Using eddy covariance and stable isotope mass balance
techniques to estimate fog water contributions to a Costa
Rican cloud forest during the dry season

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Abstract

Fog deposition, precipitation, throughfall, and stemflow were measured in a windward tropical montane cloud forest near Monteverde, Costa Rica, for a 65-day period during the dry season of 2003. Net fog deposition was measured directly with the eddy covariance (EC) method and amounted to 1.2 ± 0.1 mm day⁻¹ (mean ± standard error). Fog water deposition was 5–9% of incident rainfall for the entire period, which is at the low end of previously reported values. Stable isotope concentrations (δ¹⁸O and δ²H) were determined in a large number of samples of each water component. Mass balance-based estimates of fog deposition were 1.0 ± 0.3 mm d⁻¹ and 5.0 ± 2.7 mm d⁻¹ (mean ± SE) when δ¹⁸O and δ²H were used as tracer, respectively. Comparisons between direct fog deposition measurements and the results of the mass-balance model using δ¹⁸O as a tracer indicated that the latter might be a good tool to estimate fog deposition in the absence of direct measurement under many (but not all) conditions. At 506 mm, measured water inputs over the 65 days (fog plus rain) fell short by 46 mm compared to the canopy output of 552 mm (throughfall, stemflow, and interception evaporation). The discrepancy is attributed to underestimation of rainfall during conditions of high wind.

Keywords: Fog, Stable Isotope Tracer, Interception, Tropical Montane Cloud Forest, Costa Rica

Introduction

Montane cloud forests are widely believed to receive significant extra amounts of water through the capture of passing low cloud (fog). The quantification of this additional water input is of great practical importance where upland watersheds with cloud forests supply water to downstream populations (Zadroga, 1981; Brown et al., 1996; Rhodes et al., 2010). Fog water inputs are usually quantified indirectly, be it through comparison of rainfall and crown drip during times with and without fog (e.g. Harr, 1982; Sigmon et al., 1989; Hafkenscheid et al., 2002; Holder, 2003), modeling (e.g. Lovett, 1984; Yin and Arp, 1994; Walmsley et al., 1996; Ritter et al., 2008), or, by simply using some kind of passive “fog” gauge (e.g. Juvik and Ekern, 1978; Goodman, 1985; cf. Bruijnzeel et al., 2005). The drawback of indirect methods is that the quantification of fog deposition is dependent on correct rainfall and net
precipitation measurements and, by necessity, represents net amounts because of
unmeasured losses of water evaporated from the wetted canopy. Reliance on fog
gauges introduces the problem of separating contributions by fog and (wind-driven or
inclined) rain to the overall catch (McJannet et al., 2007; cf. Frumau et al., 2010a,b;
Giambelluca et al., 2010; Tanaka et al., 2010). An additional problem concerns the
translation of water amounts collected by a vertical gauge surface to effective
hydrological input onto a horizontal plane, and the impossibility of any type of fog
gauge to represent natural vegetation. The distinction between fog and rain water
inputs is crucial, because the latter are – due to the larger droplet sizes involved –
deposited independently of the surface cover. Fog water, however, is strongly
influenced by turbulence. Because of the rougher and larger surface area of forest
canopies, fog water deposition is much larger over forests than over, for example,
pasture (e.g. Thalmann et al., 2002).

This paper presents the results of direct net fog water deposition
measurements by means of the eddy covariance method (Beswick et al., 1991;
Eugster et al., 2006; Beiderwieden et al., 2008) made above a windward montane
cloud forest in northern Costa Rica. The results are compared with those obtained
with a mass-balance model using the stable isotopes $^{18}$O and $^2$H as tracers (cf. Guswa
et al., 2007; Scholl et al., 2010). To further validate the direct fog deposition
measurements, the remaining components of the wet-canopy water budget equation
(Holwerda et al., 2006a) were measured or calculated and the different approaches
evaluated.

Materials and methods

Site description

Hydrological and micrometeorological measurements were made between 10
February and 13 May 2003 at 1,460 m.a.s.l. in the San Gerardo headwater area within
the Caño Negro drainage basin on the exposed Atlantic slopes of the Cordillera de
Tilarán in northern Costa Rica, ~10 km NE of the town of Santa Elena (10° 21’ 33"
N, 84° 48’ 5” W). The meteorological measurements were made on top of a 24 m tall
scaffolding tower situated about 200 m from the crest of a fully forested 10° slope of
N350E exposure. Measurements of net precipitation were made on a nearby slope
with a somewhat different exposure and gradient (slope 30°, N270E). The forest was
a windward lower montane cloud forest having its main canopy surface at 21–22 m, with epiphyte-laden emergent trees extending above this level by several metres. Overall epiphyte biomass was determined at 16.2 t ha$^{-1}$ (Köhler et al., 2007). Tree ferns and palms were common in the understory. Long-term rainfall data for the upper Atlantic slopes are not available, but conventionally measured rainfall input (rain only) between 1 July 2003 and 30 June 2004 at the site was c. 6,000 mm (K.F.A. Frumau, unpublished data). A somewhat drier period tends to occur in the area between February and April, with monthly rainfalls of generally less than 150 mm, vs. 500 mm or more during the remainder of the year (Clark et al., 2000). Due to the prevailing high wind speeds there is a major horizontal precipitation component in the form of wind-driven rain (mostly drizzle) and fog (cf. Clark et al., 1998; Frumau et al., 2010a,b; Häger and Dohrenbusch, 2010). Tobón et al. (2010) provide further basic information on site climate.

Methods and instrumentation

Net fog water deposition was measured directly by the eddy covariance technique. Net deposition is defined as the difference between gross deposition – the water that is actually deposited on the leaves or on other surfaces – and formation of fog droplets due to condensation. The latter constitutes a counteracting, upward flux which reduces the measured flux at the height of the eddy covariance set-up (see Eugster et al. (2006) for details). Eddy covariance flux measurements are directly measuring deposition rates, and thus the only assumptions that need to be made are that: (i) the measurements are representative for a larger surface area (homogeneity of upwind canopy surface and topography), and (ii) turbulent conditions are stationary during the measurements (e.g. no abrupt changes in wind direction and wind speed). The measurements were performed with a three-dimensional ultrasonic anemometer (model 1199 HSE, Gill Instruments Ltd., Lymington, UK) coupled with an active high-speed FM-100 cloud particle spectrometer (Droplet Measurement Technologies Inc., Boulder, CO, USA). Fog droplets were continuously measured in 40 size classes between 2 and 50 μm diameter and recorded together with the 3-dimensional wind speed information at a frequency of 12.5 times per second. Internal measurements were carried out 100 times per second, and therefore each of the recorded outputs
represented the average of eight measurements. For further details on the eddy covariance measurements the reader is referred to Burkard \textit{et al.} (2003) and Eugster \textit{et al.} (2006). Vertical rainfall was measured by two standard rain gauges (100 cm$^2$ orifice) that were manually emptied on a daily basis, and one automatic tipping-bucket rain gauge (200 cm$^2$ orifice, 0.2 mm per tip). The precipitation measurements were corrected for aerodynamic losses around the gauge due to wind following the procedure of Førland \textit{et al.} (1996), and for the effects of sloping ground according to Sharon (1980). Horizontal precipitation (i.e. fog and wind-driven rain) was measured using a modification of the cylindrical louvered gauge of Juvik and Ekern (1978) (Frumau \textit{et al.}, 2010a). Throughfall (\textit{TF}) was measured with the roving gauge technique using 60 totalizers with an orifice of 100 cm$^2$ each (cf. Lloyd and Marques, 1988; Holwerda \textit{et al.}, 2006b). Stemflow (\textit{SF}) was measured on 30 trees using spiral gutters and made up $< 1\%$ of uncorrected rainfall (K.F.A. Frumau and C. Tobón, unpublished data). Wet-canopy evaporation was calculated with the wet-canopy version (i.e. surface resistance $r_s=0$) of the Penman-Monteith equation (Monteith, 1965).

\textit{<Table 1>}

In addition to the eddy covariance measurements, fog water deposition was also estimated with a mixing model as described by Brunel \textit{et al.} (1995), using the stable isotopes $^{18}\text{O}$ and $^2\text{H}$ as tracers. Samples for the determination of isotope concentrations were taken on a nominally daily basis from rain, fog, \textit{TF} and \textit{SF}. Exact durations for \textit{TF} sampling are given in Table 1, whereas more detailed information can be found in the raw data set (http://doi.pangaea.de/10.1594/PANGAEA. 735614).

Fog water was collected using a modified Caltech Active Strand Cloudwater Collector (CASCC; Demoz \textit{et al.}, 1996) with a shielded inlet to avoid raindrops ($>100\ \mu\text{m}$) from being collected (Figure 1). The teflon strands collect all fog droplets larger than approximately 5–7 $\mu\text{m}$. CASCC sampling was executed automatically (including transfer to a closed flask to prevent re-evaporation; cf. Scholl \textit{et al.}, 2010) whenever visibility was $< 500\ \text{m}$. At the end of each sampling period a representative subsample was taken from the collected fog water for analysis. Rain water was collected with a sampler built according to the specifications of IAEA (2002) whereas a locally constructed, rotating gauge with a vertical orifice (RGVO) was used to sample wind-driven rain (horizontal precipitation) (Figure 2). A representative subsample of the water collected by each individual \textit{TF} and \textit{SF} collector was used for
isotope analysis. For days on which samples were available from all water types
collected over the same time interval, the proportions of fog and rain water in TF were
calculated using the following mixing model containing two end members:

\[ f = \frac{\delta_{TF} - \delta_F}{\delta_F - \delta_P}, \]  

(1)

where \( f \) is the fraction of rain water in TF and the various subscripts of \( \delta \)
denote the respective isotopic ratios of either \( \delta^{18}O \) or \( \delta^2H \) in TF, fog (F) and rain (P)
with reference to the Vienna Standard Mean Ocean Water (V-SMOV). Thus, \( \delta_{TF} \) is a
placeholder for the \( \delta^{18}O_{TF} \) or \( \delta^2H_{TF} \) tracer. Correspondingly \( \delta_F \) and \( \delta_P \) represent \( \delta^{18}O_F \)
and \( \delta^2H_F \) or \( \delta^{18}O_P \) and \( \delta^2H_P \), respectively, in Eq. (1). Cases where \( \delta_{TF} \) was outside the
range given by \( \delta_F \) and \( \delta_P \) were rejected.

<Figure 1>

<Figure 2>

Results and discussion

Isotopic signatures of fog, rain, throughfall, and stemflow water

In total, 566 water samples were collected during the 65-day field period. Figure 3
shows the isotopic signatures of RGVO, rain, fog, and throughfall water together with
the global meteoric water line (GMWL), the local meteoric water line as determined
by Rhodes et al. (2006), and a local meteoric water line based on the rain water
samples collected by the present study. Since the scatter was large (as may be
expected from short-term sampling), only rain water samples with \( \delta^{18}O < 0 \% \) and
\( \delta^2H < -20 \% \) were used, yielding the following relation: \( \delta^2H = (7.59 \pm 0.23) \delta^{18}O +
(3.90 \pm 1.49) \% \) V-SMOV (r² = 0.991, n=11). The presently derived mixing water
line for dry season conditions is flatter than the one reported by Rhodes et al. (2006)
for the two full years between June 2003 and April 2005. The difference in slope
between the two local meteoric water lines is consistent with the expectation that
winter (colder temperatures) precipitation should lead to lower slopes. In addition,
enhanced evaporation during dry season conditions also tends to produce a lower
slope (cf. Clark and Fritz, 1997).
Figure 3

Fog deposition

Average net fog deposition measured by the eddy covariance system for conditions with visibility below 1,000 m was 0.05 mm h\(^{-1}\) or 14.2 mg \cdot m\(^{-2}\) s\(^{-1}\). This rate is similar to the fog deposition measured with the same equipment in an elfin cloud forest setting near Pico del Este in Puerto Rico (0.04 mm h\(^{-1}\) or 10.2 mg \cdot m\(^{-2}\) s\(^{-1}\); Eugster et al., 2006; Holwerda et al., 2006a) and lies within the range of reported values measured with this technique outside the tropics (Beswick et al., 1991; Vong and Kowalski, 1995; Vermeulen et al., 1997; Burkard et al., 2003). The average daily deposition rate of 1.2 ± 0.1 mm also lies within the range of 0.2–4.0 mm d\(^{-1}\) of reported cloud water interception rates in tropical montane areas as obtained by various indirect methods (Bruijnzeel and Proctor, 1995; Bruijnzeel, 2005). Fog deposition expressed as a percentage of rainfall (5%) was at the low end of the spectrum reported by Bruijnzeel and Proctor (1995) and Bruijnzeel (2005) (4–281% of corresponding rainfall). Whilst the observed daily deposition rates are plausible, therefore, the contribution by fog water to total water input proved rather small. Based on the direct measurements, fog water added a mere 19 mm of water to the forest water budget during the 65-day measurement period during which a possibly unusually low fog frequency of 26% (i.e. times with horizontal visibility of 1000 m or less) was observed. The higher than normal position of the cloud base, and the associated lack of fog, were caused by the occurrence of the “temporales del pacífico” weather pattern (Clark et al., 2000). During several days, the field site was climatically speaking situated on the leeward side of the Continental Divide due to the occurrence of the associated warm and dry western winds. According to Clark et al. (2000), this type of weather system tends to occur mostly during the hurricane season (August–October) and its occurrence in March 2003 may have led to non-representative conditions. However, Clark et al. (2000) also report that during 20–25% of all hours during the dry season the upper slopes and ridges along the Continental Divide in the (leeward) area of nearby Monteverde are immersed in clouds and are thus affected by fog. These percentages compare well with the visibility-based observation of 26% fog occurrence during the present field period. Therefore, the inferred 5% fog contribution during the study period may be typical for
the dry season after all, although longer-term observations would be needed to
confirm this (cf. Guswa et al., 2007; Lawton et al., 2010).

Isotope concentrations of all water types were available for 31 sampling
days (Table 1). The fractions of fog water in throughfall (TF) as calculated with the
mixing model of Eq. (1) were outside the acceptable range of 0–100% on 14 days
(45%) and 21 days (68%) for δ¹⁸O and δ³H, respectively. Most likely, the time series
of available samples for the individual components indicated effects of dynamic
changes in weather conditions. For example, Eugster (2007) reported that at a similar
site in Puerto Rico, δ¹⁸O in fog water tended to be related more closely to values
found in precipitation falling 36–60 hours prior to the fog event. This may explain
why fog water sometimes exhibits a more negative isotopic signature than
precipitation. Whilst this has no consequences for the application of the type of tracer
mixing model used here, such findings may help to understand why in only 55% of all
cases TF had a δ¹⁸O signature intermediate between the values of the two end
members (i.e. fog and precipitation). At 32%, this fraction was even lower for δ³H (cf.
Table 1).

Therefore, δ¹⁸O was considered to be the more reliable tracer for
determining the fraction of fog water in TF samples. The fractions obtained for the
remaining days using δ¹⁸O as a tracer are shown in Figure 4. The calculated fractions
of fog water in stemflow (SF) were all outside the acceptable range. Therefore, SF
was assumed to receive the same share of fog water as determined for corresponding
TF. Since SF is a very small component compared to TF, this assumption does not
introduce a large additional uncertainty in estimated amounts of daily fog deposition.

<Figure 4>

The eddy covariance-based fog water fluxes (EC) and the deposition rates
estimated with the mass balance approach for δ¹⁸O were in the same order of
magnitude as indicated by the 1:1 line, except for two events with unrealistically high
deposition rates in view of the prevailing wind speeds and fog liquid water content
(see inset in Figure 5). Because the correlations were higher when δ¹⁸O was used as a
tracer ($r = 0.72, p = 0.009$) instead of δ³H ($r = 0.54, p = 0.045$), the numbers given
below pertain to the results obtained with δ¹⁸O. Overall, fog deposition as calculated
with the mixing model may be considered to represent the gross fog water flux at the
canopy level whereas the EC-based flux represents the net fog water flux. On average,
the gross fog water flux was 1.8 times the directly measured amount (excluding the
two events that gave unrealistic results; Figure 5, inset). The corresponding values
were $0.37 \pm 0.06 \text{ mm d}^{-1}$ for the EC (net flux) and $0.66 \pm 0.13 \text{ mm d}^{-1}$ for the mixing
model (gross flux; n=14 events) or 5% and 9% of incident rainfall, respectively.
Eugster et al. (2006) reported the gross fog water flux at the canopy level for an elfin
cloud forest site in Puerto Rico to be 1.74 times the net flux measured by eddy
covariance, a value that is consistent with the presently derived factor. In view of this
similarity in the difference between gross and net fog water fluxes, a factor of 1.8 may
also be representative for other tropical montane cloud forest sites and illustrates the
importance of fog droplet formation as the air moves upslope. As stated earlier, this
condensation counteracts the deposition of fog droplets onto the vegetation surface.

<Figure 5>

Wet-canopy water balance

For the computation of the wet-canopy water balance, a period of 65 days with
uninterrupted measurements of all components was selected (9 March–13 May 2003).
For this period, the following amounts (all in mm) were determined:

\[ 487_{\text{(corrected rainfall)}} + 19_{\text{(direct fog)}} \approx 497_{\text{(TF)}} + 50_{\text{(wet-canopy evaporation)}} + 5_{\text{(SF)}} \]  

For these 65 days, the average daily difference between canopy inputs (rain and fog)
and outputs ($TF, SF$, evaporation) was not statistically significant (paired Wilcoxon
rank sum test, 95% confidence level, $p = 0.30$). However, during a two-day storm
event with high wind speeds and inclined rainfall, the difference between inputs and
outputs became quite large (see Figure 6: days 91 and 92, or 1 and 2 April 2003).
If it is assumed that the uncertainty in the $TF$ measurements (which made up 97% of
the total output during these two days) was small due to the use of a large number of
collectors (cf. Lloyd and Marques, 1988; Holwerda et al., 2006b), then it is most
likely that the “missing” amounts during these two days reflect an underestimation of
the inputs rather than an overestimation of the output components.

<Figure 6>
If the unaccounted water would have been due to underestimated fog deposition alone, then a daily deposition rate of more than 18 mm would have been required, which would seem unrealistically high in view of the published range reported by Bruijnzeel (2005). In addition, the mixing model-based fraction of fog water in TF was very small for large TF events (Figure 4), which is indicative of the fact that fog inputs were only significant at times when precipitation rates were comparatively low. For example, a daily TF total of 10 mm would yield a contribution of ~5% by fog according to the mixing model (Eq. (1)). Measured daily TF totals for 1 and 2 April 2003 were very much larger (165 and 134 mm, respectively, with corresponding measured rainfall amounts of 134 and 44 mm, respectively). Whilst no isotopic information was available for these extreme events, based on Figure 4 it would be expected that the associated fraction of fog water in TF for these two events would be well below 5%. This suggests that total fog deposition must have been less than 15 mm during these two days (note that the eddy covariance system measured a total amount of 5.5 mm). Therefore, it is concluded that the bulk of the unexplained gap of 46 mm in the overall wet-canopy water balance (Eq. (2)) was due to underestimation of rainfall, despite the application of corrections for aerodynamic losses around the gauge and for slope effects. This conclusion is supported by measurements made with the louvered cylindrical gauge (MJU) and the rotating vertical orifice gauge (RVOG), both of which collected large volumes of water during these two days. The MJU recorded 459 mm and 100 mm of horizontal precipitation for 1 and 2 April, respectively. Furthermore, isotopic values of the water collected with the RVOG showed a clear contrast to those of fog water (as collected by the modified CASCC) throughout the measuring campaign (Figure 7), whereas no significant difference was found with the δ-values in rain water, particularly for δ²H (Figure 7b). It is most likely, therefore, that the water collected by the rotating gauge during the storm events of 1 and 2 April was mostly wind-driven rain.

<Figure 7>

Conclusions

The components of the wet-canopy water balance of a windward montane cloud forest in north-western Costa Rica were measured or calculated for a period of 65 days during the dry season of 2003. There was no statistically significant difference
between totals of canopy inputs (fog and rain) and outputs (throughfall, stemflow and
wet-canopy evaporation) over this period if expressed in daily terms. Fog inputs
ranged between 5% (eddy covariance-based net flux measurements) and 9% (tracer-
based mixing model using $\delta^{18}$O) of incident rainfall. Rainfall was corrected for the
effects of sloping ground and aerodynamic losses around the gauge. On average, the
corrected amounts were 27% higher. However, for an extreme composite storm event
with strong winds and therefore substantial inclined or near-horizontal rainfall, the
applied corrections were insufficient and rainfall was still underestimated. During the
same event, throughfall greatly exceeded incoming rainfall and a cylindrical louvered
screen gauge collected large amounts of water, confirming the occurrence of near-
horizontal precipitation.

The mixing model for $\delta^{18}$O was found to be a good tool to assess the
fraction of fog water in throughfall during 16 out of 31 precipitation events.
However, the method needs further refinement as several relevant questions remain
unsolved, including: (i) Why did the method not work well for stemflow samples? (ii)
Why does $\delta^{18}$O appear to be a useful tracer for this purpose whereas $\delta^{2}$H yielded
completely different and arguably less reliable results? (iii) Does isotopic
fractionation occur when fog water is sampled with an Active Strand Cloud Water
Collector? And (iv) how large is the effect of evaporation on isotopic concentrations
in throughfall water?

Longer-term measurements of both directly measured net fog deposition
and isotopic composition of fog, rain and throughfall water are needed to unravel the
existence of relationships between isotopic signatures in fog and rain, and the time
lags between the two (Eugster, 2007). This is expected to increase confidence in the
idea that the isotope mixing approach could usefully replace the expensive and
sophisticated eddy covariance instrumentation. However, it would first be necessary
to understand why the results obtained with $^{2}$H as a tracer differed so much from those
based on $^{18}$O (see also Scholl et al., 2010) at this wind-exposed location, when Rhodes
et al. (2006) found isotopic values in the precipitation at nearby (leeward)
Monteverde to follow the global meteoric water line.

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Table Caption

Table 1: Events with concurrent fog, precipitation, and measurable throughfall (TF) to allow for application of the isotope tracer model according to Eq. (1). Estimates of fog water contributions in sampled TF given as percentages and absolute amounts (mm d$^{-1}$) for both $\delta^{18}$O and $\delta^2$H, although only the values obtained with $\delta^{18}$O as the tracer appear to provide realistic results. Eddy covariance (EC) fog water fluxes relate to the 24 hour period prior to the time when TF samples were collected.

Figure Captions

Figure 1: Schematic representation of the CASCC fog collector.

Figure 2: Locally-built rotating gauge with vertical orifice (RGVO) to capture horizontal precipitation.

Figure 3: Isotopic ratios in water collected with the rotating gauge with vertical orifice (RGVO), and in rain, fog and throughfall water. The global mixing water line (GMWL) of $\delta^2$H = 12 + 8.5 $\delta^{18}$O, and two local mixing water lines are added for comparison (see text for details).

Figure 4: Measured daily throughfall amounts and corresponding fractions of fog water in throughfall as calculated with the mixing model of Eq. (1) using $\delta^{18}$O as the tracer at the San Gerardo cloud forest site.

Figure 5: Directly measured (eddy covariance-based) daily net fog water deposition rates vs. rates calculated with the mixing model of Eq. (1) using $^{18}$O as the tracer ($r^2 = 0.52, p = 0.009$) at the San Gerardo cloud forest site.

Figure 6: The daily wet-canopy water balance at the San Gerardo forest site between 19 March and 13 May 2003. Inputs are displayed by positive values and dark bars, outputs are negative with grey bars, whereas the deviation from a closed budget is indicated by the bold line.
**Figure 7:** Box plots of isotopic signatures of source waters: (a) oxygen isotopic ratios ($\delta^{18}$O), (b) hydrogen isotopic ratios ($\delta^2$H). Each box shows the inter-quartile range with its median (horizontal line). Whiskers show the data range up to 1.5 times the interquartile range. Values outside this distribution are denoted by open circles. Identical letters denote similarity (Wilcoxon rank sum test, $p \geq 0.05$), different letters indicate significant differences ($p < 0.05$). RGVO denotes rotating gauge with vertical orifice.
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<th>Duration (hours)</th>
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<th>Throughfall</th>
<th>Precipitation</th>
<th>Tracer Model</th>
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**SE:** 1141.0 0.4 5.4 4.63 0.58 4.30 0.65 4.44 7.6 0.3 9.4 2.7 0.066

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Costa Rica Monte Verde

\[
\delta^2 H = 7.6 \delta^{18}O + 3.9\%\text{o}
\]

GMWL

Rhodes et al. (2006)

\[
\delta^{18}O \text{ [%]} \text{ in } H_2O
\]

\[
\delta^2 H \text{ [%]} \text{ in } H_2O
\]
Calculated (mm day$^{-1}$) vs. Measured (mm day$^{-1}$)
\[ \delta^{18}O \text{[permil]} \text{in } H_2O \]

(a) 

(b) 

\[ \delta^2H \text{[permil]} \text{in } H_2O \]