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Mixing and transport of water in a karst catchment: a case study from precipitation via seepage to the spring

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Abstract. One of the best-known and largest karst areas in Germany, the Blautopf Catchment, offers unique access to waters of the unsaturated zone through a large cave system. It was investigated with stable isotopes (^{18}O/^{16}O and D/H ratios expressed in permille = ‰) in precipitation, seepage- and groundwater as tracers for water flow, mixing, and storage. The precipitation showed a distinct seasonality with δ^{18}O values between −2.9 and −24.6‰ during summer and winter, respectively. However, the isotope signals in seepage water in the caves as well as the discharge were almost completely buffered and ranged around an average δ^{18}O value of −10‰. This value was also close to the long-term average value of local precipitation, −9.3‰. The homogeneous isotopic composition of the Blautopf Spring was unexpected, as its highly variable discharge (0.3 to 32 $\mathrm{m^3\,s^{-1}}$) is typical for a fast responsive karst system. These isotopic similarities could be explained by nearly complete mixing of the water already in the vadose zone. The data set therefore presents a case study to narrow down zones of mixing in karst catchments. It also confirms the minor role of the fast conduit system in the water balance of the Blautopf Catchment.

1 Introduction

Understanding of water pathways and movements in the vadose zone is a prerequisite for evaluation of the risk for groundwater pollution. In karst areas such evaluations become particularly important as about 25% of the world's population rely on karst sources for potable water supply (Ford and Williams, 1989). Classifications of karst system by Cruz Jr. et al. (2005), Genty and Deflande (1998) and Mangin (1974) who define three main flow compartments:

1. the non-karst recharge area consisting of soils or non carbonaceous bedrock
2. the epikarst and
3. the saturated zone.

Next to soils and the vadose zone for mixing, the influence of the epikarst was recently investigated in more detail as it is assumed to play a major role in mixing of waters due to is finer fracture systems and associated longer residence times of water (Aquilina et al., 2006; Clemens et al., 1999; Perrin et al., 2003; Sauter, 1995). According to Mangin (1973), epikarst is a perched saturated zone above the groundwater table that stores part of the infiltrated water. In order to describe the variable flow character of karst systems, it is also necessary to consider the conduits that are embedded in the fissured-porous matrix (Kiraly, 1998; Liedl and Sauter, 1998; , 2000). Even though the latter are assumed to play a minor role in water fluxes through karst systems, they may play an important role for storage of pollutants. Since pollutants are difficult to trace, particularly in small fissures, it helps in a first instance to outline how water mixes underground in karst systems. Tracers that are homogeneously distributed over large areas – such as stable isotopes of water – can therefore indirectly help to assess risk of diffuse pollution for catchment-wide water recharge considerations. In contrast to focused tracer tests with dyes or salts, such more widely distributed tracers may help to characterize diffuse

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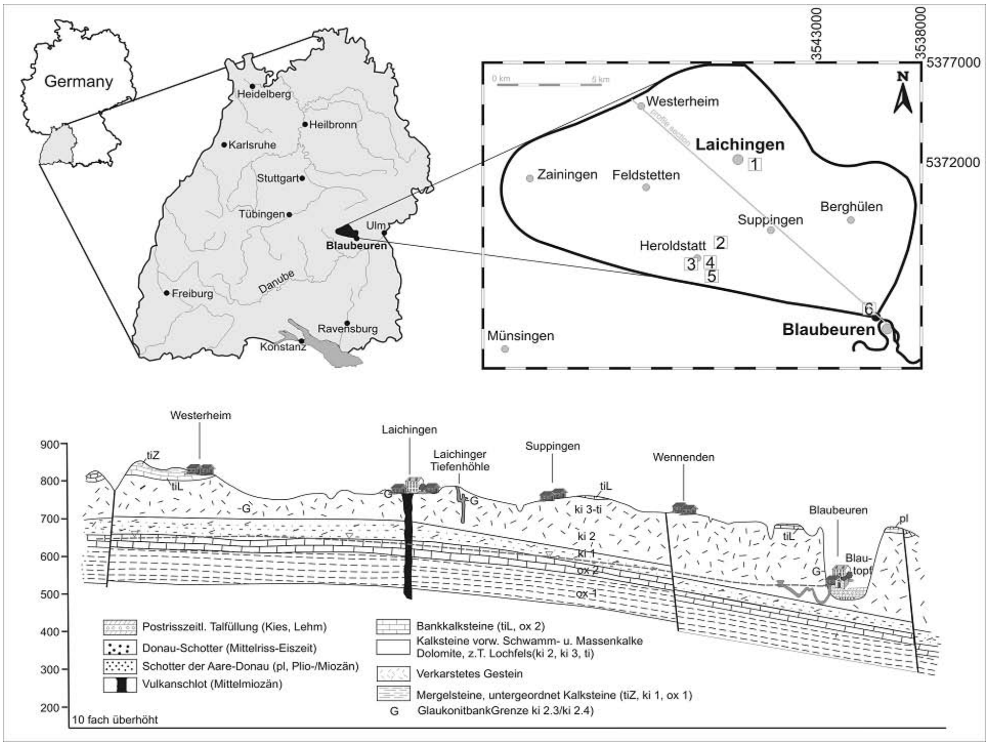

Fig. 1. Top: the catchment area with the Blautopf Spring and the investigated caves; 1=Laichinger Tiefenhöhle (LTH), 2=Hawaii-Schacht (HWS), 3=precipitation sampling point, 4=sewage plant of Heroldstatt, 5=Sontheimer Höhle (SH) and 6=Blautopf.
Bottom: profile through the area from NW to SE.

infiltration. This works if stable isotope ratios are homogeneous over larger areas and altitude effects can be assumed to be minor (Clark and Fritz, 1997). If so, isotope signals in precipitation can be thought to give the same input signal for areas of several hundred square kilometers such as the Blautopf Catchment. Specifically, ^{18}O/^{16}O and/or D/H ratios are suitable tools because they are constituents of water molecules and thus act as already present conservative tracers (Maloszewski et al., 2002).

In this study the main focus was to investigate diffuse recharge and transport processes in a typical karst system at the catchment scale. The objective was to investigate the mixing behaviour of the entire system rather than to focus on the fast flow paths of the infiltrated water. This goal was approached by comparison between the isotopic composition of precipitation and discharge and allowed to decide if mixing occurs in such a fast responsive system or if precipitation reaches the spring unaltered. Furthermore, with caves being present in a well-developed unsaturated zone of up to 150 m thickness, it was possible to investigate to which degree mixing of the water takes place in the unsaturated zone and the epikarst.

The setting of the Blautopf Catchment with its caves enabled convenient sampling of the unsaturated and saturated zones and therefore was ideal to provide new insights into how these compartments are linked. This approach may also help to evaluate the risk of groundwater contamination by diffuse pollution and can provide important insights into water balances.

2 Materials and methods

2.1 Sampling sites

General information: The Blautopf Catchment is situated on the “Schwäbische Alb” (Fig. 1), which together with the “Fränkische Alb” makes up the largest karst area in Germany (Villinger, 1997). The catchment area is rural and has a size of about 165 km^2 of which ∼31% is covered by forests while more than 60% is agricultural land (Köberle, 2005).

The Blautopf Catchment has more than 50 caves. Three of them have been chosen for our investigation (Fig. 1). Two of them, the “Laichinger Tiefenhöhle” (LTH; 9°41′36″ E, 48°28′43″ N) and the “Sontheimer Höhle” (SH 9°40′52″ E, 48°25′52″ N), are publicly accessible, while the third, the “Hawaii-Schacht” (HWS; 9°41′02″ E, 48°27′29″ N), is not accessible to the general public. The depths below surface were 33 m for LTH, 45 m for SH and 8 m for HWS. While HWS is situated in a dry valley, the entrance of SH is situated in a hill slope and the LTH is located beneath a plain.

The Schwäbische Alb has a typical continental climate with an annual average temperature of 6.5 °C (1961 to 1990) (Müller-Westermeier et al., 1999). The average precipitation in the Blautopf Catchment is higher in the northwestern part with 1100 mm a^{-1} and decreases towards the southeastern part to average values of 800 mm a^{-1} (Keller, 2003) while the mean groundwater recharge in the Blautopf Catchment is about 500 mm a^{-1} (Armbruster, 2002).

On average the soil cover is about 50 cm and the main soil type is a rendzic leptosol. Underneath this soil cover the thickness of the vadose zone varies between 100 and 150 m. The thickness of the saturated zone was not determined precisely in this study, but is estimated to range between 50 and 120 m. A comprehensive overview of the hydrology of the Blautopf Catchment is described in Villinger (1978). Upstream of the Blautopf Spring, a large cave system with phreatic and vadose zones has been explored up to a length of about 4 km from the spring (www.blautopf.org).

Geological and hydrogeological settings: The Blautopf Catchment is situated in the Upper White Jurassic Formation, which mainly consists of limestones and marls. The layers dip southeast. Few tectonic structures are present and have only low displacements (Fig. 1b). The catchment has two main karst units. The upper one is situated between the "Untere Felsenkalk-Formation" and the "Hängende Bankkalk-Formation" and partially forms an individual aquifer system that is limited at its lower parts by the "Lucasomamergel Formation" that has a low permeability character typical of marly slates. In cases where the limestone is massive, it is differentiated between "Untere" and "Obere Massenkalk-Formation". The lower unit, a low permeability marl known as "Impressamergel," serves as the basement of the entire karst aquifer system of the Blautopf Catchment.

The mean discharge of the Blautopf Spring – the principal outlet of the system – was determined to be 2.43 m^3 s^{-1} between 1980 and 2003. However, it shows considerable variability with the highest discharge close to 32 m^3 s^{-1} and the lowest of 0.3 m^3 s^{-1}. This variation is typical for a karst spring and indicates a strong karstification of large parts of the aquifer. According to Selg et al. (2006), rain events and snowmelts can be partially detected in the groundwater recharge of the Blautopf within a short retardation time of 1 to 2 days, while the mean transit time of the groundwater is around 13 years (Bauer and Selg, 2006).

2.2 Sampling and analyses

Samples for stable isotope analyses were collected in the caves and the Blautopf Spring between March 2005 and May 2006. In the same time period precipitation was collected with the aim of sampling the most representative precipitation events of this period including long-term snowfall and thunderstorms. A rain collector, equipped with a funnel that reached almost to the bottom to prevent evaporative loss, was placed at the village of Heroldstatt (9°40′01″ E, 48°26′39″ N; altitude ∼780 m above sea level). Most samples were collected after several precipitation events and then transferred into 20-mL vials with tight screw caps to avoid secondary evaporation effects. Afterwards they were stored upside down at 4°C in the dark. Note that throughout the sampling period not all rain events were collected for isotope analyses, however the ones presented here with isotope data establish a sufficient data base for this case study. While making sure that most strong precipitation events were analysed isotopically, we can assume that the smaller precipitation events (not sampled for isotope analyses) are isotopically similar to their previous or later counterparts or did not affect the cumulative isotopic signature by mass.

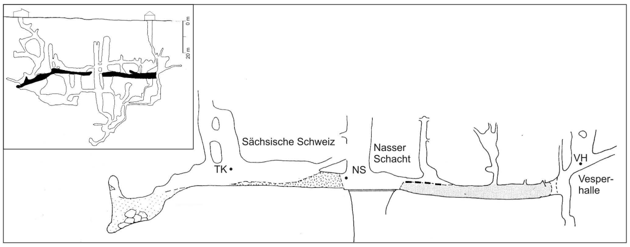

Fig. 2. Position profile of the sampling sites in the Laichinger Tiefenhöhle, TK: Sächsische Schweiz, NS: Nasser Schacht and VH: Vesperhalle (changed according to Burger et al. (1993). Horizontal distances between TK and NS are 20 m and between NS and VH 40 m.

The cave seepage waters were collected at three different locations HWS, LTH and SH (Fig. 1). In the LTH three further sampling locations with different distances to the surface were chosen to investigate a variety of possible flow paths and residence times. They are the "Vesperhalle" (VH), "Nasser Schacht" (NS) and "Sächsische Schweiz" (TK). Exact locations of these sampling sites are displayed in Fig. 2 and range between about 33 and 35 m below the surface. The seepage water was collected with a vial, the filling time of which took several minutes in winter and up to half an hour in summer, but no precise seepage fluxes were determined. Samples were taken in the LTH at time intervals ranging from days to weeks (Table 1). During events such as snowmelts or thunderstorms, samples were taken more frequently at time intervals of days whenever possible. Samples from the two other caves were only sampled for general comparison. Note that more frequent sampling was often not possible due to safety considerations and limited access to the caves.

The discharge water of the entire catchment was collected in the Blautopf Lake from a depth of 20 cm below the surface of the and a few meters before the outflow at the weir. At this depth the water was not influenced by admixture of any precipitation events as a strong enough outward discharge of the spring-ensured supply of fresh water purely from the cave system.

Table 1. All stable Isotope data for ^{18}O/^{16}O and D/H ratios of collected water samples with sampling dates and cumulative precipitation amounts between sampling dates (LTH=Laichinger Tiefenhöle, NS=Nasser Schacht, VH=Vesperhalle, HWS=Hawaii Schacht, TK=Sächsische Schweiz, SH= Sontheimer Höhle, BLT=Blautopf Spring). All values are expressed in permille versus the VPDB standard.

Precipitation				LTH main hall			LTH NSH		LTH VSP		LTH TK		HWS		SH		Blautopf		
date	mm	δ^{18}O	δD	date	δ^{18}O	δD	Date	δ^{18}O	date	δ^{18}O	date	δ^{18}O	date	δ^{18}O	date	δ^{18}O	date	δ^{18}O	δD
06.03.05	7.0	−5.7	−32	09.02.05	−10.1	−73	12.11.05	−10.2	12.11.05	−9.3	26.04.05	−9.9	05.05.05	−10.3	26.04.05	−9.9	07.03.05	−10.0	−71
23.03.05	30.5	−9.8		28.02.05	−9.9	−73	21.11.05	−9.8	21.11.05	−9.9	07.05.05	−9.7	14.05.05	−10.6	07.05.05	−9.7	19.03.05	−9.9	−72
23.05.05	227.5	−6.5		07.03.05	−10.1	−73	02.12.05	−9.2	02.12.05	−10.0	18.05.05	−9.8	09.07.05	−9.5	10.05.05	−10.0	21.03.05	−9.9	−72
05.06.05	25.0	−5.9	−39	14.03.05	−9.9	−73	12.12.05	−9.8	12.12.05	−10.0	18.07.05	−9.6			18.05.05	−9.8	22.03.05	−9.8	−70
02.07.05	35.0	−8.5	−61	22.03.05	−10.0		19.12.05	−9.9	19.12.05	−10.1	25.08.05	−9.4			18.07.05	−9.6	24.03.05	−10.0	−72
05.07.05	38.5	−9.3	−69	25.03.05	−10.1	−72	30.12.05	−9.7	30.12.05	−9.8	13.12.05	−9.6			25.08.05	−9.4	30.03.05	−10.0	
09.07.05	19.0	−7.7	−54	29.03.05	−10.2	−73	09.01.06	−10.0	09.01.06	−9.8	17.01.06	−9.8			13.12.05	−9.6	24.04.05	−10.5	−71
12.07.05	16.0	−7.7	−55	06.04.05	−10.0		16.01.06	−9.6	16.01.06	−10.0	18.02.06	−9.7			17.01.06	−9.8	26.05.05	−9.9	−71
19.07.05	35.0	−2.9	−15	10.04.05	−10.2		23.01.06	−9.9	23.01.06	−9.9					18.02.06	−9.7	26.05.05	−9.7	−69
25.07.05	22.0	−9.0		20.04.05	−10.0		01.02.06	−9.8	01.02.06	−9.5							19.06.05	−9.8	−70
26.07.05	26.0	−8.3	−59	26.04.05	−9.6	−71	12.02.06	−9.6	12.02.06	−9.4							07.07.05	−9.8	
03.08.05	33.0	−3.8	−19	07.05.05	−10.0		17.02.06	−9.8	17.02.06	−9.7							07.07.05	−9.8	
22.08.05	65.0	−7.2	−53	12.05.05	−9.9	−72	20.02.06	−9.9	20.02.06	−9.8							26.07.05	−10.0	−67
23.08.05	20.0	−8.5		14.05.05	−9.8		27.02.06	−9.7	27.02.06	−9.7							22.08.05	−9.7	
26.08.05	12.0	−7.6	−51	26.05.05	−9.8	−70	03.03.06	−9.6	03.03.06	−9.9							26.05.05	−9.9	
03.05.05	31.0	−6.1	−42	19.06.05	−9.9	−71	11.03.06	−9.7	11.03.06	−10.1							06.06.05	−9.6	−70
11.05.05	57.0	−7.5	−49	26.06.05	−10.1	−73	17.03.06	−9.8	17.03.06	−10.0							30.06.05	−9.8	
13.05.05	15.0	−10.7		09.07.05	−10.1		24.03.06	−9.8	24.03.06	−9.8							20.11.05	−10.1	−70
17.05.05	28.0	−9.4	−66	28.07.05	−10.2		29.03.06	−9.9	29.03.06	−10.4							02.12.05	−10.0	−70
30.05.05	5.0	−6.6	−40	15.08.05	−10.1	−72	31.03.06	−10.6	30.03.06	−10.2							31.12.05	−10.0	−70
02.06.05	20.0	−7.9	−53	25.08.05	−10.0		05.04.06	−9.8	31.03.06	−9.9							22.01.06	−9.9	
03.06.05	20.0	−8.0	−44	26.08.05	−10.3	−73	13.04.06	−9.9	13.04.06	−10.2							18.02.06	−10.0	−70
04.06.05	8.0	−7.8		07.05.05	−10.1	−73	20.04.06	−9.8	20.04.06	−10.4							31.03.06	−10.5	
05.06.05	5.0	−6.9		15.05.05	−10.2		01.05.06	−10.2	27.04.06	−10.3							01.04.06	−10.5	−70
03.11.05	98.0	−7.2	−47	18.05.05	−10.0	−71	10.05.06	−9.9	01.05.06	−10.5							22.04.06	−9.9	−71
05.11.05	21.0	−11.4	−81	25.05.05	−10.1		14.05.06	−9.9	14.05.06	−10.3							14.05.06	−9.8	
22.11.05	40.0	−14.9	−112	30.05.05	−10.1	−72													
17.12.05	117.5	−9.2	−65	16.06.05	−10.1														
18.12.05	1.0	−10.7		22.06.05	−10.1														
28.12.05	34.0	−11.6	−73	29.06.05	−10.3	−72													
30.12.05	20.0	−17.3	−125	12.11.05	−10.1														
09.02.06	55.5	−10.5	−74	21.11.05	−10.1														
10.02.06	10.0	−11.3		28.11.05	−10.1	−72													
11.02.06	49.0	−15.4		28.11.05	−10.2														
12.02.06	1.0	−13.5	−97	28.11.05	−9.9	−71													
27.02.06	26.5	−15.3	−111	30.11.05	−9.9														
03.03.06	17.0	−12.9		02.12.05	−10.1														
04.03.06	20.0	−16.7	−125	12.12.05	−9.9														
05.03.06	42.0	−22.4		19.12.05	−9.9														
06.03.06	17.0	−24.6		09.01.06	−9.8	−68													
09.03.06	10.0	−11.9		16.01.06	−9.6	−70													
10.03.06	23.0	−9.5		23.01.06	−9.6	−68													
11.03.06	1.0	−9.1		01.02.06	−9.7	−68													
14.03.06	1.0	−16.2	−111	12.02.06	−9.5	−69													
22.03.06	5.0	−9.3	−64	17.02.06	−9.6														
27.03.06	25.5	−7.6		27.02.06	−9.7	−69													
29.03.06	11.0	−8.6	−53	03.03.06	−9.8														
01.04.06	12.0	−7.5	−52	11.03.06	−9.7	−70													
06.04.06	68.0	−10.4		17.03.06	−9.9														
11.04.06	32.0	−16.8	−125	29.03.06	−10.6	−72													
18.04.06	67.0	−5.6	−38	31.03.06	−10.6														
26.04.06	28.0	−7.2		05.04.06	−10.2														
28.04.06	15.0	−8.4	−55	05.04.06	−10.0	−71													
10.05.06	14.0	−11.2		13.04.06	−10.0														
14.05.06	10.0	−5.6	−37	20.04.06	−9.9	−73													
17.05.06	30.0	−5.1	−33	27.04.06	−9.9														
19.05.06	15.0	−4.6		01.05.06	−10.0														
				10.05.06	−10.2														
				10.05.06	−9.9														
				14.05.06	−10.3	−71													

Stable isotope ratios of the water were measured at the Department for Geochemistry at the Centre for Applied Geosciences (ZAG). A Thermo-Finnigan isotope ratio mass spectrometer (IRMS, Model MAT 252) was used to determine the ^{18}O/^{16}O and D/H ratios after equilibration with CO_2 and by reduction to H_2 gas, respectively. Both parameters were calculated with respect to the international standard VSMOW (Vienna Standard Mean Ocean Water) using the following equation:

$$\delta_{\text{sample}} = \left[\frac{R_{\text{sample}} - R_{\text{VSMOW}}}{R_{\text{VSMOW}}}\right] \cdot 1000 \quad (1)$$

where R is the ratio ^{18}O/^{16}O or D/H. This notation dictates that more positive values are enriched in the heavier isotope (i.e. ^{18}O or D). The one σ standard deviation for repeat measurements was ±0.2‰ for δ^{18}O and ±1 for δD. The weighted mean isotopic composition for the precipitation was calculated with:

$$\overline{C_w} = \frac{\sum Q_t C_t}{\sum Q_t} \quad (2)$$

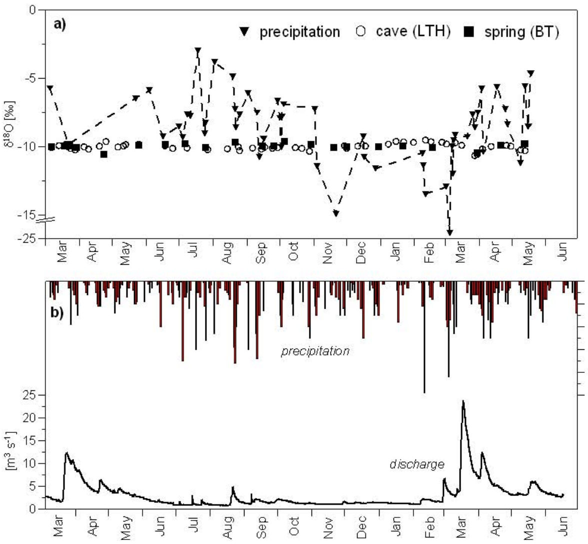

Fig. 3. **(a)** δ^{18}O composition of the rainfall (Heroldstatt), the spring (Blautopf) and the seepage water (Laichinger Tiefenhöhle) and **(b)** precipitation and the discharge amounts.

where Q_t is the cumulative rain amount between events [mm] and C_t the δ^{18}O signal of the precipitation water [in permille = ‰] at time t.

Data for precipitation were provided by the sewage plant in Heroldstatt (9°40′42″ E, 48°26′30″ N) that has an altitude of 728 m above sea level and is located 0.6 km away from the precipitation sampling station for isotopes. A Hellmann apparatus was used to determine the precipitation amounts. The discharge at the Blautopf Spring was continuously recorded by the Landesanstalt für Umwelt, Messungen und Naturschutz Baden-Württemberg (Karlsruhe).

3 Results

57 samples were measured for ^{18}O/^{16}O ratios in precipitation, 26 for the spring, and a sum of 132 for all cave seepage waters. They are listed in table 1 together with sampling dates and precipitation amounts. For selected samples the hydrogen isotope values (δD) were measured and with those of the δ^{18}O a local meteoric water line was established (Table 1, Fig. 4).

Figure 3a shows the isotopic variability of the precipitation. The δ^{18}O values reveal clear seasonality patterns with maximum values in summer (−2.9‰) and minimum values in winter (−24.6‰). The δ^{18}O values were also weighted by cumulative precipitation amounts between sampling events and yielded a value of −9.3‰ for the period from March 2005 to May 2006. For comparison, Bauer and Selg (2006) determined a weighted mean average of δ^{18}O of −9.5‰ at the station "Münsingen" that is at a distance of 15 Km from Heroldstatt. With lateral distribution patterns of δ^{18}O in the catchment being relatively homogeneous and assuming negligible altitude effects, few such sampling points can be used to represent the isotopic input for the entire catchment.

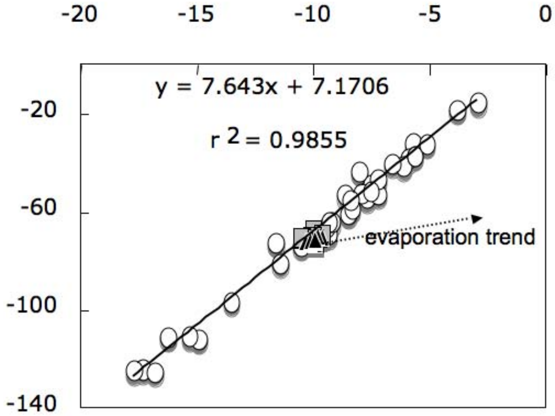

Fig. 4. Local meteoric water line of the Blautopf Catchment precipitation (open symbols) with evaporation trend (dashed arrow) and seepage and spring water (closed symbols). The Number of points that make up meteoric water line is n=36, while standard error of slope and intercept are 0.159 and 3.641.

The samples of the seepage and the spring water did only vary in a narrow range. They showed oxygen values between −9.5 and −10.6‰ for LTH while the other locations in the caves showed very similar results with δ^{18}O values ranging from −9.3 to −10.5, −9.2 to −10.6, −9.4 to −9.9 and −9.5 to −10.6‰ for VH, NS, TK and HWS, respectively. Location NS is known for a fast response to strong precipitation events; however, even at this subsurface location no significant seasonality in the δ^{18}O signal was found. For comparison, Nordhoff (2005) measured δ^{18}O values in the "Zaininger Höhle" that is also located in the Blautopf Catchment and found similar δ^{18}O values in the drip water (−10.5 to −11.2‰). These values overlap, but are nonetheless up to 0.6‰ lighter than our most negative measurements. A deviation towards these more negative values most likely reflects the influences from a different sampling year or the admixture of faster inflowing waters from snowmelts. Overall, however, they match our values well.

With their isotope values ranging around −10‰, the cave drip as well as the Blautopf Spring waters were slightly more negative than the weighted average of the precipitation. This can be explained by the fact that the amount of soil and groundwater recharge during winter was to a lesser extent reduced by evapotranspirative processes than summer recharge. This means that more water with more negative isotope signals recharged during the cold season. The result is a drift towards slightly more negative values of water in the subsurface and the Blautopf Spring. Nonetheless, the differences between Blautopf discharge and weighted recharge are too small to establish a proper mass balance to weigh summer versus winter precipitation.

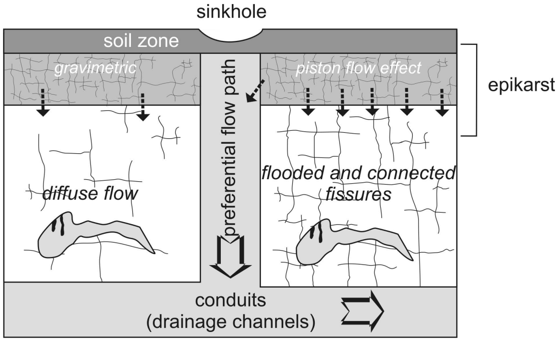

Fig. 5. Schematic representation of the different flow paths during base flow conditions (left) and high flow (right).

The hydrogen isotope composition (δD) ranged between -68 and -73‰ for the LTH and -67 and -72‰ for the Blautopf, while the precipitation varied between -15 and -125‰. Plotting the δ^{18}O versus δD values of the precipitation yields a linear relationship for the Blautopf Catchment that is known as the local meteoric water line (Fig. 4). The isotopic values of cave seepage and Blautopf discharge samples all fell on this line and only small variations in the isotope values of the Blautopf samples were found. If they were influenced by evaporation prior to recharge or from the open surface of the Blautopf, they would follow the typical evaporation trend that is outlined with the dashed arrow in Fig. 4. Since this is not the case, the local precipitation must indeed be responsible for the recharge of the Blautopf Spring with negligible alteration of the isotope signal.

4 Discussion

The similarity between cave seepage waters indicates that a significant homogenisation of the water must occur in the upper unsaturated zone regardless of the length of flow path. For instance, even the sampling location HWS, which is only 8 m beneath the surface, shows such buffering. This is further confirmed by the similarity between spring discharge and cave seepage waters, which, in turn, also have a value very close to the weighted mean δ^{18}O value of the precipitation. The assumed mechanism to mask the annual isotopic variation of the precipitation is considerable mixing of recharge already in the unsaturated zone.

This conforms to other findings of Caballero et al. (1996) who also collected water from wells to show influences of an aquifer system in Nerja in southern Spain and by Perrin et al. (2003) who sampled spring water from an about 500 m long karstic network near Basel in Switzerland. Both studies demonstrate similarity between recharge and discharge and thus mixing. Other studies by Fuller et al. (2008) also show buffering of the recharge water by comparing isotope analyses of cave drip waters and local precipitation.

If such homogenisation takes place in the epikarst, interactions of slow water movement and storage are plausible mechanisms. While base flow preferentially enables gravimetric movement of more easily mobilised water in fast conduit systems, stronger rain events can also flood and subsequently connect smaller fissures (Fig. 5). In such a case, the hydraulic pressure can mobilise pre-event water out of the storage zone towards the larger conduits in a piston flow effect. This concept could explain mixing in the seepage water while the main function of the fast conduit system remains transport of the already mixed water. Cruz Jr. et al. (2005) stated that karst seepage flow is largely influenced by storage capacity. They also found that the drip discharge is often delayed in time, depending on thickness and character of the unsaturated zone. This finding supports the assumption that the main mixing and storage processes occur in the upper part of the unsaturated zone. Hydrochemical and isotope studies from various regions for instance from the Arabika Massif in New Zealand and from New Mexico demonstrate that a delay in flow caused by storage in the epikarst can range from several days to a few months (Klimchouk and Jablokova, 1989; Williams, 1983). On the other hand, seasonal variations of δ^{18}O were found to be significantly reduced after about 3.5 years of residence time in the soil and epikarst zone in the neighboring Fränkische Alb (Stichler and Herrmann, 1983). With the current data set it is not possible to determine exact travel times of water. Nonetheless, the above research findings provide the boundary conditions for residence times of water in the unsaturated zone. Einsiedl (2005) and Einsiedl and Mayer (2005) established that the fissured-porous aquifer, especially the rock matrix, is the main location of water storage, whereas the soil and the epikarst only have a low storage capacity. Nonetheless, the rock matrix in the Blautopf Catchment, especially in the environment of the Laichinger Tiefenhöhle consists of the "Lochfelsfazies" with a high porosity. Perrin et al. (2003) also stipulated that the soil and the epikarst subsystems appear to act as an important storage element. However, with the current data set, a differentiation between these compartments is not possible. In any case, the homogenisation of the isotopic composition seems to take place close to the surface. This conclusion is confirmed by others who found a good match between the isotopic composition of drip and the soil waters in Brazil (Cruz Jr. et al., 2005).

The good agreement in isotope numbers between cave seepage and Blautopf discharge also implies that only a minor part of heavy precipitation events bypasses the epikarst and soil zone in preferential flow paths. This is confirmed by the fact that even high discharge seems to provoke only a slight change of the isotopic composition in the Blautopf Spring. The proposition that only a small part of the precipitation reaches the discharge directly was also confirmed with modeling where the conductive part of the complete discharge was determined to be only about 1% even though during extreme events the fast conduit discharge can reach 5 to

10% of the total flow (Bauer and Selg, 2006).

The possibility of a connection with adjacent basins could also be tested, particularly if cave systems spread beyond the surface area of the catchment. Since all isotope data presented of the Blautopf case study lie on the meteoric water line, we can assume that the Blautopf Spring has been fed by local recharge. Alternatively, if caves extent to adjacent catchments, they have received recharge of similar isotopic composition.

A calculation of proportions such as summer recharge to winter discharge was not possible as this requires different output and input isotopic compositions. However, these compositions could not be determined, as the isotope signals were already too mixed in the cave. Therefore, the given results do not enable quantification of mixing proportions, as the weighted average of precipitation, cave seepage- and groundwater discharge through the Blautopf Spring are too similar.

An investigation of persistent pollutants (POPs) in the same area produced findings that match the isotope investigation presented here. It showed that the largest amounts of POPs reached the saturated zone shortly after high discharge events such as snow melts. This can be explained by the piston flow effect that mobilizes particles deposited in the fissures of the epikarst with increasing pressures resulting from higher precipitation amounts. After the fissures are flooded and connected, the infiltrated water is able to transport the particles towards the receiving stream. The Blautopf Spring reacts very fast to snow melts and heavy rain events, thus confirming it to have a saturated conduit system (Birk et al., 2004).

It is also interesting to compare the above results to the nearby Gallusquelle where the δ^{18}O signal of the discharge decreased with smaller amounts (Sauter, 1992). The explanation for such a trend is the mobilization of old winter recharge that was stored in lower aquifer zones and only released from storage during low-flow conditions. Such tendencies could not be observed in the Blautopf Spring. An explanation for this discrepancy could be that the discharge amount from the Gallusquelle, on average $0.5\,\mathrm{m^3\,s^{-1}}$, is much less than the Blautopf discharge, which has an average of about $2.4\,\mathrm{m^3\,s^{-1}}$. The Blautopf cave system therefore establishes a comparatively larger mixing pool where such delay effects might be masked. Further studies on the Gallus Quelle showed that its spring hydrograph does not reveal temporal recharge distributions (Geyer et al., 2008). This supports the isotope results on the Blautopf Catchment, although the work presented here rather focuses on mixing in the unsaturated zone directly after the recharge.

5 Conclusions

By investigating the karst aquifer of the Blautopf Catchment with water stable isotopes the following conclusions could be drawn:

(i) The variations of the stable isotope signal of the precipitation were not found in the Blautopf discharge, which was homogeneous throughout the year. This indicates that considerable mixing must take place in the subsurface of the catchment. It also confirms that fast conduit systems play a minor role in the water balance.

(ii) The stable isotope signal of the precipitation was already buffered in the vadose zone and the cave seepage water showed only small variations in its isotopic composition, which was very similar to the isotope value of the Blautopf Spring (i.e. groundwater) and the weighted averages of the annual precipitation. This is in contrast to the isotope curve of the precipitation and indicates a considerable mixing in the unsaturated zone.

(iii) At present it is difficult to decide which compartment in the unsaturated zone is most responsible for mixing the incoming water masses; however, the most likely candidates are the soil and epikarst compartments.

The mixing of water seemed to be maintained even during high discharge (e.g. after snowmelts), as demonstrated by the homogeneous isotope values of the Blautopf Spring, which consistently ranged, around -10‰. Nonetheless, other investigations showed increased mobilisation of pollutants during such times. This may be explained through involvement of the low permeability fracture system of the epikarst that may hold back and release pollutants over several years.

Future work should focus on investigations of the buffer capacity of the soil and epikarst zone and more research should be devoted to the bedrock matrix. Further dynamic tracers such as tritium isotopes could reveal better insight into travel times of subsurface water masses, while higher sample frequencies may be able to resolve quantification of events such as snow melts and heavy precipitation and the role of the fast conduit system.

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