₄, N₂O, HNO₃, and NO₂, and this list was recently extended to include N₂O₅, ClONO₂, CFC-11 and CFC-12. Here we present preliminary results of retrievals of the third set of species under consideration for inclusion in the operational processor: HCN, CF₄, HCFC-22, COF₂ and CCl₄.

I. INTRODUCTION

The Michelson Interferometer for Passive Atmospheric Sounding (MIPAS), which operated on the Envisat satellite from 2002-2012, is a Fourier transform spectrometer for the measurement of emission spectra at the Earth's limb. It operates in the near- to mid-infrared where many of the main atmospheric trace gases have detectable emission features. The initial operational products were profiles of Temperature, H₂O, O₃, HNO₃, CH₄, N₂O and NO₂, and this list was recently extended to include N₂O₅, ClONO₂, CFC-11 and CFC-12.

In this paper the preliminary results of a third set of species, HCN, CFC-14 (CF₄), HCFC-22, COF₂, CCl₄, SF₆, OCS, HOCl and C₂H₆, retrieved using the Oxford L2 processor, MORSE (Multispectral Optimal Retrievals using Sequential Estimation), are presented.

HCN, OCS and C₂H₆ are tracers of biomass burning (Rinsland et al., 1998; Li et al., 2000;

Notholt et al., 2003; Logan et al., 1981). The relatively long lifetimes for HCN and C₂H₆ make them indicators of how transport redistributes pollutants on a global scale (Rinsland et al., 2005). CCl₄, CFC-14, HCFC-22 and SF₆ are mainly from anthropogenic emissions. For example CFC-14 are produced primarily as a by-product during electrolytic aluminum production and SF₆ is mainly from insulating electrical equipment. SF₆ and CF₄ are extremely long-lived species and often used as tracers for the 'age of air'. HOCl is considered to be a reservoir for active chlorine, ClO_x, and odd hydrogen, HO_x, in the stratosphere (von Clarmann et al., 2012). It is produced primarily by the reaction of ClO and HO₂ (peroxy radical) and is destroyed mainly by photo-dissociation, which returns OH and Cl radicals (Hickson et al., 2007).

Here we also examine fluorine species collectively measured by MIPAS. Stratospheric fluorine has important effects on the atmosphere, especially fluorine in long-lived greenhouse

gases. Over the past few decades, the major sources of fluorine in the stratosphere are the man-made chlorofluorocarbons CFCs and HCFCs. Photolysis of these compounds forms COF_2 . The COF_2 molecule has been shown to be the second most abundant stratospheric fluorine reservoir (Kaye et al., 1991).

II. ZONAL MEAN DISTRIBUTIONS

The Oxford L2 processor MORSE has been used to retrieve these new species with the microwindows shown in Fig.1. Here we analyze these new retrieved species to establish their zonal mean for the period of 2010 March.

For each gas, we eliminated those data points that are cloud-affected and where a priori has a significant contribution, in other words, the retrieved random error greater than 50% of the volume mixing ratio (VMR). A 5σ global spike test is then applied to each species to eliminate unrealistic data. The percentage of profiles removed by the spike test is shown in Table 1. The largest percentage showed in the table is 21.5% from CFC-14. Reasons for these spike test failures have yet to be investigated. As the total number of profiles for each species for one month is over 32,000, there are still remaining a large number of profiles, over 25,000 profiles, to have a reliable sample basis for the further study.

The remaining profiles are used construct monthly zonal mean together with a standard deviation defined as the standard deviation of profiles contribute to each grid point, which is a combination of random error and atmosphere variability.

Zonal plots of species CCl_4 , OCS, HCFC-22, SF_6 , C_2H_6 and COF_2 in Fig. 2 show the expected structure for tropospheric source gases. The

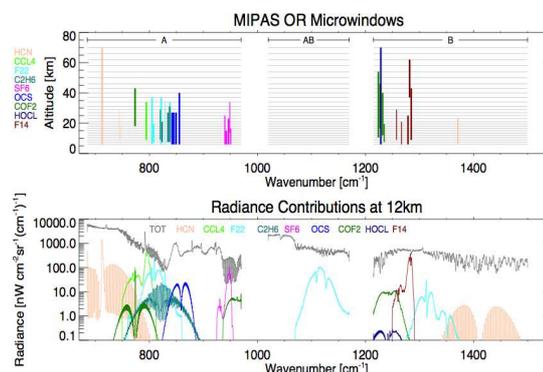


Fig. 1, Microwindows for the new species. The upper panel shows the microwindows selected for these new species retrievals. The lower panel show the spectral signatures of these species.

Table 1, percentage of removed profiles by 5σ spike test.

Species	Ratio (%)
CCl_4	1.9
COF_2	12.5
HCFC-22	0.5
HCN	5.2
CFC-14	21.5
SF_6	12.3
HOCl	0.03
C_2H_6	18.7
CFC-11	1.6
CFC-12	2.6
OCS	2.0

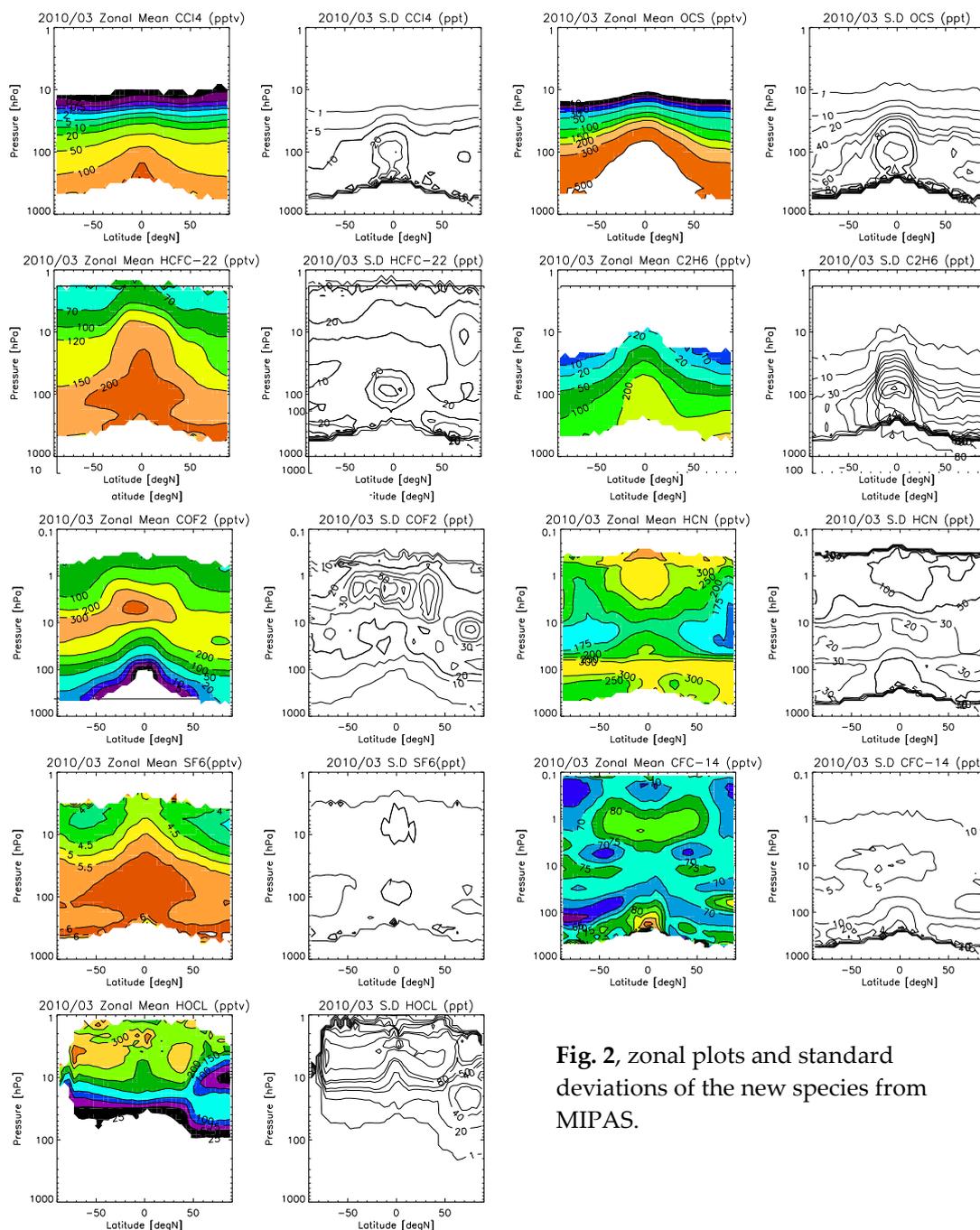


Fig. 2, zonal plots and standard deviations of the new species from MIPAS.

plot of COF_2 also well represents the maximum of VMR around the middle of the stratosphere over equator. This occurs because

COF_2 is an intermediate product in the degradation of CFCs in the stratosphere, which results in an increase of VMR. Also because COF_2 is destroyed by photolysis and reaction

with O(1D) in the upper stratosphere, which results in a decrease of VMR.

There are some unexpected features in the zonal plots for species CFC-14 and HCN. For example, a maximum VMR of HCN occurs near the stratopause over the equator, which seems unrealistic and requires comparison with other data sets. Similar for CFC-14 there is a maximum in the upper stratosphere over equator, which is unrealistic as well. Due to its complexity, HOCl species need further study before the data could be used for quantitative research.

III. Total Fluorine

The fluorine species measured by MIPAS are COF_2 , CFC-11, CFC-12, CFC-14, CFC-22 and SF_6 from which the total fluorine can be computed as $[F] = 2[\text{COF}_2] + [\text{CFC-11}] + 2[\text{CFC-12}] + 4[\text{CFC-14}] + 2[\text{CFC-22}] + 6[\text{SF}_6]$. Mahieu et. al. (2008) show most of the stratospheric fluorine species eventually form Hydrogen Fluoride (HF), which is not measured by MIPAS. Other fluorine containing species are comparable small compared with those measured by MIPAS and HF.

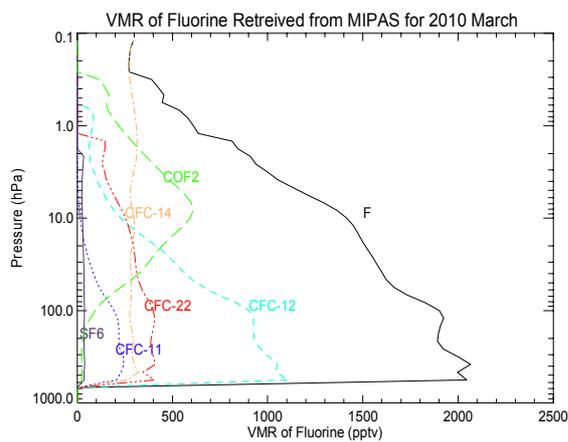


Fig. 3. The vertical profiles of all the fluorine containing species and the total fluorine retrieved by MIPAS.

Figure 3 shows the vertical profiles of all the fluorine species and total fluorine (F) measured by MIPAS. In the lower stratosphere and upper troposphere, the atmospheric fluorine is mainly contributed by CFC-12. COF_2 contributes nearly half of the fluorine VMR at 10hPa pressure level, while CFC-14 dominates in the upper stratosphere. The total [F] decreases with altitude as they are eventually formed into HF, which is not measured by MIPAS. The expected HF zonal plot for 2010 March is constructed by the following, $[\text{HF}] = [\text{Fmax}] - [\text{F}]$, where [F] is the total fluorine zonal mean measured by MIPAS and [Fmax] is the maximum value of [F]. This plot (Fig. 4) is further compared with the zonal plot of HF (fig. 5) produced by Jones et al., 2012. Fig 5 is a three-month combined zonal average from ACE-FTS data during September-October-November. Fig4 and Fig 5 is for brief comparison of MIPAS data with ACE-FTS data of HF zonal means.

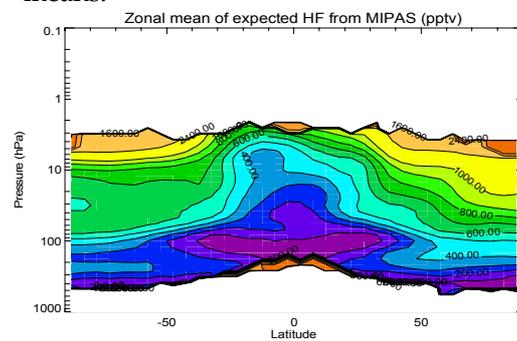


Fig. 4. expected zonal plot of HF from MIPAS

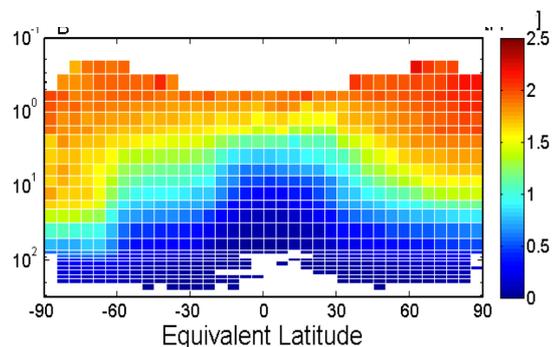


Fig. 5. zonal plot of HF from ACE-FTS (Jones et al., 2012)

IV. CONCLUSIONS AND FUTURE WORK

Plausible distributions of HCFC-22, COF₂, CCl₄, SF₆, OCS, HOCl and C₂H₆ retrieved by MIPAS, which CFC-14 and HCN have some anomalies requiring further investigation. However, further comparison with ACE-FTS, other MIPAS processor and model results are required for further justification.

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