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The stable isotope amount effect: New insights from NEXRAD echo tops, Luquillo Mountains, Puerto Rico

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[1] The stable isotope amount effect has often been invoked to explain patterns of isotopic composition of rainfall in the tropics. This paper describes a new approach, correlating the isotopic composition of precipitation with cloud height and atmospheric temperature using NEXRAD radar echo tops, which are a measure of the maximum altitude of rainfall within the clouds. The seasonal differences in echo top altitudes and their corresponding temperatures are correlated with the isotopic composition of rainfall. These results offer another factor to consider in interpretation of the seasonal variation in isotopic composition of tropical rainfall, which has previously been linked to amount or rainout effects and not to temperature effects. Rain and cloud water isotope collectors in the Luquillo Mountains in northeastern Puerto Rico were sampled monthly for three years and precipitation was analyzed for δ^{18}O and δ^{2}H. Precipitation enriched in ^{18}O and ^{2}H occurred during the winter dry season (approximately December–May) and was associated with a weather pattern of trade wind showers and frontal systems. During the summer rainy season (approximately June–November), precipitation was depleted in ^{18}O and ^{2}H and originated in low pressure systems and convection associated with waves embedded in the prevailing easterly airflow. Rain substantially depleted in ^{18}O and ^{2}H compared to the aforementioned weather patterns occurred during large low pressure systems. Weather analysis showed that 29% of rain input to the Luquillo Mountains was trade wind orographic rainfall, and 30% of rainfall could be attributed to easterly waves and low pressure systems. Isotopic signatures associated with these major climate patterns can be used to determine their influence on streamflow and groundwater recharge and to monitor possible effects of climate change on regional water resources.

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1. Introduction

[2] It is important to understand the local variations in hydrogen (δ^{2}H) and oxygen (δ^{18}O) isotopic composition of rainfall to fully utilize isotopic techniques in climate change and hydrological studies. The International Atomic Energy Agency (IAEA) and World Meteorological Organization (WMO) have operated the Global Network of Isotopes in Precipitation (GNIP) since 1961. This program maintains a database of monthly precipitation isotope values at selected sites worldwide. Early work by *Dansgaard* [1964] using the initial data established a global meteoric water line and noted the main control on isotopic composition of precipitation as being condensation temperature, with evaporation and exchange below the cloud and seasonal shifts of water vapor source area as additional factors explaining variations in the isotopic composition of rain. *Rozanski et al.* [1993], working with as much as 30 years of the GNIP data, thoroughly reviewed the precipitation isotope literature and reiterated the importance of temperature and rainout effects, which are reflected by sampling site attributes of latitude, altitude, and distance inland. Seasonal patterns of isotopic composition of rain on the continents at high and midlatitudes were correlated with seasonal differences in land surface air temperature, with higher (enriched in the heavier isotopes) isotopic values in the summer and lower (lighter, or depleted in the heavier isotopes) isotopic values in the winter. Both *Dansgaard* [1964] and *Rozanski et al.* [1993], and many investigators since, have noted that monthly data from tropical stations in the GNIP network showed a correlation between the amount of precipitation and its isotopic composition, while there was a poor correlation between isotopic composition and surface temperature for the sites. Higher values of δ^{2}H and δ^{18}O were observed during months with less rainfall, and lower values of δ^{2}H and δ^{18}O correlated with higher precipitation amounts. This was called the amount effect by *Dansgaard* [1964]; it is discussed in detail in a later section of this paper. More recent work using global-scale climate models has expanded the concepts outlined in earlier work, showing that atmospheric circulation patterns affect seasonal cycles of isotopic composition [*Feng et al.*, 2009].

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[3] Puerto Rico is a tropical island in the Caribbean (latitude 18.3°N) with a climate dominated by easterly trade winds. Orographic showers occur on a near-daily basis on the windward slopes of mountains in the trade wind latitudes. The 1,077 m high Luquillo mountain range, on the eastern end of Puerto Rico, is directly impacted by the east-northeast trade winds blowing over the ocean and the rainfall maximum for the island is at this location. A summary of the consensus results of 21 atmosphere-ocean general circulation models in a report by the Intergovernmental Panel on Climate Change [*Christensen et al.*, 2007] indicates that Puerto Rico is in an area that is projected to become drier over the remainder of the century, as well as being subject to more frequent intense precipitation events. Assessments of climate change by *Scatena* [1998] and of rainfall by *Heartsill-Scalley et al.* [2007] also presented evidence of a drying climate in the Luquillo Mountains, and periodic droughts occur in relation to the North Atlantic Oscillation (NAO) and El Nino–Southern Oscillation (ENSO) cycles [*Larsen*, 2000]. Changes in temperature and humidity due to deforestation, defoliation, urbanization or global climate change could cause a rise in cloud base altitude (ceiling height) by as much as a few hundred meters, which may lead to a decline in trade wind orographic precipitation amounts and in land area receiving the precipitation [*Richardson et al.*, 2003; *Lawton et al.*, 2001; *Still et al.*, 1999; *Scatena and Larsen*, 1991]. Alternatively, the elevation range receiving precipitation could change due to lowering of the trade wind inversion [*Sperling et al.*, 2004], changes in the vertical lapse rate [*Giambelluca et al.*, 2008], or changes in vegetative cover [*Ray et al.*, 2006; *van der Molen et al.*, 2006]. With continuing land use change and rising global temperatures, information on the present climate patterns and their contribution to water supply is useful as a baseline against which future changes may be quantified.

[4] Previous work in the Hawaiian Islands [*Scholl et al.*, 1996, 2002, 2007] examined δ^2H and δ^{18}O of precipitation in detail for a trade wind dominated tropical climate. During a two year study at windward (1950 m) and leeward (1220 m) sites on Maui, Hawaii, there was no seasonal pattern evident in δ^2H and δ^{18}O values of monthly precipitation [*Scholl et al.*, 2007]. The studies showed that trade wind orographic precipitation (rain and cloud water) had a distinct and repeatable isotopic signature that was enriched in ^{2}H and ^{18}O, compared to that of rain from larger synoptic-scale weather patterns such as low pressure and frontal systems. The higher clouds of storm systems, with precipitation forming at lower temperatures, were hypothesized to be the reason that the rainfall was depleted in ^{2}H and ^{18}O compared to the trade wind orographic precipitation. Many investigators [i.e., *Clark and Fritz*, 1997; *Friedman et al.*, 2002; *Kohn and Welker*, 2005] have noted that the temperature within clouds controls precipitation isotopic composition, but in-cloud temperatures are not often measured. With the advent of online access to a large variety of weather data, it is now possible to evaluate in more detail the in-cloud temperatures and other weather parameters that can affect δ^2H and δ^{18}O of local precipitation.

[5] In the current study, the hypothesis that the isotopic composition of rainfall is correlated with cloud height was tested using measurements of the altitude of rain within the clouds, which provided an estimate of the range of condensation and liquid/vapor equilibration temperatures for the rain. Estimates of the contribution of different precipitation sources to total rainfall were also made, to establish a baseline for interpreting possible effects of climate change in the Luquillo Mountains. Monthly rain samples were collected from 9 sites in the Luquillo Mountains and analyzed for δ^2H and δ^{18}O. The weather type and the echo top altitude (maximum altitude of rainfall within clouds) for individual rain events were compiled and averaged over each monthly isotope sample collection period for two years of the study, May 2005 to May 2007. Correlations between echo top altitude, sample volume, rainfall intensity and isotopic composition of rainfall were evaluated, and the isotopic signatures of precipitation from different seasonal weather patterns were identified. The results provide a new perspective on the observed amount effect in tropical precipitation that may be extrapolated to other areas in the trade wind latitudes.

2. Methods and Geographic Setting

2.1. Study Area

[6] The Luquillo Mountains, with summits as high as 1,077 m, are on the eastern end of the island of Puerto Rico and include the 113 km^2 Luquillo Experimental Forest within El Yunque National Forest. Monthly rain samples were collected for δ^2H and δ^{18}O analysis at 9 sites located along a windward-leeward transect over the Luquillo mountain range (Figure 1). Separate cloud water samples were also collected at three of the sites using passive cloud water collectors, which do not entirely exclude rainfall, but provide an estimate of the isotopic composition of precipitation that is not collected by standard funnel-type rain collectors. The altitude of the sampling sites ranged from 1 m near the northern coast to 1,050 m on Pico del Este. The study area ranges from subtropical montane cloud, wet and rain forest to lowland moist forest and shrubland [*Helmer et al.*, 2002]. Sampling sites were open to the sky, though we cannot rule out canopy influence at some sites. Monthly sampling began in April 2005; data from April 2005 to April 2008 are reported here. The detailed weather analyses were done for the first 2 years of the study, May 2005 to May 2007.

2.2. Climatological Setting

[7] In the Caribbean region, the climate is strongly influenced by easterly trade winds, especially in the winter months [*Granger*, 1985; *Taylor and Alfero*, 2005]. The trade winds and sea breeze, as well as synoptic features such as easterly waves, fronts, and low pressure systems, interact with topographically driven influences to control the spatial distribution of rainfall [*Carter and Elsner*, 1996]. Precipitation patterns are also influenced by the NAO and ENSO [*Jury et al.*, 2007]. The prevailing wind direction is from the east with the trade wind flow varying from southeast to northeast. In the trade wind latitudes, there is a narrow (~300 m thick) layer of increasing temperatures in the atmosphere at around 2500 m altitude, called the trade wind inversion. Under normal trade wind weather conditions, the vertical development of cumulus clouds is limited to the altitude of the inversion [*Gutnick*, 1958; *Johnson et al.*, 1999]. The inversion is present more often in the winter

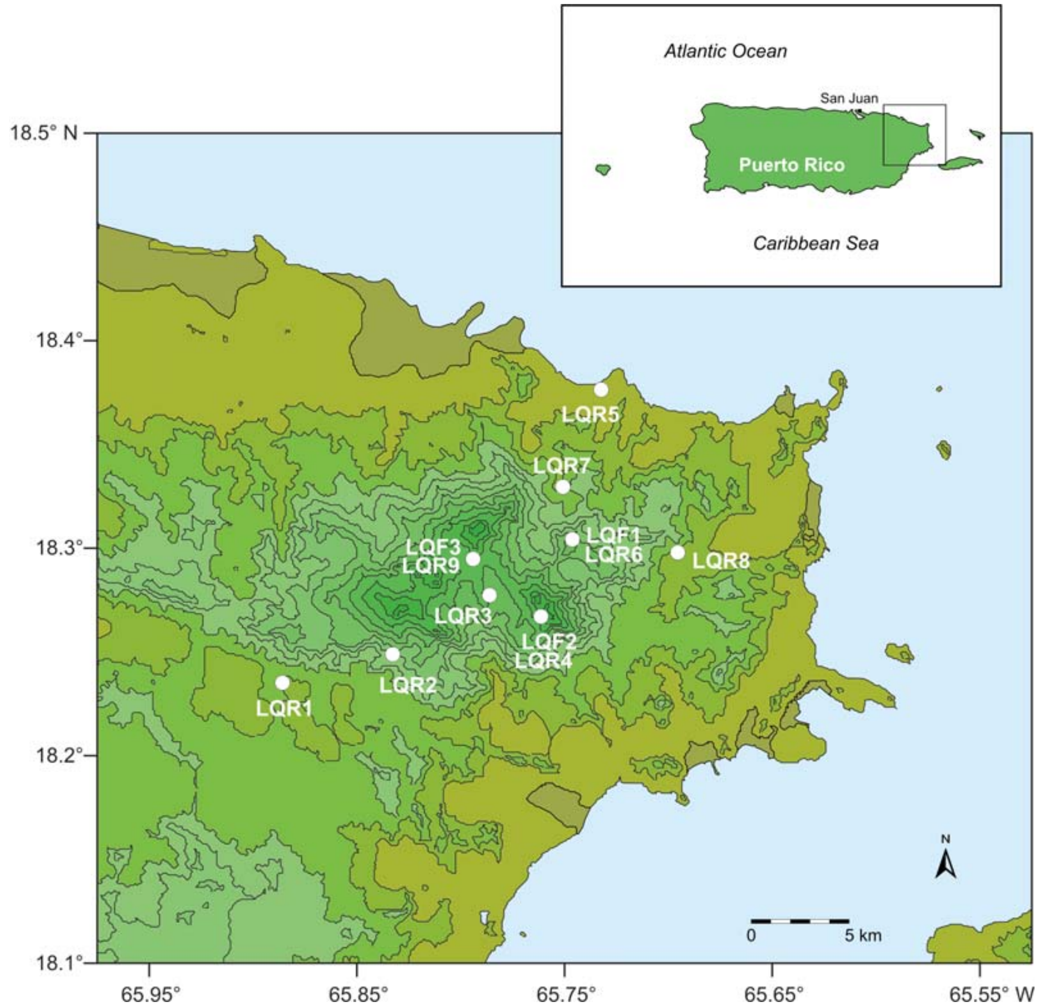

Figure 1. Map of eastern Puerto Rico, showing locations of the precipitation sampling sites. Contour intervals are 1, 50, and 100 m beginning at the coastline, and every 100 m thereafter. The Rio Icacos weather station is located at site LQR3.

months than in the summer and fall months [*Gutnick*, 1958]. Seasonal weather patterns for the Caribbean region are broadly divided into dry and rainy seasons with the rainy season defined by the passage of easterly waves that bring much of the rainfall to the region [*Taylor and Alfero*, 2005; *Grist*, 2002]. Because of the orographic influence on rainfall in the Luquillo Mountains, rainfall amounts are high year round, and the dry season is evidenced by occasional days without rain and smaller monthly rainfall totals. The approximate seasonal divisions are June through November for the rainy season and December through May for the dry season [*Taylor and Alfero*, 2005]. For this study, the summer/fall rainy seasons are defined by the beginning and end of the easterly wave weather pattern.

[8] Long-term climate records from several stations in and near the study area indicate a seasonal fluctuation in mean temperature of about 3–4°C [*Schellekens et al.*, 2004] (see also Luquillo LTER, Luquillo Experimental Forest Long Term Ecological Research Network site data, 2008, http://luq.lternet.edu/data/and National Weather Service Southern Region headquarters climate records, 2007, http://www.srh.noaa.gov). The Luquillo Mountains receive high rainfall; reported averages are 3,864 mm a^{-1} for the area [*Garcia-Martino et al.*, 1996] and 4,280 mm a^{-1} for the Rio Icacos watershed [*Peters et al.*, 2006]. Rainfall increases with altitude, from about 2,500 to 4,500 mm a^{-1} over a 1,200 m range of altitude [*Garcia-Martino et al.*, 1996].

2.3. Sample Collection and Analysis

[9] Cumulative rain samples for isotopic analysis were collected monthly in 20 L HDPE rectangular carboys. A funnel glued into the cap was sized accordingly for each site 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 carboy to make a 1 cm thick layer over the water sample to prevent evaporation and subsequent isotopic fractionation [*Scholl et al.*, 2002, 2007]. Samples were collected by replacing the funnel cap with a spigot cap, rotating the carboy so the oil layer was above the outlet, and dispensing the sample through a coarse, qualitative filter into a 60 mL glass bottle with a conical insert cap. The filter paper served to remove residual oil from the sample. Volume of the entire monthly sample was then measured to determine the rainfall amount.

[10] Cumulative cloud water samples for isotopic analysis were collected monthly at 3 sites at altitudes of 482, 770, and 1051 m. The passive cloud water collectors were adapted from the design of *Falconer and Falconer* [1980]. These consisted of a 32 cm tall frame supporting a 19 cm diameter cylindrical array of tightly strung Teflon monofilament (0.4 mm diameter). The cylinder was seated on a funnel that drained the cloud water to a 20 or 40 L carboy or tank containing mineral oil. For two of the collectors, a circular sheet aluminum "roof" (76 cm diameter) was mounted over the cylinder to exclude vertically falling rain; the other collector was mounted on a tower under a larger rain shield. Collector efficiency varied with wind speed and the collectors did not exclude all wind-driven rainfall. Samples were collected as described above for rainfall.

[11] Stable isotope samples were analyzed for $\delta^{18}O$ and $\delta^{2}H$ in the U.S. Geological Survey Reston Stable Isotope Laboratory. Oxygen and hydrogen isotopic results are reported relative to Vienna Standard Mean Ocean Water (VSMOW) on scales normalized such that the isotopic composition of SLAP reference water is −55.5‰ and −428‰, respectively. Deuterium ($\delta^{2}H$) values of the water samples were determined by equilibration with gaseous hydrogen and automated analysis [*Coplen et al.*, 1991]; one sigma uncertainty is ±1‰. Oxygen-18 ($\delta^{18}O$) values were determined by equilibration with carbon dioxide and automated analysis using the method of *Epstein and Mayeda* [1953]; one sigma uncertainty is ±0.1‰.

2.4. Weather Analyses

[12] Four of the precipitation sampling sites were collocated with weather stations or stand-alone tipping bucket rain gauges. The Rio Icacos site in the Luquillo Mountains (616 m, LQR3 on Figure 1) had two rain gauges in the same area, so missing data could be filled in and a complete rainfall record was obtained for the period of study. The rain event record from the Icacos site was used for the weather type and echo top analyses. The timing of larger rain events at the Icacos site correlated on a daily basis with that of other stations in the study area, and the site location in the mountains ensured that all the trade wind orographic rain showers were accounted for, even though they may not have affected the lower altitude stations. Rainfall was recorded with 5 to15 min resolution. Rain events were defined as periods of rainfall with rainless intervals of less than 3 h; a break in rainfall of more than 3 h denoted a new rain event.

[13] Rain events were categorized using descriptive text summaries from the National Weather Service (NWS) office in San Juan, PR (National Weather Service regional weather summary for Puerto Rico, 2005–2007, http://www.srh.noaa.gov/productview.php?pil=SJURWSPR&version=0). The weather summaries are posted 4 times per day, they described the synoptic and local scale weather patterns affecting the island, and they often included details on the rainfall-producing mechanisms for eastern Puerto Rico. Rain event size and duration were determined as described above for the Rio Icacos data set, and events were sorted by size within each monthly precipitation collection period. Weather types were assigned for events in order of size until ≥80% of the total rainfall for the sampling period was accounted for; this included an average of 12 events per sample period. Rain events of a few millimeters were usually not included. These small rain events were analyzed for several of the sampling periods. Analysis of 100% of the rainfall during those periods showed that the small rain events were generally on the same day as larger events and were from the same weather systems, so using ≥80% of the total volume was sufficient to characterize the weather pattern for each sampling period.

[14] The major weather categories were fronts, trade wind orographic showers associated with high pressure systems, troughs, low pressure systems, tropical storms, and easterly waves. Most of the weather systems that bring rainfall to eastern Puerto Rico are likely affected to some extent by orography [*Smith*, 2006; *Roe*, 2005], but for this study, we use the term orographic precipitation to mean rainfall originating under trade wind conditions, in the absence of larger-scale weather systems. In the weather summaries, showers during high-pressure system trade wind weather patterns were distinguished from showers associated with atmospheric instability during easterly waves. In addition, there were two less distinct categories that we labeled "showers and thunderstorms" and "showers." The showers were variously described as mountain showers, scattered showers, heavy showers, and passing showers. For events in the showers category, the weather summary did not usually contain information on the weather that caused the rainfall. This rain was assumed to be from orographic uplift, and the sea breeze and atmospheric instability associated with land surface heating. Five percent of the rain events had no weather description because the summaries were not available. Rainfall intensity in mm h^{-1} was calculated for each rain event and the median intensity for each weather category was determined. The median value was used because the ranges of intensity values were large, and the mean values were generally not representative of the most frequent intensity for each weather type.

2.5. Echo Top Analyses and Atmospheric Temperature Estimates

[15] Echo tops are a radar product from the NWS that provides the maximum altitude of radar-detected precipitation over the duration of a rain event. Echo tops are "the height above ground of the center of the radar beam using the tilt or scan that contains the highest elevation where reflectivities greater than 18 dBZ can be detected" (National Weather Service glossary, 2008, http://www.weather.gov/glossary/). NEXRAD data are available for Puerto Rico from NOAA's National Climatic Data Center (NOAA, NCDC radar resources, http://www.ncdc.noaa.gov/oa/radar/radarresources.html and NCDC Java NEXRAD tools, http://www.ncdc.noaa.gov/oa/radar/jnx/index.php).

[16] The echo top data were available as raster (image) files in 5 to 15 min increments over the duration of a rain event. Echo top altitudes were found for the 4 to 6 largest rain events during each monthly sampling period. These events accounted for 43 to 82% (average of 54%) of the rainfall and correspondingly, the volume of the isotope sample, during each period. Analyzing only the largest events was found to provide a satisfactory average echo top altitude for the monthly period because most of the smaller events in a given sample period were part of the same multiday weather systems as the largest events. The trade wind showers, however, tended to be underrepresented in the analysis, so in order to obtain average echo top

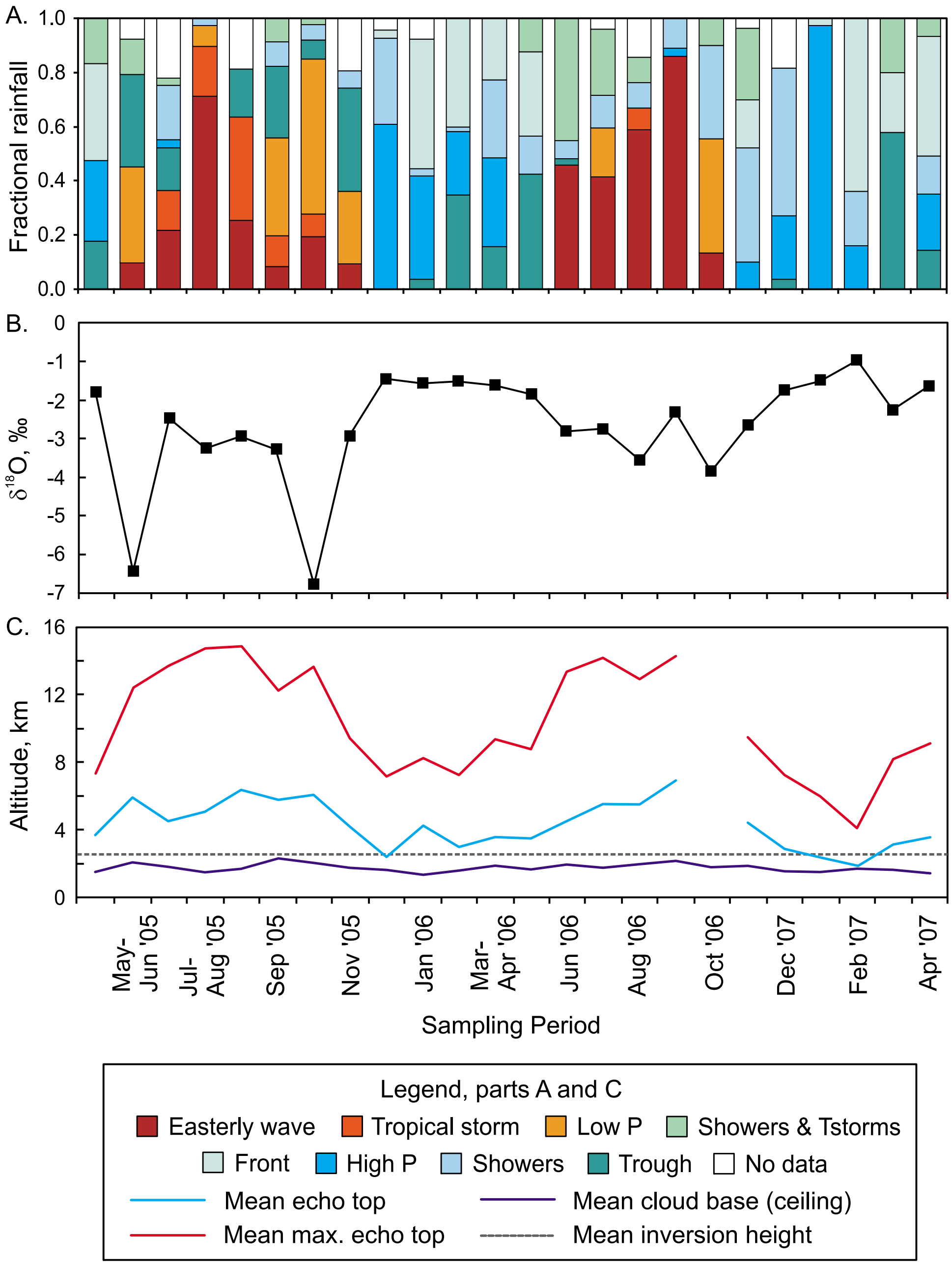

Figure 2. (a) Fraction of rainfall contributed by different weather types during each monthly sampling period. (b) Values of $\delta^{18}O$ measured at the Icacos station, over the period of the weather analysis. (c) Maximum and mean echo top altitudes and cloud base at San Juan Airport averaged for each sampling period, and average altitude of the trade wind inversion for Puerto Rico [*Gutnick*, 1958]. Data are shown for the period April 2005 to May 2007; exact dates for the sampling periods are given in Table 1.

estimates for all of the different rain sources, echo tops were also analyzed for six of the smaller trade wind orographic events. Raster files covering the duration of each event at 6 min intervals were downloaded from the NCDC web site (http://www.ncdc.noaa.gov/oa/radar/radarresources.html and http://www.ncdc.noaa.gov/oa/radar/jnx/index.php). Echo top values were represented by pixels with a vertical resolution of 1,524 m of altitude and a horizontal resolution of 4 $\times$ 4 km. An average altitude was assigned to each 1,524 m echo top interval for the analysis. For each data file, echo top altitudes for all pixels within a 531 km^2 circle encompassing the study area were accumulated, then an average echo top altitude was calculated for the entire rain event. An average echo top altitude for each monthly sampling period was calculated by weighting the echo top values by each event's rainfall amount. The maximum echo top altitude within the study area boundaries was also recorded for each event and averaged for each sampling period.

[17] Although echo tops are related to cloud height, they are not necessarily the same as cloud tops, and the echo top may be at a lower altitude than the cloud top. Echo top

Table 1. Volume-Weighted Average Isotopic Composition of Rain or Cloud Water From Each Site, April 2005 through April 2008[a]

Collector ID	Sample Type	Site Name	Latitude (°N)	Longitude (°W)	Altitude (m)	VWA δ^2H (‰)	VWA δ^{18}O (‰)
LQR1	R	Rio Gurabo[b]	18.234	65.885	71	−14.5	−3.30
LQR2	R	Pueblito del Rio[b]	18.248	65.832	341	−12.4	−3.10
LQR3	R	Rio Icacos[b]	18.277	65.786	616	−10.8	−3.05
LQR4	R	Pico del Este	18.270	65.760	1,051	−14.8	−3.76
LQF2	CW	Pico del Este	18.270	65.760	1,051	−3.4	−2.42
LQR5	R	Mata de Platanos	18.376	65.733	1	−8.7	−2.53
LQR6	R	Bisley[c]	18.304	65.746	482	−11.4	−3.12
LQF1	CW	Bisley[c]	18.304	65.746	482	−8.4	−2.74
LQR7	R	Rio Mameyes nr. Sabana[b]	18.329	65.751	84	−6.8	−2.43
LQR8	R	Rio Fajardo[b]	18.299	65.695	42	−9.5	−2.73
LQR9	R	Aviary	18.295	65.794	770	−7.7	−2.81
LQF3	CW	Aviary	18.295	65.794	770	−3.6	−2.49

[a]R, rain; CW, cloud water; VWA, volume-weighted average.
[b]Site with U.S. Geological Survey stream gauge and/or precipitation gauge.
[c]Samples were collected above the canopy on a meteorological tower at the Bisley site.

altitudes are relevant for comparison to the isotopic composition of rain because the corresponding air temperature at this altitude is an indication of the lowest temperature at which water vapor may be condensing and equilibrating with cloud droplets. An estimate of the atmospheric temperatures was obtained from archived sounding profiles based on the National Centers for Environmental Prediction Eta model (now the NAM model) EDAS 40 km data set (NOAA, Air Resources Laboratory Archived Meteorology data http://www.arl.noaa.gov/ready/ametus.html and information http://www.arl.noaa.gov/edas40.php) using the average echo top altitudes for each event. The modeled temperature profiles incorporate radiosonde and aircraft observations from the nearest NWS station, which is San Juan airport, 29 km from the study area. An estimate of cloud base altitude was obtained from ceilometer measurements from the San Juan Airport, located near sea level in an urban area. The measurements from the airport were higher than cloud base observed in the mountains, but no measurements were available from the study area.

3. Results

3.1. Seasonal Weather Patterns in the Study Area

[18] Detailed analyses of the weather patterns that brought rainfall to the study area were done for the period May 2005 to May 2007. Figure 2a shows the fraction of the total rainfall contributed by each weather type during each monthly sampling period. The weather analysis in Figure 2a illustrates the distinctly different rainfall sources during the rainy and dry seasons in eastern Puerto Rico. Much of the rainfall in the rainy seasons (June through November) was from deep convection associated with easterly waves and from low pressure systems, including tropical storms. The dry seasons (December through May) were characterized by trade wind orographic showers associated with high pressure systems, and fronts. Troughs and showers with thunderstorms occurred in both seasons, except thunderstorms were not noted in the January–March timeframe during either year.

3.2. Isotopic Composition of Rain and Cloud Water

[19] The volume-weighted average isotopic composition of rain and cloud water for the period April 2005 through April 2008 is given for each site in Table 1. The range of individual monthly values was −7.25 to −0.03‰ for δ^{18}O and −46 to +13.9‰ for δ^2H (Table 2). Rainfall amounts for each sampling period are given for the Icacos (LQR3) site, and ranged from 129 to 778 mm (Table 2). Figure 3 shows the spatial and temporal variation in δ^{18}O composition of rainfall from all sites in the study area from April 2005 through April 2008. Isotopic values of rainfall generally decreased with increasing altitude, as would be expected due to progressive fractionation along a coast-to-inland gradient and lower temperatures with increasing altitude [*Clark and Fritz*, 1997]. The linear regressions describing differences in isotopic composition of rain with altitude on the windward side of the study area were δ^{18}O = −0.0012 (altitude, m) −2.48, R^2 = 0.90; and δ^2H = −0.006 (altitude, m) −8.1, R^2 = 0.77. The seasonal pattern of isotopic composition is similar at all the sites, with lower δ^{18}O values during the summer rainy season and higher values during the winter dry season, and substantially lower isotopic values during sampling periods affected by large storms. The δ^2H and δ^{18}O of the monthly samples were generally higher at the low altitude sites and lower at high altitude sites, although geographic location also appeared to be a factor affecting rain isotopic composition (Figure 3). Sites on the leeward (southwest) side of the Luquillo range (LQR1 and LQR2) had relatively high δ^2H and δ^{18}O values for their altitude during most collection periods. The LQR8 site, in a river valley at 42 m, was located some distance inland and had relatively low δ^2H and δ^{18}O values, despite its low altitude. Values of δ^2H are not shown, but the seasonal pattern is the same.

[20] Figure 2b shows the δ^{18}O values of rainfall measured at the Icacos site (LQR3) during each sampling period of the 2 year weather analysis. The seasonal cycle in isotopic composition is apparent, with lower δ^{18}O values (around −3‰) during the summer/fall rainy season and higher δ^{18}O values (around −1.5‰) during the winter/spring dry season. The substantially lower δ^{18}O values (around −6.5‰) were associated with low pressure systems during the affected sampling period. The seasonal transitions in isotopic composition can be matched to the transitions between the rainy and dry season weather types shown in Figure 2a.

[21] From previous work comparing the isotopic composition of cloud water and rain, it was expected that cloud

Table 2. Stable Isotope Values δ^2H and $\delta^{18}O$ From Nine Sample Locations and Rainfall Measured at the USGS Icacos Rain Gauge

End Date of Sample Period[b]	Rainfall Amount (mm)	Values of δ^2H for Cumulative Precipitation Samples, April 2005 to April 2008 (‰)[a]											
		LQR1	LQR2	LQR3	LQR4	LQR5	LQR6	LQR7	LQR8	LQR9	LQF1	LQF2	LQF3
						Values of δ^2H							
05/15/05	261	−30.4	−34.3	0.9	−7.2	−13.1	−17.1	−4.6	−17.2	–	−27.7	−5.0	–
06/13/05	536	−32.0	−35.0	−40.7	−44.0	−36.7	−38.7	−38.1	−35.4	–	−38.7	−13.1	–
07/12/05	295	−14.3	−6.1	−6.1	−9.3	−10.0	−3.9	−2.3	−5.4	–	−7.1	−4.7	–
08/10/05	202	−10.2	−14.2	−14.7	−16.5	−4.8	−12.5	−9.5	−10.7	–	−14.2	−7.1	–
09/06/05	129	−5.9	−7.3	−9.9	−13.4	−6.6	−9.0	−9.7	−7.1	–	−11.5	−6.0	–
10/04/05	398	−37.3	−14.1	−13.6	−16.0	−10.6	−13.2	−12.6	−22.9	–	−14.3	−13.9	–
11/08/05	778	−14.5	−39.2	−39.9	−42.4	−31.3	−38.7	−32.2	−30.7	–	−33.9	−30.4	–
12/06/05	339	−7.1	−4.4	−8.6	−10.4	−4.5	−4.8	−5.3	−5.1	–	−5.9	−10.5	–
01/12/06	332	7.4	5.0	4.0	1.7	8.0	4.5	6.8	5.8	4.2	7.2	2.8	–
02/12/06	546	5.9	6.2	3.0	−0.6	8.4	4.8	6.8	7.7	3.8	5.6	3.9	–
03/16/06	186	4.5	6.3	4.5	2.1	–	5.0	6.8	6.7	3.4	2.2	4.3	–
04/25/06	530	5.3	2.2	1.2	−1.4	2.9	0.1	2.2	0.8	−0.5	−0.8	1.8	–
05/25/06	196	1.0	−1.2	1.5	−4.2	4.1	2.0	3.6	3.1	3.3	−1.0	3.1	5.2
06/22/06	376	1.3	−12.8	−9.1	−10.1	−1.3	−6.0	−5.4	−4.4	−8.8	−7.9	−3.7	−11.6
07/26/06	464	–	−9.5	−10.1	−15.7	−11.0	−8.6	−6.1	−8.3	−11.5	−9.5	−2.4	−9.0
08/27/06	509	–	−19.0	−18.6	−20.6	−9.3	−10.7	−9.1	−13.3	−13.6	−9.8	−6.5	–
09/28/06	319	−13.4	−5.8	−5.6	−11.5	−1.6	−9.1	−3.2	−2.3	−13.4	−12.6	−3.9	−14.3
11/02/06	358	−7.5	−5.6	−17.0	−12.9	−15.6	−11.2	−14.4	−12.6	−12.9	−9.5	−4.0	−13.9
12/04/06	420	–	0.8	−5.4	−7.2	−2.6	−3.4	−1.5	−0.8	−6.8	−2.3	−4.3	−3.4
01/09/07	326	3.5	3.2	1.0	0.1	4.9	4.0	4.0	5.4	2.4	3.8	4.9	2.9
02/01/07	185	11.6	7.3	4.0	1.6	6.8	4.8	8.2	6.1	3.1	6.0	4.7	3.2
03/07/07	172	13.9	10.0	9.3	5.4	10.6	8.4	9.0	–	9.6	9.4	7.5	8.3
04/02/07	131	−6.4	−15.1	−5.7	−13.5	−5.9	−9.3	−8.3	–	−7.5	−10.4	1.8	−2.6
05/04/07	504	7.1	4.9	1.1	−0.1	4.9	2.2	4.5	6.3	1.1	3.5	2.1	1.4
6/7/2007	135	−8.2	−6.0	−12.9	−9.0	2.8	−10.3	−5.8	−3.6	−12.7	–	3.7	−13.3
7/2/2007	243	−6.6	−4.8	−9.0	−10.2	−7.4	−0.1	−0.6	−2.9	−7.4	–	0.1	−5.7
8/16/2007	422	−5.0	−4.5	−4.8	−6.6	−2.2	−5.9	−5.5	−5.6	−5.2	–	−1.0	−4.6
9/12/2007	199	−9.2	−10.5	−7.5	−13.0	−5.4	−7.0	−6.1	−7.6	−4.9	–	−3.0	−5.2
10/1/2007	244	−12.1	−14.7	−9.2	−12.7	−8.8	−6.9	−7.2	−8.1	−12.1	–	−6.1	−11.1
11/8/2007	537	−34.7	−40.7	−38.9	−42.7	−42.0	−37.5	−31.4	−36.0	−45.0	–	−24.3	−46.0
12/13/2007	501	−12.8	−11.3	−14.3	−20.4	−10.2	−17.6	−12.5	−10.1	−18.9	–	−6.9	−11.6
1/16/2008	366	0.5	−1.3	0.0	−2.9	2.9	0.5	2.3	1.1	−0.8	–	2.5	2.3
2/21/2008	436	7.4	7.1	5.5	3.9	1.1	5.4	6.8	6.0	5.0	–	–	7.0
04/17/08	465	6.2	6.5	5.7	2.5	7.9	5.2	7.8	5.8	3.1	–	5.1	7.0
						Values of $\delta^{18}O$							
05/15/05	261	−5.05	−5.50	−1.80	−2.52	−2.78	−3.38	−2.05	−3.47	–	−4.71	−2.32	–
06/13/05	536	−5.36	−5.78	−6.45	−7.12	−5.75	−6.28	−6.11	−5.84	–	−6.34	−3.33	–
07/12/05	295	−3.18	−2.34	−2.46	−2.99	−2.42	−2.21	−1.78	−2.04	–	−2.32	−2.39	–
08/10/05	202	−2.58	−3.30	−3.24	−3.71	−1.83	−3.09	−2.43	−2.52	–	−3.76	−2.78	–
09/06/05	129	−2.51	−2.45	−2.94	−3.41	−2.14	−2.74	−2.44	−2.29	–	−3.07	−2.76	–
10/04/05	398	−6.19	−3.30	−3.28	−3.92	−2.78	−3.27	−3.14	−4.39	–	−3.49	−3.79	–
11/08/05	778	−3.38	−6.66	−6.80	−7.25	−5.13	−6.46	−5.32	−5.35	–	−5.77	−5.74	–
12/06/05	339	−2.42	−2.18	−2.95	−3.53	−2.46	−2.69	−2.60	−2.54	–	−2.74	−3.47	–
01/12/06	332	−0.77	−1.09	−1.47	−2.09	−0.84	−1.48	−1.04	−1.12	−1.74	−1.24	−1.97	–
02/12/06	546	−0.59	−0.67	−1.57	−2.08	−0.52	−1.41	−0.97	−0.88	−1.73	−1.39	−1.79	–
03/16/06	186	−1.40	−1.12	−1.52	−2.03	–	−1.35	−1.00	−1.06	−1.78	−1.69	−1.69	–
04/25/06	530	−0.74	−1.47	−1.62	−2.08	−1.26	−1.72	−1.27	−1.32	−1.90	−1.83	−1.70	–
05/25/06	196	−1.65	−1.90	−1.84	−2.56	−1.42	−1.60	−1.25	−1.26	−1.83	−1.68	−1.74	−1.54
06/22/06	376	−1.15	−3.05	−2.80	−3.08	−1.23	−2.07	−1.83	−1.72	−2.82	−2.33	−2.30	−3.00
07/26/06	464	–	−2.63	−2.75	−3.48	−2.48	−2.48	−2.21	−2.50	−2.82	−2.56	−1.91	−2.52
08/27/06	509	–	−3.77	−3.56	−3.92	−2.24	−2.67	−2.18	−2.79	−3.14	−2.53	−2.39	–
09/28/06	319	−3.15	−2.25	−2.32	−3.43	−1.63	−2.75	−1.94	−1.75	−3.35	−3.18	−2.44	−3.63
11/02/06	358	−2.26	−2.30	−3.85	−3.40	−3.50	−3.08	−3.41	−2.97	−3.36	−2.74	−2.40	−3.62
12/04/06	420	–	−1.85	−2.66	−3.05	−2.04	−2.44	−2.15	−2.01	−2.86	−2.39	−2.85	−2.79
01/09/07	326	−1.13	−1.17	−1.75	−2.22	−0.84	−1.62	−1.29	−1.05	−1.79	−1.59	−1.84	−1.88
02/01/07	185	−0.05	−0.49	−1.48	−2.08	−0.93	−1.42	−0.91	−1.01	−1.77	−1.37	−1.81	−1.89
03/07/07	172	−0.03	−0.28	−0.95	−1.52	−0.52	−1.04	−0.67	–	−1.07	−0.90	−1.29	−1.35
04/02/07	131	−2.16	−3.21	−2.26	−3.35	−2.23	−2.88	−2.33	–	−2.89	−2.82	−2.03	−2.50
05/04/07	504	−0.73	−1.09	−1.63	−2.11	−1.12	−1.73	−1.34	−1.15	−1.90	−1.34	−1.82	−1.87
6/7/2007	135	−2.46	−2.16	−2.96	−2.82	−0.92	−2.71	−1.94	−1.69	−3.16	–	−1.41	−3.39
7/2/2007	243	−1.83	−1.91	−2.28	−2.94	−2.06	−1.56	−1.33	−1.59	−2.36	–	−1.82	−2.37
8/16/2007	422	−1.62	−1.84	−1.84	−2.64	−1.48	−2.30	−2.00	−2.03	−2.28	–	−1.68	−2.05
9/12/2007	199	−2.64	−2.81	−2.36	−3.48	−2.08	−2.43	−2.10	−2.30	−2.22	–	−2.34	−2.46
10/1/2007	244	−2.95	−3.50	−2.73	−3.50	−2.44	−2.48	−2.33	−2.47	−3.26	–	−2.73	−3.25
11/8/2007	537	−5.78	−6.80	−6.55	−7.25	−6.59	−6.37	−5.43	−6.03	−7.47	–	−5.05	−7.66
12/13/2007	501	−3.18	−3.03	−3.71	−4.70	−2.88	−4.10	−3.32	−3.05	−4.43	–	−3.00	−3.30
1/16/2008	366	−1.66	−1.88	−1.93	−2.48	−1.28	−1.94	−1.52	−1.65	−2.23	–	−1.90	−1.85
2/21/2008	436	−0.90	−0.90	−1.41	−1.96	−1.83	−1.65	−1.19	−1.15	−1.84	–	–	−1.60
04/17/08	465	−0.69	−0.93	−1.28	−1.95	−0.63	−1.50	−0.75	−1.17	−1.81	–	−1.59	−1.31

[a]LQR samples 1–9 are rain and LQF samples 1–3 are cloud water.

[b]Samples were collected over several days; the sample period ending date shown is the median collection date for the set of samples.

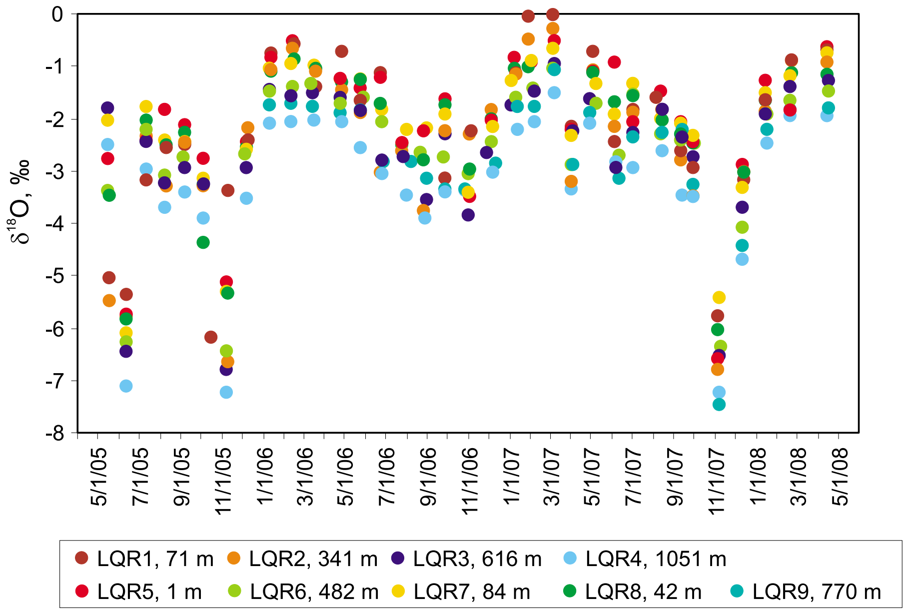

Figure 3. Values of $\delta^{18}O$ from monthly samples at nine sites in the Luquillo Mountains over the period 15 May 2005 to 17 April 2008. Points are plotted on the sample collection date and represent isotopic composition of the cumulative monthly rainfall. The altitude range for the sample sites is 1 to 1051 m. Data are given in Table 2 and location information is shown in Figure 1 and Table 1.

water would be enriched in ^{2}H and ^{18}O compared to rainfall [*Eugster et al.*, 2002; *Scholl et al.*, 2007]. The isotopic compositions of cloud water and rain were compared at the three measurement sites that had both types of collectors (Tables 1 and 2). Although the passive cloud water samplers do not entirely exclude rain, they provide an estimate of the isotopic composition of fog and cloud water that may be present on mountains above the altitude of cloud base. Cloud water samples were enriched in ^{2}H and ^{18}O compared to rain samples for the highest altitude site on Pico del Este (LQF2 in Figure 1). At the Pico del Este site, the differences between volume-weighted average $\delta^{2}H$ and $\delta^{18}O$ of rain and cloud water were 11.4‰ and 1.34‰, respectively (Table 1). At the other two sites, differences between the volume-weighted average of rain and cloud water were smaller (at LQF1, 3‰, 0.38‰; at LQF3, 4‰, 0.32‰ in $\delta^{2}H$ and $\delta^{18}O$, respectively). These sites were lower in altitude than Pico del Este and not often above cloud base, and differences greater than analytical error were not observed between rain and cloud water samples for most of the sample periods.

3.3. Echo Top Altitudes With Weather Type and Isotopic Composition of Rain

[22] Echo top altitudes were obtained for precipitation events during the period April 2005 to April 2007. Average echo top altitudes for individual precipitation events ranged from 1,072 to 8,757 m. Maximum echo top altitudes for individual events ranged from 3,810 to 17,525 m. Low pressure systems, including tropical storms, had the highest echo top altitudes and easterly waves also had relatively high echo top altitudes (Table 3). Trade wind showers associated with high pressure had the lowest echo top altitudes. Average echo top altitudes for the monthly sampling periods over two years ranged from 1,877 to 6,968 m (Figure 2c). The average atmospheric temperatures corresponding to the echo top altitudes for different weather types are also given in Table 3; these ranged from −11 to 10°C.

[23] The differences between echo top altitudes for the different weather types were assessed using an analysis of variance (ANOVA). To meet normal distribution criteria for the test, similar weather categories were lumped together, i.e., the showers and trade wind orographic showers categories were combined, and the low pressure system and tropical storm categories were combined. The ANOVA showed significant differences ($P < 0.001$) between the echo top altitudes associated with different weather types. A Holm-Sidak pairwise comparison indicated that the low pressure system and easterly wave echo tops (rainy season) were significantly different than those of the showers and the fronts (dry season). There was not a significant difference between the low pressure systems group and easterly waves, or between the showers and fronts.

[24] In Figure 4, average echo top altitudes are plotted against the average $\delta^{18}O$ values from the Icacos site for each sampling period (the Icacos site is the source of the rain event data set for which echo tops were analyzed). Rainy (summer/fall) and dry (winter/spring) season data are shown by different symbols. The seasonal designation for each sample period was based on the weather analysis shown in Figure 2a. The temperatures corresponding to the echo top altitudes are also shown, obtained from the atmospheric profiles. Values of $\delta^{18}O$ generally decrease with increasing echo top altitude and decreasing atmospheric temperature. Figure 2c shows the maximum and mean echo top altitudes, and mean cloud base altitude over time during the 2005–2007 period. The plot illustrates the seasonal changes in

Table 3. Average Echo Top Altitude Plus or Minus Standard Deviation, Average Atmospheric Temperature at the Echo Top Altitudes, Maximum Observed Echo Top Altitude for Each Weather Type, Median and Maximum Rainfall Intensity for All Events That Were Categorized by Weather Type, and Fraction of Seasonal and Total Precipitation From Different Rain Event Types in the Luquillo Mountains[a]

Rain Event Weather Type	Average Echo Top Altitude (m)	Average Atmospheric *t* for Echo Tops (°C)	Maximum Observed Echo Top Altitude, m	Number of Echo Top Events Analyzed	Median Rainfall Intensity (mm h^{-1})	Rainfall Intensity Range (mm h^{-1})	Fraction Rainy Season Rainfall	Fraction Dry Season Rainfall	Fraction of Total Rainfall
High pressure and trade wind showers	2,365 ± 589	10.3	9,906	15	1.98	0.4–13.7	0.01	0.14	0.15
Showers	2,750 ± 974	9.1	12,953	15	2.37	0.9–61.0	0.07	0.07	0.14
Fronts	3,470 ± 1,604	4.7	17,525	15	3.39	0.8–15.8	0.01	0.13	0.14
Troughs	4,335 ± 1,776	1.8	14,447	13	3.09	0.5–103.6	0.06	0.08	0.14
Showers with thunderstorms	4,748 ± 1,097	0.1	14,447	9	3.58	1.1–35.1	0.06	0.02	0.08
Easterly waves	5,292 ± 1,743	−2.9	16,001	16	3.13	0.8–50.3	0.17	0	0.17
Tropical storms	5,733 ± 1,510	−5.2	16,001	5	3.77	0.8–22.9	0.04	0	0.04
Low-pressure systems	6,723 ± 1,252	−11.1	16,001	8	4.18	0.9–19.8	0.09	0	0.09
No data							0.04	0.01	0.05

[a]Here *t* is temperature.

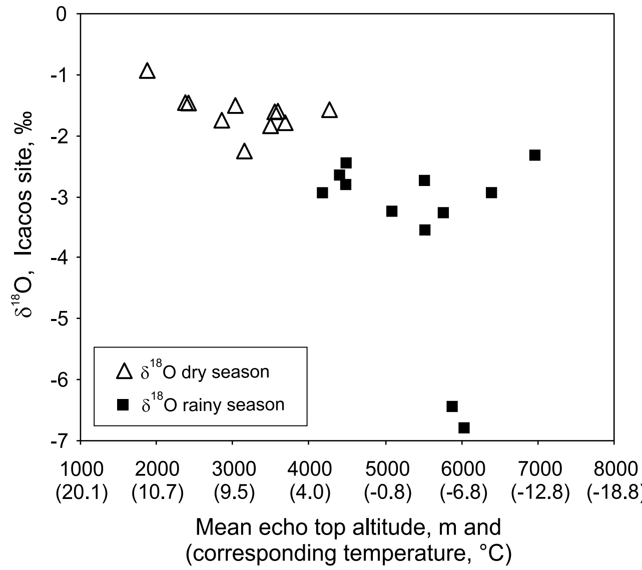

Figure 4. Relation between δ^{18}O values (Icacos site LQR3) and the mean echo top altitude and corresponding atmospheric temperature for each monthly sampling period. The δ^2H pattern, not shown, is the same.

cloud height and how cloud height corresponds with δ^{18}O values measured at the Icacos site and with weather type.

4. Correlation Analysis

[25] A Pearson correlation analysis was done with selected parameters that can affect isotopic composition of rainfall, and the correlation coefficients are shown in Table 4. The monthly measurements included in the correlation were δ^{18}O and δ^2H from the Icacos site (the source of the rain event record for the echo top analysis), average δ^{18}O and δ^2H of all the sites, average echo top altitude, sample volume (the "amount" referred to in the amount effect), median rainfall duration, and median rainfall intensity. For the Icacos site, the correlation between isotopic composition and echo top altitude was significant at $p < 0.001$, with a correlation coefficient of −0.69 (average of δ^{18}O and δ^2H coefficients), while the correlation between isotopic composition and monthly sample volume (amount) was lower, with an average correlation coefficient of −0.55 (significant at $p < 0.01$). The correlation coefficients for echo top altitude and amount using the average isotopic composition for all the sites were the same: −0.69 for echo top altitude and −0.69 for average sample volume for all the sites. The correlation coefficient between isotopic composition and median monthly rain intensity for all sites averaged −0.50 (significant at $p = 0.01$), while the correlation between median event duration and isotopic composition was not significant (average 0.06). Echo top altitude and sample volume for all the sites were somewhat correlated with an average correlation coefficient of 0.55 ($p < 0.01$).

[26] Repeating the correlation analysis and omitting the two sample periods with extremely low isotopic composition yielded different results (not shown in Table 4). For the Icacos site, the correlation between isotopic composition and echo top altitude for the Icacos site increased, with a coefficient of −0.78 (significant at $p \ll 0.001$), while the correlation between isotopic composition and sample volume was not

Table 4. Pearson Correlation Coefficients for Selected Variables Measured During the Study[a]

	δ^{18}O Icacos	δ^{2}H Icacos	δ^{18}O, Average of All Sites	δ^{2}H, Average of All Sites	Echo Tops	Volume, Icacos	Volume, Average of All Sites	Median Intensity	Median Duration
δ^{18}O Icacos	1.0								
δ^{2}H Icacos	0.99	1.0							
δ^{18}O, average all sites	0.94	0.94	1.0						
δ^{2}H, average all sites	0.93	0.94	0.99	1.0					
Echo tops	**−0.67**	**−0.71**	**−0.67**	**−0.70**	1.0				
Volume, Icacos	**−0.56**	**−0.55**	−0.48	−0.48	0.40	1.0			
Volume, average all sites	−0.59	−0.58	**−0.70**	**−0.69**	**0.55**	0.54	1.0		
Median intensity	−0.38	−0.42	−0.49	−0.52	0.47	0.35	0.52	1.0	
Median duration	0.04	0.07	0.04	0.06	−0.06	−0.02	0.14	−0.51	1.0

[a]Time period for correlation of all variables was the isotope sampling period (approximately monthly) and units are as follows: δ^{18}O and δ^{2}H (‰), average echo top altitude (m), volume (mL), median intensity of rain events (mm h^{-1}), and median duration of rain events (h). Correlations between echo top altitude, isotopic composition, and sample volume are in bold.

significant (coefficient of −0.22). For the average values of all the sites in the study area, the correlation between isotopic composition and echo top altitude increased, with a coefficient of −0.75, while the correlation between isotopic composition and volume decreased, with a coefficient of −0.51.

5. Discussion

5.1. Seasonal Patterns in Isotopic Composition of Rain

[27] Previous data on isotopic composition of precipitation from Puerto Rico are available from the GNIP database during the period 1968–1973 from a site in San Juan at 4 m altitude and about 25 km from the study area (International Atomic Energy Agency, Global network of isotopes in precipitation, GNIP database, http://isohis.iaea.org). The range of δ^{18}O values was −4.44 to +0.56‰. Monthly averages from these data show the highest isotopic values during the months of January–April and the lowest values during August, October and November (not shown), in agreement with the seasonal pattern shown in this study. *Rodriguez-Martinez* [1997] presented isotopic data for monthly rainfall samples from 4 sites in north central Puerto Rico. Values of δ^{2}H ranged from −37.1 to +15.5‰ and δ^{18}O ranged from −5.36 to +0.78‰. The average rainy season isotopic values were lower than the average dry season values, in agreement with the results found in this study. In a more recent study [*te Linde et al.*, 2001], rain, throughfall, and fog isotopic values were measured during September 1999 at 8 sites on the windward side of the Luquillo Mountains. The δ^{18}O values of individual events ranged from about −8.8 to +0.6‰. The wide range of values measured during that month indicates the substantial variability of weather systems and their associated isotopic compositions during the rainy season in Puerto Rico. *Jones et al.* [2000] and *Jones and Banner* [2003] showed a seasonal cycle in stable isotope composition of rainfall on Barbados, Puerto Rico and Guam. For all their study sites, the amount of monthly rainfall was correlated with isotopic composition, i.e., lower isotopic values corresponded to higher monthly rainfall.

[28] In the present study, rainfall was generally enriched in ^{18}O and ^{2}H during the winter months and depleted in ^{18}O and ^{2}H during the summer months (Figure 3), and the historical data described above indicate that this is a long-term pattern. The distinct seasonality of the weather patterns producing rainfall (illustrated in Figure 2a) causes the seasonal fluctuations in δ^{18}O of rainfall, as shown in Figures 2b and 3. Rainfall depleted in ^{18}O and ^{2}H occurs during the summer/fall rainy season, associated with easterly waves and low pressure systems. Rainfall enriched in ^{18}O and ^{2}H occurs during the winter/spring dry season, associated with weather patterns of trade wind orographic showers and frontal systems. These results agree quite well with the global patterns shown by *Feng et al.* [2009], but add some detail relevant to latitudes north of the Intertropical Convergence Zone (ITCZ) in the Atlantic basin. *Feng et al.* [2009] interpreted the major climatic controls on global patterns of isotopic composition as being the ITCZ and the subtropical highs. Puerto Rico is north of the area influenced by the ITCZ, and we show that the summer minimum in isotopic values there is associated with the easterly waves climate pattern. The subtropical highs also influence Puerto Rico; specifically, the trade winds and orographic effects account for most of the precipitation under high pressure conditions. The results presented here suggest the winter maximum in rainfall isotopic values in Puerto Rico is controlled by the limited cloud height under the trade wind inversion.

5.2. Relative Contribution of Rainfall During Different Weather Patterns

[29] The volume fractions of precipitation derived from each weather type for the 2 year analysis are shown in Table 3. Trade wind orographic rainfall associated with high pressure systems, together with nonthunderstorm showers, accounted for 29% of the total rainfall for the study period. The major weather types in the summer/fall rainy season (easterly waves, tropical storms, and low pressure systems) contributed 30% of the total precipitation. The other major weather types were fronts and troughs, each contributing 14% of the total precipitation, and showers with thunderstorms, which contributed 8%. The remaining 5% was from events for which there were no weather summaries available.

[30] The isotopic signature of rainfall during the dry and rainy seasons was distinctly different, as shown in the time series of Figure 3. For the period of the weather analysis, May 2005 to May 2007, the dry season volume-weighted average δ^{18}O and δ^{2}H values of precipitation were −1.5‰ and +2.3‰, respectively. The rainy season volume-weighted average δ^{18}O and δ^{2}H values were −3.7‰ and −16‰, and the average δ^{18}O and δ^{2}H values for the samples with low-pressure system rain were −5.9‰ and −36‰. Understand-

ing the isotopic signatures of the different weather patterns that contribute to the water supply will help in studies to determine the best ways to assure water supplies for both humans and ecosystems under conditions of changing climate.

5.3. Relation Between Echo Top Altitude and Isotopic Composition

[31] Figure 4 illustrates the relationship between the isotopic composition of rain and echo top altitude. The echo top values represent the average origination altitude and temperature for the largest rain events in each sample period. There is a general trend of lower δ^{18}O values with increasing echo top altitudes. Lower echo top altitudes were measured during the dry season; this corresponds to the presence of the strong trade wind inversion that limits cloud height in these latitudes. The trade wind showers and other showers had average echo tops at 2365–2750 m (Table 3), and the dry season inversion height in the Caribbean ranges from 1860 to 2830 m [*Gutnick*, 1958]. Frontal system rain events during the dry season also had relatively low echo top altitudes. The rainy season had rain events with a higher range of echo top altitudes corresponding to the higher clouds associated with convection in easterly waves and low pressure systems (Table 3).

[32] There are several factors that may explain the correspondence between echo top altitude and isotopic composition. The isotopic composition of rain is controlled by the temperature of condensation, the isotopic composition of the source vapor, and the length of time the raining air mass spends over the study area, as well as raindrops coalescing and equilibrating isotopically with surrounding vapor during the processes of circulation within the cloud and transport to the land surface [*Lee and Fung*, 2008; *Rozanski et al.*, 1993; *Dansgaard*, 1964, *Friedman et al.*, 1962]. Condensation of precipitation at lower temperatures (higher in the atmosphere) accelerates the removal of the heavier isotopologues from the vapor; with the end result that precipitation δ^{18}O and δ^{2}H values from low temperature condensation are lower (more negative). Average echo top altitudes for dry season precipitation were below the freezing layer at around 5 km [*Johnson et al.*, 1999], but the echo top altitudes during many rainy season events corresponded with subfreezing temperatures. Isotopic fractionation from evaporation, and isotopic exchange from equilibration processes may have been minimized if precipitation was frozen during part of its time within the cloud. *Friedman et al.* [1962, Table 2] noted that the travel distance calculated from the ^{2}H equilibration time for a falling raindrop ranged from 5 m to 2900 m for droplets with a radius between 0.01 and 0.15 cm. Therefore, small raindrops that have significantly lower δ^{2}H and δ^{18}O values from upper altitudes in a cloud would equilibrate to a large degree with the water vapor near the cloud base, while larger raindrops would partly retain their low δ^{2}H and δ^{18}O values due to longer equilibration times.

[33] Last, weather systems that arrive at the study area having water vapor with significantly lower δ^{2}H and δ^{18}O values than the local water vapor would produce rain with lower δ^{2}H and δ^{18}O values. Differences in atmospheric water vapor isotopic composition are implicit with differences in cloud height, as water vapor δ values decrease with increasing altitude [cf. *Ehhalt et al.*, 2005]. *Angert et al.* [2008] found that water vapor measured 6 m above land surface in the Mediterranean region varied seasonally by about 4‰ in δ^{18}O. We found isotopic composition of atmospheric water vapor to be similar during the rainy and dry seasons in Puerto Rico, but made only four measurements (described below). Future studies would benefit from atmospheric water vapor measurements made seasonally or with different types of rain events.

[34] Rainy season precipitation may encounter a large range of temperatures during transport to the land surface, depending on the altitude from which it fell. The temperature estimated from the average maximum echo top altitude during rainy season events was −59°C. Temperature at the average rainy season echo top altitude was 6°C, and average cloud base altitude from NWS ceiling height measurements at San Juan airport for the rainy season was 1,830 m, which corresponds to a temperature of 13°C. We measured atmospheric water vapor near land surface during both rainy and dry seasons in the study area and obtained average δ^{18}O and δ^{2}H values of −11.1 ± 0.4‰ and −70 ± 2.5‰ (n = 4). This vapor, at the estimated cloud base temperature of 13°C, would be in isotopic equilibrium with liquid having a δ^{18}O value of about −0.6‰ (fractionation factor from *Majoube* [1971], reprinted in work by *Clark and Fritz* [1997]). The observed δ^{18}O of the rainy season samples averaged −3‰, so the rain falling through the bottom of the cloud would have equilibrated toward a more positive δ value (−0.6‰) than the value it may have started with higher in the cloud.

[35] The dry season precipitation was from clouds with average maximum echo tops of 6,248 m and average echo tops of 2,557 m, which is the average altitude of the trade wind inversion. These correspond to temperatures of −8 and 10°C, respectively. Average dry season cloud base was 1600 m, corresponding to a temperature of 15°C. Atmospheric water vapor of the composition noted above would be in equilibrium with a condensate δ^{18}O value of about −0.8‰ at this temperature. Most of the observed dry season monthly rain samples have δ^{18}O values of −1.5‰ or greater. Assuming that many of the dry season orographic rain clouds remain below the inversion layer between 10 and 15°C, these clouds appear to produce rainfall that is close to isotopic equilibrium with the near-surface water vapor composition.

[36] Two sample periods had significantly lower δ^{18}O values compared to the rest of the record (May 2005, October 2005), but did not have the highest echo top altitudes (Figure 4). These months had low pressure systems that accounted for 30% and 50% of the monthly precipitation, respectively, and those low pressure systems are assumed to be responsible for the significant depletions in rainfall ^{18}O and ^{2}H. The low pressure systems were producing rain before arriving at the study site, and lasted several days with large amounts of rainfall. The observations suggest an extended rainout process for the storms, which would have the effect of depleting the heavier isotopes in the water vapor both within the clouds and in the atmosphere below the clouds. Raindrops from the storm system would retain their low δ^{2}H and δ^{18}O values from the upper atmosphere [*Lee and Fung*, 2008] because the effects of equilibrating with water vapor in the layer of air near the ocean and land surface would be minimal. The data from this study do not provide much insight on whether rainout

processes affected isotopic composition for other weather types. Rain event durations during this 2 year study ranged from 0.25 h (the minimum measurement interval for the rain gauge) to 47 h, and there was no significant correlation between median rain event duration and isotopic composition on the monthly time scale, although there was a correlation with rainfall intensity (Table 4). Event-based sampling would provide more detailed information regarding the idea that long-duration rain events change the isotopic composition of water vapor in the near-surface atmosphere, as was hypothesized by *Lee and Fung* [2008].

5.4. New Insights on the Amount Effect

[37] Previous work [*Dansgaard*, 1964; *Rozanski et al.*, 1993, *Gonfiantini et al.*, 2001] noted that there was little correlation between surface temperature and the isotopic composition of rain in the tropics. *Gonfiantini et al.* [2001, p. 157] also noted that "due to the so-called amount effect, the heavy isotope content of tropical precipitation is lower during the rainy season than the dry season." *Jones et al.* [2000] and *Jones and Banner* [2003] interpreted their findings in Barbados, Puerto Rico and Guam as examples of the amount effect described by *Dansgaard* [1964] and subsequent investigators. Closer to the equator at 8 to 10°N in Panama and Costa Rica, *Lachniet et al.* [2007] reported that the amount effect was the dominant control on temporal values of δ^{18}O in rain. More recent work [*Kurita et al.*, 2009; *Tindall et al.*, 2009; *Risi et al.*, 2008] has linked large-scale atmospheric processes to the amount effect observations in the GNIP database.

[38] The amount effect has been attributed to a number of factors: 1) the isotopic value of the condensate in a cloud decreases as cooling and "rainout" proceeds; 2) smaller raindrops equilibrate to a larger degree with the water vapor and temperature conditions below the cloud; and 3) small raindrops evaporate more than larger raindrops on their way to the land surface [*Dansgaard*, 1964]. *Rozanski et al.* [1993] offered additional explanations for the amount effect, including the higher rain intensity and greater extent of rainout in convective clouds [*Yapp*, 1982], and different water vapor isotopic compositions due to different source regions. *Lee and Fung* [2008] used a numerical model to examine the effects of precipitation rate and temperature on the isotopic equilibration of falling raindrops with surrounding vapor. They concluded that larger raindrops do not completely equilibrate with surrounding vapor during transit to the land surface and higher rainfall rates affect the surrounding vapor isotopic composition through evaporation and equilibration processes. Both of these processes explained the amount effect, i.e., intense rainfall having lower δ^2H and δ^{18}O values than light rainfall, and this explanation built upon the findings of *Friedman et al.* [1962] that the degree of equilibration of falling raindrops with water vapor at lower altitudes depends on droplet size and temperature. A recent effort to explain the physical basis of the amount effect in tropical precipitation using a convective precipitation model [*Risi et al.*, 2008] simulated the decrease in isotopic composition with increasing rainfall rate, but did not match measured isotopic values. This analysis did not specifically incorporate the variations in atmospheric temperature and other parameters that are associated with differences in cloud height in the tropics.

[39] The present study illustrates that the altitude range in which precipitation forms, as estimated by echo top measurements, explains some of the seasonal variation in stable isotopic composition of rain in Puerto Rico (Figure 4). The similar correlation coefficients between echo top altitude and isotopic composition and between sample volume and isotopic composition (Table 4) show that the influence of echo top altitude is as important as that of rainfall amount. When the sample periods with extreme isotopic composition in this study were removed from the correlation analysis, the correlation between amount and isotopic composition became less significant, while the correlation between echo top altitude and isotopic composition increased. The results presented in this study imply that the amount effect observed in tropical rainfall is a result of seasonal shifts in weather patterns, where rainfall amount is just one characteristic of different weather systems that also have different water vapor isotopic composition and temperatures in the rain-generating levels of the clouds. Cloud height has not previously been investigated as a factor controlling the isotopic composition of rainfall, and the amount effect has been considered to be separate from temperature effects. The interpretation presented here does not necessarily contradict the other mechanisms thought to contribute to the amount effect, because larger raindrops and higher precipitation rates may also correlate with the higher clouds in deep convective and low-pressure systems. Atmospheric water vapor isotopic composition is assumed to vary with altitude, and probably varies to some extent with air masses associated with the different climate patterns as well. However, the seasonal variation in echo top altitudes and their corresponding temperatures are quantifiable parameters that should be considered in future investigations, especially in predictive models of the isotopic composition of tropical rainfall.

6. Conclusions

[40] Combining climate analysis and echo top altitude measurements with stable isotope analysis of monthly rain samples revealed important insights into the factors controlling the isotopic composition of precipitation in the Luquillo Mountains of eastern Puerto Rico. There is a long-standing assumption that temporal patterns in the stable isotope composition of tropical rainfall are explained by the amount effect rather than temperature effects. In contrast, this study suggests that the isotopic composition of rain in eastern Puerto Rico is influenced by atmospheric temperatures (and other factors) that correspond to the different cloud heights associated with the seasonal climate patterns. Relating isotopic composition to echo top altitudes, especially for individual precipitation events, is a promising approach for prediction of rain isotopic composition in other locations in the tropics. The results from Puerto Rico can be extrapolated to the broader Caribbean and Central America region, and possibly to other areas where the trade wind inversion is present. As latitude decreases, the ITCZ, rather than easterly waves, becomes prevalent in controlling the timing of the rainy and dry seasons. If seasonal echo top altitude variations are similar, these results may also apply to tropical areas under the influence of the ITCZ.

[41] Seasonal climate patterns over the Luquillo Mountains and the Caribbean region are reflected in the isotopic signatures of precipitation. This study provides a baseline of precipitation isotopic composition related to climate patterns, and long-term isotopic records for precipitation may be a valuable tool for monitoring future changes in climate patterns in the Caribbean. The seasonal cycle of isotopic composition in rainy and dry season precipitation can also be used in hydrologic studies and in studies that utilize isotope methods to assess paleoclimate.

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