HYDROLOGICAL PROCESSES
Hydrol. Process. (2010)
Published online in Wiley Online Library
(wileyonlinelibrary.com) DOI: 10.1002/hyp.7762

Understanding the role of fog in forest hydrology: stable isotopes as tools for determining input and partitioning of cloud water in montane forests[†,‡]

Martha Scholl,[1]* Werner Eugster[2] and Reto Burkard[3]

[1] *Water Resources, US Geological Survey, Reston, VA, USA*
[2] *Institute of Plant, Animal and Agroecosystem Sciences, Swiss Federal Institute of Technology ETH, Zurich, Switzerland*
[3] *Institute of Geography, University of Bern, Bern, Switzerland*

Abstract:

Understanding the hydrology of tropical montane cloud forests (TMCF) has become essential as deforestation of mountain areas proceeds at an increased rate worldwide. Passive and active cloud-water collectors, throughfall and stemflow collectors, visibility or droplet size measurements, and micrometeorological sensors are typically used to measure the fog water inputs to ecosystems. In addition, stable isotopes may be used as a natural tracer for fog and rain. Previous studies have shown that the isotopic signature of fog tends to be more enriched in the heavier isotopes ^{2}H and ^{18}O than that of rain, due to differences in condensation temperature and history. Differences between fog and rain isotopes are largest when rain is from synoptic-scale storms, and fog or orographic cloud water is generated locally. Smaller isotopic differences have been observed between rain and fog on mountains with orographic clouds, but only a few studies have been conducted. Quantifying fog deposition using isotope methods is more difficult in forests receiving mixed precipitation, because of limitations in the ability of sampling equipment to separate fog from rain, and because fog and rain may, under some conditions, have similar isotopic composition. This article describes the various types of fog most relevant to montane cloud forests and the importance of fog water deposition in the hydrologic budget. A brief overview of isotope hydrology provides the background needed to understand isotope applications in cloud forests. A summary of previous work explains isotopic differences between rain and fog in different environments, and how monitoring the isotopic signature of surface water, soil water and tree xylem water can yield estimates of the contribution of fog water to streamflow, groundwater recharge and transpiration. Next, instrumentation to measure fog and rain, and methods to determine isotopic concentrations in plant and soil water are discussed. The article concludes with the identification of some of the more pressing research questions in this field and offers various suggestions for future research. Published in 2010 by John Wiley & Sons, Ltd.

KEY WORDS stable isotopes; cloud water; fog; oxygen-18; deuterium; cloud forest

Received 28 September 2009; Accepted 16 April 2010

INTRODUCTION

The importance of fog in the water budget of montane forests has been recognized for many years (Nagel, 1956; Kerfoot, 1968; Zadroga, 1981; Lovett *et al*., 1982; DeLay and Giambelluca, 2010; Marzol-Jaén, 2010), but there are still unresolved questions as to how cloud-affected ecosystems actually function hydrologically (Bruijnzeel 2001; Bruijnzeel *et al*., 2005; Bruijnzeel *et al*., 2010). Accurate water balances that include both fog and horizontal precipitation (i.e. precipitation not captured by a conventional rain gauge) are needed to quantify fog contributions to groundwater recharge and streamflow, to understand the role of fog water inputs in terms of nutrient and pollutant loadings and to quantify fog as a moisture source during rainless periods. Clouds with low liquid water content or fog events with low wind speeds may not deposit measurable amounts of water but may still have an effect on forest functioning via foliar uptake or the reduction of transpiration from the plants (García-Santos, 2007; McJannet *et al*., 2007b; Fischer *et al*., 2009; Limm *et al*., 2009; Schawe *et al*., 2010). Distinguishing fog events, events with fog plus rain and rain events aids in determining the rates of cloud-water interception by a forest, and how much water input would be missed by using only conventional rain gauge-based water balance techniques.

The stable isotopes of water (^{2}H and ^{18}O) are a potentially useful tool for determining the amount and transport pathways of cloud water in montane forests. To use these tools effectively requires an understanding of the underlying processes controlling stable isotope composition of natural waters. This article summarizes the results of previous studies involving stable isotopes of fog or cloud water, and gives an overview of how isotope ratios may

* Correspondence to: Martha Scholl, US Geological Survey, Reston, VA, USA. E-mail: mascholl@usgs.gov
† This article is a US Government work and is in the public domain in the USA.
‡ This paper is largely reproduced from a chapter previously published as M.A. Scholl, W. Eugster and R. Burkard (2010). Understanding the role of fog in forest hydrology: stable isotopes as tools for determining input and partitioning of cloud water in montane forests. In *Tropical Montane Cloud Forests. Science for Conservation and Management*, eds. L.A. Bruijnzeel, F.N. Scatena and L.S. Hamilton. Cambridge: Cambridge University Press, pp. 228-241. www.cambridge.org/9780521760355.

be used to provide insight into water balances and water transport in cloud forests.

A necessary first step is to define what is meant by cloud water, fog, horizontal precipitation, etc., and what one is trying to quantify in terms of the total water input received by a cloud-affected forest. In meteorology, a cloud touching the ground with a horizontal visibility less than 1 km is defined as fog. This definition does not serve well in forest hydrology, because it does not include the aspect of whether or not there is measurable precipitation from fog. The most precise way to distinguish fog from rain is by droplet size. The American Meteorological Society Glossary of Meteorology (Glickman, 2000) states: 'Fog differs from cloud only in that the base of fog is at the earth's surface while clouds are above the surface' and 'A diameter of 0·2 mm has been suggested as an upper limit to the size of drops that shall be regarded as cloud drops; larger drops fall rapidly enough so that only very strong updrafts can sustain them. Any such division is somewhat arbitrary, and active cumulus clouds sometimes contain cloud drops much larger than this'. In the present paper, the term 'fog' is used to refer to cloud droplets that are small enough to remain suspended in the air without falling. 'Cloud water' refers to the entire size spectrum of fog, drizzle and rain present in a cloud. Rain is defined as having a droplet size greater than 0·5 mm (Glickman, 2000). Furthermore, the term 'rain' is taken to refer to droplets large enough to fall into a conventional rain gauge, with the understanding that this droplet size threshold will depend on the prevailing wind conditions (Nespor and Sevruk, 1999; Holwerda *et al.*, 2006; Sieck *et al.*, 2007; Frumau *et al.*, 2010b; Giambelluca *et al.*, 2010).

Climatologically, there are several types of fog that may occur in MCF, including advection fog, sea fog, steam fog, radiation fog and orographic clouds (see Bruijnzeel *et al.*, 2005 for more detail). Advection fog is fog that is formed elsewhere and then transported horizontally, e.g. to a mountain range. In coastal regions, such advection fog may have originated as sea fog or steam fog. Sea fog forms when warm air masses move over cold ocean water, and the fog droplets represent mostly the condensate of the water vapour present in the air before it cooled below its dew point temperature. This type of advection fog occurs frequently off the Pacific coast of North and South America and affects coastal mountain ranges in those areas. Conversely, steam fog commonly forms over warm water bodies when evaporation from the water surface exceeds the capacity of the colder air above it to take up moisture, after which the excess vapour condenses to liquid water drops.

Radiation fogs occur when moist air cools below its dew point temperature. Typically, radiation fog is formed overnight in mountain valleys and basins with little or no drainage of cold air (Liu *et al.*, 2007). It rarely occurs in mountain valleys where a strong down-valley wind occurs at night. Orographic clouds (upslope or mountain fogs) form when moist air is topographically forced to rise. This may occur on a large scale where the prevailing winds blow against an entire mountain range or on a smaller scale where thermally forced winds blow upslope. The small droplets typical of fog may be mixed with larger droplets; either rain, or droplets that, over flat terrain, would be large enough to precipitate as rain, but which are now kept in the orographic clouds due to strong updrafts. Thus, orographic clouds may be accompanied by significant wind and rainfall (Giambelluca *et al.*, 2010). Because raindrops are typically several orders of magnitude larger in volume and amount of liquid water, orographic clouds may deposit much higher amounts of water than do other types of fog with smaller droplets (Bruijnzeel *et al.*, 2005).

Droplet size measurements have rarely been made at remote mountain sites and what has been obtained in most studies is an operational definition of fog deposition, based on the type of instrument or sampler used. From a water balance perspective, it is important to quantify all incoming precipitation types. This involves quantifying the size fraction of precipitation that is not measured in a standard rain gauge. Part of this may be quantified by throughfall gauges, which measure some of the fog and cloud-water deposition to the vegetation. Rain gauges, with their horizontally oriented openings and susceptibility to wind effects, do not collect the same size fractions of precipitation. Several other articles in this issue (Frumau *et al.*, 2010b; García-Santos and Bruijnzeel, 2010; Giambelluca *et al.*, 2010; Holwerda *et al.*, 2010) discuss the latter in some detail.

ISOTOPE FRACTIONATION PROCESSES RELEVANT TO CLOUD FOREST PRECIPITATION

The chemical composition of water is H_2O, a combination of two hydrogen (^1H) and one oxygen (^{16}O) atoms. A very small fraction of water molecules, however, contain either ^2H (deuterium, often also abbreviated with D) substituted in place of ^1H, or ^{18}O in place of ^{16}O. The different isotopic variations of the molecules are called isotopologues. These isotopes are stable, that is, they are not subject to radioactive decay. Because concentrations of ^{18}O and ^2H are typically very low: (i) the concentrations are expressed as the difference between the ratios (e.g. $^{18}O/^{16}O$) of a sample and a known standard, divided by the ratio of the standard; this yields values that are labelled with δ (e.g. $\delta^{18}O$) and (ii) these δ values are expressed as per mil (‰) difference from the known standard. For water samples, the Vienna Standard Mean Ocean Water (V-SMOW) is typically used as a standard; its value is 0‰ for both $\delta^{18}O$ and δ^2H. Most precipitation and natural water samples have $\delta^{18}O$ and δ^2H values that are more negative than ocean water. Because ^2H has a greater mass than ^1H, and ^{18}O has a greater mass than ^{16}O, the terms 'light' and 'heavy' have come into use when describing waters with different isotopic composition. 'Lighter' water (i.e. depleted in the heavier isotopes relative to another sample) has a more negative δ value, and 'heavier' water (enriched in the heavier isotopes relative to another sample) has a more positive δ value.

The precision of laboratory analyses for ^{18}O is generally 0·2‰ or better, and for ^{2}H it is 2‰ or better. Textbooks such as Clark and Fritz (1997) or Mook and de Vries (2001) provide more details for the interested reader.

Isotopic fractionation between vapour and liquid water involves temperature-dependent proportions of the heavier isotopes of hydrogen and oxygen partitioning into the liquid phase during either condensation or evaporation (Clark and Fritz, 1997; and references therein). The heavier isotopes have a lower diffusion velocity and are less reactive than the lighter ones because their bonds with other molecules are stronger than those of the lighter isotopes. These characteristics lead to repeatable patterns of isotopic composition for water in different parts of the hydrologic cycle.

Worldwide $\delta^{18}O$ and $\delta^{2}H$ composition of precipitation exhibits a linear relationship: $\delta^{2}H = 8{\cdot}20\ \delta^{18}O + 11{\cdot}27$, known as the global meteoric water line (GMWL) (Rozanski *et al.*, 1993, after Craig, 1961). Differences in climate and humidity between different areas cause local meteoric water lines to differ in slope and intercept from the global average. Therefore, ideally, a local meteoric water line should be used in the interpretation of the isotope hydrology of an area. The stable isotope composition of precipitation varies with temperature and the history of the water vapour mass producing the precipitation. The classic conceptual model for progressive isotopic depletion of rainfall, that is, a preferential rain-out of the heavier water, involves a moist air mass rising and cooling. As condensation occurs and rain enriched in ^{2}H and ^{18}O falls to the ground, the source vapour in the cloud becomes increasingly depleted in these heavier isotopes, causing subsequent rainfall to be more isotopically depleted (although the rain at any time is enriched relative to the vapour it condensed from). The end result of these processes is that rainfall sampled from the same vapour mass, over time or along an altitudinal transect, will become progressively depleted isotopically (Dansgaard, 1964; Siegenthaler and Oeschger, 1980; and many others). Complicating this conceptual model is the situation where the cloud intersects the land surface, and precipitation is sampled within the cloud (Figure 1). In this case, samples may have an overall isotopic composition resulting from differently sized water droplets, water droplets from different altitudes within the cloud, and evaporation and re-equilibration of falling raindrops within the cloud (Lee and Fung, 2008). There may also be additional vapour from evaporation or transpiration incorporated into the cloud. Isotopic compositions under such conditions are not as predictable, and only a few studies are available. Some clouds have stratified isotopic composition, as evidenced by isotopic analysis of concentric layers in hailstones (Jouzel *et al.*, 1975) and by modelling of isotopic distributions within clouds (Federer *et al.*, 1982; Gedzelman and Arnold, 1994).

Fog has been found to be isotopically enriched compared with rainfall in the same area, when fog and rainfall are generated by separate climatic processes, for example, in areas with distinct wet and dry seasons. Advective ocean-derived fog (Aravena *et al.*, 1989; Ingraham and Matthews, 1995; Dawson, 1998) condenses at ambient air temperature and may even equilibrate with warmer temperatures as it moves onshore. Orographic or upslope fogs may also represent early stage condensation from a moist air mass, at temperatures near those of the land surface (Ingraham and Matthews, 1988). In contrast, rain from deep convective, frontal or low-pressure systems typically condenses higher in the atmosphere at much

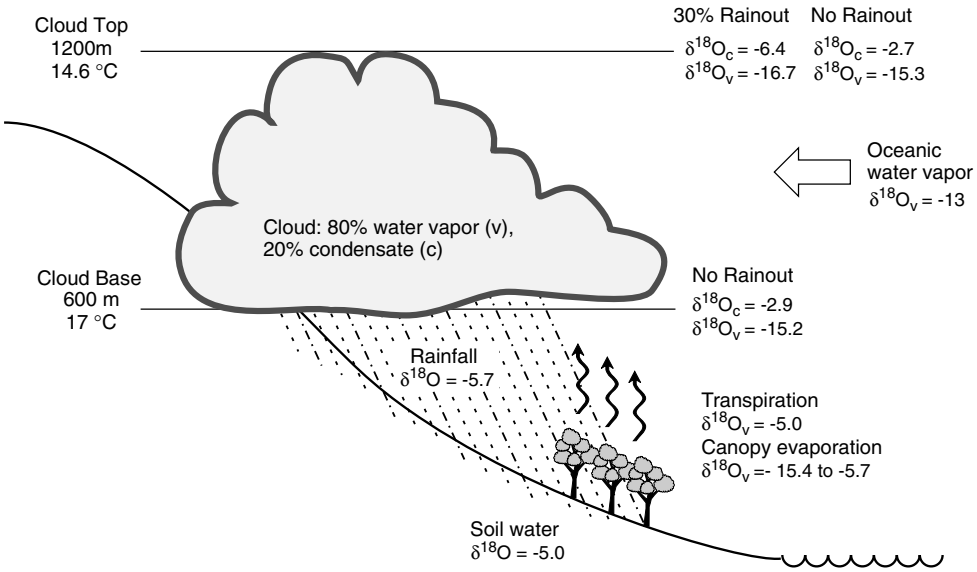

Figure 1. Isotopic transformations in the water cycle in a mountain cloud forest, illustrated using hypothetical $\delta^{18}O$ values in ‰. The example is an orographic cloud of 600 m vertical extent that originated from oceanic water vapour. The isotopic compositions of vapour ($\delta^{18}Ov$) and fog condensate ($\delta^{18}Oc$) are calculated using Rayleigh distillation equations and fractionation factors as given in Clark and Fritz (1997). Isotopic fractionation at cloud-top and cloud-base temperatures is shown in the figure. Isotopic values for two situations are illustrated, where the top of the cloud is producing rain (30% rain-out) and not raining (no rain-out), while the bottom of the cloud does not produce rain. With this small range in temperatures, loss of rain from the cloud-top is necessary for isotopic composition to differ significantly with altitude within the cloud

colder temperatures. The water vapour in high clouds is isotopically lighter to begin with and then becomes progressively lighter during rain-out (Scholl *et al.*, 2007, 2009).

When fog and rain occur as part of the same climatic process, fog droplets that condensed at (or equilibrated with) air temperature near the land surface could be more isotopically enriched than raindrops in the same cloud, as long as the raindrops formed near the top of the cloud where water vapour has a different composition and progressive vapour depletion is occurring due to rain-out processes and lower temperatures (Figure 1). This situation was postulated for the Otago uplands of New Zealand, where fog and rain often occurred simultaneously and the respective isotopic compositions fell along the same local meteoric water line (Ingraham and Mark, 2000). For mountains frequently immersed in raining orographic clouds, such as in Hawai'i (Scholl *et al.*, 2002, 2007; Table I), Puerto Rico (te Linde *et al.*, 2001; Burkard and Eugster, unpublished data in Table I; Scholl *et al.*, 2009) or Costa Rica (Burkard, 2003 and unpublished data in Table I; Schmid *et al.*, 2010), isotopic signatures of rain and fog may not be as distinct. Many measurements in these areas showed fog to be isotopically enriched compared with rain, but in some cases, isotopic signatures were similar, and measurements of individual precipitation events in both Puerto Rico and Costa Rica included instances when fog isotopic composition was more depleted than rain isotopic composition (Table I). The reasons for the latter observations are unknown, and further studies need to be done.

Throughfall is precipitation collected underneath a vegetation canopy. The definition of throughfall generally includes both precipitation that has been intercepted by the canopy and then drips to the ground, and precipitation falling directly through gaps within the canopy without interception. The intercepted precipitation may include rain and/or fog, and the canopy has a storage capacity that must be filled before the precipitation begins dripping off to the ground. Studies of isotopic composition of throughfall generally reported throughfall to be enriched relative to open-sky rainfall, although Goller *et al.* (2005) found throughfall and rain in a tropical forest in Ecuador to be similar in ^{18}O composition, and depletion of throughfall relative to rain has also been observed in some samples (Scholl *et al.*, 1995). The difference in isotopic composition between throughfall and rain is thought to be due to evaporation and exchange with atmospheric vapour during storage in the canopy, with the magnitude of the change depending on temperature, humidity and the residence time of the water in the canopy. Published isotopic enrichments of ^{18}O in throughfall relative to rain range from 0·3 in a boreal pine forest in Sweden (Saxena, 1986), to 0·38‰ in spruce and 0·36‰ in beech forests in Germany (Brodersen *et al.*, 2000), to as much as 1‰ in coniferous and deciduous forests in Georgia, USA (Kendall, 1992). Isotopic composition of throughfall can also be affected by the placement of the collector; for example Brodersen *et al.* (2000) found higher isotopic enrichment under tree crown centres than under the crown periphery. In a montane forest in Hawai'i, isotopic depletion in throughfall samples was thought to result from the collectors receiving water predominantly from isotopically depleted intense rainfall events, while the canopy blocked much of the locally generated, isotopically enriched orographic rainfall and fog drip from falling into the collectors (Scholl *et al.*, 1995).

Isotopic fractionation of water occurs during evaporation from soils, but not during the root uptake process in transpiration (Thorburn *et al.*, 1993a; Dawson and Ehleringer, 1998). Plant leaves contain water that is isotopically enriched due to evaporation, but it is generally thought that there is no significant isotopic fractionation of the vapour in the process of transpiration outflux from leaves, so that under steady-state conditions, transpired vapour is assumed to have the same isotopic composition as the water taken up by the roots (Dawson and Ehleringer, 1998; Wang and Yakir, 2000).

Gat (2000) reviewed the different sources of atmospheric vapour and how isotopes may be used to trace water sources in the atmospheric water balance. The deuterium excess (d) is defined as $d = (\delta^2H - 8\ \delta^{18}O)$. Because of differences in the fractionation of oxygen and hydrogen during evaporation at different humidity levels, precipitation from water vapour that originates from re-evaporated rainfall (vapour from canopy interception, lakes and wetlands, or falling rain) may have a larger deuterium excess value than precipitation originating from water vapour evaporated from the oceans. This parameter has been used to assess the contribution to precipitation at a particular location by recycled moisture. Examples include the Amazon Basin (Salati *et al.*, 1979; Martinelli *et al.*, 1996), Hawai'i (Scholl *et al.*, 2007) and Costa Rica (Rhodes *et al.*, 2006).

ISOTOPES IN RAINFALL AND FOG: A REVIEW

Published studies including measurements of the stable isotope content of fog span about 45 years (Table I), but are surprisingly few considering the large number of isotope hydrology studies conducted during that time. Reported isotope values for fog water cover a large range, from −71 to +13‰ for δ^2H and −10·4 to +2·7‰ for $\delta^{18}O$, depending on the temperature and vapour sources in the study areas (Table I). A scatter plot of $\delta^{18}O$ versus δ^2H values in fog or cloud water and in rainfall from the studies listed in Table I is shown in Figure 2. As is often observed for fog and rain samples from individual sites, the fog values as a group are generally enriched in the heavier isotopes compared with the rain samples, although the two groups overlap because of the large range of temperatures for the sites. Fog values plot both above and below the GMWL, but as a group, the values

Table I. Stable isotope values ($\delta^{18}O$ and $\delta^{2}H$) of fog, cloud water and rain for sites around the world

	Study	Location	Altitude (m)	Fog type	Sampling interval	Number of samples	Fog $\delta^{18}O$ (‰)	Fog $\delta^{2}H$ (‰)	Rain $\delta^{18}O$ (‰)	Rain $\delta^{2}H$ (‰)
1	Gonfiantini and Longinelli (1962)	Shipboard, off Newfoundland	Sea level	Advective oceanic	≤4h	Average of 14 fog, 18 rain	−2·4	—	−5·8	—
2	Clark *et al*. (1987)[a]	Oman	—	Orographic (monsoon)	—	—	−0·43 to +1·13	−2·1 to +10·5	—	—
3	Ingraham and Matthews (1988)	Kenya	1700	Orographic	Grab samples: 10–12 days	Average of 4	−0·75	+13	—	—
						Average of 2	−1·6	+6	—	—
4	Aravena *et al*. (1989)	Chile	—	Advective oceanic	—	Average of 13 fog, 4 rain	−1·86	−3·2	−5·6	−40
5	Ingraham and Matthews (1990, 1995)	California, northern	—	Advective oceanic	Cumulative samples, intervals not given	4-year average, three sites	−2·3	−10	−6·5	−38
							−2·8	−15	−7·0	−40
							−2·4	−10	−6·3	−36
6	Dawson (1998) and ongoing observations[b]	California, northern	—	Advective oceanic	Monthly averages, 3-year study	17 fog collectors, rain not given	−4·9 to +2·7	−8·9 to +6·4	−15·6 to −5·5	−84·6 to −28·7
7	Feild and Dawson (1998)[c]	Costa Rica	1500	Orographic	Event	Averages, 82 total	−2·9	−6·6	−2·8	−24·9
8	Dawson and Vidiella (1998)	Chile	68	Advective oceanic	Monthly, per event in summer	Averages, 212 total	−1·3	−4·6	−3·7	−32·8
9	Dawson (2000–2004, written communication)	California, northern	140	Advective oceanic	Monthly since 1/00	Averages, 97 samples	−2·3	−8·1	−8·4	−46·2
10	Dawson (2000–2004, written communication)	California, northern	128	Advective oceanic	Monthly since 1/00	Averages, 155 samples	−3·3	−7·1	−8·9	−55·3
11	Corbin *et al*. (2005)	California	9	Advective oceanic	Monthly, and per event in summer	Averages, 38 total	−2·7	−6·4	−5·3	−40·8
12	Ingraham and Mark (2000)	New Zealand	736, 870 and 1140 m	Advective	Approximately monthly, two summers	Three sites, 9–11 samples per site	−5·3 to −10·4	−30 to −71	−7·9 to −12	−50 to −87
13a	te Linde *et al*. (2001)[d]	Puerto Rico	1018	Orographic cloud (trade wind)	Daily for 5 weeks	Average of 4 fog, 4 rain	−3·8	−17	−4·1	−17

Table I. (*Continued*)

	Study	Location	Altitude (m)	Fog type	Sampling interval	Number of samples	Fog $\delta^{18}O$ (‰)	Fog $\delta^{2}H$ (‰)	Rain $\delta^{18}O$ (‰)	Rain $\delta^{2}H$ (‰)
13b	te Linde *et al.* (2001)[d]	Puerto Rico	1018	Orographic cloud (trade wind)	Daily for 5 weeks	Composite (bulk) sample	−1·9	—	−2·4	—
14a	Burkard, Eugster and Holwerda (unpublished)[e]	Puerto Rico, Pico del Este	1015	Orographic cloud (trade wind)	One sample per event, 12-h average	Fog > rain: 36	−1·21	−1·70	−1·62	−6·2
14b	Burkard, Eugster and Holwerda unpublished[e]	Puerto Rico, Pico del Este	1015	Orographic cloud (trade wind)	One sample per event, 12-h average	Fog < rain: 8	−1·32	−4·70	−0·47	−2·0
15a	Scholl *et al.* (2007)[f]	Leeward Maui	1220	Orographic (thermal)	2-year VWA of monthly samples	19	−2·7	−6	−5·5	−31
15b	Scholl *et al.* (2007)	Windward Maui	1950	Orographic cloud (trade wind)	2-year VWA of monthly samples	22	−4·1	−16	−5·5	−28
16	Still *et al.* (2003)	Costa Rica	—	—	Not given	One sample each	−4·9	−21	−8·1	−45
17a	Burkard, Schmid and Eugster, unpublished[e]	Costa Rica	1460	Orographic cloud	One sample per event, 24-h average	Fog > rain: 31	−1·99	−6·46	−2·39	−12·3
17b	Burkard, Schmid and Eugster, unpublished[e]	Costa Rica	1460	Orographic cloud	One sample per event, 24-h average	Fog < rain: 6	−3·14	−15·40	−2·23	−10·2
18	Fischer and Still (2007)[g]	California, Santa Cruz I	296	Advective oceanic	Monthly for 34 months	37 fog, 17 rain	−2·52	−11·4	−5·16	−31
19	Liu *et al.* (2007)	SW China	750	Radiation	Fog: biweekly, rain: monthly and event	116 rain, 59 fog	−3·3	−11·5	−7·9	−56·8
20	Scholl *et al.* (2009)[h]	Puerto Rico, Pico del Este	1050	Orographic cloud (trade wind)	VWA of monthly samples	36 rain, 36 fog	−2·14	−1·34	−3·68	−14·3

VWA, volume-weighted average.
[a] Data from I. Clark, written communication, 2005; data were shown in Figure 8 in Clark *et al.* (1987).
[b] Research is ongoing, data reported here are for the entire period of data collection at the site as of 2004 (T. Dawson, written communication, 2004).
[c] Values reported here are more comprehensive than those reported in the publication (T. Dawson, written communication, 2004).
[d] Values in 13a are the average of four selected events; 13b are the volume-weighted average of all the daily samples.
[e] Values are averaged separately for conditions where δD or $\delta^{18}O$ in fog was enriched compared with rain (fog > rain; 14a, 17a) and conditions with both isotopes being depleted in fog compared with rain (fog < rain; 14b, 17b).
[f] Fog averages for Maui exclude sampling periods with large storms, because rain dominated the fog collector sample.
[g] Average values are from D. Fischer, written communication. The publication gives values in graph format only.
[h] Fog averages for Pico del Este exclude three sampling periods with large storms, because rain dominated the fog collector sample.

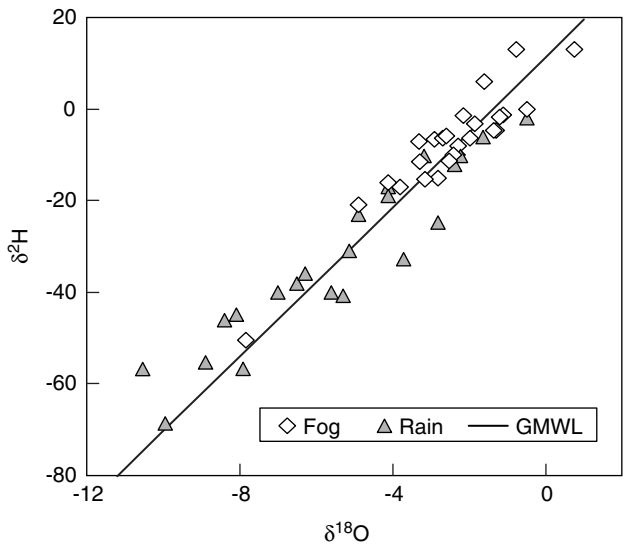

Figure 2. Fog isotopic values from around the world based on the studies listed in Table I are compared with rain isotope values from the same site (if given) and the GMWL. All values are in ‰. Single symbols are individual values, or the average value when a range was reported in the publication

are parallel to the meteoric water line, as expected for precipitation samples.

Gonfiantini and Longinelli (1962) published δ^{18}O analyses of fog and rain collected on a ship near the fishing banks off Newfoundland and Labrador. The fog was formed at the sea surface due to warmer air moving over cold water (sea fog). The authors noted that the δ^{18}O values ranged from that of sea water to water vapour in equilibrium with sea water. Although the range of δ^{18}O in fog overlapped the range of rain δ^{18}O values, the fog samples on average were isotopically enriched compared with rain in the same area.

Clark *et al*. (1987) and Ingraham and Matthews (1988), in regional isotope hydrology studies conducted in arid climates, found fog to be an important component of the local hydrology. In northern Kenya, Ingraham and Matthews (1988) sampled fog, groundwater and a river in a desert basin where isolated high mountains received orographic fog precipitation. They found the fog to be substantially isotopically enriched compared with a groundwater sample derived from rain, and groundwater in three other areas appeared to be a mixture of fog and rain. Clark *et al*. (1987) found that monsoon fog and light rain in the mountains of southern Oman constituted a source of recharge for groundwater in the mountains and in the adjacent coastal plain. These monsoon-cloud precipitation samples had isotopic signatures similar to sea water, and the precipitation was assumed to originate from a single-stage evaporation–condensation cycle near the coast.

In an isotope hydrology study of the windward side of East Maui, Hawai'i, Scholl *et al*. (2002) found isotopic values of mountain streams and springs to be unexpectedly enriched in the heavier isotopes for their altitude, compared with volume-weighted average rainfall measured in a transect up the mountainside. The best explanation for the observed isotopic composition was that fog drip contributed substantially to streamflow and shallow groundwater. This work suggested that water balances based only on streamflow and rain gauge precipitation measurements in the area could have a large degree of error. A subsequent study was done (Scholl *et al*., 2007; Table I) on both the windward and leeward sides of East Maui, with cloud-water samples collected from passive collectors at monthly intervals for 2 years. On the windward side, fog occurred as part of the trade-wind orographic clouds, which had droplet sizes ranging from fog to rain. On the leeward side, thermal heating over the land generated an upslope fog with relatively lower liquid water content. Fog was isotopically enriched compared with rain at both sites (Table I), but isotopic differences between fog and rain were larger on the leeward side, where synoptic-scale storms accounted for most of the rainfall. With few exceptions, each month's fog collector sample was isotopically enriched compared with the rain collector sample, though differences between the two samples were sometimes small (Scholl *et al*., 2007).

Near Pico del Este in the Luquillo Mountains of eastern Puerto Rico, Burkard and Eugster (Table I) sampled fog, rain, throughfall and stemflow in a follow-up study after the preliminary work of te Linde *et al*. (2001). Fog and rain from each precipitation event were sampled for approximately 1 month. Using a Caltech active strand cloud-water collector (CASCC) (Daube *et al*., 1986), fog was efficiently separated from rain even when they occurred simultaneously. The fog collector was switched on whenever visibility dropped to less than 500 m and sampling continued until the 10-min running mean visibility exceeded 500 m for several minutes. This threshold was chosen to minimize contamination by insects and dry aerosols; fog with a visibility in excess of 500 m tends to contribute very little to total fog deposition (Thalmann *et al*., 2002; Burkard *et al*., 2003). Rain and fog water samples for isotopic analysis were always taken simultaneously, such that the durations of sampling of fog and rain matched. The local type of fog is an advected cloud formed over a warm ocean, with the cloud-base below the mountain top for almost 75% of the time (Holwerda *et al*., 2006, 2010). Oxygen-18 and ^{2}H were usually (but not always) enriched in fog compared with rain (Figure 3). The difference between the isotopic composition of rain and fog, however, was quite small (Figure 3 and Table I) compared with the temporal variability caused by weather conditions and prevailing wind directions. Conditions during which fog was depleted in ^{18}O and ^{2}H relative to rain may have been partly due to time lags between fog and rain (Figure 3). During some events, a change in isotopic signature occurred 12–24 h (the minimum sampling interval used in the study) earlier in fog than in rain (Eugster, 2007). This result is consistent with the potential explanation that coalescence of rain consisting of relatively large droplets, although originating from the same air mass as

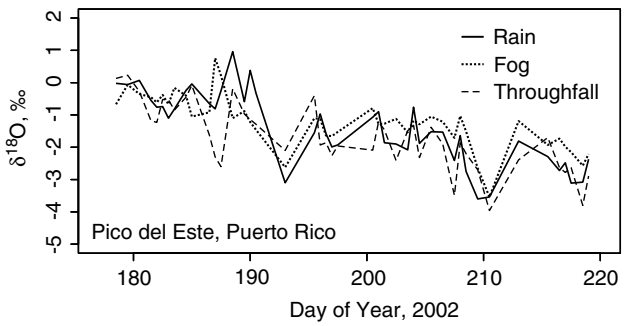

Figure 3. Isotopic signatures of $\delta^{18}O$ in rain, fog and throughfall measured in elfin cloud forest in Puerto Rico (daily means). The time traces reveal the importance of synoptic-scale changes in weather

the fog, takes longer than the coalescence of fog alone. The fact that isotopic signatures at Pico del Este did not differ much between fog and rain after considering such a time lag suggests that under these humid tropical conditions, condensation and re-evaporation processes occur in an atmospheric system saturated with water vapour. Thus, the coalescence of droplets as the air mass ages determines how much of the water is available as large droplets (rain) and what fraction remains as small droplets (fog).

The isotopic signature of composite throughfall at Pico del Este was often depleted in ^{18}O and ^{2}H relative to both rain and fog (Figure 3), which may indicate that additional processes (not fully understood as yet) could affect throughfall isotopic composition. Twenty roving collectors were randomly placed at 80 pre-defined positions, and isotopic analysis was performed on a single sub-sample after bulking the water from all collectors. Although this sampling design should average the spatial variability of throughfall amounts, it may be sensitive to the influence of isotopic 'hot spots' where the influence of rainfall contributions is disproportionately large (so-called 'drip points'; Holwerda *et al*., 2006).

Similar conditions to those described above were found in a windward cloud forest in the Monteverde area in northern Costa Rica (Burkard *et al*. in Table I; Schmid *et al*., 2010), where a few events did not correspond to the typical pattern that stable isotopes are enriched in fog compared with rain. This site, which was not as close to the ocean as the example from Puerto Rico, experienced an even wider range of isotopic concentrations depending on weather conditions. As in Puerto Rico, isotopic signatures in fog and rain followed each other closely (data not shown).

A few isotopic studies involving fog, rain and groundwater included analyses of leaf water (Aravena *et al*., 1989) or tree xylem and soil water (Ingraham and Matthews, 1995; Scholl *et al*., 2003); others used isotopes to examine the role of fog in ecosystems (Dawson, 1998; Feild and Dawson, 1998, Limm *et al*., 2009). The field studies found fog water to be isotopically enriched compared with rain water, and each study showed that the vegetation utilized fog water under some conditions. The investigation by Dawson (1998) in the redwood forests of California was the most extensive, showing conclusively that the ecosystem depended on fog as a water source as the soil dried out during the rainless summer season.

The differences in isotopic values for rain and fog in the studies listed in Table I are shown in Figure 4. When a range of values was given in the original publication, the mean values were used to calculate the difference. Both deuterium and oxygen-18 plots are shown because

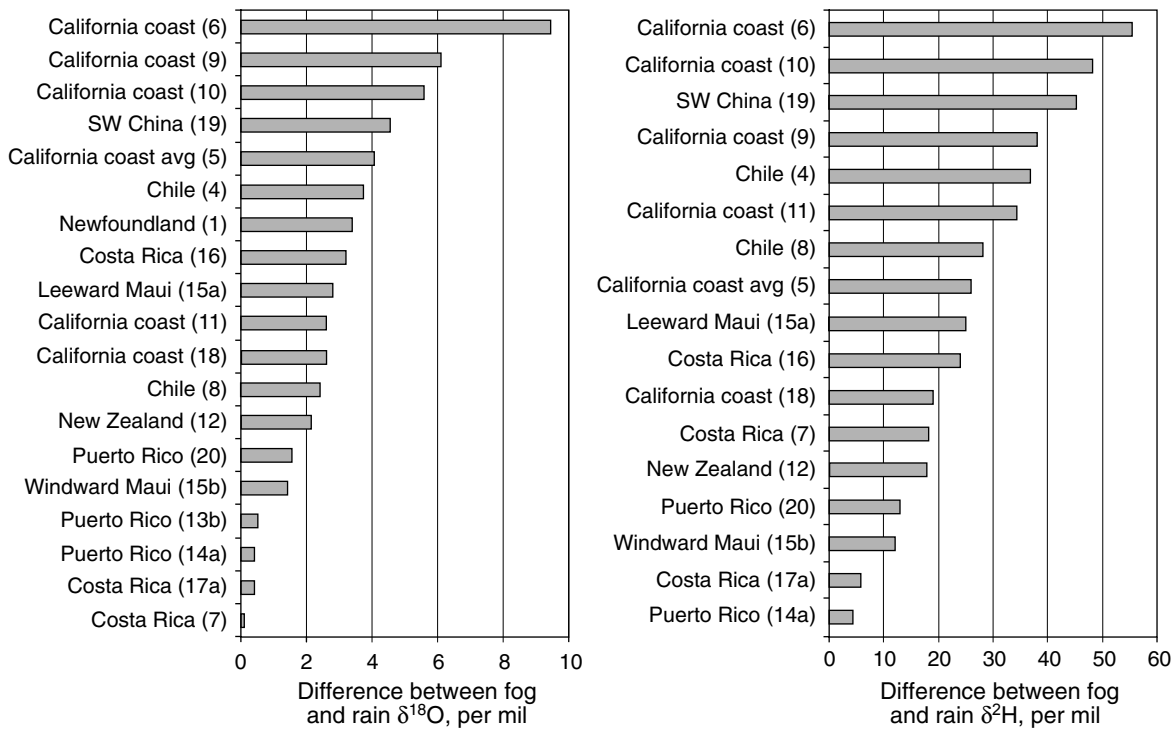

Figure 4. Magnitude of the difference between values for $\delta^{18}O$ and $\delta^{2}H$ in fog and rain, in ‰. Numbers correspond with numbered studies in Table I

some studies involved only one of the isotopes. The graphs show differences in isotopic values of fog and rain in different localities, but these should not be considered definitive as different sampling frequencies, methods and numbers of samples were associated with the different studies. The graphs indicate that the smallest differences between fog and rain (<2‰ in ^{18}O and <20‰ in ^{2}H) are associated with orographic clouds on mountains in Puerto Rico, windward Hawai'i and Costa Rica. The largest differences (>4‰ in ^{18}O and >30‰ in ^{2}H) involved advected oceanic or radiation fog, with rain as a separate climatic process (California, Chile and SW China).

To summarize the previous work, relatively few studies have examined the isotopic composition of fog, and of these, even fewer constituted more than reconnaissance-level surveys. Of the studies listed in Table I, only five involved long-term sampling, yielding average isotopic values in fog and rain over two to four years, and only three studies investigated stable isotopes in fog and rain in detail for every precipitation event during at least a month. Most of the studies found average fog isotopic composition to be more enriched than average rain; however, sampling in Puerto Rico and Costa Rica revealed situations where the reverse was true (Figure 3 and Table I). In some studies, collection methods did not entirely separate fog and rain, so that average values may not reflect true isotopic differences between fog and rain. Tracing fog water using isotopic analysis of plant water has been successful in some environments, particularly where fog and rain are governed by different climatic processes.

SAMPLING METHODS FOR STABLE ISOTOPES

Precipitation

General considerations. The main goal when collecting a precipitation sample for stable isotope analysis is to avoid changes in isotopic composition between collection and analysis. Water in a container open to the atmosphere immediately begins to change in isotopic composition because of evaporation and exchange with ambient vapour (Ingraham and Criss, 1993). If evaporation takes place in an atmosphere of high humidity (i.e. the headspace of a vented collection container), the altered sample isotopic composition will be close to the meteoric water line (Gonfiantini, 1986, reprinted in Clark and Fritz, 1997), so that the evaporation is not detectable but the sample values are incorrect (Scholl *et al*., 1995). Evaporation and exchange are minimized if the sampler is designed to inhibit evaporation, collects relatively large samples with a small surface area of sample exposed to the atmosphere, and if the collection reservoir is shielded against direct insolation. Water samples for stable isotope analysis should be collected in glass bottles with 'poly-seal' caps (caps with conical plastic insert). Mook and de Vries (2001) give a detailed discussion of general water sampling and isotopic analytical methods.

Fog, rain and throughfall collectors. Most collectors used for precipitation sampling on a time scale longer than a few hours involve some kind of system whereby the rain is collected with a funnel, or fog is collected on a vertical screen or strings, after which the water is routed to a collection bottle. There are two ways to preserve the isotopic composition of the water in a precipitation collector: (i) a layer of mineral oil is added to serve as a barrier against evaporation. Because of its greater density, precipitation entering the collector will sink below the protective oil layer. If the sampling interval is longer than a week, the oil layer needs to be about 1-cm thick, as water will evaporate through thinner layers (Scholl *et al*., 1995, 2002). (ii) The sampling container has the smallest possible area open to the atmosphere, so that the degree of evaporation or exchange is small relative to sample volume. There are many ways to accomplish this, ranging from the use of tubing extending from the stem of the funnel to the bottom of the sampling container, collecting the sample in a bag to minimize headspace, or using a plastic ball that floats to allow sample into the container and blocks the opening at other times. For any precipitation collector design, a control container with known volume and isotopic composition should be placed at the collection location to test the sampling method for evaporation effects.

To collect the small fog droplets separately from larger raindrops, an active strand cloud-water collector (known as a CASCC; Daube *et al*., 1986, 1987) may be used. This device has a fan that pulls the air from under a rain-shed across an array of strings where the fog droplets impact on Teflon or stainless steel strings and are guided to a collection bottle. The size and spacing of the strings, and the air velocity generated by the fan determine the size of the droplets captured. The collector inlet must face the wind. A drawback of this collector for remote sites is the high-power consumption of the fan. A test in the Adirondack Mountains of New York, USA (M. Scholl, unpublished data) showed that isotopic samples of cloud water collected with a small CASCC (18 × 18 cm inlet) had the same composition as samples passively collected on wire mesh, suggesting that the fan's airflow velocity does not cause significant evaporation and isotopic fractionation of the fog droplets as they impact on the strings. Further tests, however, should be done with the larger, higher-velocity CASCCs. Because CASCCs are extremely efficient, they produce the amount of water required for isotopic analysis within a short time.

Tree cores, twigs and soil water. The ^{18}O or ^{2}H isotopic composition of sap can indicate the transpiration water source for the plants in a forest (White *et al*., 1985; Thorburn *et al*., 1993b; Dawson and Ehleringer, 1998; Meinzer *et al*., 1999; and many others). Dawson (1993) and Dawson and Ehleringer (1998) provided thorough reviews of the use of plant isotope tracers in watershed hydrology and may be consulted for additional detail. Tree sap for isotopic analysis may be collected from cores

(White *et al*., 1985) or twigs (Dawson, 1993; Thorburn *et al*., 1993b). The water in the xylem is the transpiration water, so when taking core samples, sapwood should be separated from heartwood as the isotopic composition of the heartwood may represent stored water from other sources or time periods. For twig samples, twigs with mature bark and measuring at least 1-cm diameter are removed from the plant, the bark is scraped off, and twigs cut into short pieces to fit into an airtight glass jar. Samples are frozen until analysis. The commonly used methods for extracting the water from plant tissues are azeotropic distillation (Revesz and Woods, 1990; Thorburn *et al*., 1993b) and cryogenic vacuum distillation (West *et al*., 2006), after which the water is analysed for isotopic composition using standard methods.

Sampling the isotopic composition of soil water in forests involves more uncertainty than precipitation and plant water, because water infiltrating into the soil is subject to evaporation in the unsaturated zone, particularly in the top of the soil profile (Allison *et al*., 1983; Barnes and Allison, 1983; Barnes and Turner, 1998). Knowledge of the depth of the root zone for the plants of interest is helpful to make optimum use of both soil and sap isotopic data from a site. Samples for isotopic composition of soil water are obtained by extraction from soil cores or from the outflow of lysimeters. Suction-type lysimeters introduce the possibility of isotopic fractionation, although Landon *et al*. (1999) found in laboratory tests that lysimeter samples were not significantly fractionated. Soil core samples are placed in airtight glass or metal containers immediately after collection and kept refrigerated until analysis to inhibit microbial activity and evaporation. Water extraction techniques include vacuum distillation, azeotropic distillation, micro-distillation with zinc and immiscible displacement using centrifugation; Barnes and Turner (1998) reported that azeotropic distillation was generally found to be the best method.

TRACING FOG THROUGH THE FOREST WATER CYCLE

Sampling-interval considerations

Both long-term, infrequent sampling and short-term, intensive sampling strategies have been used to study the isotope hydrology of cloud forests. There are advantages and disadvantages to each approach, and the selected approach also depends on the research questions, site accessibility and funding. Short-term, event-based sampling of isotopes is important to investigate processes that may vary over short time intervals, such as interception of rainfall or fog, crown drip, transpiration and storm runoff. Some simplifying assumptions about fractionation processes within the canopy are necessary, but short-term event-based sampling may help to resolve this. Longer-term cumulative-sample studies integrate short-term variations in samples and yield a volume-weighted average isotopic value. This strategy can work well for watershed processes that involve longer time scales or for understanding spatial variability in mountainous areas. For example, the pathway from fog and rain water inputs to groundwater may in some areas be on the scale of months to years, and for such an application the variation in isotopic signature with each event can be considered negligible. Careful consideration should be taken concerning the relevant processes and their respective time scales, from which an optimum sampling strategy may be derived.

The sampling interval for precipitation also needs to be determined with consideration of the study objectives, and the climatology and precipitation patterns at the site. The stable isotope composition of rainfall commonly changes not just between events but also during the course of a precipitation event (McDonnell *et al*., 1990; Clark and Fritz, 1997, p. 50; Barnes and Turner, 1998). These changes are not predictable because of variations in cloud processes producing the rain, and because precipitation is normally sampled at a fixed location while different parts of a weather system move past. To resolve this variation, samples must be taken over the course of a precipitation event. At the opposite end of the sampling time scale, for regional hydrological studies, 6-month cumulative samples of precipitation may be an adequate resolution, provided that evaporation between rain events is prevented. Most of the studies discussed in this paper had sampling intervals ranging from daily to monthly.

Mixing models and stream hydrograph separation techniques

In locations where fog and rain have distinct isotopic signatures, a simple linear mixing model may be applicable for evaluating possible contributions of the two source waters to streamflow, plant transpiration, or groundwater recharge. For example, fog and rain are considered the two independent source water end members, which are mixed in a certain volumetric proportion to yield the resulting component (e.g. transpiration water). The fraction of transpiration that comes from fog water, f_F, is

$$f_F = \frac{\delta_T - \delta_R}{\delta_F - \delta_R} \tag{1}$$

where the isotopic ratios of ^{18}O or ^{2}H are denoted with δ, and the indexes T, F and R, indicate the sampled transpiration water (sap), fog and rain, respectively. Mixing models work best in situations where: (i) there is a large difference between average isotopic composition of fog and rain and (ii) there is no fractionation of the source water isotopes in the process of transport through the hydrologic cycle, or the fractionation is known and constant. In the case of streamflow studies or recharge over short time intervals, precipitation usually passes through the shallow soil zone, and its isotopic composition changes by mixing with pore water already present. Similarly, for water intercepted by the canopy, evaporative isotopic fractionation may be an issue. Phillips and Gregg (2001) provide a good overview of single isotope,

two-source and dual isotope, three-source mixing models with formulas for calculation of confidence intervals, which can be utilized in mixing model analyses.

Stable isotope techniques have been used for more than 30 years in watershed hydrograph separation studies. The recognition that rain events often have significantly different isotopic composition than water stored in the subsurface led to the finding that streamflow generally includes a significant proportion of pre-event water stored in the watershed, rather than just runoff from the current storm event (Sklash *et al*., 1976; Sklash and Farvolden, 1979; Buttle, 1998; and many others). These techniques may have application in determining the amount of cloud water contributing to stream baseflow in mountain forests. Another technique involves using the seasonal fluctuations in precipitation isotopes to determine residence time for water in a watershed (Maloszewski and Zuber, 1982; McGuire *et al*., 2002). Seasonal differences in rain isotopes tend to be smaller in the tropics than at higher latitudes, but the differences in precipitation isotopic composition required for the application of such techniques can occur in mountain areas with distinct rainy and dry seasons with fog providing significant moisture in the dry season (Rhodes *et al*., 2006; Liu *et al*., 2007; Scholl *et al*., 2007), or in areas having orographically generated local rainfall alternating with synoptic-scale storms (Scholl *et al*., 2007, 2009). Evaporative fractionation may also be useful as a check on other methods for determining evaporation rates of precipitation intercepted by the canopy, provided throughfall has a significant evaporative signature (Saxena, 1986; Brodersen *et al*., 2000).

In principle, stable isotopes constitute a powerful tool to determine the relative influences of fog and rain in the local water budget (Dawson, 1998; Liu *et al*., 2007), and may also yield insights into water dynamics in the plant canopy. In reality, conditions are sometimes more complex, and simple mixing models may not provide the desired information. However, these models can be a valuable approach for testing conceptual models of water flow in mountain areas affected by fog, yielding information on previously unexpected or unknown processes that prove to be relevant at a certain site.

DIRECTIONS FOR FUTURE RESEARCH

Previous studies have suggested that stable isotopes can be a useful tool in identifying the role of fog water in the hydrologic and ecological functioning of cloud-affected forests, but comparatively few studies have been conducted and several important questions remain. In areas where fog and rain are generated by separate climate processes, fog is isotopically enriched compared with rainfall, and this contrast has been used effectively to demonstrate the importance of fog water to, for example, the redwood forest of coastal California (Dawson, 1998). Tracing fog water inputs to an ecosystem is least ambiguous where fog is the only source of water for all or part of the year (Aravena *et al*. 1989; Ingraham and Matthews, 1995; Dawson, 1998; Liu *et al*., 2007). However, in areas receiving mixed fog and rain, like many montane cloud forests experiencing significant orographic cloud-water input, the isotopic composition of rain and fog has not been as well documented. The event data from the elfin cloud forest at Pico del Este in Puerto Rico (Figure 3) show conclusively that fog and rain sampled from the same cloud are often isotopically different. Other studies in climates with locally generated orographic rainfall have also found fog to be isotopically enriched compared with rain, although such differences were relatively small (Scholl *et al*., 2007, 2009). In those environments, larger differences have been found between different types of precipitation events (local orographic scale vs synoptic scale). There is a need for more studies of rain and fog water, particularly in relation to the determination of the water dynamics and sources of precipitation-dependent parts of the ecosystem such as epiphytes (Hietz, 2010; Tobón *et al*., 2010).

Because much of the precipitation input to forest soils consists of throughfall, it is important to understand the isotopic composition of throughfall if isotope techniques are to be used to understand streamflow sources, ecosystem functioning, or recharge patterns. There is some disagreement as to whether the isotopic composition of throughfall is always enriched relative to rainfall. Brodersen *et al*. (2000) shed some light on this issue, showing that the placement of the collector is important. Both throughfall and fog water may be isotopically enriched relative to rain, which may render it difficult to separate contributions by rain and fog to overall canopy interception using isotope mass balance techniques (Schmid *et al*., 2010). Similarly, large inputs of evaporatively enriched throughfall to a forest may make differentiating between fog and rain inputs more difficult in longer-term studies. It may also be possible for throughfall to become depleted by vapour exchange at high humidity (Brodersen *et al*., 2000), which may be relevant in cloud forest situations.

The design of fog collectors for stable isotope sampling also needs further work. In areas with mixed fog and rain precipitation, passive fog collectors generally collect some proportion of wind-blown rainfall, even if they have a cover to keep out the rain (Fischer and Still, 2007; McJannet *et al*., 2007a; Scholl *et al*., 2007; Frumau *et al*., 2010a,b; Giambelluca *et al*., 2010). Active collectors require a power source which makes them less practical for use in remote areas or for long periods of time. Such problems in the sampling of fog and rain have led to some uncertainty in measured isotopic compositions. Measurements that would help to resolve these questions include analysis of isotopic compositions across the range of droplet sizes within a raining cloud, and at several altitudes within a single cloud. Despite the present sampling limitations, it is clear that in hydrologic studies involving isotope techniques in mountain forests, relying on the isotopic composition of precipitation as collected in a standard funnel-type collector under open

sky could lead to misinterpretation. Given the magnitude of potential fog capture by the canopy of many cloud-affected forests, isotope samples should be analysed from rain-, throughfall- and cloud-water collectors alike to ascertain the relative contributions by rainfall and fog to overall ecosystem inputs.

ACKNOWLEDGEMENTS

We thank Douglas Burns and Karen Rice of the US Geological Survey, Sampurno Bruijnzeel of VU University, Amsterdam, and Douglas Fischer of the California State University for helpful comments on the manuscript.

REFERENCES

Allison GB, Barnes CJ, Hughes MW. 1983. Distribution of deuterium and oxygen-18 in dry soils. II. Experimental. *Journal of Hydrology* **64**: 377–397.

Aravena R, Suzuki O, Pollastri A. 1989. Coastal fog and its relation to groundwater in the IV region of northern Chile. *Chemical Geology (Isotope Geoscience Section)* **79**: 83–91.

Barnes CJ, Allison GB. 1983. The distribution of oxygen-18 and deuterium in dry soils. I. Theory. *Journal of Hydrology* **60**: 141–156.

Barnes CJ, Turner JV. 1998. Isotopic exchange in soil water. In *Isotope Tracers in Catchment Hydrology*, Kendall C, McDonnell JJ (eds). Elsevier: Amsterdam; 137–163.

Brodersen C, Pohl S, Lindenlaub M, Leibundgut C, von Wilpert K. 2000. Influence of vegetation structure on isotope content of throughfall and soil water. *Hydrological Processes* **14**: 1439–1448.

Bruijnzeel LA. 2001. Hydrology of tropical montane cloud forests: a reassessment. *Land Use and Water Resources Research* **1**: 1.1–1.8.

Bruijnzeel LA, Eugster W, Burkard R. 2005. Fog as an input to the hydrological cycle. In *Encyclopaedia of Hydrological Sciences*, Anderson MG, McDonnell JJ (eds). John Wiley: Chichester; 559–582.

Bruijnzeel LA, Mulligan M, Scatena FN. 2010. Hydrometeorology of tropical montane cloud forests: emerging patterns. *Hydrological Processes*. DOI: 10.1002/hyp.7974.

Burkard R. 2003. *Fogwater flux measurements Above different vegetation canopies*. PhD thesis, University of Bern, Bern, Switzerland.

Burkard R, Bützberger P, Eugster W. 2003. Vertical fogwater flux measurements above an elevated forest canopy at the Lägeren research site, Switzerland. *Atmospheric Environment* **37**: 2979–2990.

Buttle JM. 1998. Fundamentals of small catchment hydrology. In *Isotope Tracers in Catchment Hydrology*, Kendall C, McDonnell JJ (eds). Elsevier: Amsterdam; 1–49.

Clark ID, Fritz P. 1997. *Environmental Isotopes in Hydrogeology*. CRC Press: New York.

Clark ID, Fritz P, Quinn OP, Rippon PW, Nash H, Al Said SBBG. 1987. Modern and fossil groundwater in an arid environment: a look at the hydrogeology of southern Oman. In *Symposium on Isotope Techniques in Water Resources Development*, IAEA-SM-299/15. International Atomic Energy Agency: Vienna; 167–187.

Craig H. 1961. Isotopic variations in meteoric waters. *Science* **133**: 1702–1703.

Corbin JD, Thomsen MA, Dawson TE, D'Antonio CM. 2005. Summer water use by California coastal prairie grasses: fog, drought, and community composition. *Oecologia* **145**: 511–521.

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

Daube BC Jr, Flagan RC, Hoffmann MR. 1986. Active Cloudwater Collector. U.S. Patent nr. 4,697,462.

Daube B, Kimball KD, Lamar PA, Weathers KC. 1987. Two new ground-level cloud water sampler designs which reduce rain contamination. *Atmospheric Environment* **21**: 893–900.

Dawson TE. 1993. Water sources of plants as determined from xylem-water isotopic composition: perspectives on plant competition, distribution, and water relations. In *Stable Isotopes and Plant Carbon-Water Relations*, Ehleringer JR, Hall AE, Farquhar GD (eds). Academic Press: San Diego; 465–496.

Dawson TE. 1998. Fog in the California redwood forest: ecosystem inputs and use by plants. *Oecologia* **117**: 476–485.

Dawson TE, Ehleringer JR. 1998. Plants, isotopes and water use: a catchment-scale perspective. In *Isotope Tracers in Catchment Hydrology*, Kendall C, McDonnell JJ (eds). Elsevier: Amsterdam; 165–202.

Dawson TE, Vidiella PE. 1998. Plant-fog interactions in California and Chile. In *Proceedings of the First International Conference on Fog and Fog Collection*, Schemenauer RS, Bridgman HA. IDRC/CRDI Publication: Ottawa, Canada; 225–228.

DeLay JK, Giambelluca TW. 2010. History of cloud water interception research in Hawai'i. In *Tropical Montane Cloud Forests: Science for Conservation and Management*, Bruijnzeel LA, Scatena FN, Hamilton LS (eds). Cambridge University Press: Cambridge, UK; 332–341.

Eugster W. 2007. The relevance of fog for the vegetation: is it the water or the nutrients that matter? In *Proceedings of the Fourth International Conference on Fog, Fog Collection and Dew*, Biggs A, Cereceda P (eds). Pontificia Universidad Católica de Chile: Santiago; 359–362.

Federer B, Brichet N, Jouzel J. 1982. Stable isotopes in hailstones. Part I: the isotopic cloud model. *Journal of the Atmospheric Sciences* **39**: 1323–1335.

Feild TS, Dawson TE. 1998. Water sources used by *Didymopanax pittieri* at different life stages in a tropical cloud forest. *Ecology* **79**: 1448–1452.

Fischer DT, Still CJ. 2007. Evaluating patterns of fog water deposition and isotopic composition on the California Channel Islands. *Water Resources Research* **43**: W04420, DOI: 10.1029/2006WR005124.

Fischer DT, Still CJ, Williams AP. 2009. Significance of summer fog and overcast for drought stress and ecological functioning of coastal California endemic plant species. *Journal of Biogeography* **36**: 783–799.

Frumau KFA, Burkard R, Schmid S, Bruijnzeel LA, Tobón C, Calvo-Alvarado JC. 2010a. A comparison of the performance of three types of passive fog gauges under conditions of wind-driven fog and precipitation. *Hydrological Processes*. DOI: 10.1002/hyp.7884.

Frumau KFA, Bruijnzeel LA, Tobón C. 2010b. Scientific Briefing: Precipitation measurement and derivation of precipitation inclination in a windy mountainous area in northern Costa Rica. *Hydrological Processes*. DOI: 10.1002/hyp.7860.

García-Santos G. 2007. *An ecohydrological and soils study in a subtropical montane cloud forest in the National Park of Garajonay, La Gomera, Canary Islands*. PhD Dissertation, VU University, Amsterdam.

García-Santos G, Bruijnzeel LA. 2010. Rainfall, fog and throughfall dynamics in a sub-tropical ridge top cloud forest on La Gomera (Canary Islands, Spain). *Hydrological Processes*. DOI: 10.1002/hyp.7760.

Gat JR. 2000. Atmospheric water balance—the isotopic perspective. *Hydrological Processes* **14**: 1357–1369.

Gedzelman SD, Arnold R. 1994. Modeling the isotopic composition of precipitation. *Journal of Geophysical Research* **99**: 10,455–10,471.

Giambelluca T, DeLay J, Nullet M, Scholl M, Gingerich S. 2010. Canopy water balance of windward and leeward Hawaiian cloud forests on Haleakala, Maui, Hawaii. *Hydrological Processes*. DOI: 10.1002/hyp.7738.

Glickman TS. 2000. *Glossary of Meteorology*, 2nd edn. American Meteorological Society: Boston, MA. http://amsglossary.allenpress.com/glossary [Accessed: May 2010].

Goller R, Wilcke W, Leng M, Tobschall HJ, Wagner K. 2005. Tracing water paths through small catchments under a tropical montane rain forest in south Ecuador by an oxygen isotope approach. *Journal of Hydrology* **308**: 67–80.

Gonfiantini R. 1986. Environmental isotopes in lake studies. In *Handbook of Environmental Isotope Geochemistry, Volume 2, The Terrestrial Environment B*, Fritz P, Fontes J-Ch (eds). Elsevier: Amsterdam; 113–168.

Gonfiantini R, Longinelli A. 1962. Oxygen isotopic composition of fogs and rains from the North Atlantic. *Experientia* **18**: 222–223.

Hietz P. 2010. Ecology and ecophysiology of epiphytes in tropical montane cloud forests. In *Tropical Montane Cloud Forests: Science for Conservation and Management*, Bruijnzeel LA, Scatena FN, Hamilton LS (eds). Cambridge University Press: Cambridge, UK; 67–76.

Holwerda F, Bruijnzeel LA, Scatena FN. 2010. Comparison of passive fog gauges for determining fog duration and fog interception by a Puerto Rican elfin cloud forest. *Hydrological Processes*. DOI: 10.1002/hyp.7641.

Holwerda F, Burkard R, Eugster W, Scatena FN, Meesters AGCA, Bruijnzeel LA. 2006. Estimating fog deposition at a Puerto Rican elfin cloud forest site: comparison of the water-budget and eddy covariance methods. *Hydrological Processes* **20**: 2669–2692.

Ingraham NL, Criss RE. 1993. Effects of surface area and volume on the rate of isotopic exchange between water and water vapor. *Journal of Geophysical Research (Atmospheres)* **98**: 20,547–20,553.

Ingraham NL, Mark AF. 2000. Isotopic assessment of the hydrologic importance of fog deposition on tall snow tussock grass on southern New Zealand uplands. *Austral Ecology* **25**: 402–408.

Ingraham NL, Matthews RA. 1988. Fog drip as a source of groundwater recharge in northern Kenya. *Water Resources Research* **24**: 1406–1410.

Ingraham NL, Matthews RA. 1990. A stable isotope study of fog: the Point Reyes Peninsula, California, U.S.A. *Chemical Geology (Isotope Geoscience Section)* **80**: 281–290.

Ingraham NL, Matthews RA. 1995. The importance of fog drip water to vegetation: Point Reyes Peninsula, California. *Journal of Hydrology* **164**: 269–285.

Jouzel J, Merlivat L, Roth E. 1975. Isotopic study of hail. *Journal of Geophysical Research* **80**: 5015–5030.

Kendall C. 1992. Temporal, spatial and species effects on the oxygen and hydrogen isotopic compositions of throughfall. *EOS, Transactions of the American Geophysical Union* **73**(43): 160.

Kerfoot O. 1968. Mist precipitation on vegetation. *Forestry Abstracts* **29**: 8–20.

Landon MK, Delin GN, Komor SC, Regan CP. 1999. Comparison of the stable-isotopic composition of soil water collected from suction lysimeters, wick samplers, and cores in a sandy unsaturated zone. *Journal of Hydrology* **224**: 45–54.

Lee J-E, Fung I. 2008. "Amount effect" of water isotopes and quantitative analysis of post-condensation processes. *Hydrological Processes* **22**: 1–8.

Limm EB, Simonin KA, Bothman AG, Dawson TE. 2009. Foliar water uptake: a common water acquisition strategy for plants of the redwood forest. *Oecologia* **161**: 449–459.

Liu WJ, Liu WY, Li PJ, Gao L, Shen YX, Wang PY, Zhang YP, Li HM. 2007. Using stable isotopes to determine sources of fog drip in a tropical seasonal rain forest of Xishuangbanna, SW China. *Agricultural and Forest Meteorology* **143**: 80–91.

Lovett GM, Reiners WA, Olson RK. 1982. Cloud droplet deposition in subalpine balsam fir forests: hydrological and chemical inputs. *Science* **218**: 1303–1304.

Maloszewski P, Zuber A. 1982. Determining the turnover time of groundwater systems with the aid of environmental tracers. 1. Models and their applicability. *Journal of Hydrology* **57**: 207–231.

Martinelli LA, Victoria RL, Sternberg LSL, Ribeiro A, Moreira MZ. 1996. Using stable isotopes to determine sources of evaporated water to the atmosphere in the Amazon basin. *Journal of Hydrology* **183**: 191–204.

Marzol-Jaén V. 2010. Historical background of fog-water collection studies in the Canary Islands. In *Tropical Montane Cloud Forests: Science for Conservation and Management*, Bruijnzeel LA, Scatena FN, Hamilton LS (eds). Cambridge University Press: Cambridge, UK; 352–358.

McDonnell JJ, Bonell M, Stewart MK, Pearce AJ. 1990. Deuterium variations in storm rainfall: implications for stream hydrograph separation. *Water Resources Research* **26**: 455–458.

McGuire KJ, DeWalle DR, Gburek WJ. 2002. Evaluation of mean residence time in subsurface waters using oxygen-18 fluctuations during drought conditions in the mid-Appalachians. *Journal of Hydrology* **261**: 132–149.

McJannet DL, Wallace JS, Reddell P. 2007a. Precipitation interception in Australian tropical rainforests: II. Altitudinal gradient of cloud interception, stemflow, throughfall and interception. *Hydrological Processes* **21**: 1703–1718.

McJannet D, Fitch P, Disher M, Wallace J. 2007b. Measurements of transpiration in four tropical rainforest types of north Queensland, Australia. *Hydrological Processes* **21**: 3549–3564.

Meinzer FC, Andrade JL, Goldstein G, Holbrook NM, Cavelier J, Wright SJ. 1999. Partitioning of soil water among canopy trees in a seasonally dry tropical forest. *Oecologia* **121**: 293–301.

Mook WG, de Vries JJ. 2001. *Environmental Isotopes in the Hydrological Cycle—Principles and Applications, Volume I: Introduction—theory, methods, review*. UNESCO/IAEA: Paris/Vienna. http://www-naweb.iaea.org/napc/ih/IHS_resources_publication_hydroCycle_en.html, [Accessed: May 2010].

Nagel JF. 1956. Fog precipitation on Table Mountain. *Quarterly Journal of the Royal Meteorological Society* **82**: 452–460.

Nespor V, Sevruk B. 1999. Estimation of wind-induced error of rainfall gage measurements using a numerical simulation. *Journal of Atmospheric and Oceanic Technology* **16**: 450–464.

Phillips DJ, Gregg JW. 2001. Uncertainty in source partitioning using stable isotopes. *Oecologia* **127**: 171–179.

Revesz K, Woods PH. 1990. A method to extract soil water for stable isotope analysis. *Journal of Hydrology* **115**: 397–406.

Rhodes AL, Guswa AJ, Newell SE. 2006. Seasonal variation in the stable isotopic composition of precipitation in the tropical montane forests of Monteverde, Costa Rica. *Water Resources Research* **42**: W11402, DOI: 10.1029/2005WR004535.

Rozanski K, Araguas-Araguas L, Gonfiantini R. 1993. Isotopic patterns in modern global precipitation. In *Climate Change in Continental Isotopic Records*, Geophysical Monograph 78, Swart PK, Lohman KC, McKenzie J, Savin S (eds). American Geophysical Union: Washington, DC; 1–36.

Salati E, Dall'Olio A, Matsui E, Gat JR. 1979. Recycling of water in the Amazon basin: an isotopic study. *Water Resources Research* **15**: 1250–1258.

Saxena RK. 1986. Estimation of canopy reservoir capacity and oxygen-18 fractionation in throughfall in a pine forest. *Nordic Hydrology* **17**: 251–260.

Schawe M, Gerold G, Bach K, Gradstein SR. 2010. Hydrometeorological patterns in relation to montane forest types along an elevational gradient in the Yungas of Bolivia. In *Tropical Montane Cloud Forests: Science for Conservation and Management*, Bruijnzeel LA, Scatena FN, Hamilton LS (eds). Cambridge University Press: Cambridge, UK; 199–207.

Scholl MA, Gingerich SB, Giambelluca TW, Nullet MA, Loope, LL. 2003. Quantifying the role of cloud water in the hydrology of two montane forest sites on East Maui, Hawaii. *EOS, Transactions American Geophysical Union* **84**: F687.

Scholl MA, Gingerich SB, Tribble GW. 2002. The influence of microclimates and fog on stable isotope signatures used in interpretation of regional hydrology: East Maui, Hawaii. *Journal of Hydrology* **264**: 170–184.

Scholl MA, Giambelluca TW, Gingerich SB, Nullet MA, Loope LL. 2007. Cloud water in windward and leeward mountain forests: the stable isotope signature of orographic cloud water. *Water Resources Research* **43**: W12411, DOI: 10.1029/2007WR006011.

Scholl MA, Ingebritsen SE, Janik CJ, Kauahikaua JP. 1995. An isotope hydrology study of the Kilauea Volcano area, Hawaii. *U.S. Geological Survey Water Resources Investigations Report* 95–4213, 44 p.

Scholl MA, Shanley JB, Zegarra JP, Coplen TB. 2009. The stable isotope amount effect: new insights from NEXRAD echo tops, Luquillo Mountains, Puerto Rico. *Water Resources Research* **45**: W12407, DOI: 10.1029/2008WR007515.

Schmid S, Burkard R, Frumau KFA, Tobón C, Bruijnzeel LA, Siegwolf R, Eugster W. 2010. Using eddy covariance and stable isotope mass balance techniques to estimate fog water contributions to a Costa Rican cloud forest during the dry season. *Hydrological Processes* DOI: 10.1002/hyp.7739.

Siegenthaler U, Oeschger H. 1980. Correlation of ^{18}O in precipitation with temperature and altitude. *Nature* **285**: 314–317.

Sieck LC, Burges SJ, Steiner M. 2007. Challenges in obtaining reliable measurements of point rainfall. *Water Resources Research* **43**: W01420, DOI: 10.1029/2005WR004519.

Sklash MG, Farvolden RN. 1979. The role of groundwater in storm runoff. *Journal of Hydrology* **43**: 45–65.

Sklash MG, Farvolden RN, Fritz P. 1976. A conceptual model of watershed response to rainfall, developed through the use of oxygen-18 as a natural tracer. *Canadian Journal of Earth Sciences* **13**: 271–283.

Still CJ, Foster PN, Pounds A, Williams A. 2003. Preliminary measurements of oxygen-18 and hydrogen-2 in water samples collected from a cloud forest in Monteverde, Costa Rica. *EOS, Transactions of the American Geophysical Union, Fall Meeting Supplement* **84**: Abstract B31E-0348.

te Linde AH, Bruijnzeel LA, Groen J, Scatena FN, Meijer HAJ. 2001. Stable isotopes in rainfall and fog in the Luquillo Mountains, eastern Puerto Rico: a preliminary study. In *Proceedings of the Second International Conference on Fog and Fog Collection*, Schemenauer RS, Puxbaum H (eds). IDRC/CRDI Publication: Ottawa, Canada; 181–184.

Thalmann E, Burkard R, Wrzesinsky T, Eugster W, Klemm O. 2002. Ion fluxes from fog and rain to an agricultural and a forest ecosystem in Europe. *Atmospheric Research* **64**: 147–158.

Thorburn PJ, Hatton TJ, Walker GR. 1993a. Combining measurements of transpiration and stable isotopes of water to determine groundwater discharge from forests. *Journal of Hydrology* **150**: 563–587.

Thorburn PJ, Walker GR, Brunel J-P. 1993b. Extraction of water from *Eucalyptus* trees for analysis of deuterium and oxygen-18: laboratory and field techniques. *Plant, Cell, and Environment* **16**: 269–277.

Tobón C, Köhler L, Frumau KFA, Bruijnzeel LA, Burkard R, Schmid S. 2010. Water dynamics of epiphytic vegetation in a lower montane

cloud forest: fog interception, storage and evaporation. In *Tropical Montane Cloud Forests: Science for Conservation and Management*, Bruijnzeel LA, Scatena FN, Hamilton LS (eds). Cambridge University Press: Cambridge, UK; 261–267.

Wang X-F, Yakir D. 2000. Using stable isotopes of water in evapotranspiration studies. *Hydrological Processes* **14**: 1407–1421.

West AG, Patrickson SJ, Ehleringer JR. 2006. Water extraction times for plant and soil materials used in stable isotope analysis. *Rapid Communications in Mass Spectrometry* **20**: 1317–1321.

White JWC, Cook ER, Lawrence JR, Broecker WS. 1985. The D/H ratios of sap in trees: implications for water sources and tree ring D/H ratios. *Geochimica et Cosmochimica Acta* **49**: 237–246.

Zadroga F. 1981. The hydrological importance of a montane cloud forest area of Costa Rica. In *Tropical Agricultural Hydrology*, Lal R, Russell EW (eds). John Wiley: New York; 59–73.