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THE INFLUENCES OF HYDROLOGY ON THE RADIOGENIC AND STABLE CARBON ISOTOPE COMPOSITION OF CAVE DRIP WATER, GROTTA DI ERNESTO (ITALY)

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ABSTRACT. ^{14}C and δ^{13}C values of C-containing species in cave drip waters are mainly controlled by the C isotope composition of karst rock and soil air, as well as by soil carbon dynamics, in particular the amount of soil CO_2 in the unsaturated soil zone and the process of calcite dissolution. Here, we investigate soil carbon dynamics by analyzing the ^{14}C activity and δ^{13}C values of C dissolved in cave drip water. Monthly over a 2-yr period, we collected drip water from 2 drip sites, one fast and one relatively slow, within the shallow Grotta di Ernesto Cave (NE Italy). The ^{14}C data reveal a pronounced annual cycle. In contrast, the δ^{13}C values do not show an annual pattern and only small interannual variability compared to the δ^{13}C values of soil waters. The annual ^{14}C drip-water cycle is a function of drip-rate variability, soil moisture, and ultimately hydrology.

INTRODUCTION

Radiocarbon techniques are successfully used to determine the age of groundwater in karst systems by measuring the ^{14}C activity of the dissolved inorganic carbon (DIC) (Clark and Fritz 1997). Despite the usefulness of ^{14}C to estimate age and residence time of karst waters, which play a central role in water resource sustainability, the proportion to which carbonate bedrock dilutes the ^{14}C signal of CO_2 evolved from organic matter decay in the soil zone is still a matter of debate (Criss et al. 2007). ^{14}C activity in the recent portion of secondary mineral deposits formed in caves, known as speleothems, is commonly used to identify the ^{14}C peak related to the increased atmospheric load during the 1960s related to nuclear tests (Genty and Massault 1997). Therefore, a prerequisite for karst water and speleothem ^{14}C dating is identifying the extent of water-rock interaction. A deeper understanding of the extent of reaction with the host rock can be obtained by coupling ^{14}C and δ^{13}C measurements (Criss et al. 2007), which is the focus of the present study.

The initial ^{14}C activity of speleothems and speleothem drip water is controlled by a mixture of 2 end members, the ^{14}C content of soil CO_2, typically close to the atmospheric ^{14}C level, and the C originating from dissolution of the carbonate host rock, commonly devoid of ^{14}C. The activity ratio of the first end member is modified by the dissolution of gaseous CO_2 in soil water. Additionally, the ^{14}C activity of the acidic solution depends on the soil air ^{14}C activity, the partial pressure of soil CO_2 (pCO_2), and temperature-dependent isotope fractionation factors (Garrels and Christ 1965; Hendy 1971; Salomons and Mook 1986; Dulinski and Rozanski 1990).

Soil air carbon dioxide ($CO_{2,g}$) is composed of CO_2 from root respiration and microbial decomposition of dead organic matter. Root respiration introduces modern ^{14}C values to the total $CO_{2,g}$, whereas microbial decomposition of soil organic matter (SOM) introduces CO_2 that has the composition of past atmospheric ^{14}C activities less the small amount of ^{14}C decayed since the time the dead OM was buried within the soil. The proportion of both components to the total soil CO_2 varies interannually (Dörr and Münnich 1986). During periods with less ^{14}C change in the atmosphere, and due to the relatively short turnover time of SOM (e.g. Trumbore 2000), CO_2 derived by decomposition of SOM has near-atmospheric ^{14}C values. As a result, the total soil air ^{14}C activity approximates atmospheric ^{14}C values, except for periods with fast and significant atmospheric ^{14}C variations. The

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$\delta^{13}C$ values of the respired CO_2 derived from root respiration and decomposition of SOM are identical. For plants using the C_3 pathway of photosynthesis, the soil air CO_2 sources respire $CO_{2,g}$ whose $\delta^{13}C$ values are around –25‰ (Deines 1980). This soil air $CO_{2,g}$ then equilibrates with the soil water by converting the gaseous $CO_{2,g}$ to aqueous $CO_{2,aq}$, which, according to the pH, then dissociates to bicarbonate (HCO_3^-) and finally to the carbonate ion CO_3^{2-}. For soil air, pCO_2 values usually found in soils (McDermott 2004), and accordingly low pH values in the soil water (Cerling 1984) isotope fractionation processes between the C-species, lead to an enrichment of the ^{14}C activities and of the $\delta^{13}C$ values in the solution compared to soil air $CO_{2,g}$. The strength of the enrichment is controlled by the relative distribution of DIC species in water, which in turn depends on the soil air pCO_2 (Hendy 1970, 1971). For example, Hendy (1970) modeled this relationship for water saturated with respect to calcite and varied soil air pCO_2 from 8100 to 125,000 ppm and found changes in the ^{14}C activity from 49.4 to 63.5 pMC with $\delta^{13}C$ values varying between –11.5 and –14.9‰. The solution saturated with carbon dioxide gas subsequently enters the karst aquifer, and carbonate rock dissolution occurs until the water is saturated with respect to calcite.

Models of isotopic exchange in karst aquifers consider in general 2 limiting cases of carbonate dissolution that occur under open and closed conditions (e.g. Wendt et al. 1967; Hendy 1970; Wigley 1975; McDermott 2004). In a closed system, the aqueous solution has no contact with the infinite soil CO_2 reservoir during the dissolution process. Therefore, for each mole of carbonate ion species derived from the acid hydrolysis of the host rock, 1 mole of aqueous carbon dioxide is converted to bicarbonate. When the solution becomes saturated with respect to calcite, approximately half of the C atoms originate from the carbonate rock, which is devoid of ^{14}C, and the other half is derived from soil air CO_2 (Hendy 1971). Consequently, the apparent age of the reservoir is close to 1 half-life. In an open system, the aqueous solution keeps equilibrating with the unlimited reservoir of soil gaseous carbon dioxide during carbonate dissolution. Hence, in the open carbonate dissolution system more Ca^{2+} is dissolved than in the closed system. In this process, isotopic exchange between DIC and soil air CO_2 is responsible for a ^{14}C activity of karst water that is similar to the values of soil air CO_2. The open and closed systems are 2 "theoretical" end-member cases of carbonate dissolution in karst aquifers. In most soil-rock-cave systems, the carbonate dissolution occurs in conditions that are intermediate between completely open and completely closed systems. This intermediate system combines the characteristics of both end members with respect to the isotopic composition of the C species in solution. With a change to a more open (closed) carbonate dissolution system, we expect higher (lower) ^{14}C values, lower (higher) $\delta^{13}C$ values, and higher (lower) Ca^{2+} concentrations in the saturated aquifer and cave water. In the intermediate system, the partial pressure of CO_2 and the ^{14}C activity of soil CO_2 in the unsaturated soil zone are the dominant factors controlling the magnitude of ^{14}C activity of the dissolved C species in the waters that enter a cave.

Variability in the ^{14}C activity and $\delta^{13}C$ values of the DIC in cave drip waters allows us to set quantitative constraints on the processes occurring in the soil zone during carbonate dissolution and in the cave. This is due to the different behavior of radiogenic and stable C isotopes in soil and karst processes. On the one hand, the ^{14}C activity of soil water is depleted in ^{14}C during carbonate dissolution due to the absence of ^{14}C in the geologically old host rock. On the other hand, the strongly depleted $\delta^{13}C$ value of soil-respired CO_2 in equilibrium with C_3-dominated vegetation coverage (about –25‰) and C species in soil water is shifted towards more positive values by carbonate dissolution due to the $\delta^{13}C$ value of carbonate rock, which is typically ~0‰ for those of marine origin.

Variations in the open and closed system behavior can therefore be identified by comparing pairs of ^{14}C activity and $\delta^{13}C$ values of DIC. As described above for the Ca^{2+} concentration, lower (higher) ^{14}C activities and higher (lower) $\delta^{13}C$ values are expected in the solution, if the carbonate dissolution occurs under more closed (open) conditions. This results in an anticorrelation between both C isotopes, which, in addition, is accompanied by important Ca^{2+} concentration changes. Furthermore, a negative correlation is introduced between ^{14}C and $\delta^{13}C$ if C exchange processes between DIC of the solution and the C in the carbonate rock influence the C isotopic composition of the drip water. C exchange processes between the DIC of the solution and $CaCO_3$ occur mainly when the solution is saturated with respect to calcite. During this process, the C isotope composition of the DIC is modified, due to the small proportions of back-and-forth reaction, which occur even at chemical equilibrium. In contrast to variations in the dissolution system, C isotope exchange between DIC of the solution and host-rock carbonate does not change the Ca^{2+} concentration in the solution. The annual vegetation cycle is responsible for more depleted $\delta^{13}C$ values and higher ^{14}C activities (Dörr and Münnich 1986) in spring and summer and for higher $\delta^{13}C$ values and lower ^{14}C activities in autumn and winter. This leads to an anticorrelation, but with a different slope between ^{14}C and $\delta^{13}C$ compared to the first processes. A positive correlation is generated by the isotopic fractionation between the participating C species because the radiogenic and the stable C isotopes have the same fractionation characteristics despite the fact that the fractionation for ^{14}C is twice as high as for $\delta^{13}C$.

In the present study, C isotopes in a well-monitored mid-altitude alpine karst system are investigated to gain information on the present-day processes that influence isotopic exchange in soils of mountain regions. The ultimate goal is a better understanding of the environmental significance of the variability of C isotope values over time in speleothems, which have been, so far, interpreted in terms of vegetation changes or generic "soil processes." In particular, the aim of this study is to quantify the different processes that control annual variations in the C isotope content of DIC in cave drip waters by using a multiproxy approach coupled with monitoring studies.

CAVE LOCATION AND SAMPLE PREPARATION

Study Site

Grotta di Ernesto is a shallow cave located 1167 m asl on the northern, steep slope of Valsugana Valley (Trentino Province) in northeast Italy. It is overlain by 5–30 m of dolomitic limestone. This cave is ideally suited for this study because it is small, largely undisturbed, and one of the most extensively monitored cave sites worldwide (e.g. Borsato 1997; McDermott et al. 1999; Huang et al. 2001; Frisia et al. 2003; Borsato et al. 2007). The vegetation above the cave consists entirely of C_3 plants in a mixed forest association, with predominant *Picea abies* and subordinate *Fagus sylvatica*, plus seasonal shrubs and grass. The soil is typical of a mixed forest in the upper mountain zone with parent material mostly consisting of limestone debris, namely Calcari-mollic Cambisol according to the World Reference Base for Soil Resources 1998 (Merkli et al. 2009). In the subsurface, the 70-m-long cave passage has a temperature of ~6.6 °C all year round, which reflects the mean annual air temperature at the surface. The average mean annual precipitation measured at the nearby meteorological station Vezzena (30-yr mean) is ~1300 mm and shows bimodal distribution with maxima during spring and autumn. Taking into account evapotranspiration (calculated after Thornthwaite 1948), the highest soil infiltration occurs in autumn. Snow is usually present in the winter months and melts during March and April, resulting in an important infiltration event. The karst aquifer reservoir, which feeds the drips in the cave beneath, is well equilibrated with a mean annual soil air pCO_2 (Fairchild et al. 2000; Frisia et al. 2005).

Water samples from 2 cave drip sites were analyzed for their C isotopic composition. One of the sites, ER-G1, has a fast dripping seasonal drip, whereas the second drip site, ER-76, has a slow dripping seasonal drip. Their typical discharge is 5–10 mL/min and 0.1–0.5 mL/min, respectively. The drip rate was measured manually once a month. ER-G1 drip rates are delayed relative to precipitation events by less than 2 weeks. The exceptions are strong rainstorms (more than ~12 mm/day) where the drip ER-G1 reacts within 12 hr. In contrast to ER-G1, the drip rate of ER-76 responds to precipitation events only after 1 to 2 months (Borsato 1997).

Sample Preparation

Drip water samples were collected monthly from November 2005 to October 2007. Samples at site ER-G1 were collected during each cave visit (within 2 hr), except for July and November 2006 and September 2007 when the drip rates were too low. In these months, aggregate drip water collected during the previous month was sampled. No sample is available for February 2006 because the risk of avalanches did not permit us to reach the cave. The March 2006 sample was lost during sample preparation. Drip water from site ER-76 was sampled as 1-month aggregate samples due to the consistently low discharge with the exception of the March 2006 sample, which represents 2 months. Sample preparation for accelerator mass spectrometry (AMS) ^{14}C measurement was performed at the ^{14}C laboratory of the Heidelberg Academy of Sciences. About 100 mL of drip water was acidified with HCl *in vacuo*. The evolved CO_2-water vapor mixture was separated first by freezing the water vapor in a dry-ice cold trap. The remaining CO_2 was captured in a glass vessel cooled with liquid nitrogen. The CO_2 was then converted to C in a combustion line at 575 °C via the reaction $CO_2 + 2H_2 \rightarrow C + H_2O$ using an iron catalyst. After the C precipitated on the iron, the C-iron mixture was pressed into AMS targets and sent to the ^{14}C laboratories at Lund University (samples collected November 2005 to August 2007) and Zurich (September–October 2007), respectively (Table 1).

Table 1 ^{14}C activity and δ^{13}C results of drip water samples (sites ER-G1, ER-76). Typical error of DIC δ^{13}C measured at Innsbruck University is 0.1‰ (1 σ). Differences in δ^{13}C between AMS and Innsbruck data are due to additional fractionation effects in the ion source of the AMS.

Sample name	Sampling date	Lab nr Heidelberg (HD)	Lab nr Lund (LuS)/ Zurich (EM)	^{14}C activity (pMC)	1-σ error (pMC)	δ^{13}C (AMS) (‰)	δ^{13}C (Innsbruck) (‰)
ER-G1 47	Nov 2005	HD-24871	LuS50011	98.04	0.32	–7.9	–11.2
ER-G1 48	Dec 2005	HD-24882	LuS50012	102.07	0.36	–7.9	–12
ER-G1 49	Jan 2006	HD-24884	LuS50013	102.66	0.39	–14.1	–11.8
ER-G1 50	Feb 2006						
ER-G1 51	Mar 2006						–11.6
ER-G1 52	Apr 2006	HD-25302	LuS50082	97.13	0.34	–9.9	–11.7
ER-G1 53	May 2006	HD-25304	LuS50084	99.44	0.38	–6.8	–11.9
ER-G1 54	Jun 2006	HD-25306	LuS50086	101.33	0.36	–0.7	–12.3
ER-G1 55	Jul 2006	HD-25348	LuS50088	103.6	0.39	–13.5	–12
ER-G1 56	Aug 2006	HD-25410	LuS50090	103.4	0.38	–13.7	–11.5
ER-G1 57	Sep 2006	HD-25464	LuS50144	102.68	0.45	–5.9	–12.1
ER-G1 58	Oct 2006	HD-25596	LuS50207	101.26	0.4	–6.2	–12.2
ER-G1 59	Nov 2006	HD-25738	LuS50205	101.22	0.38	–16.2	–10.3
ER-G1 60	Dec 2006	HD-25789	LuS50208	101.45	0.39	–18.7	–12.3
ER-G1 61	Jan 2007	HD-25791	LuS50203	104.01	0.42	–16.1	–12.3
ER-G1 62	Feb 2007	HD-25822	LuS50201	99.24	0.49	3.8	–11.8
ER-G1 63	Mar 2007	HD-25974	LuS50256	100.06	0.4	–13.2	–12.1
ER-G1 64	Apr 2007	HD-25979	LuS50258	100.92	0.43	–13.1	–11.8
ER-G1 65	May 2007	HD-26047	LuS50260	101.12	0.55	–5.3	–12.8
ER-G1 66	Jun 2007	HD-26202	LuS50357	101.64	0.49	–12.3	–11.9
ER-G1 67	Jul 2007	HD-26266	LuS50361	103.89	0.39	–16.9	–12.3
ER-G1 68	Aug 2007	HD-26384	LuS50364	104	0.39	–13	–12.3
ER-G1 69	Sep 2007	HD-26475	EM1005	102.61	0.26	–11.6	–12

Table 1 ^{14}C activity and δ^{13}C results of drip water samples (sites ER-G1, ER-76). Typical error of DIC δ^{13}C measured at Innsbruck University is 0.1‰ (1 σ). Differences in δ^{13}C between AMS and Innsbruck data are due to additional fractionation effects in the ion source of the AMS. *(Continued)*

Sample name	Sampling date	Lab nr Heidelberg (HD)	Lab nr Lund (LuS)/ Zurich (EM)	^{14}C activity (pMC)	1-σ error (pMC)	δ^{13}C (AMS) (‰)	δ^{13}C (Innsbruck) (‰)
ER-G1 70	Oct 2007	HD-26477	EM1007	101.49	0.25	–11.2	–12.1
ER-76 47	Nov 2005	HD-24870	LuS50014	100.1	0.38	–12	–11.1
ER-76 48	Dec 2005	HD-24881	LuS50015	101.62	0.36	–4.7	–11
ER-76 49	Jan 2006	HD-24883	LuS50016	101.62	0.34	–1.3	–11.1
ER-76 50	Feb 2006						
ER-76 51	Mar 2006	HD-25032	LuS50017	102.27	0.42	–6.9	–10.8
ER-76 52	Apr 2006	HD-25301	LuS50091	99.13	0.41	–6.1	–10.4
ER-76 53	May 2006	HD-25303	LuS50083	99.77	0.35	–9.6	–11.6
ER-76 54	Jun 2006	HD-25305	LuS50085	100.25	0.35	–11	–12
ER-76 55	Jul 2006	HD-25349	LuS50087	101.81	0.36	–16.4	–11.5
ER-76 56	Aug 2006	HD-25409	LuS50089	98.64	0.36	–12.5	–11.6
ER-76 57	Sep 2006	HD-25463	LuS50145	101.53	0.42	–15.4	–11.1
ER-76 58	Oct 2006	HD-25596	LuS50207	100.14	0.39	–16.9	–11.6
ER-76 59	Nov 2006	HD-25738	LuS50205	99.82	0.39	–18.2	–11.1
ER-76 60	Dec 2006	HD-25788	LuS50209	98.98	0.38	–15.9	–11.4
ER-76 61	Jan 2007	HD-25790	LuS50202	101.53	0.39	–11.6	–11.3
ER-76 62	Feb 2007	HD-25821	LuS50200	101.94	0.41	–7.7	–10.7
ER-76 63	Mar 2007	HD-25973	LuS50255	93.17	0.37	–15.1	–12.2
ER-76 64	Apr 2007	HD-25978	LuS50257	102.08	0.4	–12.4	–11.2
ER-76 65	May 2007	HD-26046	LuS50259	101.81	0.46	–8.8	–12.1
ER-76 66	Jun 2007	HD-26201	LuS50356	98.68	0.36	–14	–11.1
ER-76 67	Jul 2007	HD-26265	LuS50360	100.79	0.54	–13.9	–12.1
ER-76 68	Aug 2007	HD-26384	LuS50364	101.35	0.37	–11.2	–12
ER-76 69	Sep 2007	HD-26474	EM1004	99.71	0.25	–11.6	–11.5
ER-76 70	Oct 2007	HD-26476	EM1006	100.93	0.24	–10.2	–11.6

The soil water samples were collected with a lysimeter situated above the center of the cave, nearly exactly above drip location ER-G1, and not shaded by the vegetation canopy. The lysimeter is comprised of a plastic tube with a large ceramic cup at the bottom. The water was collected with a vacuum pump. The soil water samples were collected at 1 m depth. To minimize C isotope fractionation effects, we followed the sampling procedure described in Spötl (2005) when collecting soil and drip water. The method for air sample collection and transport as suggested by Spötl (2004) was performed to minimize alterations of the stable C isotopic composition. DIC δ^{13}C and δ^{18}O values of monthly drip and soil water samples as well as δ^{13}C of air samples were analyzed at Innsbruck University (±0.1‰ precision) using a Delta$^{\text{plus}}$XL isotope ratio mass spectrometer (see Spötl 2005). δ^{13}C and δ^{18}O values are reported on the VPDB scale. All air isotope samples were analyzed within 72 hr after sampling.

The concentration of dissolved Ca^{2+} in the drip water was analyzed at Heidelberg University using an ICP-OES VISTA MXP (VARIAN) with an internal 1 σ of <1%. NIST 1643e was used as a standard, which has long-term reproducibility of 1 mg/L (3%). pH measurements were carried out in the field and directly within the cave to avoid temperature effects, by using a multiparameter 340I meter (WTW) equipped with a highly sensitive probe (±0.05 pH units) and temperature probe. Cave air pCO_2 was measured with a Vaisala Meter GM70 with GMP222 probe (accuracy at 25 °C: ±20 ppm).

RESULTS AND INTERPRETATION

δ^{13}C and δ^{18}O

Soil air and soil water δ^{13}C values of DIC as well as the O isotopic composition of soil and cave water were investigated in order to evaluate the drip water C isotope data in terms of processes influencing the annual variability. The δ^{18}O values of soil water at 1 m depth (Figure 1a) indicate a strong annual δ^{18}O cycle (~3‰) despite the lack of data in some months where it was not possible to collect soil water. In contrast, drip water δ^{18}O values show little interannual variation (~0.5‰), indicating a well-mixed karst water reservoir feeding ER-G1 (Figure 1a). Furthermore, the elevated Ca^{2+} values in soil water (Figure 1a) indicate that at 1 m below the surface, significant calcite dissolution has already occurred as also shown in other studies (e.g. Larssen et al. 1998). The concentration of soil water Ca^{2+} shows a large variation of ~35 mg/L. This variation diminishes in the karst aquifer and results in nearly constant Ca^{2+} concentrations in the drip water of location ER-G1 (Figure 1a). The same pattern is observed in the stable C isotope composition of soil air, soil water (Figure 1b), and drip water of ER-G1 and ER-76 (Figure 2) (see also Frisia et al. 2010). The δ^{13}C value of soil air and soil water has varied between November 2005 and October 2007 by 3‰ (Figure 1b). This variation is consistent with the annual cycle of soil air δ^{13}C as observed in other studies (e.g. Andrews et al. 1999; Ekblad and Högberg 2001; Bowling et al. 2002; Gorczyca et al. 2003; Steinmann et al. 2004). Maximum values are reached in winter, when vegetation respiration and dead organic material decomposition are reduced with respect to the warm seasons when the most negative values are observed. The soil air δ^{13}C shows the opposite behavior to the soil air pCO_2. Both findings can be explained by the soil respiration rate, which is lower in winter than in summer, and with the diffusion of the respired soil air CO_2 to the free atmosphere as demonstrated by Cerling (1984). The soil respiration rate, in turn, depends strongly on temperature and precipitation (Schlesinger 1977). Thus, the annual cycles of temperature and amount of precipitation explain the minimum and maximum of soil air δ^{13}C in September and March, respectively. The soil water δ^{13}C cycle is a consequence of water in isotopic equilibrium with the surrounding air. In months where no data are shown, the lysimeter was empty due to dry conditions of the atmosphere (less rain or a high amount of evapotranspiration) or frozen soil conditions. Isotope analysis on soil air started in April 2006.

The δ^{13}C data of the drip water DIC of ER-G1 and ER-76 (Figure 2) reveal only a subtle interannual variability, with only small deviations from the mean values of both drip sites. The 3‰ range seen in the soil water is completely attenuated and no clear annual cycle is visible. Hence, the variation in the DIC in drip water δ^{13}C can hardly be inferred from the soil water δ^{13}C cycle. The slow drip site ER-76 shows on average 0.5‰ more negative δ^{13}C values than the fast drip site ER-G1. The 2-yr means are –11.9‰ (ER-G1) and –11.4‰ (ER-76).

Radiocarbon Measurements

In contrast to δ^{13}C, ^{14}C measurements on DIC in drip water reveal a distinct annual pattern over the 2-yr sampling period (Figure 3). This pattern is more significant for the ^{14}C values of waters from the fast seasonal drip ER-G1 waters than for the slow seasonal drip ER-76. In the second year of ^{14}C activity measurements of ER-76, the pattern breaks down. The annual drip water characteristic consists of a trend towards increasing ^{14}C activity between November and January, followed by a strong decrease in the ^{14}C activity in February and March. Between March and July, a steady increase in ^{14}C activity occurs until the ^{14}C content decreases slightly until November. For most samples, the ^{14}C activity in DIC drip water samples of location ER-76 is lower than for drip ER-G1. The mean difference in the ^{14}C activity between both drip locations is 1.2 pMC. Furthermore, the variations of the ^{14}C content in DIC of the drip water from location ER-G1 are larger than those from ER-76.

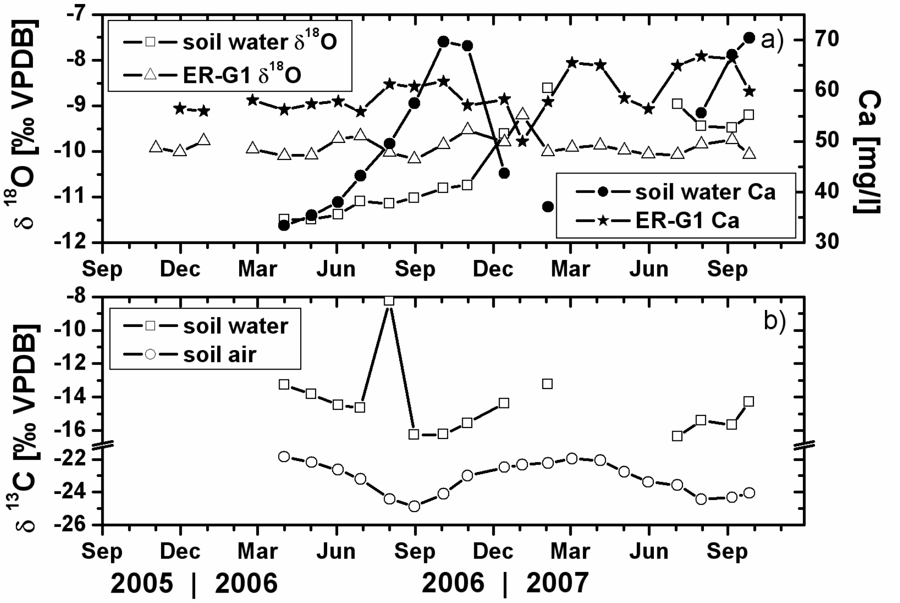

Figure 1 Monthly measured $\delta^{18}O$ values (a) of soil water (open squares) and water of drip location ER-G1 (open triangles). The large difference of the soil water collected in summer and winter is smoothed in the karst system and results in almost constant $\delta^{18}O$ values of the drip water. While soil water Ca concentrations (black circles) reveal large interannual variations, the Ca concentration of location ER-G1 (black stars) is more constant. (b) Shows the stable C isotopic composition of soil air (open circles) and soil water (open squares). The cyclicity of the $\delta^{13}C$ signal in soil air is maintained in the soil water samples.

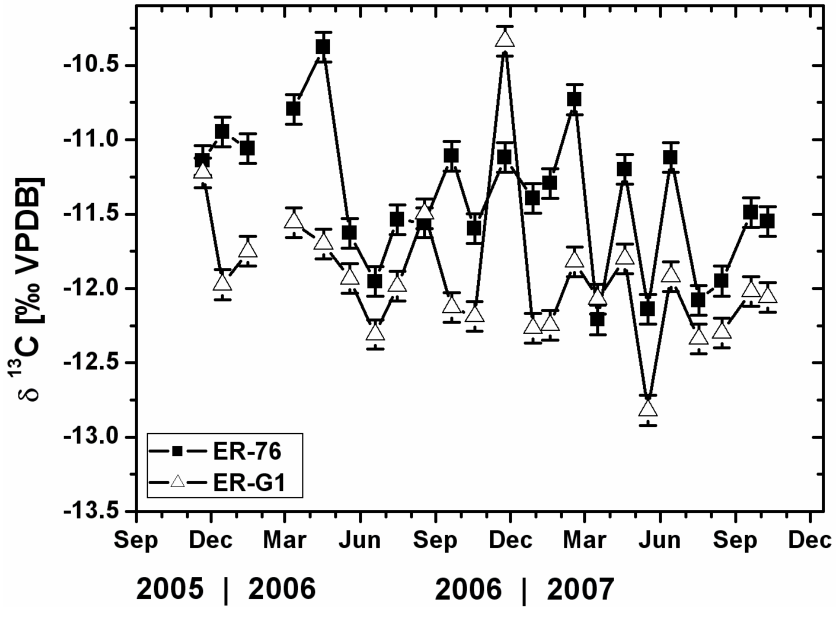

Figure 2 Monthly measured $\delta^{13}C$ data of DIC in the drip water samples collected at sites ER-G1 (open triangles) and ER-76 (black squares) are fairly constant compared to the pronounced annual cycle of soil water DIC $\delta^{13}C$ (Figure 1b).

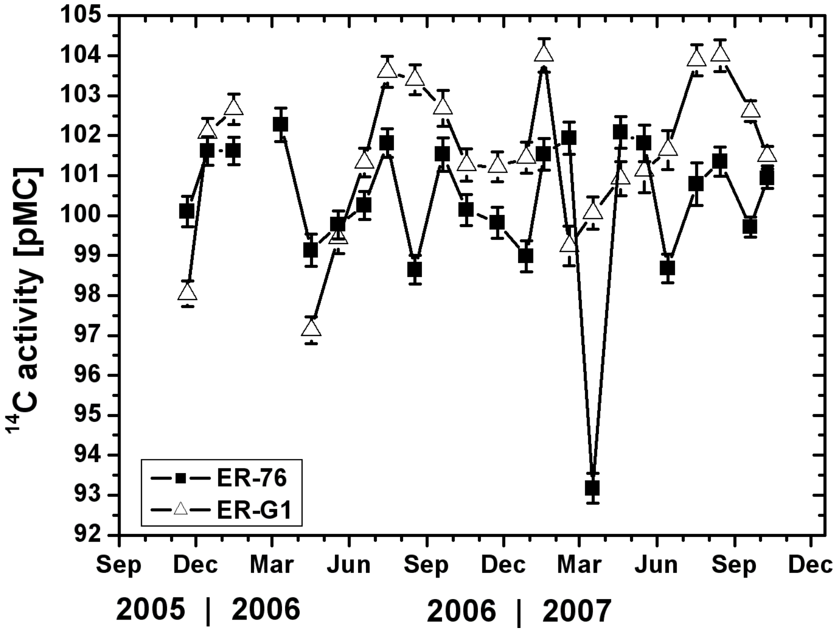

Figure 3 Monthly measured ^{14}C data of the drip water samples collected at drip locations ER-G1 (open triangles) and ER-76 (black squares) reveal a distinct annual cycle. Only the last year for ER-76 did not fit the cycle.

Fohlmeister et al. (forthcoming) derived soil parameters for the soil above Ernesto Cave, which enable computation of the ^{14}C activity of the soil air. According to these parameters, the gaseous CO_2 of the soil has a ^{14}C activity of ~110 pMC in the year 2006. The mean ^{14}C value of drip site ER-G1 is ~101.5 pMC. Neglecting the small fractionation effects for ^{14}C, the proportion of dead carbon originating from the host rock carbonate is approximately 8%.

pH Measurements and Drip Rates

A distinct annual signal has been observed in the drip water pH (Figure 4). This had been interpreted as being modulated by degassing, because it follows the seasonal cave air pCO_2 decrease (Figure 4), with higher pH in the cold season when cave pCO_2 is at its lowest values (Frisia et al. 2000, 2010). However, the chemical composition of drip water from both sites is not in chemical equilibrium with cave air CO_2. The cave air pCO_2 is constant in the whole cave at any given time due to its ventilation characteristics, which are responsible for the large range of cave air pCO_2 throughout the year. The main sources of cave air pCO_2 are the outer atmosphere in winter and gaseous CO_2 emerging from the karst in summer (Frisia et al. 2010). In both drip sites, decreasing pH values have been measured from late winter to autumn and increasing pH values from autumn to late winter. The pH of water from drip site ER-76 is more alkaline than the pH of drip water measured at the location ER-G1, but the pH variations in both drip sites are comparable.

Drip rate measurements at both locations reveal the seasonality of drips in the slow drip ER-76 and in the fast drip ER-G1 (Figure 5). The drip rate is controlled by the infiltration of meteoric water (Miorandi et al. 2010). However, calcite deposition below ER-76 occurs over a small radius and forms a stalagmite displaying a marked annual cyclicity (Frisia et al. 2003), whereas under ER-G1 deposition is spread over a large area and lacks evidence of annularity. Hence, seasonality of the drips does not necessarily translate into seasonality in the calcite precipitated from these drips.

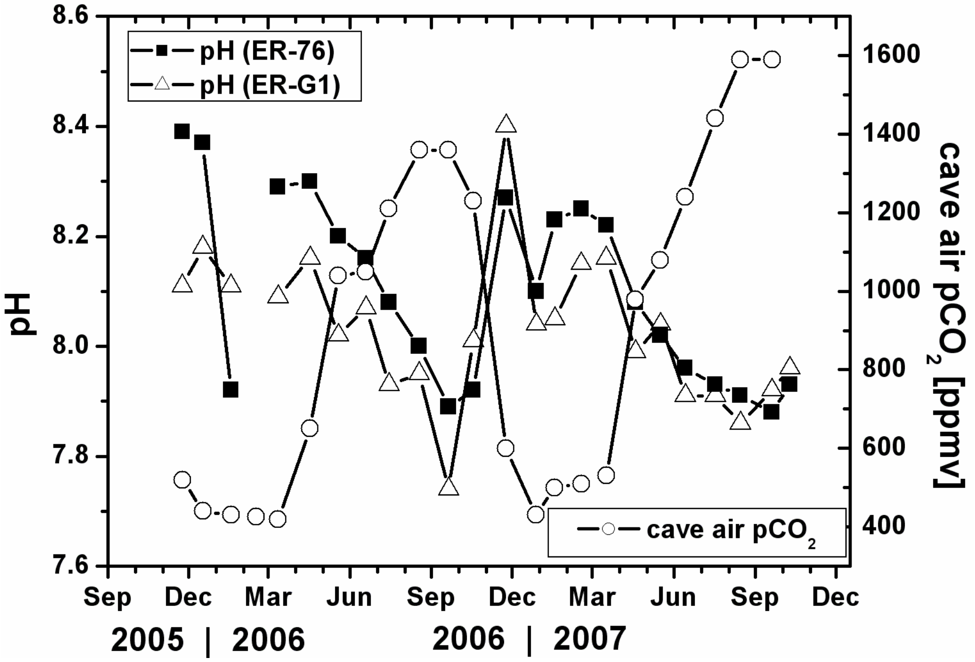

Figure 4 Monthly measured pH values of drip water from locations ER-G1 (open triangles) and ER-76 (black squares) reveal a synchronous behavior. Water from ER-76 is in general more alkaline than ER-G1. Cave air pCO_2 (open circles) shows an inverse pattern as pH resulting in a high anticorrelation between both variables ($r = -0.87$, $p < 0.0001$).

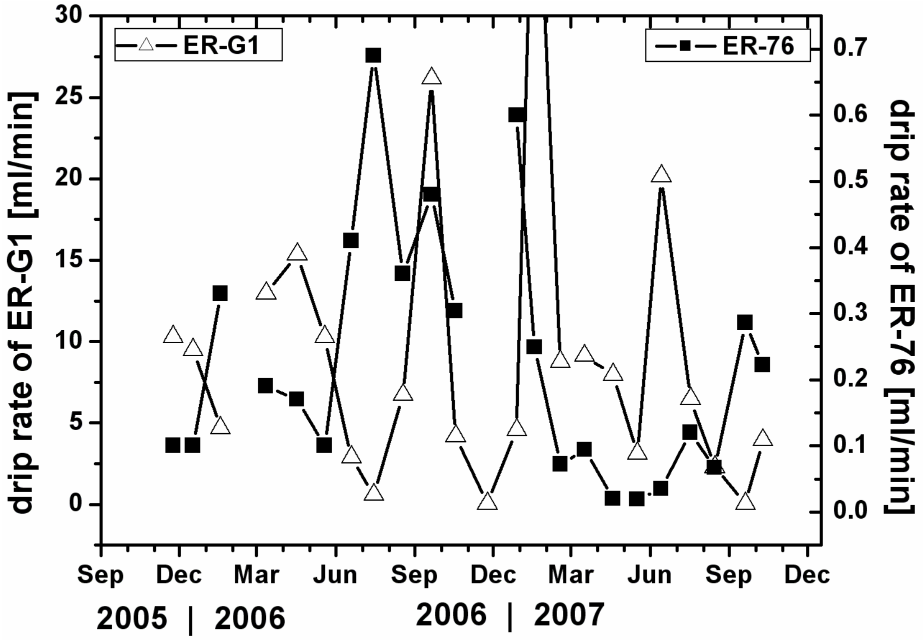

Figure 5 Drip site ER-76 (black squares) has lower drip rates than ER-G1 (open triangles). Nevertheless, both sites show large variations in drip rate, although they are not simultaneous.

DISCUSSION

Implications for Soil Processes

The smoothing of the $\delta^{18}O$ signal in drip water from location ER-G1 compared to the soil water (Figure 1a) is interpreted as mixing in the karst aquifer reservoir occurring below the sampling depth of the soil water (1 m) as stated in Fairchild et al. (2000) and Frisia et al. (2005). Due to the short-term monitoring of the oxygen isotopes in the water, it is impossible to provide any indication about the resolution of the time signal encoded in the mixed oxygen isotope values. The oxygen isotope values of drip waters at both drip sites indicate a mixed average over a minimum of 2 yr. It is reasonable, therefore, to infer that the $\delta^{13}C$ values of drip water at both monitored drips (Figure 2) also reflect some mixing in the soil and epikarst. The 3‰ variation in $\delta^{13}C$ observed in soil air and water in the 2 yr of observation is, in fact, smoothed in the aquifer reservoir and leads to a relatively constant $\delta^{13}C$ signal in the drip waters. The mixing hypothesis is also supported by the seasonal pattern of soil air and soil water $\delta^{13}C$ values (Figure 2b), because the seasonality is not reproduced by the $\delta^{13}C$ variability of the drip water. Therefore, other processes occur in the karst, which account for the small variation of $\delta^{13}C$ of DIC in drip water. These effects can be explained by interpreting the ^{14}C measurements on drip water (Figure 3). First, we will focus on drip location ER-G1, which responds quickly to precipitation events, rather than on the slow drip location ER-76.

For further consideration, we assume a groundwater reservoir above Ernesto Cave that is not completely saturated with respect to calcite. Furthermore, we assume that the groundwater has ^{14}C values generated by a calcite dissolution process under predominantly open dissolution conditions. The first condition is satisfied by the fact that when an unsaturated solution joins a reservoir the resulting solution is also unsaturated. Additionally, our assumption of the unsaturated aquifer reservoir is supported by the theoretical finding that mixing of 2 saturated solutions each in equilibrium with different pCO_2 leads to an unsaturated solution (Dreybrodt 1988). The mixed solution is expected to emerge mainly under open dissolution conditions because the carbonate dissolution occurs in the upper soil layers and the solution remains in contact with the infinite soil CO_2 reservoir. This assumption is underpinned by the $\delta^{13}C$ values of soil air and water (Figure 1b) in combination with the soil water Ca^{2+} data (Figure 1a). The mean Ca^{2+} concentration of the soil water is ~50 mg/L and, hence, large parts of the dissolution process takes place within the first meter of the soil (compare with the mean drip water Ca^{2+} content of ER-G1 [Figure 1a], which is ~60 mg/L). Figure 1b shows a mean $\delta^{13}C$ enrichment between soil air CO_2 and DIC of soil water of ~8.5‰. At a mean soil water temperature of ~7 °C and a mean soil water pH value of 7.4, the aqueous CO_2 in the solution is ~10% and the bicarbonate is ~90% of the total C in the solution. According to the fractionation constants reported in Mook and de Vries (2000) the mean $\delta^{13}C$ enrichment between soil air CO_2 and DIC of soil water should be ~8.85‰. Theoretical and measured fractionation factors are in the same range and point to calcite dissolution, which is in equilibrium with its surrounding soil air CO_2. The stable C isotope value of the host-rock carbonate of around 0 to +1‰ (published by Avanzini et al. [1997], who measured $\delta^{13}C$ on the same rock formation that also covers Grotta di Ernesto) is not seen in the soil water. Hence, open conditions of carbonate dissolution are very likely to prevail in the first meter of the soil cover.

Implications for Karst Aquifer Behavior on Drip Location ER-G1

Carbon from SOM and from carbonates are the most important C sources from which the C species in the drip water are derived. Therefore, these pools are responsible for a seasonal signal like the one shown in Figure 3. Theoretically, the annual ^{14}C activity pattern as seen in drip water can be explained by changes in the composition of the total soil CO_2 alone, which is derived from SOM reservoirs of different ages (Dörr and Münnich 1986; Tegen and Dörr 1996; Genty et al. 1998; Genty and Massault 1999; Trumbore 2000). The percentages of the different reservoirs to total soil pCO_2 change the ^{14}C composition of soil air CO_2 throughout the year. However, as argued above, any seasonal soil signal is attenuated by mixing processes in the soil above Grotta di Ernesto, and, thus the contribution from SOM of different ages is hardly responsible for the cycle observed in drip water ^{14}C. Hence, this cannot be the process driving the annual cycle in ^{14}C activity in drip water of Grotta di Ernesto.

Another effect on the C of the drip water is the degassing of CO_2 inside the cave, plus some possible equilibration of C isotopes in the solution with cave air. The degassing of the drip water observed at the same time that water was running down the stalactite (Frisia et al. 2000; Miorandi et al. 2010), did not affect the Ca^{2+} concentration because the solution must first exceed a certain SI value (Nielsen and Toft 1984) before Ca^{2+} can precipitate. During degassing, the composition of the C isotope changes, whereas the changes for ^{14}C are roughly twice as high as for $\delta^{13}C$ (Saliège and Fontes 1984; Mook and de Vries 2000). Comparing the mean $\delta^{13}C$ of soil water (about –14.4‰) and drip water (about –11.9‰) (Figure 1b) indicates that at maximum a change of 6‰ (0.6 pMC) in ^{14}C activity can occur due to the degassing of CO_2. This is an order of magnitude smaller than the variations of the ^{14}C data during the measurement period (Figure 3). Hence, the degassing process has little potential to vary the ^{14}C activity and Ca^{2+} concentration and, therefore, is not significant for the collected drip water. In addition, it is possible that C exchange between the DIC in the water and the cave air affects the carbon isotope composition of the DIC in drip water. However, at Grotta di Ernesto also cave air $\delta^{13}C$ was measured during the investigated period. Summer values of cave air $\delta^{13}C$ are about –20‰ and winter values are around –12‰ (Frisia et al. 2010). Hence, if the effect of C exchange is pronounced in the cave, then the $\delta^{13}C$ of the slow drip ER-76 should be affected most, because the drip waters of ER-76 are collected continuously over a 1-month period and, hence, have time to equilibrate. However, we did not observe variations in the $\delta^{13}C$ of the drip water, which are similar to the change of the cave air $\delta^{13}C$. We therefore conclude that the process of C exchange between DIC in drip water and cave air CO_2 is not important for the drip water that we collected.

The third possibility is that the observed variability in the ^{14}C signal of DIC in drip water originates from the carbonate dissolution processes in the soil zone and the epikarst, either by the way the carbonate dissolves or by C exchange processes between water and carbonate rock. At first, we deal with changes in the degree of open and closed carbonate dissolution conditions. As already discussed, the water in the well-mixed groundwater reservoir is undersaturated and emerges under open dissolution conditions. When the carbonate of the karst aquifer dissolves until the saturation is achieved, the condition of carbonate dissolution can vary. Under completely open dissolution conditions, much more carbonate can dissolve as compared to completely closed conditions (e.g. Hendy 1971; Salomons and Mook 1984). Variations in the Ca^{2+} concentration indicate that there are changes in the condition of calcite dissolution. These changes also control the ^{14}C activity of the drip water. If we assume, *a priori* and without loss of generality, that in the month with the highest measured Ca^{2+} concentration (66.8 mg/L, August 2007) the carbonate was dissolved under the most open conditions of all observed months, and if we assume further that the deviations from that Ca^{2+} value are due to changes in the degree of open and closed carbonate dissolution, then the Ca^{2+} concentration should correlate with the measured ^{14}C data. However, a correlation is not observed. This theoretical correlation cannot be disturbed by the degassing process in the cave because there is no potential to disturb a correlation between ^{14}C and Ca^{2+} concentration as shown above. Hence, there has to be another process overlying the varying condition of carbonate dissolution.

This process has to occur also in the karst aquifer and seems to be the C isotope exchange between DIC and the host-rock carbonate. To demonstrate the impact of the C isotope exchange on the ^{14}C activity, we use the drip rate of location ER-G1, which is a value for the residence time of the water in the karst aquifer. Figure 6 shows that there is a strong correlation between ^{14}C activity and drip rate. From very low drip rates up to drip rates of ~15 mL/min, there is a strong negative linear correlation between these 2 parameters ($r = -0.7$, $p = 0.001$). Above drip rates of ~15 mL/min, a threshold is crossed and the correlation breaks down. Above the threshold, the ^{14}C activity increases with increasing drip rate. Therefore, the correlation calculation was performed without the samples lying above the threshold, which are marked as squares within parentheses.

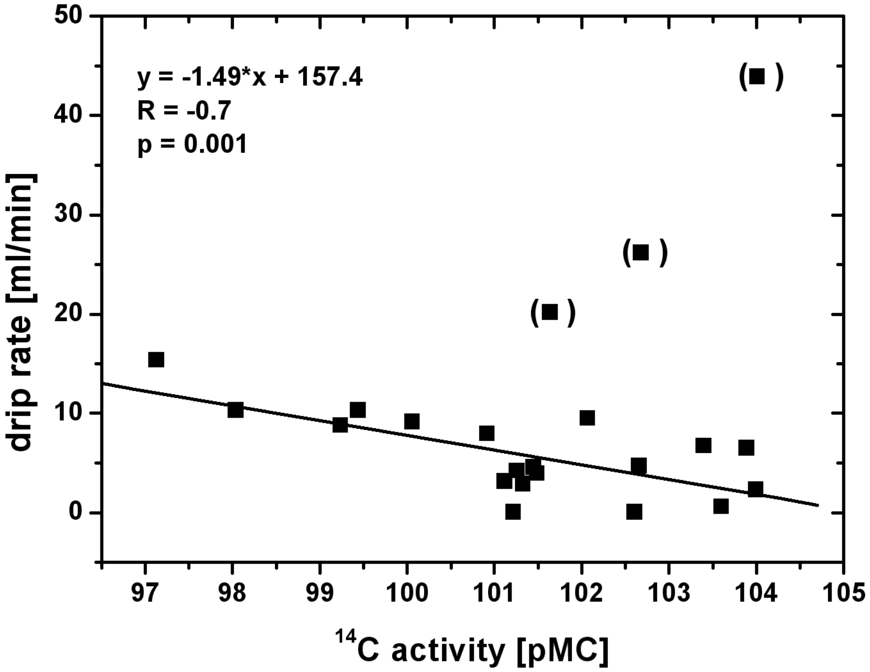

Figure 6 Correlation of monthly drip rate at ER-G1 and ^{14}C activity of DIC in drip water, indicating a strong relationship. Calculations were performed without the values in parentheses (see text).

For ER-G1, the linear correlation below the threshold can be explained by the karst residence time of the water. Water, which has a longer residence time in the karst, is allowed to exchange more C between the water and the carbonate rock. Accordingly, the drip water sampled during high drip rates has a longer residence time in the water reservoir than the water, which arrives in the cave during low drip rates. At first glance, this seems to be contradictory. However, water emerging in the cave at high drip rates came into the karst aquifer during times that experience mostly low infiltration conditions and stayed there a relatively long time until a strong infiltration event pushed this water very quickly into the cave. When the infiltration event stopped, large parts of the water from the infiltration event are shortly above the cave and this water, which has a relatively short residence time in the karst, has high ^{14}C values, and emerged in the cave during times with low drip rates.

The existence of the threshold implies that at least 2 different water flows feed drip location ER-G1. If the drip rates are below the threshold, the water is supplied by a steady flow, most likely a matrix one (Fairchild et al. 2006). Such flow allows for more C isotope exchange. The ^{14}C activity depends on this drip rate range only in the time when the water is percolating through the karst aquifer. If an enormous infiltration event occurs, a threshold is crossed and water from another flow path is added to drip location ER-G1. This process is similar to those modeled for other caves in Fairchild et al. (2006). This additional water originates from fissure flow with water having less contact with the carbonate matrix; hence, less C can be exchanged. This water has to have higher ^{14}C activities than the water of the porous flow. Therefore, the variations in the ^{14}C activity of the drip water depend on the contribution of the different sources to the total drip water. If the threshold is crossed, then the ^{14}C activity of the drip water is higher with a larger contribution of water from fissure flow, resulting in very high drip rates.

With a host rock consisting of ancient marine carbonates, an opposite behavior to that described for ^{14}C activity should be established with respect to drip water δ^{13}C (Criss et al. 2007). This is not observed due to CO_2 degassing in the cave. The degassing process disturbs the signal of the stable C isotope (expressed in δ notation) more significantly than the radiogenic C isotope in drip water (expressed in pMC). Additionally, the amount of degassing varies within the analyzed period. Using the MIX4 program (Plummer et al. 1975; Fairchild et al. 1994), we virtually added CO_2 to the drip water. The injected CO_2 amount, which was needed to achieve the saturation state of the water with respect to calcite, covers a range from 0.09 up to 0.29 mmole/L. The loss of CO_2 in the range of the calculated amount yield an enrichment in δ^{13}C of the water of about 0.2–0.6‰ if we assume isotopic equilibrium fractionation. The enrichment is larger if the fractionation does not occur in equilibrium.

Implications for Karst Aquifer Behavior on Drip Location ER-76

It is remarkable that the ^{14}C values of the slow seasonal drip ER-76 are generally lower than for the fast seasonal drip ER-G1 and that the signal is more attenuated (Figure 3). On the other hand, the δ^{13}C values (Figure 2) are higher in general. Assuming that the drip water of both drip locations is fed by the same aquifer with the same isotopic composition, the difference between the C isotopes of both drip locations is related to karst hydrology or processes within the cave. Degassing of the solution during the 1-month sampling duration is a possible explanation for the enhanced δ^{13}C values. The degassing process is being increasingly recognized as a very important cave process in a variety of environments (Spötl et al. 2005; Baldini et al. 2008), and has been documented at Grotta di Ernesto (Frisia et al. 2000). However, if only degassing acted, the enriched δ^{13}C values should be accompanied by higher ^{14}C values in the C of the drip water (Figure 3). A higher δ^{13}C value of 0.5‰ (the observed mean difference of the 2-yr period for both drip sites) would result in a higher mean ^{14}C activity of roughly 0.1 pMC in drip ER-76 compared to ER-G1. However, a lower mean value of 1.2 pMC in ER-76 was measured. Hence, degassing is not the only process responsible for higher δ^{13}C values in drip water of ER-76 compared to ER-G1. Nevertheless, degassing will surely contribute to the total δ^{13}C and ^{14}C signal of ER-76 drip water.

As mentioned previously, chemical reactions or isotopic C exchange between the solution and the soil and host rock carbonates explain lower ^{14}C activities and higher δ^{13}C contents in drip water. That means either that the dissolution process in the pathway feeding ER-76 occurred under more closed conditions than in the pathway feeding ER-G1, or that C exchange processes between the C species in solution and the C of the host rock occurred to a larger extent in ER-76 compared to ER-G1. Both drips, ER-76 and ER-G1, are classified as seasonal drips reacting to seasonal precipitation changes. Only the amount of discharge (roughly 2 orders of magnitude difference) and the soil residence time of water (around 2 months in ER-76 compared to 2 weeks for ER-G1; Borsato 1997) are different. This is a hint that for water of ER-76, C exchange between solution and carbonates is even more important than for ER-G1.

The difference in pH between both drip waters is the more alkaline drip water of ER-76 compared to the ER-G1 drip water (Figure 4). Higher pH values can be attributed to degassing processes, to a more closed carbonate dissolution process, or to a combination of both. Unfortunately, no ion measurements were performed on drip water of ER-76 during that period, so that data is unavailable to differentiate between both processes. We speculate that most of the offset in the pH between ER-76 and ER-G1 is due to a more closed dissolution condition in the karst aquifer and that the seasonal pattern of the pH is due to the same strength of degassing effects occurring for ER-G1. The sum of all 3 processes—degassing, a more closed dissolution condition, and a more important C exchange process—have the potential to explain the C isotopes measurements.

We did not find a correlation between drip rate and ^{14}C activity for drip site ER-76. The attenuation of the ^{14}C signal in drip water of ER-76 compared to ER-G1 is very likely attributed to the longer soil and karst residence time of this water, which is consistent with the more muted seasonal drip behavior of ER-76. The longer residence time leads to higher mixing in the karst aquifer. Hence, the water derived under more open conditions in 1 month and under more closed conditions during the next month can account for the observed intermediate ^{14}C values.

CONCLUSIONS

We present data from a 2-yr monitoring involving C measurements on monthly drip water samples from 2 drip sites at Ernesto Cave. The ^{14}C measurements reveal a clear annual cycle for the fast seasonal drip ER-G1. This pattern is as clearly present in the first year of ^{14}C analysis for drip site ER-76, but the seasonality is not visible in the second year. In both δ^{13}C drip water records, no relation to soil air and soil water δ^{13}C was observed. Furthermore, there is no clear relation observed between ^{14}C activity and δ^{13}C in drip water of both drips due to several processes that change the isotopic composition of the water and which are not necessarily constant over subannual timescales. The observed changes in both C isotopic compositions are attributed to C exchange processes and to small variations in the degree of the open versus closed carbonate dissolution. However, the expected variations in δ^{13}C are masked by other processes, such as isotopic fractionation due to degassing in the cave or in hydrological pathways, which cause larger changes in δ^{13}C than in ^{14}C activity. The relative change in δ^{13}C due to fractionation is in the range of 10‰ by accounting the conversion of HCO_3^- to gaseous CO_2. This value is relatively large compared to the differences of the end members contributing to the total C in the solution (about –25‰ of soil air and ~0‰ of marine-derived carbonate). For the ^{14}C activity, the difference between soil air (~100–110 pMC) and host-rock carbonate (0 pMC) is much larger than changes induced by fractionation effects (~2 pMC for the conversion of HCO_3^- to gaseous CO_2).

C isotopic composition of ER-G1 drip water is largely controlled by variations in the C exchange processes between solution and host-rock carbonate and in the second order by the degree of open versus closed calcite dissolution. At this drip location, the infiltration-dependent residence time of the water in the aquifer controls C exchange processes. A negative correlation between ^{14}C activity and drip rate is then established, because drip rate also depends on infiltration. The negative correlation is observed under a certain drip rate threshold. Above that threshold of ~15 mL/min, a positive (non-linear) relationship between ^{14}C activity and drip rate is observed.

The calcite dissolution of location ER-76 seems to occur under more closed conditions compared to ER-G1. Furthermore, C isotope exchange and additional mixing of water within the aquifer also play an important role. Additionally, degassing affects the C isotope composition due to the low drip rate and long sampling time. This all leads to a change in the C isotopic composition compared to the ER-

G1 location. Hence, no correlation between drip rate and ^{14}C is observed for ER-76. Although results and interpretation are conclusive, further monitoring is necessary to support our findings.

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