Monitoring of Cueva Larga, Puerto Rico—A First Step to Decode Speleothem Climate Records

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Abstract

This study presents results of an ongoing cave monitoring program at Cueva Larga, Puerto Rico. The monitoring includes monthly analyses of stable isotope ratios of rain and drip water, and trace element ratios of drip water and cave air parameters. Drip sites are above growing speleothems offering the unique chance to calibrate geochemical variations in speleothems in order to reconstruct past climate conditions. Seasonal rainfall patterns above Cueva Larga show characteristic stable isotope values. The wet season is characterized by more negative δ^{18}O and δD values and a maritime deuterium excess (+10‰). The dry season has more positive δ^{18}O and δD values and elevated deuterium excess (>15%). The seasonal variations in the δ^{18}O and δD values are smoothed by the soil and karst system which acts as a low-pass filter, indicating that climate proxies derived from speleothems growing in Cueva Larga may only show multiannual changes. The seepage water reservoir appears to be well-mixed. The transmission time of atmospheric signals into the drip water is site-specific ranging most likely from several months to years.

1 Introduction

Here, we present results from a cave monitoring program at Cueva Larga. The goal of monitoring the Cueva Larga (CL) cave system is to understand and quantify the processes controlling the geochemical composition of cave drip waters which is ultimately recorded in speleothems. Calibrating the speleothems' geochemical composition to climate variables is the key to correctly interpret the proxy record encoded in speleothems in terms of past climate variability.

Speleothems have successfully been used as paleoclimate records (e.g., Fairchild and Baker 2012; Fairchild et al. 2006a; Lachniet 2009). Stable oxygen isotopes and trace element ratios have proven to be reliable paleoclimate proxies in many settings (e.g., Winter et al. 2011; Lachniet 2004; Wang et al. 2001; Spötl and Mangini 2002; Fairchild and Treble 2009; Cruz et al. 2009). However, interpretation of these proxies is not always straightforward. Cave

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monitoring and drip site monitoring play a key role prior to paleoclimate reconstruction based on speleothems (James et al. 2015; Lachniet 2009; Riechelmann et al. 2011, 2013).

Speleothem geochemical composition and growth are affected by the seepage water flow systematics through the soil and karst as well as the cave environment (Fairchild and Baker 2012). Seasonal variations in the cave environment can bias the recorded signal and might lead to aliasing if not resolved at a sufficiently high resolution (Banner et al. 2007; James et al. 2015; Weedon 2003). Moreover, processes such as evaporation, temperature variations, prior calcite precipitation (PCP), and changes in drip rate and pCO_2 can potentially alter the geochemical composition of speleothems, including trace elements and stable isotopes (Deininger et al. 2012; Fairchild and Baker 2012; Mickler et al. 2006). Cave monitoring results, as presented here, are important to understand the transmission of climate signals from the surface through the vegetation cover, soil, and karst into the cave (Fairchild and Baker 2012; Fairchild et al. 2007).

In the tropics, the speleothem $\delta^{18}O$ value is commonly used to reconstruct variations in local rainfall amount over time (Lachniet 2009). Variations in $\delta^{18}O$ and δD values of rainfall in the tropics are inversely correlated with the monthly rainfall amount, which is referred to as the "amount effect" (Sect. 2.1; Dansgaard 1964). The "amount effect" is variable, and other processes such as temperature, seasonality, and moisture source can modulate the "amount effect" and result in a more complex $\delta^{18}O$ signal (Dansgaard 1964; Rozanski et al. 1993). Trace element ratios of Sr/Ca and Mg/Ca show high potential as a complementary recorder of rainfall changes (Fairchild and Treble 2009; Fairchild et al. 2000; Stoll et al. 2012).

Adjustments of rainfall patterns to future climate change scenarios are still uncertain, and changes in the hydrological cycle will affect freshwater supplies (Intergovernmental Panel on Climate Change 2014; Winter et al. 2015). Multiproxy paleorainfall records offer a unique opportunity to evaluate climate models (Braconnot et al. 2012), and speleothem records can elucidate important climate forcings on regional rainfall (e.g., Asmerom et al. 2007; Cruz et al. 2005).

Our study investigates the transmission of the atmospheric signal into cave drip water feeding growing speleothems in Cueva Larga, Puerto Rico. The focus lies on tracing variations in the water cycle, expressed by changes in local precipitation. One part is to investigate the "amount effect" to ensure that variations recorded by speleothem isotopes can be linked to changes in past rainfall amount. Rainfall samples are collected above the cave site in the northern karst region of Puerto Rico and in Mayagüez at the western coast of the island to detect the stable isotope signal of precipitation. Another part is to characterize the cave environment and record changes in drip water chemistry to study whether there is a connection to atmospheric rainfall anomalies.

The setting of Cueva Larga appears ideal for paleoclimate studies due to its remote location, the lack of an active water stream and its small entrance limiting cave ventilation. In addition, the cave is unknown to the public restricting the risk of measurement disturbances. The monitoring results are documenting the natural undisturbed conditions in Cueva Larga and are providing important insight into the climate signal transmission into the cave.

2 Background

2.1 Isotopic "Amount Effect"

Rainwater $\delta^{18}O$ values depend on complex interactions in the hydrological cycle (Dansgaard 1964; Lachniet 2009; Rozanski et al. 1993). In the tropics, the "amount effect," first described by Dansgaard (1964), usually outweighs other stable isotope effects. The "amount effect" describes a negative correlation between the monthly rainfall amount and its $\delta^{18}O$ values. Deep vertical convection systems, including tropical storms and hurricanes, have more negative $\delta^{18}O$ values than most other tropical rain events (Dansgaard 1964; Lawrence and Gedzelman 1996). In tropical cyclonic systems, atmospheric water ascends to high altitudes and Rayleigh distillation in the deep convection leads to an enrichment in light isotopes during the system's evolution (Lachniet 2009). Furthermore, the extent of subcloud raindrop evaporation has also been related to rainfall amount and intensity (Dansgaard 1964; Lachniet 2009).

In Puerto Rico, easterly waves and low-pressure systems during the rainy season have higher cloud altitudes and lower condensation temperatures than trade-wind orographic rainfall of high-pressure systems during the dry season. More recent results obtained in Puerto Rico have shown a stronger correlation between $\delta^{18}O$ values of precipitation and maximal cloud heights (Scholl et al. 2009). This implies that the "amount effect" appears to be infuenced by cloud height and varying condensation temperatures of precipitation as well. Speleothem $\delta^{18}O$ values record variations in the drip water's stable isotope composition reflecting rainfall's $\delta^{18}O$ values and allowing reconstruction of tropical rainfall amount and weather patterns over time (Fairchild and Baker 2012; Lachniet 2009).

2.2 Global Meteoric Water Line (GMWL) and Deuterium Excess (d-Excess)

The Global Meteoric Water Line (GMWL) was defined by Craig (1961) as the relationship between the δD and $\delta^{18}O$ values of monthly rainfall water samples around the globe (Eq. 1). It results from the proportional fractionation difference during phase changes between δD and $\delta^{18}O$ and kinetic isotope fractionation during evaporation at relative humidity below 100% creating a d-excess. The d-excess (Eq. 2) is caused by the higher diffusivity for the lighter deuterium carrying molecule $^{2}H^{1}H^{16}O$ than for the heavier $^{1}H^{1}H^{18}O$. The d-excess of 10‰ in the GMWL represents an average relative humidity of 85% at the water source region (Clark and Fritz 1997; Merlivat and Jouzel 1979):

$$\delta D = 8 * \delta^{18}O + 10\text{‰} \tag{1}$$

$$d = \delta D - 8 * \delta^{18}O \tag{2}$$

During condensation, the d-excess does not change and it is an indicator of the water vapor source region (Merlivat and Jouzel 1979).

2.3 Speleothem Trace Element Ratios (Sr/Ca and Mg/Ca)

Trace element ratios of Sr/Ca and Mg/Ca in cave drip water and speleothem may be used as hydrological proxies (Fairchild and Baker 2012). In certain cave settings (Fairchild et al. 2000, 2006a), it has been shown that seepage water during drier conditions exhibits higher ratios due to increased prior calcite precipitation (PCP) and selective leaching due to longer water residence times. PCP occurs upstream from the drip site and preferentially incorporates Ca in the crystal's lattice increasing the trace element ratio downstream. This may also be the case in Cueva Larga.

3 Site Description

Puerto Rico is the easternmost island of the Greater Antilles located in the northeastern Caribbean between the island of Hispaniola and the Virgin Islands (Fig. 1). From east to west, the northern karst region stretches along the north coast reaching heights of more than 400 m. Cueva Larga (CL), also known as Cueva Coroso (Fig. 1), is located in the north-central karst region (N 18°19; W 66°48) at a height of 350 msl. The area is a developed holokarst characterized by sinkholes and mogotes. A thick tropical forest covers the surface above the cave. The cave is dominantly vadose with some phreatic features. It developed in the Oligocene Lares Limestone (Monroe 1980). The entrance of CL is located along the flank of a sinkhole at the lower edge of a small hill. A narrow vertical pit forms the entrance, followed by two U-shaped depressions along the cave ceiling (Fig. 1). The main passage is nearly horizontal, strikes west–east, and forms a tube with ceiling heights of up to 30 m. The cave ends in the Collapse Room, a chamber whose roof collapsed, which is separated from the main chamber by a rise in the cave passage floor. The Collapse Room splits up in a small

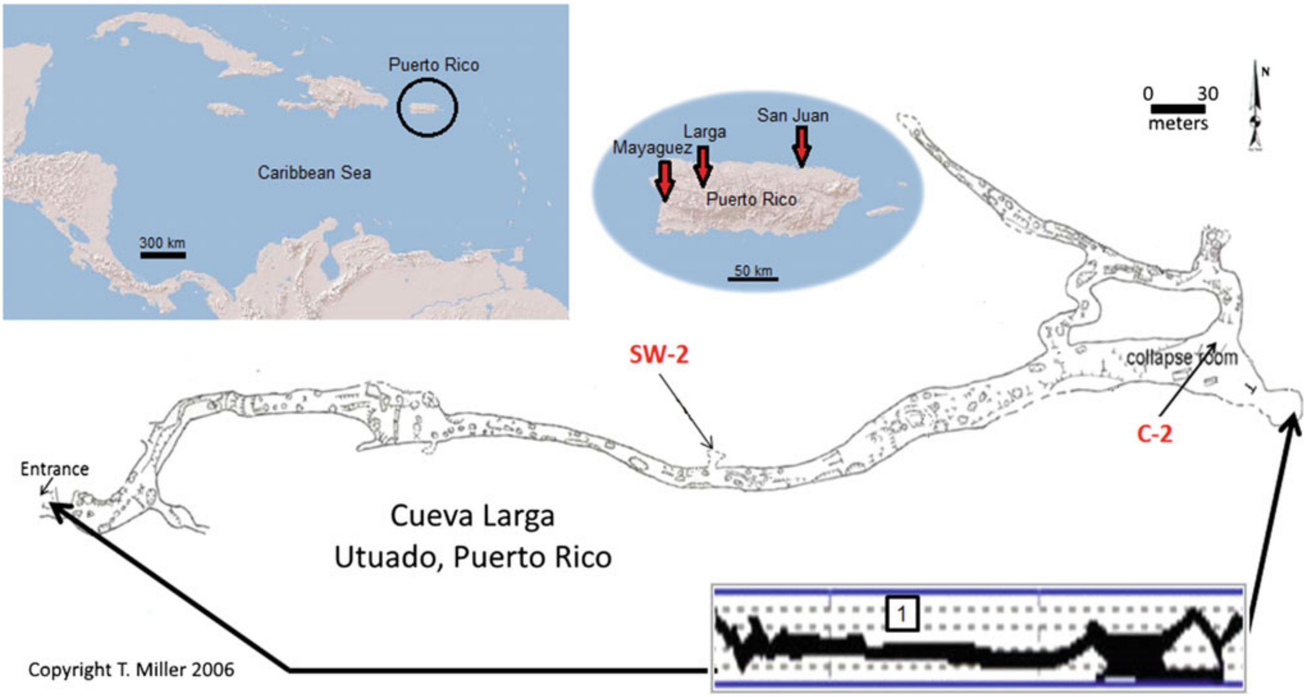

Fig. 1 Plan view of Cueva Larga (after Miller 2010) with monitored drip sites SW-2 and C-2 (*marked in red*). Also shown is an overview map of the Caribbean and a map of Puerto Rico with the locations of Cueva Larga, Mayagüez, and San Juan (*red arrows*). *Inset 1* Longitudinal section of the cave (Miller 2010)

lower- and a large upper-level passage which reconnects at the end of the cave (Fig. 1). The horizontal extent of CL is about 1440 m (Miller 2010). Here, we discuss the drip water data of drip site SW-2, located in the main passage, and site C-2, located in the Collapse Room (Fig. 1). Both sites were chosen because they feed actively growing speleothems and their drip rate is fast enough to allow instantaneous drip water sampling during each cave visit. Site SW-2 is in close proximity to a fallen speleothem which grew during the last 35 to 17 ka and the moitoring aims to improve the speleothem based climate reconstruction.

Most of the Caribbean shows a dry (Dec–Mar/Apr) and wet (Apr/May–Nov) season. The hurricane season starts at beginning of June and ends in November. During the wet season, precipitation declines during the summer months, which is referred to as the midsummer drought (Chen and Taylor 2002; Magaña et al. 1999). This rainfall pattern is also visible at Mayagüez and the Arecibo Observatory (Fig. 2). At the Arecibo Observatory, the annual rainfall amount is larger with 2137 mm/year compared to 1510 mm/year in Mayagüez. The midsummer drought is very pronounced at the mountainous Arecibo Observatory site with highest monthly rainfall amounts occurring during May. In Mayagüez, the midsummer drought is marked by a slight rainfall decrease in June, and the rainfall maximum is reached in September. Trade winds are the dominant control (85%) of air flow over Puerto Rico (Jury and Chiao 2013). In Mayagüez, the diurnal land and sea breeze are pronounced (Bennett et al. 1998), and the topography of Puerto Rico weakens the trade-wind flow creating a wake to the west of the islands, which promotes the formation of high convective afternoon thunderstorms (Jury and Chiao 2013).

Different weather patterns cause rain events throughout the year. Low-pressure systems embedded in easterly waves, tropical storms, and occasional cold fronts from the north are the main contributors of Caribbean rainfall. During the rainy season, easterly waves and low-pressure systems with cloud altitudes reaching up to 8000 m deliver the majority of rainfall, while during the dry season, trade-wind orographic rainfall of high-pressure systems with significantly lower cloud heights occurs (Scholl et al. 2009).

4 Methods

4.1 Sampling Procedure

Cueva Larga was visited every month in 2013 and 2014 and about every two months in 2015. The monitored drip site SW-2 is located in the middle section of CL about 425 m inside the cave, and site C-2 is located in the Collapse Room on top of a boulder field at the end of the cave about 790 m inside (Fig. 1). During each cave visit, pCO_2, temperature (T), and relative humidity (RH) measurements were recorded at each site. An Amprobe CO_2-100 handheld carbon dioxide meter (precision of ±30 ppm, ±5% of the reading for pCO_2 between 0 and 5000 ppm; ±0.6 °C for T and ±5% for RH above 90%) was used from January 2013 to July 2013, whereas from July 2013 to January 2015, a handheld Vaisala GM 70 with a 2000 ppm CO_2 probe (accuracy ±30 ppm + 2% of reading for pCO_2 between 0 and 2000 ppm) and a HM70 humidity and temperature probe (precision ± 0.2 °C for T and ±1.7% for RH above 90%)

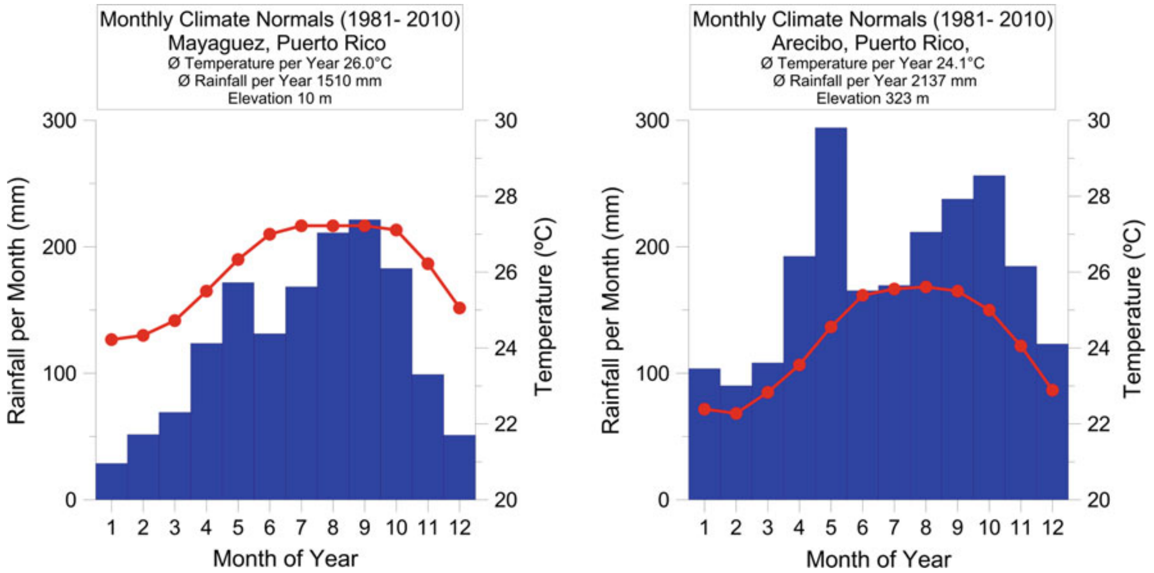

Fig. 2 Monthly climate normal 1981–2010 for Mayagüez (*left*) and Arecibo Observatory (*right*). The data were downloaded from the data query tool xmACIS (http://xmacis.rcc-acis.org/) developed and maintained by NOAA's Northeast Regional Climate Center

were used. During two cave visits, both devices were used and the measurements agreed within uncertainty.

Outside atmospheric temperature data for Cueva Larga were taken from the Arecibo Observatory weather station, located at 323 msl (about 7 m lower than the entrance of CL) about 10 km north of the cave site. (Data source: http://xmacis.rcc-acis.org/). Monthly rainwater samples were collected both above the cave site and at the University of Puerto Rico in Mayagüez (N 18°12; W 66°08, 10 msl). Rainwater samples were collected according to the GNIP (Global Network of Isotopes in Precipitation) station operation manual (IAEA 2012). At the beginning of each sampling period, the collection bucket was filled with paraffin oil that covered the buckets surface area by a height of at least 0.5 cm to prevent evaporation of the rainwater stored inside the bucket over the sampling period. After a settling period of about one week, to allow the oil to separate completely from the rainwater, the monthly rainwater sample was transferred via siphoning into transportation vials. For the Cueva Larga site, the weighted average rainfall δD and δ^{18}O values were calculated. At the cave site, rainfall samples were collected during each cave visit. In Mayagüez, rainwater samples were taken in close temporal relation to the cave site visitation in 2013. Starting in 2014, the rainwater samples in Mayagüez were taken at the beginning of each month.

Cave drip water samples were collected during each field trip. Depending on the drip rate, the collection of enough water took up to 1.5 h. Drip rates were determined via counting the number of drips within 1 min. For cation analyses, pre-acidified 15-ml Falcon tubes were used.

4.2 Analytical Methods

Monthly rainwater samples from Mayagüez were measured in the Isotope Hydrology Laboratory of the IAEA (International Atomic Energy Agency) in Vienna. Hydrogen and oxygen isotope analyses were conducted by off-axis integrated cavity output laser spectroscopy and/or dual-inlet isotope-ratio mass spectrometry.

Stable isotope ratios of rain and drip water from the CL site were analyzed at the University of Innsbruck, Austria. A first set of samples was analyzed for δ^{18}O using the CO_2 equilibration method (Thermo Scientific Delta^{plus}XL with Gasbench II) and for δD using a Thermo Scientific Thermal Combustion/Elemental Analyzer (TC/EA) and a Delta V Advantage mass spectrometer. The uncertainty was 0.15‰ for δ^{18}O and 1‰ for δD. Later samples were analyzed on a Picarro L2140-*i* CRDS. The uncertainty is 0.08‰ for δ^{18}O and 0.5‰ for δD. All results are reported relative to VSMOW.

The analyses of the cation concentrations of drip waters were performed at Heidelberg University with a Agilent ICP-OES 720 (Varian) with an internal 1σ-standard deviation of <1% for Ca^{2+}, Mg^{2+} and Sr^{2+}. An external standard, the SPS SW2 with a long-term 1sigma-reproducibility of 2.2% for Ca^{2+} (conc. 10 mg/L), 3.4% for Mg^{2+} (conc. 2 mg/L) and 3.6% for Sr^{2+} (conc. 250 µg/L) was used.

5 Results

At both sites, Mayagüez and Cueva Larga, the rainwater δ^{18}O values show a trend towards more negative values when the amount of rainfall is larger (Fig. 3). The sample period has not always been exactly one month. For Cueva Larga, the rainwater sampling period varied between 16 and 58 days and for Mayagüez the sampling period started to be monthly in the year 2014 but varied between 15 and 48 days in 2013. To account for different sampling durations, the average daily rainfall amount over the sampling period has been calculated and was multiplied by 30.4 days (the length of an average month) to express the average rainfall intensity over the sampling period in terms of monthly rainfall amount. In Fig. 3, the raw results (rainfall amounts over initial variable sampling periods) and normalized monthly results (normalized to 30.4 days) are shown together with GNIP data from San Juan between the years 1968 and 1973. The monthly rainfall δ^{18}O values show a wide scatter, but in general, lower values are observed during periods of higher rainfall amount. The linear trend indicates that a decrease of 1‰ in δ^{18}O roughly corresponds to a rainfall increase of about 220 mm/month in Mayagüez and 250 mm/month at Cueva Larga.

All data from Mayagüez plot close to the GMWL (Fig. 4). The rainfall measurements from Cueva Larga split up into two groups. One group is located near the GMWL, while the other group plots above the GMWL with elevated d-excess values between 15 and 20‰ (blue box in Fig. 4). Some of the cave drip water samples from drip sites SW-2 and C-2 were analyzed for both δD and δ^{18}O. These results are also shown in Fig. 4. Only one result falls on the GMWL. The other drip water samples plot between the GMWL and the elevated d-excess. These have been sampled between April and August 2014. All drip water values show lower stable isotope values than the weighted mean of rainfall δ^{18}O and δD ($\delta^{18}O = -2.04$‰ and $\delta D = -5.24$‰).

The d-excess values were plotted against time to investigate the temporal distribution of both rainfall groups at Cueva Larga in Fig. 5. The rainfall measurements with an elevated deuterium excess (d-excess > 15‰) were taken during the end of the dry season and early wet season (February–May; Fig. 5). While Figs. 4 and 5 point out that

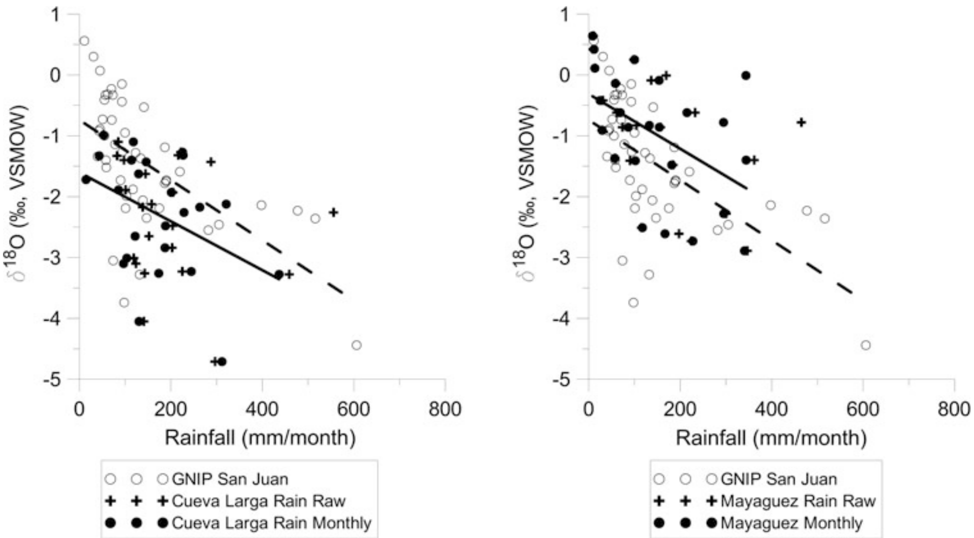

Fig. 3 δ^{18}O values of rainfall collected at Cueva Larga (*left*) and in Mayagüez (*right*). *Crosses* show the measured values for each sampling period (raw data). *Filled circles* show the rainfall δ^{18}O value relative to the normalized to rainfall amounts occurring over one month (30.4-day sampling period). *Open circles* show GNIP rainfall data from San Juan between 1968 and 1973 (downloaded from GNIP's WISER data-platform https://nucleus.iaea.org/wiser IAEA/WMO 2015). The *solid-and-dashed line* shows the linear trends of the normalized data from our measurements and the GNIP data from San Juan, respectively

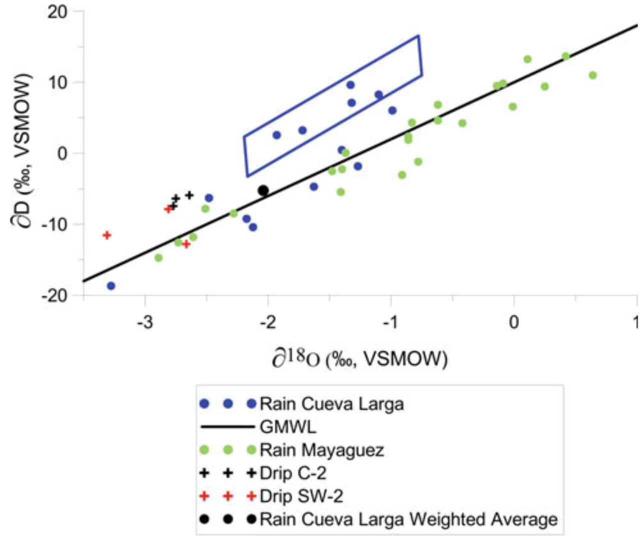

Fig. 4 Comparison of rain (*points*) and drip water data (*crosses*). The Global Meteoric Water Line (GMWL: $\delta D = 8*\delta^{18}O + 10‰$) is represented by the *black solid line*. The *blue box* marks elevated rainwater d-excess values >15‰ at Cueva Larga. The *black filled circle* shows the average isotopic composition of the rainfall weighted by rainfall amount ($\delta^{18}O = -2.04‰$ and $\delta D = -5.24‰$)

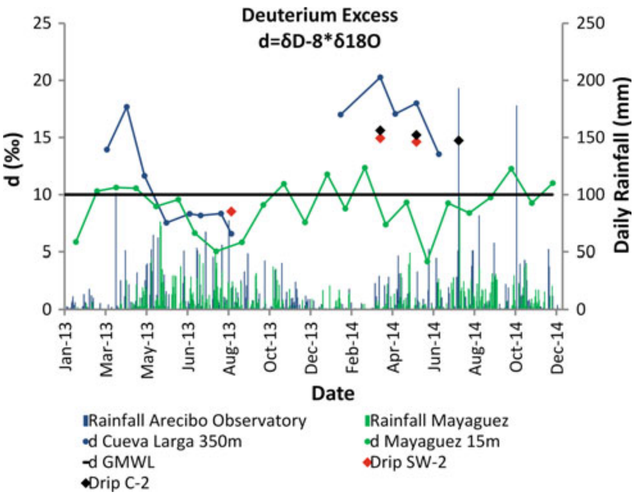

Fig. 5 Deuterium excess (d) of rainwater compared to the daily rainfall amount. The time series for Cueva Larga shows gaps, because some monthly samples have been measured only for δ^{18}O

there is a seasonality of the deuterium excess, yet insufficient data are available to establish seasonal meteoric waterlines for the Cueva Larga mountain site.

Figure 6 shows the results of cave monitoring compared to the temperature and rainfall outside the cave. The rainfall pattern shows the dry season in the winter and wet season in the summer period. Extreme daily rainfall events are related to tropical depressions and hurricanes. The highest daily rainfall amount (193 mm) was measured during hurricane Bertha (3 August 2014). Tropical depressions delivered large rainfall amounts of 178 mm (27 October 2014) and 142 mm (16 May 2015). The monthly rainfall anomaly is the difference between the observed monthly rainfall to the rainfall normal from 1981 to 2010. Figure 6 shows that monthly rainfall anomaly was negative during summer 2013 and early 2014. This trend is interrupted by the strong positive anomaly in August 2014 when hurricane Bertha passed by Puerto Rico. The following month showed normal

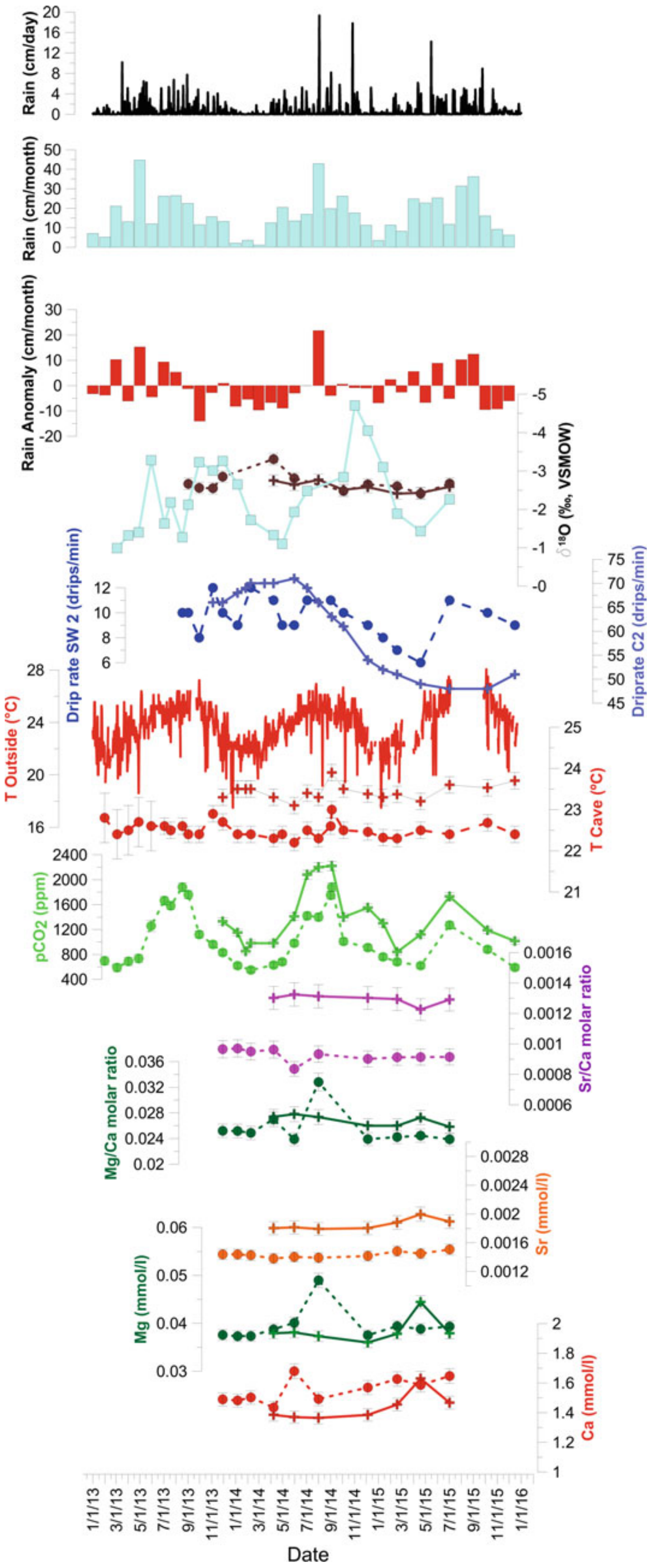

Fig. 6 Weather observation and cave monitoring results in Cueva Larga from 2013 to 2015. Data are shown for drip site SW-2 (*circles on dashed line*) and C-2 (*crosses on solid line*). The *first three plots* show the daily rainfall amount, the monthly rainfall amount, and the rainfall anomaly of each month compared to the monthly climate normal from 1981 to 2010 from the Arecibo Observatory weather station (Fig. 2). The *blue squares* show $\delta^{18}O$ results of rainwater compared to the $\delta^{18}O$ results of drip water (*in brown*). This is followed by the temperature outside and inside Cueva Larga (*red*), the cave atmospheric pCO_2 at each site (*green*), and the Sr/Ca (*pink*) and Mg/Ca (*dark green*) values. The *lowest plots* show the concentrations of Sr (*orange*), Mg (*green*), and Ca (*red*) in the drip water

rainfall amounts and some positive and negative anomalies at the end of 2015.

Inside Cueva Larga, the variations in drip rate are site-specific. The monthly observations at drip site C-2 show constant trends exceeding the annual period. Drip rate increased from November 2013 to May 2014 and then continuously decreased until October 2015. In contrast, drip site SW-2 shows variations on a shorter timescale. Rapid increases in drip rate were observed in November 2013, February 2014, July 2014, and July 2015 followed by drip rate decreases occurring over time frames of several months (Fig. 6). Assuming a drip volume of 0.23 mL/drip (Collister and Mattey 2008), we calculated the drip rate in L/s and were able to classify both drips (after Fairchild et al. 2006b) as dominated by seepage flow.

Rainfall $\delta^{18}O$ values show a seasonal signal. More negative values (down to −4.7‰) are recorded during the wet season and vice versa. In 2013, one negative peak in May (−3.28‰) is observed followed by a second negative peak (below −3‰) at the end of the rainfall season (September to December). In 2014, the negative $\delta^{18}O$ values of the summer season do not show the bimodal signal observed in 2013. More negative values are measured from July to December/January. The most negative values are up to 1.4‰ more negative than in 2013 and occur during October and November. The drip water $\delta^{18}O$ composition of drip sites C-2 and SW-2 inside Cueva Larga does not reflect the surface pattern between dry and wet season. The drip water of drip site C-2 shows no significant variations and has an average $\delta^{18}O$ value of -2.59 ± 0.12‰. Similar $\delta^{18}O$ values were measured in drip water at site SW-2 (-2.69 ± 0.23‰). Except for April and May 2014, when drip water $\delta^{18}O$ values were more negative.

Temperatures in Cueva Larga are nearly constant over time compared to the annual cycle outside the cave. In the main cave passage at site SW-2, the average temperature is 22.51 ± 0.18 °C. This is similar to the average annual temperature outside the cave, 22.5 ± 0.1 °C (calculated for two years from 4 November 2012 to 3 November 2013 and 4 November 2013 to 3 November 2013). At site C-2 in the Collapse Room near the end of Cueva Larga, the average temperature is almost 1 °C higher (23.43 ± 0.19 °C). At the transition from summer to winter (September and October), a short-lived temperature maximum was observed where temperatures increase by +0.5 °C. This is probably related to a change in cave air circulation.

Cave pCO_2 values follow the seasonal temperature cycle at the surface. Summer maxima reach up to 1880 ppm at drip site SW-2 and up to 2220 ppm at drip site C-2. Winter minima are as low as 550 ppm at drip site SW-2 and 850 ppm at drip site C-2. In contrast to temperature, the annual pCO_2 pattern is asymmetrical showing a gradual rise from May to August and a relatively rapid decrease in September.

The trace element to Ca ratios is nearly constant over the monitoring period. At drip site C-2, the average Sr/Ca ratio is $1.293 \times 10^{-3} \pm 0.029 \times 10^{-3}$ and thus higher than at drip site SW-2 with an average of $9.25 \times 10^{-4} \pm 0.38 \times 10^{-4}$. The Mg/Ca ratio is similar at both sites with an average of $2.55 \times 10^{-2} \pm 0.26 \times 10^{-2}$ at site SW-2 and $2.681 \times 10^{-2} \pm 0.077 \times 10^{-2}$ at site C-2. The Ca concentration is generally higher at drip site SW-2.

6 Discussion

Rainfall and temperature outside Cueva Larga show a seasonal cycle with increased rainfall during the summer season (Fig. 6). Plotting the $\delta^{18}O$ values of rainfall against rainfall amount (Fig. 3) reveals that periods of increased rainfall amount correspond to more negative $\delta^{18}O$ values. The linear trend at both sites shows a rainfall “amount effect” of about 4.5×10^{-3} to 4.0×10^{-3}‰/mm monthly rainfall. This “amount effect” is in agreement with the trend observed in rainfall collected in San Juan between 1968 and 1973 (Fig. 3). Unfortunately, the rainfall data (Fig. 3) show a large scatter, which makes quantification of absolute rainfall amounts from the rainfall’s isotopic composition difficult. Nonetheless, the rainfall results document the general isotopic “amount effect”, suggesting that $\delta^{18}O$ values recorded in speleothems from Cueva Larga reflect primarily variations in rainfall amount similar to other speleothem records from tropical regions (e.g., Lachniet 2004; Winter et al. 2015).

The differences in rainfall $\delta^{18}O$ values between 2013 and 2014 above Cueva Larga appear to be related to different weather patterns reaching the site. In 2014, maximum daily rainfall amounts are larger than in 2013 due to large convective rainfall systems including hurricane Bertha. Large tropical convective systems may have $\delta^{18}O$ values lower than −6‰ (Lawrence and Gedzelman 1996). The contribution of these systems seems to be responsible for the lower $\delta^{18}O$ values in 2014. The observed bimodal summer in the $\delta^{18}O$ values of 2013 may be related to the lack of large convective rainfall systems allowing the midsummer drought to appear in the rainfall $\delta^{18}O$ data. In the summer of 2014, the sampling interval was larger than in 2013 which may also have prohibited the detection of a bimodal $\delta^{18}O$ rainfall signal.

The currently available two years of observations from Cueva Larga indicate inter-annual variations in rainfall $\delta^{18}O$ values. Extending the observations to several years might resolve inter-annual isotopic rainfall variations, which are likely to be recorded in speleothems. Detailed rainfall stable isotope studies in Puerto Rico revealed that the $\delta^{18}O$ value of rainfall is complex (Scholl et al. 2009; Scholl and Murphy 2014). The correlation between maximum cloud height and rainfall $\delta^{18}O$ values is larger than the correlation to rainfall amount (Scholl et al. 2009), indicating that condensation temperature plays an important role. The evolution of rainfall downstream of Puerto Rico leads to characteristic rainfall δ^{18}O values distinguishing trade-wind orographic showers, low-pressure systems, and convective systems (Scholl and Murphy 2014). Thus, changes in weather patterns over multiannual time-spans seem to have an influence on the isotopic signal of drip water in Cueva Larga, highlighting the potential for speleothem δ^{18}O time series from this site for revealing changes in weather patterns and rainfall amounts. However, the complexity of the process occurring in the soil and karst above the cave as well as inside the cave during precipitation of speleothem calcite may make the interpretation of speleothem δ^{18}O values on inter-annual timescales difficult (Mischel et al. 2015).

In Mayagüez, δ^{18}O and δD values of the rainwater plot close to the GMWL (Fig. 4). These samples seem to be primarily controlled by different degrees of Rayleigh fractionation during rainout (Rozanski et al. 1993). At the location of Cueva Larga, the rainwater samples appear to form two groups, one group plotting on the GMWL and the other group plotting above the GMWL with d-excess values between +15 and +20‰. Currently, we do not have enough data to establish a seasonal Local Meteoric Water Line (LMWL), but it appears that the season of elevated d-excess agrees well to a LMWL ($\delta D = 8.2 * \delta^{18}O + 14$) established for the mountainous Eastern Puerto Rico by Scholl and Murphy (2014). Elevated d-excess values occur between the middle and end of the dry season and have been measured in April 2013 and from February to end of May 2014 (Fig. 5). The seasonality might be related to a greater fraction of recycled rainwater via the process of evaporation from surface and forest canopy upstream the cave site (Aemisegger et al. 2014; Peng et al. 2010; Lee et al. 2009; Price et al. 2008; Victoria et al. 1991) among other processes.

Since elevated d-excess values have not been observed at Mayagüez (Fig. 5), rainwater recycling seems to be negligible during both seasons. Mayagüez lies on the west coast of Puerto Rico in the trade-wind wake zone of the island. At this location, winds typically come from the west (Jury and Chiao 2013) bringing marine moisture with a d-excess of about 10‰. Similar observations have been made at the south coast of Puerto Rico where the primary moisture source is also maritime (Govender et al. 2013).

Inside Cueva Larga drip water δ^{18}O and δD results indicate that the wet season rainfall contributes proportionally more to the drip water than the rainfall during the dry season because all drip water measurements are more negative than the amount of weighted average isotopic composition of the rainfall (Fig. 4). This seems plausible because during the dry season a greater fraction of the rainfall will be lost to evapotranspiration than during the wet season. Currently, only three drip water samples at each site have been analyzed for δD. These results are insufficient to reveal drip water seasonality. More frequent cave drip water δ^{18}O and δD values could be used to investigate the transmission of seasonal atmospheric signals into the cave drip water in addition to the δ^{18}O drip water time series at this site. An indication of the transmission of d-excess seasonality into Cueva Larga is the observation that during the wet season in September 2013, the drip water at site SW-2 falls near the GMWL, having similar d-excess values than the rainwater at that time (Fig. 5). The rest of the few drip water d-excess observations have been made during the end of the dry season (April and May 2014) and show elevated d-excess values similar to the rainfall at that time. Additional drip water δD data with monthly sampling resolution are required for more meaningful interpretations concerning the transmission of the seasonal d-excess signal from the rainwater into the cave drip water.

Cave atmosphere pCO_2 shows an annual cycle. It reaches a minimum during winter and a maximum during summer season. Comparing the buoyancy of cave air to the outside atmosphere reveals that the combination of the seasonal temperature cycle outside the cave and the cave geometry of Cueva Larga is the main driver of alternation between a well-ventilated winter mode and a near-stagnant summer mode (Vieten et al. 2016). In particular, during winter nights, the buoyancy of the cold outside air drops markedly below the cave atmosphere's buoyancy, leading to maximal cave ventilation. During the summer mode, cave ventilation is at a minimum because most of the time the buoyancy of the cave air is lower than outside leading to stagnant ventilation conditions. Similar observations in the seasonality and magnitude of pCO_2 have been documented in temperate regions (Frisia et al. 2011; Spötl et al. 2005). Other caves show similar seasonal ventilation systematics, but different pCO_2 amplitudes, such as in Austria (Boch and Spötl 2008); Ireland (Baldini et al. 2008); France (Bourges et al. 2006); Arizona, USA (Buecher 1999); Texas, USA (Cowan et al. 2013); and Germany (Meisner et al. 2010).

The documented cave atmosphere seasonality probably leads to seasonal variations in carbonate precipitation (e.g., Kaufmann and Dreybrodt 2004; Fairchild et al. Fairchild et al. 2006a, b; Baldini et al. 2008) because cave pCO_2 is directly linked to the growth rate of speleothems where lower pCO_2 values result in higher supersaturation with respect to calcite and increasing carbonate precipitation rates (Baker et al. 2014; Dreybrodt 2012). Variations in growth rate might cause a bias toward the fast growing season in climate records deduced from speleothems and also affect the incorporation of trace elements into the crystal lattice (Fairchild et al. 2006a; Gabitov and Watson 2006). Assuming all other factors being equal, seasonal ventilation appears to cause increased growth rates during the low pCO_2 winter season even though it rains more in the summer. In the most extreme case, speleothems in Cueva Larga would only grow during winter when the cave pCO_2 falls below a threshold value allowing carbonate precipitation. Carbonate precipitation seasonality is especially important for drip sites which feed from seepage water with short transition times and negligible water mixing along the seepage path from the surface to the cave. Such sites usually exhibit seasonal variations in the drip water geochemistry linked to the seasonality above the cave. The drip water stable isotope and trace element data from Cueva Larga do not show seasonal patterns (Fig. 6). Thus, the soil and karst above the cave appear to act as a low-pass filter.

A seasonal signal similar to the rainfall $\delta^{18}O$ seasonality is not clearly detectable in the drip water data. Drip site SW-2 appears to show a slight response to rainfall seasonality in early 2014. More negative $\delta^{18}O$ values are recorded at site SW-2 (Fig. 6). This could be the signal transmitted of 2013 summer rainfall. Delay times of similar length have been observed at other cave sites (e.g., Riechelmann et al. 2011). In 2015, a corresponding signal is not visible in the drip water of site SW-2. This might be related to the relatively dry year in 2014 with most months showing a negative rainfall amount anomaly (Fig. 6). A lack of recharge during 2014 is also indicated by the decreasing drip rates at both drip sites starting in summer 2014. At site SW-2, drip rates decrease by about 45% from 11 drips/min in September 2015 to 6 drips/min in April 2015. Thus, less recharge of more negative summer rainfall during the drier summer 2014 might be the reason for the missing negative peak in drip water $\delta^{18}O$ values at drip site SW-2 in 2015. At drip site C-2, drip rates decrease by about 40% from 69 drips/min in July 2014 to 48 drips/min in July 2015 and remain low, while drip site SW-2 shows an increase in drip rate in July 2015. The increase in drip rate at drip site SW-2 seems to be related to a large rainfall event in May 2015 (140 mm rain on May 16, 2015). During 2013/2014, drip site SW-2 also shows higher drip rate variability than drip site C-2, indicating that drip rate at site SW-2 responds more directly to rainfall and recharge events above the cave.

Trace element ratios indicate that the residence time and/or the host rock composition is different above both drip sites. Sr/Ca is higher at drip site C-2 (Fig. 6) indicating longer residence times above drip site C-2 than above drip site SW-2 (Verheyden et al. 2000). This is in agreement with the slower responding drip rates and the lack of any seasonality at drip site C-2.

Sr/Ca and Mg/Ca show no seasonal variation. We do not find evidence for varying degrees in PCP. Figure 7 shows a comparison of the drip water results from both drip sites at Cueva Larga to drip water data from Brown's Folly Mine, UK (Fairchild et al. 2006b). The variable drip water composition in Brown's Folly Mine is represented by the outlined area in Fig. 7 and has been interpreted to be the result of varying degrees of PCP. In Cueva Larga, there is no evidence for such variable degrees of PCP above the cave on the annual timescale.

The water reservoir above Cueva Larga seems to be large enough to buffer seasonal rainfall variations causing no detectable changes in PCP over the monitored period. However, trace element variability in speleothems from Cueva Larga may be related to long-term changes in climate above the cave.

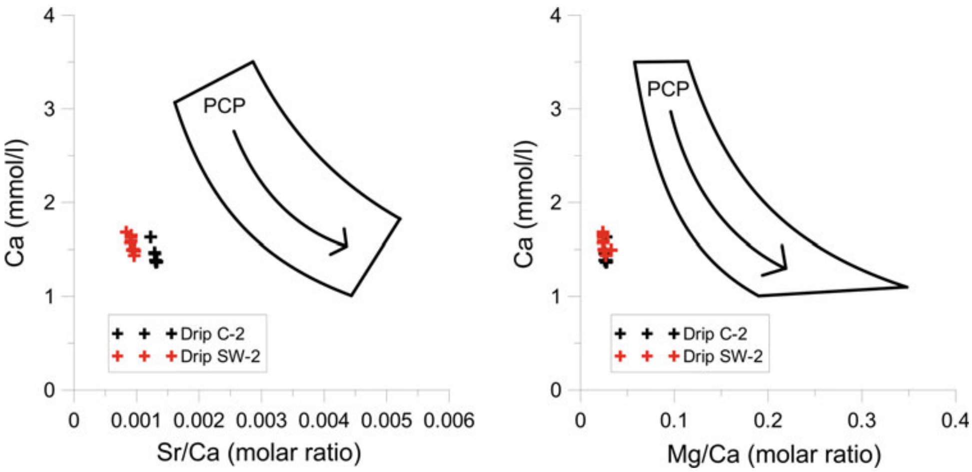

Fig. 7 Geochemical relationships of trace element ratios (Sr/Ca *left* and Mg/Ca *right*) to Ca concentration for drip sites SW-2 and C-2 in Cueva Larga. The outlined area in each plot shows similar evaluation in Brown's Folly Mine, UK (Fairchild et al. 2006a, b). The *arrow* labeled with PCP (prior calcite precipitation) shows the direction in which higher degrees of PCP along the seepage water flow path would shift the results

7 Conclusions

Two years of cave monitoring in Cueva Larga, Puerto Rico, represent a first step to investigate the response of cave drip water to climate fluctuations above the cave. The drip water geochemistry provides insight into seepage water flow and mixing processes resulting in important implications for speleothem climate records. The isotopic rainfall "amount effect" has been detected in rainfall above the cave and in Mayagüez. This is an important prerequisite for speleothem $\delta^{18}O$ values to reflect changes in the rainfall amount over Puerto Rico. Rainfall deuterium excess shows elevated values during the dry season only at Cueva Larga, whereas Mayagüez seems to be dominated by maritime water vapor sources. Drip water d-excess may enable us to estimate seepage water transition time.

Seasonality in cave ventilation results in low cave air pCO_2 in the winter season which might cause accelerated speleothem growth rates and bias speleothem climate records toward the winter season. Drip water trace element ratios lack variations, implying that changes in PCP along the seepage flow path do not have a significant effect over the monitored period.

Both drip sites seem to be fed by well-mixed sources. The lack of clear seasonality makes estimations of residence and transmission time difficult. Drip site SW-2 appears to show a response to annual rainfall changes indicating a transmission time of several months, while the transmission time for drip site C-2 appears to be larger. The well-mixed and slowly responding drip sites monitored here favor speleothems to record multiannual paleoclimate changes because the seepage water system acts as a low-pass filter.

This study shows that monitoring of drip sites is useful to decipher the effects influencing the climate signal recorded in speleothems. Environmental observations will improve speleothem paleoclimate interpretations and extending the monitoring to several years may even enable us to calibrate the speleothem proxy record to absolute changes above the cave. Some of the here presented results are preliminary and need to be verified by continuation of the cave monitoring program in Cueva Larga.

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