

The hydrologic record of karst systems: linking soil moisture to the carbon isotope signatures of soils above the Blue Spring cave system

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Abstract Speleothem carbonates are precipitated continuously from inorganic carbon dissolved in seepage water infiltrating from the land surface, that reflects a mixture of atmospheric CO₂, respired soil carbon, and epikarst sources, each with distinct $\delta^{13}\text{C}$ values. To aid in deconvolving these signatures, soil samples were collected above the Blue Spring cave system in Sparta, Tennessee, USA and subjected to a series of incubation experiments, in order to constrain the correlation between CO₂ respiration rates and soil moisture. This relationship is used to parameterize a simple mixing model which predicts the relationship between $\delta^{13}\text{C}$ and soil moisture in fluids infiltrating into the underlying cave system.

Keywords Speleothem · $\delta^{13}\text{C}$ · CO₂ respiration · Soil moisture

1 Introduction

Karst systems constitute approximately 20% of the terrestrial Earth surface and experience distinct hydrogeochemical alteration as a result of the reactivity between limestone and rainwater. Cave systems formed within the subsurface of these landscapes record a history of mineral–

water–microbe interactions through the deposition of secondary minerals. Speleothem carbonates formed in the caves offer a key means of unraveling the hydrologic conditions of the past in that they are often continuously formed over a long period of time and can be precisely dated. Previous studies have suggested that the carbon isotopic compositions ($\delta^{13}\text{C}$) in speleothem carbonates are controlled by the isotopic signature of dissolved CO₂ in seepage water, which is a function of the climate and surface hydrologic cycle (e.g. Genty et al. 2001). This signal is subsequently modified to varying degrees within the epikarst through interactions with host rocks and deep sources of organic matter (e.g. Oster et al. 2010). Thus the carbon isotopic composition of speleothems may offer a means of revealing past climate changes, but further research combining the effects of reactivity and transport are needed.

CO₂ dissolved into the seepage water which interacts with epikarst has two sources: atmospheric CO₂ and CO₂ respired by soil microorganisms. Since the $\delta^{13}\text{C}$ signature of atmospheric CO₂ is fairly constant ($\sim -7\text{‰}$) over the time scale of water infiltrating through soil, variations in the $\delta^{13}\text{C}$ of this fluid are primarily controlled by the amount of CO₂ respired within the soil and the $\delta^{13}\text{C}$ of the labile organic soil carbon. Since the $\delta^{13}\text{C}$ of the respired CO₂ can be affected by the type of vegetation (C3 or C4), where C3 plants have a lower $\delta^{13}\text{C}$ signature (-24‰ to -34‰) than C4 plants (-6‰ to -19‰) (e.g. Deines 1980), distinctions in the $\delta^{13}\text{C}$ recorded in speleothems could reflect different ecosystems in different periods of time (e.g. Dorale et al. 1998). In addition, given the large C isotopic fractionation between vegetation and atmospheric CO₂, changes in soil respiration rates can affect the mass balance between these two sources of CO₂ and thus the isotopic signature of the mixed fluid sample. Specifically,

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when the respiration rate is high, CO₂ dissolved in seepage water should appear lower, and vice versa. As the seepage water infiltrates below the soil layer, dissolution of the host carbonate will dampen the δ¹³C signature. Several aspects have been proposed explaining the variations in speleothem δ¹³C. Some studies have suggested that the respiration record is not totally erased, and thus may serve as an indicator of past changes in the hydrologic cycle (e.g. Oster et al. 2015). However, a recent study suggests that such changes can only be recorded in the speleothems when environments are described by low mean annual precipitation and temperature (Breecker 2017).

Previous studies have focused on a variety of factors that affect soil respiration rates (temperature, microbial community, pH, organic carbon composition, soil texture, and moisture). Among these, soil moisture directly reflects the surface hydrologic cycle (and ultimately climate changes), and influences the velocity at which water seeps into the underlying caves. The correlation between soil moisture and respiration rates has been studied both in lab settings and in situ soil profiles. It is commonly demonstrated that these parameters are positively correlated in arid and semi-arid systems, and negatively correlated when soil approaches saturation (e.g. Howard and Howard 1993). Multiple processes have been proposed for the cause of this correlation. A common explanation is that at lower soil moistures, water deficiency inhibits the proficiency of the microbial communities to respire. Under dry conditions, microbes are prone to enter a dormant state, reserving energy for more favorable conditions, and resulting in a lower respiration rate at lower soil moistures. In contrast, at higher soil moistures, O₂ concentrations in the soils become limiting as a result of both the low equilibrium O₂ concentration in the water and the orders of magnitude difference in the diffusion coefficient of oxygen in a liquid phase versus a gas phase. Thus, when soils approach full saturation, oxygen fugacity is insufficient to support a high oxidation rate of organic carbon, which is reflected as a negative correlation at higher soil moistures (e.g. Skopp et al. 1990).

The relationship between soil moisture and respired CO₂ also exhibits strong transient fluctuations. In particular, an extremely high soil respiration rate (manifested as a large pulse of CO₂) is observed when a long period of drought is followed by a large precipitation event (also known as the Birch effect). The validity and significance of the Birch effect has been demonstrated in previous studies over timescales of days to months, suggesting CO₂ concentration pulses large enough to support abrupt, transient shifts in the δ¹³C of dissolved soil CO₂ might be recorded by speleothem formation.

In this study, soil core samples were collected directly above the Blue Spring cave system in Sparta, Tennessee, USA, an active, instrumented cave system. Soil samples were incubated at a range of fluid saturations to constrain

the relationship between soil moisture and CO₂ respiration rate in order to predict the maximum range of the δ¹³C of water entering the epikarst above the cave. These data will be applied to calibrate parameter values in an isotope-enabled reactive transport framework (CrunchTope, Steefel et al. 2015) to advance our understanding of the connection between surface hydrologic variability and speleothem composition.

2 Methods

Blue Spring Cave is a developed cave system with approximately 62 km of mapped passage. Though much of the cave is covered with sandstones and conglomerates which prevent water infiltration and speleothem formation, seepage water is found on the edges of the cave system where the cap rock is absent, resulting in active speleothem growth. Monitoring devices have been installed both above and in the cave since June 2013 recording air temperature and humidity for both surface air and cave air, rainfall amount, soil temperature and moisture, pCO₂ and drip rate in the cave. Drip water in the cave is collected and measured monthly for chemical concentrations and δ¹³C. Soil gas wells installed above the cave enable sampling and measurement of gas concentrations and δ¹³C of soil gas as a function of depth.

Soil core samples were taken near the gas wells installed at the edge of the cave system. Cores were divided into four subsamples based on depths (0–10.7 cm, 10.7–21.3 cm, 21.3–32.0 cm, 32.0–40.0 cm), carefully sealed, and shipped to the University of Illinois Urbana-Champaign. All samples were stored at 3 degrees Celsius for approximately two months before pretreatments for incubation. Pretreatment involved air-drying for two weeks to reach residual water saturation, and sieving with a 2-mm mesh size.

Water holding capacity of the soil samples was determined prior to incubation by recording the mass of water adding to weighed air-dried soil samples until they became fully saturated. Three 75-gram air-dried subsamples are taken from each depth, and individually placed into 237-mL glass vessels (AnchorGlass). The three subsamples were subjected to distinct soil moisture contents of 30%, 60%, and 100% water holding capacity. Polyethylene tubing (McMaster-Carr) was connected to the vessels through two ports on each cap, sealed with epoxy to prevent gas leakage, and connected with luer-loc valves (Nordson Medical) to allow for sampling. Each vessel was purged with CO₂ free air for over 10 times the volume of the jars after they were sealed. CO₂ concentrations in the headspace were measured using an Infrared Gas Analyzer (LICOR-8100) once every 24 h. The vessels were again purged with CO₂ free air after every sampling processes.

3 Results

Respiration patterns are consistent across different depths of the soil profile and with different soil moistures (Fig. 1), in agreement with previous studies (e.g. Schimel et al. 1999). Respiration rates for the 60% soil moisture (black lines) are higher than 30% soil moisture (red lines) and 100% soil moisture (blue lines) for all depths of soil samples, as a result of microbe dormancy at lower moisture, and insufficient O₂ at higher moisture. A large CO₂ pulse is observed after 48 h of incubation, and it levels out to reach an equilibrium after approximately 200 h, consistent with the Birch effect. The transient peak values are two to three times higher than equilibrium respiration rates. Also, the largest differences in respiration rate as a function of soil moisture is observed in the shallower depths, while for deeper soils, moisture has little effect on respiration rates.

4 Discussion

Based on the incubation results, it is clear that CO₂ respiration rates are highly dependent on soil moisture for the samples collected from the Blue Spring site. This implies that changes in soil moisture at the field site (rainfall events, drought, etc.), will result in different amounts of

respired CO₂, resulting in a changing CO₂ concentration of the fluid infiltrating the soil at different time periods. CO₂ from both the atmosphere and this respiration source dissolve into the water infiltrating through the soil zone and form bicarbonate (HCO₃⁻) and carbonate (CO₃²⁻), while changing the pH of the solution.

As a result, increased CO₂ partial pressure in the soil zone results in a more acidic, reactive fluid infiltrating the epikarst, and this reactivity is primarily controlled by soil respiration rate. This water ultimately moves into the underlying cave where secondary carbonate minerals precipitate to form speleothems. Thus it is plausible that the soil moisture control on soil respiration rate may be preserved in the speleothem record. However modification of δ¹³C signatures through carbonate dissolution and precipitation within the epikarst must also be examined.

The inorganic carbon dissolved in the water infiltrating the soil will have the isotopic signature of the gas phase CO₂ in the soil zone. The gas phase CO₂ in the soil pores is a mixture of respired CO₂ with δ¹³C similar to the organic carbon in the soil (~ -20‰), and atmospheric CO₂ which has a δ¹³C = ~ -7‰. Therefore, the mixing of these two sources should result in a δ¹³C signature of the water entering the epikarst which reflects changes in the amount of CO₂ respired.

A mass balance calculation is presented which combines the correlation between soil moisture and respiration rates

Fig. 1 CO₂ respiration rates at different times for **a** 0–10.7 cm; **b** 10.7–21.3 cm; **c** 21.3–32.0 cm; **d** 32.0–40.0 cm depths of soil. Red, black, and blue symbols and lines represent 30%, 60%, and 100% soil moisture capacity, respectively

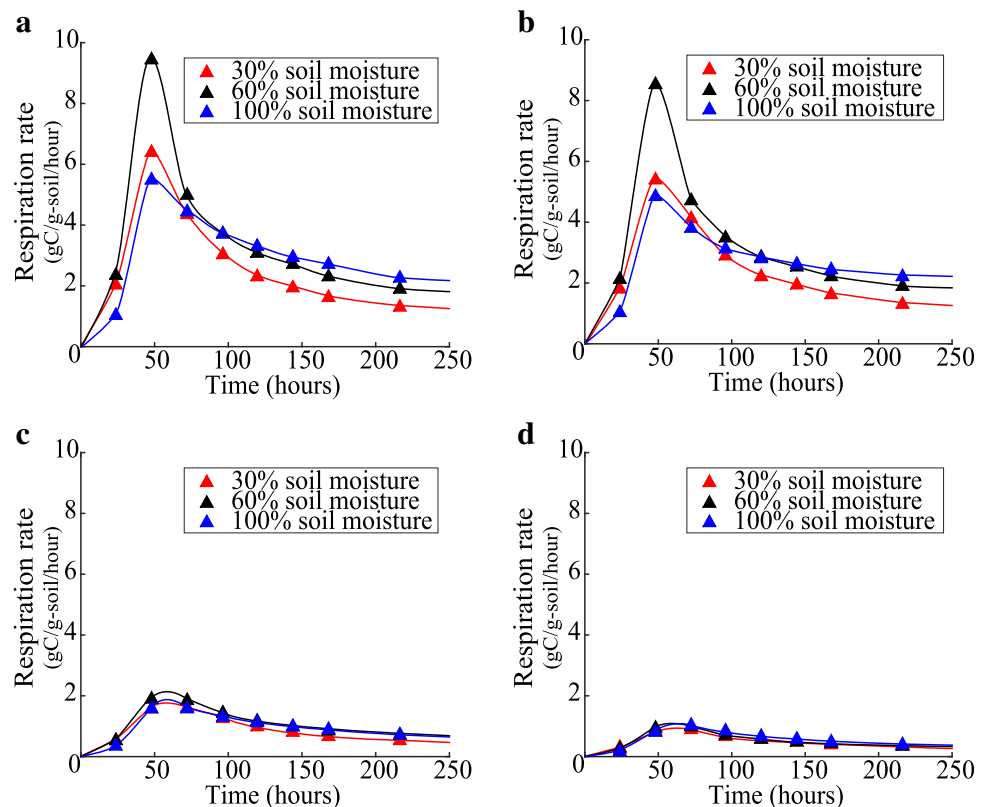
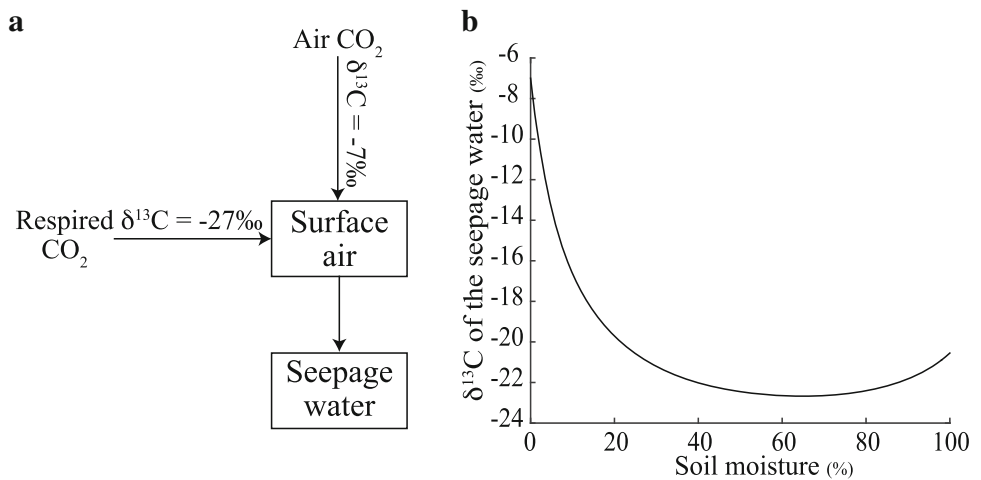


Fig. 2 **a** Diagram of the mixing box model; **b** predicted $\delta^{13}\text{C}$ of the fluid entering the epikarst as a function of soil moisture



(Fig. 1) and the correlation between respiration rates and $\delta^{13}\text{C}$ of the fluid infiltrating the epikarst, following a simple box model approach (Fig. 2a). The model shows the relationship between soil moisture and $\delta^{13}\text{C}$ of fluid entering the epikarst (Fig. 2b). $\delta^{13}\text{C}$ of the respired CO_2 is assumed to be -20‰ , and atmospheric $\delta^{13}\text{C}$ is set to -7‰ . The respired CO_2 concentration used in this simulation is taken from the data measured after 48 h of incubation for the 0–10.7 cm soil, extrapolating the three datapoints to the whole moisture range with polynomial fitting, and diluted $10 \times$ to approximate gas diffusion across an in situ soil profile. Results show that in arid and semi-arid conditions, the $\delta^{13}\text{C}$ of the soil water is negatively correlated with soil moisture, and the trend reverses when soils approach saturation. Even though respiration might not be a controlling factor in environments such as the Blue Spring cave system, which are subject to large annual precipitation rates, the ability to deconvolve the influence of respiration is vital in interpreting speleothem $\delta^{13}\text{C}$ when applying the model to other karst systems.

5 Conclusions

Soil incubation experiments were conducted for samples taken above Blue Spring cave system in Sparta, Tennessee, USA, to better understand the relationship between respiration rate and soil moisture. The results are related to $\delta^{13}\text{C}$ of the fluid exiting the soil layer and infiltrating the epikarst with a simplified mixing model, resulting in a first order prediction of how we may interpret the changes in carbon isotopic composition of speleothems in the underlying cave.

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