

“Amount effect” of water isotopes and quantitative analysis of post-condensation processes

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Abstract:

A numerical model is proposed that describes the interaction between raindrops and water vapour near the planetary boundary layer to explain the “amount effect”. This model relates the intensity to the isotopic composition of precipitation. The model resolves raindrop sizes, and explicitly includes: (1) the isotopic equilibration time of raindrops that is drop-size dependent; (2) raindrop transit times through the atmosphere; and (3) the evolution of the isotopic composition of vapour at various rain rates. At high rain rate, the precipitation through a layer is less equilibrated with the vapour because the isotopic equilibration time is long compared to the fast transit time, and there is a preponderance of large drops, which take longer to equilibrate. The $\delta^{18}\text{O}$ of vapour in the lower atmosphere becomes lower as a result of the interaction with these raindrops of low $\delta^{18}\text{O}$, and the degree of depletion of ^{18}O is higher when precipitation rates are high. The model reproduces time-series observations of isotopic composition of precipitation in Japan, and a vapour replenishment rate is inferred by either advection or evaporation of about 5% of the precipitation rate. The results could be the basis for a new parameterization of the isotopic equilibration for different precipitation types and rates in General Circulation Models (GCMs). When the model is applied to a GCM, this parameterization is important for places where precipitation occurs at cold temperatures ($< 15^\circ\text{C}$). Copyright © 2007 John Wiley & Sons, Ltd.

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INTRODUCTION

The ^{18}O and deuterium (D) contents of precipitation (see Gat, 1996, for a general review; here, the focus is mainly on ^{18}O) are observed to decrease with increasing monthly or annual mean precipitation in many tropical islands and monsoon climate regions (Dansgaard, 1964; Rozanski *et al.*, 1993), and with higher precipitation intensity in a single storm (Miyake *et al.*, 1968). This relationship, called the “amount effect”, has been used to estimate past storm activity derived from paleoproxies such as speleothems that record the isotopic history in precipitation (Fleitmann *et al.*, 2003).

Dansgaard (1964) presented three hypotheses to explain the amount effect. First, fractional removal of heavy isotopes in the condensate, or the initial rain within the cloud, is high during intense precipitation, leading to increasingly ^{18}O depleted vapour in the cloud layer because H_2^{18}O has slightly higher vapour pressure. This results in low $\delta^{18}\text{O}$ in the remaining vapour and ensuing condensate.

Second, isotopic equilibration with the enriched vapour below the cloud base is more complete with the small raindrops associated with light rains. Water vapour near the surface has higher $\delta^{18}\text{O}$ because of the effect of ^{18}O enriched vapour from the surface evaporation and little

condensation. Thus, small raindrops would adjust to the high $\delta^{18}\text{O}$ surface water vapour, and “forgets” the low isotopic composition at the cloud layer. This hypothesis was based on calculations by Bolin (1958). For different sizes of raindrops, Bolin (1958) calculated the time to reach isotopic equilibrium and showed that the isotopic adjustment time—the e-folding time to reach isotopic equilibrium) was about 90 s for a drop of radius 0.5 mm, during which it travelled about 370 m in the atmosphere. He pointed out that the isotopic adjustment time shortens with smaller raindrop size.

Third, there is a high relative loss of light isotopes (which results in a high $\delta^{18}\text{O}$ for raindrops) when raindrops evaporate below the cloud base in arid regions. This was confirmed in experiments by Stewart (1975), who showed that raindrops are enriched in heavy isotopes when they evaporate at low relative humidity. He also confirmed from those experiments that a raindrop has a thin boundary layer where the water vapour in that layer is in isotopic equilibrium with the raindrop even if the raindrop is evaporating at a relative humidity (RH) close to 0%.

In addition to the three hypotheses proposed by Dansgaard (1964), Rozanski *et al.* (1993) suggested that in heavy showers, the isotopic composition of the vapour, and hence of the precipitation beneath the storm cloud, decreases with time because of the continuous isotopic exchange with falling raindrops. This isotopic depletion of precipitation with time has been shown in a series of observations (Miyake *et al.*, 1968)

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Although researchers have been explaining the amount effect with the four hypotheses mentioned above, there has been little quantitative work on the subject. In this study, we quantify the factors that contribute to the amount effect and examine the relative importance of the four hypotheses. In particular, we emphasize how vapour evolution affects the isotopic composition of precipitation near the planetary boundary layer (PBL).

Here, a numerical model is proposed to quantify how precipitation rate affects the isotopic composition of the precipitation at different temperatures. The model is described in the following section, and illustrative results are presented in the third section. In the fourth section, the model is applied to the precipitation/isotopic observations made by Miyake *et al.* (1968), one of the few time series observations of the isotopic composition in precipitation available. The work is summarized in the final section.

MODEL DESCRIPTION

Consider an isothermal layer of height H and temperature T , where raindrops of various sizes and specified isotopic composition are “released” at the top of the layer, and fall through the layer. Isotopic exchange between the raindrops and ambient vapour occurs during transit of the raindrops through the layer. It is assumed that there is no horizontal advection in the layer, vapour is uniformly mixed, there is no interaction among raindrops during transit, and raindrop sizes do not change as a result of isotopic exchange.

Isotopic interaction with a raindrop

The rate of evaporation of a raindrop is governed by the rate of loss of water vapour through the molecular boundary air layer in contact with a raindrop (Stewart, 1975). As the drop falls, the isotopic exchange between the raindrop and the ambient vapour is modeled as a diffusive process, using the experimental relationship of Beard and Pruppacher (1971)

$$\frac{\partial m_i}{\partial t} = -4\pi r D_i (\rho_{i,r} - \rho_{i,\infty}) (c_1 + c_2 Re^{1/2} Sc_i^{1/3}) \quad (1)$$

where m is the mass of the isotopologue in a raindrop of radius r . The subscript i (16 or 18) denotes $H_2^{16}O$ and $H_2^{18}O$, respectively. $\rho_{i,r}$ and $\rho_{i,\infty}$ are the density of the $H_2^{16}O$ or $H_2^{18}O$ vapour at the boundary of the raindrop and of the surrounding air, respectively. D_i is the diffusivity of $H_2^{16}O$ or $H_2^{18}O$ in air, Re is the Reynolds number, Sc is the Schmidt number, and the parameters c_1 and c_2 are empirical functions of Re (Beard and Pruppacher, 1971). Isotopic equilibrium is maintained between the molecular boundary layer of the raindrop and the raindrop (Stewart, 1975), so that the isotopic composition of the vapour in the boundary layer is given by the equilibrium fractionation coefficient:

$$\alpha = \frac{R_{liquid}}{R_{vapour}} \quad (2)$$

Here, R_{liquid} ($=\gamma m_{18}/m_{16}$) is the number ratio of $H_2^{18}O$ to $H_2^{16}O$ in the raindrop, R_{vapour} ($=\gamma \rho_{18}/\rho_{16}$) is that for the vapour and $\gamma = 20/18$ is the ratio of the molecular weights of water molecules containing either ^{18}O or ^{16}O . The temperature-dependent equilibrium fractionation factor, $\alpha(T)$, is taken from Majoube (1971).

At 100% RH, the equation reduces to $\rho_{16,r} = \rho_{16,\infty}$. The isotopic equilibration time can be derived from Equation (2) and with, $m_{16} = \rho_l (4/3\pi r^3)$, and Equation (3):

$$m_{18,eqm} - m_{18} = (m_{18,eqm} - m_{18,0}) \exp(-t/\tau_a) \quad (3)$$

where $m_{18,0}$ and m_{18} are the initial mass and instantaneous mass of $H_2^{18}O$ in the raindrop at time t , respectively; ρ_l is the density of the raindrop, $m_{18,eqm}$ is the mass of $H_2^{18}O$ in the raindrop that is in isotopic equilibrium with the surrounding vapour. The e-folding time, τ_a , to reach isotopic equilibrium is given as (cf. Bolin, 1958):

$$\tau_a = \frac{\alpha r^2 \rho_l R_v T}{3 D_{18} e_s} (c_1 + c_2 Re^{1/2} Sc_{18}^{1/3}) \quad (4)$$

Here, R_v is the gas constant for water vapour, and e_s is the saturation vapour pressure of the water vapour at temperature T .

The transit time τ_H of the raindrop through the layer is given by $\tau_H(r) = H/v(r)$, where $v(r)$ is the size-dependent falling velocity of a raindrop (Beard and Pruppacher, 1969).

Isotopic interaction with precipitation

The raindrops are integrated using a size distribution for precipitation rates to yield the isotopic composition of precipitation. The size distribution of the number of raindrops $N(r; ppt)$ for a given precipitation rate ppt is described by the Marshall–Palmer distribution (Marshall and Palmer, 1948), an empirical relationship determined in Ottawa, Canada during the summer. $N(r; ppt)$ is an approximate negative-exponential for $r > 0.5$ mm, and has been demonstrated to apply widely (Rogers and Yau, 1989). The Marshall–Palmer number distribution was converted to a mass distribution $M(r; ppt)$ that is collected on the ground for different precipitation rates:

$$M(r; ppt) = \frac{N(r; ppt) \cdot (4/3\pi r^3) \cdot \rho_l \cdot v(r)}{\sum_r N(r; ppt) \cdot (4/3\pi r^3) \cdot \rho_l \cdot v(r)} \times ppt \quad (5)$$

This is illustrated in Figure 1. As precipitation rate increases, the total mass of raindrops in each size bin increases, and the peak of the mass distribution shifts to a larger radius. Raindrops are released at the top of the layer at every Δt , and the drops are tracked as they fall and interact with, and modify the vapour. Precipitation is defined as the mass of raindrops reaching the surface.

The isotopic composition of falling raindrops and the surrounding vapour is calculated with r ranging from 0.2 mm to 3 mm with an increment of 0.2 mm, and a time step of 0.02 s. The initial isotopic composition of

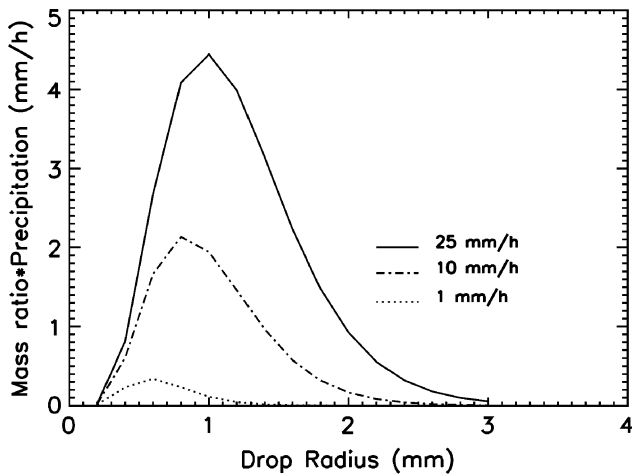


Figure 1. Mass ratio collected on the ground between 0.2 mm radius bin multiplied by the precipitation rate (cf. Equation (5)). The mass in each bin increases as precipitation rate increases and the radius peak where the ratio is maximum also increases with precipitation rate

the vapour is specified in such a way that the vapour is in equilibrium with ocean water of 0‰. The isotope composition of the vapour would be $-9.7‰$ at 20°C and $-11.6‰$ at 0°C . Raindrops with different $\delta^{18}\text{O}$ values exchange isotopes with the vapour as they fall through the layer, thus altering the isotopic composition of the vapour. $\delta^{18}\text{O}$ values are calculated for raindrops in each radius bin, and the isotopic composition of the vapour and precipitation are then calculated.

Uniform precipitation rates ppt are assumed, and the notation $\delta^{18}\text{O}_v$, $\delta^{18}\text{O}_r$ and $\delta^{18}\text{O}_{ppt}$ are used for the $\delta^{18}\text{O}$ s of vapour, raindrop and precipitation, respectively. For a specified precipitation rate, initial $\delta^{18}\text{O}_r$ is assumed to be the same for all r . $\delta^{18}\text{O}_{ppt}$ is the number weighted average of the $\delta^{18}\text{O}_r$ after transit through the layer.

Application to a General Circulation Model (GCM)

The equilibration model was applied to a GCM, and the effect of having specific equilibration will be discussed later. A water isotope module was developed using the National Center for Atmospheric Research (NCAR) Community Atmospheric Model version 2 (CAM2) at T42 resolution (approximately $2.815^\circ \times 2.815^\circ$). The vertical grid has 26 levels from the surface up to 2 hPa. Model details are documented in Collins *et al.* (2002). The model is forced by observed climatological monthly mean sea surface temperatures (Collins *et al.*, 2005).

The way water isotopes were incorporated into CAM2 is similar to that in previous model studies (Jouzel *et al.*, 1987; Hoffmann *et al.*, 1998; Mathieu *et al.*, 2002), with fractionation associated with evaporation at the surface as well as with cloud processes. For the kinetic fractionation associated with surface fluxes, the kinetic fractionation factor and sub-cloud relative humidity values proposed by Mathieu *et al.* (2002) were used. The details of the model are described in Lee (2005) and Lee *et al.* (2007).

We conducted two experiment runs: one with specified equilibration depending on precipitation rate and temperature (variable equilibration run), and the other

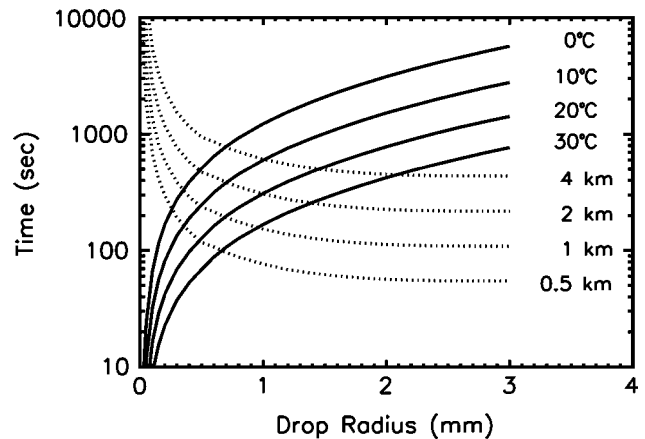


Figure 2. Time required for a spherical raindrop to reach 95% equilibrium with the surrounding water vapour at each temperature (solid lines) and residence time of the raindrop for 0.5, 1, 2, and 4 km layer (dotted lines)

with traditional 95, 45% equilibration (fixed equilibration run) for precipitation from stratiform and convective clouds, respectively (Hoffmann *et al.*, 1998). The interaction between precipitation and the surrounding vapour was parameterized as detailed earlier. The experiments were run for 20 years and, the last 10-year mean was analysed. The model can simulate water isotope ratios very similar to the observations including global meteoric water line (Lee *et al.*, 2007).

RESULTS AND DISCUSSION

Isotopic Equilibration of a Raindrop (100% RH)

Figure 2 shows, as a function of raindrop size, the time required for a single raindrop to reach 95% equilibrium ($3\tau_a$) and the transit times τ_H for different layer thicknesses $H = 0.5, 1, 2, 4$ km. Note that τ_a is independent of the initial δ_r of the raindrops (cf. Equation (4)). A typical raindrop ($r \sim 0.5$ mm) takes about 4 min to reach isotopic equilibrium. Because this equilibration time is three times the adjustment time, the result is comparable to Bolin's estimate of 90 s for τ_a (Bolin, 1958) with large differences only for raindrops smaller than 0.2 mm. A longer equilibration time is required at low temperatures and for large raindrops because of the slower diffusion per unit volume. In 4 min, a 0.5 mm raindrop travels about 1 km, altering and integrating information about the $\delta^{18}\text{O}_v$ throughout.

Isotopic Equilibration of Precipitation

A high precipitation rate implies large raindrops and numerous raindrops interacting with the vapour, significantly lowering the isotopic composition of the vapour and the ensuing raindrops. $\delta^{18}\text{O}_r$ at the top of the layer was initialized at $-10‰$, out of equilibrium with the vapour. Figure 3a shows, for different precipitation rates, the temporal evolution of $\delta^{18}\text{O}_{ppt}$ and δ_v for $H = 1$ km. As expected, $\delta^{18}\text{O}_v$ becomes more depleted as precipitation persists, and heavy rain accentuates the depletion, and in turn, $\delta^{18}\text{O}_{ppt}$ decreases with time as raindrops

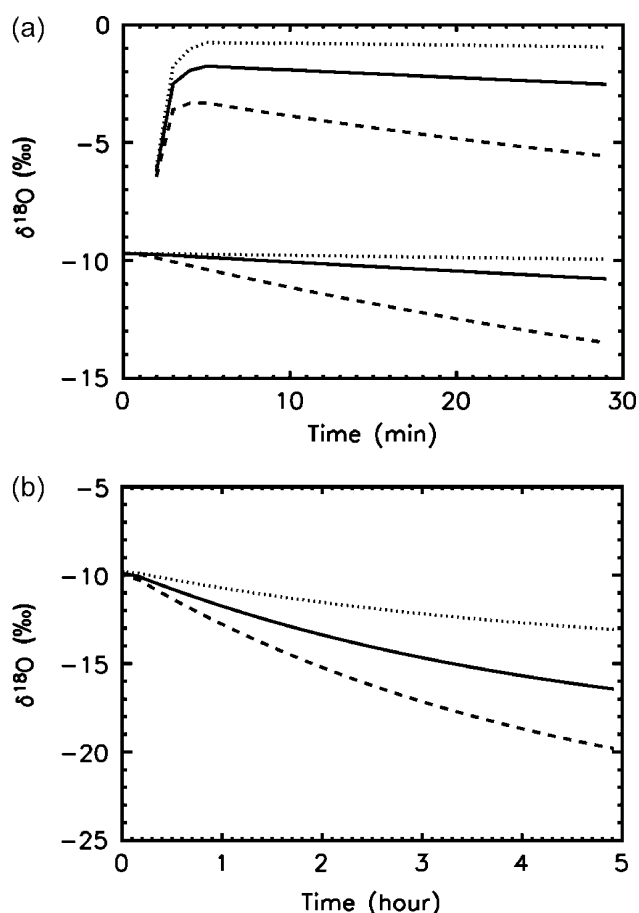


Figure 3. (a) Evolution of the isotope composition for precipitation ($\delta^{18}\text{O}_{ppt}$) (upper three lines) and surrounding water vapour (lower three lines) in 1 km layer at 20°C, 100% relative humidity, and three precipitation rates (dotted line for 1 mm h⁻¹, solid line for 5 mm h⁻¹, and dashed line for 25 mm h⁻¹). (b) Depletion of vapour ($\delta^{18}\text{O}_v$) in 1 km layer with three different initial compositions of raindrops ($\delta^{18}\text{O}_{ppt}$) (dotted line for -5‰, solid line for -10‰, and dashed line for -15‰) at 20°C, 5 mm h⁻¹ precipitation rate

interact with the increasingly depleted vapour. In the first few minutes of rainfall, $\delta^{18}\text{O}_{ppt}$ is low because large raindrops, which retain information about the initial $\delta^{18}\text{O}_r$, reach the surface first. The marked difference in $\delta^{18}\text{O}_{ppt}$ at different precipitation rates in the early stages of a storm is not related to $\delta^{18}\text{O}_v$ differences, but is due to differences in drop size distribution, transit times and equilibration times. For example, at 5 min, a 2.5‰ $\delta^{18}\text{O}_{ppt}$ difference is found between ppt of 1 mm h⁻¹ and 25 mm h⁻¹, whereas the difference in $\delta^{18}\text{O}_v$ is only about 1‰ for the same rain rates (Figure 3a). At 30 min, the difference in $\delta^{18}\text{O}_{ppt}$ between 1 mm h⁻¹ and 25 mm h⁻¹ increases to about 4‰ (Figure 3a), with the increase coming from differences in the degree of vapour depletion of ¹⁸O.

The sensitivity of $\delta^{18}\text{O}_v$ to initial values of $\delta^{18}\text{O}_r$ is plotted in Figure 3b for the same 1 km layer. With ppt of 5 mm h⁻¹ and $T = 20^\circ\text{C}$, the $\delta^{18}\text{O}_v$ difference among three different initial $\delta^{18}\text{O}_r$ increases as precipitation persists. As can be seen in Equation (3), the isotopic exchange is proportional to the difference between the initial and the equilibrium isotopic composition of the raindrop. If the initial $\delta^{18}\text{O}_r$ at the top of the layer is low

Table I. Degree of equilibration (%) for different thicknesses (m) of the atmosphere at four temperatures (30, 20, 10 and 0°C) and three precipitation rates (1, 5, 25 mm h⁻¹)

T (°C)	Rain rate (mm h ⁻¹)	500 m	1000 m
30	1	89.4	96.8
30	5	76.4	89.8
30	25	59.8	77.8
20	1	78.1	90.7
20	5	61.2	78.5
20	25	43.9	62.3
10	1	62.1	79.1
10	5	44.2	62.4
10	25	29.1	45.1
0	1	43.8	61.8
0	5	28.4	44.0
0	25	17.3	29.0

because the layer above has a high rain rate and/or low temperature, the vapour in the layer—and the ensuing raindrops at the base of the layer (cf. Equation (3))—will be more depleted in heavy isotopes. Thus, the degree of equilibration at each layer determines the isotopic composition of the subsequent vapour and precipitation.

Given τ_a and τ_H , we calculate the degree of equilibration (E ; cf. Equation (3)):

$$E = \frac{m_{18,eqm} - m_{18}}{m_{18,eqm} - m_{18,0}}$$

E at the base of the layer is shown in Table I for different temperatures, precipitation rates and layer thicknesses. At high temperature and low precipitation rate (e.g. 30°C and 1 mm h⁻¹), raindrops are almost completely equilibrated ($E = 97\%$) in the planetary boundary layer (PBL ~ 1 km). With high E , the $\delta^{18}\text{O}_{ppt}$ can be determined directly from the temperature and $\delta^{18}\text{O}_v$ in the PBL. In the PBL, isotopic equilibration decreases with increasing rain-rate and decreasing temperature: for a 5 mm h⁻¹ rain rate, the precipitation is 90% equilibrated with the vapour at 30°C, but only 62% at 10°C.

At low temperatures, a large degree of disequilibrium within the PBL is found even from moderate rain rates such as winter precipitation for maritime stratus (10°C, 5 mm h⁻¹). At 0°C and 25 mm h⁻¹, precipitation is only 29% equilibrated with surrounding vapour within the PBL. Thus, $\delta^{18}\text{O}_{ppt}$ of heavy rains from cumulonimbus towers integrates the isotopic variations of vapour from far above the PBL.

Relative humidity (RH) lower than 100%

For RH lower than 100%, kinetic fractionation occurs due to the difference in the diffusivities of H₂¹⁶O and H₂¹⁸O. As diffusion of H₂¹⁶O is faster than H₂¹⁸O, $\delta^{18}\text{O}_{ppt}$ for RH < 100% is higher than that for saturation (Stewart, 1975). At lower RH, evaporation of small drops is faster than their transit time, so that drops with r smaller than 0.6 mm do not reach the bottom of the 1 km layer at 70% RH. For an initial $\delta^{18}\text{O}_r$ and $\delta^{18}\text{O}_v$ of -10 and -9.7‰, respectively, the final $\delta^{18}\text{O}_r$ of drops

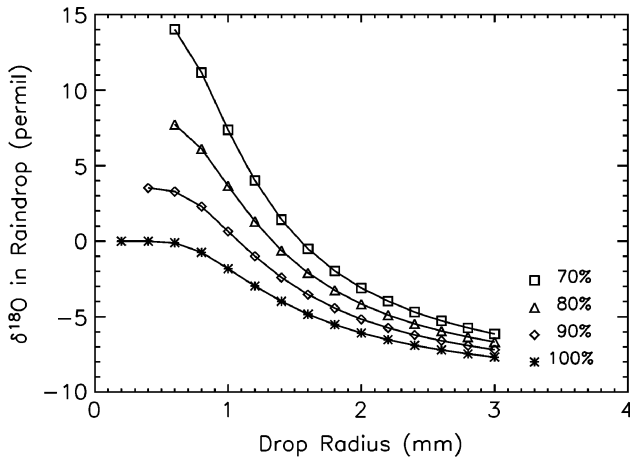


Figure 4. $\delta^{18}\text{O}$ of the raindrop on the ground for different relative humidity (70, 80, 90, and 100% relative humidity) for different raindrop size at 20°C and initial vapour $\delta^{18}\text{O}$ of -9.9‰ . Initial $\delta^{18}\text{O}$ of the raindrop is -10‰ , and missing values are for the raindrops that evaporate on the way it reaches to the ground from 1 km height

with $r = 1$ mm after 1 km is higher by 10‰ , at 70% RH than at 100% RH (Figure 4). The degree of isotopic enrichment is higher with lower relative humidity and smaller raindrop size.

NCAR GCM Results

Figure 5 shows the monthly minimum equilibration for a layer of the NCAR CAM2. NCAR GCM has 26 vertical layers, and the thickness of these layers varies from about 120 m (the lowest layer) to 1.3 km at the mid-troposphere. The layer in Figure 5 is the third layer from the surface (~ 950 hPa), and the thickness of the layer is approximately 450 m. Since Figure 5 is the monthly minimum, the mean equilibration would be higher than the values shown in Figure 5. At low latitudes, precipitation is close to 90% equilibration for stratiform clouds and more than 70% equilibration with surrounding vapour. At higher latitudes, however, the equilibration may fall to 30%. Compared to the fixed equilibration run, $\delta^{18}\text{O}_{ppt}$ is higher in low latitudes and is higher at lower in high latitudes for the variable equilibration run (Figure 6). As we expected from the equilibration values, regions where it rains in cold temperatures (southern ocean and Mediterranean climate regions) have lower $\delta^{18}\text{O}_{ppt}$.

From Figures 5 and 6, equilibration seems to be more sensitive to temperature. However, since GCM at this resolution ($\sim 2.815^\circ \times 2.815^\circ$) tends to have too many weak precipitation events and not enough intense precipitation events (Iorio *et al.*, 2004), calculated equilibration factor for precipitation from convective clouds might be too high.

APPLICATION TO OBSERVATIONS

One of the few time series measurements of the isotopic composition in precipitation is that of Miyake *et al.* (1968), who presented $\delta^{18}\text{O}_{ppt}$ through 8 h of a storm

at the top and the foot of a 720 m high mountain on Hajicho-jima Island in Japan (sample number 7 in Miyake *et al.*, 1968). The proposed model of the amount effect was tested using Miyake *et al.*'s data. It was assumed that $\delta^{18}\text{O}$ of the vapour is uniform in the 720 m layer and is in equilibrium with ocean water (0‰) at 15°C . This yields a $\delta^{18}\text{O}_v$ initial value of -10.1‰ . The $\delta^{18}\text{O}$ of the spectrum of raindrops is specified at the top of the 720 m layer to be the observed $\delta^{18}\text{O}_{ppt}$ at the top of the mountain. As information about $\delta^{18}\text{O}_v$ is not reported by Miyake *et al.* (1968), a "vapour replenishment rate" equivalent to 0, 5, or 10% of the precipitation amount was added to the model, with δ_v of the added vapour given by the initial state (-10.1‰). The replenishment rate thus represents sources of H_2^{18}O from surface evaporation or from horizontal advection. To maintain 100% RH, it was assumed that the vapour added to the box for replenishment is mixed with the vapour in the box, then the amount of vapour that is added is removed out of the box.

Figure 7 shows the observed precipitation rate, and the observed and calculated $\delta^{18}\text{O}_{ppt}$ at the foot of the mountain for different rates of replenishment. Gaps in the observed time series were filled using the mean of the adjacent values. At all replenishment rates, the model captures the general pattern of isotopic variation at the bottom of the mountain. The difference in $\delta^{18}\text{O}_{ppt}$ between the top and foot of the mountain is small at high precipitation rate (e.g., from 13:20 to 14:20) for both the modelled and observed data, as the degree of isotopic equilibration (E) is only 35% (cf. Table I) at high precipitation rates. Also, both the modelled and observed $\delta^{18}\text{O}_{ppt}$ at the bottom of the mountain becomes increasingly depleted during the same period of heavy rain since the $\delta^{18}\text{O}_v$, and therefore precipitation, is lowered as a result of high precipitation rate and low initial $\delta^{18}\text{O}_{ppt}$. In particular, the 5% replenishment case yielded $\delta^{18}\text{O}_{ppt}$ time series most similar to that observed.

There remains some uncertainty in this simple model as applied to Miyake's observations, the most important being assumptions, necessitated by the lack of information, about the temporal evolution of $\delta^{18}\text{O}_v$. We note that a $\delta^{18}\text{O}_{ppt}$ difference of 3‰ results from 0 and 10% replenishment after 8 h of rain (around at 16:00). Other uncertainties relating to the assumptions that the RH is 100% and to the assumption that $\delta^{18}\text{O}_r$ of the raindrops in the atmosphere at the height of the mountain is the same as $\delta^{18}\text{O}_{ppt}$ of the precipitation reaching the top of the mountain may not be unreasonable as the study is of a rain event in an island station.

SUMMARY

In this paper, a numerical model of the "amount effect" is proposed. The isotopic equilibration time of raindrops depends not only on drop size but also on ambient temperature. Isotopic equilibration of raindrops with the ambient vapour is incomplete if the drop-size dependent

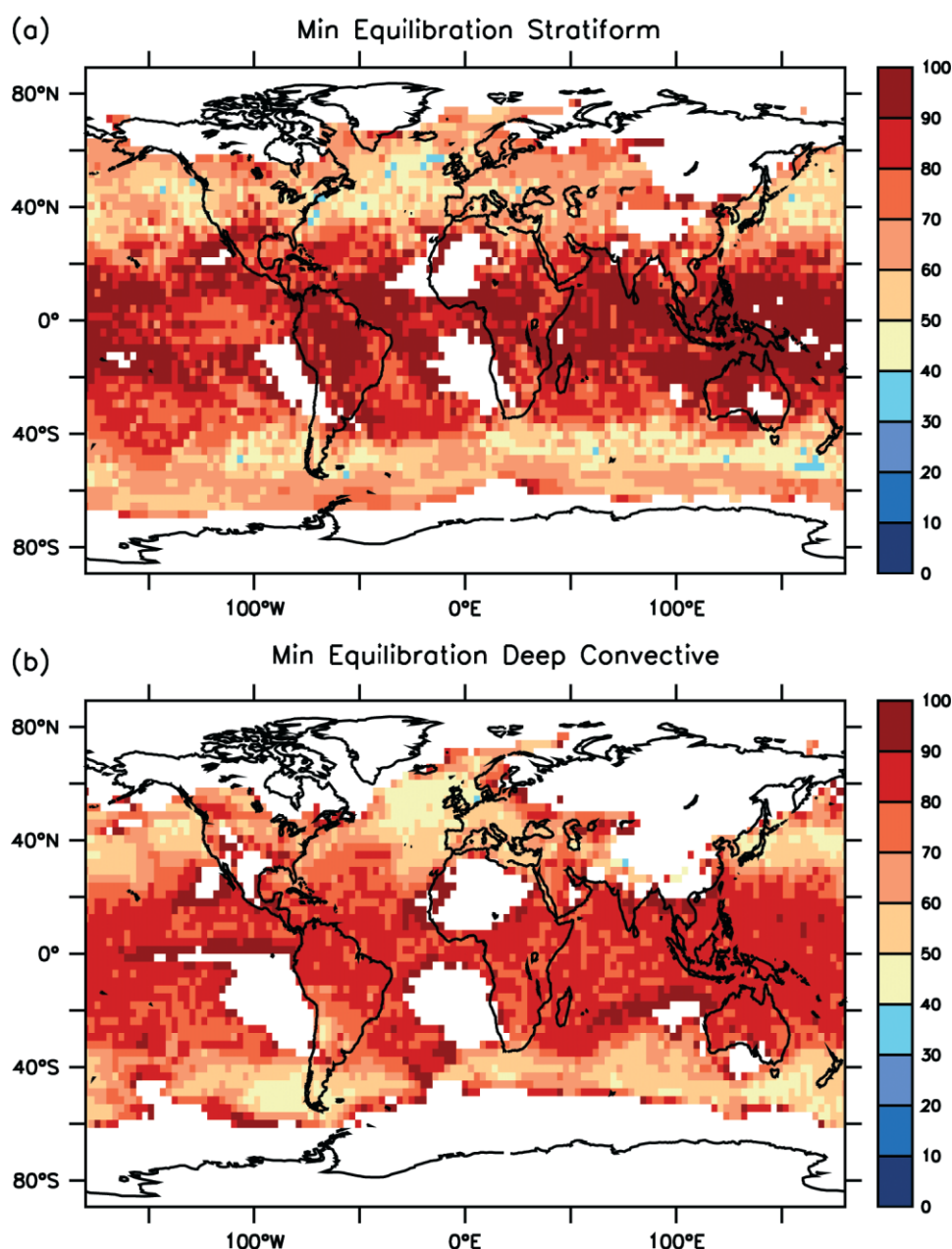


Figure 5. An example of isotopic equilibration between precipitation and surrounding water vapour from AGCM runs. Plotted values are monthly minimum for a December output at the third layer from the surface (\sim hPa), and white area is where there is no rain during the month. (a) Equilibration between precipitation from stratiform clouds and vapour, and (b) equilibration between precipitation from deep convective clouds and vapour

transit time of raindrops in a layer is shorter than the equilibration time. Large raindrops require longer equilibration time and fall faster than small raindrops, and so carry residual information of the isotopic composition of the vapour above. As the $\delta^{18}O_v$ of vapour generally decreases with height (Araguas-Araguas *et al.* 2000), the isotopic composition for large raindrops is lower than those for small raindrops at the surface. At the same time, interaction between raindrops and water vapour lowers the isotopic composition of the surrounding vapour. Although there is relatively less exchange with vapour in heavy rain, vapour below the cloud base becomes more depleted in heavy isotopes as a result of isotopic exchange with raindrops of low isotopic composition from above. This is because the total number of raindrops at all size

spectra is always high in heavy rain (Marshall–Palmer distribution). Since tropical cyclones are associated with extremely high precipitation rate, this also helps explain why the $\delta^{18}O_r$ of the rain is so low for tropical cyclones (-18 to -29‰ for Hurricane Oliva, 1994; Lawrence *et al.*, 2004) even if they are formed at low latitudes.

Surface vapour becomes depleted as a result of interaction with raindrops. This means that the surface layer of the atmosphere is not in equilibrium with seawater, especially if the area is in a region of high precipitation. Many one-dimensional models of the initial vapour source for ice cores (Dansgaard, 1964) use a surface isotopic evaporative flux that is close to the equilibrium value with seawater (Merlivat and Jouzel, 1979). Lawrence *et al.* (2004) show that the $\delta^{18}O_v$ is not in

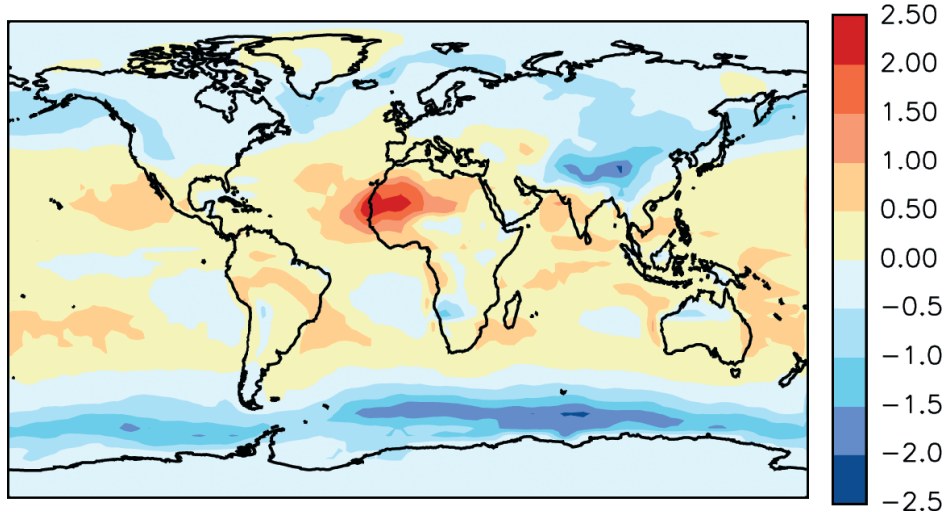


Figure 6. DJF mean difference of $\delta^{18}O_{ppt}$ from the run with the variable equilibration to fixed (95, 45%) equilibration run

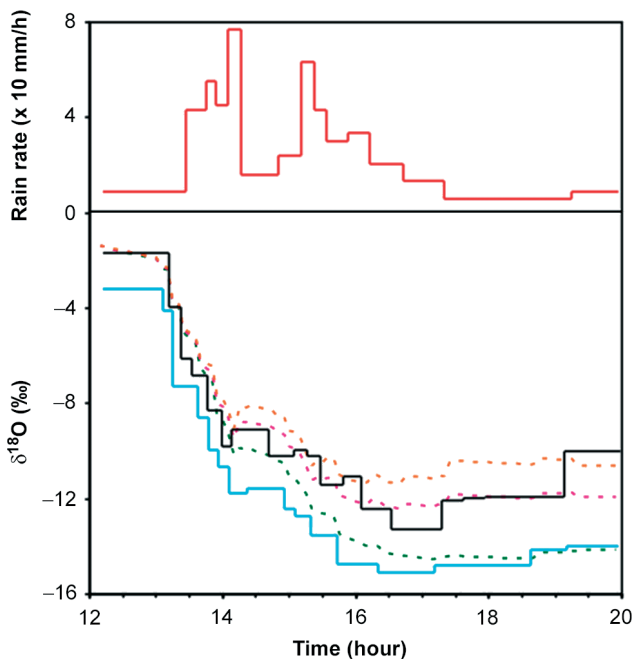


Figure 7. Top panel: Observed precipitation rate (red solid line) at the foot of the mountain in Hachijo-jima island from Miyake *et al.* (1968). Bottom panel: Observed $\delta^{18}O$ of precipitation at the top (light blue solid line) and foot (black solid line) of the mountain from Miyake *et al.* (1968) and modeled $\delta^{18}O$ at the foot of the mountain with different degrees of replenishment (green: 0%, pink: 5%, and orange: 10%)

equilibrium with ocean water over or near the sea surface in the tropics, as assumed by the Rayleigh distillation model (Dansgaard, 1964). Rather, it is slightly lower (1–2‰) than the equilibrium value during very quiescent weather, but much lower (up to 15 ‰) over stormy regions. They argue that $\delta^{18}O_v$ decreases as the precipitation intensity increases since precipitation preferentially removes heavy isotopes from the atmosphere. As Delaygue *et al.* (2000) show in their GCM results, most Antarctic moisture originates from 30°S to 60°S, a very stormy region. Thus, these results showing the disequilibrium of large raindrop sizes suggest the need for adjustment of the initial isotopic composition of vapour

in those one-dimensional models. As discussed above, the amount effect is sensitive to temperature as well as precipitation rate. At high temperature and low precipitation rate, raindrops are almost in equilibrium with the vapour in the planetary boundary layer. However, raindrops can carry isotopic information from a height of up to 8 km at low temperature and high precipitation rate. It is also emphasized that the isotopic composition of raindrops above the PBL is important for determining the subsequent isotopic composition of the vapour in the PBL. In some isotope GCMs, the percentage of equilibration is prescribed as 45% for the precipitation from convective clouds and 95% for precipitation from non-convective clouds (Hoffmann *et al.*, 1998). In particular, since a GCM has several vertical layers, and the thickness of these layers varies from about 120 m to 1.4 km (e.g. NCAR CAM 3), a fixed equilibration degree could be misleading. For example, precipitation from stratiform clouds at low temperature—such as a north-western coast of North America winter storm—will be less than 70% equilibrated with the boundary layer vapour. A 45% equilibration may be too small for moderate convective precipitation, especially at high temperatures. At the same time, it may be too large for very heavy precipitation. GCM results show that 95% equilibration is too high for precipitation at cold temperature-southern ocean and Mediterranean climate regions—and 45% may be too low for tropical convective precipitation.

Another factor that explains the amount effect is the low isotopic composition of vapour—and condensate in turn—at the high condensation rate associated with deep convection as a result of preferential condensation of heavy isotopes. As shown in Figure 3b, a low initial $\delta^{18}O$ results in a high rate of isotopic exchange. This will lower the isotopic composition of vapour and also the following raindrops.

When relative humidity is lower than 100%, raindrops will be more enriched in heavier isotopes since the diffusivity of $H_2^{16}O$ is greater than $H_2^{18}O$ as Stewart

showed (1970). Thus, relative humidity during precipitation is very important in determining whether the raindrop experiences equilibrium or kinetic fractionation. This effect is larger for small raindrops at low relative humidity.

For simplicity of simulation and interpretation, many atmospheric environmental factors were simplified for the model. Usually there is convergence and uplift of the air at the precipitation site, so the assumption that the layer is closed is not realistic. Also, a 1 km atmospheric layer cannot be well-mixed every 0.2 s. When raindrops fall through the air layer, there is coalescence between raindrops so raindrops cannot remain as they were at the top of the layer. The simplifications in the model affect the results; nonetheless, the model elucidates the underlying mechanism leading to the observed amount effect.

The quantitative evolution of the isotopic composition in vapour is also shown: when the difference of initial and equilibrium state $\delta^{18}\text{O}$ is about 10‰, there is approximately 1‰ depletion of vapour after 30 min of isotopic interaction at a typical mid-latitude rain rate of 5 mm h^{-1} . The model, when applied to the observations of Miyake *et al.* (1968), suggests a rate of vapour replenishment by either convergence or evaporation of about 5% of the precipitation. Since raindrops integrate isotopic composition of vapour from above, knowledge of the vertical isotopic profile of water vapour is crucial for understanding the isotopic composition of precipitation at the surface. The formulation presented here could be the basis for parameterizing the isotopic equilibration factors in GCMs.

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