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

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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 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 for synoptic-scale rain storms vs. local fogs or orographic clouds. Isotopic differences have also been observed between locally generated 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, due to 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 paper 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 sap can yield estimates of the contribution of fog water to streamflow, recharge and transpiration. Next, instrumentation to measure fog and rain, and methods to determine isotopic concentrations in plant- and soil water are discussed. The paper concludes with the identification of some of the more pressing research questions in this field and offers various suggestions for future research.

**Introduction**

The importance of fog in the water budget of montane cloud forests (MCF) has been recognized for many years (Kerfoot, 1968; Zadroga, 1981; Delay and Giambelluca, ch 35; Marzol-Jaén, ch 37), but there are still unresolved questions as to how cloud-affected ecosystems actually function hydrologically (Bruijnzeel, 2001; Bruijnzeel et al., 2005; Bruijnzeel and Scatena, this issue). Accurate water balances that include both fog and horizontal precipitation (precipitation not captured by a standard rain gage) 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 the reduction of transpiration from the plants (Fischer et al., 2009; Garcia Santos, 2007; McJannet et al., 2007b; Schawe et al., ch 20). Distinguishing fog events, events with fog plus rain, and rain events aids in determining rates of cloud water interception by a forest, and how much water input would be missed by using only conventional rain gage-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 MCF. To use these tools effectively requires an understanding of the underlying processes controlling stable isotope composition of natural waters. This paper summarizes the results of previous studies involving stable isotopes of fog or cloud water, and gives an overview of how isotope ratios may 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 this 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). In this paper, the term “rain” refers to droplets large enough to fall into a standard rain gage, with the understanding that this droplet size threshold will depend on the prevailing wind conditions (Nespor and Sevruk 1999; Holwerda et al., 2006; Giambelluca et al., this issue).

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 vapor 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 vapor 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 entire mountain ranges, 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., this issue). 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 gage. Part of this may be quantified by throughfall gages, which measure some of the fog and cloud water deposition to the vegetation. Rain gages, with their horizontally oriented openings and susceptibility to wind effects, do not collect the same size fractions of precipitation. Several other papers in this issue (Frumau et al.; García Santos and Bruijnzeel; Giambelluca et al.; Holwerda et al.; Mulligan et al.; Tobón et al.) discuss the latter in some detail.

**Isotope fractionation processes relevant to cloud forest precipitation**

The chemical composition of water is H₂O, a combination of two hydrogen (¹H) and one oxygen (¹⁶O) atoms. A very small fraction of water molecules, however, contain either ²H (deuterium, often also abbreviated with D) substituted in place of ¹H, or ¹⁸O in place of ¹⁶O. 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 $^2$H are typically very low, (i) the concentrations are expressed as the difference in $^{18}$O/$^{16}$O ratio between a sample and a known standard, divided by the ratio of the standard; this yields values that are labeled with δ (e.g. δ$^{18}$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; its value is 0‰ for both δ$^{18}$O and δ$^2$H. Most precipitation and natural water samples have δ$^{18}$O and δ$^2$H values that are more negative than ocean water. Because $^2$H is heavier than $^1$H, and $^{18}$O is heavier 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) has a more negative δ value, and “heavier” water (enriched with the heavier isotopes) has a more positive δ value. The precision of laboratory analyses for δ$^{18}$O is generally 0.2 ‰ or better, and for δ$^2$H is 2 ‰ or better. Textbooks such as Mook and de Vries (2001) or Clark and Fritz (1997) provide more details for the interested reader.

Isotopic fractionation between vapor 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 δ$^{18}$O and δD composition of precipitation exhibits a linear relationship: δD = 8.20 δ$^{18}$O + 11.27, 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 vapor 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 vapor 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 vapor it condensed from). The end result of these processes is that rainfall sampled from the same vapor 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 vapor 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 modeling of isotopic distributions within clouds (Gedzelman and Arnold, 1994; Federer et al., 1982).

Fog has been found to be isotopically enriched compared to 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 colder temperatures, and water vapor in the clouds may become progressively isotopically 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 and progressive vapor 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 1), Puerto Rico (te Linde et al., 2001; Burkard and Eugster, unpublished data in Table 1; Scholl et al., 2009) or Costa Rica (Burkard, 2003 and unpublished data in Table 1; Schmid, this issue?), isotopic signatures of rain and fog may not be as distinct. Many measurements in these areas showed fog to be isotopically enriched compared to 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 1). 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 vapor 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 range from an average of 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 placement of the collector; for example, Brodersen et al. (2000) found higher isotopic enrichment under tree crown centers 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 vapor in the process of transpiration outflux from leaves, so that under steady-state conditions, transpired vapor 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 vapor and how isotopes may be used to trace water sources in the atmospheric water balance. The deuterium excess (d) is defined as \( d = (\delta^2\text{H} - 8 \delta^{18}\text{O}) \). Because of differences in the fractionation of oxygen and hydrogen during evaporation at different humidity levels, precipitation from water vapor that originates from re-evaporated rainfall (vapor from canopy interception, lakes and wetlands, or falling rain) may have a larger deuterium excess value than precipitation originating from water vapor 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 40 years (Table 1), 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 δ²H and –10.4 to +2.7‰ for δ¹⁸O, depending on the temperature and vapor sources in the study areas (Table 1). A scatter plot of δ¹⁸O vs. δ²H values in fog or cloud water and in rainfall from the studies listed in Table 1 is shown in Figure 2. As is also observed for fog and rain samples from individual sites, the fog values as a group are generally enriched in the heavier isotopes compared to 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 are parallel to the meteoric water line, as expected for precipitation samples.

Gonfiantini and Longinelli (1962) published δ¹⁸O 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 δ¹⁸O values ranged from that of sea water to water vapor in equilibrium with sea water. Although the range of δ¹⁸O in fog overlapped the range of rain δ¹⁸O values, the fog samples on average were isotopically enriched compared to 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 to 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 to volume-weighted average rainfall measured in a transect up the mountain side. 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 gage precipitation measurements could have a large degree of error. A subsequent study was done (Scholl et al., 2007; Table 1) on both the windward and leeward sides of East Maui, with cloud water samples collected from passive collectors at monthly intervals for two 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 to rain at both sites (Table 1), 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 more enriched than the rain collector sample, though the two samples were frequently similar in composition (Scholl et al., 2007).

Near Pico del Este in the Luquillo Mountains of eastern Puerto Rico, Burkard and Eugster (Table 1) 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-type active strand cloud-water collector
(Daube et al., 1986), fog was efficiently separated from rain even when the two 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; Holwerda et al., this issue). Oxygen-18 and $^2$H were usually (but not always) enriched in fog compared to rain (Figure 3). The difference in the isotopic signal, however, was quite small (Figure 3 and Table 1) compared to the temporal variability caused by weather conditions and prevailing wind directions. Conditions during which fog was depleted in $^{18}$O and $^2$H 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 hours (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 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 vapor. 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 $^{18}\text{O}$ and $^2\text{H}$ 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 capture 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 1; Schmid et al., this issue), where a few events did not correspond to the typical pattern that stable isotopes are enriched in fog compared to 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 sap and soil water (Ingraham and Matthews, 1995; Scholl et al., 2003); others used isotopes to examine the role of fog in ecosystems (e.g. Dawson, 1998 and subsequent work; Feild and Dawson, 1998). These studies found fog water to be isotopically enriched compared to 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 1 are shown in Figure 4. When a range of values was given in the original paper, the mean values were used to calculate the difference. Both deuterium and oxygen-18 plots are shown because 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 fog, with rain as a separate climatic process (California and Chile).

To summarize 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 1, 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; Table 1). 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 due to evaporation and exchange with ambient vapor (Ingraham and Criss, 1993). If evaporation takes place in an atmosphere of high humidity, the altered 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 deVries (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 in 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 selected sampling method.

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 x 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 and Ehleringer (1998) and Dawson (1993) 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 most 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 analyzed for isotopic composition using standard methods.

Sampling the isotopic composition of soil water in forests involves more uncertainty than precipitation and plant water, as water infiltrating into the soil is subject to evaporation in the unsaturated zone, particularly in the top of the soil profile (Barnes and Allison, 1983; Allison et al., 1983; Barnes and Turner, 1998). Knowledge of the location 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. Extraction techniques include vacuum distillation, azeotropic distillation, microdistillation 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 during the course of a precipitation event (McDonnell et al., 1990; Clark and Fritz, 1997, p. 50; Barnes and Turner, 1998), and 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 cloud systems move past. Several convective precipitation cells with individual isotopic signatures may contribute to one single precipitation event observed at a fixed location. 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, six-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

\[
f_F = \frac{\delta_F - \delta_R}{\delta_F - \delta_R}
\]  

(1)
where the isotopic ratios of $^{18}$O or $^2$H are denoted with $\delta$, 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 passes through the unsaturated zone, and its isotopic composition changes by mixing with soil pore water already present. Similarly, for water intercepted by the canopy, evaporative isotopic fractionation may be an issue.

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; many others). These techniques may have application in determining the amount of cloud water contributing to streamflow 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 required differences in precipitation isotopes 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 (Scholl et al., 2007; Rhodes et al., 2006; Liu et al., 2007), or in areas having orographically-generated local rainfall alternating with synoptic-scale storms (Scholl et al., 2009, 2007). Evaporative
fractionation may also be useful as a check on other methods for determining the evaporation rate 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 than this, 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 to 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 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 to rain, although such differences were relatively small (Scholl et al., 2007, 2009). Larger differences have been found between different types of precipitation events (local orographic vs. synoptic-scale). There is a need for more studies of throughfall isotopic composition, as well as 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 (Tobón et al., this issue).

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. No comparable work is available for montane cloud forests. 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., this issue). 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 vapor 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., this issue; Giambelluca et al., this issue). 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 analyzed from rain-, throughfall-, and cloud-water collectors alike to ascertain the relative contributions by rainfall and fog to overall ecosystem inputs.

Acknowledgements

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Schmid et al., this issue.


Tobón et al., this issue.


Table 1. Stable isotope values ($\delta^{18}$O, $\delta^{2}$H) of fog, cloud water and rain. VWA = volume-weighted average.

<table>
<thead>
<tr>
<th>Study</th>
<th>Location</th>
<th>Altitude (m)</th>
<th>Fog type</th>
<th>Sampling interval</th>
<th>Number of samples</th>
<th>Fog $\delta^{18}$O, ‰</th>
<th>Fog $\delta^{2}$H, ‰</th>
<th>Rain $\delta^{18}$O, ‰</th>
<th>Rain $\delta^{2}$H, ‰</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Gonfiantini and Longinelli (1962)</td>
<td>Shipboard, off Newfoundland</td>
<td>Sea level</td>
<td>Advective (oceanic)</td>
<td>$\leq$ 4 hours</td>
<td>Avg. of 14 fog, 18 rain</td>
<td>-2.4</td>
<td>--</td>
<td>-5.8</td>
<td>--</td>
</tr>
<tr>
<td>2 Clark et al. (1987)</td>
<td>Oman</td>
<td>--</td>
<td>Orographic (monsoon)</td>
<td>--</td>
<td></td>
<td>-0.43 to +1.13</td>
<td>--</td>
<td>+2.1 to +10.5</td>
<td>--</td>
</tr>
<tr>
<td>3 Ingraham and Matthews (1988)</td>
<td>Kenya</td>
<td>1700</td>
<td>Orographic</td>
<td>Grab: 10-12 days:</td>
<td>Avg. of 4 rain</td>
<td>-0.75 to +1.6</td>
<td>+13 to +6</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>4 Aravena et al. (1989)</td>
<td>Chile</td>
<td>--</td>
<td>Advective (oceanic)</td>
<td>--</td>
<td>Avg. of 13 fog, 4 rain</td>
<td>-1.86</td>
<td>-3.2</td>
<td>-5.6</td>
<td>-40</td>
</tr>
<tr>
<td>5 Ingraham and Matthews (1990, 1995)</td>
<td>California, northern</td>
<td>--</td>
<td>Advective (oceanic)</td>
<td>Cumulative samples, intervals not given</td>
<td>4-year average, 3 sites</td>
<td>-2.3</td>
<td>-2.8</td>
<td>-10</td>
<td>-6.5</td>
</tr>
<tr>
<td>6 Dawson (1998) and ongoing observations</td>
<td>California, northern</td>
<td>--</td>
<td>Advective (oceanic)</td>
<td>Monthly averages, 3 year study</td>
<td>17 fog collectors, rain not given</td>
<td>+2.7 to -4.9</td>
<td>+6.4 to -8.9</td>
<td>-5.5 to -15.6</td>
<td>-28.7 to -84.6</td>
</tr>
<tr>
<td>7 Feild and Dawson (1998)</td>
<td>Costa Rica</td>
<td>1500</td>
<td>Orographic</td>
<td>Event</td>
<td>Averages, 82 total</td>
<td>-2.9</td>
<td>-6.6</td>
<td>-2.8</td>
<td>-24.9</td>
</tr>
<tr>
<td>8 Dawson and Vidiella (1998)</td>
<td>Chile</td>
<td>68</td>
<td>Advective oceanic</td>
<td>Monthly, per event in summer</td>
<td>Averages, 212 total</td>
<td>-1.3</td>
<td>-4.6</td>
<td>-3.7</td>
<td>-32.8</td>
</tr>
<tr>
<td>9 Dawson, 2000-2004 (pers. comm.)</td>
<td>California, northern</td>
<td>140</td>
<td>Advective oceanic</td>
<td>Monthly since 1/00</td>
<td>Averages, 97 samples</td>
<td>-2.3</td>
<td>-8.1</td>
<td>-8.4</td>
<td>-46.2</td>
</tr>
<tr>
<td>10 Dawson, 2000-2004 (pers. comm.)</td>
<td>California, northern</td>
<td>128</td>
<td>Advective oceanic</td>
<td>Monthly since 1/00</td>
<td>Averages, 155 samples</td>
<td>-3.3</td>
<td>-7.1</td>
<td>-8.9</td>
<td>-55.3</td>
</tr>
<tr>
<td>11 Corbin et al. (2005)</td>
<td>California</td>
<td>9</td>
<td>Advective oceanic</td>
<td>Monthly, and per event in summer</td>
<td>Averages, 38 total</td>
<td>-2.7</td>
<td>-6.4</td>
<td>-5.3</td>
<td>-40.8</td>
</tr>
<tr>
<td>12 Ingraham and Mark (2000)</td>
<td>New Zealand</td>
<td>736, 870, &amp; 1140 m</td>
<td>Advective</td>
<td>Approx. monthly, 2 summers</td>
<td>3 sites, 9 to 11 samples per site</td>
<td>-5.3 to -10.4</td>
<td>-30 to -71</td>
<td>-7.9 to -50 to -78</td>
<td></td>
</tr>
<tr>
<td>13 a te Linde et al. (2001)</td>
<td>Puerto Rico</td>
<td>1018</td>
<td>Orographic cloud (trade wind)</td>
<td>Daily for 5 weeks</td>
<td>Avg. of 4 fog, 4 rain:</td>
<td>-3.8</td>
<td>-17</td>
<td>-4.1</td>
<td>-17</td>
</tr>
<tr>
<td>13 b te Linde et al. (2001)</td>
<td>Puerto Rico</td>
<td>1018</td>
<td>Orographic cloud (trade wind)</td>
<td>Daily for 5 weeks</td>
<td>Composite (bulk) sample:</td>
<td>-1.9</td>
<td>-2.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Study</td>
<td>Location</td>
<td>Altitude (m)</td>
<td>Fog type</td>
<td>Sampling interval</td>
<td>Number of samples</td>
<td>Fog $\delta^{18}$O, ‰</td>
<td>Fog $\delta^2$H, ‰</td>
<td>Rain $\delta^{18}$O, ‰</td>
</tr>
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<td>---</td>
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</tr>
<tr>
<td>14</td>
<td>Burkard, Eugster and Holwerda unpublished</td>
<td>Puerto Rico, Pico del Este</td>
<td>1015</td>
<td>Orographic cloud (trade wind)</td>
<td>1 sample per event, 12-hr avg.</td>
<td>fog&gt;rain: 36</td>
<td>-1.21</td>
<td>-1.70</td>
<td>-1.62</td>
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<tr>
<td>14</td>
<td>Burkard, Eugster and Holwerda unpublished</td>
<td>Puerto Rico, Pico del Este</td>
<td>1015</td>
<td>Orographic cloud (trade wind)</td>
<td>1 sample per event, 12-hr avg.</td>
<td>fog&lt;rain: 8</td>
<td>-1.32</td>
<td>-4.70</td>
<td>-0.47</td>
</tr>
<tr>
<td>15</td>
<td>Scholl et al., (2007)</td>
<td>Leeward Maui</td>
<td>1220</td>
<td>Orographic (thermal)</td>
<td>2 year VWA of monthly samples</td>
<td>19</td>
<td>-2.7</td>
<td>-6</td>
<td>-5.5</td>
</tr>
<tr>
<td>15</td>
<td>Scholl et al., (2007)</td>
<td>Windward Maui</td>
<td>1950</td>
<td>Orographic cloud (trade wind)</td>
<td>2 year VWA of monthly samples</td>
<td>22</td>
<td>-4.1</td>
<td>-16</td>
<td>-5.5</td>
</tr>
<tr>
<td>17</td>
<td>Burkard, Schmid and Eugster, unpublished</td>
<td>Costa Rica</td>
<td>1460</td>
<td>Orographic cloud</td>
<td>1 sample per event, 24-hr avg.</td>
<td>fog&gt;rain: 31</td>
<td>-1.99</td>
<td>-6.46</td>
<td>-2.39</td>
</tr>
<tr>
<td>18</td>
<td>Fischer and Still, (2007)</td>
<td>California, Santa Cruz I.</td>
<td>296</td>
<td>Advective oceanic</td>
<td>Monthly for 34 months</td>
<td>37 fog, 17 rain</td>
<td>-2.52</td>
<td>-11.4</td>
<td>-5.16</td>
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<td>19</td>
<td>Liu et al., (2007)</td>
<td>SW China</td>
<td>750</td>
<td>Radiation</td>
<td>Fog: biweekly, rain: monthly and event</td>
<td>116 rain, 59 fog</td>
<td>-3.3</td>
<td>-11.5</td>
<td>-7.9</td>
</tr>
<tr>
<td>20</td>
<td>Scholl et al., (2009)</td>
<td>Puerto Rico, Pico del Este</td>
<td>1050</td>
<td>Orographic cloud (trade wind)</td>
<td>VWA of monthly samples</td>
<td>35 rain, 35 fog</td>
<td>-2.42</td>
<td>-3.4</td>
<td>-3.76</td>
</tr>
</tbody>
</table>

1. Data from I. Clark, written communication, 2005; data were shown in Figure 8 in Clark et al., 1987.
2. Research is ongoing, data reported here are for the entire period of data collection at the site as of 2004 (Dawson, written comm., 2004).
3. Values reported here are more comprehensive than those reported in the publication (Dawson, written comm., 2004).
4. Values in 13a are the average of 4 selected events; 13b is the volume-weighted average of all the daily samples.
5. Values are averaged separately for conditions where $\delta$D or $\delta^{18}$O in fog was enriched compared to rain (fog>rain; 14a, 18a) and conditions with both isotopes being depleted in fog compared to rain (fog<rain; 14b, 18b).
6. Fog averages for Maui exclude sampling periods with large storms, because rain dominated the fog collector sample.
7. Samples are bulk precipitation; averages are for wet season (17a, convective precipitation) and transitional season (17b, orographic precipitation).
8. Average values are from D. Fischer, written communication. The publication gives values in graph format only.