

TEMPORAL VARIABILITY OF CAVE-AIR CO₂ IN CENTRAL TEXAS

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Abstract: The growth rate and composition of cave calcite deposits (speleothems) are often used as proxies for past environmental change. There is, however, the potential for bias in the speleothem record due to seasonal fluctuations in calcite growth and drip-water chemistry. It has been proposed that the growth rate of speleothem calcite in Texas caves varies seasonally in response to density-driven fluctuations in cave-air CO₂, with lower growth rates in the warmer months when cave-air CO₂ is highest. We monitored CO₂ in three undeveloped caves and three tourist caves spread over 130 km in central Texas to determine whether seasonal CO₂ fluctuations are confined to tourist caves, which have been modified from their natural states, and the extent to which cave-air CO₂ is controlled by variations in cave geometry, host rocks, cave volume, and soils. Nearly 150 lateral transects into six caves over three years show that CO₂ concentrations vary seasonally in five of the caves monitored, with peak concentrations in the warmer months and lower concentrations in the cooler months. The caves occur in six stratigraphic units of lower Cretaceous marine platform carbonate rocks and vary in volume (from 100 to >100,000 m³) and geometry. Seasonal CO₂ fluctuations are regional in extent and unlikely due to human activity. Seasonal fluctuations are independent of cave geometry, volume, depth, soil thickness, and the hosting stratigraphic unit. Our findings indicate that seasonal variations in calcite deposition may introduce bias in the speleothem record, and should be considered when reconstructing paleoclimate using speleothem proxies.

INTRODUCTION

It is important to understand the mechanisms that control speleothem growth and calcite composition. It has long been known that the concentration of CO₂ in cave air can affect the growth rate of speleothems (Holland et al., 1964), but until recently, the extent to which cave-air CO₂ fluctuations might introduce bias into the speleothem record was not fully appreciated (Fairchild et al., 2007). Recent studies in the United States (Banner et al., 2007; Wong et al., 2011), Austria (Spötl et al., 2005), and Ireland (Baldini et al., 2008) have demonstrated that there is potential for bias in the paleoclimate record due to changes in speleothem deposition rate and drip-water chemistry caused by cave-air CO₂ fluctuations.

A recent study of calcite growth rates in four central Texas tourist caves reveals that in three of the caves, calcite growth varies seasonally and is inversely correlated with cave-air CO₂ concentrations (Banner et al., 2007). In the caves that experienced growth-rate variations, calcite deposition peaked in the cooler months, when cave-air CO₂ concentrations were low, while in the warmer months, elevated cave-air CO₂ concentrations inhibited drip water degassing, resulting in a significant decrease or cessation of calcite deposition. Drip rate variations were not the primary control on seasonal fluctuations in calcite growth rate, but did account for site-to-site variability in the magnitude of calcite growth rate within individual caves. The tourist caves with variable growth rates were located

over a distance of 130 km, suggesting that the potential for a regionally extensive seasonal bias in the speleothem record exists. Such regional biases in speleothem proxies (e.g., seasonal growth-rate variations, isotopic shifts) might be incorrectly interpreted as a direct result of climate conditions, not as a result of speleothem deposition being affected by cave meteorology. Therefore, it is important to determine if seasonal cave-air CO₂ fluctuations in central Texas caves are confined to tourist caves, which are modified from their natural state and receive a large number of visitors, or if they are naturally occurring.

Seasonal CO₂ fluctuations in tourist caves may result from modifications to their natural connectivity with the surface atmosphere during their development for tourism, significant human visitation, or non-anthropogenic influences. Variations in non-anthropogenic factors, such as cave volume, stratigraphic unit, cave geometry, and soil thickness, may also influence the extent and timing of CO₂ fluctuations. The hypothesis that seasonal CO₂ fluctuations in central Texas caves are regional in extent and are not unique to tourist caves was tested.

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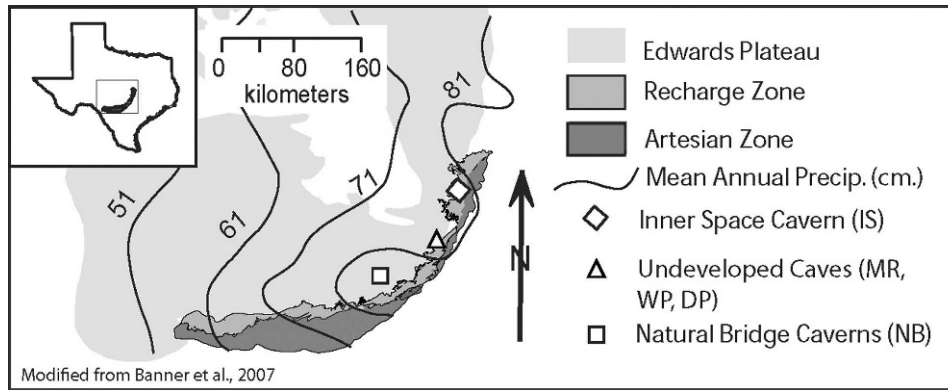


Figure 1. Map of Edwards Aquifer and cave locations on the Edwards Plateau in central Texas, USA. Note the undeveloped caves are located within 5 km of each other and are depicted as a single triangle. The two parts of Natural Bridge Caverns are adjacent and shown by a single symbol. Average annual precipitation in centimeters is shown as contours.

The timing and magnitude of CO₂ fluctuations in three undeveloped caves, District Park, Whirlpool, and Maple Run, were compared with those measured in the tourist caves with variable speleothem growth rates that were studied by Banner et al. (2007), Natural Bridge North Cavern, Natural Bridge South Cavern, and Inner Space Cavern. The undeveloped caves chosen for comparison with the tourist caves are centrally located between the tourist caves, are formed in similar stratigraphic units as the tourist caves, are overlain by similar soil and vegetation, receive similar rainfall amounts, experience similar surface temperature fluctuations, and receive little visitation outside of the monitoring trips (Fig. 1; Table 1).

STUDY AREA

The study area is located near Austin, Texas, on the Edwards Plateau, which is composed of karstified Lower Cretaceous marine carbonates overlain by a thin calcareous clay soil that supports oak and juniper savannah. Soils across the study area are thin mollisols (typically < 30 cm) and commonly contain limestone fragments sourced from the underlying bedrock (Cooke, 2005). The undeveloped caves are overlain by stony clay loams, Inner Space is overlain by silty clays and stony clays, and the two parts of Natural Bridge are overlain by extremely stony clays and gravelly clay loams (U.S. Department of Agriculture, Web Soil Survey).

All study caves, with the exception of Natural Bridge North and Natural Bridge South, are located within the Edwards Limestone, an Early Cretaceous marine limestone unit with interbedded dolomitic layers. Within the study area, the Edwards Group can be subdivided into several hydrostratigraphic units with different structural and hydrologic characteristics (Fig. 2) (Maclay and Small, 1976; Small et al., 1996). The Natural Bridge caves are located within the interbedded limestone and dolomitic units of the upper Glen Rose and lower Walnut

formations, which are also Early Cretaceous in age. Those two caves are adjacent to each other, not well connected, and have separate entrances. More detailed descriptions of the hydrology and morphology of Inner Space Caverns and the Natural Bridge caves is given by Musgrove et al. (2001), Musgrove and Banner (2004), and Banner et al. (2007).

The entrances of Natural Bridge North and Natural Bridge South are sealed by double glass doors that are only opened when tour groups enter and exit. During the development of Inner Space Cavern, an entrance tunnel approximately 4 m in diameter was excavated, and it remains unsealed. To increase visitor comfort, man-made ventilation shafts equipped with fans were installed in all three tourist caves. Ventilation fans are manually controlled and are typically used during the daytime hours in the summer months.

CONTROLS ON CAVE-AIR CO₂

CAVE VENTILATION

Cave ventilation is an important control on cave-air CO₂ concentrations, both seasonally and on shorter timescales, and is dependent on multiple factors, including fluctuations of the outside air temperature and barometric pressure, cave geometry and prevailing winds (e.g., Villar et al., 1985; Fernández et al., 1986; Hoyos et al., 1998; Buecher, 1999; Bourges et al., 2001; Spötl et al., 2005; Baldini et al., 2006; Denis et al., 2005; Bourges et al., 2006; Baldini et al., 2008; Kowalczyk and Froelich, 2010). At mid latitudes, density differences between cave and outside air caused by seasonal temperature variability exert a first order control on the seasonal ventilation of caves (James and Banner, 2007). In many caves, air temperature is near the mean annual surface temperature and varies by only a few degrees over the seasons (Moore and Sullivan, 1997), and thus, cave ventilation is primarily controlled by surface air temperature and changes in barometric pressure

Table 1. Characteristics of monitored caves and overlying soils.

Cave name	Hydrostratigraphic Unit	Cave volume (m ³) <accuracy>	Soil thickness (cm) <stdev>	USDA soil type	USDA soil series	Tourist cave	Stormwashed debris	Min/Max CO ₂ (ppm)	R ² average CO ₂ vs. distance from entrance	Transect length (m)
Inner Space Cavern (IS)	Cyclic and Marine Members of Edwards Group	75,000 <1,000>	26.2 <10.2>	Silty clays stony clays	Eckrant	Yes	None	400/7,600	0.87	450
Natural Bridge Cavern North (NBN)	Upper Glen Rose and Walnut Formation	250,000 <10,000>	23.1 <20.9>	Stony clay, gravely clay loam, exposed bedrock	Comfort & Eckrant Rock Complex	Yes	None	370/9,500	0.79	200
Natural Bridge Caverns South (NBS)	Upper Glen Rose and Walnut Formation	150,000 <2,000>	32 <17.6>	Stony clay, gravely clay loam, exposed bedrock	Comfort & Eckrant Rock Complex	Yes	None	470/38,000	0.25	400
Maple Run Cave (MR)	Leached and Collapsed Member, Grainstone Member, and Regional Dense Member of Edwards Group	450 <10>	41.9 <14.4>	Stony Clay Loam	Speck	No	Little	570/23,000	0.05/0.29 ^a	42
Whirlpool Cave (WP)	Grainstone Member and Kirschberg Member of Edwards Group	22,000 <100>	31 <21.7>	Stony Clay Loam	Speck	No	None	420/22,000	0.84	125
District Park Cave ^b (DP)	Kirschberg Member of Edwards Group	100 <2>	37.8 <18.9>	Stony Clay Loam	Speck	No	Significant	500/31,000	•••	5

^a denotes that R² value is calculated for average CO₂ and depth from cave entrance.

^b R² value not calculated for DP, because there are only two stations in the cave.

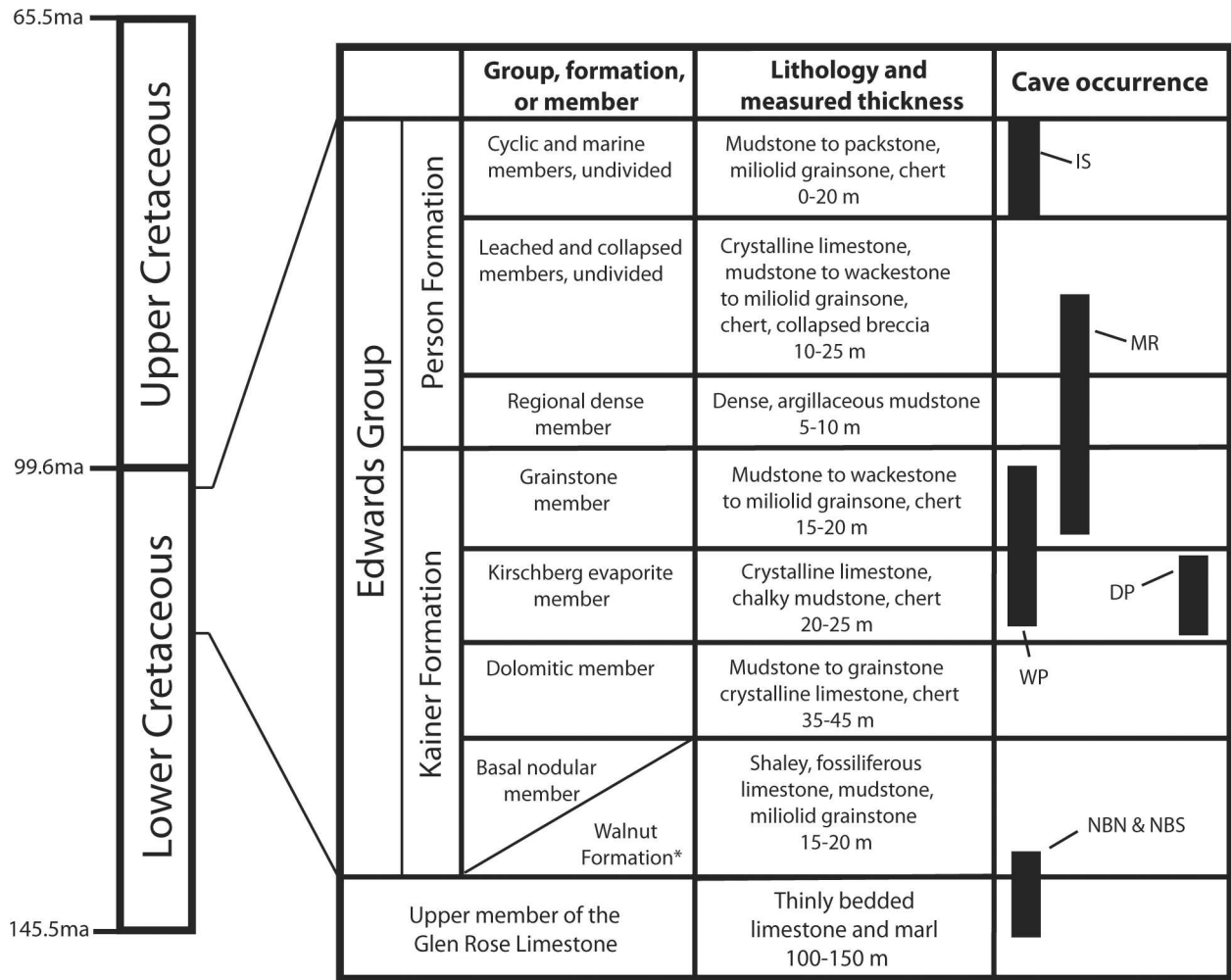


Figure 2. Stratigraphic section of the study area showing the intervals of occurrence of the caves of this study. The undeveloped caves (MR=Maple Run, DP=District Park, and WP=Whirlpool) are formed within several members of the Kainer and Person Formations. Note that MR and WP are formed in more than one member. The two parts of Natural Bridge Cavern (NBS and NBN) are adjacent and formed in the same member. Adapted from Maclay and Small (1976), Kastning (1983), and Small et al. (1996).

(Fairchild et al., 2006). Here we focus on seasonal fluctuations of cave-air CO₂ fluctuations that are primarily controlled by seasonal surface temperature fluctuations.

During warmer months, cave-air temperatures remain below outside temperature, causing the cooler, denser cave air to stagnate. During this time, the cave can be thought of as a semi-closed system, as ventilation is less efficient. As long as CO₂ sources such as degassing of drip water or advection through fractures are present, the concentration of CO₂ in the cave air will continue to rise until CO₂ inputs reach equilibrium with CO₂ removal. When cave-air temperatures are warmer than outside temperatures, ventilation becomes more efficient, because the denser outside air flows into the cave, mixing with and displacing the CO₂-rich cave air, and causing CO₂ levels within the cave to decrease. This process only applies to caves in which most of their volume is lower in elevation than the entrance(s).

The intensity of cave ventilation is governed by cave geometry (e.g., vertical vs. horizontal, large passages vs. numerous constrictions), density differences between the cave air and outside air, distance from the cave entrance, other connections with the surface via pores and fracture networks that primarily depend on the stratigraphic position of the cave, and cave volume (Batiot-Guilhe et al., 2007). In general, stronger ventilation occurs at sites near the entrance and at sites that are not separated from the entrance by constrictions (Bourges et al., 2006). Where ventilation is limited by constrictions or distance from the entrance, CO₂ levels may remain relatively constant, governed by the balance between sources and losses other than ventilation.

CAVE CO₂ SOURCES

Known sources of cave-air CO₂ include decomposition of soil organic matter by microbes (soil respiration), root

respiration, in-cave decomposition of organic matter, diffusion from deep sources, animal respiration, and degassing from CO₂-rich groundwater (Troester and White, 1984; Ek and Gewalt, 1985; Hanson et al., 2000; Baldini et al., 2006; Bourges et al., 2001; Batiot-Guilhe et al., 2007; Crossey et al., 2006). The rate of CO₂ input into a cave is dependent on several factors that may vary on multiple timescales.

Degassing of CO₂-rich vadose water is a significant input of CO₂ in most caves. The concentration of CO₂ in vadose water is primarily controlled by the concentration of CO₂ in the soil air. Soil and root respiration is likely the dominant source of soil CO₂ in the study area. The rate of respiration is affected by changes in soil temperature and soil moisture, and the highest CO₂ production occurs when soils are moist and in warm months (Amundson and Smith, 1988; Daly et al., 2008; Lloyd and Taylor, 1994; Raich and Schlesinger, 1992). As the water flows through the soil zone, it becomes enriched in CO₂ until the partial pressure of CO₂ of the water is equal to the *p*CO₂ of the soil or the water drops below the soil zone. When CO₂-charged water comes into contact with a lower *p*CO₂ environment such as a cave, CO₂ degassing occurs, and the air within that environment becomes slightly more CO₂-rich. Advection or diffusion of vadose-zone air through fractures, cracks, and dissolution cavities is also a significant means of transporting CO₂ to the cave atmosphere (Baldini et al., 2006; Batiot-Guilhe et al., 2007; Perrier and Richon, 2010).

Carbon dioxide generated from decaying organic material within caves is a significant CO₂ source for caves that collect detritus or bat guano. The significance of this contribution of CO₂ is likely to vary, depending on the ability of a given cave to capture storm-washed debris or the presence of a significant bat population. Overland flows of water into caves, sinkholes, or soil piping features are required for a significant amount of organic debris to enter the caves that we monitored. Only District Park Cave receives significant amounts of organic debris via overland stormflow.

Animal respiration is another significant source of CO₂ in a cave environment, particularly in tourist caves. The concentration of CO₂ in a human breath is approximately 40,000 ppm (Miotke, 1974). A recent study of the impacts of respired CO₂ in a cave in the Czech Republic demonstrated that human respiration is a significant source of CO₂ that is proportional to the number of people in a cave and the duration of visits (Faimon et al., 2006). Likewise Liñán et al. (2008) noted that cave CO₂ concentrations in Nerja Cave, Spain, were correlated with visitation during certain times of the year. However, some data suggests that these elevated levels of CO₂ dissipate rapidly (Faimon et al., 2006; Hoyos et al., 1998).

Three of the monitored caves are tourist caves and receive <100 to >1,000 visitors per day, while the undeveloped caves receive few visitors outside of our monitoring trips. Visitation varies greatly, but generally the

greatest numbers of visits to the tourist caves occur in mid-March and the summer months of May through August. Animals inhabiting caves will affect CO₂ concentrations in similar ways, depending on population size. A few bats are commonly found in the Natural Bridge caves, Inner Space, and Maple Run, but not in numbers significant enough to be counted (Jim Kennedy, Bat Conservation International, personal communication, April 8, 2009) or to significantly raise the concentration of CO₂ in the caves. Large mammals are unlikely to enter any of the undeveloped caves, as they are gated to exclude large mammals but allow for unimpeded airflow.

Degassing of CO₂ from phreatic water is another potential source within caves, especially where cave passages intersect the water table. Degassing occurs when high-*p*CO₂ phreatic water comes in contact with lower-*p*CO₂ cave air and will continue until the water reaches equilibrium with the air or it leaves the air-filled cave at a spring or a sump. The contribution of CO₂ from degassing of phreatic water will likely vary seasonally and in response to recharge events. Degassing of phreatic water might be a significant source of CO₂ in Inner Space and the Natural Bridge caves, as they are known to flood when aquifer levels rise after particularly heavy rainfalls. Flooding of these caves does not occur on a regular basis (seasonally), but only after prolonged periods of unusually wet conditions. A small stream flows through Natural Bride North occasionally. Degassing of phreatic water is not likely a significant source of CO₂ in Whirlpool, Maple Run, or District Park, as they are located approximately 50 m above the phreatic zone and are not known to flood.

METHODS

CO₂ concentrations were measured along transects inward from the cave entrances at sample points shown in Figure 3 using a portable Telaire 7001 CO₂ meter. From August 2006 to August 2007 the Telaire CO₂ meter was calibrated to an average atmospheric value of 380 ppm. Local atmospheric CO₂ concentrations likely differ from 380 ppm due to anthropogenic and natural variations, however these variations are likely within the instrument's range of uncertainty of 50 ppm or 5% of the total CO₂ concentration. Beginning in June 2007, a zero-point calibration was performed using argon gas. Atmospheric CO₂ concentrations were measured before and after each field transect to check for post-calibration drift. When a drift of greater than 100 ppm was detected, all data from that transect were considered unreliable and are not reported here.

Although the caves were monitored with varying frequency, ranging from weekly to monthly, each cave was visited multiple times during each season in order to assess seasonal variability. Cave-air CO₂ concentrations in tourist caves Inner Space, Natural Bridge North, and Natural Bridge South were monitored every four to six

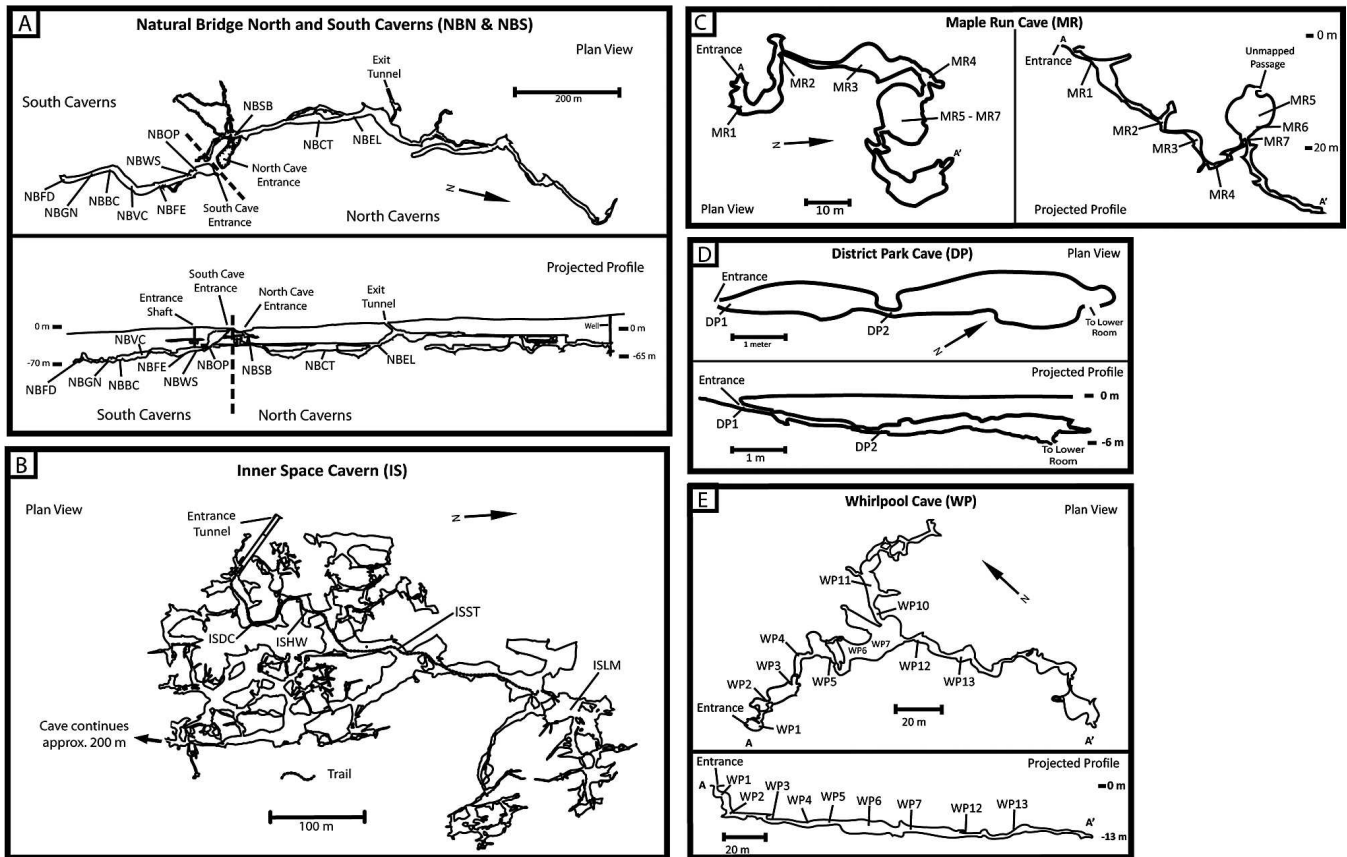


Figure 3. Maps of central Texas caves and locations of monitoring stations. Note that the entrance to cave NBN is taken as the datum for indicated depths for both NBN and NBS. Cave entrances are taken as the datum for all other depths reported. IS map adapted from Atkinson (2003), NBN and NBS maps adapted from Atkinson (2004), MR map adapted from Scott (2000), WP map adapted from Russell (1979), and DP map adapted from Russell (1988).

weeks from 2001 to May 2010. Maple Run, Whirlpool, and District Park caves were each visited two to four times monthly between July 2006 and October 2007. No transects were taken in those three caves from November 2007 to July 2008. In August 2008, monitoring resumed in those caves and continued through July 2009.

Significant increases in CO_2 concentration due to operator respiration have been reported (Baldini et al., 2006). Due to the ruggedness of the undeveloped caves, it was impractical to wear CO_2 scrubbing respirators or other devices that remove exhaled CO_2 from where measurements were being taken. Several experiments to estimate operator-caused bias were performed. Upon arriving at a measurement site, the initial CO_2 concentration was recorded. The operators then waited for a period of five minutes to determine if there was a rise in CO_2 concentration as a result of respiration. This experiment was repeated at several sites within each undeveloped cave. No increase in CO_2 concentration greater than the instrument error (50 ppm) was measured, and occasionally small decreases (20 to 30 ppm) within instrument error were measured. The meter was turned on and allowed to warm up and stabilize before reaching each measurement

site as to minimize the time required for the meter to equilibrate with the atmosphere at each measurement site. Measurements reported here were typically recorded within two to three minutes of arrival at each site, and no measurements were recorded after spending five minutes at a site. Based on this protocol, operator bias is considered to be insignificant, especially when compared to the magnitude of seasonal cave-air CO_2 fluctuations observed. The volumes of the tourist caves are so large that operator respiration is unlikely to have been a problem.

Total cave volume is reported for each cave in Table 1. All volumes were estimated from survey maps and physical measurements, and are presented here to compare relative cave volumes. To facilitate comparison between caves and between visits to each cave, a weighted mean CO_2 concentration was calculated for each transect as weighted mean = $[(C_{s1} V_{s1}) + (C_{s2} V_{s2}) + \dots] / V_t$, where C_{sx} is the CO_2 concentration measured at site x , V_{sx} is the volume of passage at site x , and V_t is the total volume of transect passages. Because cave-air CO_2 concentrations are both temporally and spatially variable, the weighted means are displayed in Figure 4 as an estimation of the magnitude and timing of seasonal variability.

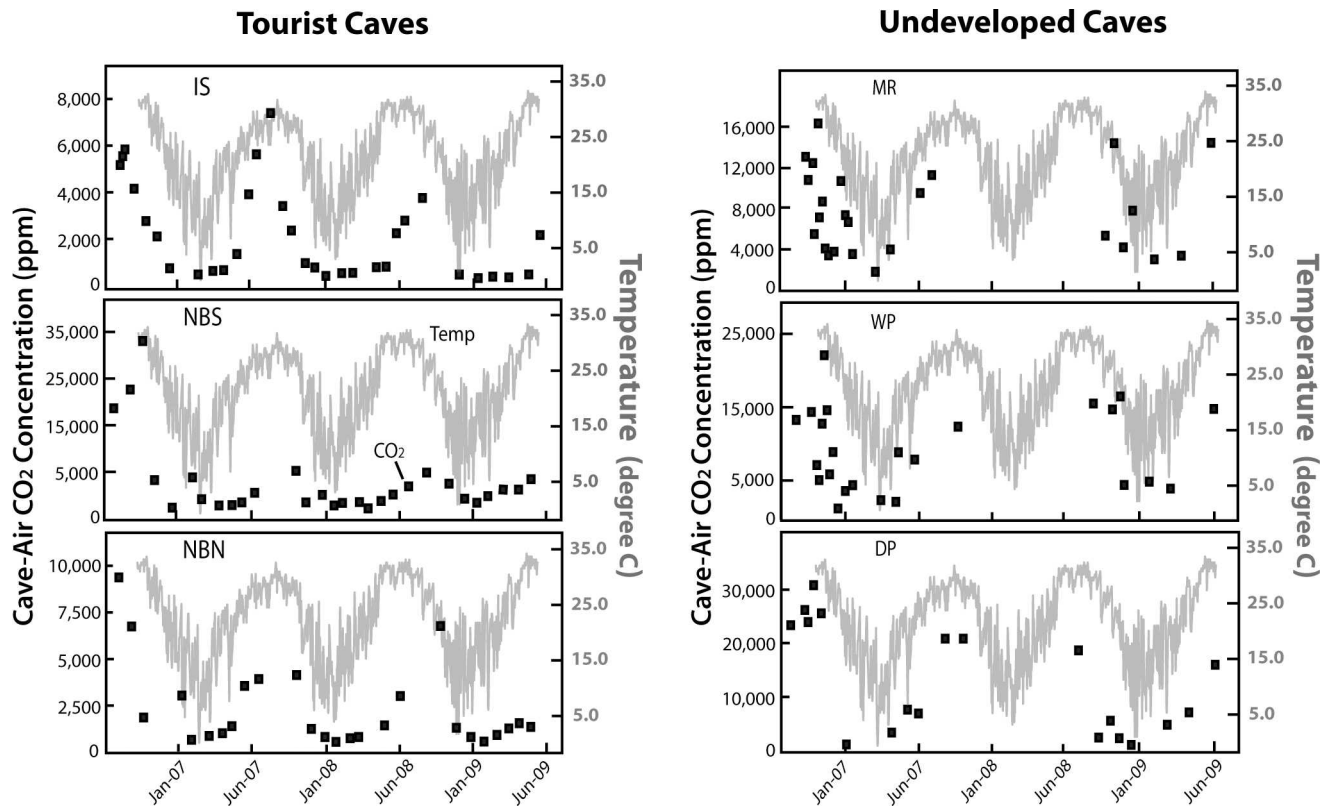


Figure 4. Time series of volume-weighted mean cave-air CO₂ concentrations measured during each transect of tourist and undeveloped caves (black squares) and outside air temperature (gray solid lines). Instrument error (5% of measurement or 50 ppm) is smaller than symbols used to represent CO₂ concentrations. Air temperature was measured at a National Climate Data Center weather station located in Austin, Texas; COOP ID: 410428). For weighted mean calculation, see text. IS is Inner Space Cavern, NBS and NBN are the parts of Natural Bridge Cavern, MR is Maple Run Cave, WP is Whirlpool Cave, and DP is District Park Cave.

Soil thicknesses were measured above each cave by hammering a 1.7-meter stake with a radius of 1 cm into the soil as far as possible (Table 1). Measurements were taken every 10 m along a 60 m transect, and a minimum of three transects were measured above each cave. Average soil thicknesses ranged from 23 cm above Natural Bridge Caverns North to 42 cm above Maple Run Cave (Table 1). Impervious cover was visually estimated by superimposing cave maps on satellite images of the land surface above the caves. Part of Inner Space is overlain by engineered fill for Interstate Highway 35 that is several meters thick, and approximately 35% of the cave is overlain by impervious cover. Natural Bridge North is overlain by approximately 20% impervious cover, and Natural Bridge South is overlain by approximately 10% impervious cover. There is no impervious cover over District Park, Whirlpool, or Maple Run caves.

RESULTS

The volume-weighted means over time of the cave-air CO₂ concentrations are presented in Figure 4. Daily

average surface temperature measured at a National Climate Data Center weather station (COOP ID: 410428) located in Austin, Texas, are also in Figure 4.

The concentration of CO₂ in the tourist and undeveloped caves show strong seasonal variability. The timing of seasonal CO₂ fluctuations was consistent between all caves, but the magnitude of CO₂ fluctuations varied considerably, especially between the undeveloped and tourist caves. CO₂ concentrations were lowest during the cooler season (November through April) and elevated throughout the warm season (May through October), and concentrations generally increased with increasing distance from the cave entrances (Fig. 5). With the exception of Maple Run and District Park, the average CO₂ concentration at each station was well correlated ($R^2 > 0.25$) with distance from the entrance (Table 1, Fig. 6). At Maple Run there is not a strong correlation between average CO₂ concentration at each station and distance from the entrance ($R^2 = 0.0$, but there is a stronger correlation between average CO₂ concentration at each station and depth ($R^2 = 0.29$; data not shown). The small size and limited number of points for District Park Cave prevented this calculation there.

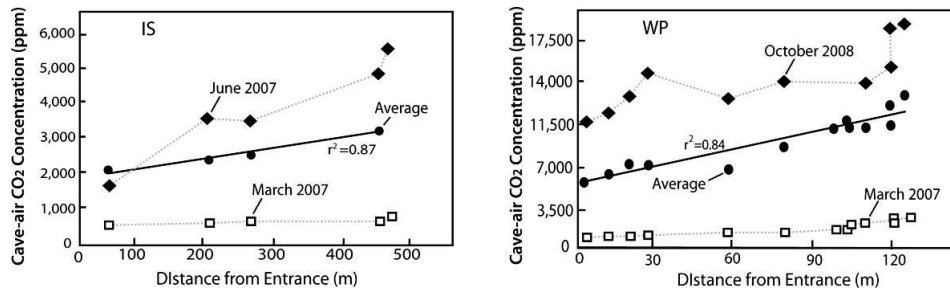


Figure 5. Representative individual warm- and cool-season CO₂ transects at Inner Space Caverns (IS) and Whirlpool Cave (WP). Mean CO₂ concentration measured during all transects at each station during study.

DISCUSSION

REGIONAL CONTROLS OF CAVE-AIR CO₂

Cave-air CO₂ concentrations varied significantly in all caves monitored. Higher CO₂ concentrations were measured during the warmer months and lower concentrations were measured during the cooler months (Fig. 4). Seasonal ventilation differences are likely driven by density differences

between outside and cave air caused by seasonal differences in outside temperatures. If anthropogenic effects were responsible for the seasonal fluctuations of cave-air CO₂, then significant CO₂ fluctuations would only occur in tourist caves; but large seasonal fluctuations of cave-air CO₂ were observed in all caves.

Although seasonal fluctuations of cave-air CO₂ were observed in the undeveloped caves and tourist caves,

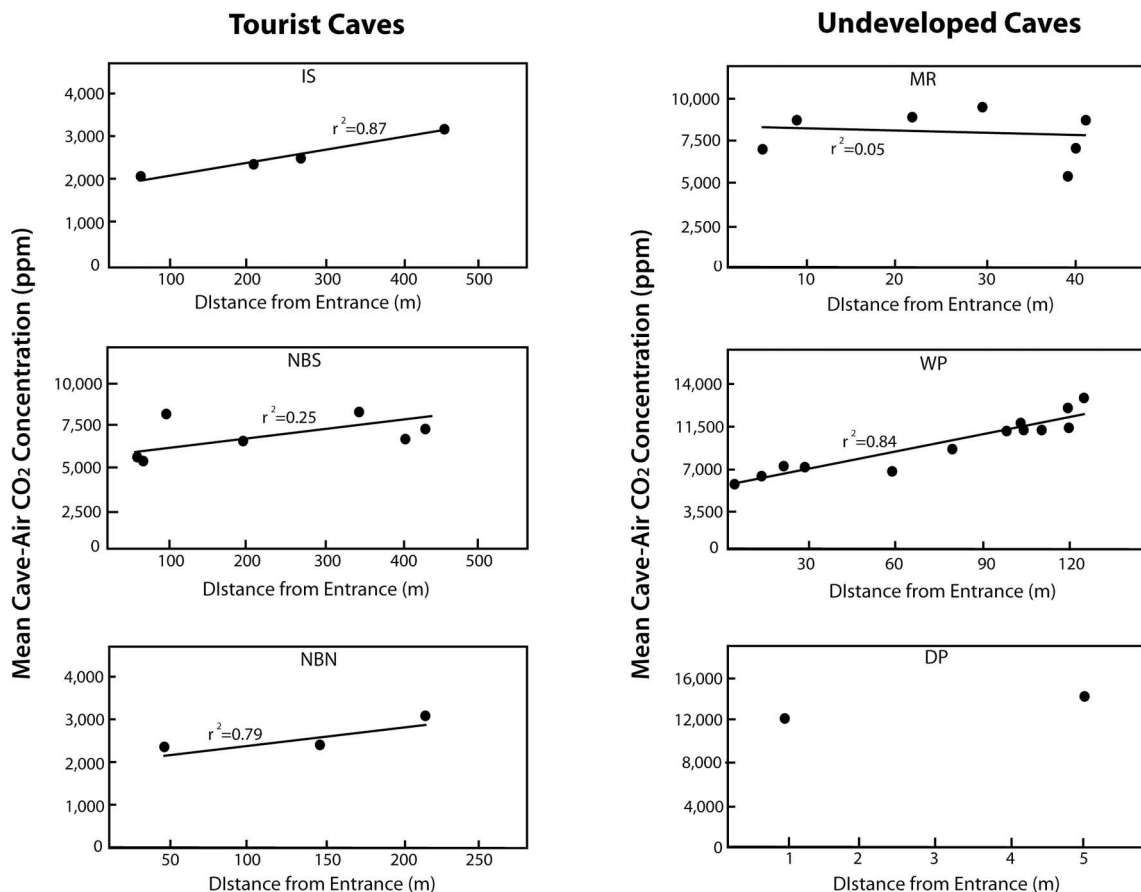


Figure 6. Mean CO₂ concentration measured at each station versus distance from the cave entrance. IS refers to Inner Space Cavern, NBS and NBN are the parts of Natural Bridge Cavern, MR is Maple Run Cave, WP is Whirlpool Cave, and DP is District Park Cave. No statistically valid r^2 value can be presented for District Park, as there are only two stations within the cave.

visitation cannot be dismissed as a significant source of CO₂ in the tourist caves without closer examination. Visitation to all three tourist caves reaches a maximum during the summer, when cave-air CO₂ levels are most elevated. There are, however, two key observations that suggest visitor respiration is not the primary control on seasonal CO₂ fluctuations. Visitation rates peak in March and July each year, but CO₂ concentrations remain elevated throughout the summer and not in March; and the highest CO₂ concentrations occur in Natural Bridge South, the least visited tourist cave (Banner et al., 2007). These lines of evidence suggest that the seasonal CO₂ fluctuations observed in the tourist caves are indeed a natural phenomenon and not due to visitation.

It is also important to note that the tourist caves use ventilation fans to remove some of the CO₂-rich air from the caves during the summer months. No detailed record of fan usage exists, but preliminary data from logging CO₂ meters installed in both caves exhibit high summertime cave-air CO₂ concentrations with no intermittent excursions to near atmospheric values. Although diurnal CO₂ fluctuations >500 ppm were routinely detected, the maximum CO₂ concentrations were measured during the afternoon hours, when fans were typically turned on. The lowest CO₂ concentrations were typically measured during the overnight hours, when the ventilation fans were typically not in use. This suggests that CO₂ inputs are sufficient to maintain elevated concentrations throughout the warmer months, even though ventilation fans undoubtedly remove CO₂-rich air from the caves. Similar diurnal patterns were observed in all undeveloped caves for which logging meters were deployed.

There was significant variety in the magnitude of seasonal cave-air CO₂ fluctuations (Fig. 4), but seasonal weather patterns cannot explain the inter-cave variability. All of the caves are located within 130 km of each other and experience similar seasonal weather patterns. Additionally, the three undeveloped caves are located within 5 km of each other and experience nearly identical seasonal and storm-scale weather patterns, yet the magnitude and exact timing of CO₂ fluctuations within these caves are not identical, suggesting that some site-specific parameters play a role in cave ventilation.

SITE-SPECIFIC CONTROLS OF CAVE-AIR CO₂

Soil thickness does not appear to be an important control on cave-air CO₂ variability in the study area. If soil thickness were an important control on cave-air CO₂ concentrations, we would expect to see variations in the average CO₂ concentrations at monitoring stations that are overlain by thicker soils relative to other stations in the same cave. At Inner Space, sites ISHW and ISST (Fig. 3) are overlain by engineered fill that is several meters thick and sites ISDC and ISLM are overlain by much thinner soils (approximately 26 cm; Table 1). If soil thickness were an important control on cave-air CO₂ variability at Inner

Space, there would likely be a weaker correlation between CO₂ concentration and distance from the cave entrance due to the highly variable soil thickness above the cave. Instead, there is a strong correlation ($R^2 = 0.87$) between average CO₂ concentration and distance from the entrance (Fig. 6).

The large differences in peak CO₂ concentrations at the caves shown in Table 1 also suggest that soil thickness is not a major control on cave-air CO₂ concentrations in the study area. Soil type and thickness (Table 1) and extent of vegetative cover are relatively uniform across the study sites, with the exception of Inner Space, but peak CO₂ concentrations vary by more than 30,000 ppm between caves. This is best illustrated by comparing the north and south parts of Natural Bridge Cavern. Vegetative cover and soil type and thickness are nearly identical above both caves (33 cm at Natural Bridge South and 34 cm at Natural Bridge North), and the caves are located adjacent to one another. Nevertheless, peak CO₂ values in the north cave did not exceed 10,000 ppm at any site, while peak CO₂ values in the south cave consistently exceeded 20,000 ppm during the summer months of 2006 and were consistently higher than the CO₂ concentrations in the north cave the following two summers (Fig. 4). It is important to note that these two caves are overlain by different amounts of impervious cover (approximately 10% of Natural Bridge South and 20% of Natural Bridge North), which could account for some of the difference in peak CO₂, but probably not the magnitude observed.

The data suggest that cave volume is an important control on the magnitude of seasonal cave-air CO₂ fluctuations. With the notable exception of Natural Bridge South during the summer of 2006, peak CO₂ concentrations in the tourist caves were significantly lower than those in the undeveloped caves (Table 1). The large passages in the tourist caves imply a greater volume of cave under a given area of the surface, so larger caves will require a greater flux of CO₂ per unit of surface area to achieve the same magnitude increase in CO₂ concentration as a smaller cave. The soils in the study area are all similar in composition and thickness, so it is likely that the amount of CO₂ production per unit area above each cave is similar. The tourist caves might have a greater flux of CO₂ into them compared to the undeveloped caves, but the volumes of the tourist caves relative to their surface footprints are much greater; and therefore, the flux of CO₂ into the tourist caves per unit volume may actually be less than the flux of CO₂ per unit volume in the undeveloped caves. Cave-air CO₂ concentrations in the smaller, undeveloped caves rarely dropped below 4,000 ppm, the threshold above which Banner et al. (2007) noticed a significant decrease in calcite growth. This suggests that smaller caves may have higher cave-air CO₂ concentrations on average, leading to less speleothem growth than larger caves located in the same region.

In the study area, cave geometry is influenced by stratigraphy (Russell, 2007; Hauwert, 2009). For example,

much of Maple Run Cave is within units that are more conducive to cave formation via leaching and collapse (Rose, 1972), and mean CO₂ concentration is better correlated with depth of the monitoring stations than distance from the entrance (Table 1). The better correlation with depth might be attributed to the ease with which air can circulate through the rock units in which the cave is formed. Much of the cave consists of connected voids in a collapsed rubble pile (Fig. 2). Airflow through the subsurface at Maple Run is likely not only through the known cave passages, but also through the void spaces within the rubble pile that surrounds much of the cave.

Initial results from high frequency monitoring at Inner Space, Maple Run, and Whirlpool verify that strong seasonal CO₂ fluctuations do occur in the caves monitored with the exception of Maple Run, which did not experience seasonal cave-air CO₂ fluctuations, but did experience large diurnal CO₂ fluctuations (Cowan et al., 2009). The lack of seasonal fluctuations in Maple Run can be attributed to diurnal ventilation of the cave caused by barometric-pressure fluctuations and its porous geologic situation. Airspeed measurements taken at the cave reveal that a volume of air nearly 15 times greater than the volume of known passage flows from it during a 9-hour period. These daily ventilation patterns in Maple Run appear to be due to the global atmospheric tide (Melcior, 1983; Wallace and Hobbs, 2006) that has been shown to affect cave meteorology (e.g., Sondag et al., 2003; Bourges et al., 2006). The apparent seasonality of cave-air CO₂ data taken in Maple Run for this study that appear in Figure 4 can be attributed to the timing of cave ventilation caused by seasonal shifts in the atmospheric tide and the timing of the visits, which typically occurred between 12:00 and 15:00 CST. Initial results from logging CO₂ meters confirm that CO₂ concentrations in Inner Space and Whirlpool do fluctuate both seasonally and diurnally. Logging CO₂ meters were only deployed in Natural Bridge North for two months and recorded diurnal CO₂ fluctuations there as well.

In contrast to Maple Run, Whirlpool, Inner Space, and Natural Bridge North are formed in stratigraphic units known for lateral cave development (Hauwert, 2009), and CO₂ concentrations in these caves is well correlated with distance from the entrance (Fig. 6). It is important to note that the undeveloped caves are in different stratigraphic units than the tourist caves (Fig. 2), and it is likely that the stratigraphic characteristics of the hosting and overlying units affect the ventilation and CO₂ inputs of the caves. Therefore, it is possible that the smaller seasonal cave-air CO₂ fluctuations in the tourist caves could be attributed to the stratigraphic units that the caves are located in, not their larger volumes. While the data suggest that stratigraphic control promoting horizontal or vertical development does influence the spatial variability of CO₂ within the caves, more monitoring of a larger number of caves in a wide range of stratigraphic units is needed to fully

understand the relative importance of this control on cave-air CO₂.

With the exception of Maple Run Cave (and maybe District Park, for which very limited data are available), cave-air CO₂ concentrations were correlated with distance from the cave entrance (Fig. 6). This is likely related to ventilation efficiency. As cooler outside air flows into a cave, it will come into contact with the cave walls, which remain at a relatively stable temperature year-round. As the denser outside air is continually warmed by the cave walls, its density will decrease and ventilation will become less efficient with distance from the entrance.

IMPLICATIONS FOR SPELEOTHEM PALEOCLIMATE STUDIES

Recent studies have proposed that there is potential for bias in the speleothem paleoclimate record due to changes in deposition rates and drip-water chemistry caused by cave-air CO₂ fluctuations (Spötl et al., 2005; Banner et al., 2007). This bias may affect speleothem proxies such as growth rate and isotope and trace element geochemistry (Baldini et al., 2008; Wong et al., 2011). These studies highlight the need to better understand the causes of cave-air CO₂ fluctuations, on what time scales the fluctuations occur, and whether cave-air CO₂ fluctuations occur on a regional scale or are specific to individual caves. The findings presented herein suggest that seasonal cave-air CO₂ changes are a regional phenomenon caused by seasonal differences in cave ventilation. Elevated CO₂ concentrations were detected in all caves during the warmer months, and lower concentrations during cooler months. This observation implies that even in regions where paleoclimate proxies are reproducible among spatially separated sites in a region, seasonal fluctuations of cave-air CO₂ may cause a seasonal bias in the speleothem paleoclimate record.

Speleothem growth-rate is often used as a proxy for rainfall. It is typically assumed that growth-layer thickness and hiatuses in growth are controlled by drip rate, which is controlled by changes in rainfall (Baker et al., 1993; Genty and Quinif, 1996; Qin et al., 1999; Musgrove et al., 2001; Polyak and Asmerom, 2001). It is likely that this assumption is valid in many instances, but there is evidence that high cave-air CO₂ concentrations can inhibit speleothem growth rates (Banner et al., 2007; Baldini et al., 2008), so the possibility should be considered that a growth rate proxy may be affected by cave-air CO₂ variations.

Cave-air CO₂ fluctuations may also affect the trace-element composition of speleothems, which has also been used as a proxy for rainfall. In caves where trace-element composition in drip water varies seasonally, periods of non-deposition due to high cave-air CO₂ concentrations might cause speleothem calcite composition to be biased toward times when cave-air CO₂ is lower and speleothem growth is faster. Precipitation of calcite from the water upgradient from the point where a speleothem is being

deposited has been shown to affect the concentration of trace elements in speleothem-forming drip water (Fairchild et al., 2006; Matthey et al., 2010; Wong, 2008) and might be reflected in the speleothem record. As modeled by Wong et al. (2011), a speleothem with a pattern of seasonally varying trace-element concentrations due to seasonal cave-air CO₂ fluctuations might be incorrectly interpreted as reflecting changes in rainfall or vadose flow paths.

Carbon and oxygen stable isotope variations are commonly used as proxies for vegetation and rainfall amounts and temperature. Similar to the bias in trace element proxies, stable isotope variations may also preserve a bias that would affect the accuracy of climate interpretations (Baldini et al., 2008). Studies have shown that $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values respond not only to environmental changes, but also to in-cave processes as well. Drip-water may undergo significant kinetic isotope effects due to rapid CO₂ degassing or Rayleigh distillation that causes departures from equilibrium isotope fractionation between HCO₃⁻ and CaCO₃ (Mickler et al., 2004, 2006). Because the rate of drip-water degassing is largely controlled by the difference between the *p*CO₂ of the drip water and cave air, the magnitude of departure from equilibrium isotope fractionation, may change as cave-air CO₂ concentrations fluctuate. In fact, a study of a modern stalagmite by Matthey et al. (2010) showed that annual growth lamina preserved seasonal $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ cycles that were attributed to cave ventilation. If this effect is not accounted for, then changes in the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ composition of speleothems might be incorrectly interpreted as reflecting climatic changes and not in-cave processes.

Although seasonal cave-air CO₂ fluctuations could introduce bias into the speleothem climate record, these fluctuations may also leave seasonal markers in speleothem calcite growth layers, which could greatly increase the resolution of paleoclimate reconstructions. With advances in analytical techniques, such as laser-ablation inductively coupled plasma mass spectrometry, it may be possible to achieve annual or sub-annual resolution from speleothems deposited in caves that experience seasonal CO₂ fluctuations. This is an exciting prospect considering that some speleothem records cover the past 200,000 years (e.g., Wang et al., 2008).

SUMMARY AND CONCLUSIONS

The results of nearly 150 lateral transects into six caves over three years show that CO₂ concentrations vary seasonally in all of the caves monitored, with peaks in CO₂ concentration in the warmer months and lower concentrations in the cooler months. These seasonal CO₂ fluctuations are attributed to seasonally variable cave ventilation that is controlled by outside temperature fluctuations. Cave-air CO₂ concentrations are lowest in the cooler months due to stronger ventilation. In the cooler months, when the outside air is cooler and denser than the

cave-air, outside air sinks into the cave and mixes with the CO₂-rich cave air, causing a decrease in the cave-air CO₂ concentration. In the warmer months, when the outside air is less dense, cave ventilation becomes much weaker and CO₂ concentrations increase.

Seasonal CO₂ fluctuations in the study area do not appear to be caused by anthropogenic influences such as cave visitation. If anthropogenic influences were controlling seasonal CO₂ fluctuations in the study area, it would be unlikely that seasonal CO₂ fluctuations would occur in the undeveloped caves, as they have not been modified greatly and receive a relatively small number of visitors. Instead, the largest CO₂ fluctuations were observed in the undeveloped caves. The timing of peak CO₂ concentrations in the tourist caves does not coincide with visitation, which peaks in March and July each year. Instead, CO₂ concentrations remain elevated throughout the summer and September. Additionally, the highest CO₂ concentrations occur in Natural Bridge South, the least visited tourist cave.

Seasonal fluctuations occurred regardless of cave volume, geometry, depth, soil thickness, and hosting stratigraphic unit. Significant seasonal CO₂ fluctuations were measured in all caves, but the magnitude of CO₂ fluctuations does appear to be influenced by cave volume and geometry. In general, the peak CO₂ concentrations in the smaller caves were much greater than peak concentrations in the larger caves. Additionally, the caves are located in seven distinct stratigraphic units. Portions of Inner Space are overlain by engineered fill that is several meters thick, but significant CO₂ fluctuations were nevertheless measured there.

It is important to note that the presence of seasonal CO₂ fluctuations does not necessarily indicate that seasonal variations in calcite deposition rates are occurring. The rate of calcite deposition is dependent on the interplay of multiple factors, including temperature, CO₂ concentration, relative humidity, the concentration of calcium in the drip water, and the drip rate. The CO₂ concentration in some caves was seldom below 4,000 ppm, the concentration at which Banner et al. (2007) observed a decrease in calcite precipitation.

To understand modern and ancient changes in speleothem deposition, it is essential that the mechanisms controlling cave ventilation be understood in greater detail. Future research should focus on seasonal and short-term (e.g., diurnal or storm scale) variations in cave ventilation and the influence of ventilation on disequilibrium calcite precipitation or periods of cessation of calcite deposition. It is clear that continuous monitoring with logging CO₂ meters will help address the complexities of cave ventilation.

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