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Long-term intercomparison of MIPAS additional species $ClONO_2$, N_2O_5, CFC-11, and CFC-12 with MIPAS-B measurements

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I. INTRODUCTION

The Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) aboard the environmental satellite ENVISAT is a limb-viewing Fourier-transform emission spectrometer working in the mid-infrared spectral region between 685 cm^{-1} and 2410 cm^{-1} [Fischer et al. 2008]. During the ten years of operation, MIPAS was able to observe temperature and a large number of climate-relevant trace gases from the upper troposphere up to the mesosphere (nominal observation mode) and even the thermosphere (special modes). For about two years after the launch of the satellite on 1 March 2002, MIPAS recorded spectra with full spectral resolution of 0.025 cm^{-1}. After anomalies in the velocity of the interferometer drive unit and a subsequent interruption of the measurements (March 2004), a lower (so-called optimized) spectral resolution of 0.0625 cm^{-1} together with a higher spatial resolution was chosen such that operational observations could restart in January 2005. Following the loss of communications with the satellite platform, there are no MIPAS data available since 8 April 2012. The description and characterization of the operational European Space Agency (ESA) processor products have been presented by Raspollini et al. [2006, 2013] and references therein. While previous operational product processing was limited to temperature and the molecules H_2O, O_3, HNO_3, CH_4, N_2O, and NO_2, the new ML2PP V6 data includes also the minor "additional" trace gases CFC-11 (CCl_3F), CFC-12 (CCl_2F_2), N_2O_5, and $ClONO_2$. In this paper we focus on the comparison of these additional species.

Several flights with MIPAS-B, the balloon version of MIPAS, have been carried out during the operational period of ENVISAT. Table 1 gives an overview of MIPAS-B flights where MIPAS-B observations coincide in space and time with MIPAS on ENVISAT (MIPAS-E) measurements. MIPAS-B limb sequences recorded during these flights are compared to the corresponding MIPAS-E overpasses. MIPAS-B was strongly involved in the ENVISAT validation activities and the high accuracy of the MIPAS-B data has been assessed in numerous MIPAS-E related validation studies [see, e.g., Cortesi et al. 2007, Höpfner et al. 2007, Milz et al. 2009, Payan et al. 2009, Ridolfi et al. 2007, Steck et al. 2007, Wang et al. 2007a, 2007b, Wetzel et al., 2007, 2013, Zhang et al. 2010a, 2010b].

II. MIPAS-B DATA ANALYSIS AND INTERCOMPARISON METHOD

MIPAS-B can be regarded as a precursor of the satellite instrument [see Friedl-Vallon et al., 2004 and references therein]. Therefore, a number of specifications are quite similar, such as spectral resolution and spectral coverage. However, for some essential parameters, the MIPAS-B performance is superior, e.g. in terms of the NESR (Noise Equivalent Spectral Radiance), and in the case of the pointing accuracy. Further improvement of the NESR is achieved by averaging multiple spectra taken at the same pointing angle. MIPAS-B measures all atmospheric parameters covered by MIPAS-E. Essential for the balloon instrument is the sophisticated line of sight stabilization system, which is based on an inertial navigation system and supplemented with an additional star reference system leading to an after all knowledge of the tangent altitude in the order of 90 m (3 σ). The MIPAS-B data processing from interferograms to calibrated spectra including instrument characterization is described in Friedl-Vallon et al. [2004] and references therein. The measurements were done typically at a 1.5 km vertical grid. Retrieval calculations of atmospheric target parameters were performed at a 1 km grid with a least squares fitting algorithm using analytical derivative spectra calculated by the Karlsruhe Optimized and Precise Radiative transfer Algorithm [KOPRA; Stiller et al. 2002; Höpfner et al. 2002]. A Tikhonov-Phillips regularization approach [Phillips, 1962, Tikhonov, 1963] constraining with respect to a first derivative a priori profile was adopted. The resulting vertical resolution is typically between 2 and 5 km for the analyzed species and is therefore comparable to or slightly better than the vertical resolution of MIPAS-E. The species $ClONO_2$, CFC-11, CFC-12, and N_2O_5 are analyzed in the spectral windows 779.7 - 780.7 cm^{-1}, 840 - 860 cm^{-1}, 918 - 924 cm^{-1}, and 1220 - 1270 cm^{-1}, respectively. Different spectral windows within these molecular bands were used for the MIPAS-E data analysis [Raspollini et al. 2013]. Spectroscopic parameters for the calculation of limb emission spectra originate from the high-resolution transmission (HITRAN) molecular absorption database [Rothman et al. 2005]. The MIPAS-B error estimation includes random noise as well as the mutual influence (covariance) of the fitted parameters, temperature errors, pointing inaccuracies, errors of non-simultaneously fitted interfering gases, and spectroscopic data errors (1 σ). For details on the MIPAS-B data analysis and error estimation, see Wetzel et al. [2012] and references therein.

Since pressure is the primary vertical coordinate of MIPAS-E, vertical profiles of the satellite sensor have been interpolated to the MIPAS-B pressure-altitude grid. Differences between measured volume mixing ratios (VMRs) of MIPAS-E and the validation instrument MIPAS-B are expressed in absolute units and relative differences. The mean difference Δx_{mean} for N profile pairs of compared observations is given as:

$$\Delta x_{mean} = \frac{1}{N}\sum_{n=1}^{N}\left(x_{E,n} - x_{B,n}\right) \quad (1)$$

where x_E and x_B are VMR values of MIPAS-E and MIPAS-B at one altitude level. The mean relative difference $\Delta x_{mean,rel}$ of a number of profile pairs is calculated by dividing the mean absolute difference by the mean profile value of the validation instrument MIPAS-B:

$$\Delta x_{mean,rel} = \frac{\Delta x_{mean}}{\frac{1}{N}\sum_{n=1}^{N} x_{B,n}} \cdot 100\% \quad . \qquad (2)$$

Differences are displayed together with the combined errors σ_{comb} of both instruments which are defined as:

$$\sigma_{comb} = \sqrt{\sigma_E^2 + \sigma_B^2} \quad , \qquad (3)$$

where σ_E and σ_B are the precision, systematic or total errors of MIPAS-E and the validation instrument, respectively.

Precision errors characterize the reproducibility of a measurement and correspond, in general, to random noise errors. Systematic errors of the V6 processor used for MIPAS-E data have been assessed in a corresponding ESA study [Raspollini et al. 2013]. The uncertainty of the calculated mean difference (standard error of the mean, SEM) is given by $\sigma/N^{0.5}$ where σ is the standard deviation (SD). A bias between both instruments is considered significant if the SEM is smaller than the bias itself. The comparison between the VMR difference and the combined systematic error (for statistical comparisons) or total error (for single comparisons) is appropriate to identify unexplained biases in the MIPAS-E observations when they exceed these combined error limits. Since the vertical resolution of the used VMR profiles of both instruments is of comparable magnitude, no smoothing by averaging kernels has been applied for the intercomparison of the observed profiles.

III. Intercomparison Results

Table 1: *Overview of MIPAS-B flights used for intercomparison with MIPAS-E. Distances and times between coincident trace gas profile pairs observed by MIPAS-E and the validation instrument refer to an altitude of 20 km (Kiruna) and 30 km (Aire-sur-l'Adour and Teresina).*

Location	Date	Distance (km)	Time difference (min)
Kiruna (Sweden, 68°N)	20 Mar 2003	16/546	14/15
	11 Mar 2009	187/248	5/6
	24 Jan 2010	109/302	5/6
Aire-sur-l'Adour (France, 44°N)	24 Sep 2002	21/588/410/146	12/13/15/16
Teresina (Brazil, 5°S)	14 Jun 2005	109/497/184/338	228/229/268/269
	06 Jun 2008	224/284/600/194	157/158/169/170

In this section, ESA operationally processed (ML2PP V6) MIPAS-E VMR profiles of the molecules $ClONO_2$, N_2O_5, CFC-11, and CFC-12 are compared to coincident MIPAS-B observations. Table 1 summarizes corresponding balloon flights in terms of date, time, locations, and differences in time and space to the satellite measurements.

Mean deviations of all coincident $ClONO_2$ profiles measured by MIPAS-B and MIPAS-E between 2002 and 2010 are shown in Figure 1. Up to 18 collocations are available per altitude. The agreement between the measured profiles appears to be quite good with a mean deviation over all altitudes of 7.2 %. Some biases are visible in limited altitude regions but they are not significant with regard to the combined error limits.

Figure 2 displays the differences concerning the molecule N_2O_5. This molecule exhibits a pronounced diurnal variation in its mixing ra-

tio. Hence, a photochemical correction using a box model [Wetzel et al. 1995], which takes into account the nighttime variation of N_2O_5, has been applied to the tropical MIPAS-E measurements where both, diurnal variation and the time difference of the observations (see Table 1), are quite large. Apart from the lowermost altitude region between 15 and 17 km (where only 2 collocations are available) there is no significant bias visible between the balloon and satellite measurements of MIPAS. The overall agreement between both sensors is fairly good with a mean deviation of -6.7 %.

The comparison for the species CFC-11 is shown in Figure 3. In contrast to the previously discussed molecules, significantly higher values are visible in the MIPAS satellite data in the complete altitude region under comparison. While below 19 km this positive bias is still within the combined systematic and total errors, it clearly exceeds these error limits above and therefore remains unexplained.

Figure 4 displays the observed differences for the molecule CFC-12. Unlike the case of CFC-11, the agreement of measured CFC-12 VMR is quite good with a mean difference of 11.5 %. No significant biases are visible at all.

IV. Conclusions

Vertical profiles of six MIPAS balloon flights between 2002 and 2010 have been used for an intercomparison study of the species $ClONO_2$, N_2O_5, CFC-11, and CFC-12, which have been processed for the first time by the operational ESA processor (ML2PP V6).

For the molecules $ClONO_2$, N_2O_5, and CFC-12 the agreement between both MIPAS instruments is generally good. No clear biases in the observed mixing ratios are visible. Furthermore, no seasonal or latitudinal dependence of deviations could be recognized. However, standard deviations are slightly larger than the combined precision errors. Concerning the species CFC-11 a significant positive bias is evident at all altitudes under comparison. Above 19 km, this bias clearly exceeds the combined systematic and total errors and remains unexplained. Hence, this molecule cannot be recommended for scientific users at the present state. Investigations are ongoing within the ESA processor development team to understand the reason of the bias.

It should also be mentioned that some single MIPAS-E profiles of these additional species exhibit retrieval oscillations which show up in VMR differences (in limited altitude regions) to MIPAS-B observations but which may in turn be smoothed out in comparisons of mean differences. Scientific users should therefore be careful in their interpretation when using single MIPAS-E profiles of these trace gases.

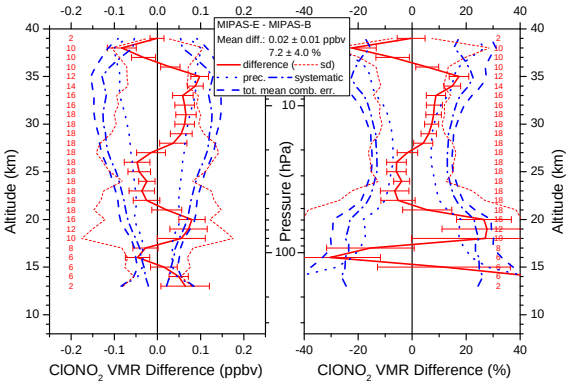

Figure 1: *Mean absolute and relative $ClONO_2$ VMR differences of all collocations between MIPAS-E and MIPAS-B (red solid lines) including standard deviation (red dotted lines) and the standard error of the mean, plotted as error bars around the mean deviation together with precision (blue dotted lines), systematic (blue dash-dotted lines) and total (blue dashed lines) mean combined errors. Red values indicate the number of collocations used for the statistical analysis. Differences of $ClONO_2$ mixing ratios are well within the combined error limits.*

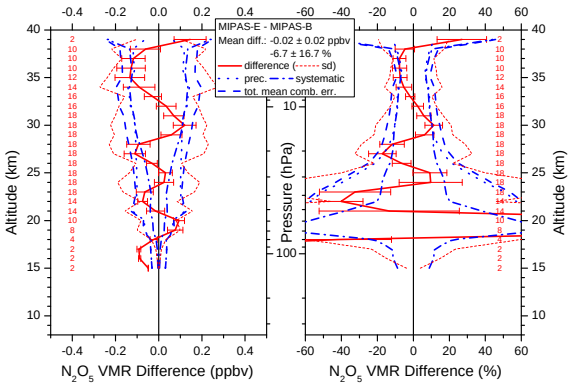

Figure 2: *Same as Figure 1, but for the molecule N_2O_5. The overall agreement of both sensors is fairly good.*

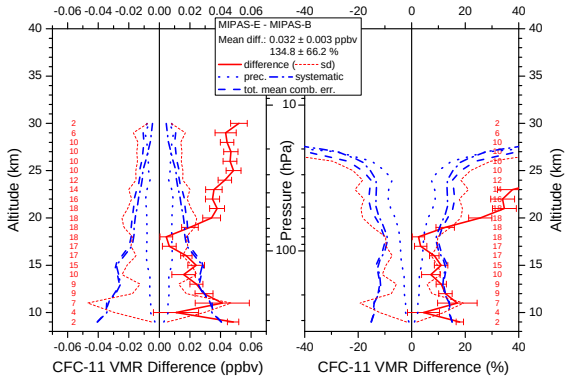

Figure 3: *Same as Figure 1, but for the species CFC-11. A positive bias is visible in the MIPAS-E data, especially above 19 km.*

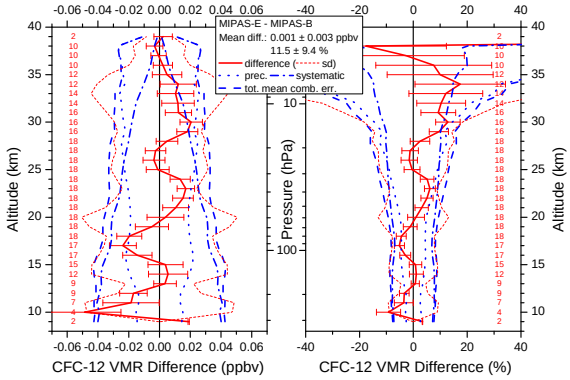

Figure 4: *Same as Figure 1, but for the molecule CFC-12. No significant bias is obvious between the measured profiles of both MIPAS instruments.*

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