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Vertical distribution of deuterium in atmospheric water vapour

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ABSTRACT

Available experimental data on the vertical deuterium distribution in atmospheric water vapour show a steep decrease of deuterium with altitude in the lower troposphere. Condensation removal of water alone does not correctly reproduce the isotopic evolution of ascending air masses and the steep deuterium profiles observed. Therefore, a multibox cloud model is proposed to explain the experimental data. In this one-dimensional model a complete isotope exchange between the falling raindrops and the vapour and cloud water at various atmospheric levels is proposed.

The observed deuterium increase near the tropopause is proposed to be at least partly due to downward mixing of isotopically heavy water vapour produced by methane decomposition in the upper atmosphere.

1. Introduction

Variations of deuterium and ^{18}O in atmospheric water vapour and precipitation are caused by isotope fractionation due to evaporation and condensation processes in the hydrologic cycle, mainly in its atmospheric part. This isotope fractionation between water vapour and liquid water favours the heavy water molecules HDO and $H_2{}^{18}O$ remaining or to going over into the liquid phase. Thus vapour loss by rain, for example during moist adiabatic cooling of an ascending air mass, leads to a depletion of D and ^{18}O in the residual water vapour, i.e. D and ^{18}O in tropospheric water vapour are expected to decrease with altitude. Since the atmospheric part of the hydrologic cycle means net transport of water from the ocean to the continent, the heavy stable isotope content of local precipitation reflects to some extent the rainout history of the moist air masses involved in the individual precipitation event. Therefore D and ^{18}O are suitable tracers for studies of the atmospheric water vapour transport with its sinks (precipitation) and sources (evaporation) on both the regional and global scale.

Eriksson (1965) used an isotope model based on a general circulation model of atmospheric water vapour and found that the vertical distribution of D and ^{18}O in the model decreased exponentially with height. From the vertically integrated horizontal vapour flux, a relation between the isotope data of rain and the local precipitable water has been derived. However, this general water vapour model simulates the spatial and time variation of the experimental isotope data of local precipitation only to a very rough approximation.

If compared with the rather extensive isotope data set of the IAEA/WMO Global Precipitation Network (IAEA 1969, 1970, 1971, 1973, 1975, 1979), relevant data for atmospheric water vapour and cloud water are until now scarce. Taylor (1972) has measured 20 vertical profiles of deuterium in tropospheric water vapour up to 5 km altitude over the Heidelberg/Mannheim area (F. R. Germany) during the period between June 1967 and June 1968. For some locations in the United States deuterium as well as tritium profiles from 1966–67 and 1971–73 have been reported by Ehhalt (1971, 1974a). These profiles have been

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discussed individually by the authors with respect to actual weather conditions (temperature, humidity) prevailing at the time of the sampling flights. Since in both cases the profiles obtained cover roughly a one year period with sufficient uniformity, the average deuterium profiles presented here should reflect to some extent the mean climatological conditions over the given sampling area. These mean profiles are summarized in Figs. 1 and 2. The deuterium content is expressed in δ-values (permill deviation from Standard Mean Ocean Water—SMOW).

In addition, Fig. 1 shows the deuterium profile in hurricane clouds as found by Ehhalt and Östlund (1970). In hail cloud studies, use has been made of the fact that the isotope fractionation between water vapour and cloud water (also ice-crystals) depends on the condensation temperature. Thus the isotope investigation of various layers of hailstone was expected to yield information on in-cloud conditions during hailstone formation. For the sake of interpretation of isotopic data of hailstones, Facy et al. (1963) proposed a simple model which describes the changes in the isotopic composition of the vapour and cloud water on the adiabatic ascent of an individual air mass without water loss by rain.

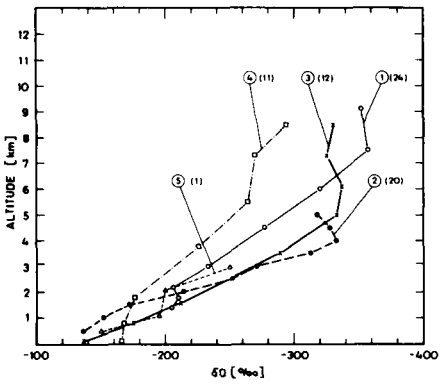

Fig. 1. Mean vertical profiles of deuterium in tropospheric water vapour over mid-latitude regions. Numbers in parentheses indicate the number of sampling flights over the given area. ①—Scottsbluff, Nebraska (Ehhalt, 1974a); ②—Heidelberg, F. R. Germany (Taylor, 1972); ③—Pacific Ocean, off-shore Santa Barbara, California (Ehhalt, 1974a); ④—Death Valley, California (Ehhalt, 1974a); ⑤—hurricane clouds (Ehhalt and Östlund, 1970).

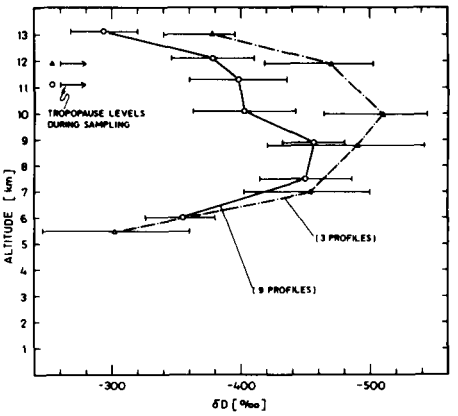

Fig. 2. Average vertical profiles of deuterium in the water vapour of the upper troposphere over mid-latitude regions. ○—Scottsbluff, Nebraska, March 1971—November 1972 (Ehhalt, 1974a). △—Palestine, Texas, November 22, 1972, March 21, 1973, September 10, 1973 (Ehhalt, 1974a).

This model has been used in the hailstone studies of Knight et al. (1975) and Jouzel et al. (1975). However, as pointed out by Knight et al. (1975), this simple model can only be qualitatively correct. Removal of cloud water and mixing with environmental air as well as initial isotopic composition of the vapour supplied to the cloud are expected to have considerable influence on the actual vertical distribution in the heavy stable isotopes. It is worth noting that model predictions with respect to the deuterium content of the liquid phase kept in hail clouds has not been checked experimentally. On the other hand, the experimental deuterium profile in hurricane clouds shows a considerably higher deuterium gradient with altitude than that predicted by the model. Ehhalt and Östlund (1970) suggested, that the isotope exchange between falling raindrops and water vapour and cloud droplets within the ascending air might have caused this steeper gradient. Ehhalt (1971) used this mechanism in his interpretation of the mean vertical profiles of the HTO-mixing ratio found over Scottsbluff, Nebraska and the Pacific Ocean in 1966–67.

A simple numerical model of the vertical distribution of deuterium in atmospheric water vapour is presented here. It includes the isotope exchange between water vapour and cloud water and falling raindrops.

2. The model

Fig. 3 shows the main features of the model. The cloud is represented by a vertical multibox system which operates like a counterflux distillation column. Moist air of known meteorological and isotope data (temperature, pressure, relative humidity, isotopic composition of water vapour) enters the first box at the bottom side of the system. On its way upwards from one box into the next one the air parcel undergoes at first dry adiabatic cooling and, eventually, after condensation, moist adiabatic cooling sets in under continuous cloud water formation. If a certain cloud water content, N_L, is reached (open model parameter), excess cloud water is removed from the system as precipitation (rain or snow), which falls downward through the boxes below.

The isotopic composition of the water vapour and liquid water in the various boxes—isotope ratios R_v and R_L—are calculated from the relation

$$\frac{dR_v}{R_v} = \frac{(\alpha - 1)\cdot dN_v - N_L \cdot d\alpha}{N_v + \alpha \cdot N_L}, \qquad R_L = \alpha \cdot R_v \quad (1)$$

used in the two-phase model of Merlivat and Jouzel (1979) for the adiabatic ascent of a closed air mass with continuous water loss by rain. In this relation N_v and N_L are the mixing ratios of the water vapour and the cloud water, respectively, α is the equilibrium isotope fractionation factor between the vapour and liquid (solid) phase, which increases with decreasing temperature. This model is an extension of the known Craig–Gordon model (Craig and Gordon, 1965). In our model the isotope ratios R_v and R_L are further influenced by isotope exchange between the total air moisture (vapour and cloud water, mixing ratio $N = N_v + N_L$) and the raindrops falling through the various boxes (cf. Fig. 3):

$$R'_v = \frac{R_L \cdot N_L + R_v \cdot N_v + \Delta N_L \cdot R_R \cdot K}{(N_L + \Delta N_L \cdot K)\cdot \alpha + N_v} \quad (2)$$

$$R'_R = R'_L = \alpha \cdot R'_v. \quad (3)$$

Here ΔN_L is the mass of raindrops within the specific box, K is the isotope exchange factor, R'_R, R'_L, R'_v are the isotopic composition of the rain, the cloud water and the water vapour in a specific box, respectively. The model yields isotope profiles on a temperature scale, which can, however, easily be transferred to an altitude scale using the proper temperature lapse rates. The following temperatures or altitudes are of particular interest: the condensation temperature being assumed to define the cloud base, the temperature of the "first rain level" in the model (i.e. the level at which the amount of condensate exceeds the presumed value, N_L, the excess, ΔN_L, being removed in the form of raindrops), the ice crystal formation and ice melting temperatures and the temperature of the cloud top.

The model yields isotope profiles for various states of the evolution of cloud formation. The isotope profile has reached its steady state, if the change in the isotope content of the water vapour in the uppermost box is sufficiently low. The isotope fractionation factor α has been calculated with the empirical formulas of Majoube (1971) and Merlivat and Nief (1965). All calculations have been performed on a desk calculator (HP 9830).

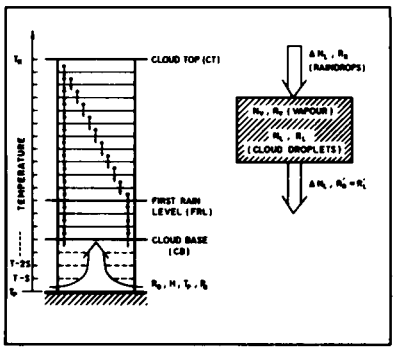

Fig. 3. Schematic diagram of the multibox cloud model. Input data: initial temperature, T_p; final temperature, T_k; initial pressure, P_0; relative humidity, H; initial isotopic composition of water vapour, R_0; cloud water mixing ratio, N_L; temperature step, S; isotope exchange factor, K.

3. Results

Model estimates of the vertical distribution of deuterium in cloud water vapour are shown in Figs. 4–6. The isotope profiles nos. 1–4 (Fig. 4) illustrate the isotopic evolution in the course of cloud formation before the steady state is reached under the assumption of complete exchange between rain and total air moisture (exchange factor $K = 1$) in each box. For comparison the δD profile obtained for the case of no exchange ($K = 0$, Merlivat-

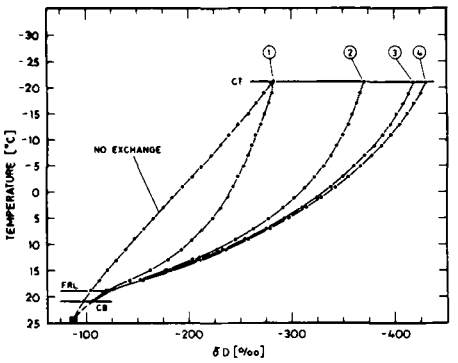

Fig. 4. Vertical distribution of deuterium content in cloud water vapour as predicted by the multibox model. The curves ① to ④ represent deuterium profiles at various stages of isotopic evolution of the cloud. The deuterium profile labelled with "no exchange" represents the model estimate if the isotope exchange between raindrops, water vapour and cloud droplets has been neglected. CB—cloud base level, FRL—first rain level, CT—cloud top level. Input data: initial temperature T_p = 25 °C; final temperature T_K = −10 °C; initial pressure P_0 = 1000 mbar; relative humidity H =80%; initial deuterium content in the water vapour R_0 = −74.7‰; cloud water mixing ratio N_L = 1 g m^{-3}; temperature step S = 2 °C; isotope exchange factor K = 1.

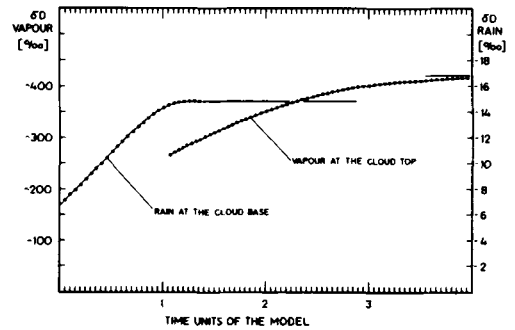

Fig. 5. Evolution of the deuterium content of rain at the cloud base and of vapour at the cloud top as predicted by the multibox model (input data as in Fig. 4). The time needed for the given air parcel to come through the whole system is called the time unit of the model.

Jouzel model) is also presented. Fig. 5 shows how fast the isotope contents of the vapour at the cloud top and of rain at the cloud base converge towards their steady state values. The time needed for a given air parcel to be transported through the entire system is called the time unit of the model.

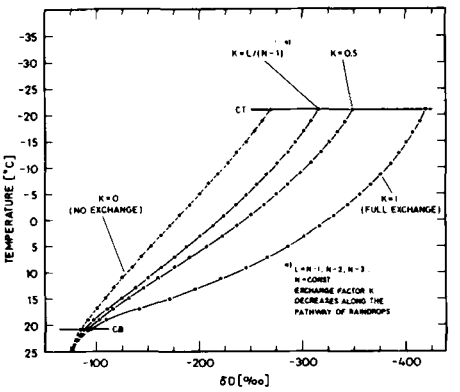

Fig. 6. Changes of the vertical deuterium distribution in the cloud water vapour induced by the isotopic exchange process between raindrops, water vapour and cloud droplets as predicted by the multibox model (input data as in Fig. 4). The curves illustrate different degrees of isotope exchange within each box (K—isotope exchange factor). CB—cloud base level.

Incomplete isotope exchange between rain and air moisture yields the isotope profiles of Fig. 6 under the assumption that only the fraction $K < 1$ of the rain falling through the individual boxes undergoes complete exchange, whereas the rest, $1 - K$, keeps the isotope content it had before entering the box. The case of incomplete exchange with decreasing K along the trajectories of the raindrops might be more realistic than that with constant K.

Other model estimates which are not shown here indicate that the deuterium profiles strongly depend on the presumed value of the cloud water mixing ratio, N_L. For small N_L values, steeper isotope profiles are obtained. Ice crystal formation in the system also influences the isotope profile considerably. The model has been tested at different ice formation–ice melting temperatures (no exchange within the boxes between these temperatures was assumed). The profiles obtained are in some cases even steeper than for the complete exchange case, but without solid phase formation in the system.

Reliable comparison between model prediction and experimental data has only been possible for the average vertical deuterium profile representing Taylor's data (Fig. 7). Only in that case can the input parameters needed to run the model be assessed with sufficient accuracy. The long-term averages of the atmospheric humidity, surface air temperature, pressure and deuterium content in monthly precipitation available for Stuttgart Station (IAEA, 1969, 1970, 1971, 1973, 1975,

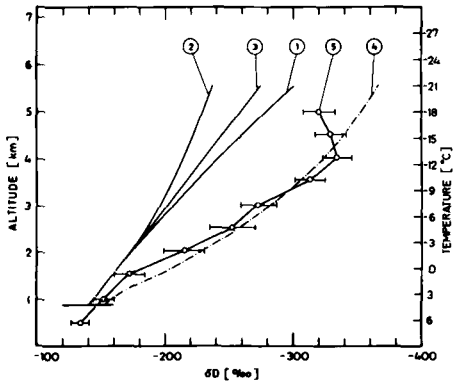

Fig. 7. Comparison between the average vertical deuterium distribution in the tropospheric water vapour over continental Europe (Taylor, 1972) and the predictions of different models. ①—Rayleigh model, ②—two-phase model without rainout, ③—two-phase model with rainout, ④—multibox model, ⑤—measurement data.

1979) have been used in the calculation. These initial model parameters are believed to be representative for the Heidelberg/Mannheim area. The deuterium content of the water vapour at ground level has been estimated using the empirical relation between the isotope content of local rain and surface air moisture ($\delta_{vapour} = \delta_{rain} - 76\%$, Zimmermann, 1978). The cloud water content, N_L, was an open model parameter. For comparison, other model estimates which have been obtained with this initial data, are also presented in this figure. The best fit of our model estimates to the experimental data has been obtained for a cloud water content of $N_L = 0.5$ g m^{-3}. In this case the model prediction for the isotope content of rain leaving the cloud base in the steady state yields $\delta D_{rain} = -58.5‰$ which has to be compared with the observed long-term mean of $-60.4‰$ at Stuttgart.

4. Discussion

Our model estimates of the vertical distribution of deuterium in atmospheric water vapour show that isotope exchange between the gaseous and liquid water within the cloud system seems to be a very effective process. This exchange is presumably responsible for the observed steep gradient of the deuterium content of tropospheric moisture. The multibox model reproduces the observed vertical deuterium profiles fairly well. Equally good fitting cannot be obtained with previous models in use.

One should, however, not overestimate the capabilities of the proposed multibox model. We tried rather to investigate the role of isotope exchange in the adiabatic ascent of a closed air mass, than to establish a comprehensive cloud model which usually requires much more initial information (e.g. Mason, 1971; Kessler, 1974; Hagen, 1979). It may also seem questionable to fit data obtained in clear air with a model which rather describes in-cloud conditions. We believe, however, that the mean isotope profile of tropospheric water vapour, which is characterized by a steep decrease of the heavy isotope content with altitude, is primarily controlled by convective processes like cloud formation. Vertical mixing of the air by eddy diffusion would rather lead to a smaller vertical isotope gradient as was pointed out by Eriksson (1965). The mean deuterium profile over the Death Valley area in California is in fact significantly less steep than the other profiles shown in Fig. 1. This might be due to the hot desert climate without rain, i.e. without isotope exchange between atmospheric moisture and falling raindrops. This specific example might serve to confirm the supposition that isotope exchange controls the steep isotope gradients observed in the lower troposphere.

As can be seen in Fig. 1, the deuterium content of the water vapour reaches a roughly constant value in the upper troposphere. Beyond this, two mean profiles shown in Fig. 2 clearly indicate an opposite sign of the isotope gradient, i.e. a fast increase of the deuterium content above 9–10 km altitude. This trend suggests a strong source of isotopically enriched water vapour in the stratosphere, which might be due to the chemical decomposition of methane gas. Numerous measurements show that methane concentration remains fairly constant in the troposphere (~1.5 p.p.m.v.) and decreases to 0.5 p.p.m.v. at 35 km altitude (Ehhalt, 1974b; Fabian et al., 1979). This decrease, as well as a detailed discussion of the atmospheric cycle of methane (Ehhalt, 1974b), strongly suggests an atmospheric sink mechanism for CH_4. At first Levy (1971) and then Ehhalt (1974b) proposed a mechanism for the chemical decomposition of methane which starts with the reaction of CH_4 with hydroxyl free radicals (OH). Water is one of the final products. The global water production rate of this process in the stratosphere

has been estimated to be 1–19 $\times$ 10^{10} kg yr^{-1} (according to Johnston and Solomon, 1979). It is commonly accepted that the upward branch of the Hadley cell is a major source for stratospheric water vapour. The air flux in the Hadley cell is estimated to be about 3.8 $\times$ 10^{17} kg yr^{-1} (Johnston and Solomon, 1979). If we take 10^{11} kg yr^{-1} as an estimate for the water vapour production rate in the stratosphere by methane decomposition, we obtain 0.26 p.p.m.m. as an average partial mixing ratio due to that water in the air returning from the stratosphere to the troposphere. This is about 10% of the total mixing ratio of stratospheric water vapour (2.5 p.p.m.m. as a typical value—Harries, 1976). The deuterium content of the atmospheric methane is approximately −110‰ (Begemann and Friedman, 1968). The question is to what extent this isotopic composition can be assigned to the water produced by the CH_4 reaction with OH radicals. Unfortunately, practically nothing is known about the isotopic composition of OH molecules; even their role in the chemistry of the upper atmosphere is still not completely understood (Warneck, 1974). Nevertheless, if the global mass balance of the hydrogen atoms leaving the troposphere in the form of CH_4 molecules and entering it again as water vapour is considered, one may expect the isotopic composition of this water vapour to be similar to the mean value reported for methane. The shape of the deuterium profile within the troposphere–stratosphere boundary layer might then be explained by the mixing of isotopically depleted water vapour of tropospheric origin with considerably heavier stratospheric vapour. It should be noted, however, that the 10% share of the water of methane origin deduced above is not sufficient to explain the observed shape of the deuterium profiles (a contribution of at least 50% would be needed, if $\delta D_{CH_4} = -110$‰ is assumed). On the other hand, this estimate is uncertain by at least a factor of 2. A more comprehensive study of the problem would be needed.

Additional useful information about the origin of stratospheric water vapour might be provided by ^{18}O. It is commonly assumed that the condensation of water vapour in the atmosphere occurs under equilibrium conditions. Tropospheric water vapour in the $\delta D - \delta^{18}O$ diagram should therefore be located close to the so-called Meteoric Water Line: $\delta D = 8 \times \delta^{18}O + 10$. This was indeed confirmed by Taylor's measurements (Taylor, 1972). Water vapour produced by CH_4 decomposition, however, derives its oxygen from the OH molecules and from the atmospheric oxygen. On the basis of the reaction schemes proposed for the OH production (Warneck, 1974), one might expect the $\delta^{18}O$ value of this water vapour to be similar to that of atmospheric oxygen (+23.5 $\pm$ 0.3‰—Kroopnick and Craig, 1972). On the other hand, tropospheric water vapour of $\delta D = -400$‰, for example, should have $\delta^{18}O = -52$‰. The characteristic shape of isotopic profiles in the upper troposphere may therefore be even more distinctive for ^{18}O than for deuterium.

The average profile based on Taylor's data (Fig. 7) already shows an increase of the deuterium content in the tropospheric water vapour above 4 km altitude. At present, one can only speculate on the reasons for this phenomenon. The impact of stratospheric water vapour seems to be rather doubtful in that case. However, the observed effect could be at least partially caused by the fact that Taylor did not use an ice crystal shielding filter at the inlet of the sampling device.

The presented multibox cloud model and the hypothesis on the role of methane-borne water in the upper atmosphere, give together a satisfactory explanation for the observed average vertical distribution of deuterium in atmospheric water vapour.

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