Temporal Variation in Stable Isotopic Composition of Rainfall and Groundwater in a Tropical Dry Forest in the Northeastern Caribbean

Y. Govender*

Center for Applied Tropical Ecology and Conservation, University of Puerto Rico, San Juan, Puerto Rico

E. Cuevas

Center for Applied Tropical Ecology and Conservation, and Department of Biology, University of Puerto Rico, San Juan, Puerto Rico

L. D. S. Sternberg

Department of Biology, University of Miami, Coral Gables, Florida

M. R. Jury

Department of Physics, University of Puerto Rico at Mayagüez, Mayagüez, Puerto Rico

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ABSTRACT: Karst topography links rainfall to groundwater recharge; therefore, possible changes in the hydrology can play an important role in ecosystem function especially in tropical dry forests where water is the most limiting resource. This study investigates the temporal variation in isotopic

* Corresponding author address: Y. Govender, Center for Applied Tropical Ecology and Conservation, University of Puerto Rico, P.O. Box 70377, San Juan, PR 00936-8377.
E-mail address: yoganig@gmail.com

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composition (δ^{18}O and δD values) of rainwater and groundwater in the Guánica Dry Forest of southwestern Puerto Rico. The study not only establishes a dataset of oxygen and hydrogen isotopic composition of rainwater to assist in local ecohydrological studies but also establishes the origin of rainfall in the semiarid region of the island. The geographical position of Puerto Rico in the northeastern Caribbean causes the study site to receive marine air masses from the North Atlantic Ocean and Caribbean Sea. This research documents the monthly to annual variability in stable isotopic composition of rainwater and estimates the source of groundwater recharge in the Guánica Dry Forest.

To calculate the local meteoric water line (LMWL), the authors analyzed the isotopic signatures of rainwater, collected at near-monthly intervals from January 2008 to December 2011. The LMWL ($\delta D = 7.79\delta^{18}O + 10.85$) is close to the global meteoric water line ($\delta D = 8.17\delta^{18}O + 11.27$). Isotopic signatures of rainwater for the Guánica Dry Forest are consistent with southeastern Caribbean, where rainfall is of marine origin with an annual cycle contributed by sea surface temperature (SST) and significant intermonthly fluctuations due to rainfall and winds during tropical weather events. The *d*-excess values in the period of data collection (2008–11) respond to the rainfall–evaporation balance, with little seasonal cycle and strong pulsing events. Comparison of rain and groundwater isotopic compositions in the United Nations Educational, Scientific and Cultural Organization (UNESCO) Man and the Biosphere Programme (MAB) Guánica Dry Forest indicates that groundwater recharge is confined to rainfall events of more than 90 mm. Imbalances between rainfall and drought place cumulative stresses on ecosystems where plants and animals synchronize their growth phenology and reproduction to climatic patterns, especially in areas with variable annual cycles. Therefore, it is useful in ecohydrological studies to determine the origins and temporal dynamics of rainfall and groundwater recharge in the Caribbean, where predictions of climate models indicate drying trends.

KEYWORDS: Rainwater isotopic analysis; Groundwater dynamics; Puerto Rico; Guánica Dry Forest

1. Introduction

Stable isotopes of water, hydrogen (δD), and oxygen (δ^{18}O) have been widely used to trace the continual recycling of water through different parts of the hydrological system. These isotopes only change through mixing and well-known fractionation processes that occur during evaporation and condensation (Craig 1961). There are cases, however, of oxygen isotope exchange between water and silicates in underground aquifers given a sufficiently high temperature and/or time. In spite of this, it is generally accepted that, once water enters the subsurface and is away from evaporative effects, δ^{18}O and δD are conservative in their mixing relationships (Craig 1961). By analyzing the natural variations of the oxygen and hydrogen isotope ratios in rainfall (δ^{18}O and δD, respectively), researchers have been able to trace the origins of rainfall and groundwater recharge (Rodriguez-Martínez 1997; Alyamani 2001; Bowen and Wilkinson 2002; Jones and Banner 2003; Rosen and Warren 2006; Price et al. 2008).

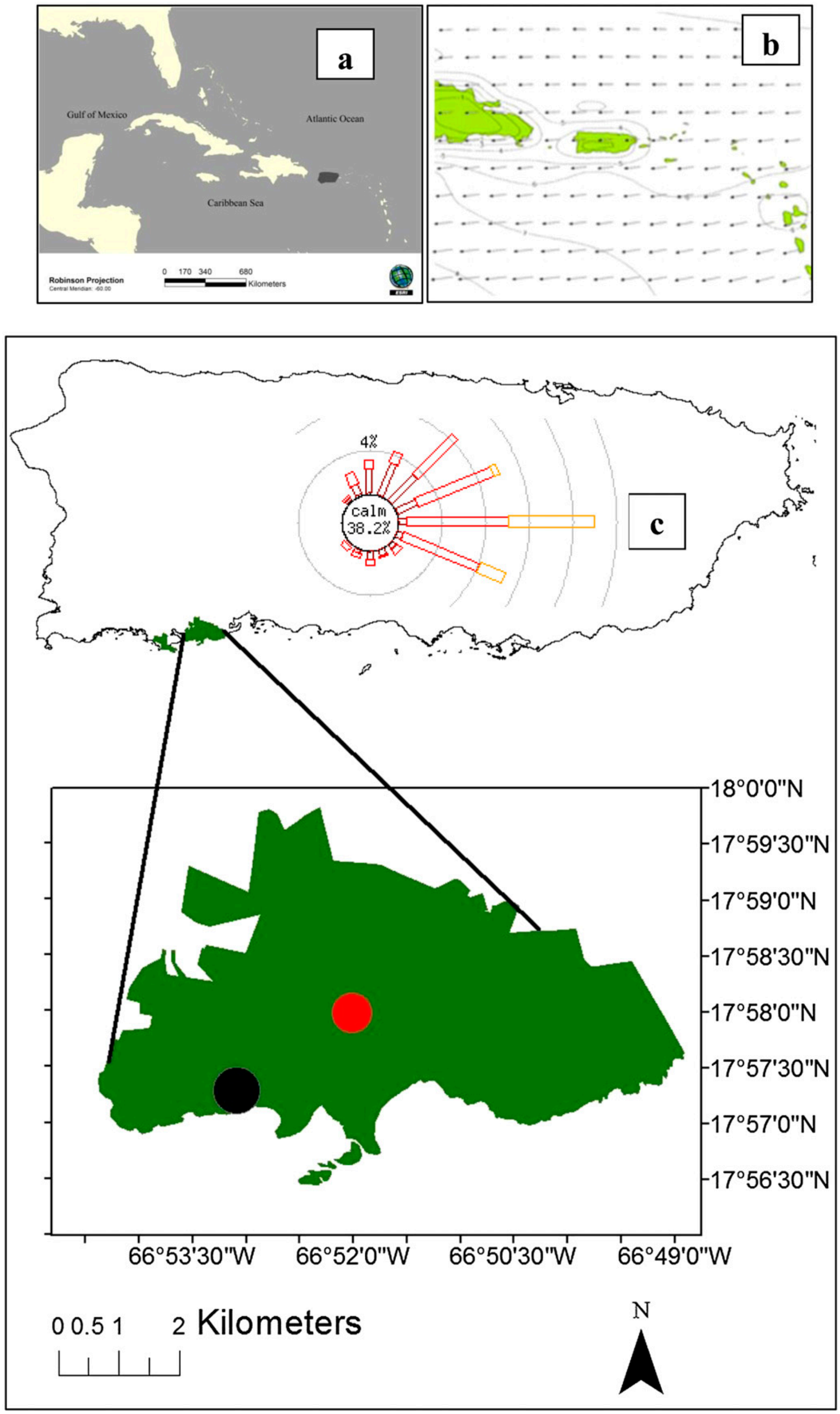
In general, δ^{18}O and δD values in rainwater fluctuate with latitude and altitude (Bowen and Wilkinson 2002), with seasons (Price et al. 2008), and by weather conditions and events such as seasonal monsoons (Alyamani 2001) and tropical storms (Gedzelman et al. 2003; Pang et al. 2004; Price et al. 2008). Dansgaard (Dansgaard 1964) found that heavy rainfall during tropical storms produces lower isotopic signatures for $\delta^{18}O$ and δD because these isotopes are progressively stripped from the water vapor toward the center of the storm. The water vapor eventually rises and condenses into rainfall with lower $\delta^{18}O$ and δD than before. Stable isotopic techniques using $\delta^{18}O$ and δD values of water are a reliable tool to trace the origins of rainfall and groundwater and can be used to detect weather events (Gedzelman et al. 2004), especially in the Caribbean, where infrequent heavy rainfall occurs in a generally dry environment (Malmgren et al. 1998; Giannini et al. 2000; Taylor et al. 2002; Jury et al. 2008).

Imbalances between rainfall and drought place cumulative stresses on ecosystems where plants and animals synchronize their reproduction and growth phenology to climatic patterns, especially in areas with a large variation in the annual cycle (Lieberman 1982; Cuevas 1995; Murphy and Lugo 1995; Drugger et al. 2004). Therefore, it is useful to determine the origins and temporal dynamics of rainfall and groundwater recharge in the Caribbean, where predictions of climate models indicate drying trends (Neelin et al. 2006; Jury and Winter 2009; Taylor et al. 2012).

Rainfall fluctuates in the Caribbean because of atmosphere–ocean interactions such as the North Atlantic Oscillation, Atlantic multidecadal oscillation (AMO), El Niño–Southern Oscillation, and shifts of the intertropical convergence zone (Hastenrath 1984; Enfield and Alfaro 1999; Giannini et al. 2000; Taylor et al. 2002; Jury et al. 2008). There is a bimodal rainfall distribution with a small peak in April–May and a broader peak in August–October separated by a midsummer dry spell in June–July (Angeles et al. 2010).

Isotopic dynamics of rainfall processes leading to groundwater recharge has been extensively studied in northern Puerto Rico, an island in the northeastern Caribbean (see Figure 1; Gomez-Gomez et al. 1991; Rodriguez-Martínez 1997; Jones and Banner 2003; Lugo et al. 2004; Heartsill-Scalley et al. 2007; Scholl et al. 2007; Scholl et al. 2009; Scholl et al. 2010). Less is known of the isotopic dynamics of rainfall in the context of ecosystem–hydrology interactions in the semiarid leeward side of Puerto Rico (Figure 2) (Medina and Cuevas 1990; Blanco et al. 2007). In southwestern Puerto Rico, the average rainfall is 796 mm yr^{-1}, with the lowest amount of rain in January and February and the highest rainfall in September and October (http://www.sercc.com/cgi-bin/sercc/cliMAIN.pl?pr3532; Figure 2). Our study site, the United Nations Educational, Scientific and Cultural Organization (UNESCO) Man and the Biosphere Programme (MAB) Guánica Dry Forest Biosphere Reserve (17.95°N, 66.85°W) in southwestern Puerto Rico, is selected because it represents a unique ecological niche (Figure 1) and is representative of hydrological dynamics of the Caribbean dry forests (Jones and Banner 2003). The Guánica Dry Forest is located between the Río Loco and Río Yauco watersheds. Preliminary isotopic studies of lateral water flow between the two areas show no connectivity between the drainage area of the aquifer of the Guánica Dry Forest and the alluvial valley surrounding it, explained by the combination of geology and topography of the region (Cruz-Quiñones 2013).

The objectives of our study are to 1) report on the early phase of a long-term data collection of rainwater oxygen and hydrogen isotopic composition in southwestern Puerto Rico, 2) document the annual cycle and variability of rainwater isotopic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composition and determine to what extent marine air masses from the North Atlantic Ocean and Caribbean Sea affect this composition, and 3) determine which rainfall events are responsible for the recharge of groundwater within the Guánica Dry Forest.

2. Methods

2.1. Sampling

We collected rainwater samples from January 2008 to December 2011 in the upper reaches of the forest and in the coastal plateau of the Guánica Dry Forest. Rainfall was collected in 1-L glass bottles that accumulated between sampling visits. The bottle was fitted with a rubber stopper that had a 6.5-cm-diameter collecting funnel and an air release port. We added 50 mL of clear mineral oil to the bottle prior to use to prevent evaporation and potential isotopic enrichment between samplings (Wilcox et al. 2004). For each sampling period, rainwater samples were extracted from the bottle with a syringe; stored in serum vacutainers, where the vacuum was established immediately by extracting with a syringe until bubbles formed; sealed with Parafilm; and placed in refrigerated containers in the field to prevent evaporation. After collection, rainfall collectors were replaced with clean 1-L bottles with mineral oil for the next sampling period. A subsample of the rainwater samples was tested for salinity using a Brix refractometer at the time of collection. Vacutainers were stored in a refrigerator (4°C) in the laboratory until analysis at the Laboratory of Stable Isotope Ecology in Tropical Ecosystems (University of Miami). A total of 49 rainwater samples were analyzed in triplicate for $\delta^{18}O$ and δD by mass spectrometry using methods described by Vendramini and Sternberg (Vendramini and Sternberg 2007). Groundwater was collected for the sampling period 2008–09 from the only existing well located at the study area (Figure 1, black dot). In November 2009, five additional nested wells were drilled in the study areas (Figure 1, red dot). The newly drilled wells were also sampled monthly. The isotopic signature of the additional wells was determined and included in the groundwater analysis. The monthly average of isotopic signature for groundwater of the six wells was then calculated and used in the analysis for this study. The $\delta^{18}O$ and δD values are reported using conventional notation relative to Vienna Standard Mean Ocean Water (VSMOW). Isotopes ratios are quantified

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Figure 1. (a) Location of Puerto Rico (shaded in black) within the Caribbean. (b) Puerto Rico and surrounding islands with mean winds in the study period (speed contours m s^{-1}). (c) Map showing study site in southwestern Puerto Rico within the UNESCO MAB Guánica Dry Forest Biosphere Reserve (area in dark green) and location of groundwater wells (red and black dots), where the wind rose with gray dot in (c) highlights trade winds (2–4 m s^{-1} in red; 4–6 m s^{-1} in yellow; longest = 18%) (source data: http://www.raws.dri.edu/cgi-bin/rawMAIN.pl?ncPGNC).

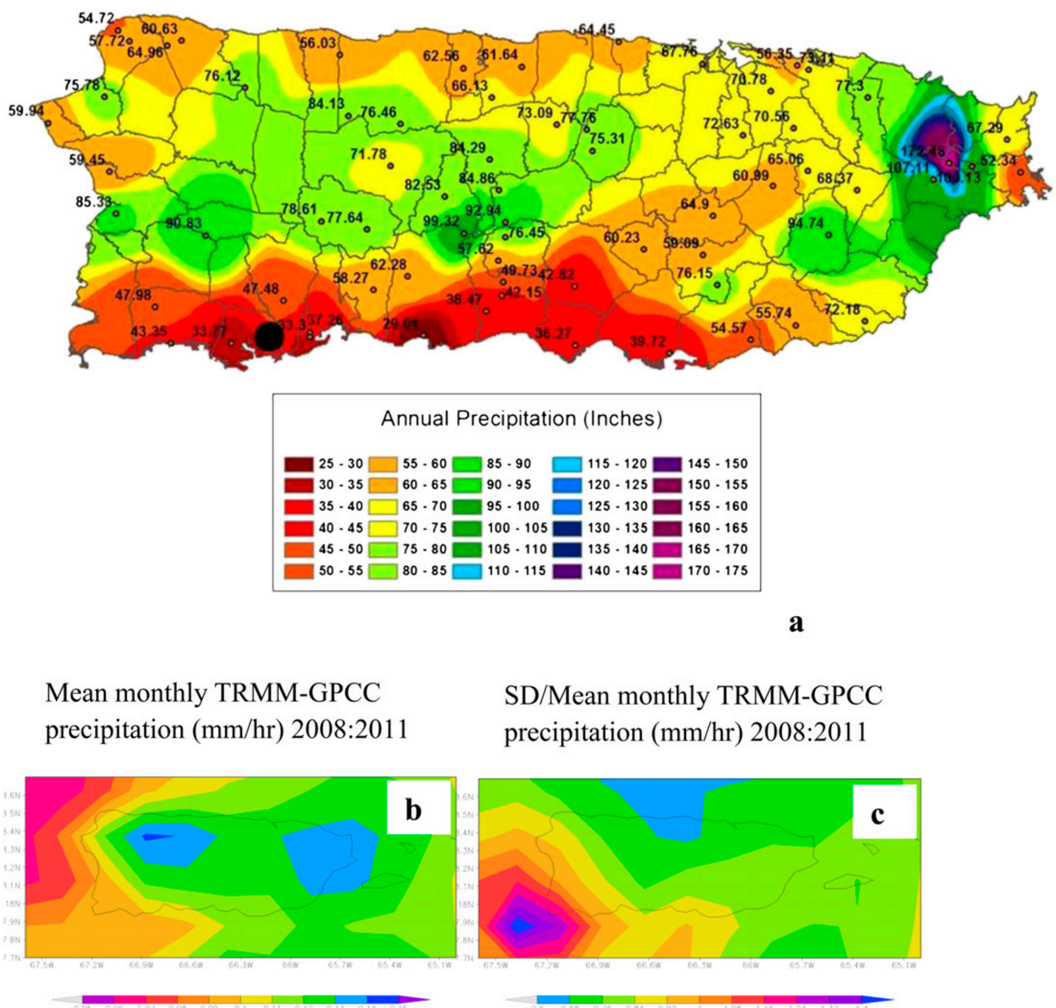

Figure 2. (a) Mean annual rainfall in Puerto Rico for 1981–2010 from National Weather Service gauges. The black dot is the study site. (b) Mean satellite-gauge merged rainfall (mm h^{-1}) in the study period and (c) its SD/mean.

as $\delta = [(R \text{ sample} - R \text{ standard})/R \text{ standard}]/1000‰$, where R is defined as D/H for δD and $^{18}O/^{16}O$ for $\delta^{18}O$ values.

2.2. Data collection

Rainfall and weather data for the Guánica Dry Forest were drawn from the National Weather Service at the Boca Station, Guánica, which has a standard rain gauge (http://www.wrcc.dri.edu/cgi-bin/rawMAIN.pl?txPGNC).

The number of days with no rainfall, the number of days with rainfall, and the total for the sampling interval were noted. Pearson's correlations were analyzed between rain categories and the isotopic signature of rainwater ($\delta^{18}O$ and δD). The rainwater *d* excess is calculated from $\delta D - (8 \times \delta^{18}O)$ in each sampling period (after Dansgaard 1964). Statistical analysis of relationship between isotopic signatures of rainfall and groundwater was done in JMP, version 7 (SAS Institute Inc., Cary, North Carolina), and Analytical Software Statistix, version 9 (Analytical Software 2009).

To determine the relationship between the isotopic signature of rainwater and groundwater and local climatic factors, we collected monthly data on sea surface temperature (SST) in a 50-km area south of Guánica (http://www.class.ncdc.noaa.gov/), rainfall minus evaporation ($P - E$) (Dee et al. 2011), and surface winds in a 30-km box over Guánica from the Coupled Forecast System (CFS; Saha et al. 2010; http://nomad1.ncep.noaa.gov/), Moderate Resolution Imaging Spectroradiometer (MODIS) satellite land surface temperature and vegetation fraction in a 5-km box at Guánica (Huete et al. 2002; http://disc.sci.gsfc.nasa.gov/giovanni/), and weather data from nearby coastal stations (http://www.ndbc.noaa.gov/). Cross correlations were calculated with a sample length of 48 months. Most variables exhibit a decorrelation of 2 months, so the degrees of freedom (df) exceeds 20 and the 90% confidence limit is reached.

To analyze the airflow trajectories for two contrasting scenarios, daily rainfall records were scrutinized. A dry period around 23 December 2008 and a wet period around 8 October 2010 were selected. The Hysplit ensemble back-trajectory model was run via the Air Resources Laboratory website (http://ready.arl.noaa.gov/) for the preceding 5 days to establish the source of air masses arriving at Guánica, Puerto Rico. MODIS SST maps were made for the monthly period around these two cases. To provide further context, the annual cycling and flood peaks were determined for Río Yauco, the closest river to the Guánica study site. The location of the surface flow gauge is 18°02′58″N, 66°50′30″W, in the Yauco municipality, of hydrologic unit 21 010 004, on the right bank, off State Road 375, about 300 ft (91 m) upstream from water extraction diversion Monserrate. Daily streamflow data from gauge 50126150 was obtained for the study period from January 2008 to December 2011 (U.S. Geological Survey 2012) and converted to log scale for analysis. In addition, AMO index data, satellite–gauge rainfall, and National Weather Service (NWS) station rainfall were obtained for comparison online (http://climexp.knmi.nl/).

3. Results and discussion

3.1. Monthly and annual fluctuation of rainfall

Our results indicate that the Guánica Dry Forest experiences large intermonthly rainfall fluctuations typical of thunderstorm environments, consistent with earlier studies (Medina and Cuevas 1990). The average monthly rainfall for the Guánica Dry Forest from January 2008 to December 2011 was 89.1 mm ± 93.1 standard deviation (SD). The lowest monthly amount recorded in the Guánica Dry forest was 1.5 mm in January 2009, while the highest monthly amount (414 mm) was in October 2010 (Table 1). Our mean rainfall was higher than the long-term average (66 mm month^{-1}) because of above-normal SST corresponding with a warm phase of the AMO. The annual cycle followed the expected pattern with highest rainfall from August to November (Table 1).

Dry conditions and low rainfall were observed from January to April and again in July (Table 1), as expected from earlier studies (Giannini et al. 2000; Taylor et al. 2002; Jury et al. 2008). The bimodality is related to higher SST and humidity in the summer

Table 1. Isotopic signature of rainwater, groundwater, and key environmental variables in the Guánica Dry Forest from 2008 to 2011. Rainfall is from the Ensenada Station, land temperature and vegetation index are from the MODIS satellite for a 5-km area of the study site, and wind speed ($m\,s^{-1}$) is from the Coupled Forecast System assimilation in a 30-km area of the study site.

Sampling period	Date sample collected	Rainwater avg $\delta^{18}O$‰	Rainwater avg δD‰	*d* excess	Rain (mm)	Rain bottle collection (mm)	Avg groundwater $\delta^{18}O$‰	Avg groundwater δD‰	SST (°C)	Land temperature (°C)	Vegetation index	Wind speed ($m\,s^{-1}$)
10 Dec 2007–14 Jan 2008	8 Jan	−2.2	−5.7	12.1	34.8		−4.7	−24.6	26.6	27.2	0.208	3.56
15 Jan–21 Feb 2008	8 Feb	−5.4	−29.2	14.2	8.9		−4.8	−25.7	26	28.4	0.198	4.99
22 Feb–27 Mar 2008	8 Mar	−1.3	7.8	18.4	32		−4.9	−26.9	25.9	29.4	0.171	3.99
28 Mar–24 Apr 2008	8 Apr	−0.3	8.3	10.7	46.2		−4.8	−27	26.2	30.3	0.188	4.12
25 Apr–22 May 2008	8 May	−1.4	3	14.2	32		−4.9	−24.7	27.5	30.8	0.182	3.66
23 May–19 Jun 2008	8 Jun	−1.5	4.5	16.5	46.7		−5	−21.8	28.3	29.2	0.188	4.12
20 Jun–29 Jul 2008	8 Jul	−2.5	2.9	22.6	15.8		−5.1	−24.8	27.8	30.6	0.184	3.9
30 Jul–21 Aug 2008	8 Aug	−0.4	6.6	10	93.7		−4.9	−26.4	29	30	0.199	3.07
22 Aug–18 Sep 2008	8 Sep	−6.5	−39.4	12.7	173		−4.8	−24.5	29	27.3	0.277	3.67
19 Sep–23 Oct 2008	8 Oct	−3.9	−16.2	15.1	355.3		−3.6	−16.9	28.8	27.1	0.266	3.23
24 Oct–20 Nov 2008	8 Nov	−7.2	−39	18.8	86.4		−4	−17.8	28.5	26.2	0.262	3.32
21 Nov–9 Dec 2008	8 Dec	−3.1	−7.2	17.9	7.9		−3.8	−27	26.9	27	0.239	4.31
10 Dec 2008–14 Jan 2009	9 Jan				1.5		−4.1	−32.3	26.1	27.4	0.227	3.81
15 Jan–19 Feb 2009	9 Feb	−2	−1.3	14.9	81.3	54.3	−4.2	−32.7	26.1	27.5	0.221	4.18
20 Feb–12 Mar 2009	9 Mar	−1.4	−4.3	6.9	30	10.6	−4.4	−37	25.8	27.7	0.214	3.74
13 Mar–16 Apr 2009	9 Apr	−0.9	−7		17.8	13.6	−4.5	−31	26.4	30	0.19	3.84
17 Apr–7 May 2009	9 May	−1.1	−3	5.8	74.9	22.2	−4.4	−33.3	27	28.2	0.211	4.37
8 May–10 Jun 2009	9 Jun	−1.5	−4.3	7.4	71.4	41.7	−4.4	−25.5	28.1	28.3	0.209	4.19
11 Jun–11 Jul 2009	9 Jul	−1.3	1.5	12.2	33.5	30.8	−4.5	−29.6	28.6	29	0.205	4.91
11 Jul–6 Aug 2009	9 Aug	−2.3	−8.7	9.4	91.7	53.1	−4.4	−28.4	28.3	29.2	0.212	4.05
7 Aug–24 Sep 2009	9 Sep*	−4.9	−28.4	11	229.9	116.3	−4.2	−22	29.1	28.9	0.234	3.6
25 Sep–8 Oct 2009	9 Oct	−2.4	−2.4	17	34	6.3	−4.4	−25.7	29.2	29.1	0.239	3.53
9 Oct–5 Nov 2009	9 Nov	−1.9	−6.3	9.2	58.9	101.3	−3.7	−19.9	28.7	27.9	0.232	2.87
6 Nov–10 Dec 2009	9 Dec	−2.2	0.3	18.1	46.5	20.2			28	27.8	0.226	3.7

Table 1. (*Continued*)

Sampling period	Date sample collected	Rainwater avg δ^{18}O‰	Rainwater avg δD‰	*d* excess	Rain (mm)	Rain bottle collection (mm)	Avg groundwater δ^{18}O‰	Avg groundwater δD‰	SST (°C)	Land temperature (°C)	Vegetation index	Wind speed (m s^{-1})
11 Dec 2009–11 Jan 2010	10 Jan	−0.5	3.7	7.9	22.4	15.2	−4.4	−26	27.1	26.4	0.193	3.51
12 Jan–4 Feb 2010	10 Feb	−0.4	10.3	13.3	23.6	24.8	−4.3	−25.7	27	29.1	0.182	2.74
5 Feb–4 Mar 2010	10 Mar	−0.8	−0.6	5.8	9.4	12.4	−4.3	−23.3	27.8	30.1	0.179	3.23
5 Mar–8 Apr 2010	10 Apr	−0.2	7.4	8.7	55.6	31.8	−4.2	−42.2	27.8	28.8	0.178	3.02
8 Apr–6 May 2010	10 May	−0.9	0.4	7.4	21.1	12.9	−4.3	−25.2	28.7	29.5	0.195	3.18
7 May–5 Jun 2010	10 Jun	−4.4	−29.7	5.5	152.4	143	−3.8	−21.3	28.9	28.1	0.242	4.12
6 Jun–8 Jul 2010	10 Jul	−3	−14.7	9.3	172.7	183.7	−3.4	−22	29	26.4	0.254	4.62
9 Jul–11 Aug 2010	10 Aug	−4.7	−26.4	11.2	232.7	91	−3.8	−22.7	29.7	28	0.254	2.49
12 Aug–9 Sep 2010	10 Sep	−2.5	−11.1	8.9	149.9	118.8	−3.7	−20.6	30	28	0.257	2.77
10 Sep–14 Oct 2010	10 Oct	−5.1	−27.6	12.9	414	209.5	−4	−22.9	29.3	26.2	0.253	2.2
15 Oct–11 Nov 2010	10 Nov	−3	−10.8	13.5	135.1	175.5	−3.3	−18.8	27.9	24.8	0.257	3.6
12 Nov–9 Dec 2010	10 Dec				2.3	2.5	−3.8	−22.6	27.4	24.5	0.251	2.97
10 Dec 2010–13 Jan 2011	11 Jan	−1.2	3.3	12.9	12.7	13.6	−3.7	−20.1	26.2	26.8	0.206	2.68
14 Jan–17 Feb 2011	11 Feb				7.1	0	−4	−23.1	26.2	27.7	0.197	2.61
18 Feb–11 Mar 2011	11 Mar	−0.5	10.5	14.1	80	24.9	−3	−15.2	26.2	28	0.192	1.94
12 Mar–7 Apr 2011	11 Apr	−0.3	16.3	19	23.4	42.1	−2.2	−3.9	27	29.7	0.182	1.93
8 Apr–12 May 2011	11 May	−0.7	4.9	10.8	33	27.2	−3	−18.4	27.5	27.3	0.201	1.65
13 May–9 Jun 2011	11 Jun	−4.3	−25.3	9.3	297.7	210.6	−4.8	−30.4	28.7	27.4	0.261	2.71
10 Jun–14 Jul 2011	11 Jul	−3.6	−22.5	5.9	67.8	200	−3.2	−21.1	28.6	27.7	0.257	3.21
15 Jul–11 Aug 2011	11 Aug	−5.3	−42.3		186.7	226.5	−4.2	−25.9	28.8	27.6	0.255	2.83
12 Aug–8 Sep 2011	11 Sep	−4.3	−22.5	11.9	86.1	224.2	−4.3	−25.4	29.2	27.7	0.265	1.65
10 Sep–6 Oct 2011	11 Oct	−3.1	−17	7.5	164.6	154.2	−3.3	−19.3	29.2	26.8	0.248	2.46
7 Oct–3 Nov 2011	11 Nov	−2.7	−13	8.3	77.2	34.2	−3.2	−15.7	28.4	26.8	0.236	1.89
4 Nov–8 Dec 2011	11 Dec	−3.7	−17.3	12.5	233.2	200.9	−3.1	−15.3	27.9	26.4	0.242	2.5

* Includes two sampling periods

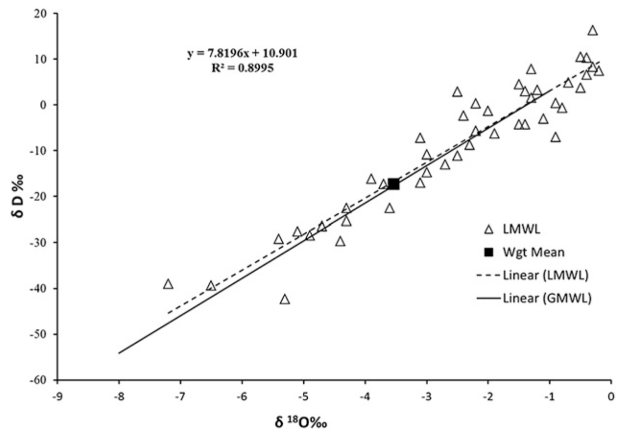

Figure 3. Scatterplot of δ^{18}O and δD for rainwater collected at the Guánica Dry Forest and the LMWL (dotted line) and GMWL (solid line) regressions (after Rozanski et al. 1993). Open triangles are monthly values; the solid square is the amount-weighted mean.

half of the year that is interrupted by a strengthening of the North Atlantic anticyclone and trade winds in June–July. Additionally, there are upper westerly winds and atmospheric aerosols from the Sahara that inhibit thunderstorm aggregation (Angeles et al. 2010). Blanco et al. (Blanco et al. 2007) suggest that rainfall departures in southwestern Puerto Rico are more influenced by coupling between the North Atlantic and eastern Pacific climates, due to reduced orographic effects.

3.2. Comparison of local rainwater isotopic signature with GMWL and vegetation index

We derived the LMWL by linear regression yielding the equation $\delta\text{D} = 7.79\,\delta^{18}\text{O} + 10.85$, $R^2 = 0.90$. The δ^{18}O and δD isotopic signatures of rainwater in the Guánica Dry Forest plot slightly to the left of the global meteoric water line (GMWL; $\delta\text{D} = 8.17\delta^{18}\text{O} + 11.27$; Figure 3). This is typical of low-latitude sites (Craig 1961), indicating that rainfall formation occurs under isotopic equilibrium conditions with similar rates of condensation and vaporization (Figure 3). There were no changes in this trend of the LMWL during the four years of the study using Bartlett's test: $X = 4.86$, df = 3, and $p = 0.18$. The mean values of δ^{18}O and δD in the Guánica Dry Forest were $-2.5‰ \pm 1.8$ SD and $-8.7‰ \pm 14.8$ SD, respectively.

The local MODIS vegetation index and rainwater isotope δD have a negative relationship (Figure 4) with $R^2 = 0.64$, meaning that vegetation productivity increases in association with isotopically depleted rainwater that occurs during the wet season in the Guánica Dry Forest. The vegetation index in the Guánica Dry Forest remains below 0.3 and correlates with a number of additional environmental variables: SST $r = +0.69$, land surface temperature $= -0.67$, $P - E = +0.50$, and rainfall SD $= +0.52$ (Table 2). Evapotranspiration is known to infuse diurnal thunderstorms that migrate across western Puerto Rico (Jury et al. 2009), but they

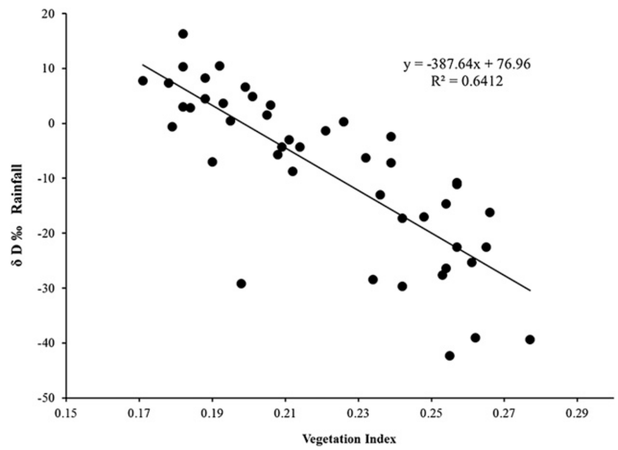

Figure 4. Relationship of rainwater δD and MODIS vegetation index at Guánica Dry Forest for 2008–11.

seldom affect Guánica. We infer that the vegetation index responds to soil water balance and has a rainfall amount as a common denominator with isotope signature.

3.3. Characteristics of rainwater isotope signatures

Our geographical position ensures that the study site receives marine air masses from the North Atlantic Ocean and Caribbean Sea. Yet the marked variability of isotopic signatures for rainwater in the Guánica Dry Forest suggests that the condition under which precipitation is formed and travels during the year was dynamic. It is known from global data that the isotopic composition of rainwater declines with the passage of seasonal weather systems (Price et al. 2008; Alyamani 2001; Scholl et al. 2007; Pang et al. 2004), especially tropical storms where $\delta^{18}O$ values can fall below −6‰ (Gedzelman et al. 2003). Here we found depleted isotopic signatures in the wet season and negative shifts following tropical storms to a $\delta^{18}O$ minimum of −7.23‰ (Table 1), consistent with results from northeastern Puerto Rico (Scholl et al. 2009) and southern Florida (Price et al. 2008). In 2008, Hurricanes Fay, Gustav, Hanna, and Ike affected Puerto Rico (Stewart and Beven 2009) and there were many depleted isotopic signatures. In 2009, fewer hurricanes affected Puerto Rico and depleted signatures were confined to August–September because of three tropical storms. Both 2010 and 2011 experienced active hurricane seasons with negative shifts following at least five tropical storms. Regional factors affecting hurricane frequency include SST and vertical wind shear (Altaii and Farrugia 2003; Gray 1968; Goldenberg et al. 2001).

We found significant differences in isotopic signatures of rainwater between months for $\delta^{18}O$ and δD (Kruskal–Wallis: $X = 4.42$ and $p = 0.0004$; $X = 2.75$ and $p = 0.012$, respectively) and seasons (Wilcox test: $Z = 2.800$ and $p = 0.005$; $Z = 2.94$ and $p = 0.003$, respectively) but little difference between years. Cross correlations between environmental variables and isotopic signatures are given in Table 2. Environmental relationships with rainwater isotopes $\delta^{18}O$ and δD include

Table 2. Cross correlation between key environmental variables and isotopic signatures. Bold values are significant above 90% confidence and indicate significant cross correlation. Note that SST, $P - E$, and rain SD are area averages.

Variables	Rainwater avg $\delta^{18}O$‰	Rainwater avg δD‰	*d* excess	Rain (mm)	Avg groundwater $\delta^{18}O$‰	Avg groundwater δD‰	SST (°C)	SFC temperature (°C)	Vegetation index	$P - E$
Rainwater avg $\delta^{18}O$‰										
Rainwater avg δD‰	**0.95**									
d excess	−0.14	0.16								
Rain (mm)	**−0.59**	**−0.61**	−0.12							
Avg groundwater $\delta^{18}O$‰	−0.02	−0.02	−0.08	0.17						
Avg groundwater δD‰	−0.17	−0.07	0.26	0.19	0.67					
SST (°C)	−0.5	−0.52	−0.18	0.58	0.22	0.25				
SFC temperature (°C)	**0.47**	**0.47**	0.11	−0.33	**−0.47**	−0.21	−0.24			
Vegetation index	**−0.79**	**−0.8**	−0.11	0.64	0.29	0.2	0.69	**−0.67**		
$P - E$	−0.31	−0.42	−0.44	0.47	0.19	0.23	0.73	−0.07	**0.5**	
Precipitation SD	−0.3	−0.36	−0.27	0.55	0.31	0.27	0.69	−0.3	**0.52**	**0.75**
Wind speed ($m\,s^{-1}$)	0	0.02	0.07	−0.24	**−0.54**	**−0.48**	−0.21	0.22	−0.17	−0.34

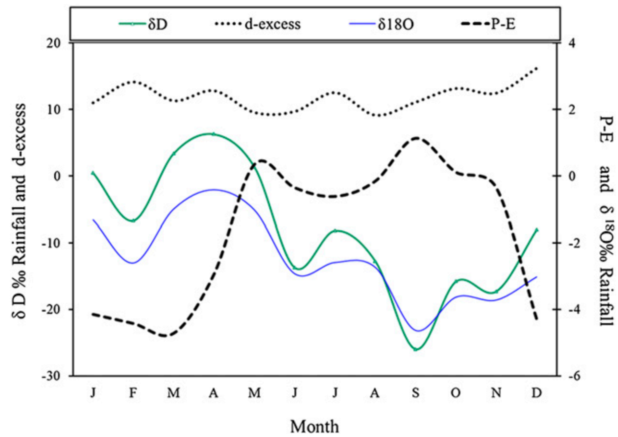

Figure 5. Mean annual cycle (2008–11) of rainwater isotopes, *d* excess, and $P - E$ in the study period.

rainfall amount (as expected from Dansgaard 1964) $r = -0.60$, SST (-0.50) that varies in its annual cycle from 26° to 29°C (Table 1), and MODIS land surface temperatures ($+0.47$). For δD additional links are found with the difference between $P - E$ and the SD of rainfall. Other weather variables were unrelated with the isotopic signatures of rainwater, possibly because of the steadiness of trade winds (mean 91° ± 15 SD). We also found an inverse relationship between the vegetation fraction index and the oxygen and hydrogen isotope ratio of rainfall. The vegetation index here is more likely the dependent variable, as increased rainfall associated with a more depleted isotopic composition would also cause an increase in the vegetation index confirming the results of Murphy and Lugo (Murphy and Lugo 1995) where leaf area index increased during wet periods and decreased during dry periods in the forest.

Risi et al. (Risi et al. 2008) explain the "amount effect" in two ways: 1) re-evaporation of the falling rain and the diffusive exchanges with the surrounding vapor and 2) recycling of subcloud vapor feeding the storm system. Besides the amount effect, Scholl et al. (Scholl et al. 2009) found that in northeastern Puerto Rico the altitude of rainfall formation, based on cloud-top temperature, explained seasonal changes in isotopic signatures.

The *d*-excess value characterizes the source of water vapor and secondary processes affecting atmospheric moisture such as SST and wind. We found that *d* excess exhibited a flat annual cycle typical of marine conditions. The *d* excess of the dry season is generally above that in the wet season: December and February > 14‰ versus May and August < 10‰, when water vapor is sourced from the subtropical North Atlantic. The *d* excess of the Guánica Dry Forest varies by year [analysis of variance (ANOVA): $F = 4.915$ and $p = 0.006$], with 2010 having lower values and 2008 higher (Figure 5 and Table 1). A significant relationship between *d* excess and $P - E$ was found, $r = -0.44$ (Table 2).

While *d* excess exhibits a minimal range, the mean annual cycle of rainwater isotope signatures for δ^{18}O and δD (Figure 5) reach a plateau at the end of the dry season when lower SST inhibits condensation. From May to September the isotope signatures decline, as SST increases and the rate of condensation exceeds

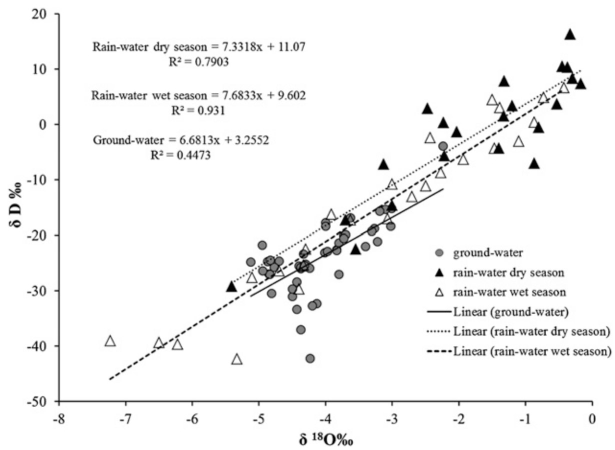

Figure 6. The δ^{18}O vs δD relationship for rainwater in dry months (solid triangles), rainwater in wet months (open triangles), and groundwater collected at Guánica Dry Forest (gray circles) and their regression lines.

evaporation. From October to December there is a gradual recovery. The mean annual cycle of $P - E$ is a mirror image of the isotope signatures except for a delay in May. In the following section we investigate groundwater isotopic signatures for the Guánica Dry Forest.

3.4. Comparison of isotopic signature of rainwater and groundwater

The δ^{18}O and δD regression for rainwater in dry months lies above wet months, which in turn lies above groundwater (Figure 6). We derived the LMWL as $\delta D‰ = 7.0 \times \delta^{18}O + 10.3$ for rainwater in dry months, $\delta D‰ = 7.37 \times \delta^{18}O + 8.0$ for rainwater in wet months, and $6.65 \times \delta^{18}O + 3.06$ for groundwater. The rainwater isotopic relationship is stronger in the wet season than in the dry season ($R^2 = 0.90$ versus 0.73). The groundwater isotopic signature in the Guánica Dry Forest had a mean $\delta^{18}O = -4.09‰ \pm 0.63$ SD and mean $\delta D = -24.10‰ \pm 6.26$ SD. There were significant differences in the groundwater signature between years (ANOVA δ^{18}O: $F = 10.86$ and $p > 0.001$; δD: $F = 6.16$ and $p = 0.004$ with 3 df), with the isotopic signature in 2011 being most depleted (Table 1) by the passage of Tropical Storms Emily, Irene, and Maria.

We found no difference in slope between LMWL for dry and wet seasons for rainwater [Bartlett test: $F = 0.95$, df = 1 (42), and $p = 0.34$] and groundwater [Bartlett test: $F = 1.74$, df = 21 (23), and $p = 0.21$]. Further isotopic ratios of groundwater had a slightly lower slope than that of LMWL, indicating little evaporation before rainwater percolates to groundwater for most of the year. Mean surface evaporation rates at Guánica Dry Forest, from CFS estimates during the study period, range from 92 mm month^{-1} in the wet season (May, August, and September) to 118 mm month^{-1} in the dry season (December and February) with SD ~12 mm month^{-1}. Such high values with narrow annual range and small SD are typical of subtropical marine trade wind zones, compounded by Guánica being south facing and exposed to the prevailing winds.

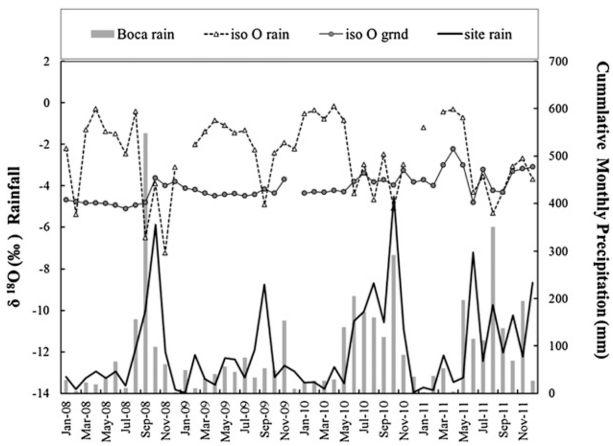

Figure 7. Temporal fluctuations of δ^{18}O isotopic signatures of rainwater and groundwater and cumulative monthly rainfall collected from the study site in glass bottles and amount of rainfall recorded at the nearest National Weather Service station in Boca, Guánica.

Like other studies, we found that recharge of the aquifer depends on rainfall amount (Rodriguez-Martínez 1997; Jones and Banner 2003). Here the groundwater isotopic signature was similar to that observed in months where rainfall exceeded ~90 mm month^{-1} (Figure 7). In the dry season there is no recharge and the isotopic signature groundwater does not match that of the scarce rainfall during these months. The close offset between the wet season rainwater and groundwater LMWL (Figure 6) indicates fast recharge rates during the wet season that are compounded by the limestone geology of Guánica Dry Forest, which has little water retention capacity (Murphy and Lugo 1995). Cross correlations of groundwater δ^{18}O were significant with CFS wind speed ($r = -0.54$, $p < 0.05$) and MODIS land surface temperature ($r = -0.47$, $p < 0.05$) (Table 2). These factors may directly affect the isotopic composition of rainfall prior to infiltration into the groundwater system.

An analysis of airflow trajectories arriving at Guánica Dry Forest is made for contrasting dry and wet periods. Daily rainfall records indicate a period of little rain before 23 December 2008 as opposed to heavy rains before 8 October 2010. Ensemble 5-day back trajectories in the dry period were consistently from the east-northeast, denoting a source region over the subtropical North Atlantic (Figure 8a). In contrast, our back-trajectory analysis in the wet period shows airflow arriving from the southwestern Caribbean and the northern edge of South America. SSTs (Figure 8b) were ~3°C lower in the 2008 dry spell than in the 2010 wet spell, while rainwater δ^{18}O values increased 4.1‰ in the former and decreased 2.6‰ in the latter (Table 1).

In addition to pairwise analysis of environmental influences on isotopic signatures, a multivariate analysis was performed by backward stepwise regression. First, all variables were included, then the less influential variables were removed according to their p value, and finally the model coefficients were compared with the respective pairwise values to remove colinear variables. Rainwater δ^{18}O is fitted by the vegetation index and V wind component, both with negative

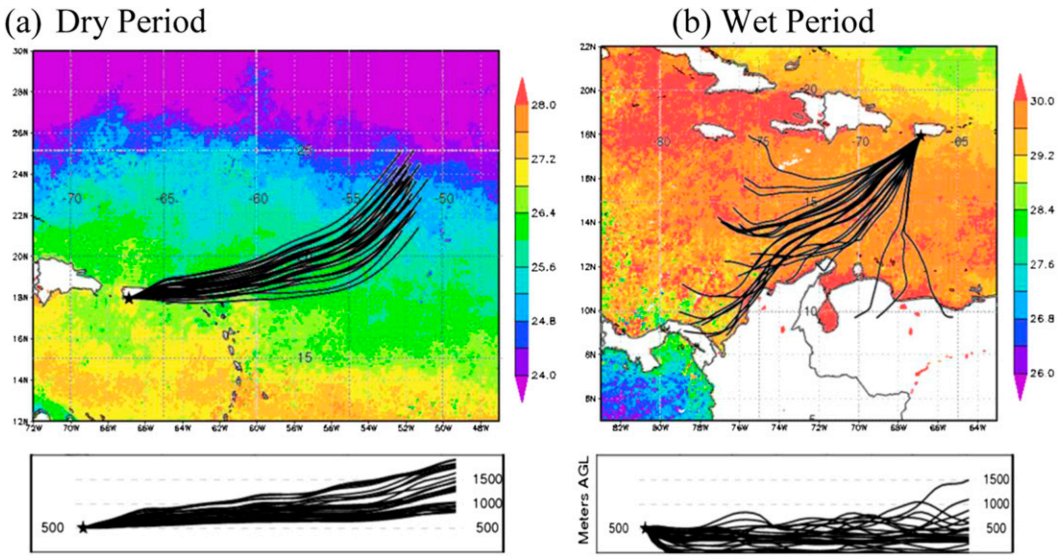

Figure 8. Analysis of (a) ensemble 5-day back trajectories ending 23 Dec 2008 and 8 Oct 2010 and (b) MODIS SST maps encompassing the same (left) dry and (right) wet periods at Guánica. (bottom) Vertical sections are given with height (m). Scales vary slightly.

coefficients providing an adjusted $R^2 = 0.61$. The rainwater δD is fitted by site rain and the vegetation index, with the latter more significant, and the adjusted $R^2 = 0.62$. The environmental algorithm for the *d* excess has a low adjusted $R^2 = 0.21$, contributed by the SD of maximum temperature and $P - E$. Similarly the groundwater δD has a weak adjusted $R^2 = 0.21$ with only the wind speed selected for input. The groundwater δ^{18}O achieves a higher $R^2 = 0.43$, contributed by surface temperature, wind speed, and the *V* wind component. In general, thermodynamic variables like rain, temperature, and vegetation replicate the annual cycle, while kinematic variables like wind speed or *V* wind contribute the intermonth fluctuations.

4. Summary

Puerto Rico's subtropical location ensures that the island receives marine air masses from the North Atlantic Ocean and Caribbean Sea. The Guánica Dry Forest study site is in the rain shadow on the southwestern coast where evaporation induces a surface water deficit of about -20 mm month^{-1}. Rainfall above a threshold to affect *d* excess occurs only during the irregular passage of tropical storms and hurricanes. There is an inverse relationship between the oxygen and hydrogen isotope ratio of rainfall and vegetation fraction index. Both are affected by depleted isotopic composition in periods of deep convection during late summer. Interannual variability could be related to factors such as AMO phase as suggested by long-term streamflow records near Guánica (Figure 9) and by local rainfall ($r = +0.67$).

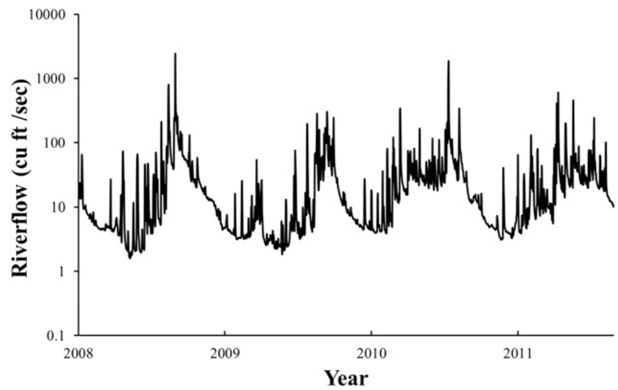

Figure 9. Annual cycling and flood peaks on log scale of Río Yauco. Data are generated from daily streamflow of USGS gauge 50126150, from January 2008 to December 2011. Tick marks indicate the month January of the corresponding year.

While a near-monthly sampling interval cannot match the weather events that induce monthly variability, there is evidence that groundwater recharge in the Guánica Dry Forest is dependent on pulses of rainfall whose timing and amounts are critical for the local hydrology. As noted elsewhere in Puerto Rico (Jones and Banner 2003; Scholl et al. 2009), groundwater recharge is confined to tropical storm events with rainfall more than 90 mm. Since global climate models predict an overall drying for the Caribbean (Neelin et al. 2006; Planos-Gutiérrez and Limia-Martínez 2007; Jury and Winter 2009), rainfall and groundwater recharge in the Guánica Dry Forest may decline in future, leading to ecosystem regime shifts. Our study provides an initial baseline for the observation of these shifts and for optimizing resource management decisions of tropical dry forest in a changing Caribbean climate.

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