

# LETTER TO THE EDITOR

Dear Prof. Dr. Haynes,

this letter concerns the revision of the ACPD manuscript (acp-2014-631) “Simulation of the isotopic composition of stratospheric water vapour – Part 1: Description and evaluation of the EMAC model“ by R. Eichinger, P. Jöckel, S. Brinkop, M. Werner and S. Lossow.

As requested by the referees and announced by our replies to the referee’s comments we have now conducted a number of changes in the manuscript. This includes small changes in the method, a new model simulation and renewed (and one additional) figures with slightly different results and a hereof revised discussion. The conclusions, however, remain the same.

For your overview, we summarised the most important points here:

1. In the new simulation, we changed the fixed tropospheric value of  $\delta D(\text{CH}_4)$  from  $-68\text{‰}$  to  $-86\text{‰}$ . This causes much better agreement between the model and the balloon measurements in  $\delta D(\text{CH}_4)$ .
2. Moreover, (after consulting referee #2 for details) we extended the calculation of the chemical tendency of HDO with a parameter that takes into account the storage of deuterium in HD during the reaction. Not surprisingly, this generates stratospheric HDO mixing ratios lower than before and therewith less agreement between model and satellite observations in the upper stratosphere. Moreover, this supports the upward propagation of the  $\delta D(\text{CH}_4)$  tape recorder, because the “overshadowing effect” through chemically produced high  $\delta D(\text{CH}_4)$  in the upper stratosphere weakens.
3. We included an additional figure with the  $\text{H}_2\text{O}$  mixing ratios as function of altitude (Fig. 5) for the four months, analogously to HDO in Fig. 4. This allows a better analysis of the insufficiencies in the representation of HDO. Our answer to this point in the reply to referee #2 was incomplete, since the new simulation (with point 2) was not available yet. First order effects (from  $\text{H}_2\text{O}$ ) do determine HDO largely, still, the lack of the fractionation effects during chemical reactions are clearly deteriorating the results of HDO.

4. Due to point 2, now the  $\delta D(\text{H}_2\text{O})$  tape recorder is not as well comparable to that of Randel et al. (2012) anymore. Still, the main conclusions, (i) that there is a tape recorder signal in  $\delta D(\text{H}_2\text{O})$ , (ii) which, in strength, ranges between the two satellite retrievals and (iii) that this  $\delta D(\text{H}_2\text{O})$  tape recorder becomes less obvious through the sparse temporal sampling of ACE-FTS can be maintained.

Please find below the differences between the discussion manuscript and the revised manuscript (as latexdiff) and the same for the supplement (apart from changing Fig. 5, here, only few minor changes were necessary) as well as the comments of the referees and our corresponding answers.

Best regards

Roland, Patrick, Sabine, Martin and Stefan

# Simulation of the isotopic composition of stratospheric water vapour – Part 1: Description and evaluation of the EMAC model

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**Abstract.** This modelling study aims on an improved understanding of the processes, that determine the water vapour budget in the stratosphere by means of the investigation of water isotope ratios. At first, an additional (and separate from the actual) hydrological cycle has been introduced into the chemistry-climate model EMAC, including the water isotopologues HDO and H<sub>2</sub><sup>18</sup>O and their physical fractionation processes. Additionally an explicit computation of the contribution of methane oxidation to H<sub>2</sub>O and HDO has been incorporated. The model expansions allow detailed analyses of water vapour and its isotope ratio with respect to deuterium throughout the stratosphere and in the transition region to the troposphere. In order to assure the correct representation of the water isotopologues in the model's hydrological cycle, the expanded system has been evaluated in several steps. The physical fractionation effects have been evaluated by comparison of the simulated isotopic composition of precipitation with measurements from a ground-based network (GNIP) and with the results from the isotopologue-enabled general circulation model ECHAM5-wiso. The model's representation of the chemical HDO precursor CH<sub>3</sub>D in the stratosphere has been confirmed by a comparison with chemical transport models (1-D, CHEM2D) and measurements from radiosonde flights. Finally, the simulated stratospheric HDO and the isotopic composition of water vapour have been evaluated, with respect to retrievals from three different satellite instruments (MIPAS, ACE-FTS, SMR). Discrepancies in stratospheric water vapour isotope ratios between two of the three satellite retrievals can now partly be explained.

## 1 Introduction

30 30% of the temperature change since 1980 can be attributed to the radiative forcing of increased stratospheric water vapour (Solomon et al., 2010) and 10% of the global total ozone decline from 1960 to 1999 can be explained by the water vapour increase (Stenke and Grewe, 2005). However, the mechanisms driving long-term changes in stratospheric water vapour are not well understood (Füglistaler et al., 2009). Stratospheric water vapour is determined by in situ methane oxidation and the intrusion of water vapour through the tropical tropopause layer (TTL). The seasonal cycle of lower stratospheric water vapour in the tropics is characterised by the tape recorder (Mote et al., 1996), which exhibits a hydrated lower stratosphere in boreal summer and fall and a dry lower stratosphere in boreal winter and spring. Thus, most of the water vapour enters the stratosphere during boreal summer when the tropopause temperatures are higher and Monsoon systems (e.g. Gettelman and Kinnison, 2004) as well as enhanced deep convection over the tropics (e.g. Khaykin et al., 2009) cause augmented transport of water vapour into the TTL. The contribution of the individual mechanisms ~~on~~ to the overall budget of stratospheric water vapour, however, is poorly quantified.

The application of water isotopologues in tracer studies has the potential to answer ~~the open questions~~, open questions concerning the stratospheric water vapour budget. The different vapour pressures and binding energies of the respective water isotopologues lead to fractionation effects during phase transitions and chemical reactions. The individ-

ual processes, which control the water vapour budget in the stratosphere, thus leave an isotopic fingerprint in the respective water vapour compound (Johnson et al., 2001). Direct injection of ice into the stratosphere through deep convection, dehydration of air during ascent by in situ formation of cirrus clouds and the in-mixing of older stratospheric air lead to an offset of the isotope ratios in the upper troposphere and lower stratosphere (UTLS) from simple Rayleigh distillation (see Steinwagner et al., 2010). The mechanisms, which are responsible for the intrusion of water vapour into the stratosphere, can hence be separated through the isotopic signature.

Recent satellite retrievals from three different instruments (SMR, MIPAS, ACE-FTS, see Urban et al., 2007; Steinwagner et al., 2007; Nassar et al., 2007) allow to obtain a global picture of the water isotopologue HDO and the water vapour isotope ratio  $\delta D(H_2O)$  ( $\delta D(H_2O) = \frac{[HDO]/[H_2O]}{R_{VSMOW}} - 1$ ; ( $R_{VSMOW} = 155.76 \cdot 10^{-6}$ ; Hagemann et al., 1970); (VSMOW: Vienna Standard Mean Ocean Water; IAEA, 2009)

$R_{VSMOW} = 155.76 \cdot 10^{-6}$  Hagemann et al. (1970); VSMOW: Vienna Standard Mean Ocean Water, IAEA (2009)) in the stratosphere and in the transition region to the troposphere. In some regions the different satellite retrievals, however, show considerable deviations when comparing profiles and annual cycles of HDO mixing ratios and isotope ratios, respectively (Lossow et al., 2011). Furthermore, Steinwagner et al. (2010) found a tape recorder signal in  $\delta D(H_2O)$  in the tropical stratosphere in the MIPAS observations, comparable to the known tape recorder in water vapour mixing ratios. In contrast, Randel et al. (2012) did not find an analogue upward propagation of the seasonal cycle of water vapour isotope ratios in the stratosphere when analysing ACE-FTS data. Speculations about this discrepancy mainly focus on the different sampling techniques and retrieval algorithms. Consequently, in order to improve the understanding of the basic structure of  $\delta D(H_2O)$  in the stratosphere, comprehensive modelling of the physical and chemical isotope processes in a well resolved global chemistry climate model (CCM) with explicit stratospheric dynamics is necessary.

For this purpose, the hitherto, a GCM (General Circulation model) study by Schmidt et al. (2005) including HDO and focussing on the UTLS region only featured a relatively coarse vertical resolution in the stratosphere and only a prescribed tendency for chemical influences on HDO. Here, the water isotopologue HDO is here implemented into the EMAC (ECHAM MESSy Atmospheric Chemistry; MESSy: Modular Earth Submodel System) model (Jöckel et al., 2005, 2010). EMAC provides the opportunity to accurately analyse troposphere-stratosphere exchange processes on a global scale. Depending on the vertical resolution when used with 90 layers in the vertical, its base model (ECHAM5; Roeckner et al., 2003) possesses a highly well resolved tropopause region (the vertical resolution near the tropopause

is about 500 m; see Jöckel et al., 2006) and explicit stratospheric dynamics. Moreover, EMAC includes optional chemical processes, which are needed for the computation of methane oxidation, which is crucial for the representation of  $H_2O$  and HDO in the stratosphere.

Confirmation of the correct representation of the fractionation processes during phase transitions in EMAC is achieved through the evaluation of the isotope ratios in precipitation. The consideration of the influence of methane oxidation on atmospheric HDO requires the computation of the methane isotopologue  $CH_3D$ . In a next step, this tracer is evaluated with respect to chemical transport models (CHEM1D, CHEM2D, Ridal et al., 2001; Ridal and Siskind, 2002) (1-D measurements from radiosonde stratospheric balloon flights (Röckmann et al., 2011). At last, the HDO mixing ratios and  $\delta D(H_2O)$  in the stratosphere are compared with the observations from satellites. This approach yields a more complete picture of the isotopic composition of stratospheric water vapour and provides insights into the discrepancies between the respective satellite retrievals. Comprehensive analyses of stratospheric  $\delta D(H_2O)$  in EMAC will be presented in the companion part 2 of this article (Eichinger et al., 2014). Here, the These model results will be investigated with respect to the sensitivity and the origin of the  $\delta D(H_2O)$  tape recorder and the role of convective ice lofting on the pattern is analysed.

## 2 Model description and simulation setup

The MESSy-conform MESSy submodel H2OISO ( $H_2O$  ISotopologues) has been incorporated into the EMAC model system. This submodel comprises tracers (see Jöckel et al., 2008) for the three stable water isotopologues  $H_2^{16}O$  ('normal' water, hereafter denoted as  $H_2O$ ),  $H_2^{18}O$  and HDO for all three phases (vapour, liquid and ice), respectively. Moreover, it contains an additional hydrological cycle, identical to the model's actual hydrological cycle, which includes all processes that modify the tracers and the corresponding fractionation effects for the isotopologues during phase transitions. The modular approach of MESSy allows the optional usage of the H2OISO submodel for all users in future EMAC versions. Besides this structural difference, the implementation of the water isotopologues follows previous studies with ECHAM3 (Hoffmann et al., 1998), ECHAM4 (Werner et al., 2001) and ECHAM5 (Werner et al., 2011). Supplementary to these previous studies, the chemical fractionation effects during the formation of water vapour through methane oxidation were are considered. Since observations of water isotopologues in the stratosphere are mostly available for  $H_2O$  and HDO, only, the more elaborate accounting for the chemical fractionation of  $H_2^{18}O$  was not conducted in this study. Hence, here  $H_2^{18}O$  basically only serves for the evaluation of the model in the troposphere. The physical isotope effects of

HDO and H<sub>2</sub><sup>18</sup>O only differ by the corresponding fractionation factors.

## 2.1 Water isotopologues in the hydrological cycle of EMAC

The hydrological cycle in the H2OISO submodel reproduces the actual hydrological cycle of the EMAC model. The tracers for H<sub>2</sub>O in the gaseous (H<sub>2</sub>O<sub>vap</sub>), the liquid (H<sub>2</sub>O<sub>liq</sub>) and the ice (H<sub>2</sub>O<sub>ice</sub>) phase were tested to be equal to the standard ECHAM variables for the water vapour (Q), the liquid water (XL) and the ice water (XI) content, respectively. Small numerical errors (the maxima are at-in the order of 10<sup>-20</sup> kg/kg/s for water vapour and 10<sup>-22</sup> kg/kg/s for liquid water and ice), which arise due to the coding design, are corrected after each time step, in order to prevent the two hydrological cycles from diverging. Moreover, we assured that these numerical errors are small enough to not deteriorate the calculation of the water isotopologues.

For the water isotopologues, fractionation effects occur during phase changes. Equilibrium and kinetic fractionation during the evaporation of water from oceans is described by the bulk formula by-of Hoffmann et al. (1998). The surface flux for the water isotopologues depends on the isotope ratio of the ocean, the wind speed above the surface, the sea surface temperature, the specific humidity and the isotopic composition of the vapour above the surface (Hoffmann et al., 1998). As in the study by Werner et al. (2011), the isotope ratio of the ocean is prescribed with a global gridded data set based on the <sup>18</sup>O isotopic composition in sea water by LeGrande and Schmidt (2006). Since there is no equivalent data set for the deuterium isotopic composition, the HDO content is prescribed with-as eight times the H<sub>2</sub><sup>18</sup>O mixing isotope ratios. This is in accordance with global observations (Craig and Gordon, 1965). Due to the limitations of the applied land surface scheme in the EMAC model, we neglect any isotope fractionation from land surfaces. The land surface scheme in EMAC is identical to the scheme in the ECHAM5 model. A more detailed description of this simplification is given in Werner et al. (2011). As for water vapour, liquid water and ice in the actual hydrological cycle, the advection of the new water isotopologue tracers follows the flux form semi-Lagrangian (FFSL) scheme by Lin and Rood (1996).

The cloud and convection ~~parameterisation routines~~ parameterisations (CLOUD and CONVECT) in EMAC include a number of phase transitions and therefore several different fractionation effects. Again, the implementation follows the study of Werner et al. (2011). During the formation of clouds, condensation of water vapour to liquid water and deposition of vapour to cloud ice take place. For condensation within clouds, a closed system is assumed. The condensate is taken on to be in contact, and hence in isotopic equilibrium, with the surrounding vapour during the entire process. This also applies for the evaporation of cloud water, where,

in contrast to evaporation from the ocean, a closed system is assumed. An open system is used for the deposition of water vapour to ice. Due to the low diffusivities of the isotopologues in the ice phase, no exchange happens between ice and vapour. The effective fractionation factor  $\alpha_{eff}$  is used here, including a function for the supersaturation  $S$ . Werner et al. (2011) adjusted this function to  $S = 1.01 - 0.0045 \cdot T_{cond}$  (with  $T_{cond} - T_{cond}$  as the condensation temperature during ice crystal formation, given in °C), in order to attain realistic isotope ratios in Antarctic snow. Since the focus of the present study lies on the tropopause region, where also low temperatures have a major effect on kinetic fractionation through deposition, as a first estimate, the values from Werner et al. (2011) have been taken. During the melting of ice and the freezing of water, no fractionation is assumed. Other in-cloud processes like sedimentation of ice, autoconversion, accretion and aggregation include no fractionation effects either. The isotopic (non-)equilibrium factor  $\alpha_{eff}$ , which describes a fractionation process between a falling raindrop and the surrounding water vapour, may vary with time. Its value depends on the humidity, the temperature, the diffusivity of the water molecules and the droplet size. Since these processes are not resolved in GCMs, the fractionation during reevaporation of raindrops falling through undersaturated air can only be approximated. Following Hoffmann et al. (1998), an isotopic equilibration of 45% is assumed for large drops from convective rain and 95% for small drops falling from stratiform clouds. Due to their low exchange rates, snow and ice do not reequilibrate at all, which leads to more depleted isotope ratios in solid precipitation.

## 2.2 Stratospheric isotope chemistry for water and methane

The EMAC model contains the submodel CH4, which provides a simplified methane oxidation mechanism to take into account the chemical production of water vapour. It includes a tracer for methane (the CH<sub>4</sub> tracer), which experiences a source from the surface (here as lower boundary conditions from the submodel TNUDGE, see next section; alternatively as methane fluxes, provided by the submodel OFFEMIS (see Jöckel et al., 2010)) and a sink in form of methane oxidation. Solutions are calculated for the four oxidation reactions, which are determined by the mixing ratios of the three oxidation partners (Cl, OH, O(<sup>1</sup>D)) and the photolysis rate. The photolysis rate  $j_{CH_4}$  ( $= r_{hv}$ ) is here calculated in the MESSy submodel JVAL (for details, see Landgraf and Crutzen, 1998) (for details, see Landgraf et al., 2012) passed on to the submodel CH4 (alternatively it can be prescribed). The rates for the oxidation of methane with the reaction partners Cl, OH and O(<sup>1</sup>D)) are calculated within the submodel CH4. First, the first order reaction coefficients  $k_{OH}$  for OH,  $k_{Cl}$  for Cl and  $k_{O1D}$  for O(<sup>1</sup>D)) are determined. While  $k_{O1D} = 1.75 \cdot 10^{-10} \text{ cm}^3/\text{s}$  is constant,  $k_{OH}$  and  $k_{Cl}$

are temperature ( $T$  in K) dependent and are computed by

$$k_{OH} = 1.85 \cdot 10^{-20} \cdot \exp\left(2.82 \cdot \log(T) - \frac{987}{T}\right) \frac{\text{cm}^3}{\text{s}} \quad (1)$$

and

$$k_{Cl} = 6.6 \cdot 10^{-12} \cdot \exp\left(-\frac{1240}{T}\right) \frac{\text{cm}^3}{\text{s}}. \quad (2)$$

Subsequently the [rates-pseudo first order rate coefficients](#) for the reactions with methane are

$$r_{O1D} = k_{O1D} \cdot c_{air} \cdot O(^1D) \quad (3)$$

$$r_{Cl} = k_{Cl} \cdot c_{air} \cdot Cl \quad (4)$$

$$r_{OH} = k_{OH} \cdot c_{air} \cdot OH, \quad (5)$$

with  $O(^1D)$ ,  $Cl$  and  $OH$  representing the prescribed mixing ratios (in  $\text{mol/mol}$ ) of the respective species and  $c_{air}$  the concentration of dry air molecules (in  $\text{cm}^{-3}$ ), which is calculated by

$$c_{air} = \frac{N_A \cdot 10^{-6} \cdot p}{R_{gas} \cdot T \cdot \left[1 + \left(\frac{M_{air}}{M_{H_2O}} - 1\right) \cdot Q\right]}. \quad (6)$$

Here  $N_A$  denotes the Avogadro Constant ( $6.022045 \cdot 10^{23} \text{ mol}^{-1}$ ),  $p$  the pressure (in Pa),  $R_{gas}$  the universal gas constant ( $8.314409 \text{ J/K/mol}$ ),  $T$  the temperature (in K),  $M_{air}$  the molar mass of dry air ( $28.97 \text{ g/mol}$ ),  $M_{H_2O}$  the molar mass of water ( $18.02 \text{ g/mol}$ ) and  $Q$  the specific humidity (in  $\text{kg/kg}$ ).

The tendency for the methane tracer (in  $\text{mol/mol/s}$ ) is then given by

$$\frac{\partial(CH_4)}{\partial t} = -1 \cdot CH_4 \cdot (r_{O1D} + r_{Cl} + r_{OH} + r_{h\nu}), \quad (7)$$

where  $CH_4$  is the methane mixing ratio (in  $\text{mol/mol}$ ) of the previous time step and the  $-1$  accounts for the fact that this is a pure sink reaction for the methane tracer. To calculate the tendency for the specific humidity due to methane oxidation,

$$\left. \frac{\partial Q}{\partial t} \right|_C = \frac{-2 \cdot \frac{\partial(CH_4)}{\partial t}}{\frac{M_{air}}{M_{H_2O}} \left(\frac{1}{1-Q}\right)^2} \quad (8)$$

is applied. The subscript  $C$  denotes, that this is the chemical tendency of  $Q$ . This division is to convert the tendency from  $\text{mol/mol/s}$  to  $\text{kg/kg/s}$ . The negative sign here accounts for the fact that methane oxidation is a source for water vapour and the factor 2 for the reaction of the four hydrogen atoms of one methane molecule into two water molecules.

In order to take into account the chemical production of HDO, analogously a parameterisation for the oxidation of

$\text{CH}_3\text{D}$  has been devised. A tracer for  $\text{CH}_3\text{D}$ , the most abundant deuterium isotopologue of methane, was included for this purpose. The coefficients for the mass-dependent kinetic isotope effects (KIE) for the reactions of  $\text{CH}_3\text{D}$  with  $\text{OH}$ ,  $\text{O}(^1\text{D})$  and  $\text{Cl}$  have been determined in laboratory measurements by Saueressig et al. (1996, 2001). They are partly temperature dependent and can be described with the function  $\text{KIE}(T) = A \cdot \exp(B/T)$ . The values for  $A$  and  $B$  and their temperature ranges are given in Tab. 1 (see also Röckmann et al., 2011). The absorption cross-section of  $\text{CH}_3\text{D}$  is shifted

**Table 1.** Temperature dependent kinetic isotope fractionation coefficients for the reaction with  $\text{CH}_3\text{D}$ . The kinetic isotope effect is determined by  $\text{KIE}(T) = A \cdot \exp(B/T)$  for the given temperature range (see Röckmann et al., 2011).

Reactant	$T$ range	$A$	$B$
OH		1.097	$49 \pm 22$
$\text{O}(^1\text{D})$	224-295	1.066	0
Cl	223-295	1.278	$51.31 \pm 19.1$

0.9 nm blueward relative to  $\text{CH}_4$  (Nair et al., 2005). For the photodissociation of  $\text{CH}_3\text{D}$ , this results in the fractionation factor  $\text{KIE}_{h\nu} = 0.995$  in the atmosphere of Mars (see also Nixon et al., 2012). This approach is here applied onto the Earth's atmosphere, since the photodissociation characteristics of methane do not differ from one planet of the solar system to another.

As for physical kinetic fraction processes, the Rayleigh equation

$$R = R_0 \left(\frac{N}{N_0}\right)^{\text{KIE}^{-1}-1} \quad (9)$$

is applied for the fractionation processes in the chemical reactions. Inserting the isotope ratios ( $R_0$  and  $R$ ) and the total mixing ratios ( $N_0$  and  $N$ ) before and after the reaction, leads to

$$\frac{CH_3D - \frac{\partial(CH_3D)}{\partial t}}{CH_4 - \frac{\partial(CH_4)}{\partial t}} = \frac{CH_3D}{CH_4} \left(\frac{CH_4 - \frac{\partial(CH_4)}{\partial t}}{CH_4}\right)^{\text{KIE}^{-1}-1} \quad (10)$$

Using Eq. 7 for  $\partial(CH_4)/\partial t$  and considering that the KIE is different for each of the reactions, the tendency of the  $\text{CH}_3\text{D}$  tracer is given by

$$\begin{aligned} \frac{\partial(CH_3D)}{\partial t} = & CH_3D \cdot \\ & \left[ \left(1 - (1 + r_{OH})^{\text{KIE}_{OH}^{-1}}\right) + \left(1 - (1 + r_{Cl})^{\text{KIE}_{Cl}^{-1}}\right) + \right. \\ & \left. \left(1 - (1 + r_{O1D})^{\text{KIE}_{O1D}^{-1}}\right) + \left(1 - (1 + r_{h\nu})^{\text{KIE}_{h\nu}^{-1}}\right) \right]. \end{aligned} \quad (11)$$

In order to calculate the tendency of the HDO tracer from the tendency of the CH<sub>3</sub>D tracer (i.e. the chemical tendency of HDO), analogously to Eq. 8,

$$\left. \frac{\partial(HDO)}{\partial t} \right|_C = \frac{-1 \cdot \frac{\partial(CH_3D)}{\partial t}}{\frac{M_{air}}{M_{HDO}} \left( \frac{1}{1-HDO} \right)^2}, \quad (12)$$

is applied. Here, we use the specific humidity and the molar mass of HDO ( $M_{HDO} = 19.02$  g/mol) instead of  $Q$  and  $M_{H_2O}$  and the factor 1 instead of 2, because the oxidation of one CH<sub>3</sub>D molecule can only produce one HDO molecule.

This simple parameterisation, however, neglects the intermediate reactions between CH<sub>3</sub>D and HDO with molecular hydrogen and its isotopologue HD. While H<sub>2</sub> is fairly constant throughout the stratosphere and therefore can be neglected for the CH<sub>4</sub> conversion to H<sub>2</sub>O,  $\delta D(H_2)$  increases with altitude due to chemical isotope fractionation effects (see Röckmann et al., 2003; Rhee et al., 2006). Hence, some deuterium is stored in HD during this process and therefore one CH<sub>3</sub>D molecule translates into a little less than exactly one HDO molecule (see also, Rahn et al., 2003). In order to account for this, we apply the stratospheric relation

$$HD = -6.32 \cdot 10^{-5} \cdot CH_4 + 0.297 \quad (13)$$

derived from measurements by McCarthy et al. (2004). The time derivative of HD in dependence of the time derivative of CH<sub>4</sub> can now be used to account for the stored deuterium in HD and thus for the reduction of chemically formed HDO. Therefore, Eq. 12 was extended to

$$\left. \frac{\partial(HDO)}{\partial t} \right|_C = \frac{-\frac{\partial(CH_3D)}{\partial t} + 6.32 \cdot 10^{-5} \cdot \frac{\partial(CH_4)}{\partial t}}{\frac{M_{air}}{M_{HDO}} \left( \frac{1}{1-HDO} \right)^2}. \quad (14)$$

This approach still neglects a number of effects that may be important for the chemical production of HDO: Firstly, the other, rather rare methane isotopologues CH<sub>2</sub>D<sub>2</sub>, CHD<sub>3</sub> and CD<sub>4</sub> as well as the reaction partner OD (an isotopologue of the hydroxyl radical) are not considered. Secondly, the entire cycle of molecular hydrogen and its isotopologue HD is fractionation effects during the formation of HDO by HD are not taken into consideration. The intermediate reactions between CH<sub>3</sub>D and HDO involving HD also include fractionation effects (see e.g. Röckmann et al., 2003; Rhee et al., 2006). Most of these, however, are poorly quantified (Zahn et al., 2006) and therefore neglected for this initial study. These simplifications have to be kept in mind when evaluating the model results in the stratosphere.

Emissions of CH<sub>3</sub>D could be defined with the aid of an extension (for deuterium) of the MESSy isotope scheme of Gromov et al. (2010). However, this task requires the integration of the full chemistry scheme and therefore goes beyond the scope of our study, which mainly focuses on stratospheric and upper tropospheric processes. This leads to another simplification: In accordance with Ridal and Siskind (2002) Rhee et al. (2006) the isotope ratio of methane was fixed to  $-68\text{‰}$ – $-86\text{‰}$  in the troposphere (i.e. here, below 500 hPa). This is within the range of the climatological in between the stratospheric entry values of  $\delta D(CH_4)$  ( $\delta D(CH_4)$  is also based on VS-MOW) value, which methane possesses when entering the stratosphere in the tropics, derived from measurements by Irion et al. (1996), found by Rahn et al. (2003) ( $-90\text{‰}$ ), Röckmann et al. (2003) ( $-80\text{‰}$ ) and Röckmann et al. (2011) ( $-81\text{‰}$ ) and also within the range of recent aircraft measurements presented by Umezawa et al. (2012).

### 2.3 Simulation setup

For this study, an EMAC (v2.42) model simulation, in T42L90MA resolution was performed. This corresponds to an approximate horizontal grid box size of  $2.8^\circ \times 2.8^\circ$ , 90 vertical layers layers in the vertical and explicitly resolved stratospheric dynamics. The uppermost model layer is centered around 0.01 hPa. The MESSy submodels, which were applied in this simulation (in addition to the described H2OISO and CH4 submodels and the ECHAM5 base model from EMAC version 2.42) are listed and described in the appendix. The time step of the simulation was twelve minutes and the output was set to produce instantaneous values with an interval of eleven hours. The EMAC model provides the possibility to use several different convection schemes. In all the simulations conducted for this study, the “Tiedtke-Nordeng” convection scheme (Tiedtke, 1989) (Tiedtke, 1989; Nordeng, 1994) was applied. Before starting the actual simulation, a 20 year free running simulation was carried out to obtain steady-state initial values for water, methane and their isotopologues. From these initial conditions a simulation with specified dynamics (i.e. in “nudged” mode) was started, which means a Newtonian relaxation of the divergence, the vorticity, the temperature and the logarithm of the surface pressure towards reference data. Here, the relaxation is performed up to 1 hPa towards the ERA-INTERIM reanalysis data (ECMWF; Dee et al., 2011). This guarantees, that not only the climatic state, but also the meteorological situation of the model simulation corresponds to the actual states and allows a direct comparison of the model results with satellite or in situ measurements. The simulation starts at the beginning of the year 2011 and terminates at the end of the year 2010. From the steady-state conditions, which are used for the initialisation, the model again needs several years to adjust to the

conditions of the “nudged” mode. The first eight years are hence not considered for the analysis. Only the 21 years from 1990 ~~until 2011~~ to 2010 are evaluated. Transient greenhouse gas concentrations are prescribed throughout the atmosphere. Methane is prescribed at the lower boundary through the sub-model TNUDGE, based on observations. The mixing ratios of OH, Cl, O(<sup>1</sup>D) are prescribed (monthly averages) from a previous “nudged”, transient EMAC simulation with full chemistry. The same applies for ozone, which is needed to calculate the photolysis rate in the submodel JVAL. As mentioned above, the methane oxidation is calculated in the CH<sub>4</sub> submodel.

### 3 Model evaluation

Before evaluating the model simulation with respect to the isotopic composition of water vapour in the stratosphere, we show that the basis for this is established in the EMAC model. This includes the correct representation of the physical water isotope effects in the troposphere and the chemical HDO precursor CH<sub>3</sub>D in the stratosphere, as well as its sink reactions. Subsequently stratospheric HDO mixing ratios and  $\delta D(H_2O)$  are compared to satellite observations.

#### 3.1 Water isotope ratios in precipitation

The isotopic composition in precipitation allows to ~~conclude various fractionation processes~~ evaluate various isotope fractionation effects (Dansgaard, 1964). Hence, the representation of the isotope physics in the model can be evaluated by examining the isotope ratios in precipitation. This has been conducted in many studies with isotopologue-enabled GCMs (e.g. Risi et al., 2010; Werner et al., 2011).

The GNIP (Global Network of Isotopes in Precipitation) measurement survey provides a comprehensive data base for this purpose. The International Atomic Energy Agency (IAEA) and the World Meteorological Organisation (WMO) have started GNIP in 1961. Since its start, more than 800 meteorological stations in 101 countries have collected samples of the water isotopologues HDO and H<sub>2</sub><sup>18</sup>O in precipitation (IAEA, 2009). Some of these stations provided monthly precipitation measurements for several decades, most of them, however, operated for a much shorter period, only. This data set serves as a basis for the evaluation of the simulated isotope ratios in the troposphere. Good qualitative agreement was achieved when comparing the general global patterns in annual mean precipitation, as well as in the seasonal cycles between GNIP and EMAC. Details can be found in the supplement.

The isotopologue-enabled GCM ECHAM5-wiso (water isotopologues) has also been tested successfully against GNIP data, as well as against other water isotopologue measurements (see Werner et al., 2011). Several model resolutions have been applied for this study. The results of the

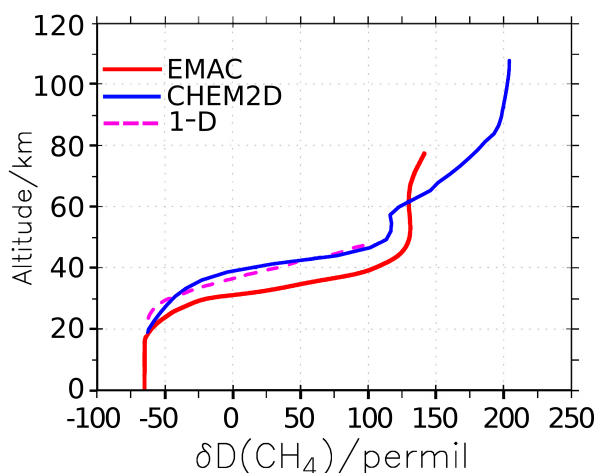
lowest of these horizontal resolutions (T31  $\sim$  3.75° x 3.75°) was largely reproduced with the EMAC model (see supplement). Since the model physics and dynamics of the two models, including the hydrological cycle and the implementation of the water isotopologues (as described in Sect. 2), are almost identical, this is not surprising. However, it is a prerequisite for assuring the correct representation of the tropospheric isotope composition of water. A detailed comparison between EMAC and ECHAM5-wiso is given in the supplement. The good quantitative agreement of this comparison supports the conclusion, that the EMAC model with the H2OISO submodel represents the state of the art of GCMs with an explicit representation of the water isotopologues HDO and H<sub>2</sub><sup>18</sup>O in the troposphere.

#### 3.2 CH<sub>3</sub>D in the stratosphere

The simulated CH<sub>3</sub>D is compared to results from the ~~CHEM1D-1-D~~ model by Ridal et al. (2001) and the CHEM2D model by Ridal and Siskind (2002). These models comprise an oxidation scheme, where CH<sub>3</sub>D produces HDO through a number of chemical reactions. This oxidation scheme was developed for the ~~CHEM1D-1-D~~ model. For the CHEM2D model, it was extended for higher altitudes and included into the Naval Research Laboratory two-dimensional chemical/dynamical model. In Ridal (2002) and Ridal and Siskind (2002) the two chemical transport models have shown good general agreement with measurements from the ATMOS (Atmospheric Trace MOlecule Spectroscopy) instrument (Irion et al., 1996). ATMOS provides global data for CH<sub>3</sub>D and HDO, however, with large uncertainties. The equatorial values of  $\delta D(CH_4)$  of EMAC, CHEM2D and ~~CHEM1D-the 1-D model~~ are presented in Fig. 1.

~~Since in all three models, the~~ The tropospheric values of  $\delta D(CH_4)$  ~~are fixed (–68‰ in EMAC and in the CHEM2D, and the 1-D model are fixed to –68‰ and –65‰ in CHEM1D), they,~~ respectively. For a better comparison with these models, an additional EMAC simulation was carried out, with the only difference, that this value was set from –86‰ to –68‰ (see Sect. 2.2). Therefore, the model results do not differ below the tropopause. Moreover, the overall dependence of  $\delta D(CH_4)$  on altitude qualitatively agrees in all the three model simulations. Between 20 and 50 km altitude the methane isotope ratio increases from –68‰ to around +120‰ in CHEM2D and ~~CHEM1D-the 1-D model~~, and to around +130‰ in EMAC. Especially the increase in the lower stratosphere is much stronger in EMAC, which leads to rather large discrepancies in the altitude range between 30 and 40 km. Between 50 and 60 km, both, CHEM2D and EMAC, show almost no change in  $\delta D(CH_4)$  with altitude, ~~CHEM1D-the 1-D model~~ does not extend above 50 km. This is the transition region between the altitudes of the chemical and the photolytic methane oxidation. The photodissociation, which becomes important above 60 km and increases continuously above,





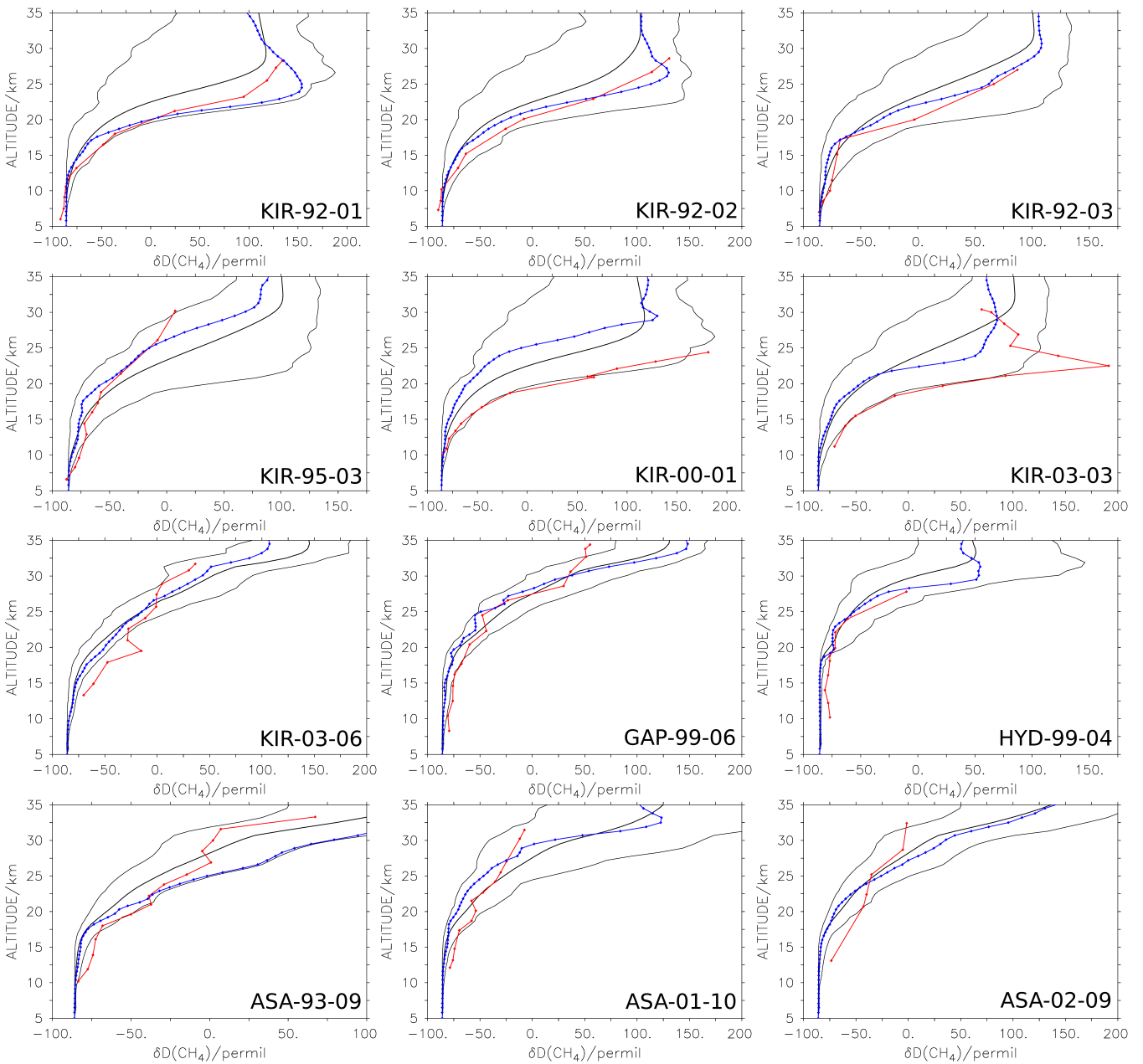
**Fig. 1.** Comparison of equatorial averages of  $\delta\text{D}(\text{CH}_4)$  with altitude between EMAC (red), CHEM2D (blue) by Ridal and Siskind (2002) and CHEM1D the 1-D model (dashed purple) by Ridal et al. (2001).

is much stronger in CHEM2D at first. This is somewhat surprising, because there is no fractionation included for the photolysis of  $\text{CH}_3\text{D}$  in the CHEM2D model. Even though the fractionation for photolysis in EMAC is very small, the photolysis of  $\text{CH}_3\text{D}$  is expected to be of similar strength as in CHEM2D. The discrepancy is hence likely caused by the differences in the calculation of the photolysis rates in EMAC and CHEM2D. Since the mid of the uppermost layer of the EMAC model in the applied resolution is at 80 km, a comparison further above is not possible.

Measurements of  $\text{CH}_3\text{D}$  in the stratosphere are sparse. Röckmann et al. (2011), however, collected 13 samples altitude profiles from stratospheric balloon borne air measurements, which were provided by the Max-Planck Institute (MPI) for Solar System Research and by the Institute for Atmospheric and Environmental Sciences of the University of Frankfurt. The mixing ratios and the isotopic composition of  $\text{CH}_4$  were measured, using a high-precision continuous flow isotope ratio mass spectrometry system (Brass and Röckmann, 2010). Twelve of these balloon flights can be used for direct intercomparison with the data from the EMAC simulation. One flight (Flight ID: HYD-87-03) was conducted in 1987. Since the model results are considered to be in steady-state only from 1990 on, this sample profile is not taken into account for the evaluation. In Fig. 2, twelve panels are presented, with showing the balloon borne data and the EMAC results of  $\delta\text{D}(\text{CH}_4)$  with as function of altitude, between 5 and 35 km. The flight IDs, included in the panels provide information about the location, the month and the year of the balloon flights (see caption). To provide an estimate about the average and the annual variability of

$\delta\text{D}(\text{CH}_4)$  in the model simulation, additionally, the averages, maxima and minima of the 21 simulation years of the respective months at the location of the launch are included in the panels.

In general, a good qualitative agreement can be observed is achieved between the measured and the simulated data. Both simulation and measurements, show an increase of the methane isotope ratios from tropospheric values to values between  $-100\text{‰}$  and  $-200\text{‰}$   $100\text{‰}$  and  $200\text{‰}$  at 25 to 35 km in the Arctic region and to values between  $0$  and  $-100\text{‰}$   $0\text{‰}$  and  $100\text{‰}$  in the mid-latitude and tropical regions. The balloon borne samples profiles are mostly lying within the extremes of the simulation and close to the simulated values from the same day and location. The measured  $\delta\text{D}(\text{CH}_4)$  values in the troposphere and lower stratosphere, however, are systematically lower than the simulated values. In contrast to the  $-68\text{‰}$  for stratospheric entry values of  $\delta\text{D}(\text{CH}_4)$ , suggested by Ridal and Siskind (2002), Röckmann et al. (2011) assess the typical tropospheric  $\delta\text{D}(\text{CH}_4)$  value to be  $-81\text{‰}$ . This explains the constant offset at lower altitudes between the two data sets and, it adjusted, is also expected to reduce the differences at higher altitudes. However, since firstly, as Ridal and Siskind (2002) we focus on the stratospheric entry values of  $\delta\text{D}(\text{CH}_4)$  in the inner tropics and secondly, this uncertainty at these altitudes has only little relevance for the HDO mixing ratios, we did not perform this adjustment. The simulated are in good agreement with the chosen value of  $-86\text{‰}$  from the study by Rhee et al. (2006). The step increase of  $\delta\text{D}(\text{CH}_4)$  above 25 to 25 km in the simulation can only be seen in the measurements in of the Arctic region (KIR). The In the mid-latitude (GAP and ASA) samples show profiles, the  $\delta\text{D}(\text{CH}_4)$  increase with height is smaller, which leads to partly large deviations at these altitudes. The differences in the profiles of the KIR-00-01 and the KIR-03-03 samples profiles between simulation and balloon flights are exceptional. Apart from the lower stratospheric regions (and the values above in sample two uppermost data points in the KIR-03-03) profile, the measured  $\delta\text{D}(\text{CH}_4)$  values are constantly higher than the simulated values. These two samples profiles are associated with special meteorological and thus chemical situations. The KIR-03-03 sample data comprises a mesospheric enclosure and during the sampling of the KIR-00-01 data, a strong Arctic vortex was present (Röckmann et al., 2011). These phenomena can also be observed in the simulation, due to the “nudging” these special meteorological situations and the associated chemical situations are broadly represented. However, the horizontal resolution of the model simulation is too coarse, to resolve sharp horizontal gradients around the site of the balloon launch. Also, the balloons Moreover, the balloon’s drift off the launching site while ascending can cause deviations of such magnitudes. Also, this may be related to omitting the chemical cycle of  $\text{H}_2$  and  $\text{HD}$ , since isotopically very heavy  $\text{H}_2$  might have been reconverted to  $\text{CH}_4$  in these profiles.

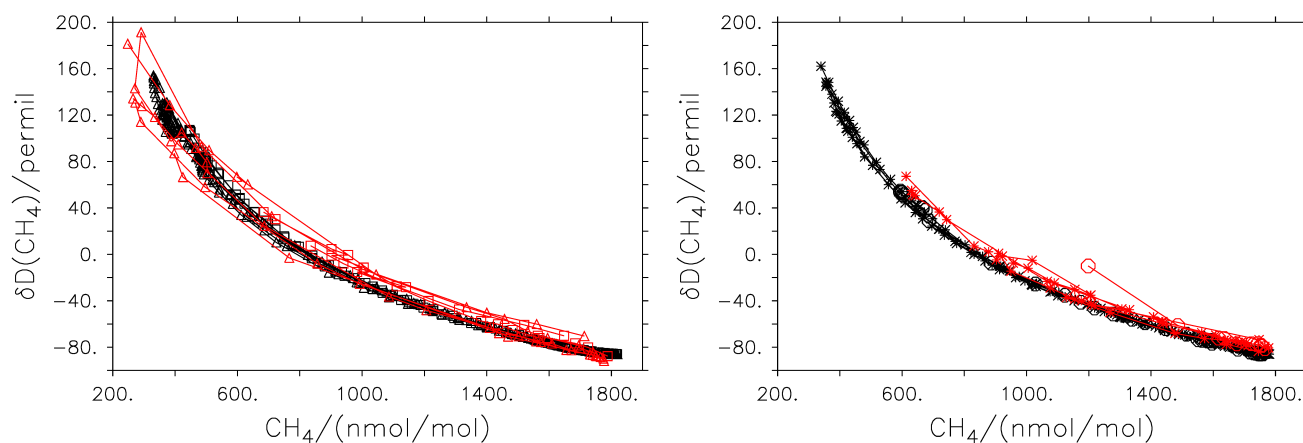


**Fig. 2.** Comparison of  $\delta D(CH_4)$  vertical profiles between EMAC and balloon borne data by Röckmann et al. (2011). The red lines show the observations and the blue lines show the EMAC data of the same day at the location of the balloon launch. The black lines represent the simulated averages, minima and maxima of the 21 monthly averages of the respective month at the location of the balloon launch. The flight IDs, included in the panels denote the location, the year and the month of the balloon flight. KIR: Kiruna, Sweden (67.9°N, 21.10°E); GAP: Gap, France (44.44°N, 6.14°E); HYD: Hyderabad, India (17.5°N, 78.60°E); ASA: Aire sur l’ Adour, France (43.70°N, 0.30°W).

Another method for evaluating the methane isotope chemistry is assessing the relation of  $\delta D(CH_4)$  to the  $CH_4$  mixing ratio. The  $\delta D(CH_4)$  values of the same data as in Fig. 2, from 5 to 35 km altitude, are plotted versus the  $CH_4$  mixing ratios in Fig. 3. The figure is divided into the launches in the polar

region (KIR) in the left panel and the launches in mid- (ASA, GAP) and tropical (HYD) latitudes in the right panel.

Again a constant offset. Again, overall consistency between the simulation and the measurements can be seen is visible. Apart from a single exception (the measurement from the HYD-99-04 sample profile, right panel) the simu-



**Fig. 3.** Comparison of the relations of  $\delta D(\text{CH}_4)$  to  $\text{CH}_4$  between EMAC (black) and balloon borne data (red; data as in Fig. 2). The left panel shows the Arctic samples data (KIR,  $\triangle$ : vortex,  $\square$ : non-vortex) and the right panel shows the mid-latitude (\*) and tropical samples data ( $\circ$ ). The altitude range is 5 to 35 km.

lated  $\delta D(\text{CH}_4)$  values are generally higher for the same as function of the methane mixing ratios – agree very well with the measurements. Decreasing the fixed tropospheric value can reduce this offset. The slope of increasing isotope ratios with decreasing methane mixing ratios is in very good agreement almost identical. Since these compact tracer-tracer correlations are generally found for trace gases whose life times are longer than the transport times (Plumb and Ko, 2004), it implies that the chemical removal of the  $\text{CH}_3\text{D}$  tracer in relation to the removal of the  $\text{CH}_4$  tracer is well represented, despite the simplified chemistry parameterisation.

### 3.3 HDO in the stratosphere

During the first decade of the 21st century, three satellite missions collected data applicable for the retrieval of the water isotopologue HDO in the stratosphere. The MIPAS (Michelson Interferometer for Passive Atmospheric Sounding) instrument on Envisat (Environmental Satellite) allowed the retrieval of HDO by measuring the thermal emission in the mid-infrared. This high-resolution Fourier transform spectrometer measured at the atmospheric limb and provided data for HDO retrievals in full spectral resolution from July 2002 to March 2004, roughly in the altitude range between 10 and 50 km. It orbits the Earth sun-synchronously 14 times a day. The vertical resolution for the retrieval of HDO is around 5 km between the tropopause and 30 km altitude, above it degrades ( $\sim 8$  km at 40 km) (Steinwagner et al., 2007; Lossow et al., 2011). The Odin satellite also orbits the Earth sun-synchronously and carries the SMR (Sub-Millimetre Radiometer) instrument, among other purposes to passively measure HDO on the global scale roughly on one day per week. It operates in the microwave range. Data has

been retrieved from the start of the mission in 2001 until today, at altitudes between roughly 20 and 70 km with a vertical resolution of around 3 km (Urban et al., 2007). The ACE-FTS (Atmospheric Chemistry Experiment Fourier Transform Spectrometer) instrument circularly orbits the Earth on the SCISAT satellite and obtains Fourier transform absorption spectra from solar occultation measurements. It has a vertical resolution between 2 and 6 km and a comparably limited spatial sampling. The ACE orbit is optimised for measurements in mid- and high latitudes, the tropics are only covered during the four months of February, April, August and October (Nassar et al., 2007; Randel et al., 2012).

Lossow et al. (2011) collected data of the three instruments for intercomparison and concluded a good consistency between MIPAS and ACE-FTS at altitudes above 20 km. Below this altitude, issues like different cloud filtering and measurement techniques as well as different vertical resolutions cause large deviations. Generally, in the stratosphere the MIPAS and the ACE-FTS data agree favourably, the SMR data shows considerably dryer conditions, especially below 30 km. This is mainly due to uncertainties in the different spectroscopies of the instruments (Lossow et al., 2011).

These data could now also be used to evaluate the HDO simulated by EMAC. In Fig. 4, the tropical ( $15^\circ\text{S}$  to  $15^\circ\text{N}$ ) values of the HDO mixing ratios of the three satellite instruments and the EMAC model are presented. Additionally to the data of MIPAS, SMR and version 2.2 of ACE-FTS shown by Lossow et al. (2011), here also version 3.0 of ACE-FTS is included, which reaches higher up in the stratosphere, compared to version 2.2. Since ACE-FTS only provides data for four months per year in this region, the panels show averages for February, April, August and October. Since the years of the ACE-FTS and the MIPAS satellite retrievals do not

overlap, a direct comparison is not possible. However, tests have shown, that the averages of the periods of the individual retrievals do not show substantial differences between each other and between the average of the entire simulation. In order to get a good estimate for the comparison of the model with all retrievals and for the annual variability, the averages, the minima and the maxima of the respective months have been taken from the entire 21 years of the EMAC simulation. Since, at first order, the HDO mixing ratios follow those of H<sub>2</sub>O, the profiles of H<sub>2</sub>O of EMAC and of the mentioned satellite retrievals are shown in Fig. 5 in the same manner, in order to allow a more detailed discussion of the results.

The EMAC data is generally dryer in HDO and in H<sub>2</sub>O compared to the MIPAS and the ACE-FTS profiles in each of the presented months at all altitudes. For water vapour in the UTLS, this offset has already been shown by Jöckel et al. (2006) and is consistent with the slightly too cold hygropause in the nudging data (see e.g. Liu et al., 2010). Only between 30 and 35 km the HDO–H<sub>2</sub>O profiles of EMAC increase stronger than in the satellite data and reach the level of MIPAS and ACE-FTS HDO–H<sub>2</sub>O mixing ratios. For HDO, this is not the case, its increase with height at these altitudes is rather similar between EMAC and the satellite retrievals and therefore the offset remains. In the altitude range between 16 and 30 km HDO in the EMAC simulation quantitatively corresponds well with the Odin retrieval. In this region also local maxima and minima, which can be seen in all four satellite profiles are reproduced qualitatively in EMAC. These reveal the seasonal cycle of HDO. However, especially for and H<sub>2</sub>O. Due to the spectral band that is used to derive these parameters by SMR, in this special case, H<sub>2</sub>O can not be retrieved below 20 km while the limit for HDO is between 17 and 18 km. Especially for April and August, the local HDO minimum between 25 and 30 km in the EMAC data is not as pronounced as in the satellite retrievals. Above the the local minima the HDO mixing ratios of all satellite profiles increase strongly with altitude to values around 1.1 nmol/mol at 50 km, while the EMAC simulation shows HDO mixing ratios of only 0.6 nmol/mol at these altitudes. This is in H<sub>2</sub>O, this behaviour is observable as well, however, only at altitudes above around 40 km and at a significantly smaller magnitude. Therefore, to some extent, this is most likely due to the assumptions made in the chemistry parameterisation for HDO, which does not include the influence of the isotopic composition of molecular hydrogenon HDO–fractionation effects during the reactions concerning molecular hydrogen. Also the simplified methane oxidation scheme itself, however, plays a role here.

### 3.4 The stratospheric $\delta D$ tape recorder

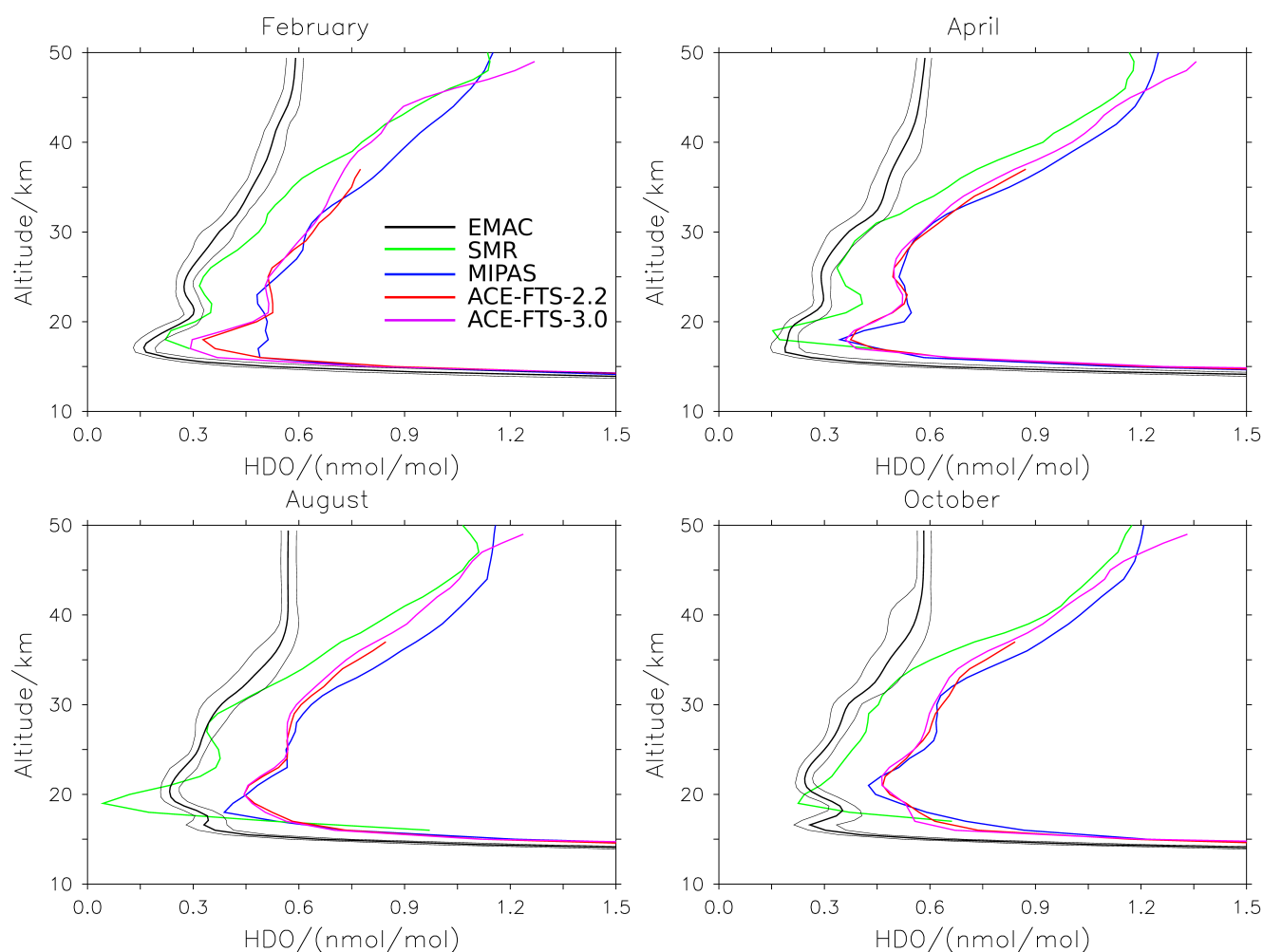
The tape recorder signal in H<sub>2</sub>O, HDO and  $\delta D(H_2O)$  in the EMAC simulation is evaluated with respect to the MIPAS data. The satellite and the model data are compared in Fig. 6.

The left panels show the EMAC results and the right panels show the MIPAS retrieval.

Overall, there is only a rather weak agreement between EMAC and MIPAS in all three quantities. As already shown in the previous section, a persistent (all altitudes, all seasons) dry bias in H<sub>2</sub>O and HDO is visible in the EMAC simulation. This offset has also been shown by Jöckel et al. (2006) and is consistent with the slightly too cold hygropause in the nudging data (see e.g. Liu et al., 2010). Also  $\delta D(H_2O)$  is slightly too high in the upper stratosphere and generally too low in the lower throughout the stratosphere. In the lower stratosphere, some of these differences can be explained with the coarse vertical resolution of the MIPAS retrieval, which smoothes the hygropause (see Steinwagner et al., 2007). The overestimation of  $\delta D(H_2O)$  in EMAC at around corresponds to the altitudes ( $\sim$ ), where HDO increases more strongly in the simulation, as seen in Fig. 4. In the upper stratosphere, the underestimation by the model can be associated to the assumptions in the chemistry parameterisation. In the lower stratosphere, the strongest deviations in  $\delta D(H_2O)$  can be observed during NH summer, when MIPAS observations show  $\delta D(H_2O)$  values around  $-500\text{‰}$  and the  $\delta D(H_2O)$  values in EMAC do not exceed  $-600\text{‰}$ . A tape recorder signal can be seen in all three quantities for both, model and observations, although with different amplitudes and a phase shift of two to three months. While the maxima of the tape recorder in the lower stratosphere in EMAC are found during summer, the satellite data show them at the beginning of autumn. This can partly (at maximum one month) be an artefact of the MIPAS retrieval and its coarse vertical sampling, but has to be kept in mind and compared with other data sets. The tape recorder signals in HDO and H<sub>2</sub>O fade out at around 30 km in both, model and observations. The  $\delta D(H_2O)$  tape recorder signal in MIPAS reaches these altitudes as well, the EMAC  $\delta D(H_2O)$  tape recorder, in contrast, fades out below somewhat lower already.

The amplitude of the tape recorder in EMAC is larger for H<sub>2</sub>O and smaller for HDO and  $\delta D(H_2O)$ , respectively, compared to the MIPAS data. Above 28 km, the  $\delta D(H_2O)$  tape recorder becomes overshadowed by chemically produced high  $\delta D(H_2O)$  values. This effect is further investigated in part 2 of the article (Eichinger et al., 2014). The MIPAS  $\delta D(H_2O)$  tape recorder might be amplified artificially by the offsets in vertical resolution between H<sub>2</sub>O and HDO (Orbe et al., 2013). A correction of this error is likely to reveal a  $\delta D(H_2O)$  tape recorder signal with smaller amplitude in the MIPAS retrieval.

By analysing ACE-FTS data, Randel et al. (2012) found a tape recorder signal in H<sub>2</sub>O and in HDO, but could not find a corresponding pattern in  $\delta D(H_2O)$ . The lower stratosphere in Fig. 7 of Randel et al. (2012) shows distinct seasonally varying maxima and minima of  $\delta D(H_2O)$ , these, however, hardly propagate upwards in time. For comparison with the



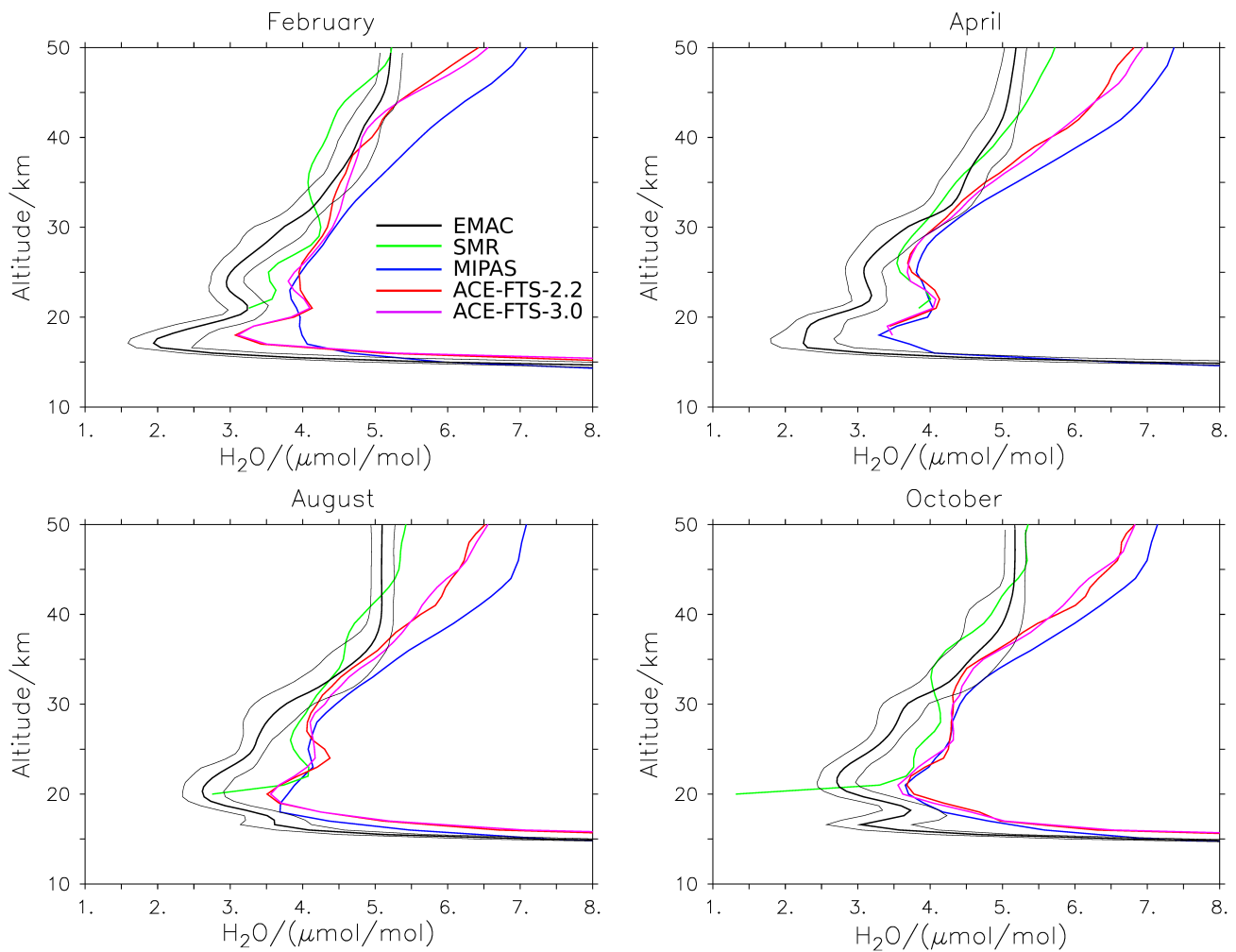
**Fig. 4.** Comparison of HDO mixing ratio-altitude profiles between EMAC and various satellite observations. Black: Averages, minima and maxima of 21 monthly averages of the EMAC simulation for the respective months; green: Odin/SMR; blue: ENVISAT/MIPAS; red: SCISAT/ACE-FTS-2.2; purple: SCISAT/ACE-FTS-3.0.

ACE-FTS data, the tropical  $\text{H}_2\text{O}$ , HDO and  $\delta\text{D}(\text{H}_2\text{O})$  in the stratosphere of the EMAC simulation are displayed in Fig. 7 for the same period and altitudes as in Randel et al. (2012).

The left panels show the monthly averages of the respective values. ~~Quantitatively~~ Qualitatively these agree fairly well with the ACE-FTS observations by Randel et al. (2012). The increase of ~~the quantities~~ HDO and therewith  $\delta\text{D}(\text{H}_2\text{O})$  with altitude in the stratosphere is ~~represented well~~ too weak, however. At 30 km  $\delta\text{D}(\text{H}_2\text{O})$  exhibits values ~~around  $-500\text{‰}$ , which matches with below  $-600\text{‰}$ , while in the~~ ACE-FTS data retrieval values of around  $-500\text{‰}$  can be seen. Similarly to the comparison with the MIPAS retrieval, ~~however,~~ also the lower stratosphere in EMAC is dryer ~~especially in~~ in  $\text{H}_2\text{O}$  and in HDO. Still, a clear tape recorder signal can be observed in all three panels, with minimum values in the

lower stratosphere during boreal winter and maxima during boreal summer.

For the right panels, the EMAC data has been filtered, using only the four months (February, April, August and October), which are also available in the ACE-FTS retrieval, to estimate the influence of the sparse temporal sampling on the tape recorder signals. This filtering somewhat blurs the tape recorder in all three panels, compared to the full data set. Especially the tape recorder in  $\delta\text{D}(\text{H}_2\text{O})$  ~~however,~~ appears to lose some of its upward motion at around 20 km and generally becomes less obvious. Therefore, it can be assumed, that the sparse temporal sampling of ACE-FTS data is an issue in the evaluation of the  $\delta\text{D}(\text{H}_2\text{O})$  tape recorder and may well contribute to the indistinctness of the signal in the study by Randel et al. (2012).



**Fig. 5.** Comparison of  $\text{H}_2\text{O}$  mixing ratio-altitude profiles between EMAC and various satellite observations. Black: Averages, minima and maxima of 21 monthly averages of the EMAC simulation for the respective months; green: Odin/SMR; blue: ENVISAT/MIPAS; red: SCISAT/ACE-FTS-2.2; purple: SCISAT/ACE-FTS-3.0.

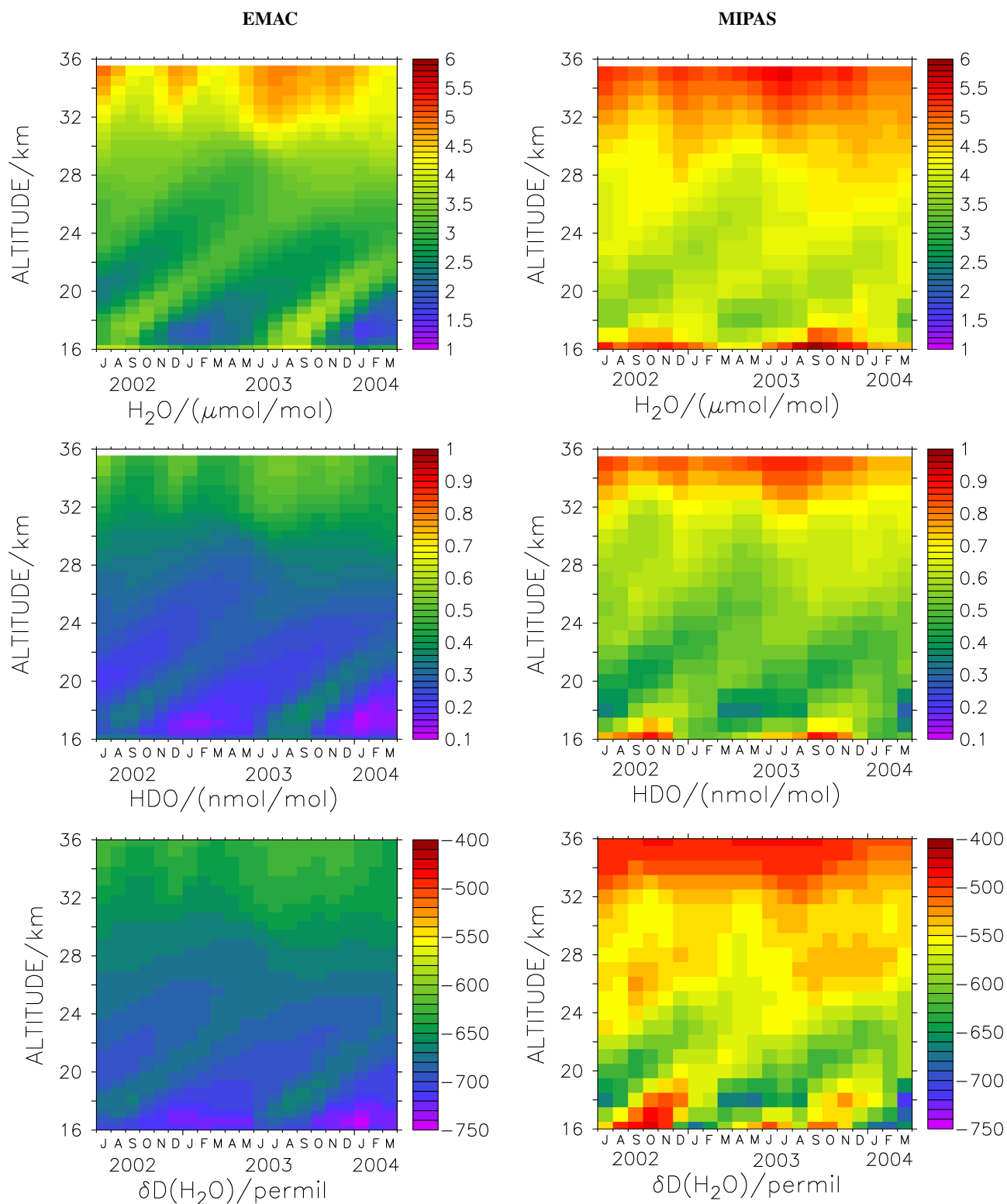
Due to its instrumental design, the SMR satellite instru-<sup>860</sup> ment measures  $\text{H}_2\text{O}$  and HDO orbitally shifted. This means, that  $\text{H}_2\text{O}$  and HDO are never measured at the same time and implies inaccuracies for the calculation of  $\delta\text{D}(\text{H}_2\text{O})$ . A comparison of the  $\delta\text{D}(\text{H}_2\text{O})$  tape recorder signal between EMAC and SMR has therefore not been conducted.<sup>865</sup>

### 3.5 Summary and discussion

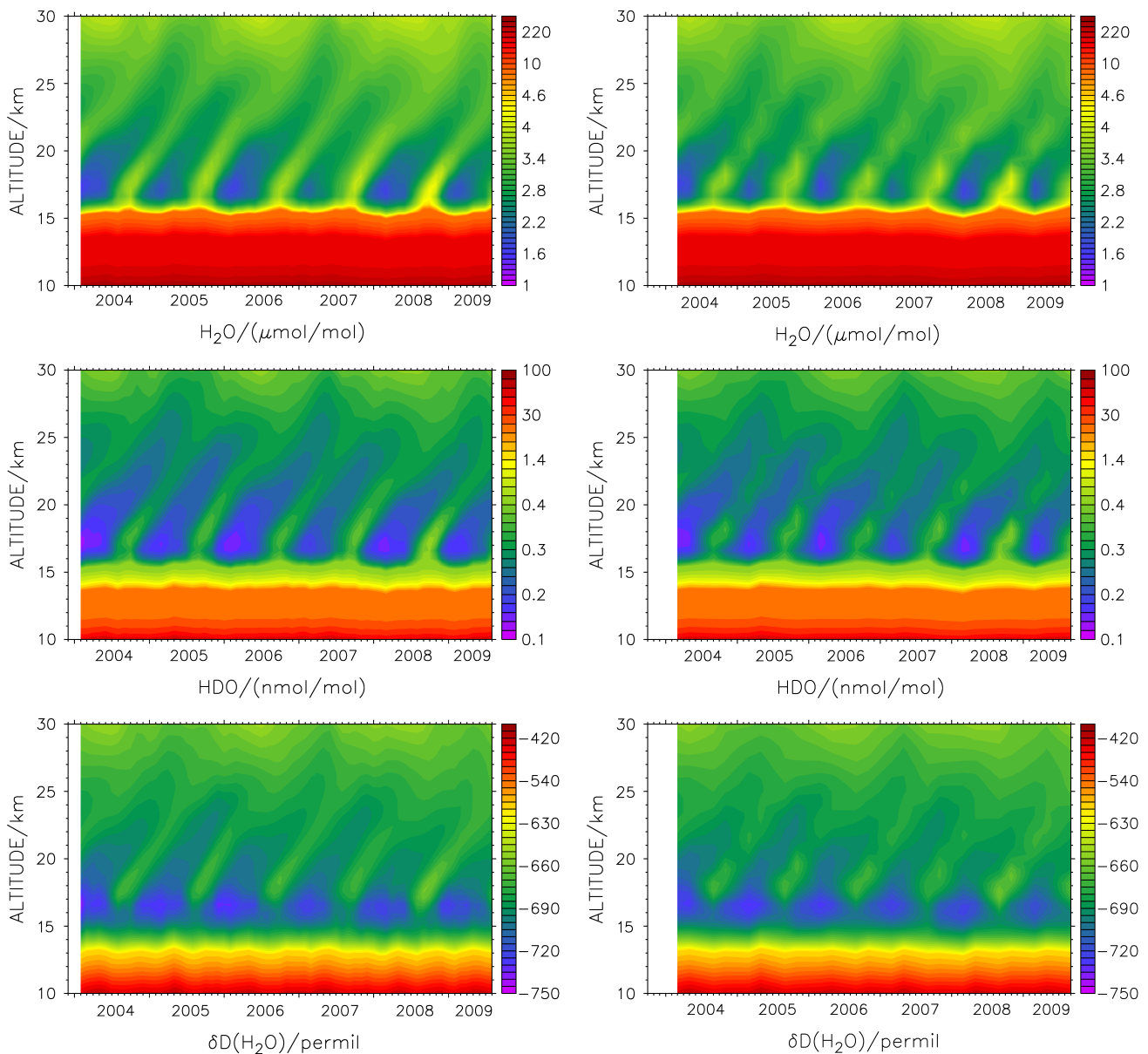
The results of the EMAC simulations were first assessed with respect to the isotope ratios in precipitation, in order to<sup>870</sup> ensure the correct representation of the physical processes in the troposphere. The EMAC results agree very well with GNIP (IAEA, 2009) data and are almost identical with results from the ECHAM5-wiso (Werner et al., 2011) model. Hence the physical processes and fractionation effects of the<sup>875</sup>

water isotopologues in the hydrological cycle of EMAC are represented satisfactorily (see supplement).

The chemical HDO precursor  $\text{CH}_3\text{D}$  in the stratosphere was evaluated next. Here, a good qualitative agreement with chemically elaborate transport models by Ridal et al. (2001) and Ridal and Siskind (2002), as well as with radiosonde-balloon flights by Röckmann et al. (2011) is shown. Quantitative differences can merely be speculated about. Differences in the model dynamics as well as in the fractionation coefficients can play a role in the model-model intercomparison. The climatological value of tropospheric  $\delta\text{D}(\text{CH}_4)$ , the contribute to disagreements between the model results. The coarse horizontal resolution of the model, the possible drift of the balloon and associated local meteorological features and especially the sparsity of



**Fig. 6.** Altitude-time diagrams of  $\text{H}_2\text{O}$ ,  $\text{HDO}$  and  $\delta\text{D}(\text{H}_2\text{O})$  in the tropics (15°S-15°N). Left: EMAC simulation, right: MIPAS observations.



**Fig. 7.** Altitude-time diagrams of  $\text{H}_2\text{O}$ ,  $\text{HDO}$  and  $\delta\text{D}(\text{H}_2\text{O})$  in the tropics ( $15^\circ\text{S}$ - $15^\circ\text{N}$ ) from the EMAC simulation. Left: monthly averages; right: averages of only February, April, August and October, as in Randel et al. (2012). The plotting algorithm linearly interpolates between the available months.

the measurements are the main issues in the comparison of  $\delta\text{D}(\text{CH}_4)$  in EMAC with observations.

As desired by Röckmann et al. (2011), this modelling approach can assist for further studies, especially concerning the investigation of the isotope effects of the chemical sink reactions of methane isotopologues. **Anyhow, For instance, Kaiser et al. (2002) and Röckmann et al. (2003) discuss the application of apparent rather than laboratory based fractionation factors ( $KIE_{app} = \sqrt{KIE}$ ) for long-lived trace gases that are removed in the stratosphere. While in the**

EMAC simulation the laboratory based fractionation factors lead to very good agreement with measurements, according to Röckmann et al. (2001) turbulent diffusion and mixing of air masses lead to significantly smaller fractionation factors. Anyhow, also more extensive measurements are desired for further evaluation of the methane isotope ratios in the stratosphere.

The mixing ratios of  $\text{HDO}$  and  $\text{H}_2\text{O}$  were compared with the results of satellite retrievals. Inconsistencies be-



tween the individual satellite retrievals (see Lossow et al., 2011) ~~make it delicate~~ render it difficult to define a distinct result. In the UTLS, the HDO profiles of EMAC agree well with the SMR satellite ~~retrieval observations, but~~ the H<sub>2</sub>O retrieval of SMR only reaches down to around 20 km. Compared to the ACE-FTS and the MIPAS satellite profiles, retrieved from measurements in the mid-infrared, the UTLS appears to be too dry in H<sub>2</sub>O and in HDO in the EMAC model. ~~A possible explanation for this, however, also is the lack of the representation of ice overshooting convection in the here applied convection scheme (Tiedtke-Nordeng; Tiedtke, 1989). According to Dessler et al. (2007), a more complete representation of this effect can enhance the mixing ratios of HDO, while H<sub>2</sub>O is not significantly affected. The O~~ this dry bias had already been discussed (see Jöckel et al., 2006) and HDO is, at first order, determined by H<sub>2</sub>O, this dry bias for HDO is not surprising. Reasons for this are the slightly too cold hygropause in the nudging data (see e.g. Liu et al., 2010) and the coarse horizontal resolution of the model. However, due to the rather low vertical resolution of the satellite observations, ~~on the other hand, blur the hygropause. Hence, the HDO mixing ratios at the tropopause might be overestimated (see e.g., Steinwagner et al., 2007). Between the hygropause is blurred in the retrievals and therefore, H<sub>2</sub>O as well as HDO are overestimated in MIPAS (see e.g., Steinwagner et al., 2007).~~

For H<sub>2</sub>O, this offset weakens between 30 and 40 km and becomes stronger again further above. At around 35 km ~~the simulated HDO, the simulated H<sub>2</sub>O~~ increases stronger with altitude than the satellite observations show. ~~This is most likely to be a chemical effect, since it is~~ Above 40 km, simulated H<sub>2</sub>O increases at much smaller rates compared to the satellite observations. These inconsistencies are most likely caused by the simplified methane oxidation scheme, since they are obvious during all the four months where observations of ACE-FTS are available. ~~This can be linked to the fractionation factors in the sink reaction of CH<sub>3</sub>D, because also  $\delta D(CH_4)$  is overestimated at these altitudes, especially in the tropical and mid-latitude profiles. A revision of the applied kinetic fractionation parameters and their temperature dependence (which were taken from Röckmann et al., 2011), is necessary to analyse this offset. The HDO mixing ratios above are underestimated by the EMAC model. This~~

HDO in contrast shows a too weak increase with altitude from around 30 km upwards. Largely, this is attributable to the lack of the intermediate reactions containing HD in the CH<sub>3</sub>D oxidation chain in the model, ~~which include isotope effects~~. Although we accounted for the deuterium storage in HD (using a relation by McCarthy et al., 2004), the isotope effects of the intermediate reactions on HDO are not taken into account in the model. As has been shown by Rahn et al. (2003) and Röckmann et al. (2003), stratospheric  $\delta D(H_2)$  increases with altitude, while the mixing

ratios of molecular hydrogen ~~is~~ are rather constant. ~~The conversion of isotopically very heavy molecular hydrogen to water would therefore increase the HDO mixing ratios strongly, while leaving H<sub>2</sub>O largely unaffected.~~ Additionally, the influence of the oxidation of CH<sub>3</sub>D itself also increases with altitude. This implies, that the importance of the intermediate reaction with HD on HDO, which is not implemented ~~considered~~ here, increases with altitude too. ~~That simplification~~ Our simplifications can therefore explain the offset in HDO mixing ratios between the EMAC simulation and the satellite retrievals ~~above~~ and the different behaviour of H<sub>2</sub>O and HDO. This leads to too low  $\delta D(H_2O)$  values in the upper parts of the stratosphere.

In future studies, the chemical deficiencies of the H<sub>2</sub>OISO submodel can be reduced, by including ~~a~~ an explicit representation of HD to take into account the intermediate reactions from CH<sub>3</sub>D to HDO. However, according to Zahn et al. (2006) the reaction rates of HD and especially the fractionation effects of these reactions are poorly quantified and hence can be subject ~~of~~ to large uncertainties. As an alternative, however more sophisticated modelling approach, the water isotopologues can be included to the isotope scheme by Gromov et al. (2010), by extending it to the deuterium cycle. This features a number of isotopic species and reactions, which also affect the hydrogen reactions. ~~Furthermore, the usage of other convection schemes may generate more suitable results of HDO in the UTLS. This, however, requires the implementation of the water isotopologues into the alternative convection schemes.~~

The tape recorder signals of H<sub>2</sub>O, HDO and  $\delta D(H_2O)$  of the EMAC simulation were compared to the MIPAS retrieval (see Steinwagner et al., 2007, 2010). In the lower stratosphere, EMAC and MIPAS are closest during winter, where the differences can mostly be explained with the low vertical resolution of the MIPAS sampling. The summer months, however, show much stronger deviations between model and observations, with too low values in all quantities in the simulation, especially however, in HDO and  $\delta D(H_2O)$ . This suggests deficiencies in the model physics, most likely for example the underrepresentation of overshooting convection. ~~Furthermore, a hardly explainable phase shift and, especially in in the convection scheme (Tiedtke-Nordeng; Tiedtke, 1989; Nordeng, 1994) applied here. According to studies by Dessler et al. (2007) and Bolot et al. (2013) a more complete representation of this effect can enhance the mixing ratios of HDO, while H<sub>2</sub>O is not hardly affected. This would increase  $\delta D(H_2O)$ ; inconsistent amplitudes and vertical propagations between the tape recorder signals are observed. The in the UTLS especially during NH summer, since convective events are more frequent during that time of the year. Thus, a better representation of the  $\delta D(H_2O)$  tape recorder in the model could be achieved. However, the inconsistent vertical resolutions between H<sub>2</sub>O and HDO in the MIPAS retrieval can~~

be the reason of ~~an a spurious~~ amplification of the  $\delta D(H_2O)$  tape recorder signal in the observations (Orbe et al., 2013). The correction of this artefact in the MIPAS data is subject of current investigations and may ~~lead to more consistency~~ ~~in the also~~ lead to a better agreement between the EMAC ~~and MIPAS~~ amplitudes of the  $\delta D(H_2O)$  ~~recorders between EMAC and MIPAS~~ tape recorders.

The influence of convective ice lofting on the isotopic composition of stratospheric water vapour in this simulation is analysed in part 2 of the article (Eichinger et al., 2014). In future studies, the quality of other convection schemes could be tested with respect to the results of HDO in the UTLS and a possibly better representation of overshooting convection. This, however, requires the implementation of the water isotopologues into the alternative convection schemes.

The phase shift of two to three months between the tape recorders of MIPAS and EMAC, which can be observed in all three quantities, is not easily explainable. Due to the coarse vertical resolution of the MIPAS retrieval there might be a delay in the retrieved tape recorder signals of up to one month. There is no evidence that the seasonality of convection in EMAC is in phase shifted. Simulated patterns of moisture in the UTLS compare well with observations and analyses of the seasonal cycle of zonal mean precipitation (convective and large-scale clouds) and integrated water vapour conducted by Hagemann et al. (2006) and Tost et al. (2006) also show accordance with observations.

The seasonal cycle of lower stratospheric  $\delta D(H_2O)$  in the ACE-FTS retrieval (see Randel et al., 2012) shows a different behaviour than that of the MIPAS retrieval and the EMAC simulation. The too low ~~HDO mixing ratios~~  $\delta D(H_2O)$  values in EMAC compared to ACE-FTS, especially during summer ~~and in the upper stratosphere~~, are consistent, however, Randel et al. (2012) ~~can would~~ not find the tape recorder signal in  $\delta D(H_2O)$ . The  $\delta D(H_2O)$  tape recorder in EMAC is weaker than the corresponding signals in  $H_2O$  and HDO. Still, the pattern is clearly recognisable ~~in the lower stratosphere~~. A possible reason for the lack of the upward propagation of the seasonal cycle of  $\delta D(H_2O)$  in the ACE-FTS observations is the sparse temporal sampling of the instrument in the tropics. A filtering of the EMAC data to its sampling reduces the apparent temporal upward motion of the  $\delta D(H_2O)$  tape recorder in the ~~lower stratosphere and the signal fades out at even lower altitudes. In fact, this filtering makes the UTLS between around 17 and 20 km. Since~~  $\delta D(H_2O)$  ~~does not increase strongly enough with altitude in the EMAC simulation due to the incomplete chemistry, a weaker~~  $\delta D(H_2O)$  tape recorder signal is expected for the correction of this effect. It would blur the tape recorder signal in EMAC above 20 km and therewith suppress its upward propagation. Below around 25 km, however, the chemical influence is very weak and thus some tape recorder signal will remain. The effect of methane oxidation on the  $\delta D(H_2O)$

tape recorder ~~hardly recognisable and therewith more similar to the ACE-FTS retrieval~~ will be analysed more deeply in the companion part 2 of the article.

~~In order to constitute~~ For more quantitative comparisons between models and observations, more sophisticated methods will be applied in future evaluations. The vertical resolution of the EMAC data can be transformed to the resolution of the respective satellite retrieval using their averaging ~~kernel~~ kernels. Also, the cloud filtering methods used for the satellite data can be applied ~~onto to~~ the model data. This elaborate evaluation can possibly assist to reduce the discrepancies between model results and observations and reveal the model ~~'s~~ and the measurement ~~'s~~ insufficiencies more precisely. In ~~this the present and in the companion (Part 2)~~ study, however, a more comprehensive understanding of the  $\delta D(H_2O)$  tape recorder is desired, which can best be achieved with the complete data record.

#### 4 Conclusions

The EMAC model system has been extended with the sub-model H2OISO, which contains a separate hydrological cycle, comprising the water isotopologues HDO and  $H_2^{18}O$  and their physical fractionation effects. The good agreement with measurement data and the ECHAM5-wiso model ~~lead leads~~ to the conclusion, that this expanded model system represents the state of the art of water isotopologue-enabled atmosphere GCMs. Moreover, a parameterisation of the oxidation of  $CH_3D$  was included to the H2OISO submodel. The sink reactions of  $CH_3D$ , which include reaction- and partly temperature-dependent kinetic fractionation effects, determine the chemical production of HDO. This rather simple parameterisation for the methane isotopologue  $CH_3D$  is apparently quite robust and can be applied for further studies concerning the isotopic composition of methane in the stratosphere. The comparison of stratospheric HDO profiles with satellite observations reveals a qualitatively good agreement. ~~In some regions, however, However,~~ systematic discrepancies can be observed. These can be associated with uncertainties in the convection scheme, ~~the kinetic fractionation coefficients in the chemical reactions and the simplified reaction chain, which does not consider the simplified representation of methane oxidation and, especially in the upper stratosphere, the negligence of the fractionation effects involving~~ molecular hydrogen. The comparison of the stratospheric tape recorder signal in  $H_2O$ , HDO and  $\delta D(H_2O)$  between EMAC and satellite observations is difficult. Considering all the uncertainties in the measurements and in the model, the overall representations of the tape recorder signals in EMAC are reasonable. The  $\delta D(H_2O)$  tape recorder simulated by EMAC at least partly resolves the discrepancies between the divergent conclusions from the MIPAS and the ACE-FTS satellite retrievals. The EMAC  $\delta D(H_2O)$  tape

recorder ranges between the pronounced tape recorder from MIPAS and the missing upward propagation of the seasonal signal in ACE-FTS observations. The ~~revision-revisions~~ of the individual insufficiencies of the retrievals ~~and the model~~, however, are expected to ~~alter the observations towards the EMAC results.~~ ~~generate more compatible results.~~ Despite the quantitative differences in stratospheric  $\delta D(H_2O)$  between EMAC and satellite observations, the conclusion can be drawn, that the new MESSy submodel H2OISO, used in the framework of the EMAC model, provides the possibility to attain additional insights into the mechanisms, which control the stratospheric water vapour budget. The physical and chemical properties of the isotopic composition of water allow new ~~investigation measures~~ ~~investigations~~, with respect to the processes and pathways, which control the stratospheric water vapour budget. The H2OISO submodel will be available in future EMAC versions as an additional option for all users.

## Appendix A

### Applied MESSy submodels

CLLOUD: Original **cloud** and cover routines from ECHAM5 as MESSy submodel (Roeckner et al., 2006, and references therein).

CONVECT: This submodel calculates the process of **Convection**. It consists of an interface to choose different convection schemes and the calculations themselves (Tost et al., 2006).

CVTRANS: The **Convective Tracer Transport** submodel calculates the transport of tracers due to convection. It uses a monotonic, positive definite and mass conserving algorithm following the bulk approach (Tost, 2006).

GWAVE: Hines non-orographic **gravity wave** routines from ECHAM5 as MESSy submodel (Roeckner et al., 2006).

RAD4ALL: ECHAM5 radiation scheme as MESSy submodel (Roeckner et al., 2006; Jöckel et al., 2006).

TROPOP: Submodel for **Tropopause** (WMO + PV) and other diagnostics (Jöckel et al., 2006).

JVAL: This submodel is for fast online calculation of **J-values** (photolysis rate coefficients) using cloud water content and cloudiness calculated by the base model and/or climatological ozone and climatological aerosol (~~based on Landgraf and Crutzen, 1998~~) (~~see Landgraf and Crutzen, 1998~~).

TNUDGE: The submodel 'Tracer **Nudg(e)**ing' is used for Newtonian relaxation of user-defined tracers as pseudo-emissions (Kerkweg et al., 2006).

Supplementary material related to this article is available online at <http://www.atmospheric-chemistry-and-physics.net/journal.html> (see Landgraf and Crutzen, 1998).

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# Supplement of

## Simulation of the isotopic composition of stratospheric water vapour – Part 1: Description and evaluation of the EMAC model

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## 1 Introduction

This supplement includes details about the evaluation of the H2OISO submodel within the framework of the EMAC model in the troposphere. For this purpose, the  $^{18}\text{O}$  and D water isotope ratios in precipitation are compared to long-term ground station measurements (GNIP) and to another isotopologue-enabled atmosphere GCM (ECHAM5-wiso).

## 2 Evaluation of EMAC H2OISO in the troposphere

Before applying the EMAC H2OISO submodel in the stratosphere an evaluation of the physical processes in the troposphere was conducted. The representation of the isotope physics in the model can be validated by examining the isotope ratios in precipitation, because these allow to ~~conclude various fractionation processes~~ evaluate various isotope fractionation effects (Dansgaard, 1964).

In addition to the EMAC simulation described in the manuscript, another simulation has been carried out for this evaluation. It constitutes a simpler setup (MESSy submodels: H2OISO, CLOUD, CONVECT, CVTRANS, GWAVE, RAD4ALL, TROPOP) without stratospheric chemistry and a resolution of T31L39MA ( $\sim 3.75^\circ \times 3.75^\circ$ , 39 vertical layers, middle atmospheric dynamics). This simulation was performed in “free running” mode, i.e., without Newtonian relaxation to meteorological reference data. The time step of the simulation was twelve minutes and the output is set to produce averaged values for each month. As boundary condition the monthly averages of the climatological sea surface temperatures and sea ice conditions (AMIP-II; Hurrell et al., 2008) of the period from 1987 to 2006 were used repeatedly for every year. The last 10 years of a 15 year simulation are used for the evaluation.

### 2.1 Comparison with ground station measurements (GNIP)

Fig. 1 and Fig. 2 show the annual averages of  $\delta^{18}\text{O}(\text{H}_2\text{O})$  and  $\delta\text{D}(\text{H}_2\text{O})$  in precipitation from the two described EMAC simulations, the GNIP database, and the absolute differences between the respective simulation and the GNIP data (see captions). For the lower panels, the annual values of the entire GNIP database were mapped to the respective model grid and subsequently, the absolute value of the difference between the GNIP and the EMAC data was calculated.

Apart from the much lower values of  $\delta\text{D}(\text{H}_2\text{O})$ , compared to  $\delta^{18}\text{O}(\text{H}_2\text{O})$ , which is due to the stronger fractionation in HDO, panels (a) and (b) of Fig. 1 and Fig. 2 show the same patterns. These correspond well between model and measurements (c). On the model grid, only small deviations can be observed between the two model simulations of different resolutions in the respective panels (a) and (b).

The respective panels (d) and (e) reveal large differences in certain regions. The northern regions of Canada and Greenland, the Asian mountains and South Africa show considerable deviations. These can be explained by general discordances in precipitation between model and reality and the poor representation of the model orography. Partly, slight improvements can be seen in the T42L90MA resolution compared to the T31L39MA resolution.

In order to provide an estimate of the representation of the seasonal cycle of  $\delta\text{D}(\text{H}_2\text{O})$  in precipitation between the GNIP measurements and the EMAC model, the monthly averages of the respectively available periods are compared in Fig. 3. For that, particular regions of different climate zones have been defined, chosen to include as many GNIP stations as possible. The defined regions can be seen in the upper left panel of the figure, which also includes the absolute differences of  $\delta\text{D}(\text{H}_2\text{O})$  in precipitation from Fig. 2. The regions are labeled with (A) for northern Canada and Greenland, (B) for the Caribbean and parts of Middle and South America, (C) for Patagonia, (D) for Central Europe, (E) for the Middle East, (F) for South Africa and (G) for the eastern parts of China. Additionally to the monthly averages, the standard deviations are included for the two model simulations to provide an estimate of the variation of  $\delta\text{D}(\text{H}_2\text{O})$ .

In general, the seasonal cycles of the measurements and the simulations correlate well. Some of the regions, however, show large offsets, partly during the entire year, partly in specific seasons. In most cases, the simulation with higher resolution (T42L90MA, green) is closer to the GNIP data, some panels, though, show the opposite. This is due to the different climatic states of both simulations, since the overall temperatures in the T42L90MA simulation are slightly higher than in the T31L39MA simulation and the temperatures determine the strength of the fractionation.

Similar evaluations have been conducted, e.g., by Risi et al. (2010) for the LMDZ-iso model and by Werner et al. (2011) for the ECHAM5-wiso model, albeit, by comparing individual stations instead of regions. These results also feature qualitative good agreement with quantitative comparable deviations in certain climate zones.



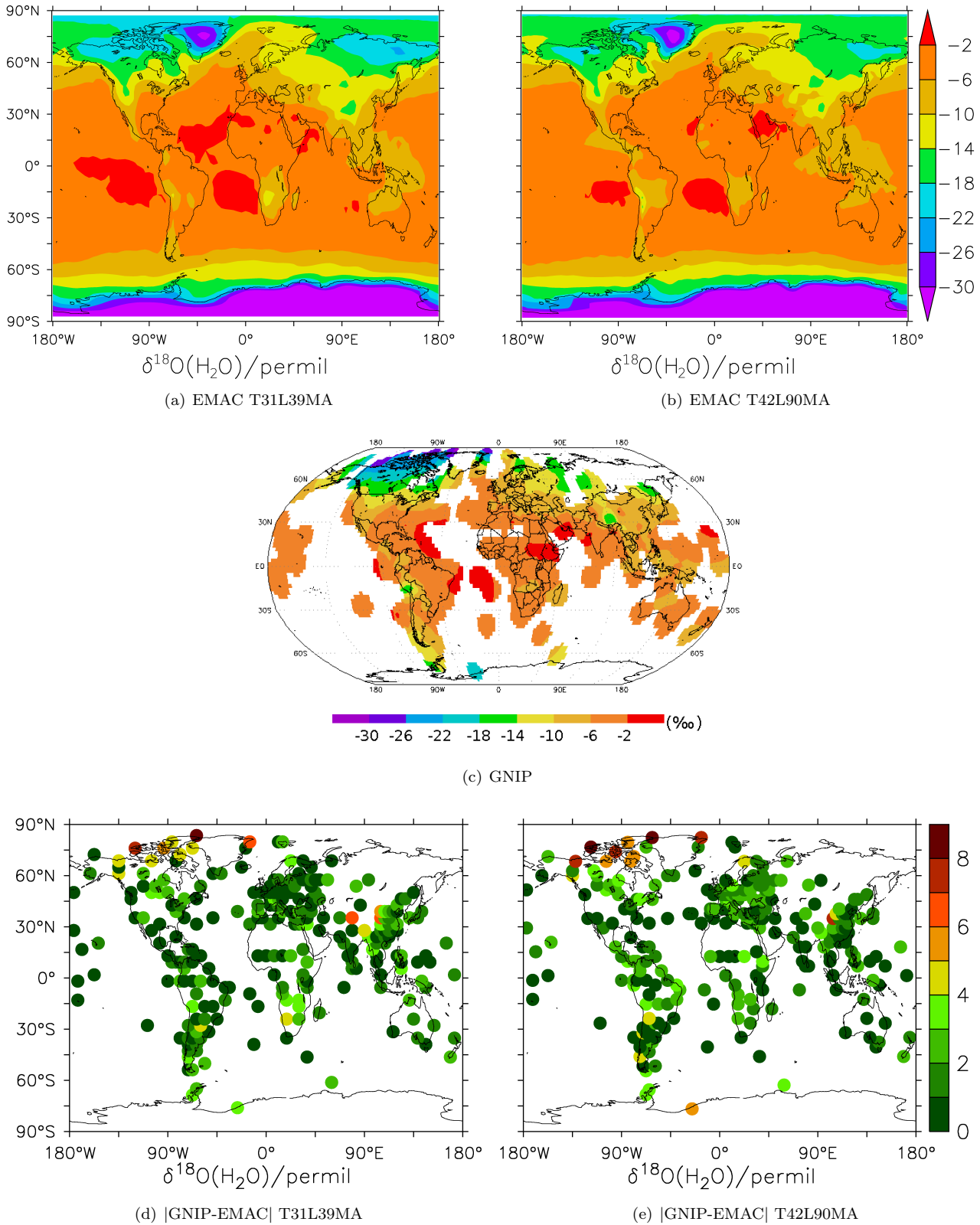


Figure 1:  $\delta^{18}\text{O}(\text{H}_2\text{O})$  in precipitation. EMAC, GNIP and the absolute values of GNIP minus EMAC. EMAC simulations are annual averages of the T31L39MA (a) and the T42L90 (b) simulation. The GNIP data image (c) is taken from IAEA (2001). The absolute differences between GNIP and EMAC are shown for the T31L39MA (d) and for the T42L90MA (e) resolution.

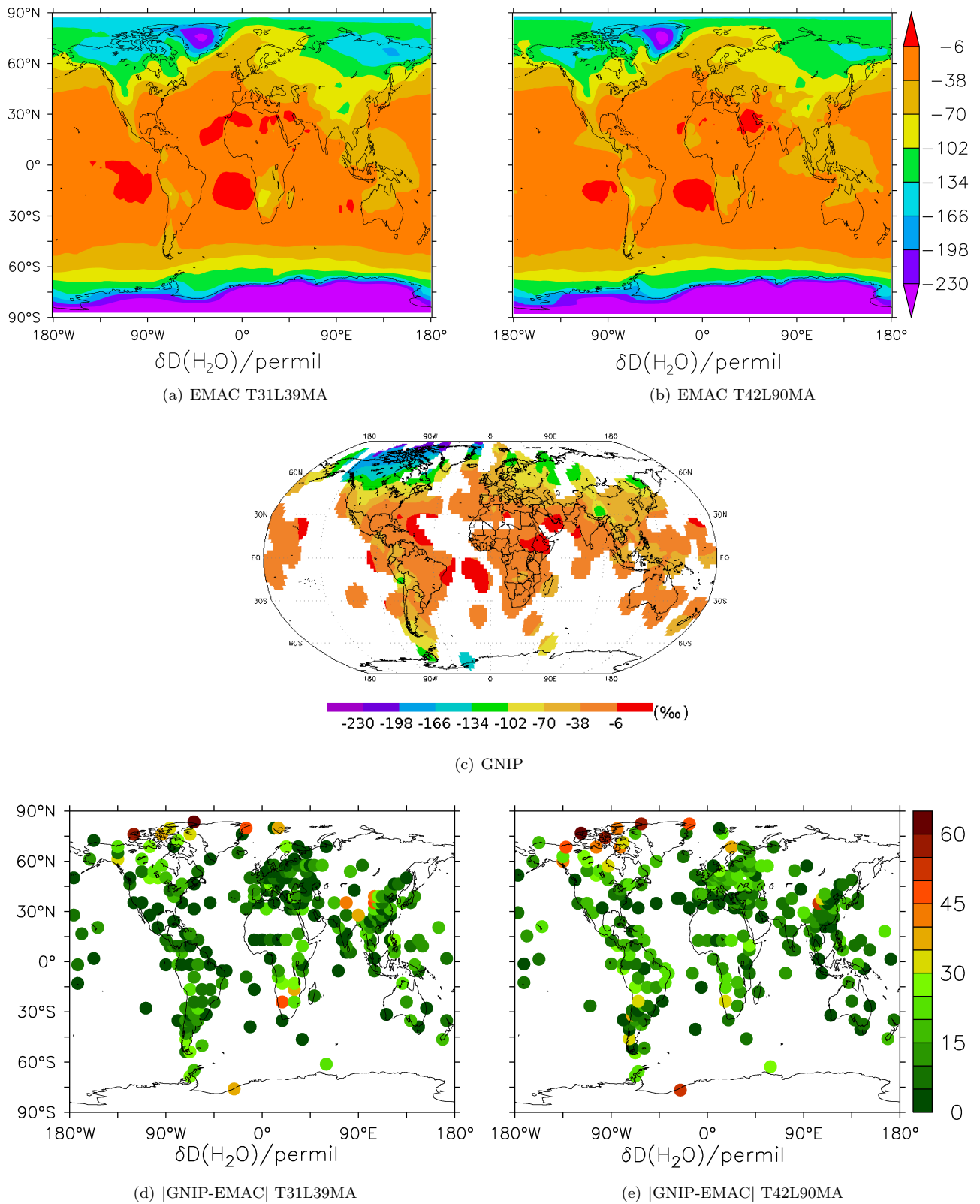


Figure 2:  $\delta D(H_2O)$  in precipitation. EMAC, GNIP and the absolute values of GNIP minus EMAC. EMAC simulations are annual averages of the T31L39MA (a) and the T42L90 (b) simulation. The GNIP data image (c) is taken from IAEA (2001). The absolute differences between GNIP and EMAC are shown for the T31L39MA (d) and for the T42L90MA (e) resolution.

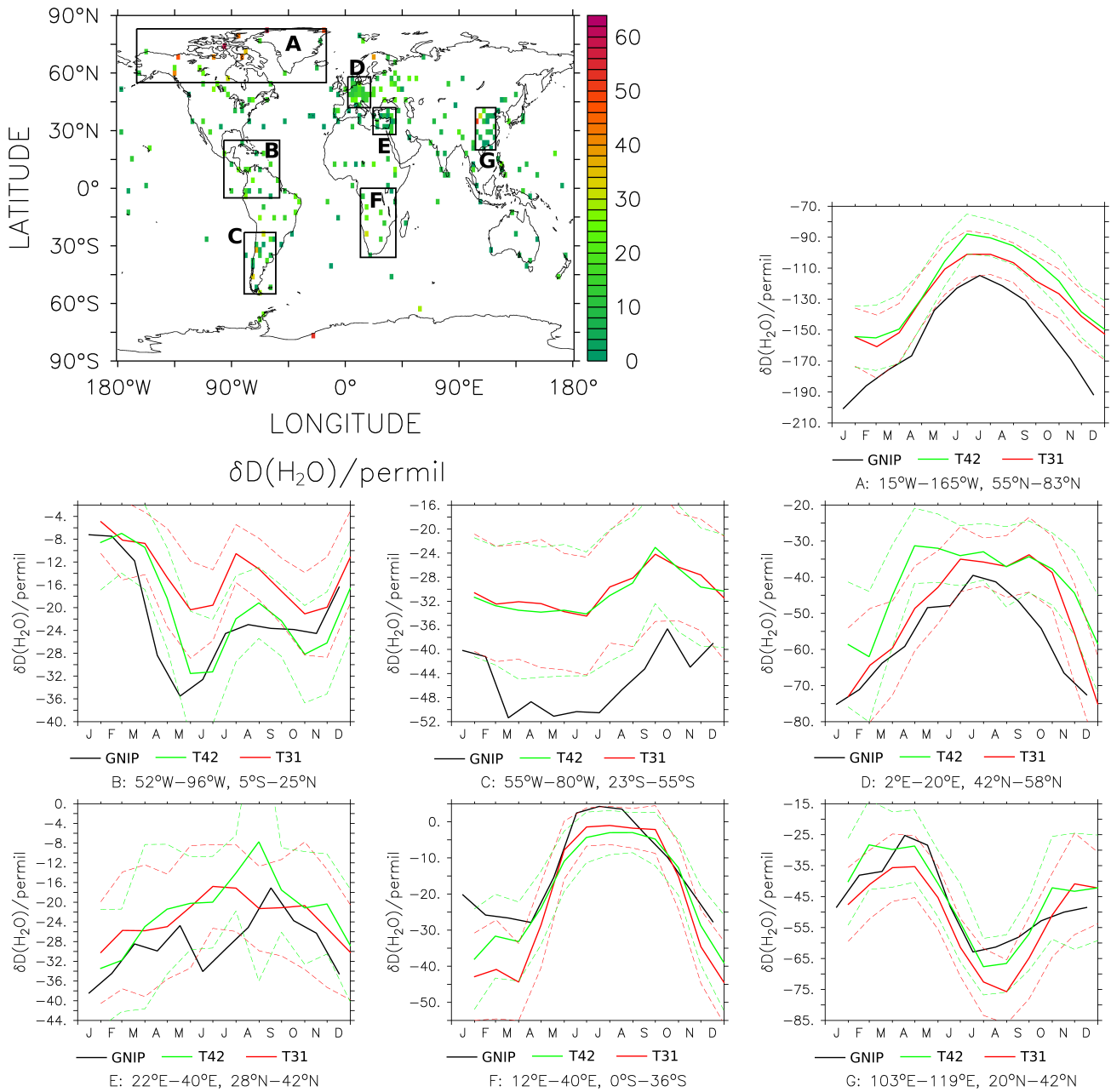


Figure 3: Comparison of the seasonal cycle of  $\delta D(H_2O)$  in precipitation between GNIP data and the two EMAC simulations (T31L39MA and T42L90MA) for selected regions. The map shows the difference between GNIP and EMAC from Fig. 2 and the selected regions (A to G), and the individual panels show monthly averages of the three data sets and the standard deviations (dashed lines) for the two model simulations.

## 2.2 Comparison with ECHAM5-wiso

One of the most recent isotopologue-enabled atmosphere GCMs and the most similar to EMAC is the ECHAM5-wiso model. ECHAM5-wiso has been evaluated successfully against GNIP data in the model resolutions T31L19, T63L31 and T159L31 by Werner et al. (2011). Fig. 4 shows the annual averages of  $\delta^{18}\text{O}(\text{H}_2\text{O})$  in precipitation, globally (top) and for Europe (bottom). The left panels show the T31L39MA and the right panels the T42L90MA resolution. The data is displayed identical to Fig. 1 and Fig. 2 in Werner et al. (2011).

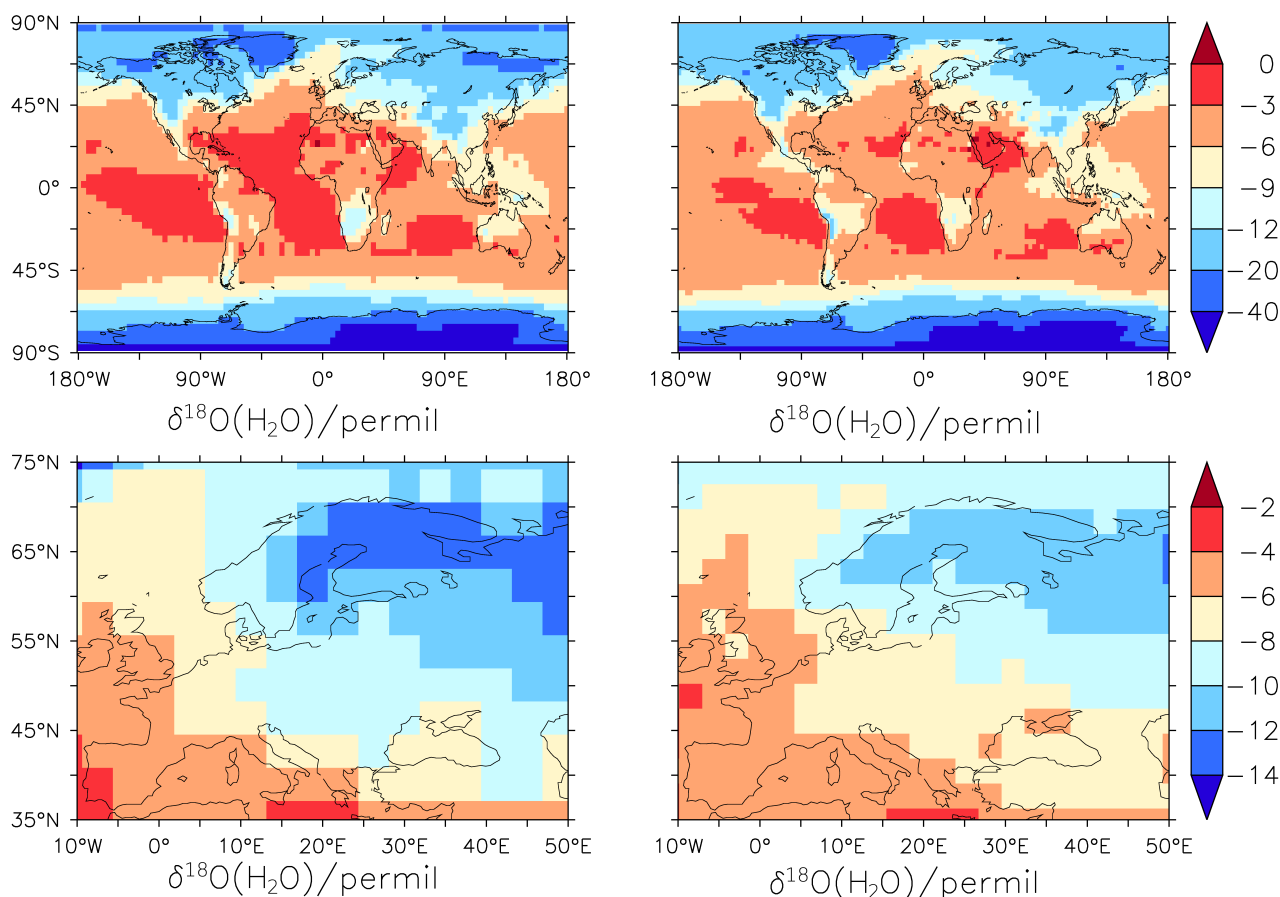


Figure 4: Averaged annual  $\delta^{18}\text{O}(\text{H}_2\text{O})$  in precipitation for the T31L39MA (left panels) and the T42L90MA (right panels) resolution, presented globally (top) and for Europe (bottom).

The patterns and values of the figures agree very well with the ECHAM5-wiso simulations. Especially the ECHAM5-wiso T31L19 simulation shows almost identical results as the T31L39MA simulation of EMAC. The small differences originate mainly from the different boundary conditions, i.e. the sea surface temperatures. The T42L90MA simulation of EMAC fits in, as an intermediate result between the T31L19 and the T63L31 setups of ECHAM5-wiso. The zoom on Europe constitutes only little differences between the two EMAC simulations. The T42L90MA resolution is horizontally still not detailed enough to represent orographic features like the altitude effect in the Alps, which can be observed in the T63L31 and the T159L31 resolution of the ECHAM5-wiso study. The low  $\delta^{18}\text{O}(\text{H}_2\text{O})$  values in Scandinavia and western Russia can not be seen as pronounced anymore in the simulation with higher resolution. This can be explained with the generally warmer conditions in this region in this simulation.

~~The The EMAC simulated averages of  $\delta\text{D}(\text{H}_2\text{O})$  in precipitation in Antarctica of the (in T42L90MA resolution) are compared with the results from the ECHAM5-wiso model (in T159L31 resolution) from Werner et al. (2011) in Fig. 5 and Fig. 5 in Werner et al. (2011).~~ This is conducted, in order to evaluate the fractionation effects at very low temperatures and in the ice phase, which also becomes important when analysing the upper troposphere and the lower stratosphere.

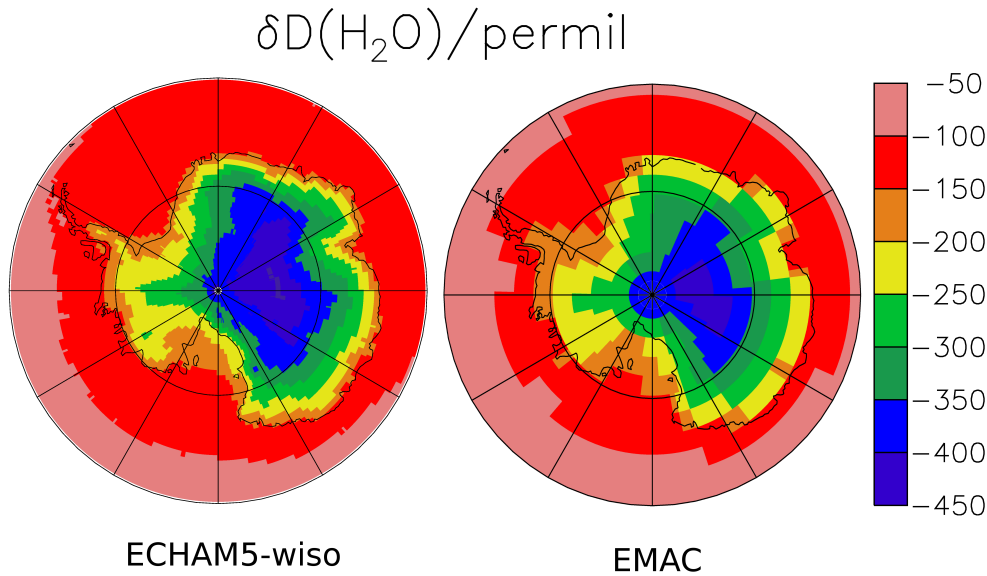


Figure 5: Annual average of  $\delta D(H_2O)$  in precipitation in Antarctica from [the ECHAM5-wiso \(in T159L31\) \(Werner et al., 2011\)](#) and [EMAC \(T42L90MA simulation\)](#).

Despite the differences in horizontal resolution, the  $\delta D(H_2O)$  in precipitation in Antarctica between the two simulations quantitatively agree very well. The comparison of these results from Werner et al. (2011) with observations compiled by Masson-Delmotte et al. (2008) generally revealed a good agreement. Particular discrepancies can be explained by unresolved effects or general model biases (see Werner et al., 2011).

### 3 Conclusions

The comparison of the EMAC model results with GNIP data generally shows a good agreement, considering the main characteristics, which can be observed in the isotopic composition in precipitation. In most of the regions, also the values, the amplitude and the seasonal cycles compare well with the GNIP measurements. Some regions, though, show considerable differences between model and observations. Since the isotopic composition of precipitation strongly depends on parameters like evaporation and condensation temperatures, the seasonal cycle of the precipitation and also small scale features of the latter, the isotope ratios are very sensitive to the climate conditions. An exact match between model and observations is hence not to be expected. Considering the inaccuracies of the model, but also the difficulties in compiling a representative data set out of partly sparse measurements, the deviations are in a reasonable range.

The results of the simulations of the EMAC model and the ECHAM5-wiso (Werner et al., 2011) model agree very well. Since the hydrological cycles of the two models are basically equal, this was expected. The representation of the isotopologues in the hydrological cycle of the ECHAM5-wiso model technically bases on previous isotopologue-enabled GCMs like ECHAM3 by Hoffmann et al. (1998) and ECHAM4 by Werner et al. (2001). Comprehensive GCM intercomparison studies for stable water isotopologues have been conducted in the SWING (Stable Water Isotope Intercomparison Group) project (Noone, 2006), where also the previous isotopologue-enabled ECHAM versions successfully participated. Hence the conclusion can be drawn, that the EMAC model with the H2OISO submodel represents the state of the art of atmosphere GCMs with explicit representation of the water isotopologues HDO and  $H_2^{18}O$  in the troposphere.

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# Comments on “Simulation of isotopic composition of stratospheric water vapor - Part 1“ by R Eichinger

This paper describes the implementation of water and methane isotopes into the chemistry-climate model EMAC and presents a preliminary comparison with some satellite and balloon-borne datasets.

This is not a very ambitious paper: 1) no particular science question is being addressed, this is left for future studies; 2) the satellite-model comparison remains rather crude compared to the state of the art, without any account for instrument sensitivity or cloud masking.

But it’s a serious and well-written paper. So I have only minor comments in section 1, but also optional suggestions in section 2.

## 1 Minor comments

- p 23810 l 2: remove coma. Beware of similar coma problems at other places.
- p 23810 l 14: What does MESSy stand for?
- p 23810: is it the first general circulation model that is used for looking at the stratosphere or TTL region? Add some review of previous studies on the subject, and cite for example [Schmidt et al., 2005].
- p 23810 l 16: “Depending on the” -> “When used with”
- p 23813 l 5: “condensation” -> “condensation to liquid”?
- p 23822 l 19: “it” -> “if”
- p 23826 l 27: you cannot cite a paper in preparation
- p 23827 l 22: “however” seems out of place

## 2 General suggestions

If the authors want to give more added value to the paper beyond the simple description of a technical achievement, here are some suggestions:

- Improve the model-data comparison technique by taking into account instrument sensitivity (through averaging kernels), spatio-temporal sampling, and cloud masking (e.g. [Risi et al., 2012, Yoshimura et al., 2011]...). This would allow to investigate in more detail and more convincingly the sources of model-data and data-data differences. This extension of the work is suggested in p 23831, and it’s not so difficult to actually do it.
- Investigate in more detail the sources of model-data disagreement, if these persist after using the more rigorous model-data comparison methods above. In particular, what explains the phase shift of the  $\delta D$  tape recorder? What does it say about the model physics? Was this problem already noticed in other models? What does it say about the potential of water isotopic observations to address questions about the stratospheric water budget?

## Références

- [Risi et al., 2012] Risi, C., Noone, D., Worden, J., Frankenberg, C., Stiller, G., Kiefer, M., Funke, B., Walker, K., Bernath, P., Schneider, M., Wunch, D., Sherlock, V., Deutscher, N., Griffith, D., Wernberg, P., Bony, S., Jeonghoon Lee, D. B., Uemura, R., and Sturm, C. (2012). Process-evaluation of tropical and subtropical tropospheric humidity simulated by general circulation models using water vapor isotopic observations. Part 1 : model-data intercomparison. *J. Geophys. Res.*, 117 :D05303.
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- [Yoshimura et al., 2011] Yoshimura, K., Frankenberg, C., Lee, J., Kanimatsu, M., Worden, J., and Röckmann, T. (2011). Comparison of an isotopic atmospheric general circulation model with new quasi-global satellite measurements of water vapor isotopologues. *J. Geophys. Res.*, 116 :D19118, doi :10.1029/2011JD016035.



Dear referee,

thank you very much for your valuable comments and suggestions. Please find below our reply to all your points.

1. Minor comments:

- Point 1: Thank you, further comma mistakes will be revised during the typesetting process.
- Point 2: MESSy: Modular Earth Submodel System; we will add this in the manuscript.
- Point 3: To our knowledge Schmidt et al. (2005) is the only publication, analysing dD in the TTL and above in an AGCM modelling study. We will include this to the introduction and mention the crucial weaknesses of the applied model in that study (vertical resolution and prescribed chemical HDO tendency).

All other points will be changed accordingly, thanks for reading carefully.

2. General suggestions

- Point 1: This is a very true point. However, for the start, we decided not to carry out this task for mainly two reasons:
  - P1. In order to make an exact one to one comparison between model and satellite data, the model output firstly has to be sampled along the satellite orbits at the exact time and place of the satellite overpass. Then, the cloud filtering and the averaging kernel will be applied. The cloud filtering also involves statistically complex measures. Firstly, the question arises if the observed or the simulated clouds have to be taken for filtering. Taking the observed only, may induce effects in the lower stratosphere through the cloud events, which may take place at other times in the model. Filtering the results by both modeled and observed clouds, requires a statistical evaluation of the number of the remaining co-localised profiles. This elaborate evaluation, in fact, does go beyond the scope of this initial study, but is planned for future projects.
  - P2. As is, the comparison 'simply' shows the best estimate of the model and of the satellite retrievals to describe reality. The meaning of this way of comparing the two approaches, lies in drawing conclusions from the existence or nonexistence, respectively, of the tape recorder signal.
- Point 2: These questions are also very important. Yet, their basis is the more detailed evaluation towards particular satellite retrievals from Point 1. Therefore, we will have to leave them open for now. The focus of this article (apart from the description and evaluation of the model) is the diverging results from the different satellite retrievals w.r.t the dD tape recorder. Since

this is the first study with a global climate chemistry model, which addresses this question, we consider these details as secondary for now. The general question rather is, if such a signal is to be expected or not. Please also note that the addressed science question (the reason for the formation of the dD tape recorder and its sensitivity) is investigated in Part 2 of the article.

Please comment in case you consider certain parts of these explanations as indispensable for the manuscript, or have any issues with them.

# Reply to referee 2

## GENERAL REMARKS

- *The paper describes the basic performance of a water isotope module of the EMAC model in the stratosphere. The description is largely clear, but the analysis is not very deep and sometimes a bit superficial. The discussion around the tape recorder isotope effect is interesting, because some effects that could contribute to the discrepancy between published observations are discussed, even if the issue cannot be resolved.*

*There are two technical issues that could have been done better in the model setup. The first is rather simple: The entry value of  $dD$  in  $CH_4$  to the stratosphere was set to -68 per mill, which is clearly too high compared to high precision measurements (based on the presently accepted relation to the VSMOW scale). The value apparently originates from a previous model study that also incorporated this high value. In the comparison with this model, this therefore does not lead to problems, but in the comparison to the data it introduces a significant shift. The authors decided not to correct for that, but it is very easy to rescale the values and I suggest to perform this correction. I suggest to correct the model entry value to the experimental value in order to show the values on the adequate scale.*

*The second issue is a bit more problematic, namely leaving out molecular hydrogen in the mass balance, in particular for Deuterium. The authors acknowledge the issue, but still do not take it into account. The argumentation why this is done is questionable, certainly not convincing (focussing on the stratospheric entry values should be done with the correct values). Whereas the individual fractionations are indeed partly not well quantified, the correlation between  $CH_3D$  and  $HD$  (and  $CH_4$ ) is well established (see McCarthy et al., doi:10.1029/2003JD004003, 2004, Rahn et al, doi:10.1038/nature01917, 2003, cite these papers!) It should be easy to add a parameter for this effect in eq 12, where the  $CH_3D$  change is translated to  $HDO$ . Basically it is not precisely 1 molecule of  $HDO$  that is formed from one  $CH_3D$ , but a bit less, since some of the deuterium will be stored in  $HD$ . The correlations can be obtained from the data in McCarthy et al and conversions from the other stratospheric datasets (Rahn, Rockmann, Rhee). In the present form, the deuterium mass balance is wrong. Although there is only 0.5 ppm of water in the stratosphere, the isotopic composition varies by several hundred per*

*mill, so the effect is estimated to be several tens of per mill. The fact that it has not been taken into account is then cited later several times as possible cause of a discrepancy, so it is really a shame that it was not simply done!*

*The comparison of HDO between the model and satellite instruments is not very strong, if it is presented without a similar comparison of HHO. The first order effects of HDO are related to HHO (more HHO, more HDO), so such a comparison should be done with HHO, where the uncertainties in the satellites are likely smaller. The dry bias of EMAC compared to some satellite datasets is discussed, but the effect on HDO is not always adequately discussed. For example, spatial changes in HDO in the stratosphere would in first order be due to spatial changes in HHO. Differences in fractionation constants will only lead to second order effects and are most likely not responsible for the larger changes in HDO that are discussed.*

*The fact that the incorporation of laboratory based KIEs into a global model with independent OH, O1D and Cl fields leads to a very good agreement with the observed isotope-mole fraction relation as shown in Fig 3 could be discussed in more detail. It is not straightforward, since also mixing effects are important for the isotopic composition in the stratosphere.*

Thank you very much for reading carefully and for giving advice and help. Please find our answers to your specific comments (in blue) in the next sections, assigned to the comments in your uploaded pdf.

## SPECIFIC COMMENTS

- 23808-4 *separate from what? not clear*  
“separate“ from the actual hydrological cycle. Will be changed to “additional (and separate from the actual hydrological cycle)“
- 23808-7 *HHO and*  
Thanks, will be corrected
- 23808-7 *does it also include 18O?*  
No, it does not. <sup>18</sup>O is included in the ”physical“ hydrological cycle, chemistry has not been implemented for it, though.
- 23808-8 *also 18O?*  
No, see above.
- 23809-11 *to*  
Thanks, will be corrected

- 23810-27 *stratospheric balloon*

Thanks, will be corrected

- 23812-19 *this should be delta values (so isotope ratio differences) not mixing ratios*

Indeed, thanks.

- 23814-11/13 *CH<sub>4</sub>*

Not sure what you are referring to here. Here we denote the CH<sub>4</sub> submodel, hence the 4 is not a subscript. We will add submodel behind it to make it more clear.

- 23814-21 *pseudeo first order rate coefficients*

Thanks, will be corrected

- 23817-7 *Effect of HD*

23817-15 *This is an important constraint. Whereas the individual fractionations are indeed not well quantified, the correlation between CH<sub>3</sub>D and HD (and CH<sub>4</sub>) is well established (see McCarthy et al., doi:10.1029/2003JD004003, 2004, Rahn et al, doi:10.1038/nature01917, 2003, cite these papers! It is relatively easy to add a parameter for this effect in eq 12, where the CH<sub>3</sub>D change is translated to HDO. In the present form, the deuterium mass balance is wrong. Although there is only 0.5 ppm of water in the stratosphere, the isotopic composition varies by several hundred per mill, so the effect is estimated to be several ten per mill.*

Thank you very much for your help. We will approximate this parameter for our calculation, with:

$$\frac{\partial[HD]}{\partial t} = -6.32 \cdot 10^{-5} \cdot \frac{\partial[CH_4]}{\partial t}$$

derived from McCarthy et al. (2004). With

$$\frac{\partial[HDO]}{\partial t} = -\frac{\partial[CH_3D]}{\partial t} - \frac{\partial[HD]}{\partial t},$$

this yields for our equation 12:

$$\frac{\partial[HDO]}{\partial t} = -\frac{\frac{\partial[CH_3D]}{\partial t}}{y} + \frac{6.32 \cdot 10^{-5} \cdot \frac{\partial[CH_4]}{\partial t}}{y}$$

with  $y = \frac{M_{air}}{M_{HDO}} \left( \frac{1}{1-HDO} \right)^2$  only dependent on HDO.

We will perform this correction, carry out another simulation, replot everything present it and change the concerned paragraphs accordingly.

- 23818-1 *I cannot find quickly where this value originates from, but it is wrong. I fear that in one of the earlier publications the digits were transposed from -86. This*

*is what many high precision measurements show, -68 is far too high (see Umezawa, [www.atmos-chem-phys.net/12/8095/2012/](http://www.atmos-chem-phys.net/12/8095/2012/), Rice et al., doi:10.1029/2002JD003042, 2003, Rockmann et al., 2011). You have cited the last one, should also cite the others. The Irion paper does not really provide information of acceptable quality and is not valid as validation.*

Thank you. We will perform another simulation and use the value -86‰, as indicated in Rhee et al. (2006). We will replot all the figures and change the text accordingly.

- 23819-16 ???

Reformulated to: allows to evaluate various isotope fractionation effects

- 23821-4 *Too high, see above, but for model comparison not a problem*

For this figure we will still use the -68‰, in order to have the direct comparison.

- 23821-15 *what does at first mean here*

Thanks, not sensible, we delete "at first".

- 23821-23 *there are many more, in the cited paper, and in Rice et al., JGR 2003. I see, below you say flights, not samples.*

Change "samples" to "altitude profiles".

- 23822-3 *showing*

Thanks, will be corrected.

- 23822-3 *as function of*

Thanks, will be corrected.

- 23822-11 ??? *This would be a decrease, when you start at -68 you probably mean 100 and 200 and 0 and 100. BUT at least the simulation at GAP also shows values up to 150*

Indeed, we confused the signs, thank you.

- 23822-20 *What does it mean? You focus on the strat entry values? You seem to compare the entire stratosphere. And if you focussed on the entry values, you should take a lower value.*

Sentence will be deleted.

- 23823-5 *This may also be related to omitting H<sub>2</sub> and HD, since it could be that in the upper stratosphere a large fraction of the originally very heavy H<sub>2</sub> was converted to CH<sub>4</sub> in these samples.*

Thank you, we will add this possible explanation in the text.

- 23824-26 *HDO is so much influenced by HHO, that an "evaluation" of the HDO mole fractions without HHO is not a very strong evaluation, and maybe it is better done with HHO than with HDO. It makes more sense in the Lossow study because of the spectroscopic challenges, but the model has no measurement artifacts...*

23825-11 *I assume that EMAC is then also simply dryer in HHO. If not, it would reflect a different isotope RATIO, which would be more worthwhile to study.*

23826-4 *See comments above, so there is a dry bias in HHO in EMAC compared to MIPAS, so it is not a surprise that there is also a dry bias in HDO*

Thank you, this is indeed a very important point, which we did not consider enough. We will add a comparison of satellite and model data of HHO in the same manner as presented here for HDO and, depending on the outcome, change the results, discussion and conclusion sections accordingly.

In fact, the H<sub>2</sub>O profiles and their deviations from the satellite measurements are very similar to the HDO profiles and deviations. First order differences will certainly have to be due to this, fractionation effects and also the lack of the incorporation of HD seem to play a minor role.

- 23827-13 *If the delta value is -500 per mill and matches the observations, then the dry bias must be the same for HHO and HDO, not be higher in HDO.*

Will be corrected to: in H<sub>2</sub>O and HDO.

- 23829-1 *applied here*

Thanks, will be corrected.

- 23829-3 *Bot you showed that H2O is also dry biased*

Yes, but this effect could especially change HDO and thus increase  $\delta D(H_2O)$  in the lower stratosphere during boreal summer, when the differences in  $\delta D(H_2O)$  between model and satellite observations are largest. We will add a sentence, in order to clarify this.

- 23829-6 *Also here, the comparison has to be made relative to the HHO change. If this also increases stronger as in the satellite observations, than this has nothing to do with fractionation, but total chemical conversion.*

Thank you very much, we will add this, see above.

- 23829-16 *cite Rahn et al 2003*

Thanks, will be included.

- 23829-24 *As mentioned above, it could be taken into account as a relatively simple modification to the conversion equation from CH<sub>3</sub>D to HDO, no need for explicit fractionations in all steps*

Thanks, see above

- 23830-13 *could that not also be due to seasonality of convection?*

We do not expect a general phase shift of convection in EMAC compared to reality. Simulated patterns of moisture on the 390 K isentrope compare well with the observations of Randel et al. (2013, Nature Geosci.) in the time evolution of minimum and maximum values due to the seasonal shift of convection. Yet, the seasonal cycle of convection can only be evaluated indirectly by an analysis of the distribution of precipitation or by the redistribution of heat, momentum and moisture in the atmosphere. This kind of analyses have already been performed for the EMAC and ECHAM models and published in (see Tost et al., 2006, ACP; Hagemann et al., 2006, J. Climate). They found that the seasonal cycle of zonal mean precipitation (convective and large-scale clouds) and integrated water vapour, which were evaluated from different EMAC and ECHAM model simulations are in accordance with observations.

Though, we found that due to the coarse vertical resolution of the MIPAS retrieval, there might be a possible delay in the retrieved tape recorder of up to 1 month at maximum possible in the MIPAS data.

- 23831-3 *allow*

Thanks, will be corrected.

- 23831-9 *in which study? DO you mean the present study? Or a future study?*

Will be changed to: In the present and in the companion study...

- 23831-19 *This could be discussed more thoroughly in the paper*

Thank you for the hint, we will add more information about this.

- 23831-26 *As mentioned above, it can be more than just fractionations*

Yes, will be taken care of, see above.

## SUPPLEMENT

- Page 3 *reformulate*

Will be reformulated to: to evaluate various isotope fractionation effects

- Page 4 *why do you show the only the absolute differences, This suppresses potentially interesting information.*

The display would become confusing and thus hard to interpret. Anyway, the regions which show large discrepancies are evaluated in detail in Fig. 3.



- Page 7 ???

Sentence reformulated to: The simulated averages of  $\delta D(H_2O)$  in precipitation in Antarctica (in T42L90MA resolution) in Fig. 5 are compared with the results from the ECHAM5-wiso model (in T159L31 resolution) in Werner et al. (2011).

- Page 8 *Why don't you show the Werner et al data for comparison?*

We will use the data from Werner et al. (2011) and replot the figure for the manuscript. Showing the figure directly would have caused license issues with JGR.