Journal of Hydrology 394 (2010) 396–406

Contents lists available at ScienceDirect

Journal of Hydrology

journal homepage: www.elsevier.com/locate/jhydrol

Dating cave drip water by tritium

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ARTICLE INFO

Article history:
Received 29 December 2009
Received in revised form 22 May 2010
Accepted 20 September 2010

This manuscript was handled by P. Baveye, Editor-in-Chief, with the assistance of Barbara J. Mahler, Associate Editor

Keywords:
Karst hydrology
Radioactive tracer
Speleothems
Groundwater dating
Stable isotopes

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 (^3H). 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 ^3H–^3He 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. $\delta^{18}O$ values can reveal changes in past temperatures and precipitation (Vollweiler et al., 2006; Wang et al., 2008). In some cases $\delta^{13}C$ 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). $\delta^{18}O$, $\delta^{13}C$, 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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doi:10.1016/j.jhydrol.2010.09.015

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