Massbalance of stratospheric deuterated water

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Methane and molecular hydrogen are the only relevant chemical sources for water in the stratosphere. Hydrogen is only changed between these three major species and the sum of total hydrogen ($H_2O+H_2+2CH_4$) is conserved. This holds also for total deuterium (D_{total}=HDO+HD+CH_3D). We use a new dataset of stratospheric HDO and H_2O inferred from measurements with the Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) between 20 and 40 km in the period September 2002 to August 2003 to investigate conservation of D_{total} and deviations from balance in the stratosphere.

The MIPAS data are combined with values for HD and CH_3D measured by isotope ratio mass spectrometry of airsamples obtained on balloon and stratospheric aircraft. Our measurements strongly support a first order linear relationship between HDO and water and the slope is in line with results obtained from HD and CH_3D data. This means that for the global stratosphere mass balance for deuterated water is fullfilled. As total deuterium conservation has to be assumed for most of the stratosphere, this demonstrates the reliability of the MIPAS HDO results.

Given this general agreement, we are able to analyze deviations in certain regions, in particular at high latitudes. Here, two processes can play a role: At lower altitudes, water can be removed from the gas phase reservoirs by formation of PSC and subsequent sedimentation processes, which disturbs D_{total} conservation. At higher altitudes, mesospheric air enriched in D due to photolysis of water descends in winter. The seasonality of this event impacts the linear correlation for HD and CH_3D which are likely not to hold there.

We conclude that the analysis of correlations between deuterated water and water in the stratosphere turns out to be a new and valuable tool for further improvement of our understanding of stratospheric transport processes and chemistry which more and more get into the focus as early indicators for climate change related topics.