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MULTI-YEAR CAVE DRIPWATER FREQUENCY AND HYDROCHEMICAL MONITORING OF THREE CAVES IN EASTERN NORTH AMERICA: IMPLICATIONS FOR SPELEOTHEM PALEOCLIMATOLOGY

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Abstract

A cave monitoring program of three caves in southeastern West Virginia, USA, was undertaken from September 2011 to December 2013. Culverson Creek Cave, Buckeye Creek Cave, and Lost World Caverns were continuously monitored for temperature and relative humidity, revealing a highly-stable environment year-round. The caves were visited approximately every three months during the study period, when discrete CO_2 measurements were taken, revealing a seasonal ventilation cycle characteristic of temperate-region caves. Dripwaters from 12 sampling stations were collected throughout the first year, from which the isotopic results show the relationship between cave dripwaters and meteoric precipitation. Two sampling periods, those of March 2012 and October 2012, were distinctly different than most of the other isotope values that fell on, or very near, the Global Meteoric Water Line (GMWL). The March 2012 dripwater isotopes were very negative, resulting from several days of heavy meteoric precipitation preceding the collection time that likely pushed water through the vadose zone that had accumulated in the previous winter months. The October 2012 samples displayed a positive linear trend, falling to the right of the GMWL, indicating that those samples were comprised of waters with evaporative loss. Drip frequency loggers placed above the cave allow a direct comparison between surface precipitation and six cave drip-frequency loggers, placed strategically throughout the study caves. These frequency data help to characterize the drips, where one was shown to be highly responsive and underwent flow-switching. Two are shown to have a seasonal-response and three demonstrated no response, characteristic of slow seepage flow. Stalagmites formed as a result of the latter are generally regarded as the most suitable for long-term paleoclimate studies. Monitoring programs performed prior to stalagmite collection for paleoclimate reconstructions could aid in the selection of suitable samples, thereby preserving priceless cave formations, as well as aiding in the interpretation of geochemical proxy variations in speleothem calcite.

Introduction

Speleothems as paleoclimate archives have been increasingly utilized over the past few decades (Baker et al., 1997; Dorale et al., 1998; Roberts et al., 1998; Hellstrom and McCulloch, 2000; Wang et al., 2001; Poore et al., 2003; Dykoski et al., 2005; Cheng et al., 2006; Spötl et al., 2006; Vollweiler et al., 2006; Borsato et al., 2007; Cruz et al., 2007; Mattey et al., 2008; Lambert and Aharon, 2010; Stríkis et al., 2011). Stalagmites are the product of cave dripwaters, which have complex surface-to-cave hydrologic pathways, seasonal distributions, and unique hydrochemical histories. Isotopic and trace element variation between coeval speleothems underscores the importance of an understanding of dripwater variability, as speleothem records may represent different aspects of the climate system. The complexity of hydrologic evolution from the soil zone through the vadose and phreatic zones in the epikarst has prohibited a complete understanding of the hydrologic histories of individual cave drips. However, the dripwater frequency and modern hydrochemistry of dripwaters can give clues as to the hydrologic pathway of the individual drips and may aid in the interpretation of stalagmite records.

Speleothems form due to the CO_2 degassing of supersaturated waters, which is governed by soil gas CO_2 and the cave air CO_2 concentrations (Fairchild et al., 2006). Upon entering the cave atmosphere, the dripwaters with high CO_2 encounter the lower-CO_2 cave air, thereby driving the precipitation and deposition of calcite as the CO_2 degasses. Density-driven seasonal ventilation exerts a significant control on the annual growth distribution of calcite laminae, as the concentration of cave air CO_2 is generally highest in the warmer months, because the relatively colder cave air remains in the topographic lows of the cave. In contrast, the cold, dense air of the colder months sinks into the cave, thereby increasing ventilation and lowering cave air CO_2 (Fairchild and Baker, 2012).

Previous work on karst vadose hydrology and speleothem geochemistry has focused on three major themes: drip variability and flow regimes (Smart and Friederich, 1986; Baker et al., 1997; Baker and Brunsdon, 2003), hydrochemical studies of dripwaters (Huang et al., 2001; Tooth and Fairchild, 2003; McDonald et al., 2004, 2007; Karmann et al., 2007; Lambert and Aharon, 2010, 2011), and experimental/quantitative models of calcite deposition and/or isotopic evolution (Buhmann and Dreybrodt, 1985; Dreybrodt, 1996; Wackerbarth et al., 2010). Many recent studies have included

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aspects of the three themes (Baldini et al., 2006, 2008; Verheyden et al., 2008; Sherwin and Baldini, 2011). In a pioneering study of discharge from a karst aquifer in Mendip Hills, UK, Smart and Friederich (1986) determined that for cave drips with low recharge rates, flow within the aquifer is predominantly vertical and slow through the matrix (seepage). However, with increasingly higher drip rates, flow switches recharge to vertical shafts (fracture) and overflow behavior was observed as rapid responses to rainfall events. An understanding of the variation of flow routes of speleothem-forming dripwaters would aid in the interpretation of paleoclimate records.

Setting

Culverson Creek Cave (CCC), Buckeye Creek Cave (BCC) and Lost World Caverns (LWC), in Greenbrier County, southeastern West Virginia (Fig. 1), were selected for a monitoring study for several reasons: 1) stalagmites from CCC and BCC have been used in numerous paleoclimate studies (Springer et al., 2008, 2009, 2014; Hardt et al., 2010; Buckles and Rowe, 2016), 2) the caves are located near one another with relative ease of access, and 3) the caves exhibit a wide range of morphologies and drip behaviors. These caves are formed within the Union Limestone Member (massive limestone with abundant chert and marine fossils) of the Greenbrier Group, which is Mississippian in age and is composed of interbedded limestone, shale, and sandstone (Dasher and Balfour, 1994). The Union Limestone ranges from 100 to 325 feet below the top of the Greenbrier Series and is notable due to its purity, containing 62–91 % of calcium carbonate with low amounts of magnesium carbonate (Reger and Price, 1926).

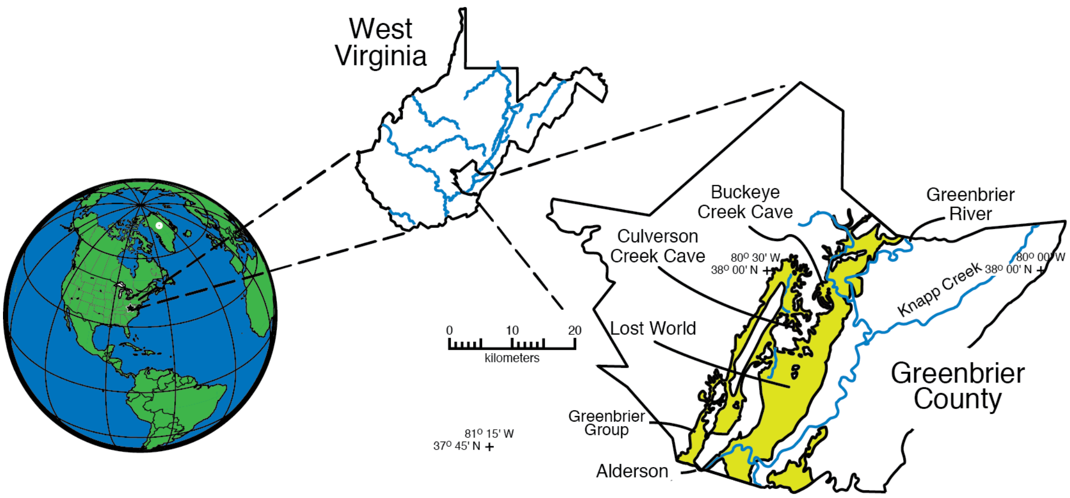

Figure 1. Regional map of Greenbrier County, West Virginia, showing the locations of Buckeye Creek Cave (37°58'33.37" N, 80°23'58.66" W), Culverson Creek Cave (37°56'11.15" N, 80°25'23.51" W), and Lost World Caverns (37°49'56.94" N, 80°26'47.53" W) in the Greenbrier Group.

CCC is a large, shallow cave system with multiple entrances, though only the portion of the cave used in this study (Peterbilt Passage) is shown (Fig. 2). The nearest entrance to the monitoring station is called the SSS entrance, which is a small, stream passage that is prone to flooding during periods of extended precipitation or snowmelt.

BCC is a large cave system with multiple, horizontal networks above the basal Buckeye Creek stream passage, and is accessed through the Buckeye Creek entrance (Fig. 3). This cave system is also prone to flooding, with the narrow canyon (located approximately 250 m from the entrance) and the near-siphon, Watergate Sump, being especially sensitive to rises in water level. Two monitoring stations were established, with Station 1 located in the basal stream passage to the east of the canyon, and Station 2 further back in the cave on the secondary level. Periodic flooding of the Watergate Sump proved to be a significant barrier to accessing Station 2.

LWC, formerly Grapevine Cave, is a heavily decorated cave located approximately 16 km from the entrance to BCC (Fig. 4). LWC has two main sections: the commercial section and the wild section, which are separated by a narrow passage of breakdown rubble. LWC receives tourists year-round, and the commercial section is frequented by visitors daily. The wild section is used for cave tours, though on a less frequent basis. LWC was ideal for an examination of the intra-cave variability in dripwater frequency and hydrochemistry for this monitoring study because it is accessible year-round, not prone to flooding, and has a wide variety of speleothem formations and drips. However, it was less ideal for CO_2 measurements due to the unquantified, anthropogenic contribution of year-round visitors and artificial ventilation at the entrance to the commercial section.

Methods

In August 2011, surficial and cave monitoring stations were established at the three study caves to record meteoric precipitation frequency, cave microclimate, and the drip frequency and isotopic characteristics of dripwaters. Dripwater station locations were chosen to represent the variability of drip behaviors present in each cave. Trips to the study

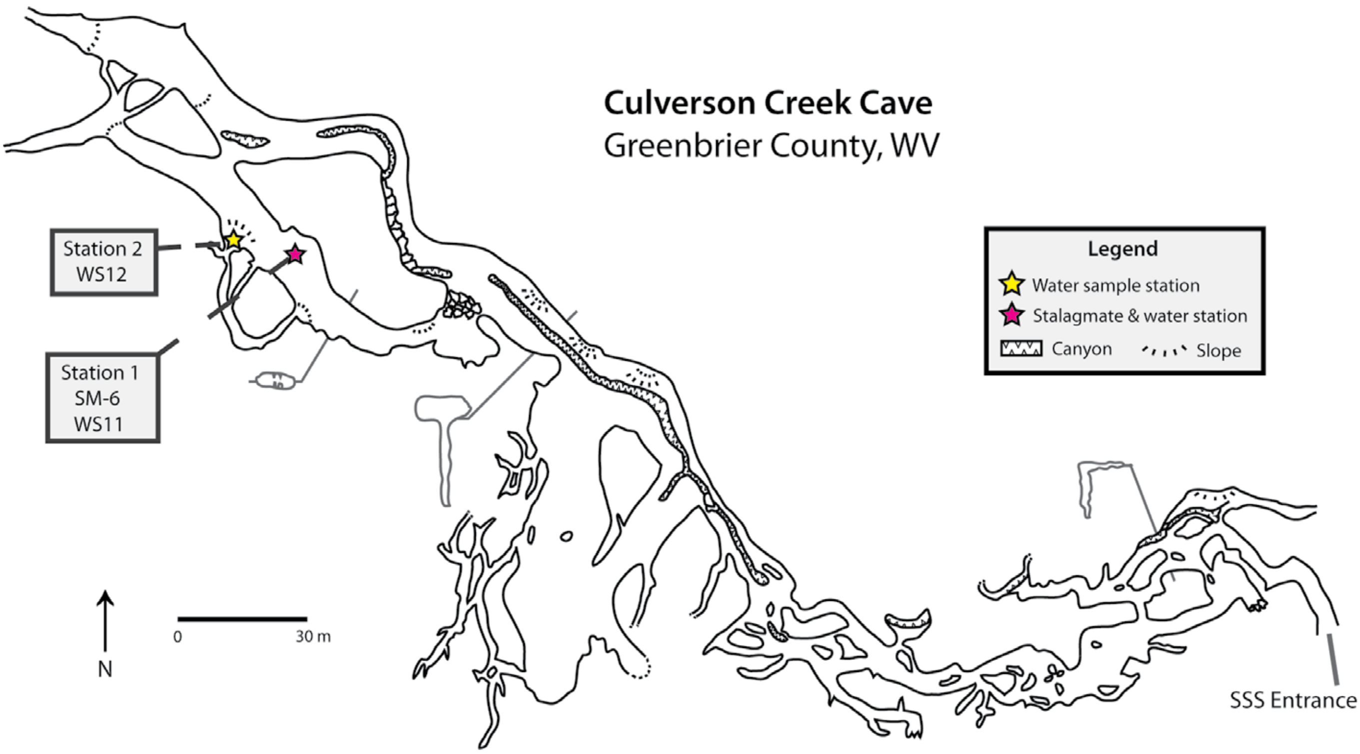

Figure 2. Map of Culverson Creek Cave, Greenbrier County, W.Va., with monitoring stations labeled (SM = Stalagmite; WS = Water Sample). Modified from map published in Dasher and Balfour, 1994.

caves were undertaken approximately every three months during the 2.5-year period (August 2011to December 2013) to retrieve data from the continuous data loggers, obtain discrete CO_2 measurements, and obtain water samples for isotopic analysis.

Cave temperature and relative humidity were measured continuously in each of the caves over the study period at 30-minute intervals with EasyLogger USB RH/Temp loggers, manufactured by Lascar Electronics, UK that recorded

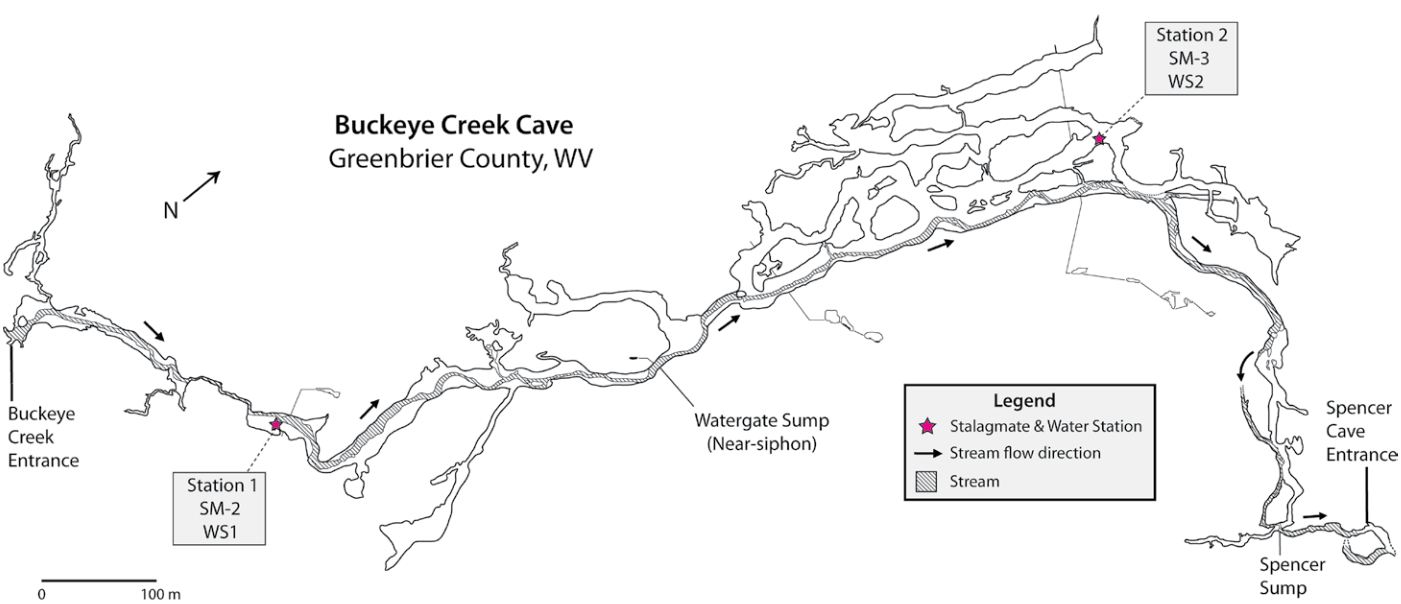

Figure 3. Map of Buckeye Creek Cave, Greenbrier County, W.Va. Modified from original survey sketches (West Virginia Association for Cave Studies), with monitoring stations labeled (SM = Stalagmite; WS = Water Sample).

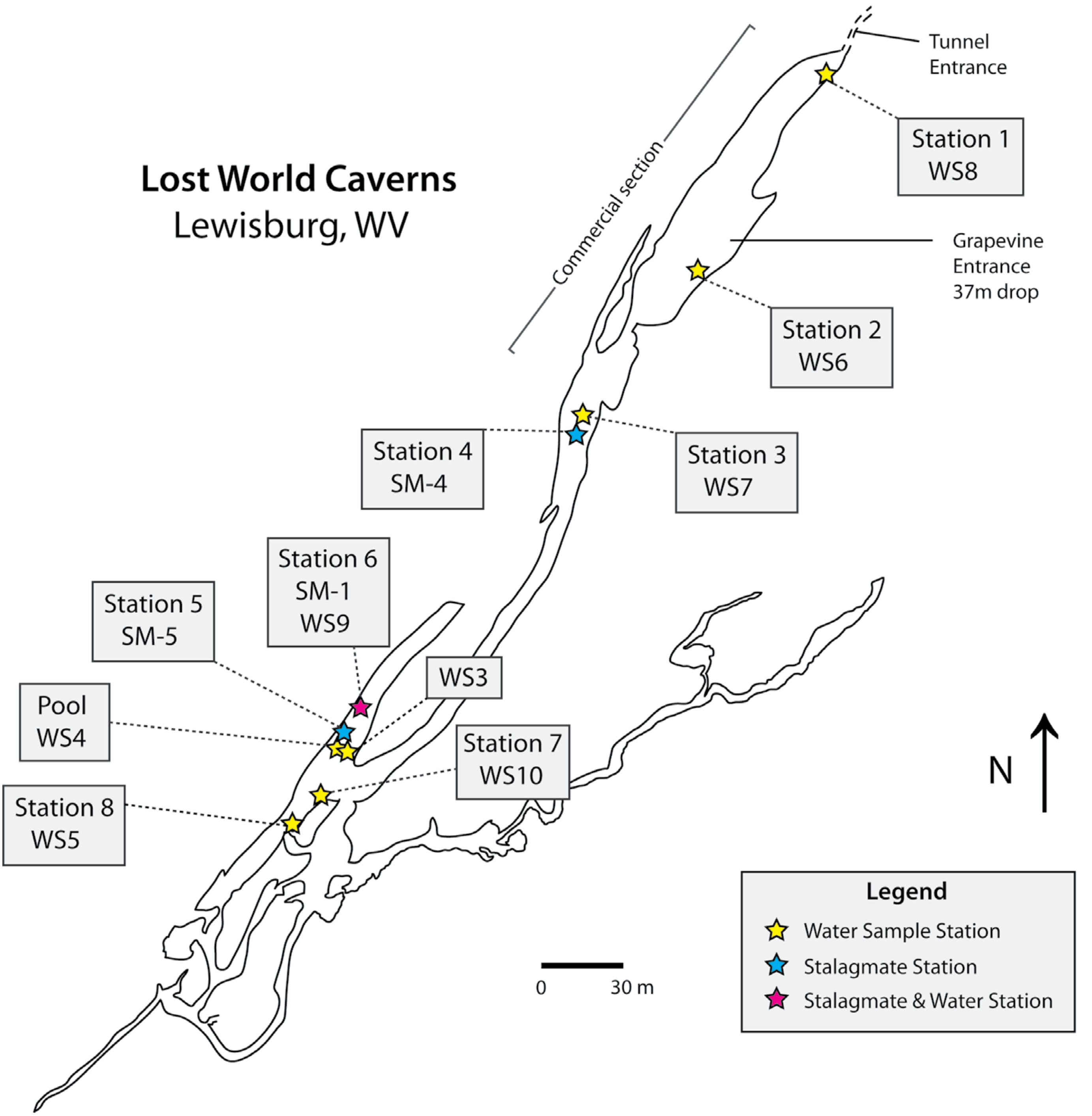

Figure 4. Map of Lost World Caverns, Lewisburg, W.Va., with monitoring stations labeled (SM = Stalagmite; WS = Water Sample). West Virginia Association for Cave Studies.

values at 1.0 degree and 0.5 % increments. Cave air CO_2 concentrations were measured during each of the sampling trips using a 0 to 10,000 ppm K33-ELG data logger, manufactured and calibrated by Dataq Instruments.

During each of the sampling trips, two visits to each of the study caves were to obtain enough dripwater for multiple analyses. Throughout the first set of cave trips, water catchment cups were deployed under drip sites (designated Water Sampling Stations, Table 1) and allowed to accumulate between 24 to 48 hours, after which dripwater samples were then collected. The relative humidity values remained high (99.7–99.99 %) throughout the entire study interval for all three caves. While potential, in-cave evaporation of dripwater is possible, simply due to the time necessary to collect enough dripwater, headspace was minimized in water sampling containers to reduce the possibility of evaporation of waters in transit.

Table 1. Dripwater source characteristics for WS1 – 12 (water sample) from Buckeye Creek Cave (BCC), Culverson Creek Cave (CCC), and Lost World Caverns (LWC) in southeastern West Virginia, USA.

Cave	Sample	Description	Notes
BCC	WS1	Stalactite-fed	Shared with Station 1 (SM-2)
	WS2	Stalactite-fed	Shared with Station 2 (SM-3)
LWC	WS3	Stalactite-fed	High-rate drip on side of large flowstone
	WS4	Pool water	
	WS5	Stalactite-fed	Periodically inactive/very slow drip
	WS6	Stalactite-fed	
	WS7	Stalactite-fed	
	WS8	Stalactite-fed	High-rate drip on side of large stalagmite
	WS9	Fed by soda straw	Soda straw approx. 30 cm in length
	WS10	Stalactite-fed	
CCC	WS11	Fed by collection of stalactites	
	WS12	Fed by collection of soda straws	

Upon collection, dripwater samples were stored in VWR high-density, polyethylene bottles. On several occasions some of the samples did not accumulate enough water to allow complete analyses to be performed. Isotopic analyses were performed at Texas State University. $\delta^{18}O$ and δD were measured using a Los Gatos Research Liquid Water Stable Isotope Analyzer (Model 908-0008), and are reported relative to the V-SMOW (Vienna Standard Mean Ocean Water) laboratory standard, with accuracies of ±0.3 ‰ for δD and ±0.1 ‰ for $\delta^{18}O$.

Figure 5. Set-up of Stalagmite monitoring station SM-4; temporary platforms for Stalagmite drip loggers were built with aluminum foil onto actively-growing stalagmites for the study duration.

Meteoric precipitation and cave dripwater frequency were monitored using Driptych Pluvimate and Stalagmite drip-frequency acoustic loggers with a 10-minute interval. One Pluvimate was placed at the surface of LWC and one at CCC (BCC is within 5 km, so the logger provides surface precipitation data relevant to both CCC and BCC). Six stalagmites were installed on top of actively-growing stalagmites (two in BCC, three in LWC, and one in CCC), under drips that exhibited different behaviors, in an effort to document a variety of dripwater responses to surface precipitation events.

Estimating the amount of meteoric water infiltrating the cave is important, as the effects of evapotranspiration can be substantial. This is accomplished through the calculation of Water Excess (*WE*), which serves as an indicator for the amount of infiltration. *WE* was calculated for Lewisburg, W.Va. (Genty and Deflandre, 1998) $WE = R - ETP$ [mm/month] where R is the total rainfall per month (mm) and ETP is the estimated monthly evapotranspiration, which was calculated using the Thornthwaite method (Thornthwaite, 1954) $ETP = 16(10\theta/I)^{a}F(\lambda)$ [mm/month] where θ = monthly temperature in degrees C; $a = (6.75 \times 10^{-7})I^{3} - (7.71 \times 10^{-5})I^{2} + (1.79 \times 10^{-2})I + 0.49239$; I = annual thermal index, which is the sum of the 12 monthly i indices; $i = (\theta/5)^{1.514}$; $F(\lambda)$ = latitude index (for 38 °N).

Table 2. Cave temperature, relative humidity, and CO2 measurements during sampling trips for the study period. Sampling sites were the commercial and wild sections of Lost World Caverns (LWC), Culverson Creek Cave (CCC), and Buckeye Creek Cave (BCC).

Location	Date	Temp., °C	RH, %	CO_2, ppm
LWC (Commercial)	8/23/2011	11.67	100	3654
	10/22/2011	11.67	100	2492
	12/29/2011	11.67	100	955
	3/12/2012	11.67	100	941
	6/18/2012	11.67	99.5	1635
	10/2/2012	11.67	99.5	1147
	1/15/2013	11.67	99.5	1424
	8/10/2013	11.67	100	3011
	12/7/2013	11.67	99.5	1380
	Average	11.67[a]	99.9[a]	1848.78
	Std. Dev.	0[a]	0.24[a]	973.69
LWC (Wild)	8/23/2011	11.67	100	1746
	10/22/2011	11.67	100	2673
	12/28/2011	11.67	100	2010
	3/12/2012	11.67	100	1461
	6/18/2012	11.67	99.5	2169
	10/2/2012	11.67	99.5	2500
	1/15/2013	11.67	99.5	1614
	8/10/2013	11.67	100	4745
	12/7/2013	11.67	99.5	1379
	Average	11.67[a]	99.9	2255.22
	Std. Dev.	0[a]	0.24	1035.01
CCC	8/22/2011	11.67	100	640
	10/22/2011	11.67	100	746
	1/4/2012	11.67	100	999
	3/14/2012	11.67	100	1180
	6/22/2012	11.67	99.5	826
	9/29/2012	11.67	100	557
	1/4/2013	12.23	99.5	693
	8/11/2013	12.23	99.5	1341
	12/7/2013	...	...	...
	Average	11.83[a]	99.97[a]	872.75
	Std. Dev.	1.09[a]	0.13[a]	276.21
BCC	8/21/2011	11.11	100	634
	10/22/2011	11.11	100	785
	1/4/2012	10.56	100	1002
	3/14/2012	10.56	100	1293
	6/22/2012	10.56	100	1077
	9/30/2012	10.00	100	1158
	1/4/2013	10.00	100	1280
	8/11/2013	9.44	100	1857
	12/7/2013	...	...	...
	Average	10.44[a]	100[a]	1135.75
	Std. Dev.	1.0^{5}a	0[a]	370.78

[a] Indicates values calculated from larger dataset.

Results

The microclimate monitoring results for the studied caves confirm very humid, temperature-stable environments. The average surface temperature for the region (Lewisburg, W.Va.) over the study interval was 10.6 °C, with a seasonal range of 10 °C (Menne et al., 2012; NOAA National Climatic Data Center), which falls within the temperature range of the studied caves (9.44 to 11.67 °C). While it is well established that temperatures in the interior of caves generally represent the annual surface temperature of the region (Poulson and White, 1969), this is an important aspect in speleothem paleoclimatology as the $\delta^{18}O$ of speleothem calcite is governed by the isotopic composition of the dripwater and the cave temperature (Lachniet, 2009). The average temperature and relative humidity measurements of the three caves were highly consistent year-round (Table 2).

Temperatures in BCC were slightly lower and relative humidity slightly higher than the other two caves, both likely due to the streamflow of Buckeye Creek through BCC. The low sensitivity of these instruments (recording only whole temperature unit increments (1.0 °C) and 0.5 % steps for relative humidity values) made them less than ideal for cave monitoring studies, as slight seasonal variations would not be recorded.

Carbon dioxide concentrations were obtained as discrete measurements during the water sampling trips (Fig. 6). Minor variability for CCC and BCC was observed, with LWC exhibiting the widest range of values. The CO_2 values range from 941 to 4,745 ppm for LWC, 557 to 1,341 ppm for CCC, and 634 to 1,857 ppm for BCC. The

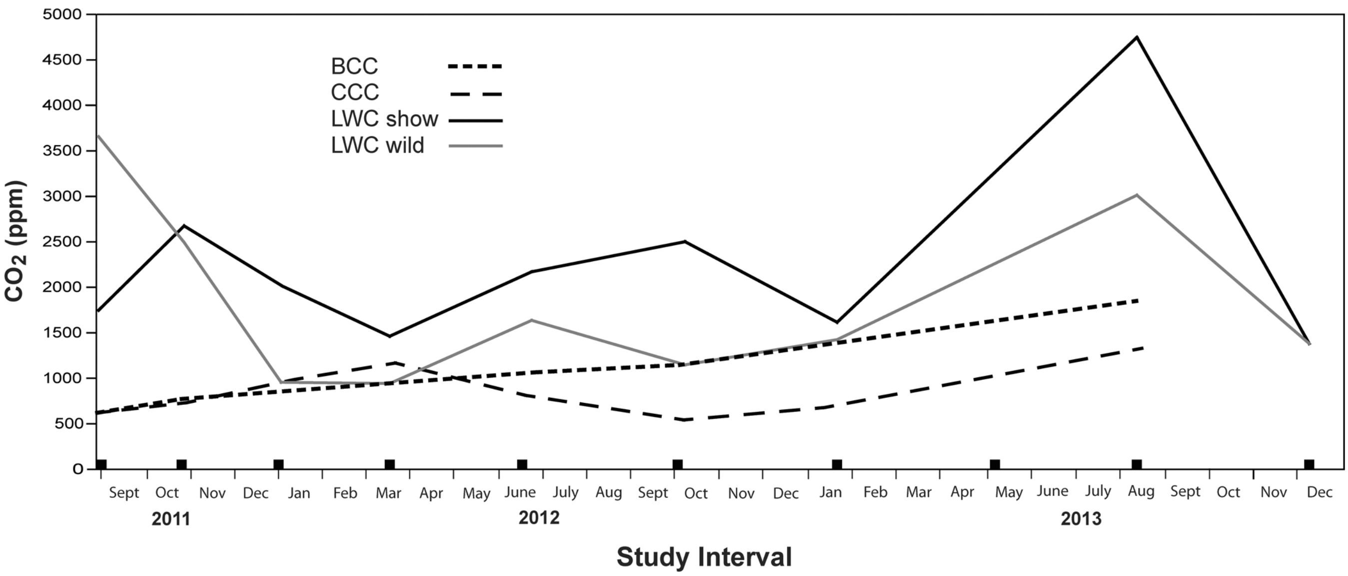

Figure 6. Periodic CO2 concentration values (ppm) for Buckeye Creek Cave (BCC), Culverson Creek Cave (CCC), and the show and wild sections of Lost World Caverns (LWC). Measurements were obtained during sampling trips (black boxes) which occurred approximately every three months during the study interval from August 2011 to December 2013. Note: values for BCC and CCC were not obtained during the December 2013 trip due to flooding.

discrete CO_2 measurements taken at each of the caves during each sampling trip permitted brief glimpses into the seasonal ventilation cycle.

CCC had the highest values in March 2012 and August 2013, but was the lowest overall, with a maximum of 1,341 ppm. Surprisingly, BCC displayed a linear trend over the study interval and also experienced the maximum of 1,857 ppm in August 2013. LWC, a show cave with year-round visitors, had the highest CO_2 concentrations with a maximum of 4,745 ppm, though it is impossible in this study to separate the natural and anthropogenic components.

Pluvimate and Stalagmite drip logger results are shown for the monitoring interval for CCC (Fig. 7), BCC (Fig. 8), and LWC (Fig. 9), as compared to monthly instrumental climate data from Lewisburg, W.Va. (ncdc.noaa.gov). The drip-logger frequency data can be found in supplemental data. The objective for the drip-frequency loggers was to compare high-resolution surface, meteoric precipitation frequency to several cave drips in an attempt to characterize the drip behavior and flow paths. This objective was met with varying degrees of success as several difficulties were experienced, including software/hardware failure, inaccessible instrumentation (i.e., flooding and sumped passages), and harsh-climate effects on the surface loggers, which resulted in gaps to monitoring data (dashed lines, Figs. 7–9). Additionally, the funnels covering the Pluvimate loggers were occasionally clogged with debris (e.g., leaf litter, wasp nests), as well as ice in some winter months. Because of these problems, a qualitative comparison is more appropriate for the drip frequency results.

For CCC, surface temperature and rainfall records for the region (Fig. 7a, b) show a wet spring and dry summer for 2012, and both show a wet spring and summer for 2013, as illustrated by the several intense rainfall events (>5k counts) recorded by PM-2, which occurred from June 2013 to August 2013 (Fig. 7c). *WE* was calculated for this region (Fig. 7d; note inverted axis to align with Fig. 7c) (Genty and Deflandre, 1998). During months when ETP (mm) exceeded precipitation (mm), it is assumed that no infiltration occurred. June 2012 to August, 2012, as well as July 2013 and October, 2013 were such months, when *WE* calculations produced negative results (exhibited as zero on Fig. 7d for ease of display) and can be considered zero as water excess.

WE is an important consideration in understanding the cave drip frequency and response to precipitation events. For example, the surface precipitation (Fig. 7c) during the months of June 2013 to August 2013 show many substantial precipitation events. However, the increase in evapotranspiration during these summer months meant that *WE* was minimal during this period, as opposed to the winter months during the study interval. When the highest *WE* values were calculated SM-6, the Stalagmite in CCC exhibited only a small response to surface precipitation events, as drip counts increased from two to three drips per 10-minute recording intervals, corresponding to a discharge of 0.014 to 0.028 mL/min, based on the typical stalactite water-drop volume of 0.14 mL, as reported by Genty and Deflandre, 1998 (Fig. 7e). The relationship between water-drop volume and the opening from which it drops was established by Collister and Mattey (2008). However, measurements of stalactite and soda straw apertures were not possible in this study due to inaccessibility.

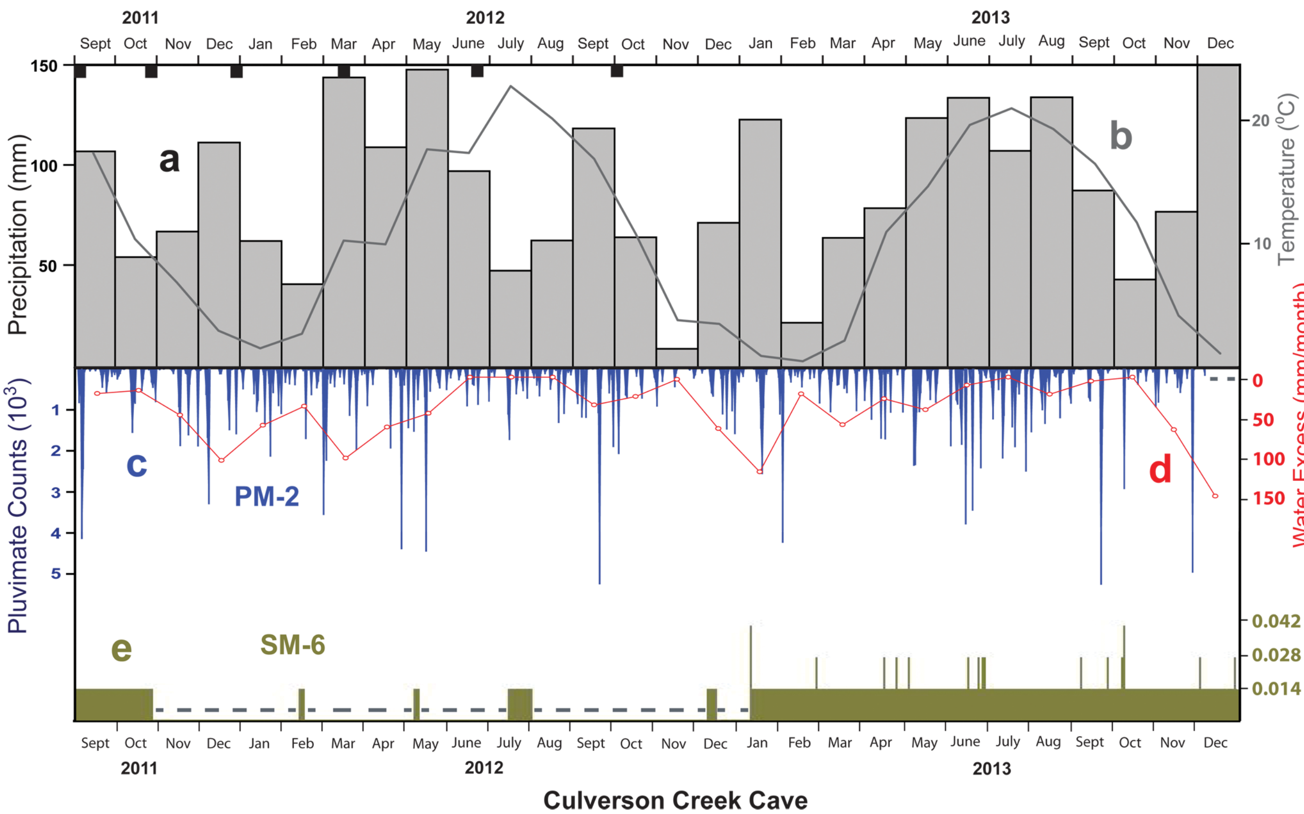

Figure 7. Drip frequency monitoring results for Culverson Creek Cave, where a) monthly precipitation totals (mm) (bar graph), and b) monthly temperature averages (°C) for Lewisburg, W.Va. (ncdc.noaa.gov); c) surface meteoric, precipitation drip-frequency logger data (PM-2) are shown as daily drip counts; d) water excess (mm/month) for Lewisburg, W.Va; and e) cave dripwater discharge (mL/min) of drip-frequency logger (SM-6). Black boxes on the top time axis denote cave dripwater sampling periods. Dashed lines indicate gaps in data.

The two Stalagmite loggers in BCC (SM-2 and SM-3) displayed very different responses to the surface precipitation (PM-2) events (Fig. 8). SM-2 (Fig. 8e) was especially responsive to surface precipitation events during the months of December to June of both 2012 and 2013. From June to November of the same years, however, the drip rate decreased to a baseline value and became largely unresponsive to precipitation events. The quiescence of SM-2 cave drips during the early summer is likely due to both a decrease in rainfall and an increase in evapotranspiration, which results in minimal infiltration of water into the epikarst. SM-3 (Fig. 8f) displays seepage flow behavior and responded to drips most similarly to SM-6 (Fig. 7e) and never exceeds three drips per interval. The data gaps for SM-3 are due to site inaccessibility of the station during sampling trips for data retrieval.

The cave drip frequency results for LWC exhibit a wide range of behaviors. The surface precipitation logger (PM-3) recorded quite similar results (Fig. 9c) as PM-2, with the main difference being the presence of two, brief data-gap intervals in 2013. SM-1 was highly responsive to surface precipitation events (Fig. 9e), with a high drip volume until late November 2012. Then, the drip suddenly changed behavior to a low-volume drip with a baseline of approximately 16 drips per sampling interval, corresponding to a discharge of 0.224 mL/min (Fig. 9f). This sudden change is not believed to be an instrumental or placement error as SM-1 was tested for functionality and correct placement. These test results demonstrated that the equipment was functioning properly and recording drips in the correct location. These data are, therefore, considered to reflect the changing behavior of the drip throughout the study interval. The drip data for SM-1 continued at this low-flow, relatively unresponsive state for the rest of the study.

Drip logger SM-4 displays seasonal behavior (Fig. 9g) similar to that of SM-2 (Fig. 8e), where the drip is most active between the winter to early summer months and decreases to a baseline flow of two to three drops per sampling interval, corresponding to a discharge of 0.028 mL/min to 0.042 mL/min during the rest of the year. SM-4 experienced the maximum drips during the March 2012 to May 2012-period, coincident with the period of highest rainfall of that year. Interestingly, the large rain event, which occurred in late September 2012, did not bring SM-4 above the baseline flow, likely due to the relatively dry state of the epikarst from low infiltration during the summer months (low rainfall and high

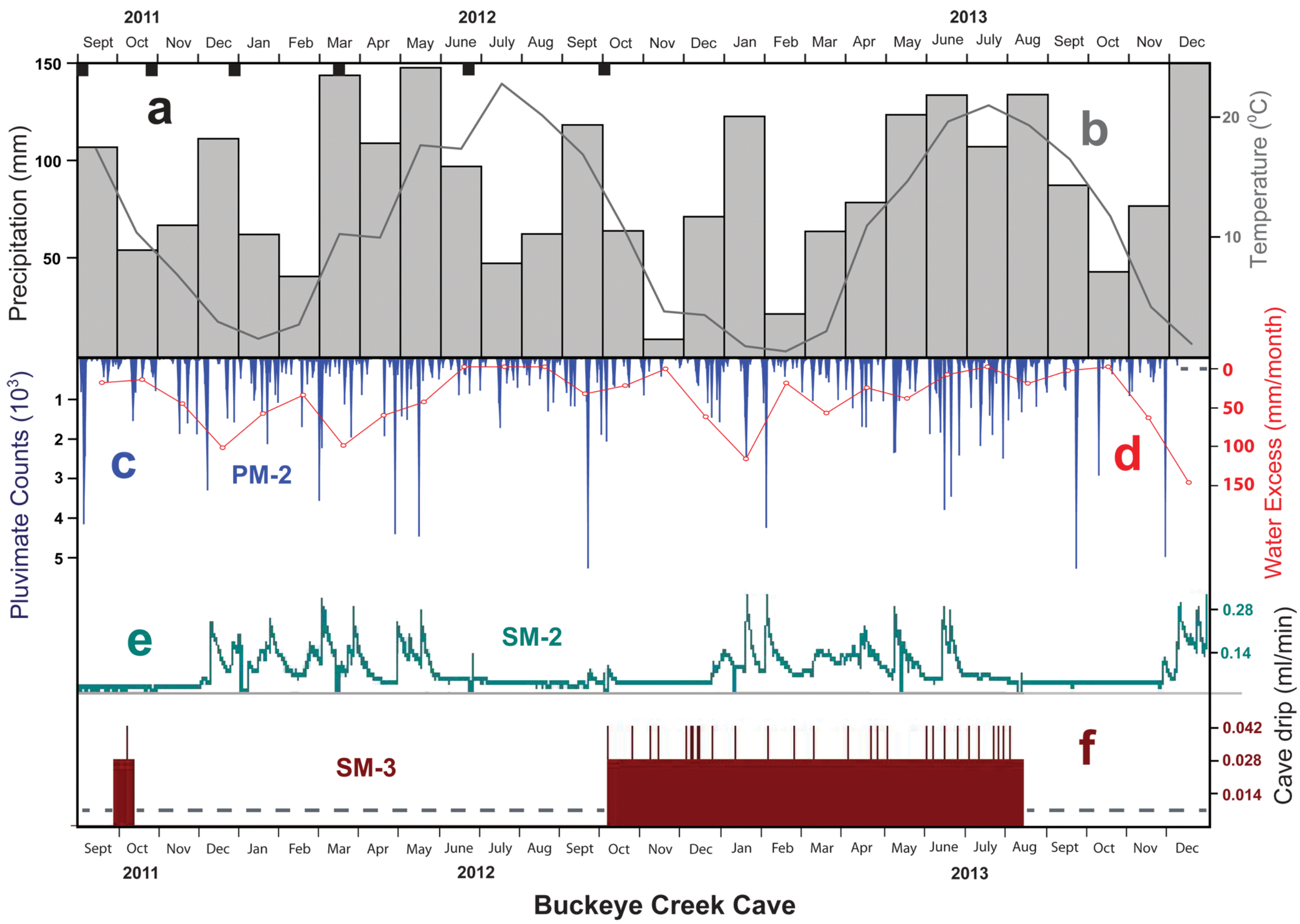

Figure 8. Drip-frequency monitoring results for Buckeye Creek Cave, where a) monthly precipitation totals (mm) (bar graph) and b) monthly temperature averages (° C) for Lewisburg, W.Va. (ncdc.noaa.gov); c) surface meteoric precipitation drip frequency logger data (PM-2) are displayed as daily counts; d) water excess (mm/month) for Lewisburg, W.Va.; and e) cave dripwater discharge (mL/min) of drip-frequency loggers (SM-2); and f) SM-3. Black boxes on the top time axis denote cave dripwater sampling periods. Dashed lines indicate gaps in data.

evapotranspiration). The final drip logger, SM-5 (Fig. 9h) displayed seepage-flow behavior similar to both SM-6 (Fig. 7e) and SM-3 (Fig. 8f). There were unknown instrumental and/or possible user error problems with SM-5 and SM-6, which resulted in gaps of the recorded data at random periods (however, the gaps in SM-3 are due to site inaccessibility).

Isotope ($\delta^{18}O$ and δD) values of water samples were obtained for each sampling trip (Fig. 10, see supplemental data) and are compared to the Global Meteoric Water Line (GMWL) (Craig, 1961) and Local Meteoric Water Line of the closest Global Network of Isotopes in Precipitation (GNIP) station in Coshocton, Ohio (IAEA/WMO, 2016). If dripwaters retain the isotopic signature of their parent meteoric waters, then it follows that these values should plot near those of the LMWL (see Discussion).

The comparison of cave dripwaters to the GMWL (Fig. 10) allows for the identification of possible fractionation processes from surface to cave dripwaters, as the values would presumably be identical under equilibrium conditions. This is the case with most of the dripwater samples, which fall within the range of the meteoric waters used to plot the Local Mean Water Line (LMWL, Coshocton, Ohio GNIP station, ncdc.noaa.gov). The two dripwater batches that deviate from this line are March 2012 and October 2012 (a few samples overlap with October 2011 as well). The October 2012 and October 2013 isotope values are the most positive, falling off the LWML to the side, typical of waters that have experienced evaporative loss. The dripwaters sampled in both October 2012 and October 2013 likely comprised waters that had accumulated in the epikarst during the summer months, which had experienced significant evaporation in the soil zone.

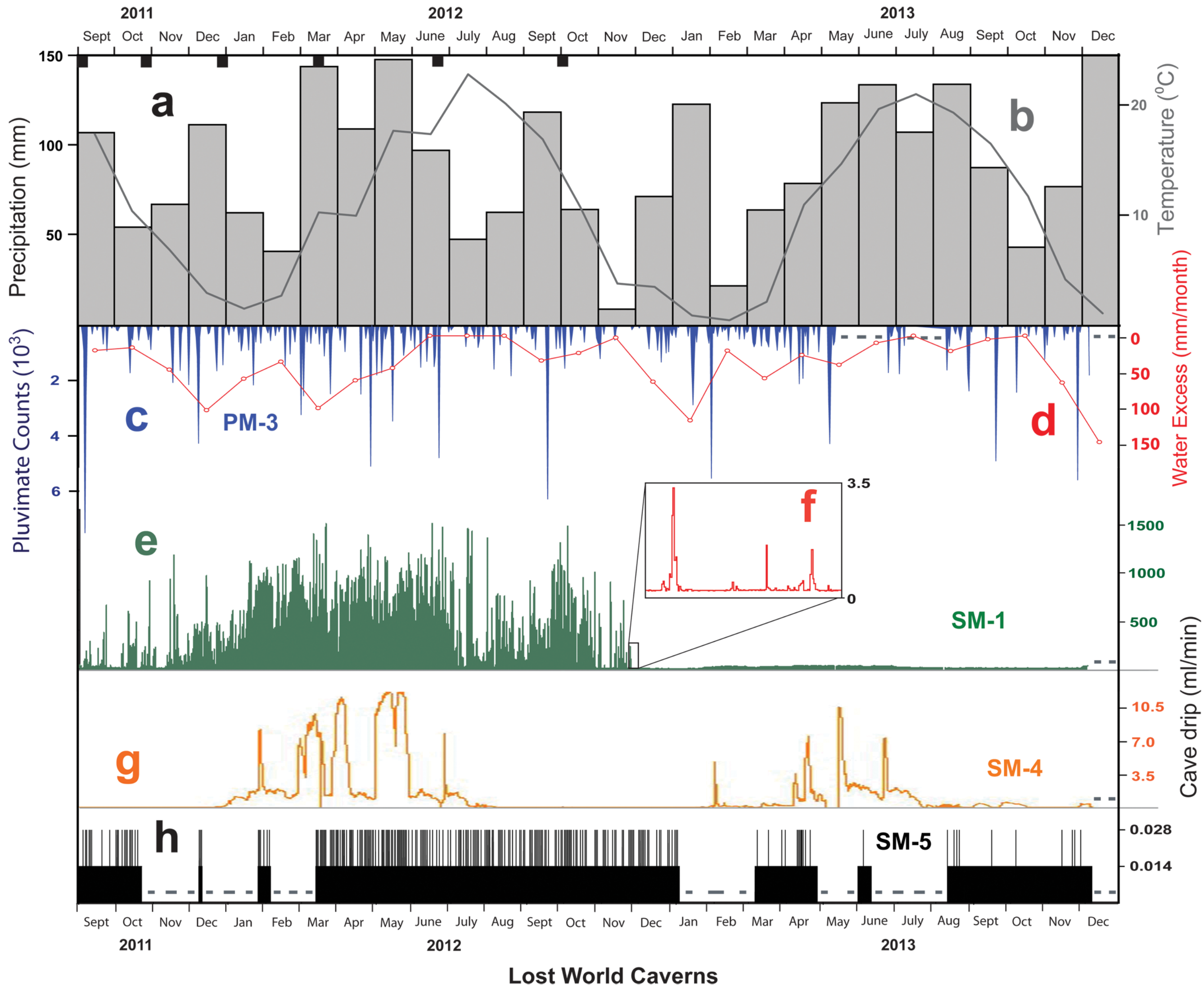

Figure 9. Drip frequency monitoring results for Lost World Caverns, where a) monthly precipitation totals (mm) (bar graph) and b) monthly temperature averages (° C) for Lewisburg, W.Va. (ncdc.noaa.gov); c) surface meteoric, precipitation drip-frequency logger data (PM-3) are displayed as daily counts; d) water excess (mm/month) for Lewisburg, W.Va; e) cave dripwater discharge (mL/min) of drip-frequency loggers (SM-1); f) inset for SM-1 (Note: scale); g) SM-4; and h) SM-5. Black boxes on the top time axis denote cave dripwater sampling periods. Dashed lines indicate gaps in data.

Discussion

Cave Drip Characterization

The stalagmite drip frequency data over the 28-month study interval recorded three primary drip behaviors in response to meteoric precipitation: no response, where the drip frequency is generally slow and unchanging throughout the year (SM-3, SM-5, and SM -6); seasonal response, where cave drips are only active (or more active) for part of the year (SM-2, SM-4); and highly responsive, where a strong relationship exists between meteoric, precipitation frequency and cave drip frequency (SM-1). The decrease in drip frequency of SM-1 that began in December 2012, and persisted until the end of the study, may represent flow-switching, where a very high-frequency drip becomes blocked and entirely or partially reroutes through a different outlet (Baldini et al., 2006).

The important role of *WE* in cave infiltration is emphasized in the results that display a seasonal response (SM-2, SM-4, Figs. 8 and 9), as the drips are most frequent during the winter to early summer months, when WE values are at their highest for the year. The large meteoric precipitation events that occurred during non-recharge months (Fig. 8c) do not produce a subsequent increase in cave drip frequency (e.g., the large rain event which occurred in late September 2013), like those which occur when *WE* values are high.

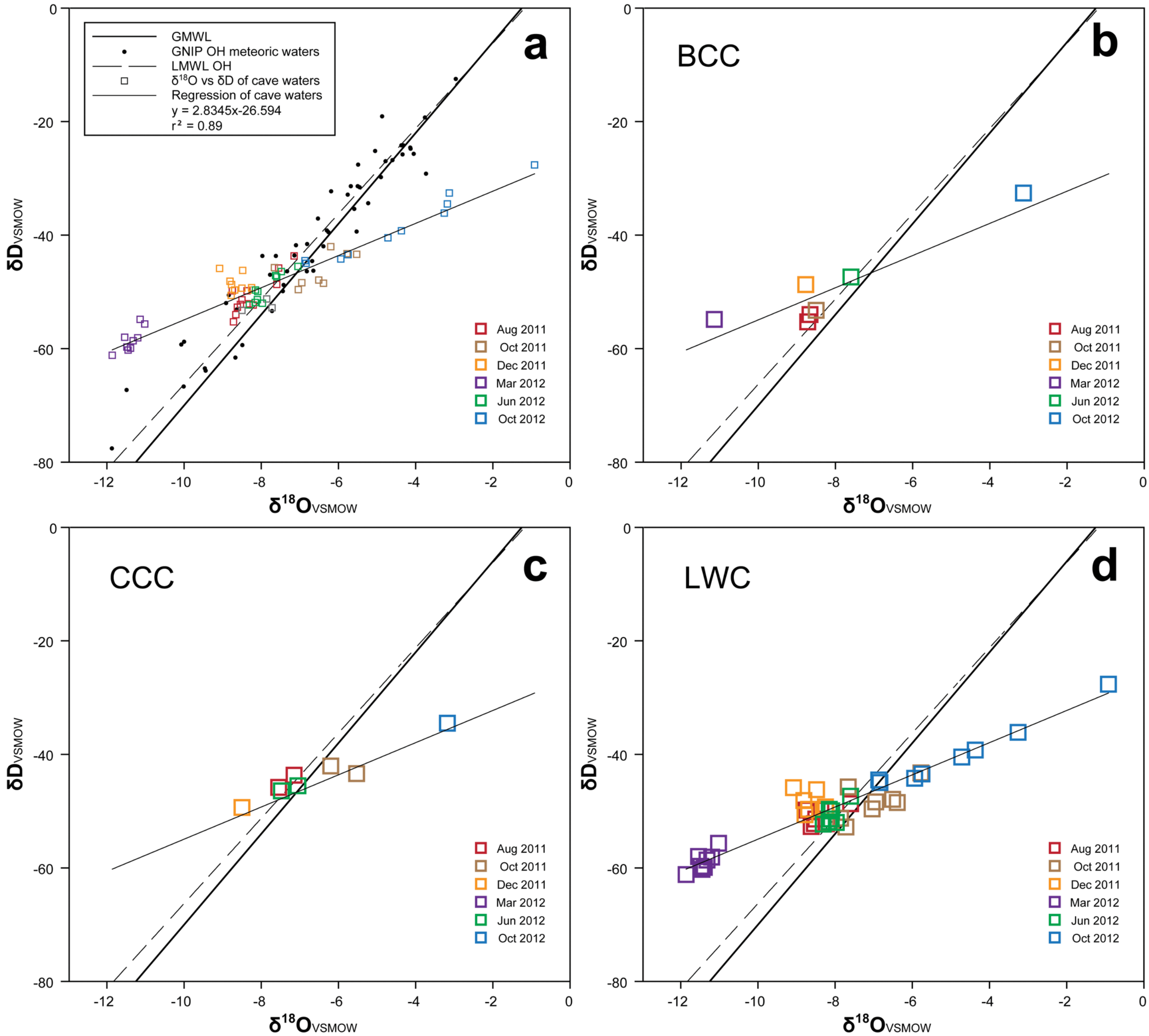

Figure 10. a) Cross-plot of cave dripwater sample δD and δ18O values standardized to VSMOW (squares; this study). Global Meteoric Water Line (GMWL) (thick black line) as δD = 8 × δ18O + 10 ‰ (Craig, 1961). Global Network of Isotopes in Precipitation (GNIP) of meteoric precipitation from closest station in Coshocton, Ohio (black dots), whose regression line provides the Local Meteoric Water Line (LMWL, dashed line) (y = 7.5096x + 8.8099; R2 = 0.9729), combined cave dripwater samples (this study) (y = 2.8345x − 26.594; R2 = 0.8900), b) cave dripwater samples from Buckeye Creek Cave; c) cave dripwater samples from Culverson Creek Cave; and d) cave dripwater samples from Lost World Caverns.

Cause of Low Dripwater Isotope Values for March 2012 Samples

The low δD and $\delta^{18}O$ isotope values of the March 2012 water samples are enigmatic, but are likely related to the anomalously-high rainfall in March 2012 (nearly twice the amount compared to March 2013). The cave dripwater samples were collected on March 12, 2012, 10 to 12 days after several substantial rain events that occurred from February 29, 2012 to March 2, 2012, as identified through pluvimate data. There are four scenarios that may account for these isotope values: the source of the moist air masses, which resulted in said rain events, was of polar or high altitude origin; the waters in the vadose zone had experienced significant evaporation resulting in kinetic, disequilibrium effects of the water vapor that could re-condense to dripwaters (Dansgaard, 1964); cave dripwater samples experienced substantial evaporation during the collection process; and the influx of the substantial amount of rain flushed out the wa-

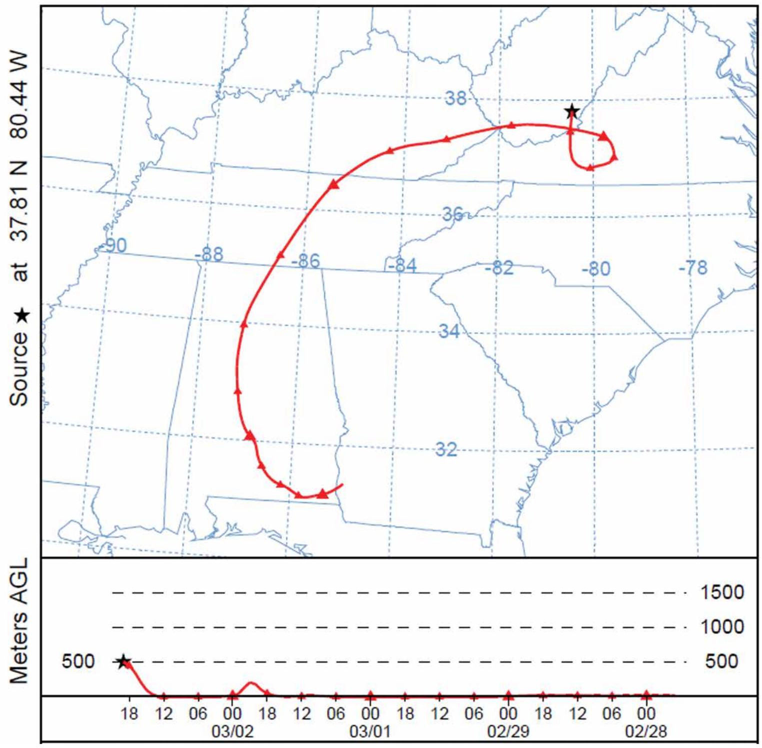

Figure 11. Hybrid Single Particle Lagrangian Integrated Trajectory Model (HYSPLIT), backward trajectory analysis for the study area during the interval of February 28 2012 to March 2, 2012 (Stein et al., 2015).

ters from the vadose zone that were comprised of meteoric precipitation, which had occurred during the cold winter months (December to February) of the preceding winter.

Scenario 1 can be tested using the back-trajectory analysis feature of the National Oceanic and Atmospheric Administration's (NOAA) Hybrid Single Particle Lagrangian Integrated Trajectory Model (HYSPLIT), which is used to calculate the trajectories of air parcels, utilizing archived weather data (Stein et al., 2015). A backward trajectory analysis was performed for the study area during the interval of February 28, 2012 to March 2, 2012, and this revealed that the air masses originated to the south of the study area at low altitudes (Fig. 11), which eliminates this scenario as a possible cause of the negative-dripwater isotope values.

Scenario 2 recognizes the possibility for kinetic, disequilibrium effects resulting from the evaporation of waters in the vadose zone. If re-condensed, the isotopic values of the resulting waters would be more negative. This scenario is unlikely to be the cause of the negative values of the March 2012 dripwater samples for two reasons. First, the water vapors, resulting from evaporation in the vadose zone, cannot be expected to remain in place and re-condense in-situ as the vadose zone is not a closed system. Second, the likelihood of this scenario is lessened by the fact that all dripwater samples from all three study caves exhibited similar negative isotopic values despite different vadose zone thicknesses and morphologies, and different drip behaviors. While evaporation and disequilibrium effects of waters in the vadose zone may occur under specific circumstances, it is highly unlikely that vadose zone evaporation during the winter months affected all three caves and all resulting dripwater samples to the same magnitude.

Scenario 3 probes the possibility that cave dripwater samples experienced substantial evaporation during the collection process. While this occurrence cannot be definitively ruled out, it is unlikely. All stalagmite loggers that were actively logging during the February 2012 to March 2012 interval (SM-1, SM-2, and SM-4) recorded relatively high drip rates, which minimized time for dripwater sample collection. The CO_2 (ppm) values measured during the March 2012 sampling period were 941 to 1,461 ppm. While CO_2 concentrations are typically lower in caves during the cold winter months due to seasonal ventilation effects, these values are likely not low enough to drive the evaporation of samples to such a degree for all three study caves.

Scenario 4 states that the influx of meteoric precipitation during the late February 2012 to early March 2012 period to the study region effectively flushed out the waters that had accumulated in the vadose zone during the preceding winter months. The meteoric precipitation falling in the cold winter months would be more negative and fall to the left of the GMWL (Dansgaard, 1964). Because all of the dripwater samples from the three caves had similar negative isotope values, this scenario is the most likely. While Scenarios 2 and 3 cannot be completely ruled out, it is unlikely that such specific circumstances would be active in all three study caves, affecting all of the dripwater samples to the same degree.

Implications for Using Speleothems for Paleoclimate Studies

This study highlights the wide range of concurrent drip behaviors that can be found in caves. From the frequency monitoring of six cave drips, one was shown to be highly responsive, two demonstrated a seasonal response, and the remaining three exhibited slow, exceedingly stable, year-round drip behavior. If these stalagmites were collected and sampled geochemically ($\delta^{18}O$, $\delta^{13}C$, trace metals, etc.) for the purpose of paleoclimate reconstructions, they would likely record very different geochemical records of the same time period simply because they are recording different aspects of the hydrologic system. For paleoclimate studies of long-term climate changes, the ideal stalagmites would be the result of slow, steady drip behaviors. While it is not feasible to perform multi-year cave monitoring research programs for every stalagmite utilized in paleoclimate studies, such a monitoring program would aid in the identification and collection of only the most appropriate and promising stalagmite samples. This conservative approach would be beneficial not only for the preservation of priceless cave formations, but it would also aid in the interpretation of the relationship between proxy values and meteoric precipitation.

Conclusions

The wide range of cave drip behaviors and isotopic values over this 28-month study highlight the dynamic nature of these systems, as well as the importance in understanding the geochemical implications of resulting speleothem calcite to paleoclimate reconstructions. The drip frequency results of the six Stalagmite loggers used in this study revealed one high-frequency drip that underwent flow-switching during the study (SM-1), two seasonal drips that were most active during the winter to early summer months (SM-2 and SM-4), and three seepage flow drips that were very slow and constant throughout the year (SM-6, SM-3, and SM-5). If stalagmites forming under these drips were used in paleoclimate reconstructions, they would likely preserve very different climate signals. SM-1 would be unsuitable as the high-frequency drip would likely dissolve more calcite than it deposited, as a small dissolution pit is present at the top of the stalagmite. The calcite laminae precipitating from the seasonal drips would likely be biased to the winter to early summer months, when most of the drips were recorded. The seepage drips, however, would most likely preserve a long-term climate signal with minimal seasonal bias and would be the most suitable for long-term paleoclimate reconstructions.

Most of the dripwater isotope values fall within the range of meteoric waters, as would be expected for mixed karst waters. However, two important sets of outliers are present in these data. March 2012 dripwaters present, as an isotopically-distinct group, that is likely the result of heavy rainfall infiltrating the vadose zone, and flushing out the isotopically-negative waters that had accumulated during the previous cold winter months. Dripwaters from October 2012 (and to a lesser extent, October 2011) likely represent heavily-evaporated soil waters from the summer months previous. These dripwater data allow for a greater understanding of the seasonal variations of isotope values, and aid in the identification of dripwaters that have undergone disequilibrium processes in the soil and epikarst zones.

While cave monitoring programs have inherent difficulties (time/financial commitment, instrument failure, etc.), they are essential in understanding the climatological implications of speleothem geochemistry. The prior monitoring and selection of stalagmites for paleoclimate reconstructions based on its drip characteristics would not only allow for a better understanding of what the geochemical proxies represent in the climate system but would also help to conserve stalagmites if only the most appropriate were collected.

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