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 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 to these tools, stable isotopes may also be used as a natural tracer for fog and rain. Previous studies show that the isotopic signature of fog tends to be more enriched in the heavier isotopes ²H and ¹⁸O than that of rain, due to differing condensation temperature and history. An overview of these studies shows that the difference between fog and rain isotopes is largest for synoptic scale rainstorms vs. local fogs. Differences are also seen in locally generated rain and fog on mountains with orographic clouds, but less is known about isotopic signatures in this environment as only a few of these studies have been done.

Quantifying fog deposition using isotope methods is difficult in cloud forests that receive mixed precipitation, due to limitations in the ability of the sampling equipment to separate fog from rain, but recent studies have shown that isotopes can be a powerful tool to determine the relative influence of fog and rain in the local hydrological budget.

We first describe the types of fog most relevant to mountain cloud forests and the importance of fog water deposition in the hydrological budget. A brief overview of isotope hydrology provides the background needed to understand their application in the hydrological context of cloud forests. A summary of previous work explains 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. Instrumentation to measure fog and rain, and methods to determine isotopic concentrations in plant and soil water are discussed. After discussion of how to derive quantitative estimates from isotopic concentration ratios found in water samples, with considerations on the adequate sampling interval and strategy for various scientific applications, the paper concludes with some of the open questions and directions for future research in this field.
Introduction

The importance of fog in the water balance of montane cloud forests has been recognized for a number of years (Bruijnzeel, 2001), but there are still many unresolved questions as to how these ecohydrological systems function, partly due to difficulties in quantifying fog water input, and partly due to the complex and interdisciplinary nature of forest hydrology. To understand the hydrology of tropical montane cloud forests, accurate water balances that include fog and horizontal precipitation (precipitation not captured by a standard rain gage) are needed. It is also important to quantify fog contribution to recharge and streamflow, and to understand the role of fog water in forest ecosystems in terms of nutrient and pollutant inputs, and as a moisture source during rainless periods. Clouds with low water content or low wind speeds may not deposit measurable amounts on instruments, but still have important effects on the forest via interception of droplets by the canopy and reduction of transpiration from plants. Distinguishing fog events, fog/rain events, and rain events aids in determining the rates of cloud water deposition to a forest, and how much water input would be missed by using conventional rain gage-based water balance techniques.

The stable isotopes of water (\(^{2}\text{H} \text{ and }^{18}\text{O}\)) are potentially useful tools in the set of techniques 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 paper summarizes the previous studies that have been done involving stable isotopes of fog or cloud water (including results from mountain cloud forest studies currently in progress), and gives an overview of how isotopes 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, mist, horizontal precipitation, etc., and what we are trying to quantify in terms of precipitation received by forests. 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 a droplet size greater than 0.5 mm (Glickman, 2000); in this paper, rain will generally refer to droplets that are large enough to fall into a standard rain gage, with the understanding that this size will depend on the wind conditions.

Climatologically, there are several types of fog that may occur in montane forests, including advection fog, sea fog, steam fog, radiation fog, and orographic clouds. Advection fog is fog that was formed elsewhere and is then transported horizontally 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 droplets are mostly the condensate of the water vapor that was in the air before it cooled below its dew point temperature. This type
of fog occurs frequently off the Pacific coast of North and South America due to cold-water upwelling, and affects coastal mountain ranges in those areas. Steam fog most commonly forms over warm water bodies when evaporation from the water surface exceeds the capacity of a cold air mass above it. This type of fog may also affect mountain areas in the tropics. 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 cold air drainage flow. It is not very frequent in mountain valleys where a strong down-valley wind occurs at night. Orographic clouds (upslope fogs) form when moist air is topographically forced to rise, either on a large scale, as in areas where prevailing winds blow against mountain ranges, or on a smaller scale, where thermally forced winds blow upslope. Small droplets typical of fog may be mixed with larger droplets that over flat terrain would be large enough to precipitate as rain, but which are kept in the orographic clouds due to strong updrafts. Thus, orographic clouds may be accompanied by significant wind and rainfall. Since raindrops are orders of magnitude larger in volume and amount of liquid water, orographic clouds may deposit much higher amounts of water than advective fogs with small droplets only.

Droplet size measurements are infrequently made at remote mountain sites, and what has been obtained in most studies is an operational definition of fog deposition, based on the instrument or sampler used to measure it. From a water balance perspective, we are concerned with quantifying all incoming precipitation, which involves measuring the size fraction of precipitation that is not measured in a standard tipping bucket rain gage, and the amount that a standard rain gage may miss due to differences in collection efficiency compared to a vegetation surface. Other papers in this volume discuss in detail the different types and relative accuracy of fog collectors.

**Isotope Fractionation Processes Relevant to Cloud Forest Precipitation**

The chemical composition of water is H₂O, thus a combination of two hydrogen (¹H) with one oxygen (¹⁶O) atoms. A very small fraction of that water, however, is not composed of molecules containing the most abundant ¹H and ¹⁶O atoms, but contains molecules with 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. There is also a very rare stable isotope, ¹⁵O, as well as the radioactive ³H, which are not considered here. Because concentrations of the ¹⁸O and ²H isotopologues are very low, there are two conventions that were adopted to deal with these small numbers: (1) concentrations are expressed as the difference in ¹⁸O/¹⁶O ratio between a sample and a known standard divided by the ratio of the standard, which yields values that are labeled with δ (e.g., δ¹⁸O), and (2) 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. A δ of 0‰ represents a water sample that perfectly matches this ocean water standard, and most precipitation and natural water samples have δ¹⁸O and δD values that are more negative than ocean water. Because ²H is heavier than ¹H, and ¹⁸O is heavier than ¹⁶O, the terms “light” and “heavy” have come into use when describing waters with different isotopic composition. “Lighter” water (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 ¹⁸O is generally 0.2 ‰ or better, and the precision for the ²H analysis
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 earlier references therein). The heavier isotopologues have a lower diffusion velocity and are less reactive than the lighter isotopologues; and bonds with other molecules are stronger than those of the lighter isotopologues. These characteristics lead to repeatable patterns of isotopic composition for water in different parts of the hydrologic cycle.

The condensation process in clouds is similar enough worldwide that the $\delta^{18}O$ and $\delta^D$ composition of precipitation has been found to have a linear relation: $\delta^D = 8.20 \delta^{18}O + 11.27$, known as the global meteoric water line (GMWL) (Rozanski et al., 1993, after Craig, 1961). Conditions of climate and humidity in different areas cause meteoric water lines to differ in slope and intercept from the global average, so ideally, a local meteoric water line is used in 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 that is producing the precipitation. The classic conceptual model for progressive isotopic depletion of rainfall, that is, a preferential rainout of the heavier water, involves a moist air mass rising and cooling. As condensation occurs and rain enriched in $^2H$ 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). There may be additional vapor from evaporation or transpiration incorporated into the cloud, and there can be evaporative isotopic enrichment and temperature-based re-equilibration of falling raindrops below the cloud. The end result of these processes is that rainfall sampled from the same vapor mass, over time or along an altitude transect, will become progressively isotopically depleted (Dansgaard, 1964; Siegenthaler and Oeschger, 1980; 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 isotopic composition resulting from different-size water droplets, water droplets from different altitudes in the cloud, and evaporation and re-equilibration of falling raindrops within the cloud. Isotopic composition of the precipitation in this case is not as predictable, and few studies have been done under these conditions. What is known is that 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 in clouds (Gedzelman and Arnold, 1994, Federer et al., 1982).
Figure 1. Isotopic transformations in the water cycle in a mountain cloud forest, illustrated using hypothetical $\delta^{18}O$ values in per mil. The example is an orographic cloud of 600 m vertical extent that originated from oceanic water vapor. The isotopic compositions of vapor ($\delta^{18}O_v$) and condensate or fog ($\delta^{18}O_c$) are calculated using Rayleigh distillation equations and fractionation factors in Clark and Fritz (1997). The isotopic fractionation occurs at the cloud-top and cloud-base temperatures shown in the figure. Isotopic values for two situations are illustrated, where the top of the cloud is raining (30% rainout) and not raining (no rainout), 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.

Fog has been found to be isotopically enriched compared to rainfall for the same area when fog and rainfall are separate climate processes; for instance, 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 an early-stage condensation from a moist air mass, at temperatures near land surface (Ingraham and Matthews, 1988). In contrast, wet-season rains from frontal or low-pressure systems condense higher in the atmosphere at much colder temperatures, and the cloud as a whole becomes progressively isotopically lighter during the rainout process.

When fog and rain occur as part of the same climate process, fog droplets that have condensed at or equilibrated with the air temperature near the land surface could be more isotopically enriched than raindrops in the same cloud, if the raindrops are formed near the top of the cloud and progressive vapor depletion is occurring due to rainout processes and lower temperatures (Figure 1). This situation was postulated for the Otago uplands of New Zealand, where fog and rain were often simultaneous and their compositions fell along the same local
meteoric water line (Ingraham and Mark, 2000). For mountains frequently immersed in raining orographic clouds, such as Hawaii (Scholl et al., 2002 and Table 1), Puerto Rico (te Linde, 2000; Burkard and Eugster, Table 1) or Costa Rica (Burkard et al., Table 1; Rhodes et al., this volume), isotopic signatures of rain and fog may not be as distinct. Many of the measurements in these areas showed fog to be isotopically enriched compared to rain, but in a significant number of cases, isotopic signatures of fog and rain were similar, and measurements of individual precipitation events in both Puerto Rico and Costa Rica showed instances when fog isotopic composition was more depleted than rain isotopic composition (Table 1).

Orographic cloud heights are often capped by an inversion layer in the atmosphere in the trade wind latitudes, or the clouds may occur as standing clouds associated with a mountain range. In the case of a limited altitude range for the cloud, the isotopic composition of all the precipitation in the orographic cloud may be similar (Figure 1). Like the areas where fog and rainfall are separate climate processes, all precipitation formed during the orographic cloud process will tend to be more isotopically enriched than precipitation from frontal or low pressure systems, where clouds extend several kilometers up into the atmosphere, with correspondingly colder temperatures and ice formation as part of the precipitation process.

Throughfall is precipitation that is collected under 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 that falls directly through the canopy without interception. The intercepted precipitation may include rain and/or fog, and the canopy has a ‘storage capacity’ that must be reached before the precipitation begins dripping off to the ground. Published studies have generally found throughfall to be enriched relative to open sky rainfall, although depletion of throughfall relative to rainfall is also seen in some samples. 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, and the magnitude of the change depends on temperature, humidity, and residence time of water in the canopy. Published isotopic enrichments in $^{18}$O range from an average of 0.3 ‰ in a 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 forest in Georgia, USA (Kendall, 1992). Isotopic composition of throughfall is also affected by placement of the sampler; for example, Brodersen et al. (2000) found higher isotopic enrichment in samplers placed under tree crown centers than those under the crown periphery. In a study on Hawaii, isotopic depletion in throughfall samples was thought to result from throughfall collectors receiving predominantly isotopically depleted intense rainfall from storms, while the canopy blocked much of the locally generated, isotopically enriched rainfall and fog from getting 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 (Dawson and Ehleringer, 1998; Thorburn et al., 1993a). 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 (Wang and Yakir, 2000; Dawson and Ehleringer, 1998), so that under steady state conditions, transpired vapor is assumed to have the same isotopic composition as the water taken in by the roots.

Gat (2000) gives a review of the different sources of atmospheric vapor and how isotopes may be used to trace water sources in the atmospheric water balance. Because of differences in fractionation of oxygen and hydrogen during evaporation at different humidity levels, precipitation from water vapor that originates from re-evaporated rainfall (such as canopy
interception, lakes, and wetlands) may have a larger deuterium excess value than precipitation originating from water vapor evaporated from the oceans (deuterium excess, d, is defined as d = \( \delta^2H - 8\delta^{18}O \)). This effect has been used to examine the role of recycled moisture in the Amazon Basin (Martinelli et al., 1996; Salati et al., 1979), and in Costa Rica (Rhodes et al., this volume).

**Previous Studies**

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 that have been done during that time. Fog isotope values have a large range, from –71 to +13 in deuterium and –10.4 to +2.7 in oxygen-18, depending on the temperatures and vapor sources in the study areas (Table 1). A \( \delta^{18}O/\delta D \) plot of fog/cloud water and rain isotopes from studies listed in Table 1 is shown in Figure 2. The fog values plot both above and below the GMWL, but as a group, the values are parallel to the meteoric water line as is expected for precipitation samples. As with fog and rain samples from individual sites, the fog values as a group are generally isotopically enriched compared to the rain samples, although the two groups overlap because of the large range of temperatures for the sites.

![Figure 2](image_url)

Figure 2. Fog isotopic values from around the world, from the studies listed in Table 1, compared to rain isotope values from the same site (if given) and the Global Meteoric Water Line (GMWL). All values are in ‰. Single symbols are individual values, or in some cases the average was taken when a range was reported in the publication.
Gonfiantini and Longinelli (1962) published oxygen-18 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 $\delta^{18}O$ values ranged from seawater to water vapor in equilibrium with seawater. Although the range of fog $\delta^{18}O$ overlapped the range of rain $\delta^{18}O$ values, the fog samples on average were quite isotopically enriched compared to rain in the same area.

Clark et al. (1987) and Ingraham and Matthews (1988), in regional isotope hydrology studies of arid climates, both 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 receive orographic fog precipitation. They found the fog water to be substantially 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) did an isotopic study of groundwater resources of southern Oman. The monsoon fog and light rain that occurred in the mountains was found to be a source of recharge for groundwater in the mountains and the adjacent coastal plain. Monsoon-cloud precipitation samples had isotopic signatures similar to seawater, 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, Hawaii, Scholl et al. (2002) found isotopic values of mountain streams and springs to be unexpectedly isotopically enriched for their altitude, based on volume-weighted average rainfall measured in a transect up the mountain side. The best explanation for the 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., 2003, Table 1) on both the windward and leeward sides of East Maui, with fog samples collected from passive cloudwater collectors at monthly intervals for 2 years. On the windward side, fog was part of the trade wind orographic cloud with a range of droplet sizes from fog to rain. On the leeward side, thermal heating over land generated an upslope fog with relatively lower 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 very close in composition (data not shown). This similarity may be because precipitation at the sites was often mixed fog and rain that may have had similar isotopic composition, and also because the fog collector did not entirely exclude wind-blown rain.
Near Pico del Este in the Caribbean National Forest of Puerto Rico, Burkard and Eugster (Table 1) sampled fog, rain, throughfall, and stemflow in a follow-up study after te Linde (2000). Fog and rain were sampled from each precipitation event for approximately 1 month. With a Caltech type active strand cloudwater collector (Daube et al. 1986), fog was efficiently separated from rain even when both occurred simultaneously. The fog collector was switched on whenever visibility dropped to less than 500 m. This threshold was chosen in order to minimize contamination by insects and dry aerosols since fog with visibility greater than 500 m contributed very little to total deposition (Burkard et al. 2003, Thalmann et al. 2002). Sampling continued until the 10-minute running mean visibility exceeded 500 m for several minutes. Rain was collected with standard equipment. Rain and fog water subsamples for isotopic analysis were always taken simultaneously, such that the durations of sampling of fog and rain match. The type of fog is an advected cloud formed over a warm ocean that has its base below the mountaintop almost 75% of the time. Isotopic concentrations of $^{18}$O 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, Table 1) compared to the temporal variability that depended on weather conditions and prevailing winds. Conditions where 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 is seen 12 to 24 hours (the minimum sampling interval in our study) earlier in fog than rain. This result is consistent with the potential explanation that coalescence of rain with large droplets from the same air mass as fog takes longer than for coalescence of fog alone. The fact that isotopic signatures are not much different between fog and rain when such a time lag is considered suggests that under these humid tropic conditions, condensation and re-evaporation processes occur in an atmospheric system saturated with water vapor. Thus the
coagulation 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 from the site was often depleted in $^{18}$O and $^2$H relative to both rain and fog, which may indicate that additional processes that are not yet fully understood affect throughfall. Twenty roving throughfall collectors were randomly placed at 80 predefined positions, and isotopic analysis was done on a representative subsample of the water from all collectors. Although this sampling design should capture the spatial variability of throughfall amounts, it may be sensitive for isotopic hot-spots that may be present at special drip-points.

Similar conditions to those described above were found in the Monteverde area in Costa Rica (Burkard and Eugster, Table 1), where a few cases did not correspond to the typical pattern that stable isotopes are enriched in fog compared to rain. The Costa Rica site, which is not as close to the ocean as the Pico del Este in Puerto Rico, experienced an even wider range of isotopic concentrations that varied with weather conditions (data not shown). Similar to Puerto Rico, the isotopic signatures in fog and rain follow each other closely.

Rhodes et al. (this volume) analyzed samples of bulk precipitation and throughfall for stable isotopes at Monteverde, Costa Rica. The bulk precipitation samples spanned the wet and transitional seasons, when the precipitation source changes from convection associated with the Intertropical Convergence Zone (ITCZ) to orographic uplift. Samples from the orographic precipitation were assumed to include rain and mist, and were isotopically heavier than samples collected from ITCZ rainfall (Table 1). Concurrent fog and rain samplers deployed for a period in January had similar isotopic composition.

A few of the isotopic studies involving fog, rain and groundwater included analyses of leaf water (Aravena et al., 1989) or tree sap and soil (Ingraham and Matthews, 1995; Scholl et al., 2003); others used isotopes to examine the role of fog in ecosystems (Dawson, 1998 and ongoing; Feild and Dawson, 1998). These studies found fog water to be isotopically enriched compared to rain water, and each study showed use of fog water by the vegetation 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 the fog as water source.
The differences between rain and fog isotopic values for each study listed in Table 1 are shown in Figure 4. When a range of values was given, the mean values were used to calculate the difference, and both deuterium and oxygen-18 plots are shown, as some of the studies involved only one of the isotopes. The plots show differences between fog and rain isotopic values in different localities, but should not be considered definitive as there are only 15 values and each study involved different sampling frequency, methods, and numbers of samples. Despite the lack of uniformity of the studies, the plots do indicate that the smallest differences between fog and rain isotopes (0-1‰ in $^18$O and 0-8‰ in $^2$H) were from the studies involving orographic clouds on mountains in Puerto Rico, windward Hawaii and Costa Rica, and the largest differences between fog and rain isotopes (>3.5‰ in $^18$O and >25‰ in $^2$H) were from studies involving advected oceanic fog with rain as a separate climate process (California and Chile).

To summarize previous work, relatively few studies have been done on the isotopic composition of fog, and of those, even fewer have involved more than a reconnaissance-level survey of an area. Of the studies listed in Table 1, only three involved long-term sampling, yielding average fog and rain isotopic values from 2 to 4 year studies, and three studies investigated fog and rain isotopes in detail for every precipitation event over a period of time. Most of the studies found average fog isotopic composition to be more enriched than average.

![Figure 4. Magnitude of difference between fog and rain isotopes for oxygen-18 and deuterium. The numbers are keyed to numbered studies in Table 1.](image)
rain isotopic composition, however, the research that involved sampling each event in Puerto Rico and Costa Rica indicated that there were situations where the reverse is true (Burkard and Eugster, Burkard et al., Table 1). For some of the studies, the collection methods did not entirely separate fog and rain precipitation, so that average values may not reflect the true differences between fog and rain isotopic composition. The research that has involved tracing fog water using isotopic analyses of the water in plants indicates that this approach can be successful in some environments, particularly when fog and rain are governed by different climatic processes.

**Sampling Methods for Stable Isotopes**

**Precipitation**

*General considerations*

The main goal in collection of 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, as Fig. 2-8), so that evaporation will not be evident by relative enrichment of the oxygen-18 in the precipitation sample (Scholl et al, 1995). Evaporation and exchange are minimized if the field sampler is designed to collect relatively large samples, with a small surface area of sample and limited exchange with the atmosphere, and the collection reservoir placed underground or otherwise out of direct sun.

After collection, water samples for stable isotope analysis are transferred to narrow-mouth glass bottles with polyseal caps (these have a conical plastic insert in the cap that makes a tight seal). The samples are not quantitatively filtered, but residual oil and large particles may be removed from the samples by putting them through a qualitative filter, taking care to do it quickly so evaporation is minimal. See Mook and deVries (2001) for a complete discussion of water sampling and isotopic analysis methods.

*Fog, rain and throughfall collectors*

Most collectors for precipitation sampling on a time scale longer than a few hours involve some kind of system where the rain is collected in a funnel or fog is collected on a screen or strings, then the water is routed to a collection bottle. There are two ways to preserve the isotopic composition of the water in the precipitation collector during the sampling period: 1) a layer of oil may be poured into the collector to serve as a barrier to prevent evaporation in the container; the precipitation sample entering the container moves below the oil because of its higher density. The oil should be non-biodegradable, such as mineral oil. If the sampling intervals are longer than a week, the oil layer needs to be at least 1 cm thick, as water will evaporate through thinner layers. 2) 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. With tubing extending from the stem of a
collection funnel to the bottom of the sampling container, the surface area available for evaporation is very small. Samples may be collected in polypropylene bags, so that there is no airspace in the sample container. A loop in the tubing that remains full of water after precipitation events can provide a barrier to sample evaporation, though this may not work well with small samples. The aperture of the container or funnel may be blocked with a plastic ball that floats to allow water to flow under it into the container. For any long-term precipitation collector design, a control container with known volume and isotopic composition should be placed in the collection location.

To collect the small fog droplets separately from large raindrops, an active strand fog collector (Daube et al., 1986, 1987) may be used. This instrument has a fan that pulls air from under a rain-shed across an array of string harps where droplets impact on the 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 that can be efficiently captured in this way. The collector inlet must face the wind, and therefore is best suited for locations with known wind directions from a narrow sector, as is typically the case in mountainous areas. A drawback to this collector is the high power consumption for the fan, and this collection method needs testing to make sure the fan’s airflow velocity does not cause evaporation and isotopic fractionation of the fog droplets as they impact on the strings. Because these collectors are extremely efficient, they produce the required amount of water for isotopic analysis within a short time.

**Tree cores and twigs, soils**

The $^{18}\text{O}$ or $^{2}\text{H}$ 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; others). Dawson and Ehleringer (1998) and Dawson (1993) provide a thorough review of plant isotope tracers in catchment hydrology; those references may be consulted for more detail than is given here. Tree sap for isotopic analysis may be collected from cores (White, 1985) or twigs (Dawson, 1993; Thorburn et al., 1993). 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, mature, fully suberized twigs of at least 1 cm diameter are quickly removed from the plant, bark is scraped off, and twigs are cut into short pieces to fit into an airtight glass jar. Samples are then 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 distillation (Ehleringer and Osmond, 1989), then the extracted 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 the soil is subject to evaporation in the unsaturated zone, particularly in the top of the soil profile (Barnes and Turner, 1998; Barnes and Allison, 1983; Allison et al., 1983). Knowledge of the location of the root zone for the plants of interest is helpful to make 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 pan or weighing-type lysimeters. Suction-type lysimeters introduce the possibility of isotopic
fractionation, and this method should be tested thoroughly before use. Soil samples from cores are placed into airtight glass or metal containers immediately after collection and refrigerated until analysis (to inhibit microbial activity and evaporation). Extraction techniques include vacuum distillation, azeotropic distillation, microdistillation with zinc, and immiscible displacement using centrifugation, with azeotropic distillation found to be the best method except for gypsum-rich soils (Barnes and Turner, 1998).

**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 approach also depends on the research questions, site accessibility, and funding. Short-term event-based sampling of precipitation isotopes is important to investigate the processes in the forest water cycle that occur on short time scales, such as transpiration, stream runoff, and canopy interception and throughfall. Some simplifying assumptions on fractionation processes within the canopy are necessary, but short-term event-based sampling may help to resolve these processes and their temporal behavior. Longer-term cumulative-sample studies incorporate the short-term variation in samples and yield a volume-weighted average isotopic value. This sampling strategy can work well for catchment 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 ground water 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 considerations should be taken concerning the relevant processes and their respective time scale, from which an optimum sampling strategy may be derived. In any case, the cost of isotopic analyses will force most applications to aim for a less frequent sampling than would be desirable.

The sampling interval for precipitation also needs to be determined with consideration of 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 the 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 by. In this way, several convective precipitation cells with individual isotopic signatures could contribute to one single precipitation event observed at a fixed location. To resolve this variation, several 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 included here 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, \( F/T \), is

\[
\frac{F}{T} = \frac{\delta_T - \delta_R}{\delta_F - \delta_R},
\]

where the isotopic ratios of \(^{18}\text{O}\) or \(^2\text{H}\) are denoted with \(\delta\), and the indexes T, F, and R, indicate the sample (transpiration water (sap) T, fog F, and rain R) that provided the respective isotopic ratio information. Mixing models work best in situations where either: 1) there is no fractionation of the source water isotopes in the process of transport through the hydrological cycle, or 2) 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. Similarly, for water intercepted by the canopy, evaporative isotopic fractionation may be an issue. In these cases, the problem might require a three or even four end-member mixing model.

Stable isotope techniques have been used for about 25 years in small-catchment 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 catchment, rather than just runoff from the current storm event (Sklash et al., 1976, Sklash and Farvolden, 1979; Buttle, 1998). 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 catchment (McGuire et al., 2002; Maloszewski and Zuber, 1982). Seasonal differences in rain isotopes tend to be small in the tropics due to the small yearly range of temperature, but the requisite differences in precipitation isotopes can occur in mountain catchments where there are distinct rainy and dry seasons with fog providing moisture in the dry season; or in areas having predominantly orographic rainfall with infrequent synoptic scale storms. Evaporative fractionation may also be useful as a check on other methods for determining the evaporation rate for precipitation intercepted by the canopy, if throughfall has a significant evaporative signature (Saxena, 1986; Brodersen et al., 2000).

In principle, stable isotopes should be a powerful tool to determine the relative influences of fog and rain in the local hydrological budget, 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 could 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 are relevant at a certain site.
Directions for future research

Previous studies have suggested that isotopes can be useful tools in identifying the role of fog water in the hydrological and ecological functioning of forests, but little of this work has been done and many questions remain. In areas where fog and rain are separate climate processes, fog is isotopically enriched compared to rainfall, due to large differences in the temperature of condensation of the water vapor, as well as the history of the air mass producing the precipitation. Isotope tracer techniques worked well to show the importance of fog water to the redwood ecosystem in California (Dawson, 1998), and tracing fog input to an ecosystem is least ambiguous in places where fog is the only source of water for all or part of a year. In areas with mixed fog and rain precipitation, like many mountain cloud forests with orographic precipitation, the isotopic composition of rain and fog has not been as well documented. Burkard and Eugster (Table 1, Figure 3) show conclusively that fog and rain sampled from the same cloud are isotopically different, and in most of the studies cited here fog has been found to be isotopically enriched relative to rain, but differences between fog and rain are relatively small, and the largest differences may be between different types of precipitation events (orographic vs. synoptic). In this situation, isotope techniques may be most useful on the catchment-hydrology scale, for answering questions about sources of transpiration water, recharge, and shallow groundwater. However, for applications such as streamflow generation on the scale of hours, throughfall isotopic composition, or determining water sources for mist-dependent parts of the ecosystem such as epiphytes, more studies to determine the isotopic differences between fog and rain in the same cloud are needed.

There is some disagreement about 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 drip may be isotopically enriched relative to rain, so it may be difficult to sort out rain and fog contributions to canopy interception using isotopic composition. Similarly, large inputs of evaporatively enriched throughfall to a forest may make differentiating between fog and rain input more difficult, especially 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 could be relevant in the humid tropics. Because much of the precipitation input to forests is throughfall, it is important to understand the isotopic composition of throughfall if isotope techniques are to be used in an area.

The design of fog collectors for stable isotope samples needs further work. In areas with mixed fog and rain precipitation, passive fog collectors generally collect some proportion of windblown rainfall, even if they have a cover. Active collectors require a power source, so they may not be usable in remote areas or for long periods of time. These problems in sampling fog and rain have led to uncertainty in measurements of the isotopic compositions. Measurements that would help resolve these questions about isotopic composition of fog and rain include analyses of isotopic composition over the range of droplet sizes in a raining cloud, and isotope measurements of droplets with altitude in a single cloud. Despite the sampling limitations, it is clear that in hydrological studies involving isotope techniques in mountain forests, relying on the isotopic composition of precipitation collected in a standard funnel-type collector under open sky could lead to misinterpretation. Given the importance of cloud water collection by the canopy to the total water input to a forest, isotope samples should be analyzed from rain collectors, throughfall collectors, and cloud water collectors.
Acknowledgements

We thank Dr. Douglas Burns and Dr. Karen Rice of the U.S. Geological Survey, and an anonymous reviewer, for their helpful comments on the manuscript.

References


<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 $\delta^D$, ‰</th>
<th>Rain $\delta^{18}O$, ‰</th>
<th>Rain $\delta^D$, ‰</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Gonfiantini &amp; 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>
</tr>
<tr>
<td>2</td>
<td>Clark et al., 1987</td>
<td>Oman</td>
<td>Advective orographic (monsoon)</td>
<td>--</td>
<td>-0.5 to +0.7</td>
<td>+2 to +10</td>
<td>--</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Ingraham &amp; Matthews, 1988</td>
<td>Kenya</td>
<td>Advective orographic</td>
<td>Grab: 10-12 days:</td>
<td>Avg. of 4 Avg. of 2</td>
<td>-0.75 -1.6</td>
<td>+13 +6</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>4</td>
<td>Aravena, 1989</td>
<td>Chile</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</td>
<td>Ingraham &amp; Matthews, 1990, 1995</td>
<td>California</td>
<td>--</td>
<td>Advective (oceanic)</td>
<td>Cumulative samples, intervals not given</td>
<td>4-year average, 3 sites</td>
<td>-2.3 -2.8 -2.4</td>
<td>-10 -15 -10</td>
<td>-6.5</td>
</tr>
<tr>
<td>6</td>
<td>Dawson, 1998 and ongoing</td>
<td>California</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</td>
<td>Feild and Dawson, 1998</td>
<td>Costa Rica</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</td>
<td>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>
</tr>
<tr>
<td>9</td>
<td>Dawson, 2000-2004 (pers. comm.)</td>
<td>California</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>
</tr>
<tr>
<td>10</td>
<td>Dawson, 2000-2004 (pers. comm.)</td>
<td>California</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>
</tr>
<tr>
<td>11</td>
<td>Corbin et al., in press</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>
</tr>
<tr>
<td>12</td>
<td>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 -12</td>
</tr>
<tr>
<td>13</td>
<td>Linde, 2000</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>
</tr>
</tbody>
</table>
Table 1. Fog and rain isotope values from the literature from past and current studies.

<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 $\delta D$, ‰</th>
<th>Rain $\delta^{18}O$, ‰</th>
<th>Rain $\delta D$, ‰</th>
</tr>
</thead>
<tbody>
<tr>
<td>13 b</td>
<td>4te Linde, 2000</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>
</tr>
<tr>
<td>14 a</td>
<td>Burkard &amp; Eugster, unpub.</td>
<td>Puerto Rico</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>
</tr>
<tr>
<td>14 b</td>
<td>Burkard &amp; Eugster, unpub.</td>
<td>Puerto Rico</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 a</td>
<td>Scholl et al, unpub.</td>
<td>Leeward Maui</td>
<td>1220</td>
<td>Orographic cloud (thermal)</td>
<td>2 year avg. of monthly samples</td>
<td>19</td>
<td>-2.6</td>
<td>-6</td>
<td>-4.1</td>
</tr>
<tr>
<td>15 b</td>
<td>Scholl et al, unpub.</td>
<td>Windward Maui</td>
<td>1950</td>
<td>Orographic cloud (trade wind)</td>
<td>2 year avg. of monthly samples</td>
<td>22</td>
<td>-4.1</td>
<td>-16</td>
<td>-4.9</td>
</tr>
<tr>
<td>16</td>
<td>Still et al., 2003</td>
<td>Costa Rica</td>
<td>--</td>
<td>Not given</td>
<td>1 sample each</td>
<td>-4.9</td>
<td>-21</td>
<td>-8.1</td>
<td>-45</td>
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<tr>
<td>17 a</td>
<td>Rhodes &amp; Guswa, this volume</td>
<td>Costa Rica</td>
<td>1460</td>
<td>Bulk precipitation incl. fog</td>
<td>Variable; avg. for each season</td>
<td>10 wet season</td>
<td>-7.5</td>
<td>-49</td>
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</tr>
<tr>
<td>17 b</td>
<td>Rhodes &amp; Guswa, unpub.</td>
<td>Costa Rica</td>
<td>1460</td>
<td>Bulk precipitation incl. fog</td>
<td>Variable; avg. for each season</td>
<td>3 transitional season</td>
<td>-1.9</td>
<td>+4</td>
<td></td>
</tr>
<tr>
<td>18 a</td>
<td>Burkard, Schmid &amp; Eugster, unpub.</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>
</tbody>
</table>

1 Ranges were estimated from Figure 8 in Clark et al., 1987, data were not given
2 Research is ongoing, data reported here are for the entire period of data collection at the site to date (Dawson, pers. comm., 2004)
3 Values reported here are more comprehensive than those reported in the publication (Dawson, pers. 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 average for leeward Maui excludes months with large storms, because rain filled fog collector
7 Samples are bulk precipitation; averages are for wet season (17a, convective precipitation) and transitional season (17b, orographic precipitation).