**Atmospheric
Chemistry
and Physics
Discussions**

Stable water isotopologue ratios in fog and cloud droplets are not size-dependent

J. K. Spiegel[1], F. Aemisegger[2], M. Scholl[3], F. G. Wienhold[2], J. L. Collett Jr.[4], T. Lee[4], D. van Pinxteren[5], S. Mertes[5], A. Tilgner[5], H. Herrmann[5], R. A. Werner[1], N. Buchmann[1], and W. Eugster[1]

[1]Institute of Agricultural Sciences, ETH Zurich, Zurich, Switzerland
[2]Institute for Atmospheric and Climate Science, ETH Zurich, Zurich, Switzerland
[3]US Geological Survey, Reston, VA, USA
[4]Department of Atmospheric Science, Colorado State University, Fort Collins, Colorado, USA
[5]Leibniz Institute for Tropospheric Research, Leipzig, Germany

Stable water isotopologue ratios in cloud droplets are not size-dependent

J. K. Spiegel et al.

Title Page

Abstract	Introduction
Conclusions	References
Tables	Figures

◄◄ ►►

◄ ►

Back Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Stable water isotopologue ratios in cloud droplets are not size-dependent

J. K. Spiegel et al.

Abstract

In this work, we present the first observations of stable water isotopologue ratios in cloud droplets of different sizes collected simultaneously. We address the question whether the isotope ratio of droplets in a cloud varies as a function of droplet size. Sam-
ples were collected from a ground intercepted cloud (=fog) during the Hill Cap Cloud Thuringia 2010 campaign (HCCT-2010) using a three-stage Caltech Active Strand Cloud water Collector (CASCC). An instrument test revealed that no artificial isotopic fractionation occurs during sample collection with the CASCC. Furthermore, we could experimentally confirm the hypothesis that the δ values of cloud droplets of the rele-
vant droplet sizes (µm-range) were not significantly different and thus can be assumed to be in isotopic equilibrium immediately with the surrounding water vapor. However, at the dissolution period of the cloud differences in isotope ratios of the different droplet sizes tended to be larger. This is likely to result from the cloud's heterogeneity, implying that larger and smaller cloud droplets have been collected at different moments in time,
delivering isotope ratios from different collection times.

1 Introduction

In order to use stable water isotopologues ($^1H_2^{16}O$, $^1H^2H^{16}O$, and $^1H_2^{18}O$) as a tool to assess paleoclimatical (e.g. Dansgaard et al., 1993; Petit et al., 1999), ecological (e.g. Yakir and Sternberg, 2000; Farquhar et al., 2007) and hydrological questions (e.g. Dansgaard, 1964), a quantitative understanding of processes involving stable water isotopologues in the hydrosphere is needed. Important mechanisms herein are cloud and precipitation formation (Jouzel, 1986). Cloud modeling is one way to gain insights into these processes (Jouzel, 1986). In recent years, modeling efforts focused on the explanation of observed trends of isotope ratios in precipitation, both on a local and a global scale (Lee and Fung, 2007; Risi et al., 2008), aiming for a better understanding

of e.g. the "amount effect". This effect describes the on-going depletion of precipitation water in heavy isotopologues with increasing rain intensity.

An important assumption used in cloud models is that the cloud droplets are in isotopic equilibrium with the surrounding water vapor, leading to cloud droplets which do not differ in isotope ratios for different droplet sizes (Jouzel, 1986). This assumption was first presented by Bolin (1958) who carried out a theoretical analysis of tritium isotope exchange between single freely falling rain droplets and their environment, based on the laboratory work by Kinzer and Gunn (1951). Additionally, laboratory studies of the isotopic exchange rate of single falling droplets (Friedman et al., 1962; Booker, 1964; Stewart, 1975) further strengthened Bolin's work. Based on a theoretical framework, Jouzel et al. (1975) demonstrated that a cloud droplet with radius less than 30 µm could be considered to be in isotopic equilibrium with water vapor independent of the cloud conditions. However, to our knowledge, no measurements in clouds or fog have been carried out so far to confirm that the results from single falling droplets can be applied to an ensemble of cloud droplets with multiple and more complex interactions, and that droplets do not differ in isotope ratio for different sizes. Due to different inertia, droplets of different sizes are affected differently by cloud dynamics: larger droplets settle faster, while smaller droplets might be transported higher in the cloud (Gedzelman and Arnold, 1994). Thus, different droplet sizes could carry isotopic information from different locations in the cloud. Moreover, as the equilibrium vapor pressure increases with increasing curvatures, larger droplets slowly grow at the expense of smaller ones and might therefore have longer life times, which could additionally influence the isotope ratio of the droplets.

In this study, we present the first experimental evidence that there is no difference in isotope ratios for different droplet sizes in hill cap clouds. The work is structured as follows. First, we present the measurement site and the sampling method, followed by the model of a single isolated cloud droplet. Then, the results are presented and discussed, conclusions are drawn, and recommendations are given for future cloud water sampling for isotope ratio analysis.

2 Materials and Methods

2.1 Measurement site and HCCT-2010 field experiment

Cloud data were gathered during the Hill Cap Cloud Thuringia 2010 (HCCT-2010) field campaign, which took place close to the summit of Schmücke (50°39′N, 10°46′E, 937 m a.s.l, Germany) in September and October 2010. In total, cloud samples from 13 different cloud events (presented in more detail in Spiegel et al., 2012) were collected using a three-stage Caltech Active Strand Cloud water Collector (CASCC, Sect. 2.2).

From a meteorological point of view the cloud that was probed at Schmücke should be called fog – as fog is a cloud that touches the ground (Pruppacher and Klett, 1997). However, from a process based point of view, the microphysical processes within the cloud do not change at the moment when an advected cloud touches the ground. We therefore use the terms fog and cloud interchangeably throughout this work. In addition to the collection of cloud water samples, other cloud properties were monitored as well in the framework of the HCCT-2010 campaign. In this work, we use the liquid water content (LWC) and the effective radius (R_{eff}). LWC is the sum of the volumes of cloud droplets per unit air volume, and R_{eff} is defined as the radius yielding the same volume to surface ratio as the ambient cloud droplet size distribution. LWC and R_{eff} were measured with a Particulate Volume Monitor (PVM-100, Gerber Scientific, USA) which determines the LWC via light scattering by the present droplets (Gerber, 1991; Arends et al., 1994). As the total surface of the droplets is also measured by the PVM-100, the R_{eff} (which is the LWC divided by the total surface) of the cloud droplets can be retrieved.

2.2 Collection of cloud water samples

In order to obtain size resolved cloud water samples a three-stage CASCC was used, mounted on a tower 20 m above ground (see Fig. 1). The three-stage CASCC is a modified version of the size-fractionating CASCC designed for the collection of cloud

droplets in two size fractions (Demoz et al., 1996). The working principle is as follows. Cloud droplets are drawn by a fan through a duct, and are collected by means of impaction. For increasing particle size their inertia decreases the ability to follow the gas stream line. By introducing obstacles into the flow, droplets of a certain size – corresponding to the obstacle morphology – can be inertially collected from the air flow (Demoz et al., 1996). In the three-stage CASCC, stages one to three consist of banks of Teflon rods of three different sizes which are used as impaction obstacles. The rods are inclined, allowing the collected fog water to flow into a Teflon sample trough (one per stage) then through a Teflon tube into a closed polyethylene collection bottle (one per stage). The larger the diameter of the rods, the larger the collected droplets are at the particular stage. We ran the CASCC with a volume flow of $19\,\mathrm{m^3\,min^{-1}}$, leading to 50 % size cuts (modeling result) at approximately 22, 16 and 4 µm droplet diameter for stages one, two and three, respectively (Raja et al., 2008).

As droplets collected on adjacent stages overlap in size, measured composition differences are somewhat conservative estimates of actual differences in composition versus droplet size. The size of the largest droplets capable of entering the CASCC and being collected in the first stage depends on the ambient wind conditions and is estimated to be in the range of 100 µm, well above the volume mode of typical cloud droplet size distributions. When rain was expected, we deployed the collector with a downward facing inlet to inhibit raindrops entering the CASCC.

Sampling times varied between 1 to 3 h per cloud sample depending on the cloud conditions. Then the polyethylene bottles were detached from the sampler and the cloud water for isotope ratio analysis was immediately filled into glass vials (1.5 ml) that were closed to inhibit additional evaporation which might change the isotope ratio. Additionally, during the campaign, six test samples for isotopic fractionation were collected (later on referred to as DI-samples), by spraying deionized water (DI; with known δ value) into the cleaned sampler using a commercially available spraying bottle. The procedure lasted around 30 min until each of the sampling bottles was filled with approximately 250 ml. To ensure saturated conditions inside the CASCC during

the collection of these samples, the fan was turned off. Different CASCC versions have frequently been used for the collection of cloud water for chemical analysis (e.g. Moore et al., 2004a,b; Collett Jr. et al., 2008; Kaul et al., 2011). One-stage CASCCs have already been used for isotope ratio analysis (Schmid et al., 2010) and MiniCASCCs have been recommended as an appropriate tool for sample collection for isotope ratio analysis (Michna et al., 2007; Scholl et al., 2011). As cloudy air is slightly supersaturated, we expect equilibrium isotopic fractionation to dominate. The saturated conditions persist within the CASCC and we therefore assume that no additional isotopic fractionation occurs during sampling. Consequently, the cloud water within the collection bottle represents the average δ value for the collection time of each stage.

2.3 Stable water isotopologue analyses

Each cloud sample consisted of three vials each from one stage of the CASCC. The cloud water was analysed for δ^2H and δ^{18}O values using the high-temperature carbon reduction method by coupling a high-temperature elemental analyser (TC/EA; Finnigan MAT, Bremen, Germany) to a Delta^{plus}XP isotope ratio mass spectrometer (IRMS) via a ConFlo III interface (both Finnigan MAT). The measurement set-up of the carbon reduction tube followed the "MPI-BGC method" (see Gehre et al., 2004, for details). Hydrogen and oxygen ratios R_{sample} (^{2}H^{1}H and ^{18}O^{16}O) were expressed as $10^3 \times \delta^2$H and $10^3 \times \delta^{18}$O (in this text we use the ‰ sign behind the numbers in order to improve readability) in relation to the Vienna Standard Mean Ocean Water ($R_{V\text{-SMOW}}$) normalized such that the SLAP (=Standard Light Antarctic Precipitation) reference water was -55.5‰ for δ^{18}O and -428‰ for δ^2H (Coplen, 1988, 2011):

$$\delta = \frac{R_{sample}}{R_{V\text{-SMOW}}} - 1. \tag{1}$$

The precision of this measurement was assessed by measuring a quality control lab standard water (WP-0503-Z0010B, once in an analytical measurement sequence which

comprises 60 samples), resulting in an uncertainty of 0.3 δ units and 0.04 δ units (peak-jump) over all measurements for δ^2H and δ^{18}O, respectively. Each vial was measured three times. Reported δ values are the mean values of these three measurements including standard error.

2.4 Isotopic equilibration time of a motionless droplet

In this section, we present the simplified model for a motionless droplet in order to deduce a theoretical estimate for the isotopic equilibration time of a cloud droplet. In contrast to earlier studies treating mostly larger rain droplets (e.g. Friedman et al., 1962; Jouzel, 1986; Lee and Fung, 2007), we chose the model of the motionless droplet, as settling velocities of cloud droplets are small (from 3.5×10^{-5} m s^{-1} to 0.07 m s^{-1} for droplets of 1 to 50 µm in diameter according to Seinfeld and Pandis (2006)) and thus ventilation effects that affect the mass transfer can be ignored. Due to the high diffusion coefficients within water, individual rain and cloud droplets can be considered to be isotopically homogeneous (Jouzel, 1986). Cloud droplets grow and shrink via the exchange of mass with the surrounding (saturated) vapor by a diffusion in air. Considering a motionless cloud droplet the rate of change of droplet, mass is given by Pruppacher and Klett (1997):

$$\frac{\partial m_i}{\partial t} = 4 \pi r D_i \left(\rho_{i,r} - \rho_{i,\infty} \right), \tag{2}$$

where m_i is the mass of the isotopologue in a cloud droplet with radius r and with i standing either for ^{1}H$_2$^{16}O, ^{1}H^{2}H^{16}O, and ^{1}H$_2$^{18}O, respectively. D_i are the diffusivities for the different isotopologues (for this study we took diffusivity values from Cappa et al., 2003), and $\rho_{i,r}$ and $\rho_{i,\infty}$ are the vapor densities of the isotopologues i at the droplet surface (r) and the surrounding air (∞), respectively. Equation (2) is valid for droplets larger than the mean free path λ of air molecules which is 0.0651 µm at 1 atm and 298 K according to Seinfeld and Pandis (2006). Non-continuum effects of very small cloud droplets are not considered, as the contribution of these cloud droplets to the collected

cloud water is small due to their small volume. The equilibrium isotopic fractionation coefficient α_k (here we use equations presented by Criss, 1999, to calculate α_k, with k standing either for $^1H^2H^{16}O$, and $^1H_2^{18}O$) for the phase change from liquid to vapor is defined as:

$$\alpha_k = \frac{R_{c,k}}{R_{v,k}} = \frac{\frac{m_k}{m_{16}}}{\frac{\rho_k}{\rho_{16}}}, \tag{3}$$

with $R_{c,k}$ denoting the corresponding isotope ratio in the condensed phase and $R_{v,k}$ being the isotope ratio in the vapor phase for the isotopologue k. Using Eq. (3), the ideal gas equation ($\rho_{16} = \frac{e_w}{R_{vw}T}$), and $m_{16} = 4/3\,r^3\pi$, the solution for Eq. (2) is:

$$m_{eq,k} - m_k(t) = \left(m_{eq,k} - m_k(0)\right)\exp(-t/\tau_k). \tag{4}$$

where $m_k(t)$ and $m_k(0)$ are the mass of isotopologue k in the droplet at the time t and $t = 0$, respectively, and $m_{eq,k}$ is the mass of isotopologue k in the droplet when the droplet is in isotopic equilibrium with the surrounding vapor. τ_k is the e-folding time, which is the time interval in which $m_{eq,k} - m_k(t)$ decreased by a factor e in comparison to the initial difference $m_{eq,k} - m_k(0)$:

$$\tau_k = \frac{\alpha_k\,r^2\,\rho_l\,R_{wv}\,T}{3D_k\,e_w}, \tag{5}$$

where $R_{wv} = 461.5$ J kg^{-1} K^{-1} is the gas constant for water vapor and e_w is the saturation vapor pressure of water vapor at temperature T in (K). Using the e-folding time τ_k (Eq. 5), the time required to reach 99 % ($t_{99} = 4.5 \times \tau_k$) of isotopic equilibrium with the surrounding air is reported in the subsequent section.

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

|◄ | ►|

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

3 Results and Discussion

3.1 Equilibration times for droplet sizes in fog and clouds

For temperature and air pressure conditions found during HCCT-2010, the isotopic equilibration time t_{99} is less than 30 s for all relevant droplet sizes in fog and smallest for the smallest droplet diameters that were sampled (Fig. 2). The calculated value of t_{99} decreased slightly with temperature and was smaller for $^1H_2^{18}O$ than for $^1H^2H^{16}O$ (as $\alpha_{^1H^2H^{16}O} > \alpha_{^1H_2^{18}O}$ for this temperature range and $D_{^1H^2H^{16}O} > D_{^1H_2^{18}O}$). However, these t_{99} values were calculated for a single motionless droplet. Extending the analysis from one single droplet to an ensemble of droplets has been discussed by Jouzel et al. (1975) who came to the conclusion that this step would reduce the equilibration time, as the droplets also grow due to collision and coalescence. In summary, this implies that cloud droplets are in principle almost instantaneously in isotopic equilibrium with the surrounding water vapor. Based on these equilibration times, we do not expect that differences in δ values among droplet sizes can be measured with the conventional CASCC sampling technique, as the sampling intervals of 1 to 3 h were much larger than the equilibration times.

3.2 Collector performance

Six DI-samples have been collected and analyzed for isotope ratio. A two-way ANOVA with the factors collection time (Time) and size stages (Size, Table 1) revealed that there was no significant difference in δ values between the deionized water ($\delta^2H_{DI} = -63.2 \pm 0.76$ ‰ and $\delta^{18}O_{DI} = -9.63 \pm 0.05$ ‰) and the DI-samples, independent of the ambient meteorological conditions. This agrees with the findings from Sect. 3.1 and the assumptions made in Sect. 2.2: As the fan was turned off, the exchange of water vapor between the saturated water vapor volume inside the CASCC (which resulted from continuously spraying deionized water into the CASCC) and the non-saturated conditions outside the CASCC was small. Therefore, the isotope ratio of both water vapor

and droplets in the CASCC was mainly determined by the isotope ratio of the deionized water. As the collected water in the collection bottles did not differ significantly in isotope ratio from the deionized water used for spraying, we conclude that no isotopic fractionation occurs during sampling. Hence, the collected cloud water samples are
5   representative of the actual isotope ratio of the cloud droplets.

3.3   Hydrogen and Oxygen isotope ratios of cloud water

During HCCT-2010 cloud water was collected for isotope ratio analysis during 13 non-precipitating cloud events with temperatures >0 °C such that warm clouds only were sampled. The events lasted between 3 and 15 h, mostly at night time, resulting in 1 to 8
10   cloud samples per event, depending on the collection time per sample (1 to 3 h). Each cloud sample consisted of the three vials from the three stages of the CASCC. For the discussion of the temporal evolution of the isotope ratio during the cloud events as well as for details and the general interpretation we refer to Spiegel et al. (2012), and hence use the same numbering as in Spiegel et al. (2012).
15   In events 1, 5, 7, 8 and 12, cloud water could not be analyzed for all stages, as either the vials broke (event 7) or insufficient cloud water had been collected (events 1, 5, 7 and 12). So in total, 115 vials could be used for the following analysis.

δ values varied over the whole measurement campaign from −77‰ to −15‰ (δ^2H) and from −12.1‰ to −3.9‰ (δ^{18}O; Fig. 3) and were slightly more depleted in heavy
20   isotopologues than the δ values that have been measured in fog so far (tabulated in Scholl et al., 2011, from −71‰ to +13‰ for δ^2H and −10.4‰ to +2.7‰ for δ^{18}O). Nevertheless, the spread of our data was comparable to what has been measured before.

The variability in δ values over time was generally larger than the differences be-
25   tween the different size fractions from the fog collector (Fig. 3). Additionally, there was no clear tendency of cloud water from one size fraction being more enriched in heavy isotopologues than cloud water from the others. In order to quantitatively determine whether there was a difference between the isotope ratio for the different droplet sizes,

we carried out a two-way ANOVA for each event separately, comprising at least two samples (Table 1). As the focus of the ANOVA was on the differences between droplet sizes, we chose both the elapsed time (Time in Table 1) and the collector stage (Size in Table 1) as factors. To account for the increasing probability of type I error (rejecting the null hypothesis although it is true) due to 18 independent ANOVAs, we adjusted the significance level $\alpha = 0.05$ using the Bonferroni criterion: $\alpha_{adj} = 0.05/18 = 2.7 \times 10^{-3}$ (Legendre and Legendre, 1998). The vials taken from the different stages of the collector did not differ significantly (significance level $p < \alpha_{adj}$) in their δ^2H and δ^{18}O values. As the Bonferroni criterion often leads to a very small α_{adj}, we also used Holm's procedure (Holm, 1979) to account for multiple testing, which did not change the results.

Hence, these data are the first stable water isotopologue data for size resolved cloud droplet sampling, providing empirical evidence that there is no difference in isotope ratios for different cloud droplet sizes of the same cloud measured at the same time. Still, for most of the events, the samples differed significantly with respect to elapsed time. A detailed analysis concerning this temporal evolution is given by Spiegel et al. (2012).

3.4 Cloud dissolution

Although the two-step ANOVA showed that the differences among the stages were not significant, the maximal differences among the stages ($\Delta_{st} = \max_{i,j=1,2,3} \left(\left| \delta_i - \delta_j \right| \right)$) tended to be larger for the first and the last data points during the course of the event as well as for certain single sample events (Fig. 3). This is discussed by a more detailed investigation of the cloud sampling intervals in which Δ_{st} was above the 90-percentile both for δ^2H and δ^{18}O: the last cloud samples of event 10 and 11 (Fig. 3 and Fig. 4) as well as the sample of event 4 (only one cloud sample collected with the following δ values including standard errors for stage 1, 2, and 3: -72 ± 0.3‰, -74 ± 0.3‰, and -72 ± 0.2 (δ^2H) and -10.9 ± 0.02‰, -11.4 ± 0.03‰ and -11.0 ± 0.10‰ (δ^{18}O)). These cloud samples were collected during the dissolution period of the cloud as the LWC decreased during the sampling interval (only shown for event 11 in Fig. 5c), but still

remained above zero, indicating at least saturated sampling conditions. For event 10 and 11, the effective radius (R_{eff}) simultaneously increased, as the smaller droplets evaporate first when supersaturation decreases. For event 4, the R_{eff} varied strongly during the whole sampling interval. So it is likely that the cloud water was not collected

5 simultaneously in the different stages for these cloud samples, as not all droplet sizes were present during the whole sampling interval. For example, for event 11 the cloud water of stage 3 was probably collected at the beginning of the sampling interval, while the other two stages continued collecting cloud water until the end of the sampling interval when the smaller droplets already were evaporated. Consequently, we assume

10 that the differences in isotope ratios among the stages for these cloud samples should be considered the result of different collection times for the different size stages, which can be regarded as a collection artifact.

4 Conclusions

In this work, we present the first size-resolved measurements of stable water isotopo-

15 logue ratios in cloud droplets. Our result confirms our expectation that differences in isotope ratios measured simultaneously in three size fractions are within the analytical precision of the IRMS (Table 1). This result is independent of the isotope ratio itself and valid for the whole range of δ values of the collected samples. Our equipment analysis also verified that there is no isotopic fractionation of samples collected in a large-size

20 active-strand cloud collector (CASCC). Based on our measurements and the theory presented we therefore expect no difference in δ values of all droplet sizes in fog. Our suggestions for future studies are (1) that non-size resolved sampling of cloud droplets is adequate and representative to measure the isotope ratio of cloud droplets of all sizes, and (2) as the isotope ratio of cloud water evolves with time, it is desirable to test

25 shorter sampling intervals (e.g. 15 to 30 min) to better resolve the temporal evolution of the isotope ratio of the cloud droplets.

References

Arends, B. G., Kos, G. P. A., Maser, R., Schell, D., Wobrock, W., Winkler, P., Ogren, J. A., Noone, K. J., Hallberg, A., Svenningsson, I. B., Wiedensohler, A., Hansson, H. C., Berner, A., Solly, I., and Kruisz, C.: Microphysics of clouds at Kleiner Feldberg, J. Atmos. Chem., 19, 59–85, doi:10.1007/BF00696583, 1994. 12666

Bolin, B.: On the use of tritium as a tracer for water in nature, in: Proc. Sec. Intern. Conf. Peaceful Uses of Atomic Energy, Vol.18, pp. 336–344, International Meteorological Inst., Stockholm, Geneva, 1958. 12665

Booker, D.: Exchange between water droplets and tritiated water vapour, Q. J. R. Metorol. Soc., 91, 73–79, 1964. 12665

Cappa, C. D., Hendricks, M. B., DePaolo, D. J., and Cohen, R. C.: Isotopic fractionation of water during evaporation, J. Geophys. Res., 108, 4525, doi:10.1029/2003JD003597, 2003. 12669, 12681

Collett, Jr., J., Herckes, P., Youngster, S., and Lee, T.: Processing of atmospheric organic matter by California radiation fogs, Atmos. Res., 87, 232–241, doi:10.1016/j.atmosres.2007.11.005, 2008. 12668

Coplen, T. B.: Normalization of oxygen and hydrogen isotope data, Chem. Geol., 72, 293–297, doi:10.1016/0168-9622(88)90042-5, 1988. 12668

Coplen, T. B.: Guidelines and recommended terms for expression of stable-isotope-ratio and gas-ratio measurement results, Rapid Commun. Mass Spectrom., 25, 2538–2560, doi:10.1002/rcm.5129, 2011. 12668

Criss, R. E.: Principles of Stable Isotope Distribution, Oxford University Press, Oxford, 1999. 12670

Dansgaard, W.: Stable isotopes in precipitation, Tellus, 16, 436–468, 1964. 12664

Dansgaard, W., Johnsen, S., Clausen, H., Dahl-Jensen, D., Gundestrup, N., Hammer, C., Hvidberg, C., Steffensen, J., Sveinbjörnsdottir, A., Jouzel, J., and Bond, G.: Evidence for general instability of past climate from a 250-kyr ice-core record, Nature, 364, 218–220, 1993. 12664

Demoz, B., Collett Jr., J. L., and Daube Jr., B.: On the Caltech active strand cloudwater collectors, Atmos. Res., 41, 47–62, doi:10.1016/0169-8095(95)00044-5, 1996. 12667

Farquhar, G. D., Cernusak, L. A., and Barnes, B.: Heavy water fractionation during transpiration., Plant Physiol., 143, 11–8, doi:10.1104/pp.106.093278, 2007. 12664

Friedman, I., Machta, L., and Soller, R.: Water-vapor exchange between a water droplet and its environment, J. Geophys. Res., 57, 2761–2766, 1962. 12665, 12669

Gedzelman, S. and Arnold, R.: Modeling the isotopic composition of precipitation, J. Geophys. Res., 99, 10 455–10 471, 1994. 12665

Gehre, M., Geilmann, H., Richter, J., Werner, R., and Brand, W.: Continuous flow ^{2}H/^{1}H and and ^{18}O/^{16}O analysis of water samples with dual inlet precision, Rapid Commun. Mass Spectrom., 18, 2650–2660, 2004. 12668

Gerber, H.: Direct measurement of suspended particulate volume concentration and far-infrared extinction coefficient with a laser-diffraction instrument, Appl. Opt., 30, 4824–31, 1991. 12666

Hall, W. and Pruppacher, H.: The survival of ice particles falling from cirrus clouds in subsaturated air., Journal of Atmospheric Sciences, 33, 1995–2006, 1976. 12681

Holm, S.: A simple sequentially rejective multiple test procedure, Scand. J. Stat., 6, 65–70, 1979. 12673

Jouzel, J.: Isotopes in Clouds Physics: Multiphase and Multistage Condensation Processes, in: Handbook of Environmental Isotope Geochemistry, Volume 2, The Terrestrial Environment, B, edited by Fritz, P. and Fontes, J., chap. 2, pp. 61–112, Elsevier Science Publischer B.V, Amsterdam, 1986. 12664, 12665, 12669

Jouzel, J., Merlivat, L., and Roth, E.: Isotopic study of hail, J. Geophys. Res., 80, 5015–5030, doi:10.1029/JC080i036p05015, 1975. 12665, 12671

Kaul, D. S., Gupta, T., Tripathi, S. N., Tare, V., and Collett, J. L.: Secondary organic aerosol: a comparison between foggy and nonfoggy days., Environ. Sci. Technol., 45, 7307–13, doi:10.1021/es201081d, 2011. 12668

Kinzer, G. D. and Gunn, R.: The evaporation, temperature and thermal relaxation-time of freely falling waterdrops, J. Meteor., 8, 71–83, 1951. 12665

Lee, J.-E. and Fung, I.: Amount effect of water isotopes and quantitative analysis of post-condensation processes, Hydrol. Process., p. DOI:10.1002/hyp.6637, doi:10.1002/hyp, 2007. 12664, 12669

Legendre, P. and Legendre, L.: Numerical Ecology, 20, Elsevier Science, 1998. 12673, 12679

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

◄ | ►

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Michna, P., Schenk, J., Wanner, H., and Eugster, W.: MiniCASCC – A battery driven fog collector for ecological applications, in: Proceedings of the Fourth International Conference on Fog, Fog Collection and Dew, La Serena, Chile, 22-27 July 200, July, 169–172, 2007. 12668

Moore, K. F., Sherman, D. E., Reilly, J. E., and Collett Jr., J. L.: Drop size-dependent chemical composition in clouds and fogs. Part I. Observations, Atmos. Environ., 38, 1389–1402, doi:10.1016/j.atmosenv.2003.12.013, 2004a. 12668

Moore, K. F., Sherman, D. E., Reilly, J. E., Hannigan, M. P., Lee, T., and Collett Jr., J. L.: Drop size-dependent chemical composition of clouds and fogs. Part II: Relevance to interpreting the aerosol/trace gas/fog system, Atmos. Environ., 38, 1403–1415, doi:10.1016/j.atmosenv.2003.12.014, 2004b. 12668

Petit, J., Jouzel, J., Raynaud, D., Barkov, N., Barnola, J., Basile, I., Bender, M., Chappellaz, J., Davis, M., Delaygue, G., and Others: Climate and atmospheric history of the past 420,000 years from the Vostok ice core, Antarctica, Nature, 399, 429–436, 1999. 12664

Pruppacher, H. R. and Klett, J. D.: Microphysics of Clouds and Precipitation, Kluwer Academic Publishers, Dordrecht, 1997. 12666, 12669

Raja, S., Raghunathan, R., Yu, X.-Y., Lee, T., Chen, J., Kommalapati, R. R., Murugesan, K., Shen, X., Qingzhong, Y., Valsaraj, K. T., and Collett, J. L.: Fog chemistry in the Texas – Louisiana Gulf Coast corridor, Atmos. Environ., 42, 2048–2061, doi:10.1016/j.atmosenv.2007.12.004, 2008. 12667

Risi, C., Bony, S., Vimeux, F., Descroix, L., Ibrahim, B., Lebreton, E., Mamadou, I., and Sultan, B.: What controls the isotopic composition of the African monsoon precipitation? Insights from event-based precipitation collected during the 2006 AMMA field campaign, Geophys. Res. Lett., 35, L24808, doi:10.1029/2008GL035920, 2008. 12664

Schmid, S., Burkard, R., Frumau, K., Tobon, C., Bruijnzeel, L., Siegwolf, R., and Eugster, W.: Using eddy covariance and stable isotope mass balance techniques to estimate fog water contributions to a Costa Rican cloud forest during the dry season, Hydrol. Process., 25, 429–437, doi:10.1002/hyp.7739, 2010. 12668

Scholl, M., Eugster, W., and Burkard, R.: Understanding the role of fog in forest hydrology: stable isotopes as tools for determining input and partitioning of cloud water in montane forests, Hydrol. Process., 25, 353–366, doi:10.1002/hyp.7762, 2011. 12668, 12672

Seinfeld, J. H. and Pandis, S. N.: Atmospheric Chemistry and Physics: From Air Polution to Climate Change, John Wiley and Sons, New Jersey, USA, 2006. 12669

Stable water isotopologue ratios in cloud droplets are not size-dependent

J. K. Spiegel et al.

Spiegel, J. K., Aemisegger, F., Scholl, M., Wienhold, F. G., Collett Jr., J. L., Lee, T., van Pinxteren, D., Tilgner, A., Mertes, S., Herrmann, H.and Werner, R. A., Buchmann, N., and Eugster, W.: Temporal evolution of stable water isotopologues in cloud droplets during HCCT-2010, Atmos. CHem. Phys. DIscuss., accepted, 2012. 12666, 12672, 12673

5 Stewart, M.: Stable isotope fractionation due to evaporation and isotopic exchange of falling water drops: application to atmospheric processes and evaporation of lakes, J. Geophys. Res., 80, 1133–1146, 1975. 12665

Yakir, D. and Sternberg, L. d. S. L.: The use of stable isotopes to study ecosystem gas exchange, Oecologia, 123, 297–311, doi:10.1007/s004420051016, 2000. 12664

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

◄◄ | ►►

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Table 1. F- and p-values for a two way ANOVA (factors: Time and Size) for the measured δ^2H and δ^{18}O values (DI-samples and cloud events) comprising more than one cloud sample. For events 1, 5, 7 and 12 the ANOVA was only performed for δ values from the large and the small stage, as at least one δ value for the middle stage was missing. Bold indicates that the null hypothesis needs to be rejected at a significance level $\alpha = 0.05$ (H_0 (events): cloud water from all vials have the same δ values; H_0 (DI-samples): water from all vials have the same δ values as the DI water). As these were 18 independent tests, we applied the Bonferroni correction (Legendre and Legendre, 1998) resulting in an adjusted significant level $\alpha_{adj} = 0.05/18 = 2.7 \times 10^{-3}$ against which the p-values were compared.

| | δ^2H | | | | δ^{18}O | | | |
| | Size | | Time | | Size | | Time | |
Event	F-value	p-value	F-value	p-value	F-value	p-value	F-value	p-value
DI-samples	0.5	0.6297	1.6	0.2508	0.1	0.9047	2.48	0.1158
1	0.7	0.4255	**67.1**	**<10^{-5}**	7.1	0.0373	**81.0**	**<10^{-5}**
3	9.0	0.1001	161.4	0.0061	2.6	0.2792	68.3	0.0143
5	4.5	0.2802	0.7	0.5677	33.4	0.1091	2.9	0.3403
6	0.1	0.8980	3.7	0.0811	2.4	0.1739	11.9	0.0062
7	3.8	0.1914	**1360.6**	**0.0007**	98.3	0.0100	**25205.0**	**<10^{-5}**
9	0.8	0.4943	**197.5**	**<10^{-5}**	0.8	0.4703	**69.0**	**<10^{-5}**
10	4.4	0.0338	**81.07**	**<10^{-5}**	1.0	0.3817	**13.3**	**<10^{-5}**
11	0.1	0.8782	15.0	0.0139	0.2	0.8536	6.5	0.0550
12	0.6	0.52	**478.76**	**0.0021**	2.3	0.2721	**1348.2**	**0.0007**
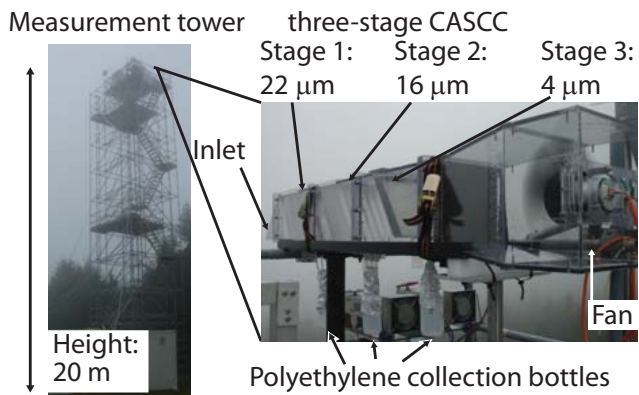
Fig. 1. Pictures of the measurement tower at Schmücke (50°39′ N, 10°46′ E, 937 m a.s.l, Germany) and of the three-stage Caltech Active Strand Cloudwater Collector (CASCC, as described in Sect. 2.2) mounted on its top. The figure includes the 50 % cut-off sizes for cloud droplet diameters collected at the different stages: stage 1 collects droplets larger than ≈22 μm, stage 2 droplets from 16 to 22 μm and stage 3 from 16 to 4 μm.
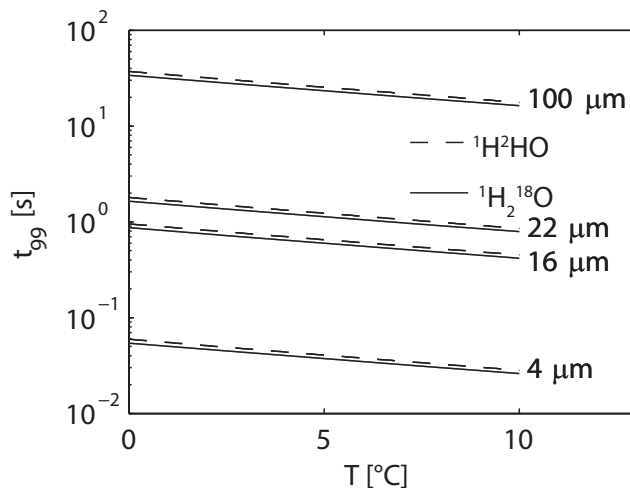
Fig. 2. Time required for a single spherical cloud droplet to reach 99 % isotopic equilibrium (both for δ^2H and δ^{18}O) with the surrounding vapor at air temperatures prevailing at Schmücke. t_{99} is depicted for four different droplet diameters: 22 μm, 16 μm and 4 μm corresponding to the cut-off sizes of the three stages of the CASCC, and 100 μm which we assume to be the diameter of the largest droplets that enter the CASCC. D_k values ($k = {}^1$H^{2}H^{16}O, and ^{1}H$_2{}^{18}$O) were deduced from the relations to $D_{{}^1\text{H}_2{}^{16}\text{O}}$ (Cappa et al., 2003), and $D_{{}^1\text{H}^2\text{H}^{16}\text{O}}$ was derived from campaign temperature and the air pressure value (900 hPa) using the relation presented by Hall and Pruppacher (1976).
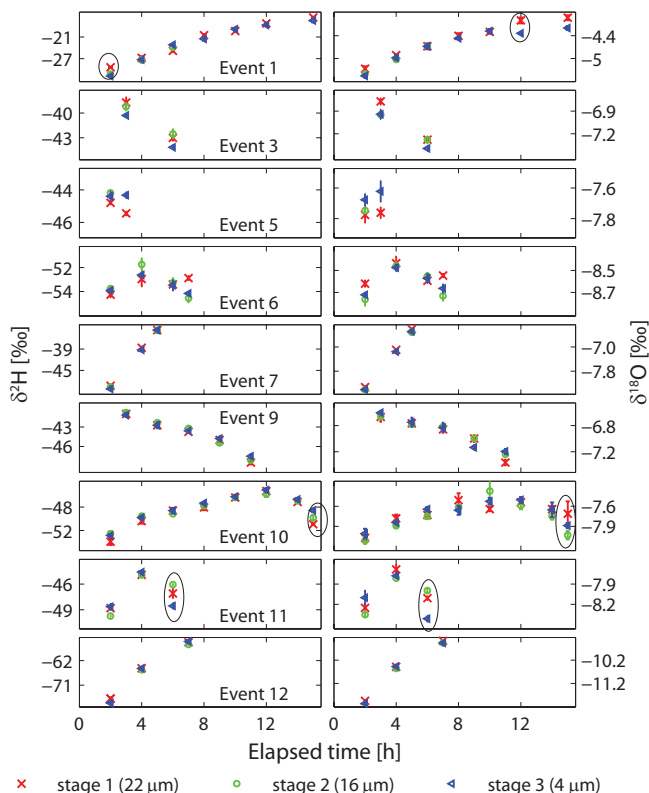
Fig. 3. Temporal evolution of the δ^2H and δ^{18}O values for all measured cloud events during HCCT lasting longer than one measurement point: δ values for the different stages are shown in different colors and different symbols and denoted with their cut-off diameters in brackets. Measurement error in terms of standard errors of the IRMS measurements are shown as error bars. Cloud samples exceeding the Δ_{st} 90-percentile threshold (see Fig. 4 for further details) are marked with an ellipse
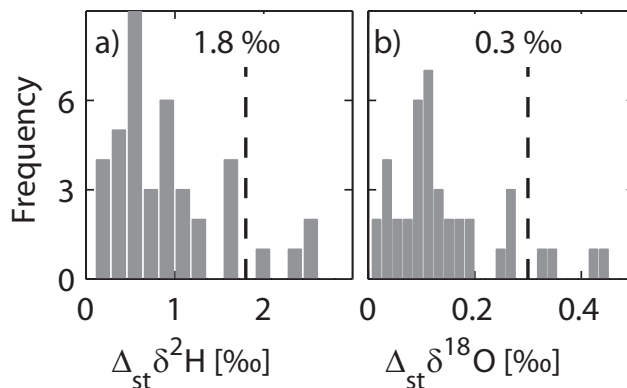
Fig. 4. Histograms for the maximum differences in δ^2H **(a)** and δ^{18}O **(b)** values among vials of the three stages collected by the CASCC ($\Delta_{st} = \max_{i,j=1,2,3}\left(\left|\delta_i - \delta_j\right|\right)$) for all cloud samples. The dashed line denotes the 90-percentile of the Δ_{st} distribution (1.8 ‰ or 0.3 ‰).
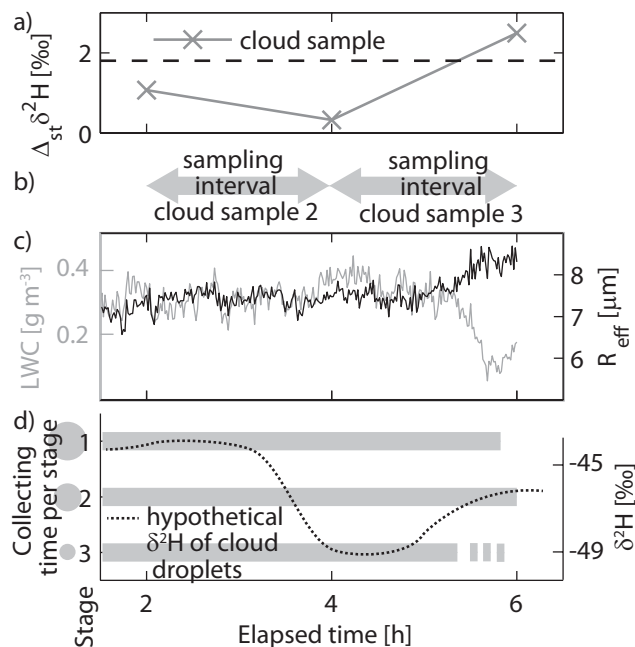
Fig. 5. $\Delta_{st}\delta^2$H for event 11 **(a)** including the 1.8‰ threshold as a dashed line and sampling intervals **(b)** of cloud sample 2 and 3 (1 is not shown). The liquid water content (LWC) measured with the Particulate Volume Monitor (PVM-100), including the effective radius (R_{eff}) **(c)**. Hypothetical collecting times (estimated from the measurements in panel **(c)**) for the three different CASCC stages which might result from the LWC are depicted (**d**, left axis) and hypothetical δ^2H evolution in cloud droplets (**d**, right axis).