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Dating cave drip water by tritium

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SUMMARY

Speleothems are increasingly used as an archive of past climate, but some of the proxy signals encoded in these deposits reflect hydrological characteristics of the karst aquifer (and not necessarily climate variability). A central aspect in karst hydrology is the time required for the rainwater to reach the point of discharge in a cave, e.g. the tip of the stalactite. One promising approach in determining this residence time is drip-water dating by tritium (^{3}H). In contrast to traditional tritium dating, we do not refer directly to tritium concentrations in precipitation as input function, but to an infiltration-weighted annual mean of the rainwater values. Using concentration differences between this infiltration-weighted mean and the drip water, an age is calculated from the radioactive decay law, assuming piston flow.

The approach was tested in three adjacent caves in northwestern Germany which were monitored for about two years. All of the studied drip sites yielded drip water ages between 2 and 4 years with uncertainties on the order of 1 year. These results were confirmed at several drip sites by oxygen isotope data which show rather constant values with insignificant intra-annual variability. Attempts to apply the ^{3}H–^{3}He method resulted in comparable ages, despite several complicating factors.

1. Introduction

Karst environments have long been studied with regard to their hydrologic behavior (Atkinson, 1977; Eisenlohr et al., 1997; Labat et al., 2002; Baker and Brunsdon, 2003; Fairchild et al., 2006), the use of karst water for drinking water supply (Zötl, 1985; Drew and Hötzl, 1999; Bakalowicz, 2005), and the influence of climate change and anthropogenic impact on these vulnerable environments (Kaçaroğlu, 1999; Ma et al., 2004; Zhengtao et al., 2009). More recently, karst terrains have gained additional scientific interest because cave deposits are increasingly used as important paleoclimate archives (e.g. Fleitmann et al., 2003; Mangini et al., 2005; Wang et al., 2008). Calcite precipitated in caves (speleothems) contains valuable proxy records of past climate and environmental conditions (Harmon et al., 2004; McDermott et al., 2005), e.g. δ^{18}O values can reveal changes in past temperatures and precipitation (Vollweiler et al., 2006; Wang et al., 2008). In some cases δ^{13}C can be used to constrain past vegetation changes (Dorale et al., 1998), whereas the Mg/Ca ratio has been interpreted as an indicator of precipitation and recharge under certain conditions (McDonald et al., 2004; Cruz et al., 2007). Furthermore, dissolved noble gases in fluid inclusions of stalagmites can give insight into past temperature changes (Kluge et al., 2008a). δ^{18}O, δ^{13}C, and elements have a high potential as up to seasonal resolution can be achieved for certain speleothems (Treble et al., 2005; Mattey et al., 2008). In order to correctly interpret high-resolution signals it is necessary to have a quantitative understanding of the geochemical processes (Tooth and Fairchild, 2003; Baldini et al., 2006) and especially the residence time in the karst aquifer, as well as of the processes occurring during calcite deposition (e.g. Spötl et al., 2005). Karst groundwater encountered in caves shows a wide spectrum of flow types, ranging from very slow dripping seepage flow to rather high-discharge types, including shaft flow and subcutaneous flow (Smart and Friedrich, 1987). Drip sites feeding actively forming stalagmites are typically of the seepage-flow type (i.e. low discharge, low variability), the seasonal-drip type (i.e. low discharge, but seasonal variability), or of the vadose-flow type (higher discharge, commonly giving rise to sheet-like flowstone deposits, e.g. Baker et al., 1997). In terms of mean

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residence time, seepage flow sites tend to show the longest delay between infiltration in the recharge area and emergence at the drip site and therefore essentially are low-pass filters which eliminate high frequency variability. Stalagmites forming beneath such drips will be particularly suited for the investigation of climate variability on multi-annual, decadal or even longer scales, but will fail to record short-lived extreme climatic events, such as extraordinarily wet or dry seasons (e.g. Baldini et al., 2006). Multi-annual monitoring of different cave drip sites is therefore required to choose suitable stalagmites and to constrain the relation between the measured stalagmite signals and meteorological or climatological variables.

Various methods have been developed and tested in order to assess the residence time of vadose groundwater in karst systems. Some of the most promising methods used so far are based on variations in the luminescence of the drip water, long-term time series of tritium (^{3}H) or oxygen isotopes interpreted in terms of lumped-parameter models as well as attempts of ^{3}H–^{3}He dating. The intensity of luminescence due to the (varying) content of organic matter in the drip water provides some information on the delay between rainwater infiltration and discharge into the cave chamber (Baker et al., 1999, 2000). However, the interpretation of luminescence data is difficult on annual and multi-annual time scales due to possible changes in the organic carbon production and non-linear luminescence-discharge effects (Baker et al., 2000). Long-term measurements of other tracers such as δ^{18}O, δD, and tritium are a valuable approach which yields rather well constrained residence times in the framework of lumped-parameter models (e.g. Maloszewski et al., 2002; Einsiedl et al., 2009). This method is useful if long-term monitoring is possible (e.g. large karst springs), but is commonly not feasible for cave studies. Combined measurements of tritium and ^{3}He provide a well established method for dating of young groundwater (Torgersen et al., 1979; Schlosser et al., 1988; Cook and Solomon, 1997). Recently, first attempts to apply the ^{3}H–^{3}He dating method to date drip water in caves have been made (Yamada et al., 2008; Kluge et al., 2010). However, because this gas-tracer method is expected to only determine the residence time in saturated parts of the overlying karst and poses considerable challenges for sampling low-flow drips in caves, it may not be generally applicable to constrain drip water ages.

Water tracing using fluorescent dyes is widely used in karst hydrogeology in "point-to-point" mode to define the trajectory and mean travel time taken by groundwater flowing in rather wide conduits (e.g. Käss, 1998; Benischke et al., 2007; Goldscheider et al., 2008) but it has only rarely been applied to seepage water in the context of speleothem studies (e.g. Tooth, 1998; Williams, 2008). This is due to the much longer observation intervals as compared to conduit flow which reflects the high degree of dispersion and retention, as well as possible absorption, e.g. on clay minerals, and chemical alteration or even complete loss of fluorescence (e.g. Flury and Wai, 2003). A dye tracer experiment was carried out above one of the caves studied here (Dechen Cave), but the dye was never detected inside the cave.

Young groundwater (less than 50 years old) can be dated by comparing tritium values with the regional input function of tritium in precipitation (Clark and Fritz, 1997; Solomon and Cook, 2000). Despite the widespread use of tritium in groundwater hydrology it has been rarely applied to date cave drip water (e.g. Kaufman et al., 2003). In the early days of the method, the pronounced "bomb-peak" produced by thermonuclear bomb tests in the early 1960s provided a strong marker (e.g. Münnich et al., 1967). Maximum values in Northern Hemisphere precipitation reached ca. 5000 TU (TU = Tritium units = tritium atoms per 10^{18} H atoms). Today, the tritium concentration of meteoric precipitation approaches pre-bomb levels of about 5 TU (Clark and Fritz, 1997; Gat et al., 2001) leaving only small inter-annual variations of the input. There is still a pronounced seasonal variation of tritium in precipitation (5–20 TU) which, however, is damped by mixing of the infiltrating water in the soil zone.

With regard to the residence time of water in the karst aquifer several studies concluded that the delay between rainfall and the arrival of this water on the stalagmite is in the range of weeks to months (Baker and Barnes, 1998; Baker et al., 1999, 2000; Frappier et al., 2002). In such cases, seasonal variations of tritium and stable isotopes in precipitation should be reflected in the drip water, such that time series of both tracers hold the potential for dating based on the phase shift between precipitation and drip water. In other caves, however, mean groundwater residence times are much longer (often exceeding 1 year), as shown by studies by Kaufman et al. (2003) or Yamada et al. (2008) and by our own work (Kluge et al., 2008b). In such cases, we propose that the monthly atmospheric tritium input values should be weighted by the seasonal variation of the amount of infiltration in order to obtain a smoothed tritium input function. We attempted to determine the age of drip water based on the radioactive decay of tritium in the aquifer in reference to the only slightly changing infiltration-weighted tritium concentrations in the recharging groundwater of the last 20 years.

In the following we present this methodology and discuss its application to drips from three caves in northwestern Germany.

2. Study sites and sampling

Three neighboring caves in the Rhenish Slate Mountains of northwestern Germany (B7 Cave, Bunker Cave and Dechen Cave, 51°22′N, 7°40′E) were investigated in this study. The caves are situated in massive limestone of Devonian age about 180 m above sea level and were mainly formed during the Pleistocene (Hammerschmidt et al., 1995). B7 Cave is situated at a depth of about 40–60 m below the surface, whereas the rock overburden at Dechen and Bunker Cave is about 15–30 m thick (Grebe, 1993; Niggemann et al., 2003; Hammerschmidt and Niggemann, 2007). The karstified limestone surface is covered by brown loamy soil (average thickness 1 m) containing limestone clasts. The vegetation above the caves consists of deciduous forest (mainly ash and maple) and shrubs. The study area has a temperate climate with precipitation throughout the year (annual mean 900 mm, 1961–1990). Annual precipitation for 2006, 2007, and 2008 (795, 1095, and 874 mm) at the weather station Hagen-Fley (2006, 2007, located 15 km from the caves) and at the German Cave Museum (2008), located at the entrance of the Dechen Cave, was comparable to the long-term mean. The mean annual air temperature is 9.5 °C (1961–1990) with a monthly winter minimum of 2–3 °C and a monthly summer maximum of 17–18 °C (station Hagen-Fley of the German National Meteorological Service DWD, 1961–1990). Due to summer evapotranspiration the main infiltration occurs during winter months.

Bunker Cave has been monitored since 2006 and a summary of the monitoring data is given by Riechelmann et al. (2009). The sampling locations relevant to this study are shown in Fig. 1. For tritium dating, rain water was collected on the roof of the German Cave Museum at Dechen Cave. Aliquots were taken for tritium and stable isotope analysis from the monthly precipitation sum. Cave drip water was also sampled for the same parameters on a monthly basis, but these represent "instantaneous" measurements (collecting water from individual drip sites for 3–4 h). The slow dripping site TS 5 in Bunker Cave (Fig. 1) is an exception; there, water was continuously collected in a container and an aliquot was taken each month for isotope analysis. For further details on sampling and drip characteristics the reader is referred to Riechelmann et al. (2009).

Additionally, drip water samples for noble gas analysis were collected in the three caves using copper tube samplers similar to

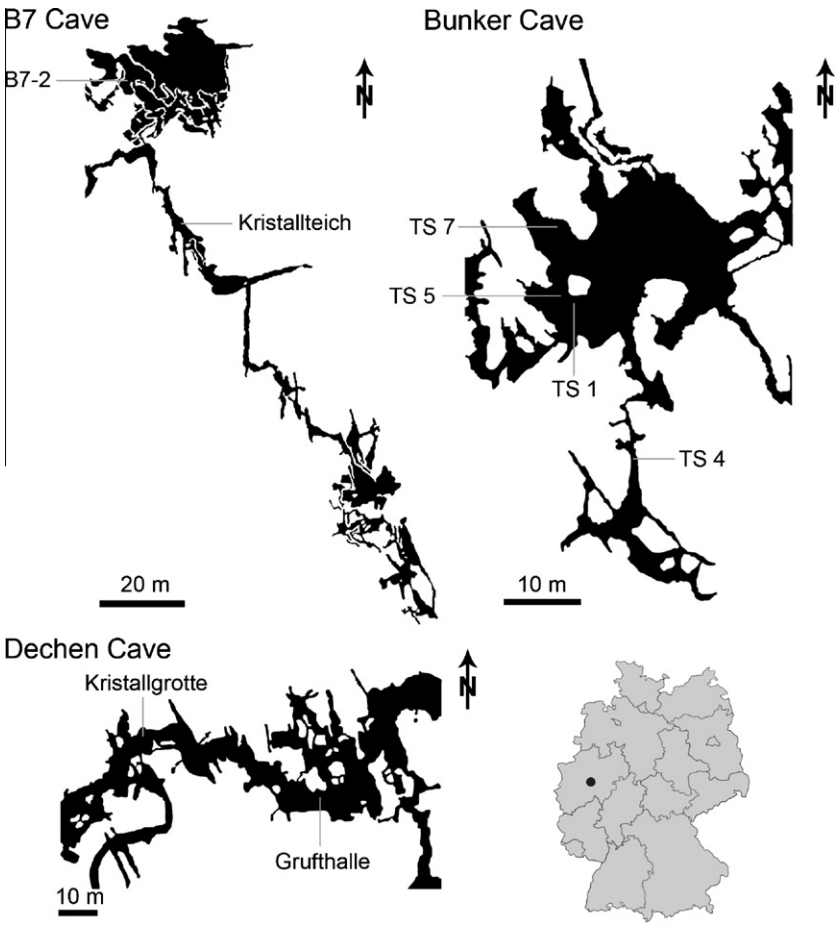

Fig. 1. Partial plan views of Bunker Cave, Dechen Cave and B7 Cave. Sampling locations are marked. The black dot on the map of Germany at the lower right marks the location of the cave region.

those used for noble gas sampling of groundwater but with a reduced size of about 6 ml due to the much smaller amount of available water. Water was collected by a funnel positioned just below the dripping stalactite or other point of entry of the drip water into the cave and then flowed slowly through flexible tubing to the copper tube sampler, which was sealed after flushing it several times.

Long-term measurements of tritium in rain water were conducted on samples from the meteorological station Hof of the DWD (50°18′N, 11°52′E, 567 m asl), about 320 km east of the cave region (Table 1). Tritium data from stations closer to the study area are comparable to the results from Hof but cover a shorter monitoring period (Fig. 2).

3. Methods

3.1. Tritium drip-water dating

The presented method is based on the radioactive hydrogen isotope tritium. It has a half-live of 12.32 years (Lucas and Unterweger, 2000) and is used in studies of groundwater and surface water to distinguish old (>50 years) from more recently infiltrated water (Clark and Fritz, 1997). The tritium "bomb-peak" of the early 1960s with maximum values of about 5000 TU has provided an ideal tool for dating of young groundwater and karstwater (Clark and Fritz, 1997; Kaufman et al., 2003). In recent years, however,

Table 1
Inter-annual mean and 1σ standard deviation of tritium concentrations of monthly precipitation samples taken at the station Hof. The values were calculated based on data from 1995 to 2005. Precipitation values from 2007 to 2009 from the German Cave Museum at the entrance of Dechen Cave are shown for comparison. All values are given in tritium units (TU). The uncertainties of the German Cave Museum rain values refer to the 1σ measurement uncertainty.

Month	Rainwater at Hof (mean)	Variability (1σ)	Precipitation at Dechen Cave		
			2007	2008	2009
January	8.0	2.8		6.1 ± 1.0	8.5 ± 1.2
February	8.2	2.2		5.0 ± 1.2	7.4 ± 1.0
March	9.8	2.8		8.4 ± 0.9	7.4 ± 1.4
April	12.0	2.1		13.5 ± 1.1	9.9 ± 1.1
May	13.9	4.0		12.3 ± 1.0	12.5 ± 1.3
June	14.1	2.8		10.6 ± 1.0	16.4 ± 1.4
July	14.5	3.4		7.9 ± 1.3	12.5 ± 1.3
August	13.2	2.1		13.4 ± 1.3	
September	10.0	3.9		12.4 ± 1.3	
October	8.3	2.4		11.2 ± 1.2	
November	8.5	2.5	9.2 ± 1.2	11.2 ± 1.4	
December	7.5	2.0		11.4 ± 1.5	

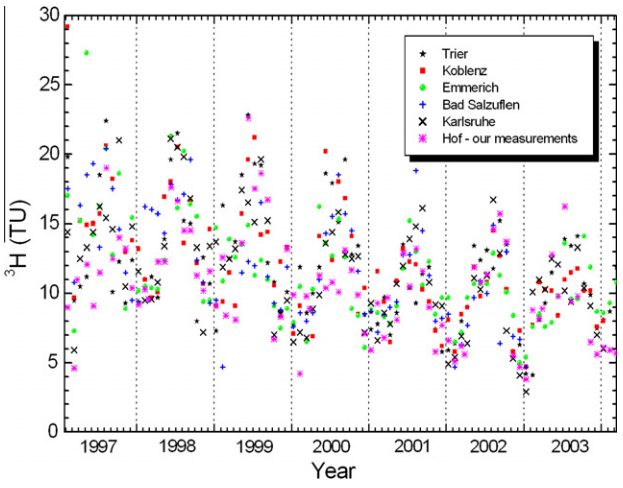

Fig. 2. Tritium data of different stations in Germany. The ^{3}H values from Hof refer to measurements performed at Heidelberg University, the other stations are from the GNIP data base (IAEA/WMO, 2006). The distances from the study area to Emmerich, Bad Salzuflen and Koblenz are about 110 km, to Trier 200 km, to Karlsruhe 270 km, and to Hof 320 km.

it has become increasingly difficult to use the high activities around the "bomb-peak" as a time marker due to the dispersion of the signal in the aquifer, non-unique solutions caused by fluctuations in the input (Clark and Fritz, 1997), and decay-reduced activities comparable to present-day precipitation values.

In the last 20 years the tritium concentration in rain water has only decreased slightly. The data from the weather station Hof in Germany show a pronounced seasonal cycle which varies between 5 TU in winter and 20 TU in summer (Fig. 3) with an annual mean of 10.7 TU (1995–2005), which is approaching pre-bomb values. Kaufman and Libby (1954) and Roether (1967) estimated the natural (pre-bomb) tritium value to ca. 5 TU in central Europe, von Butlar and Libby (1955) measured an average of ca. 2 TU in western European rivers and ca. 3 TU in Spanish wines. Tritium is naturally produced by cosmic radiation in the upper troposphere and the lower stratosphere and is transported to the troposphere through tropopause discontinuities especially in mid latitudes during late winter and spring (Gat et al., 2001). This mechanism causes the seasonal pattern of high tritium precipitation values during late winter and spring, and lower concentrations in periods of less frequent intrusions of stratospheric air into the troposphere. The variability of natural tritium levels is influenced by the extent and location of the stratosphere–troposphere exchange as well as

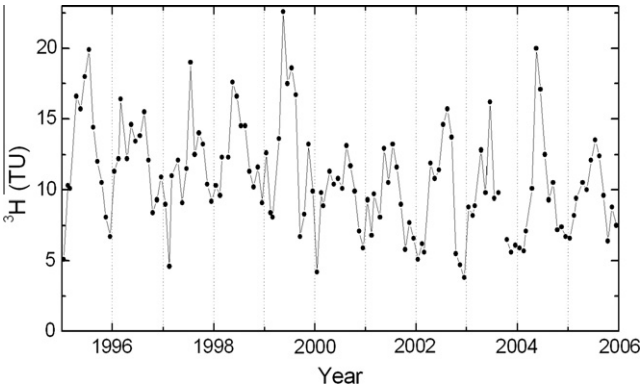

Fig. 3. Tritium concentration in monthly collected rain water. The samples were taken at weather station Hof, about 320 km east of the cave region. The measurement uncertainty (1σ) is about 1 TU.

changes in the tritium production caused by (solar activity-modulated) fluctuations in the cosmic-ray flux (Simpson, 1960). The groundwater tritium level can be furthermore influenced by variations in the infiltration.

Water percolating through the vadose zone of a karst system consists of different components including direct flow through fractures and conduits (underground stream courses), contributions of a long-term storage component, and a flow fraction from the porous-fissured aquifer (an aquifer type containing mobile water in fissures and stagnant water in the porous matrix; Maloszewski et al., 2002; Fairchild et al., 2006). However, in many cases the flow fraction from the porous-fissured aquifer, comprising rather well mixed infiltration-weighted rain water, is the dominating component. Maloszewski et al. (2002), for example, concluded that this fraction constitutes more than 80% at the outflow of two karstic springs in the Alps. The relative contribution of the different components can be studied using δ^{18}O values in precipitation and drip water (Perrin et al., 2003; Long and Putnam, 2004). In the case of Bunker Cave δ^{18}O values of individual drips in general agree well with the infiltration-weighted mean of rainwater above the cave (Fig. 4).

We therefore use the annual infiltration-weighted means C_0 of tritium as reference values for the calculation of residence times in the karst aquifer. Leaving effects of mixing and exchange with older stagnant reservoir water bodies aside (discussion in Section 5), the tritium concentration in the karst aquifer is only reduced by radioactive decay:

$$C_{\mathrm{drip}} = C_0 \cdot e^{-\lambda t} \tag{1}$$

$\lambda = 1.541 \times 10^{-4}\ \mathrm{d}^{-1}$ decay constant of tritium.
C_{drip} tritium concentration of the drip water.
t time required for the water to reach the drip site.

As the infiltration values C_0 are still changing slightly it is most precise to use a local time-dependent input curve $C_0(t)$. The residence time t can then be calculated by intersecting the decay-corrected drip water curve ($C_{\mathrm{drip}} \cdot e^{\lambda t}$) with the input curve $C_0(t)$:

$$C_{\mathrm{drip}} \cdot e^{\lambda t} = C_0(t) \tag{2}$$

This procedure is explained exemplarily in Fig. 5. It shows the actual infiltration-weighted values in the cave region and linear fits to two segments of the time series which are used to construct an input curve $C_0(t)$. The dashed line of sample B7-2 (2 February 2008, downward-pointing triangle) to the linear fit represents the decay curve of its initial infiltration-weighted value. The intersection of this line with the input curve gives the date of the water infiltration, which is early 2005 for B7-2. The dotted lines above and below refer to the decay curve either of the maximum or the minimum tritium concentration of the sample within the 1σ uncertainty. Their intersections with the input curve yield the range of infiltration dates (early 2004, end of 2005). The uncertainty of the reference curve has to be added to this range (see below).

The annual infiltration-weighted tritium values were calculated using the monthly mean tritium values from Hof and the weather data from Hagen-Fley. For 2006 and 2007 we used the monthly mean tritium values from Hof averaged over the 1995–2005 period. As the infiltration-weighted annual values vary slightly we use linear fits of annual tritium values versus time as a reference input function for the recharging water in the karst system from 1996–2007 (Fig. 5).

During the last decade tritium concentrations have been approaching rather invariant pre-bomb values, which is already visible in the Bunker Cave data after the year 2000. The low scatter may enable the determination of a constant tritium reference value in the future and a simple residence time calculation based on Eq.

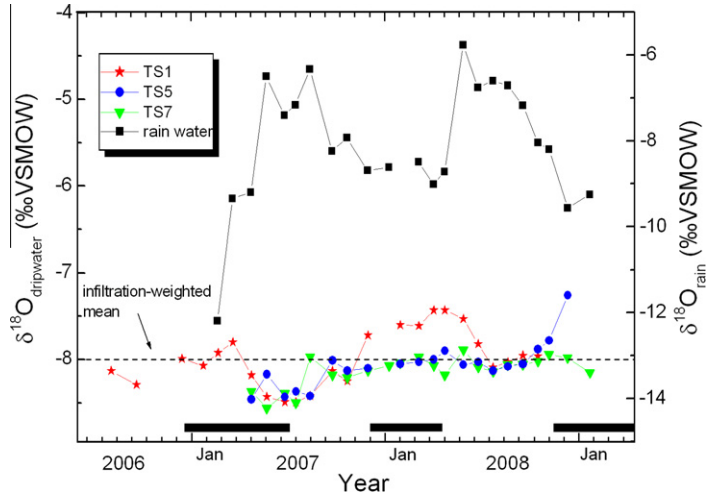

Fig. 4. $\delta^{18}O$ of rainfall (right axis) above Bunker Cave and different drip sites in Bunker Cave (TS1, TS5 and TS7, left axis). Note the different vertical scales. Periods of major infiltration are indicated by black horizontal bars at the bottom. The infiltration-weighted mean $\delta^{18}O$ value is indicated by the dashed horizontal line and corresponds well to the drip water values. The data are from Riechelmann et al. (2009).

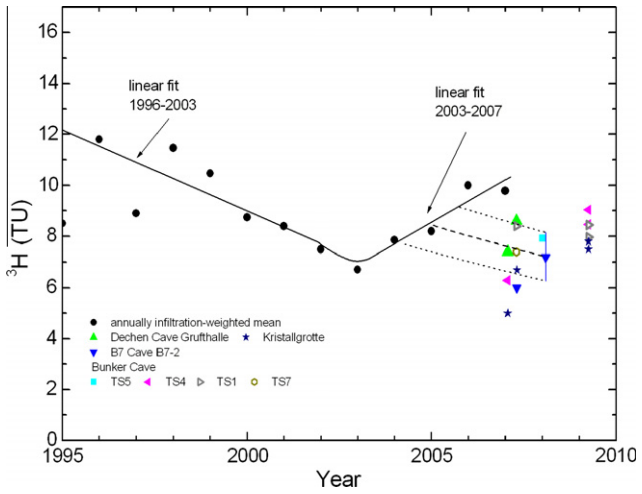

Fig. 5. Calculated annual tritium values in recharging groundwater in the study area (black circles). The calculation of these infiltration-weighted annual means is based on the mean monthly tritium values at Hof and the infiltration data derived from the weather station Hagen-Fley. Two linear fit segments are used to construct a reference tritium curve $C_0(t)$ from the annual values. Drip water values are shown for comparison. Uncertainties for the drip water samples are between 0.4 and 1 TU (1σ). The dashed line represents a decay extrapolation of a drip water sample and shows the period of infiltration at the cross section with the input curve. The adjacent dotted lines give an estimate for the age uncertainty.

(1) only. The slight increase of the tritium input observed in the period 2003–2007 (Fig. 5) is also favorable for tritium dating. In some regions, however, tritium input concentrations may continue to decrease rather strongly. If the decrease in the infiltration-weighted values is similar to the radioactive decay of tritium, then no meaningful residence time determination is possible as the calculated ages will be associated with large uncertainties (compare period 1995–2003 in Fig. 5). At sites with very low tritium input, e.g. in tropical latitudes or on the Southern Hemisphere, high-precision tritium measurements are a prerequisite for the application of the method proposed here.

The uncertainty of the residence time in the karst aquifer was derived by accounting for both the measurement uncertainty of the drip water tritium values and the uncertainty of the tritium reference curve for the infiltrating water. The latter uncertainty was calculated from the standard deviation of the annual means from the linear fit that was used to approximate $C_0(t)$. For the period 2003–2007 this standard deviation amounts to about 5% of the infiltration reference value. The tritium values at different stations within Germany show a variability of 5% (2001–2003). This uncertainty was added to the total uncertainty of the reference curve by Gaussian error propagation. The uncertainty of the reference curve was then added by Gaussian error propagation to the sample uncertainty. The experimental error of the tritium samples was propagated into an age error by increasing or decreasing the sample values by their 1σ uncertainties and then finding the intersections of the corresponding decay curves with the reference curve.

Data from a meteorological station at Hagen-Fley (100 m asl, about 15 km from the cave) and Hemer (200 m above sea level, 8 km from the cave) were used for the calculation of the infiltration-weighted mean of tritium using Haude's formula (Haude, 1955) for the potential evapotranspiration ET_{pot}:

$$ET_{pot} = x \cdot P_{14}(1 - H_{14}/100) \quad [\text{in mm/d}] \tag{3}$$

x refers to monthly weighting corresponding to the active vegetation (values for x are given in Hölting and Coldewey, 2009), P_{14} is the saturation vapor pressure (in mbar) at 2 pm, and H_{14} is the relative humidity in % at 2 pm. The evapotranspiration was calculated on a daily basis and is therefore assumed to have a small uncertainty. Schiff (1975) confirmed that Haude's formula rather precisely reproduces actual evapotranspiration values in central Europe.

3.2. ^3H–^3He dating

The combined measurement of ^3H and ^3He is a valuable tool in groundwater hydrology to determine ages of young water (e.g. Schlosser et al., 1988; Cook and Solomon, 1997; Solomon and Cook, 2000). In addition to the common application in groundwater it has recently also been used for dating of cave drip water (Yamada et al., 2008; Kluge et al., 2008b). ^3H–^3He dating is based on the ^3H and the tritiogenic $^3He_{trit}$ concentration prevailing in the water at the time of sampling:

$$t = t_{1/2}/\ln 2 \cdot \ln(^3\text{He}_{\text{trit}}(t)/^3\text{H}(t) + 1) \tag{4}$$

where $t_{1/2}$ is the half-life of ^3H and t is the ^3H–^3He age. The initial input value of ^3H is not required for the calculation of a water age. The tritiogenic $^3He_{trit}$ is derived from the measured ^3He by

subtracting the equilibrium component and a possible excess air and radiogenic component.

In the following only the main aspects are summarized in order to explain the background of the ^3H–^3He ages for some of the investigated drips used to compare with the tritium-derived ages. The details of the sampling technique for noble gases and the data evaluation procedures used to derive ^3H–^3He ages of drip waters are discussed elsewhere (Kluge et al., 2010). The determination of the tritiogenic $^3He_{trit}$ was kept as simple as possible. Because no significant radiogenic He component was found in the drip waters, tritiogenic $^3He_{trit}$ was calculated only from the measured ^4He concentrations and $^3He/^4He$ ratios and the calculated atmospheric equilibrium concentrations of He, according to the simplified equations discussed in Kipfer et al. (2002). The heavy noble gases (Ar, Kr, Xe) were only used to estimate noble gas temperatures (NGTs) as a basis for the calculation of atmospheric equilibrium concentrations. Noble-gas data were evaluated using the inverse modeling technique of Aeschbach-Hertig et al. (1999) to estimate the equilibration temperature and the amount of excess air, i.e. the super-saturation of atmospheric gases that typically exists in groundwater (Heaton and Vogel, 1981). The data were evaluated based on several models taking into account the composition of excess air in groundwater (Aeschbach-Hertig et al., 2000; Kipfer et al., 2002). No indication of significant fractionation of excess air relative to atmospheric air was found in our samples.

The advantages of the ^3H–^3He method are the high-precision with uncertainties of only a few months and the fact that ^3H input values are not required. However, ^3He is a gas tracer and can therefore be affected by diffusive gas loss in unsaturated parts of an aquifer, especially in karst areas (Kluge et al., 2010). Therefore, ^3H–^3He ages must be interpreted carefully in such environments.

3.3. Experimental methods

The tritium concentration was measured in Heidelberg by decay counting (Weiss et al., 1976; Grothe, 1992) and in Bremen using the ^3He ingrowth method (Clarke et al., 1976; Sültenfuß et al., 2009). Typical uncertainties are about 1 TU for samples measured by decay counting and as low as 0.4 TU in the case of the ingrowth method.

Noble gases (^3He, ^4He, ^{20}Ne, ^{22}Ne, ^{36}Ar, ^{40}Ar, ^{84}Kr, ^{132}Xe) were analyzed in a sector-field mass spectrometer (GV 5400) working in static mode. The gas separation and measurement follow the procedures described by Beyerle et al. (2000) and Friedrich (2007). Typical uncertainties for the noble gas concentrations are below 1% for Ne and Ar, about 1% for Kr and ^4He, about 2% for Xe, and below 2% for the $^3He/^4He$ ratio. In two runs we experienced problems with the ^3He measurement which raised the uncertainty to 4% and for two samples up to 10%.

The oxygen isotopic composition of water samples was analyzed by isotope ratio mass spectrometry at the University of Innsbruck (Spötl et al., 2005) and the data are given with reference to the VSMOW standard. Typical uncertainties (1σ) are about 0.08 ‰.

4. Results

Continuous measurements of tritium in rain water at the weather station Hof show a strong seasonal variability but only a weak long-term trend over the last 20 years (Fig. 3). Tritium measurements of rain water in the study area show the same seasonal pattern (Fig. 6) and similar amplitudes in winter and summer (Table 1). An exemplary calculation of the infiltration-weighted tritium means of 2006 and 2007, based on samples for tritium in precipitation taken at the German Cave Museum (2007–2009) and data from the weather stations Hagen-Fley and Hemer, yielded the same values as a calculation using the monthly mean tritium values from Hof and the infiltration data from both weather stations near the cave site (9.99 and 9.78 TU vs. 9.73 and 9.81 TU, respectively). Therefore, it is reasonable to use the monthly mean tritium values from Hof, as they are based on a longer monitoring period.

The tritium concentration of the sampled drip sites varies between 5 and 9.5 TU (Table 2). Samples taken from the same drip site at different times show little variation, mainly corresponding to past changes in the infiltration input values. However, tritium values of individual drip sites vary significantly even within a single cave, reflecting complex flow regimes. Drip site TS 5 in Bunker Cave was monitored for tritium for one and a half years and showed invariant values with a mean value of 8.0 ± 0.6 TU (Fig. 7).

The $\delta^{18}O$ values of the rain water vary between −9.5‰ in winter and −5.5‰ in summer (Fig. 4). The infiltration-weighted mean is −8.0‰, which is well reflected in the drip water values of the Bunker Cave (−7.5‰ to −8.5‰) and especially in their annual means (−7.9‰ to −8.2‰). Only drip site TS1 shows a slight variability. Drip site TS4 provided only water during periods of infiltration and has a relatively high $\delta^{18}O$ value, which may be due to evaporation in the vadose zone. Monitoring of B7 Cave between 1997 and 1998 showed low variability of three investigated drip sites (±0.6‰; Niggemann, 2000) with a mean of −8.4‰. Note that while the infiltration-weighted mean of the $\delta^{18}O$ values of precipitation corresponds well to the drip water data, calculating precipitation-weighted $\delta^{18}O$ values for the infiltrating water in the monitoring period 2006–2008 results in higher annual means (about −7.6‰), which are not found in the drip water. Therefore, we only use the infiltration-weighted tritium values for the following considerations.

The noble gas samples of drip water yielded NGTs of about 10 °C (Kluge et al., 2010), which are comparable to the present-day cave temperatures (Niggemann, 2000; Riechelmann et al., 2009; Pflitsch et al., 2000). Most samples contained no excess air, indicating equilibration either in the unsaturated zone above the cave (at a soil temperature similar to the cave temperature) or in the cave itself. However, the samples from B7 Cave (drip site B7-2) contained significant excesses of atmospheric noble gases (about 10% excess Ne), indicating dissolution of trapped air during the passage through the overlying karst and thus the existence of a saturated zone, i.e. a perched aquifer above B7 Cave.

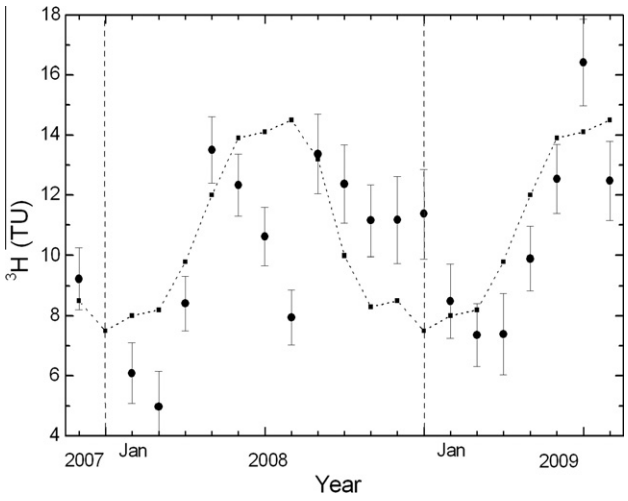

Fig. 6. Tritium concentration in rain water collected at Dechen Cave (roof of the German Cave Museum). The dotted line shows the progression of the mean monthly values (black squares) calculated from the 1995 to 2005 data of Hof. Errors are 1σ uncertainties.

Table 2
Results of tritium measurements at Bunker Cave, Dechen Cave, and B7 Cave. As most drip sites were sampled repeatedly, an error-weighted mean of all ^{3}H ages per drip site is given. Age estimations from ^{3}H–^{3}He and the delay in δ^{18}O are given as well. The δ^{18}O delay gives the apparent delay and is therefore only a minimum estimate for the residence time. δ^{18}O was not measured (n.m.) in samples from Dechen Cave.

Drip site	Date	^{3}H (TU)	^{3}H age (years)	^{3}H–^{3}He age (years)	δ^{18}O delay (years)
Bunker Cave					
TS1	24 April 2007	8.4 ± 0.9	1.6 ± 0.9	–	–
TS1	March 2009	8.4 ± 0.4	2.7 ± 0.7	–	–
TS1	March 2009	8.0 ± 0.4	3.1 ± 0.7	–	–
TS1	Mean	–	2.6 ± 0.8	–	0.5–0.8
TS4	23 January 2007	6.3 ± 1.1	3.2 ± 1.2	–	–
TS4	March 2009	9.0 ± 0.4	2.2 ± 0.7	–	–
TS4	March 2009	8.5 ± 0.4	2.7 ± 0.7	–	–
TS4	Mean	–	2.6 ± 0.5	–	Constant s.
TS5	2007–2009	8.0 ± 0.6	2.3 ± 0.5	–	Constant s.
TS7	24 April 2007	7.4 ± 1.0	2.4 ± 1.0	2.1 ± 1.0	–
TS7	24 April 2007	7.5 ± 0.4	2.3 ± 0.6	–	–
TS7	Mean	–	2.3 ± 0.6	–	Constant s.
Dechen Cave					
Grufthalle	23 January 2007	7.4 ± 1.0	2.2 ± 1.0	–	–
Grufthalle	24 April 2007	8.6 ± 1.0	1.4 ± 1.0	3.0 ± 0.8	–
Grufthalle	Mean	–	1.8 ± 0.6	–	n.m.
Kristallgrotte	23 January 2007	5.0 ± 1.0	4.6 ± 1.2[a]	–	–
Kristallgrotte	24 April 2007	6.7 ± 0.9	3.0 ± 1.0	0.7 ± 1.1	–
Kristallgrotte	March 2009	7.8 ± 0.4	3.3 ± 0.7	–	–
Kristallgrotte	March 2009	7.5 ± 0.6	3.5 ± 0.8	–	–
Kristallgrotte	Mean	–	3.5 ± 0.7	–	n.m.
B7 Cave					
B7-2	25 April 2007	6.0 ± 0.9	3.7 ± 1.0	2.4 ± 1.3	–
B7-2	25 April 2007	6.0 ± 0.9		1.7 ± 1.3	–
B7-2	2 February 2008	7.2 ± 1.0	3.1 ± 1.0	–	–
B7-2	Mean	–	3.4 ± 0.7	–	Constant s.
Kristallteich	2 February 2008	8.4 ± 1.0	2.0 ± 1.0	–	Constant s.

"Constant s." = constant δ^{18}O signal. The ^{3}H errors are 1σ uncertainties.
[a] Age result outside the reference period (2003–2007) of the fit.

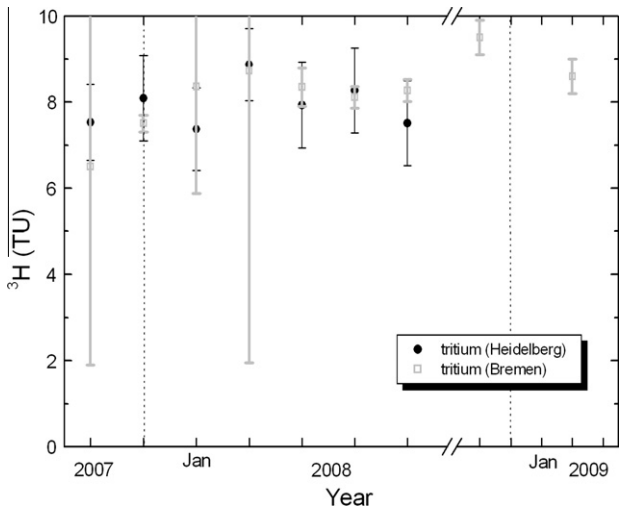

Fig. 7. Tritium concentration of drip site TS5 in Bunker Cave. Tritium was measured in Heidelberg by decay counting and on the same samples in Bremen by the ^{3}He ingrowth method. Large error bars in two Bremen samples are due to background correction. Errors are 1σ uncertainties.

The ^{3}H–^{3}He dating was complicated by several factors described in detail by Kluge et al. (2010). At least at one site gas exchange with the cave air occurred and probably reduced the ^{3}He-based gas tracer age. In two samples air contamination had very likely occurred. In several additional samples experimental problems caused relatively high uncertainties of the ^{3}He/^{4}He ratios, which severely affected the significance of the calculated ages. From one site we have good noble-gas data but no tritium results. Therefore, in the following we only use the reliable ^{3}H–^{3}He age results of five samples for comparison with the tritium ages (Table 2). These ages range between zero and three years.

To constrain the obtained ages the flow regime and the drip behavior of the investigated sites are of special importance. Site B7-2 in B7 Cave is a continuously dripping stalactite with a discharge of several ml per minute (seepage flow regime). In contrast, all drip sites in Bunker Cave analyzed for tritium are seasonal drips with intermediate discharge (0.002–15 ml/min, Fig. 8). TS1 has the highest discharge with values between 0.2 and 15 ml/min (Riechelmann et al., 2009). All drips (except B7-2 in B7 Cave) are influenced by the seasonal infiltration pattern leading to higher discharge in response to winter recharge of the aquifer (Fig. 8).

5. Discussion

The calculated infiltration-weighted annual mean tritium values show a decrease until 2003 and a slight increase afterwards. Hence, an input curve consisting of two linear segments (Fig. 5) was used to calculate drip water ages based on Eq. (2). The obtained ages range from 1.4 to 3.7 years (Table 2), with the exception of one probably older sample, for which no intersection with the input curve was found. At sites where δ^{18}O monitoring was carried out, the representativeness of the measured tritium in the drip water with respect to seasonal variations was evaluated using the stable isotope results. The drip sites TS1, TS5, and TS 7 show δ^{18}O values of about −8‰, which correspond to the infiltration-weighted mean of the precipitation. Because all drip sites (with

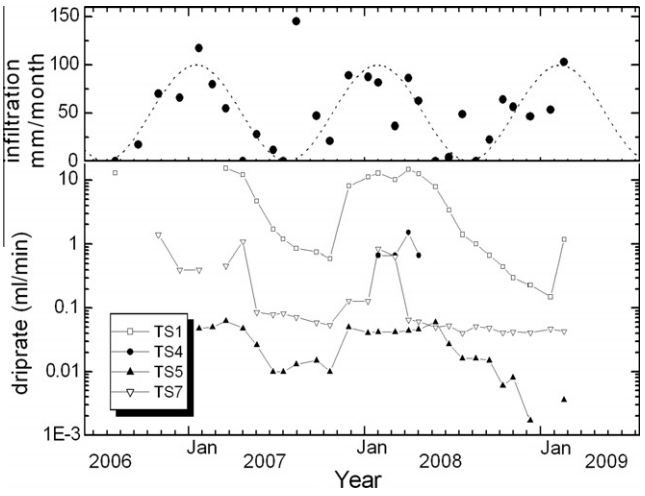

Fig. 8. Infiltration in the cave region (upper panel) and discharge of four drip sites in Bunker Cave (lower panel). Data from Riechelmann et al. (2009). For better visibility a sinus function (dashed line) is adjusted to the seasonal infiltration pattern.

the exception of TS1) lack a seasonal signal, it is reasonable to assume that the tritium results are representative, i.e. they are not influenced by seasonal variability.

When comparing ages derived from tritium with ^3H–^3He ages it has to be considered that the two methods are not necessarily measuring the same time period. Whereas the tritium method, based on radioactive decay of the water-bound ^3H, reflects the entire passage from a mixed soil water reservoir to the drip site, the ^3H–^3He clock, based on the accumulation of tritiogenic ^3He, only starts ticking when the water is isolated from gas exchange with soil air (e.g. Kipfer et al., 2002). The method is usually thought to provide residence times of groundwater in the saturated zone (Solomon and Cook, 2000). Since air-filled caves are obviously not saturated, it is in fact conceivable that the percolating water is never completely isolated on its way to the drip site, thus a zero ^3H–^3He should be expected. The finding of significant ^3H–^3He ages in drip waters may indicate the existence of perched groundwater lenses in the epikarst zone above the caves. In any case, it is expected that ^3H–^3He ages represent only a lower limit of the entire water transit time from the Earth's surface to the drip site.

In Bunker Cave, drip site TS1 shows a seasonal trend in $\delta^{18}O$ which appears to be delayed by 6–9 months relative to the isotope signal of meteoric precipitation, suggesting a mean residence time in the same time range. The tritium age, however, is higher with an error-weighted mean of three measurements of 2.6 ± 0.8 years. TS4, TS5, and TS7 yield similar tritium ages of 2.6 ± 0.5, 2.3 ± 0.5 years, and 2.3 ± 0.6 years, respectively. The result for TS5 is based on tritium ages averaged over an extended period (14 months), whereas the results for the other sites are mean values of a few samples (Table 2). The rather constant $\delta^{18}O$ values of TS5 and TS7 (Fig. 4) exclude ages below 1 year and therefore confirm the multi-year residence times derived from tritium. These results are further supported by a comparable ^3H–^3He age for site TS7 of 2.1 ± 1.0 years.

Logging of site TS5 showed a discharge of about 0.01 ml/min from August 2007 to November 2007, rising to 0.045 ml/min in November (mean annual discharge ca 15 l). The discharge of TS7 and TS4 is 10 and 150 l year^{-1}, respectively, based on drip data from 2007 to 2008 (Riechelmann et al., 2009). These low values demonstrate that only a very small portion of the epikarst is drained by these drips sites. In contrast, discharge at drip site TS1 is significantly higher (3000 l year^{-1}) based on manual drip measurements (Riechelmann et al., 2009) and indicates supply from a large reservoir. Considering the rather uniform tritium concentrations and ages as well as the stable isotope values it appears likely that most drip sites in Bunker Cave are connected to the same reservoir and are only distinguished by different flow-path properties. The significant (i.e. from zero distinguishable) ^3H–^3He age of drip TS7, which is comparable to the tritium age, is consistent with the existence of a saturated zone above Bunker Cave, although excess air was not found in any of the drips of this cave. No springs exist in the vicinity of the cave. Permanent water-filled ponds, however, are present in adjacent caves indicating the existence of water-impermeable layers or areas sealed by sinter and possibly saturated zones such as perched water lenses.

In Dechen Cave two drip sites were sampled several times for tritium. At drip site Grufthalle the tritium concentrations are close to the weighted mean of infiltration water suggesting a low age. The error-weighted mean of the calculated ages is 1.8 ± 0.6 years (Table 2). The ^3H–^3He age implies a significantly higher age (3.0 ± 0.8 years), which is exceptional and difficult to explain other than by noting that the ages agree within the 2σ uncertainty range. In contrast, tritium concentrations at drip site Kristallgrotte are very low and comparable to the lowest monthly mean value of rain water. This strongly suggests a long residence time based on the tritium concentrations and Eq. (2). The error-weighted mean of four measurements is 3.5 ± 0.7 years. The ^3H–^3He age in Kristallgrotte is much lower (0.7 years) indicating gas loss during percolation through the karst aquifer.

Two sites were investigated in B7 Cave. At site B7-2 drip water was sampled twice. The tritium ages are 3.7 and 3.1 years, respectively, with an error-weighted mean of 3.4 ± 0.7 years. Two noble gas samples yielded slightly lower ^3H–^3He ages of 2.4 and 1.7 years. B7-2 is a very fast dripping site with a discharge of about 8–10 l/day. The rather constant drip behavior suggests a perched aquifer with a large water reservoir and therefore long residence time. The significantly from zero distinct ^3H–^3He ages and in particular the existence of excess air (about 10% excess Ne) in the drip water of B7-2 confirm this assumption. Water samples from a small cave pool in B7 Cave were taken for comparison. There, the tritium concentration is close to the infiltration-weighted mean indicating direct water supply with fast percolation and a corresponding tritium age of about 2 years. ^3H–^3He data from the pool are altered due to degassing to the cave atmosphere and cannot be used to cross-check these results.

In a karst hydrological setting apparent groundwater ages are inherently mixtures of ages referring to different flow types. Low ages suggest a dominant fissure-flow component, whereas high ages result from seepage flow or mixing with water retained in perched aquifers. Mixing of water from different sources is a serious complication for estimating drip-water residence times. During base flow rather old water from the porous karst matrix prevails, whereas a considerable amount of rather young water is provided by fissure flow following recharge events (direct or quick flow). Tracers such as oxygen isotopes and tritium help to separate the two fractions (Maloszewski et al., 2002). We monitored tritium values at drip site TS5 (Bunker Cave) between November 2007 and February 2009. Although infiltration varied considerably throughout these years, the monthly tritium values in the drip water remained constant. $\delta^{18}O$ values from Bunker Cave show a similar picture, i.e. they correspond to the weighted mean of rainfall and show little intra-annual variability. These observations strongly suggest that the contribution from direct fissure flow is low in these drip sites. An admixture of about 20% of direct flow water can change the $\delta^{18}O$ value by up to 0.4‰. This value is higher than those observed at most of the drip sites in Bunker Cave; only TS1 may have a contribution of direct flow in this range. The contribution of an older, stagnant water body component can be

investigated using tritium. Assuming the same initial tritium content of 9 TU a 30% contribution of 10 year-old matrix water lowers the value of a 2.5 year old main component by 0.8 TU. A high fraction of low-tritium stagnant water would lead to a significant drop in the measured tritium content. TS5 did not show significant events during the monitoring period 2007–2009. Limited seasonal variations in the different source fractions (e.g. a rise from 5% to 10% direct flow contribution) are possible despite the fact that we did not detect significant events for both the fast-flow contribution in most monitored sites in Bunker Cave and the stagnant water contribution in TS5. An assessment of the age uncertainty due to varying fractions of different flow types requires high-precision long-term monitoring and the application of a lumped parameter model. Due to the limited monitoring at our sites no reasonable age uncertainty estimates related to flow variations are possible. These uncertainties, however, are probably small provided that the above mentioned observations can be confirmed by the ongoing monitoring. Therefore, the measured ^{3}H ages are regarded as a reasonable approximation of the "real age" of the drip water consisting of the aforementioned components, i.e. a dominant water component from the porous-fissured aquifer with small contributions of direct flow and stagnant water.

The application of tritium ages is limited primarily by the degree of variation of tritium in the infiltration water and to a lower extent by the measurement uncertainty of the water samples. In this study, tritium in the infiltration water shows a linear trend from 2003 to 2007 with minor scatter and a maximum deviation of the single years from the linear trend of 0.6 TU. For drip water samples a measurement uncertainty of 0.3 TU or slightly lower can be achieved using the ingrowth method with an ingrowth period of about 6 months and 50 ml water samples. Using such small analytical uncertainties, calculated drip water ages yield uncertainties of less than 1 year. Thus, in principle it is feasible to achieve reasonable and relatively precise drip water ages using dating by tritium.

The following protocol is recommended for determining the age of drip water. Meteorological data and monthly mean tritium values from a nearby station should be used for the calculation of the infiltration-weighted mean. Drip sites of interest should be sampled for tritium at least four times a year. In order to unambiguously identify the drip behavior periods of low recharge and periods immediately following heavy rainfall events should be included in the sampling program. A significant difference between these two sets of data (low recharge and storm events) suggests a short residence time (<2 years), which should be cross-checked by a second tracer, e.g. $\delta^{18}O$. Rather constant signals suggest a long residence time and are a prerequisite for the applicability of the tritium method for constraining the drip water age. Finally, tritium measurements with an uncertainty of 0.2–0.4 TU and rather flat tritium reference curves allow a precise determination of the drip water age with an error as low as 0.5 years.

Although our work supports the feasibility of ^{3}H–^{3}He dating of drip water, it also indicates some limitations, which were not fully discussed in the work of Yamada et al. (2008). Aspects limiting the applicability of ^{3}H–^{3}He dating are the existence of unsaturated conditions above caves and the difficulties of gas-tracer sampling at drip sites. The fact that ^{3}He is a gas tracer, which accumulates only under saturated conditions and can quickly be lost to the soil or cave air under unsaturated conditions, implies that only minimum ages of drip water can be derived, which are related to the existence of saturated zones above the drip site. Tritium, in contrast, provides constraints on the entire residence time and is not affected by degassing. Collection of samples undisturbed by contact with cave air is particularly difficult at sites with low drip rates. The resulting requirement of small samples renders precise He isotope measurements challenging. In contrast, water can be collected over a long period for tritium measurement. Despite these limitations, the combination of tritium and ^{3}H–^{3}He dating has potential for studies in karst hydrology, e.g. to identify saturated parts of the flow system.

6. Conclusions

The increasing use of speleothems as climate archives emphasizes the need for a quantitative understanding of the proxy signals. An important parameter is the residence time of water feeding stalagmites. We have applied for the first time a tritium method to drip-water dating which is based on an input curve derived by infiltration-weighting of precipitation data. The residence (or percolation) time can be reliably determined using combined tritium measurements of rain water and drip water and the additional meteorological information pertaining to the monthly infiltration. The infiltration-weighted tritium value in the recharge area of the studied caves in northwestern Germany has only been varying slightly over the last 10 years (between 7 and 10 TU). The achievable precision for the residence time can be better than ±1 year and requires tritium to be determined to better than ±1 TU as well as the input curve to be relatively flat.

For short timescales (<1 year) tritium data are not sufficiently precise, but monitoring of stable isotopes in rainfall and drip water provides useful constraints on the residence time. ^{3}H–^{3}He dating provides additional information on the transit time of soil water to the drip sites. A comparison of tritium and ^{3}H–^{3}He ages as well as additional noble-gas data (Ne) provides information regarding the existence of perched groundwater zones above the caves, which seem to exist at least at some of the sites studied here.

The three studied caves show rather similar residence times and little variability of karst water ages within a single cave. The tritium ages range from 1.4 to 3.7 years with a mean of 2.8 years, indicating similar response to precipitation events and hence to climate. Due to the residence time of about 3 years it is unlikely that seasonal extremes can be detected and consequently speleothems in these caves will be valuable archives of changes on a multi-annual time scale. At sites with rather fast percolation seasonality and possibly even extreme meteorological events (e.g. droughts) may be recorded in speleothems, whereas drip sites with higher water ages will act as low-pass filters and speleothems there will be sensitive recorders of climate variability on the decadal scale. Drip-water dating is therefore an important tool in speleothem-based paleoclimate studies which should be an integral part of any high-resolution proxy-calibration study.

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