Cloud water in windward and leeward mountain forests: The stable isotope signature of orographic cloud water

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[1] Cloud water can be a significant hydrologic input to mountain forests. Because it is a precipitation source that is vulnerable to climate change, it is important to quantify amounts of cloud water input at watershed and regional scales. During this study, cloud water and rain samples were collected monthly for 2 years at sites on windward and leeward East Maui. The difference in isotopic composition between volume-weighted average cloud water and rain samples was 1.4‰ δ^{18}O and 12‰ δ^{2}H for the windward site and 2.8‰ δ^{18}O and 25‰ δ^{2}H for the leeward site, with the cloud water samples enriched in ^{18}O and ^{2}H relative to the rain samples. A summary of previous literature shows that fog and/or cloud water is enriched in ^{18}O and ^{2}H compared to rain at many locations around the world; this study documents cloud water and rain isotopic composition resulting from weather patterns common to montane environments in the trade wind latitudes. An end-member isotopic composition for cloud water was identified for each site and was used in an isotopic mixing model to estimate the proportion of precipitation input from orographic clouds. Orographic cloud water input was 37% of the total precipitation at the windward site and 46% at the leeward site. This represents an estimate of water input to the forest that could be altered by changes in cloud base altitude resulting from global climate change or deforestation.

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1. Introduction

[2] Cloud water or fog is an integral component of the hydrology of many coastal and mountain environments. Much of the research on cloud forests has been done in tropical and subtropical forests, because deforestation and climate change in those areas threatens local water supplies, biodiversity, and survival of endemic species [*Still et al.*, 1999; *Bruijnzeel and Hamilton*, 2000; *Foster*, 2001; *Lawton et al.*, 2001; *Food and Agriculture Organization of the United Nations*, 2003; *Pounds et al.*, 2006]. Studies in Central and South America [*Cavelier and Goldstein*, 1989; *Stadtmuller and Agudelo*, 1990; *Rhodes et al.*, 2006], Hawaii [*Juvik and Ekern*, 1978; *Juvik and Nullet*, 1995; *Scholl et al.*, 2002], Australia [*McJannet et al.*, 2007] and the Caribbean islands [*Asbury et al.*, 1994; *Hafkenscheid*, 2000; *Holwerda et al.*, 2006] illustrated various aspects of the role of cloud water in tropical forest hydrology, ecology and chemistry. Temperate mountain forests are also subject to immersion in clouds or fog, and this water source is important in these forests as well; for example, the West Coast of the United States [*Harr*, 1982; *Ingwerson*, 1985; *Ingraham and Matthews*, 1990, 1995; *Collett et al.*, 1991; *Dawson*, 1998; *Fischer and Still*, 2007]; Newfoundland [*Yin and Arp*, 1994]; Switzerland [*Burkard et al.*, 2003]; and Chile [*Aravena et al.*, 1989; *Cereceda et al.*, 2002].

[3] A large body of work was done in the 1980s and 1990s on the role of cloud water in acid precipitation in the mountain forests of the Eastern United States and Canada [*Vong et al.*, 1991; *Schemenauer et al.*, 1995; *Anderson et al.*, 1999; *Isil*, 2000]. Some of this research focused on quantifying the amount of cloud water deposition to temperate forests using models [*Lovett*, 1984; *Mueller*, 1991; *Mueller et al.*, 1991; *Walmsley et al.*, 1996, 1999]. The models helped to assess the importance of different atmospheric and forest variables on cloud water deposition. Estimated fog/cloud water flux rates from the models were 0.13–0.3 mm h^{-1} [*Lovett*, 1984]; 0.1–0.69 mm h^{-1} [*Walmsley et al.*, 1996]; and 0.55 mm h^{-1} [*Mueller et al.*, 1991]. A later analysis using GIS techniques applied to previously studied areas in the Eastern United States yielded estimates of cloud water deposition in mountain areas above 600 m to be 2–50% of the total precipitation [*Sickles and Grimm*, 2003]. *Garcia-Santos et al.* [2004] found that half of the annual water input to a forest in the Canary Islands was from fog precipitation. In Australia's Wet Tropics, cloud interception contributed up to 66% of the monthly water input to the forest [*McJannet et al.*, 2007]. *Bruijnzeel* [2001] compiled studies of cloud water interception in tropical montane cloud forests. The cloud water deposition

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amounts ranged from 0.15–2.43 mm d^{-1} using a variety of methods (fog gauges, excess throughfall, net precipitation). *Bruijnzeel* [2001] also noted that stream water yields from watersheds in tropical montane cloud forests are higher than from other tropical forest watersheds with similar rainfall, because of the added moisture input and lower transpiration rates for trees immersed in clouds. In Costa Rica, *Lawton et al.* [2001] hypothesized that downslope deforestation led to a higher cloud base altitude, decreasing cloud water input to the Monteverde cloud forest and threatening the survival of several endemic species. In a forested watershed in a foggy environment in Oregon, USA, *Ingwersen* [1985] found that streamflow decreased after logging, but increased several years later after understory grew back, presumably because fog interception by the vegetation had resumed. *Dawson* [1998], using stable isotope techniques, found that 34% of the annual hydrologic input to a redwood forest in California was from fog drip, and showed that the presence of trees significantly influenced the amount of fog water input to the ecosystem.

[4] All these studies show that cloud water input is a significant component of the hydrology of forested mountain watersheds above cloud base altitude. The importance of cloud water to the survival of vegetation and the role of vegetation in scavenging cloud water have been recognized and discussed, but because cloud water is difficult to measure, relatively few quantitative studies of cloud water in the forest water budget have been conducted. Deforestation and climate change in these mountainous areas will alter the water budget, but there has not been enough research done to quantify these changes or to predict the extent of changes [*Bruijnzeel*, 2001]. Isotope hydrology techniques represent a possibility for answering some of these questions, and isotope techniques have been used in a few studies, mostly on the California coast [*Ingraham and Matthews*, 1990, 1995; *Dawson*, 1998; *Corbin et al.*, 2005; *Fischer and Still*, 2007]. If fog or cloud water is shown to have a unique isotopic composition in the different types of environments where it occurs, another tool will be available to conduct studies at watershed and regional scales.

1.1. Isotope Processes in Rain and Clouds

[5] The classic conceptual model for progressive isotopic depletion of rainfall as an air mass moves along involves moist air rising and cooling. As condensation occurs and rain enriched in ^{18}O and ^{2}H falls to the ground, the source vapor in the cloud becomes increasingly depleted in these heavier isotopes, causing subsequent rainfall to be isotopically depleted (isotopically lighter). The end result of this process 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; *Ingraham and Taylor*, 1991]. Variations occur in different locations because of differences in temperature, vapor sources and weather systems, and there can be evaporative isotopic enrichment and temperature-based reequilibration of falling raindrops below the cloud. This conceptual model is adapted here for the situation where the cloud intersects the land surface on a mountain slope, and precipitation is sampled within the cloud. In this case, precipitation samples may have an isotopic composition resulting from differently sized water droplets, different altitudes of droplet formation in the cloud, and incorporation of local water vapor from evaporation or transpiration. There have been very few measurements of isotopic composition of the precipitation within clouds.

[6] Previous work on Hawaii and Maui islands [*Scholl et al.*, 1996, 2002] established that in this trade wind climate, rain formed during the orographic cloud process is isotopically enriched compared to rain from frontal or low-pressure systems. This is because of differences in temperature at the altitude of rain and cloud formation. Clouds in synoptic-scale rain systems may extend several kilometers up into the atmosphere, with lower temperatures and ice formation as part of the precipitation process. Lower temperatures accelerate the isotopic depletion process that occurs as the heavier isotopes in water vapor partition into the droplets of condensate. Trade wind orographic clouds are typically limited to elevations of 600–2400 m [*Giambelluca and Nullet*, 1991]. In these lower-altitude clouds, higher temperatures and incorporation of local vapor will limit depletion of heavy isotopes in the cloud. Therefore all rain formed during the orographic cloud process will tend to be more isotopically enriched than rain from frontal or low-pressure systems [*Scholl et al.*, 1996, 2002].

[7] The current study was undertaken with two main objectives: (1) to determine whether orographic cloud water could be reliably distinguished from other types of precipitation using $\delta^{18}O$ and $\delta^{2}H$ and (2) to quantify and compare cloud water deposition in windward and leeward environments for an island in the trade wind latitudes. This paper includes a summary of previously published studies reporting isotopic composition of fog or cloud water, and data from a 2-year field study on the windward and leeward sides of the island of Maui, Hawaii, USA (Figure 1). The present work focuses on establishing the isotopic signature of cloud water in windward and leeward environments that have different precipitation patterns, and determining the proportion of orographic cloud water in precipitation on windward and leeward Maui.

2. Methods

2.1. Terminology

[8] The terms cloud water, horizontal precipitation, and fog have been used in previous publications and will also be used in this paper. There are different ways to define the mixed precipitation that occurs in clouds. 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''. Many studies are concerned with quantifying fog or cloud water as the size fraction of total precipitation that goes unmeasured using standard tipping bucket gage instrumentation. In this paper the focus is on orographic cloud water of all droplet sizes, associated with either trade wind or sea breeze weather patterns. Isotopic composition is a marker for vapor source and condensation history, so precipitation isotope ratios identify a process (orographic versus synoptic-scale

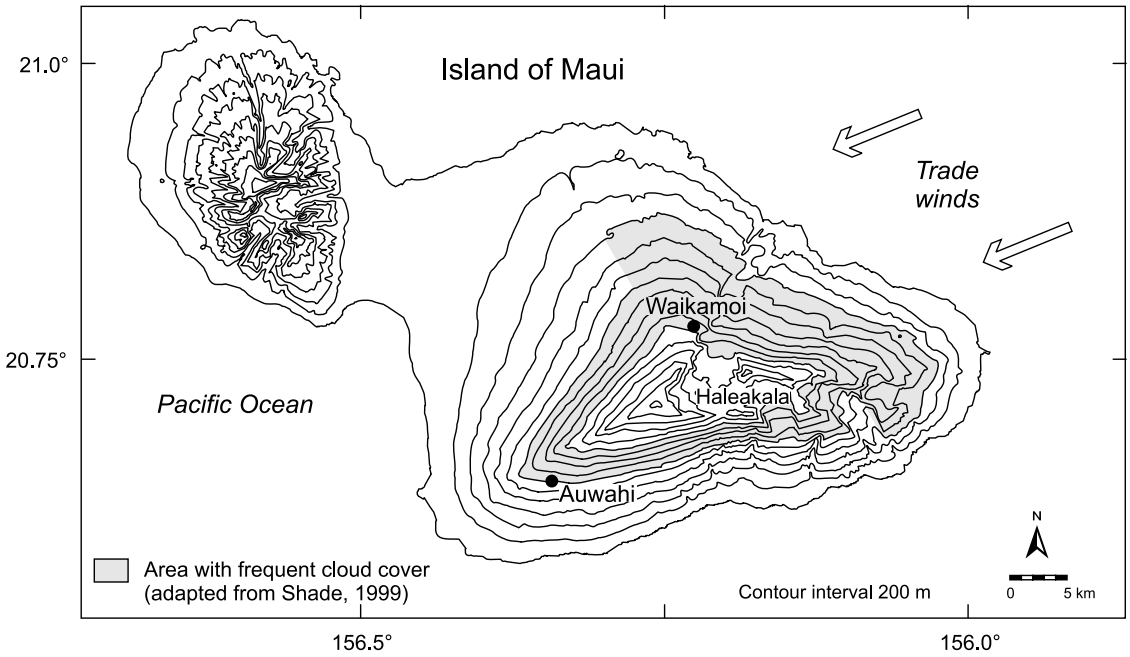

Figure 1. Map of the island of Maui, Hawaii, USA, showing East Maui (Haleakala) Volcano, location of windward (Waikamoi Preserve) and leeward (Auwahi) study sites, and altitudinal cloud belt (adapted from *Shade* [1999]).

precipitation) rather than directly identifying a droplet size fraction. It is not clear whether isotopic composition is correlated with precipitation droplet size; this study could not address that question very well with cumulative monthly samples. Event-based sample collection or collection of different droplet size fractions would provide better information. The following terminology is used in this paper: fog generally refers to cloud droplets that are small enough to remain suspended in the air without falling, and "foggy" refers to sampling periods with more cloud water than rain. Cloud water refers to fog, drizzle and windblown rain with a range of droplet sizes that may be present in a cloud. Rain refers 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. Horizontal precipitation is often associated with cloud water, and is used in describing precipitation that is measured by vertically oriented collection devices. The rain collectors in our study sampled predominantly vertically falling raindrops, whereas the cloud water collectors sampled a greater range of droplet sizes in precipitation. Therefore we assume that rain collectors collected rain from synoptic-scale storms and from orographic clouds, while the cloud water collectors sampled rain from storms and orographic clouds and in addition, the smaller droplet sizes in orographic clouds.

2.2. Study Sites

[9] This study involved two sites, one each on the windward and leeward sides of East Maui (Haleakala volcano), which is a 1450 km^2, 3055-m high volcano making up about 75% of the landmass of the island of Maui (Figure 1). The upper slopes of the volcano are dissected lava flows; areas with high rainfall have parallel streams flowing to the ocean in steep-sided, narrow watersheds. The windward side of the island faces the east-northeast trade winds, so that orographic precipitation occurs nearly daily. The cloud belt extends approximately from 600 to 2000 m altitude [*Giambelluca and Nullet*, 1991]. Orographic rainfall is highest (>7 m a^{-1}) at around 800 m altitude, then rainfall decreases with increasing altitude (about 1.5 m a^{-1} at 2300 m and <1 m a^{-1} at the summit [*Giambelluca et al.*, 1986]). Around 2000 m altitude, a temperature inversion occurs in the atmosphere about 80 percent of the time. Orographic uplift is capped at the level of the inversion, so it acts as a climatological boundary in the Hawaiian Islands. Rainfall above the mean inversion level is less frequent, and comes from synoptic-scale storms or frontal systems [*Schroeder*, 1993]. The leeward slopes where our study site was located are dry, and a large proportion of the annual precipitation comes from storm systems [*Giambelluca and Schroeder*, 1998]. A diurnal sea breeze/land breeze pattern causes anabatic upslope flow on the leeward slopes, creating a cloud zone from about 1200 to 1800 m [*Giambelluca and Nullet*, 1991]. The processes producing orographic cloud precipitation at the windward and leeward sites are completely separate; clouds from the windward side of the island do not reach the leeward site under normal trade wind conditions. In the case of synoptic-scale weather systems, the same system may affect both sites, but there are usually differences due to windward/leeward effects in those storms as well.

2.2.1. Windward Site

[10] The windward site (Waikamoi Preserve, Figure 1) was located in the upper Honomanu Stream drainage basin at 1950 m altitude, at the upper montane forest transition to alpine scrub [*Kitayama and Mueller-Dombois*, 1994]. This area is the upper boundary of the ohia (*Metrosideros polymorpha*) rain forest/cloud forest. Mean annual rainfall is about 2700 mm a^{-1} [*Giambelluca et al.*, 1986]; the site is near the top of the trade wind orographic rainfall zone, which has maximum rainfall at lower altitudes on the mountain slope. Average monthly temperatures at the site ranged from 9.7° to 13.8°C over the course of the study.

The small headwater stream, an unnamed tributary of Honomanu Stream, was generally <1 m wide and it was flowing on all but one sampling date over the 2-year duration of the study. Soil cover is relatively thin on these rocky slopes but is present in many areas. The weather station and cloud water collectors were located in the open shrub land on a slope facing the prevailing wind direction, which was generally east-southeast during the day (trade winds were not from the northeast here, probably due to local topography) and southeasterly to southwesterly at night.

2.2.2. Leeward Site

[11] The leeward site (Auwahi) was located within remnants of formerly diverse (50 native tree species) dry forest on private land of Ulupalakua Ranch. This area contains numerous endangered endemic Hawaiian plant species. A 4-hectare area has been fenced for collaborative experimental native forest restoration [*Medeiros et al.*, 1998; *Medeiros*, 2006]; the instruments for the current project were located in an adjacent enclosure. Mean annual rainfall is about 1000 mm a^{-1} [*Giambelluca et al.*, 1986]. Average monthly temperatures at the site ranged from 13.9° to 18.3°C during the study. This area is near the lower boundary of the altitudinal cloud belt that forms from thermal (sea breeze) air flow. The land is rocky with little soil, and the vegetation (outside the fenced, restored forest/shrubland area) consists of isolated small trees, shrubs and a carpet of nonnative kikuyu grass (*Pennisetum clandestinum*). There are no perennial streams in this part of leeward East Maui. The sampling equipment was located on a steep south-southwest-facing slope at 1220 m altitude. Prevailing wind direction was easterly during the day and northeasterly at night. The weather station was located on an exposed ridge about 70 m away.

2.3. Data Collection

[12] The windward site data collection began in August 2001 and ended in August 2003. The leeward site data collection began in November 2001 (delayed because the area had to be fenced against cattle) and ended in November 2003. Rainfall amounts were measured with a 6″ diameter tipping bucket rain gage and reported as hourly values. Wind speed and direction, incident radiation, air, surface and soil temperature, soil heat flux and soil moisture, and relative humidity were measured with weather stations; these data were averaged to hourly values. Four throughfall collectors with three 6-m-long collection troughs (0.7 m^2 collection area) were placed under the canopy at each site. All three troughs ran into a custom-made large-capacity tipping bucket rain gage. Samples of throughfall for measurement of isotopic composition were not collected. Cloud water deposition (amount and frequency) was measured with a 1 m^2 screen fog collector (SFC) [*Schemenauer and Cereceda*, 1994]. Horizontal precipitation on the SFCs was measured using tipping bucket gages and data loggers; the leeward SFC used a standard tipping bucket rain gage and the windward SFC required a large-capacity tipping bucket gage as used in the throughfall collectors.

[13] Cumulative rain samples for isotopic analysis were collected approximately monthly in a 5-gallon HDPE screw top pail with an o-ring sealed lid. A funnel glued into the lid was sized to collect a month of rainfall without the container overflowing. The funnel contained a small amount of polyester fiber to filter debris. Mineral oil was added to the pail to make a 1-cm thick layer over the water sample to prevent evaporation and isotopic fractionation [*Scholl et al.*, 1996, 2002].

[14] Cumulative cloud water samples for isotopic analysis were collected using passive cylindrical cloud water collectors (adapted from *Falconer and Falconer* [1980]). These consisted of two toothed disks 18.7 cm in diameter connected by 32-cm tall aluminum posts. Teflon monofilament (0.4 mm diameter) was strung between the disks to form a cylindrical collector with 360 filaments. The cylinder was mounted on a large funnel so cloud water that collected on the filaments dripped into the funnel and went through tubing to a 5- or 10-gallon container containing mineral oil. The total one-sided cross-sectional surface area of the filaments exposed to wind-carried cloud water during a precipitation event was 466.6 cm^2. A circular sheet aluminum ''roof'' (76-cm diameter) was mounted over the cylinder to exclude vertically falling rain. This collector sampled cloud water from any wind direction, and we assume that collector efficiency varied with wind speed and the collectors did not exclude wind-driven rainfall. At each site visit, cumulative rain and cloud water collectors were sampled for stable isotopes by removing a sample from below the oil layer, running it through a double layer of qualitative paper filters to remove residual oil, and into a 60-mL glass bottle with polyseal cap. Sample volume was measured, then oil was replaced and sample containers were redeployed [*Scholl et al.*, 1996, 2002].

[15] Sampling was performed approximately monthly, but sampling periods varied in length from 24–68 days. The weather station and tipping bucket gages were connected to data loggers which were downloaded approximately every 2 months. The tipping bucket gages recorded the time of each tip, and these data were consolidated to hourly rainfall values. Data loggers measured 15-min averages from the other instruments; these were averaged to hourly values.

[16] Stable isotope samples were analyzed for $\delta^{18}O$ and $\delta^{2}H$ in the USGS Reston Stable Isotope Laboratory. Oxygen and hydrogen isotopic results are reported in per mil (‰) relative to Vienna Standard Mean Ocean Water (VSMOW). Deuterium ($\delta^{2}H$) analyses of the water samples were done by equilibration with gaseous hydrogen and automated analysis; precision is around ±1‰. Oxygen 18 ($\delta^{18}O$) analyses were done by equilibration with carbon dioxide and automated analysis; precision is around ±0.1‰. Rain isotope results are presented as the volume-weighted average (VWA) from all the data and as average values from two sets of sample periods, those with and without synoptic-scale storms. A VWA for cloud water was calculated only for the periods with no synoptic-scale storms, as an average of all the data would weight the isotopic value toward the months when the (significantly depleted) rain from large storms entered the collector.

[17] Cloud water collection rates for the cylindrical isotope collector were calculated as the collected volume divided by the number of hours of cloud events in the sampling period, as determined by the record from the screen fog collector. Collection rates for comparison to a previous study near the leeward site [*Juvik and Hughes*, 1997] were calculated for the cylindrical and SFC collectors, using the collected volume divided by the number of days in

Table 1. Average Site Parameters, Cloud Water Collection Rates, and Percentage of Orographic Cloud Water Obtained From the Mixing Model Analysis, for the Windward and Leeward Sites

	Windward	Leeward
Mean temperature during study, °C	11.9	16.5
Mean wind speed, m s^{-1}	2.69	2.86
Mean wind speed during cloud deposition events, m s^{-1}	2.92	2.93
Prevailing wind direction, day	ESE	E
Prevailing wind direction, night	SE-SW	NE
Annual Rainfall, mm	2700	1027
Mean number of CW deposition events per sampling period[a]	22	14
Mean CW collection rate,[b] L m^{-2} h^{-1}	1.84	0.51
Range of monthly CW collection rates, L m^{-2} h^{-1}	0.84–4.6	0.08–1.3
Proportion of total precipitation from orographic CW	37%	46%

[a]Deposition event is defined by periods of SFC tipping bucket gage activity separated by 3 hours or more.
[b]Calculated from monthly volume in cylindrical cloud water isotope collector, includes some rainfall caught by collector.

the sampling period and the cross-sectional surface area of the collecting surface (0.047 m^2 for the monofilament on the cylinder and 0.6 m^2 for the shade cloth on the SFC).

3. Results and Discussion

3.1. Cloud Water Collection Rates and Correlation With Throughfall

[18] Cloud water interception by a forest canopy depends on a number of variables including wind speed, cloud liquid water content, and vegetation surface area; and is estimated by water balance methods, models, or eddy correlation methods. Although rates of cloud water collection by the collectors used in this study cannot be directly compared to other inputs in the water budget for the sites, the rates were calculated to show differences between the sites, to compare to previous studies in the area, and as an estimate of cloud water input from orographic precipitation.

[19] At the windward site, cloud water collection rates (volume collected/surface area of monofilament/total hours of fog events in sampling period) for the cylindrical collector were relatively high, from 0.84 to 4.6 L m^{-2} h^{-1} with a mean rate of 1.84 L m^{-2} h^{-1}. The rates are high because the trade wind weather brings frequent clouds with a range of droplet sizes (including drizzle and rain). At the leeward site, cloud water collection rates were lower, ranging from 0.08 to 1.3 L m^{-2} h^{-1} with a mean of 0.51 L m^{-2} h^{-1} (Table 1), about 28% of the amount at the windward site. The average number of cloud events per sampling period at the leeward site was 64% of the number at the windward site, however, and wind speed was similar (Table 1). Though we did not measure cloud liquid water content during the study, the deposition rates are consistent with the assumption that cloud liquid water content was less, and droplet sizes smaller, at the leeward site.

[20] The cloud water collection rate for leeward Maui can be compared to rates found by *Juvik and Hughes* [1997] for the nearby Kahikinui area, using collectors made from one square meter of shade cloth, similar to the SFCs [*Schemenauer and Cereceda*, 1994] used in the present study. Their fog catch rates were 1.56 and 1.67 L m^{-2} d^{-1} at two sites at 1350 m, and 1.61 L m^{-2} d^{-1} at one site at 2200 m. The average rates over the 2-year study period from our leeward Auwahi site (1220 m) were 1.32 and 1.34 L m^{-2} d^{-1} from the cylindrical and SFC collectors, respectively. (Both rates were calculated as volume in the collector/area of the collection surface/days in sampling period) The rates found in the present study were lower, but the site was at slightly lower altitude, so the result is consistent with *Juvik and Hughes*' [1997] finding that cloud water collection rates increased with increasing altitude.

[21] Collection volumes from the cylindrical cloud water samplers are plotted against throughfall at both sites (Figure 2) for sampling periods where data from both types of collectors were available. At the windward site, throughfall correlates well (R^2 = 0.76) with volumes collected by the cylindrical cloud water collectors during each sampling period (Figure 2a). At the leeward site (Figure 2b), throughfall and cloud water volumes were much lower than at the windward site, presumably because most cloud precipitation events at the leeward site involved lower–water content clouds. There is a weak correlation between throughfall and cloud water volume collected during the sampling period at throughfall amounts below 50 mm. The four higher-throughfall sampling periods included synoptic-scale rain events, and the cloud water collector/throughfall relationship appeared to be different during these events, which involved heavy rainfall. The poor correlation between throughfall and cloud water collector at this site may be

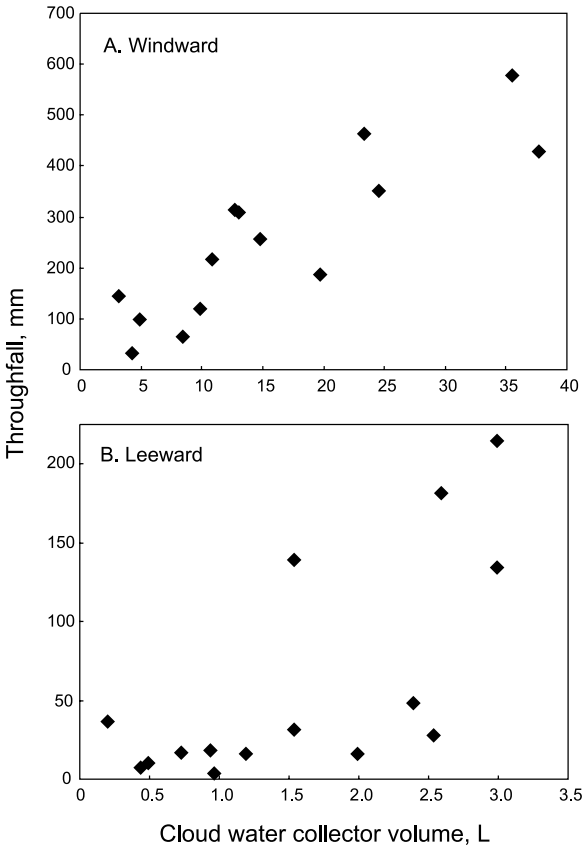

Figure 2. Total throughfall amounts and cloud water volumes (from cylindrical collectors) for each sampling period for the (a) windward and (b) leeward sites. Note the different x and y scales in Figures 2a and 2b.

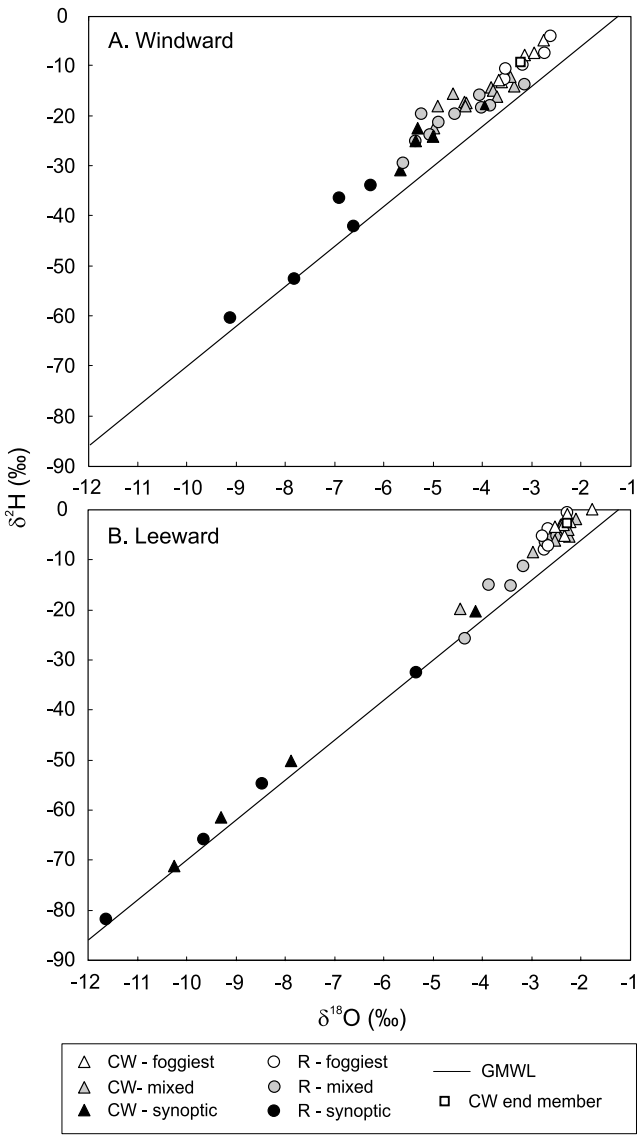

Figure 3. Cloud water samples from (a) windward and (b) leeward sites, relative to the global meteoric water line (GMWL). Samples are divided into precipitation type categories based on cloud water (CW) to rain (R) volume ratios and weather descriptions for the sampling period. Also shown are the cloud water end-members used in the mixing model analysis.

because the vegetation canopy has to reach its storage capacity before throughfall commences and evaporation losses may occur during the process; in contrast, the cloud water collector's vertical monofilaments drain cloud water rapidly into the container. Throughfall and cloud water volume comparisons from both sites indicate that the monofilament-type cloud water samplers may be useful for characterizing cloud water input to the vegetation, as was also noted by *Mueller and Imhoff* [1989] and *Fischer and Still* [2007] for conifer ecosystems.

3.2. Isotopic Composition of Cloud Water and Rain

[22] Figure 3 shows the $\delta^{18}O$ and $\delta^{2}H$ composition of all monthly samples from the cloud water and rain collectors at both sites, relative to the global meteoric water line (GMWL) represented as $\delta^{2}H = 8\delta^{18}O + 10$ [*Craig*, 1961]. The cloud water (CW) and rain (R) samples are divided into categories of sample periods designated as foggiest, synoptic, and mixed. The foggiest sampling periods were determined by calculating a cloud water (CW) to rain (R) ratio using the volumes in the cloud water and rain isotope collectors: (volume CW − volume R)/volume R. The sampling periods with highest CW:R ratio and lowest rainfall were found, then written records from the National Weather Service [*Pacific Region Headquarters*, 2003] were examined to confirm that these foggiest sampling periods had no large synoptic-scale rain events (monthly hydrologic reports and daily weather summaries from August 2001 to November 2003 were obtained online during the study). The foggiest sample periods include precipitation events from locally condensed orographic clouds, driven by trade winds at the windward site and by thermal upslope (sea breeze) winds at the leeward site. The weather during each of these periods was notably dry except for light windward showers in the mountain areas of the island [*Pacific Region Headquarters*, 2003]. "Synoptic" sampling periods had one or more large, synoptic-scale events that dominated the sample composition; these were identified by the depleted isotopic composition of the sample and confirmed using the weather summaries for the sampling period (discussed in detail below). "Mixed" sampling periods included all the other samples. These periods had a mixture of weather types that brought precipitation: windward showers driven by trade winds, cold fronts, shear lines, and weak upper level troughs and low-pressure systems.

[23] The precipitation at the windward site falls along a continuum of isotopic compositions, from isotopically enriched samples during orographic cloud water–dominated periods to isotopically depleted precipitation samples during periods with synoptic-scale weather (Figure 3a). The mixed periods were assumed to have varying proportions of orographic cloud water and precipitation from other weather systems, so that each cumulative sample was a mixture of different types of precipitation with different isotopic signatures. The wide distribution of isotopic compositions along the GMWL at the windward site indicates variable precipitation event types during most sample periods, with the weather type (water vapor source), cloud height (temperature) and degree of rainout controlling the isotopic composition of the precipitation.

[24] At the leeward site, the pattern is different. Most of the nonsynoptic samples have similar isotopic composition, and the foggiest period samples are not much different in composition from most of the group of samples designated as mixed (Figure 3b). This site is in the rain shadow of Haleakala, and so does not receive rain from weather systems carried in the trade wind flow as the windward site does. At this site, the majority of precipitation samples fall into two categories, either orographic cloud precipitation or synoptic-scale precipitation, with few samples in between. The samples in between the two types, like the windward site, represent a mixture of precipitation types over those sampling periods. At both sites, many of the synoptic rain samples fall along the global meteoric water line, while the other samples (orographic cloud water and mixed precipitation events for the monthly period) plot above the GMWL.

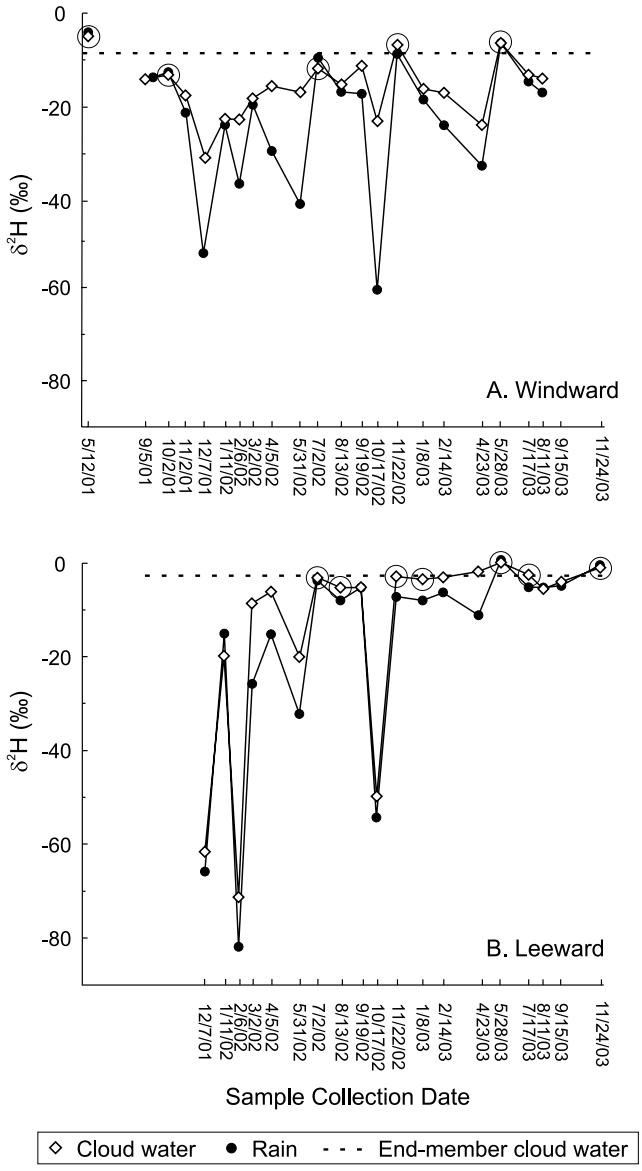

Figure 4. Time series of δ^2H values from the (a) windward and (b) leeward study sites. Circled samples are those that were used to compute the end-member cloud water isotopic composition, denoted by the dashed line.

[25] Isotopic values (δ^2H) over time for cumulative rain and cloud water samples collected at the windward and leeward sites on East Maui are shown in Figure 4 (the δ^{18}O values, not shown, have the same pattern). For most of the sampling periods, cloud water samples at both sites were isotopically enriched compared to samples from the rain collector (Figure 4). During other sampling periods, the isotopic composition of cloud water and rain was the same (within analytical error) and in two cases (11 January 2002 at the leeward site and 2 July 2002 at the windward site), cloud water was isotopically depleted relative to rain. Average isotopic composition of cloud water was enriched compared to average isotopic composition of rain, although the ranges of values overlap (Table 2). Paired t tests for samples from cloud water and rain collectors at the windward and leeward sites showed that the isotopic difference between cloud water and rain samples was significant at $p < 0.01$.

[26] The pattern of isotopic composition over time shows samples that were significantly isotopically depleted (δ^2H values < -30‰) during four periods at the leeward site (Figure 4b) and five at the windward site (Figure 4a). In all these cases, one or more synoptic-scale weather systems brought heavy rainfall to the island and can account for the significantly depleted isotopic composition of the samples. Weather records [*Pacific Region Headquarters*, 2003] showed that the first two periods (ending 7 December 2002 and 6 February 2002) were dominated by rain from low-pressure systems with heavy rainfall and winds from the south or southwest (known locally as "Kona" storms). The sample period ending 31 May 2002 included several low-pressure systems bringing high rainfall to both sites. The period ending 17 October 2002 was dominated by rainfall from a cold front. For the sampling period ending 23 April 2003, there were two cold fronts, and thunderstorms associated with a low-pressure system caused heavy precipitation on windward slopes of the island. For all the storm-affected sampling periods at the windward site, samples from the cloud water collector were significantly isotopically enriched compared to the rain collector. This observation supports the idea that storm rainfall accounted for most of the precipitation in the rain collector, while the cloud water collector received a significant proportion of precipitation from local orographic clouds in addition to the storm events. For the storm-affected periods at the leeward site, the isotopic composition of samples from the cloud water collector was closer to that in the rain collectors, indicating that storm event water in

Table 2. Range, Average ±1 Standard Deviation, Volume-Weighted Average (VWA), and End-Member Values of δ^{18}O and δ^2H for Cloud Water (CW) and Rain at Windward and Leeward Sites on East Maui[a]

	Windward δ^{18}O	Windward δ^2H	Leeward δ^{18}O	Leeward δ^2H
CW range (all)	−5.67 to −2.76	−30.0 to −4.9	−4.46 to −1.77	−19.9 to +0.1
CW average, NS	−3.9 ± 0.7	−14 ± 5	−2.4 ± 0.3	−4 ± 2
CW VWA, NS	−4.1	−16	−2.7	−6
CW end-member	−3.23 ± 0.41 n = 5	−9.2 ± 3.6 n = 5	−2.27 ± 0.24 n = 7	−2.6 ± 1.8 n = 7
Rain range (all)	−9.12 to −2.75	−60.4 to −7.4	−11.63 to −1.55	−81.8 to +0.6
Rain average, NS	−4.1 ± 1.0	−17 ± 7	−2.8 ± 0.7	−8 ± 7
Rain average, S	−7.4 ± 1.1	−45 ± 11	−8.8 ± 2.6	−59 ± 21
Rain VWA	−5.5	−28	−5.5	−31
d-excess range		13 to 21		11 to 17
d-excess average		16.7 ± 2.2		14.5 ± 1.7

[a]Deuterium excess (d-excess) values for cloud water are also shown. Values are in ‰ relative to VSMOW. Rain averages are reported for two sets of sampling periods, those with (S) and without (NS) synoptic-scale storm events. CW averages are shown for the periods without storm events (NS) only.

the cloud water collector was mixed with fewer, and/or lower–water content, cloud events. Isotopic composition measured by the cloud water collector at the leeward site was relatively uniform, other than the storm periods noted above. The average isotopic composition for periods not affected by storms was $-2.4 \pm 0.3‰$ $\delta^{18}O$ and $-4 \pm 2‰$ $\delta^{2}H$ (Table 2). The small standard deviation suggests that cloud water precipitation events at the leeward site were similar in origin and condensation history. Samples from the windward cloud water collector showed more variability, with average isotopic composition of $-3.9 \pm 0.7‰$ $\delta^{18}O$ and $-14 \pm 5‰$ $\delta^{2}H$, indicating that observed isotopic compositions resulted from mixtures of different precipitation events with varying vapor sources, cloud altitudes, and rainout histories.

[27] The composition of the cloud water end-members used in the mixing models discussed later in this paper is shown relative to the GMWL in Figure 3 and as a dashed line on Figure 4. Of the 11 sampling periods with the highest cloud water to rainwater (CW:RW) volume ratios, values from the 5 sampling periods with the lowest rainfall (the foggiest periods) were averaged to determine the end-member isotopic composition for the windward site cloud water: $-3.23 \pm 0.43‰$ $\delta^{18}O$ and $-9.2 \pm 3.6‰$ $\delta^{2}H$ (Table 2 and Figure 3a). The 5 sampling periods are shown circled on Figure 4a. Each of these sampling periods was very dry or had typical trade wind weather, with no large synoptic-scale rain events [*Pacific Region Headquarters*, 2003]. The 11 sampling periods with highest CW:RW ratios were distributed over the months of May through November, which corresponds with the season of most frequent trade winds [*National Climatic Data Center*, 2007]. End-member isotopic composition for the leeward site cloud water was $-2.27 \pm 0.24‰$ $\delta^{18}O$; $-2.6 \pm 1.8‰$ $\delta^{2}H$, based on the 7 sampling periods with highest CW:RW ratio and lowest rainfall (Table 2 and Figure 3b). These sampling periods were distributed equally in summer and winter months, and were not limited to the trade wind season. Note that the end-members for each site (Figure 3) are an average of the cloud water samples from the foggiest sampling periods and therefore are not the most isotopically enriched samples.

3.3. Evaluating Isotopic Differences With Droplet Size Within Clouds

[28] When fog and rain occur in the same cloud, fog droplets that have condensed at or equilibrated with the air temperature near the land surface may be isotopically enriched relative to raindrops. This would occur if the raindrops are formed near the top of the cloud and progressive vapor depletion is occurring in the cloud because of rainout processes and lower temperatures [*Scholl et al.*, 2002]. 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]. On the other hand, if cloud condensation occurs near the land surface sampling point, the isotopic composition of all the precipitation collected from an orographic cloud may be similar, which seems to be the case for many of the monthly samples in this study.

[29] Cloud water and rain isotope values from the foggiest periods (the ones used to calculate the end-member cloud water composition) may be compared to evaluate isotopic differences between rain and cloud water in orographic clouds. At the windward site, the cloud water and rain samples from the foggiest periods (circled on Figure 4) were similar, suggesting that the isotopic composition of orographic clouds was often similar across droplet sizes. At the leeward site, the rain collector had significantly isotopically depleted water during 2 of the 7 periods; otherwise, the cloud water and rain composition were similar. These isotope data were from cumulative monthly samples, and information on the number and precipitation rate of the events that occurred during these periods was available from the screen fog collector. At the windward site, the average number of cloud water events during the foggiest periods was similar to other periods; however, the average precipitation rate for events during those periods was lower than the average for all periods, implying smaller droplet sizes. At the leeward site, the average number of events during the foggiest periods was higher than the average of the other sampling periods, and the precipitation rate was similar to periods with more rain (data not shown). Weather records support the assumption that the ''foggiest period'' samples represent time intervals when cloud height was limited to around 2000 m by the atmospheric inversion layer and the precipitation represented condensation of local vapor that did not evolve much isotopically from a rainout process. For the sampling periods dominated by orographic precipitation (NS in Table 2), the average difference in isotopic composition between cloud water and rain samples was small (0.3‰ $\delta^{18}O$ and 4‰ $\delta^{2}H$). Also note that the VWA for cloud water is not significantly different than the average nonstorm rain at either site (Table 2). The average difference between cloud water and rain from synoptic-scale precipitation (S in Table 2) was much greater (5.0‰ $\delta^{18}O$ and 44‰ $\delta^{2}H$), as would be expected from the differing cloud heights and minimum temperatures for the two types of precipitation. In this study area, it appears that isotopic composition is often similar for all droplet sizes in the orographic cloud. The cumulative monthly data collected in this study cannot entirely rule out different isotopic composition for different droplet sizes within an orographic cloud, however, and better information would be obtained from measurements of droplet size distribution during cloud events and the ability to sample different droplet size fractions.

3.4. Comparison With Published Isotopic Values for Fog and Cloud Water

[30] Published studies including measurements of the stable isotope content of fog and cloud water are few. Some of these previous studies were multiyear efforts, notably the ones done in California [*Ingraham and Matthews*, 1990, 1995; *Dawson*, 1998; *Corbin et al.*, 2005; *Fischer and Still*, 2007], but most of the studies in tropical mountain environments with orographic precipitation involved short-term data collection or are not published in the peer-reviewed literature [*te Linde*, 2000; *Eugster et al.*, 2002; *Schmid*, 2004; *Scholl et al.*, 2006]. Fog or cloud water isotope values measured worldwide have a large range, from -10.4 to $+2.7‰$ $\delta^{18}O$ and -71 to $+13‰$ $\delta^{2}H$, depending on the temperature range and vapor sources in the study areas [*Scholl et al.*, 2007]. Most of the studies used sample collection methods similar to this study, and reported average fog or cloud water isotopic composition to be more

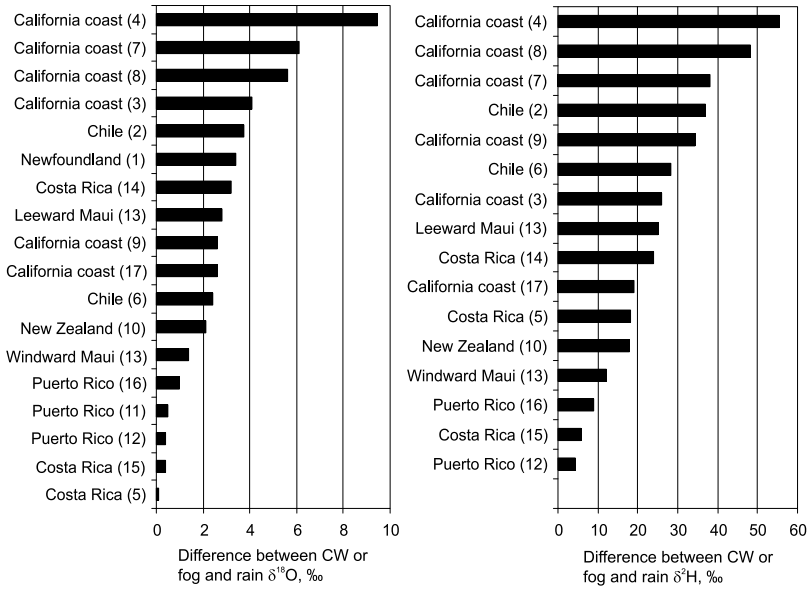

Figure 5. Differences between rain and cloud water (CW) or rain and fog in published and unpublished studies where both types of precipitation were analyzed for δ^2H or δ^{18}O content. The majority of these studies used passive fog or cloud water collectors, studies 12 and 15 used active strand collectors [*Daube et al.*, 1986]. The numbers following each site name correspond to the following references: 1, *Gonfiantini and Longinelli* [1962]; 2, *Aravena et al.* [1989]; 3, *Ingraham and Matthews* [1990, 1995], average of values reported for three sites; 4, *Dawson* [1998] and T. E. Dawson (personal communication, 2004); 5, *Feild and Dawson* [1998]; 6, *Dawson and Vidiella* [1998]; 7 and 8, T. E. Dawson (personal communication, 2004); 9, *Corbin et al.* [2005]; 10, *Ingraham and Mark* [2000]; 11, *te Linde* [2000]; 12, *Eugster et al.* [2002] and W. Eugster (personal communication, 2006); 13, this study; 14, *Still et al.* [2003]; 15, *Schmid* [2004] and W. Eugster (personal communication, 2006); 16, *Scholl et al.* [2006] and unpublished data (April 2005 to April 2007); and 17, *Fischer and Still* [2007]. For numbers 7, 8, 11, 12, 14, 15, and 16, data are from abstracts, theses, and work in progress.

enriched than average rain isotopic composition at the same site. Exceptions have been noted in several studies where some of the fog samples were found to be isotopically depleted compared to rain samples (the majority of fog samples were enriched compared to rain). These occurrences of isotopically depleted fog were measured during event-based sampling with an active strand collector in Puerto Rico and Costa Rica (W. Eugster, personal communication, 2006); by passive collectors on an above-canopy meteorological tower in Puerto Rico [*Scholl et al.*, 2006]; and in two monthly samples from this study. The reasons for these observations have not been conclusively determined. Further studies need to be done, and fog samples that are isotopically depleted relative to rain samples should be considered a possibility in orographic environments. The majority of the studies, and the long-term average values that have been published, show fog or cloud water to be isotopically enriched compared to rain. Figure 5 shows the relative size of differences in measured δ^{18}O and/or δ^2H between fog or cloud water and rain for various studies (some of the studies only reported one isotope ratio). The largest differences between fog and rain isotopes (>3.5‰ δ^{18}O and >25‰ δ^2H) were from studies in California and Chile, where oceanic advective fog occurs during summer and rain occurs as a separate climate process during winter. The smallest differences between fog and rain isotopes (<2‰ δ^{18}O and <15‰ δ^2H) were from studies involving orographic clouds on mountain slopes in Puerto Rico, Costa Rica and Hawaii (Figure 5).

[31] The difference between cloud water and rain isotopes for the windward and leeward sites in this study was calculated using the volume-weighted average (VWA) of all the rain samples and the VWA of cloud water samples (Table 2), which excluded the sample periods with large synoptic-scale storms. The differences between VWA rain and VWA cloud water were 1.4‰ δ^{18}O and 12‰ δ^2H at the windward site, and 2.8‰ and 25‰ in δ^{18}O and δ^2H at the leeward site. These differences are shown in comparison to other locations in Figure 5. The difference between isotopic composition of rain and cloud water was larger for leeward Maui than for windward Maui. The magnitude of the difference at the leeward site was similar to the Pacific Coast in California and Chile, where fog and rain occur in different seasons, from distinctly different weather patterns. Similarly, at the leeward Maui site the rain and cloud water collectors effectively separated different types of precipitation because cloud events were similar in origin and isotopic composition and were separate from the infrequent larger rain storms. At the windward site, orographic precipitation events were often simultaneously collected in both the rain and cloud water collectors, and we assume that some of these events had isotopic composition that was the same for both sample types. There was also a greater variety of precipitation event types, and the isotopic signature of each type of event was diluted by the other precipitation events during a sampling period. These sampling issues probably contributed to the smaller average isotopic difference between rain and cloud water (Figure 5). In this windward

Table 3. Average Isotopic Values for Cloud Water and Rain From the Leeward Maui Altitude Transect, Sampled Monthly From February to August 2003[a]

Leeward Site Altitude, m	δ^{18}O Cloud Water, ‰	δ^{2}H Cloud Water, ‰	δ^{18}O Rain, ‰	δ^{2}H Rain, ‰
1220	−2.09	−2.5	−2.52	−5.3
1585	−2.80	−6.8	−3.38	−10.1
1830	−3.00	−8.3	−3.39	−11.7

[a]The 1220 m site is the site in the 2-year study.

orographic precipitation environment, more frequent sampling would allow better separation of event types and isotopic signatures of the different precipitation types. Despite the sampling limitations, the relatively long-term average values from this study indicate there are measurable differences between cloud water and rain in this type of environment.

3.5. Water Vapor Sources and *d*-Excess for Orographic Cloud Water

[32] The volume-weighted average rain composition at the windward site is similar to the leeward site, though the windward site is at a higher altitude (Table 2). In general, higher-altitude rain would be expected to be isotopically depleted compared to lower-altitude rain [*Dansgaard*, 1964], but in this case, the similar rain compositions were not surprising. Prior studies on the islands of Hawaii and Maui [*Scholl et al.*, 1996, 2002] showed that leeward isotope/altitude gradients had the same slope, but were isotopically depleted compared to windward gradients. This is because more of the precipitation on the leeward sides of the islands is from synoptic-scale rain events with isotopically depleted rain. The windward cloud water, however, was isotopically depleted compared to the leeward cloud water, both in average and end-member composition (Table 2 and Figure 3). The windward site, at 1950 m, is 730 m higher than the leeward site. To test whether higher-altitude cloud water on the leeward side was similar to the windward side, rain and cloud water were collected from 13 February to 13 August 2003 at two additional, higher-altitude sites on the leeward side of Maui (Table 3). Increasing cloud water isotopic depletion was observed with increasing altitude for these collectors. The average value from the 1830 m leeward site was −3.0‰ δ^{18}O, −8‰ δ^{2}H; significantly isotopically enriched compared to −4.0‰ δ^{18}O, −15‰ δ^{2}H at 1900 m on the windward side for the same time period (Table 3). This suggests that source vapor composition and rainout processes, rather than condensation temperature, are responsible for the differences in isotopic composition of cloud water between the two sites.

[33] Isotopic fractionation factors [*Majoube*, 1971; from *Clark and Fritz*, 1997] were used to calculate the vapor composition that would result in each end-member cloud water isotopic composition, on the basis of the 2-year average site temperature for the windward and leeward study sites. For the windward site, vapor in equilibrium with the cloud water end-member (Table 2) at the average site temperature of 11.9°C would have a value of −13.7‰ δ^{18}O, −100‰ δ^{2}H. For the leeward site, the cloud water end-member would result from condensation of a vapor with −12.3‰ δ^{18}O, −88‰ δ^{2}H at 16.5°C. These calculated water vapor compositions are within the range of tropical oceanic water vapor δ^{18}O compositions of about −11 to −14‰ measured in the north Pacific [*Craig and Gordon*, 1965] and −8.8 to −24.0‰ measured during three sampling campaigns near Kwajalein, Mexico, and Florida [*Lawrence et al.*, 2004]. The δ^{18}O value for the leeward site end-member cloud water source vapor (−12.3‰) is more enriched than the windward source vapor (−13.7‰). These results are consistent with the leeward site having clouds that condensed from vapor near the site, whereas at the windward site, the clouds may form at lower altitude and evolve isotopically by removal of precipitation while moving upslope.

[34] Windward-leeward differences in amount and isotopic composition of cloud water may be partially due to differences in forest cover on the mountain slopes. Forest cover can affect both moisture content and vapor isotopic composition of the atmosphere through transpiration and reevaporation of canopy-intercepted precipitation [*Moreira et al.*, 1997; *Lai et al.*, 2006]. Much of the windward-side mountain slope of East Maui is forested and is a protected watershed for the island. Though it formerly had extensive forest, leeward East Maui has undergone deforestation over recent centuries by tree harvest, ungulate browsing and fire, so that no more than 5% of the former forest remains [*Medeiros et al.*, 1998; *Medeiros*, 2006]. Assuming that water vapor in air over the ocean has the same initial isotopic composition on the windward and leeward sides of the island, the observed differences in cloud water isotopic composition may result from the addition of vapor from transpiration or evaporation of canopy interception. Assuming a δ^{18}O value of −13‰ [*Craig and Gordon*, 1965] for atmospheric vapor above the ocean and below cloud base, vapor derived from partial evaporation of precipitation would be isotopically depleted compared to this oceanic vapor, and transpiration vapor would be isotopically enriched (transpiration returns soil water and groundwater unfractionated as vapor to the atmosphere and is assumed to have the composition of VWA rainfall). Both processes would add moisture to the atmosphere. Clouds with higher moisture content condense more water and if water is removed by precipitation or interception, the isotopic composition becomes more depleted through rainout as the cloud moves up the slope. Thus the forest cover may contribute to both the greater amounts of cloud water deposition and the depleted isotopic composition for clouds on the windward side.

[35] Since transpiration does not involve isotopic fractionation, water vapor from transpiration cannot be distinguished in a mixture with ocean-derived vapor. Evaporation causes isotopic fractionation, however, so evaporated water vapor can be traced as a source of rainfall using the d-excess parameter $d = \delta^{2}H - 8\delta^{18}O$ [*Dansgaard*, 1964]. Studies in the Amazon Basin estimated that 48–80% of rainfall originated from an evapotranspiration vapor source, thereby recycling water within the basin [e.g., *Salati et al.*, 1979; *Gat and Matsui*, 1991; *Martinelli et al.*, 1996], and d-excess indicated that up to 40% of that source could be attributed to evaporation [*Gat and Matsui*, 1991]. Values for d-excess calculated from the monthly samples in the present study ranged from 13–21‰ at the windward site, and from 11–17‰ at the leeward site (Table 2). Figure 3 illustrates the d-excess, which is graphically represented as a sample's offset

from the GMWL in the direction of increasing δ^2H. Both sites have relatively high d-excess values for orographic cloud water compared to synoptic rain. The extensive forest cover (from near sea level to 2000 m) and the absence of any large surface water bodies suggest canopy interception and streams as the most likely source of evaporated water vapor for the windward site. For the leeward site, a source of evaporated vapor could be the soil, or water vapor carried in the airflow from the southeastern part of the island, which is forested and has streams because the mountain slopes are not in the rain shadow of the 3055 m peak of Haleakala. The average d-excess at the windward site was 16.7 ± 2.2‰ compared to 14.5 ± 1.7‰ at the leeward site (Table 2). A two-sample t test indicated that d-excess was significantly different between the sites ($p \leq 0.001$). The higher d-excess at the windward site supports the idea of recycled (evaporated) vapor being a larger component of the vapor source for rainfall at the windward site than at the leeward site. These d-excess values are within the range of those at Monteverde, Costa Rica, another trade wind affected location, where *Rhodes et al.* [2006] found values of d-excess as high as 20‰ in the transitional and dry seasons, indicating a substantial contribution from windward slope recycled moisture.

3.6. Mixing Model Analyses to Determine Proportion of Cloud Water in Precipitation

[36] The stable isotope composition of samples from the cloud water collector was used in a two end-member mixing model to estimate the proportion of orographic cloud water, as opposed to other types of precipitation, that occurred in each sample period:

$$f_{CWnet} = \frac{\delta_{CW} - \delta_{RWend}}{\delta_{CWend} - \delta_{RWend}}$$

where f_{CWnet} was the net fraction of cloud water in the sample, δ_{CW} was the isotopic composition of the cloud water collector monthly sample, δ_{CWend} was the isotopic composition of the cloud water end-member, and δ_{RWend} was the isotopic composition of the rain collector monthly sample. The cloud water end-member was constant for each site, while the rain end-member changed each month depending on the precipitation history.

[37] The isotope mixing model analysis required two assumptions: (1) cloud droplets from locally condensed low-altitude clouds have a composition that is isotopically enriched compared to raindrops from higher-altitude clouds, and (2) there is no isotopic fractionation during the cloud water collection process. The first assumption is supported by the temporal data shown in Figure 4, which illustrate that during sampling periods that had large synoptic-scale rain events, the samples from the cloud water collector were significantly isotopically enriched compared to those from the rain collector, whereas for the foggiest periods, cloud water and rain isotopic composition were similar. The observations from this study show that cloud droplets from trade wind orographic clouds have significantly different composition than rain from weather systems that involve higher-altitude clouds, and suggest that many of the orographic cloud events have water droplets with similar isotopic composition. The second assumption, that there was no isotopic fractionation during sample collection of cloud water, has not been tested because it is difficult to reproduce natural conditions experimentally without introducing isotopic fractionation. The relative humidity at the sites during rain and cloud events was 98–100% and water collected on the monofilament drains quickly into the collector, leaving little opportunity for evaporative enrichment of the sample after deposition on the sampler. *Fischer and Still* [2007], in a study of fog in California, found that fog collector designs with monofilament minimized evaporative enrichment because they retain less water than mesh-type fog collectors. The isotope mixing model approach utilized the differences in precipitation type, so that for sampling periods with both orographic and other types of rain events, the mixing model could be used to obtain an estimate of orographic cloud water input. The isotope-based estimates of orographic cloud water include the proportion contributed by rain-sized droplets, because the sampling method collected orographic cloud water with a range of droplet sizes.

[38] For each monthly sample, the fraction of cloud water in the cloud water sample was calculated using the mixing model, then that fraction was applied to the collected volume. Results were summed for the entire study period and divided by the total collected volume to obtain the proportion of orographic cloud water for the site. For 7 of the 19 sampling periods at the leeward site and 6 of the 21 periods at the windward site, the rain sample and cloud water sample were not significantly different; or the sample composition was the same as, or more enriched than, the cloud water end-member; or in two cases, the rain sample was isotopically enriched compared to the cloud water sample. In these cases, the mixing model result was incorrect. If the sample's composition was isotopically enriched compared to, or within the analytical error of the cloud water end-member; the entire sample was assumed to be orographic cloud water (5 cases at the leeward site, 3 at the windward site); otherwise the data were not used in the mixing model analysis.

[39] Table 1 shows the percentage of total precipitation in the cloud water collectors that was from an orographic cloud source. The mixing model analysis was done with both the δ^{18}O and δ^2H data. Results from both isotopic ratios were similar, and the percentages reported in Table 1 are the average of the two. Uncertainty estimates for orographic cloud water input to the sites were obtained by repeating the mixing model analysis with end-member values plus and minus one standard deviation from the mean value (Table 2). This yielded a range of percentage values for the cloud water input to each site. Of the total volume of precipitation collected in the cloud water collectors during the study, 37% was orographic cloud water at the windward site, with a possible range of 29–48%. At the leeward site, 46% of the precipitation collected was orographic cloud water, with a possible range of 34–49%. The higher percentage at the leeward site reflects the similarity of cloud water precipitation events and the low frequency of rain storms, so that more of the sampling periods had isotopic composition indicating a high percentage of cloud water in the collectors. The 37% at the windward site represents the proportion of precipitation that occurred under trade wind conditions with locally condensed vapor. This is probably an underestimate of the total amount of orographic cloud precipitation on the windward slopes, but

may represent a weather pattern that would be different or absent if cloud base altitude changed. The leeward site had a smaller total volume of precipitation, so that the 46% from an orographic cloud source at the leeward site represents only 15% of the cloud water volume estimated for the windward site.

4. Conclusions

[40] Cloud water can be a significant hydrologic input to mountain forests, but it is difficult to quantify. In this study, cloud water was found to have a clearly identifiable isotopic signature that represented orographically driven condensation from local vapor sources. Using an isotopic mixing model approach, cloud water was estimated to be 37% of the total precipitation collected in cloud water collectors at the windward site, and 46% of the total at the leeward site over the 2-year study period. Despite the larger fraction of cloud water in leeward precipitation, the corresponding cloud water volume at the leeward site was only 15% of that at the windward site, in general agreement with average cloud water collection rates, which were 1.84 L m^{-2} h^{-1} for the windward site and 0.51 L m^{-2} h^{-1} for the leeward site.

[41] The results from the isotopic mixing model analysis indicate that orographic clouds are an important source of water to the ecosystem at both windward and leeward sites. If climate change or deforestation affects the height or mechanism of formation of orographic clouds [*Still et al.*, 1999; *Lawton et al.*, 2001], substantial changes in the water budget would result at these sites. The leeward side of this trade wind affected island is particularly vulnerable, as cloud water input is the main source of water between infrequent large rainstorms.

[42] These results can be extrapolated to other environments where precipitation patterns include a distinct orographic precipitation regime separate from synoptic-scale weather. The precipitation isotope patterns noted in this study may be particularly relevant for interpretation of watershed isotopic studies in environments where cloud water isotopic composition may not be represented in rain samples but is evident in stream water composition.

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