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**Storage and
transport in cave
seepage**

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Storage and transport in cave seepage- and groundwater in a South German karst system

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Received: 17 April 2008 – Accepted: 6 May 2008 – Published: 4 June 2008

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Published by Copernicus Publications on behalf of the European Geosciences Union.

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Abstract

We investigated one of the best-known and second largest karst areas in Germany (Blautopf Catchment) that offers a unique access waters of the unsaturated zone through a large cave system. As tracers for water flow and storage we measured stable isotopes ($^{18}\text{O}/^{16}\text{O}$ and D/H ratios) in precipitation, seepage- and groundwater. The precipitation showed a distinct seasonal cycle with $\delta^{18}\text{O}$ values between -2.6 and -22.6‰ during summer and winter, respectively. However, the isotope signals in seepage water in the caves as well as the discharge were completely buffered and ranged around an average $\delta^{18}\text{O}$ value of -10‰ . This value also matched the long-term average of the precipitation. In addition, the homogeneous isotopic composition of the Blautopf Spring was against expectation for its highly variable discharge (0.3 to $32\text{ m}^3\text{ s}^{-1}$) that is typical for a fast responsive karst system. We explain the isotopic similarity between cave seepage and the Blautopf Spring (as an integral signal for groundwater) by nearly complete mixing of the water already in the vadose zone. The latter can be divided into the compartments soil, epikarst and rock matrix that all have good storage capacities and also allow diffusive exchange of solutes between mobile and less mobile matrix water. The above approach revealed new aspects about turnover and flow paths of the infiltrated water and thus helps to constrain the risk by pollution to the groundwater.

1 Introduction

Understanding of water pathways and movements in the vadose and phreatic zones 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). A brief classification to karst systems is summarised by Cruz et al. (2005), Genty and Deflande (1998), Mangin (1974) who define three flow compartments:

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

Particularly the influence of the epikarst was recently investigated in more detail as it is assumed to play a major role in mixing and mobilising of waters (Sauter, 1995; Aquilina et al., 2006; Perrin et al., 2003; Clemens et al., 1999). According to Mangin (1973), epikarst is a perched saturated zone above the groundwater table that stores part of the infiltrated water. To describe the variable flow character of karst systems, it also is necessary to consider the conduits that are embedded in the fissured-porous matrix (Liedl and Sauter, 1998, 2000; Kiraly, 1998).

Tracer tests are useful tools particularly for investigation of flow dynamics in karst systems. Such tests with salts or dyes were previously carried out in the Blautopf Catchment for instance in sinkholes. They were able to reveal information about the fast conduit system. However, the latter usually presents only a small part of the subsurface water balance (Bauer and Selg, 2006). Therefore more widely distributed tracers such as stable isotopes are needed to help assess risks from diffuse pollution for the total catchment. This works, if stable isotope changes in space are homogeneous and altitude effects (Clark and Fritz, 1997) can be assumed to be minor. If so, isotope signals in precipitation can be thought to give the same input signal for areas of several hundred square kilometres such as the Blautopf Catchment. Water stable isotopes can therefore help to draw conclusions about the hydrodynamic parameters of the total karstic-fissured-porous system.

Specifically, $^{18}\text{O}/^{16}\text{O}$ and/or D/H ratios are suitable tools because they are constituents of water molecules and thus act as ubiquitous conservative tracers (Maloszewski et al., 2002).

In this study the main focus was on the overall diffuse recharge and transport processes in a karst system at the catchment scale. The objective was to determine the relevance and mixing behaviour of the entire system rather than focussing on the

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fast flow paths of the infiltrated water. In our approach, comparison between the isotopic composition of precipitation and discharge allowed to decide if mixing occurs in such a fast responsive system or if precipitation reaches the spring relatively unaltered. Furthermore, with caves being present in a well-developed unsaturated zone of up to 150 m thickness, we were also able to narrow down where mixing occurs and how much of this process is restricted to this zone that lies at the receiving end of the flow path.

The setting of the Blautopf Catchment with its caves enabled convenient sampling of the unsaturated and saturated zone and therefore was ideal to provide new insights how these compartments are linked. Such information is fundamental for understanding subsurface water movement. It may also help to evaluate the risk of groundwater contamination caused mainly by diffuse pollution and can give important insights to water balances and ultimately contaminant transport.

2 Materials and methods

2.1 Sampling sites

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 165 km² of which ~31% is covered by forests while more than 60% agricultural land (Köberle, 2005).

The Blautopf Catchment has more than 50 caves. We have chosen three of them for our investigation (Fig. 1). They are called “Laichinger Tiefenhöhle” (LTH) and “Sontheimer Höhle” (SH) that are public show-caves and the “Hawaii-Schacht” (HWS) that is not accessible to the general public.

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 north-western part with

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1100 mm a⁻¹ and decreases towards the south-eastern part to average values of 800 mm a⁻¹ (Keller, 2003). The mean groundwater recharge in the Blautopf Catchment is about 500 mm a⁻¹ (Armbruster, 2002). The mean discharge of the Blautopf spring – the principal outlet of the system – was determined with 2.43 m³ s⁻¹ between 1980 and 2003. However, it shows considerable variability with the highest discharge of close to 32 m³ s⁻¹ and the lowest of 0.3 m³ s⁻¹. The Blautopf Spring responds within several days to extreme precipitation events and snow melts. This indicates a strong karstification of large parts of the aquifer that is mostly composed of the fissured Kimmeridge and Tithon Limestones of the upper Jurassic (Villinger, 1987).

In 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 (Postigo-Rebello, 2006¹). 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 around 4 km from the spring (www.blautopf.org).

2.2 Stable isotope sampling and analyses

Samples for stable isotope analyses were collected in the caves and the Blautopf Spring between February 2005 and July 2006. In the same time period precipitation was collected with the aim to sample most precipitation events of this period including long-term snowfall and thunderstorms. A commercially available rain collector was placed at the village of Heroldstatt (9°40'01" E, 48°26'39" N; altitude ~780 m above sea level). After each sampling event, samples were transferred into 20-mL vials with

¹Postigo-Rebello, C.: Effects of plant transpiration on water and carbon cycling in the blautopf catchment (south-west germany), Zentrum für Angewandte Geowissenschaften (ZAG), Universität Tübingen, unpublished, Tübingen, 82 pp., 2006.

tight screw caps to avoid secondary evaporation effects. Afterwards they were stored upside down at 4°C in the dark.

The cave seepage waters were collected at three different locations HWS, LTH and SH (Fig. 1). In the LTH three sampling locations with different distances to the surface were chosen to investigate a variety of possible flow paths and residence times. They were the “Vesperhalle” (VH), “Nasser Schacht” (NS) and “Sächsische Schweiz” (TK). Exact locations of these sampling sites are displayed in Fig. 2. 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. The discharge water was collected in the Blautopf Spring from a depth of 20 cm below the surface and a few meters before the outflow. At this location a constant flow ensured supply of freshly discharged water.

Overall, 69 samples were measured for precipitation, 26 for the spring and a sum of 139 for all cave seepage waters. For some selected samples the hydrogen values were measured and allowed establishing a local meteoric water line (Postigo-Rebello, 2006).

2.3 Analyses

Stable isotopes 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 $^{18}\text{O}/^{16}\text{O}$ and D/H ratios after equilibration with CO_2 and by combustion 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 $^{18}\text{O}/^{16}\text{O}$ or D/H. The one σ standard deviation for repeat measurements was $\pm 0.2\%$ for $\delta^{18}\text{O}$ and ± 1 for δD . The weighted mean isotopic composition

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for the precipitation was calculated with:

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

where Q_t is the rain amount [L m^{-2}] and C_t the $\delta^{18}\text{O}$ signal of the precipitation water at time t .

5 2.4 Climatic data

Data for precipitation were provided by the sewage plant in Heroldstatt ($9^\circ 40' 42''$ E, $48^\circ 26' 30''$ 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. It was emptied every morning and the maximum and minimum temperatures were also recorded each day. The amount of snow was established by melting.

The discharge at the Blautopf Spring was continuously recorded by the Landesanstalt für Umwelt, Messungen und Naturschutz Baden-Württemberg (Karlsruhe).

3 Results and discussion

15 3.1 Input of the isotope signal

The $\delta^{18}\text{O}$ data for precipitation varied between -2.6 and -22.6‰ and between -15 and -125‰ for δD . The weighted mean concentration for $\delta^{18}\text{O}$ in the period from May 2005 to April 2006 was determined with -9.4‰ ($n=11$, January is missing). Figure 3 shows the isotopic variability of the rainfall. For comparison, Bauer and Selg (2006) determined a weighted mean average of $\delta^{18}\text{O}$ of -9.5‰ at the station Münsingen that is at a distance of 15 km from Heroldstatt. Our $\delta^{18}\text{O}$ values showed clear seasonality patterns with maximum values in summer and minimum values in winter. With

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lateral distribution patterns of $\delta^{18}\text{O}$ in the catchment being relative homogeneous and assuming relatively small altitude effects one sampling point can be used to represent the isotopic input for the entire catchment.

3.2 Local meteoric water line

5 When plotting the $\delta^{18}\text{O}$ and δD values of the precipitation, a linear relationship is established that is typical for the area (Fig. 4). It is known as the local meteoric water line and was established for the Blautopf Catchment by Postigo-Rebollo (2006). The isotopic values of seepage and Blautopf discharge samples all fell on this line (Fig. 4). This indicates negligible effects of evaporation near the surface, or during transit from
10 the surface to the cave that can be a concern during warm conditions (Cruz Jr et al., 2005). However, in temperate zones such as in the Blautopf area, this effect is negligible and our findings show that the local precipitation is indeed responsible for the recharge of the spring without any alteration of the isotope signal.

3.3 Isotope signal of the seepage and spring water

15 The samples of the seepage and the spring water did only vary in a narrow range (Figs. 3 and 4). They showed oxygen values between -9.5 and -10.6‰ (LTH). Corresponding to this, the δD values ranged between -70 and -73‰ for the LTH and -67 and -72‰ for the Blautopf (data listed in Table 1). The other locations in the caves showed very similar results with $\delta^{18}\text{O}$ 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, SH and HWS, respectively. Location NS is known for a fast response to strong precipitation events, however even at this subsurface location no strong seasonality in the $\delta^{18}\text{O}$ signal was found. Nordhoff
20 (2005) measured $\delta^{18}\text{O}$ values in the “Zaininger Höhle” that is also located in the Blautopf Catchment and found similar $\delta^{18}\text{O}$ values in the drip water (-10.5 to -11.2‰).
25 This similarity between cave seepage waters already indicates that a significant homogenisation of the water must occur in the unsaturated zone regardless of the length

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of flow path.

Furthermore, the similarity of spring discharge and cave seepage waters show that the isotopic variability from the precipitation must already be buffered in the unsaturated zone above the caves. This is also confirmed by the cave seepage water representing almost the weighted mean $\delta^{18}\text{O}$ value of the precipitation that was calculated with a value of -9.4‰ . In other words, the variability of the annual isotopic variation of the precipitation was hardly found in the cave drip water. Even with the monthly average values for the drip water, we only found insignificant changes towards the more negative winter values. Similarly heavy rain events during summer only produced slight isotopic increases in the drip water of caves. Even the base flow measured at the Blautopf Spring and the weighted average of the precipitation water (weighted over the sampling period of more than a year) showed very similar and homogeneous isotope signals. The isotope values of the Blautopf Spring in this study confirmed the results found by Bauer and Selg (2006), who determined values between -9.7 and -10.2‰ for the Blautopf discharge. This also conforms to other findings where similar buffering of the isotope signal of the precipitation was found in other karst areas in Israel, Spain, Switzerland and USA (Aaylon et al., 1998; Yonge et al., 1985; Caballero et al., 1996; Perrin et al., 2003).

Cruz et al. (2005) stated that the dynamics of karst seepage flow are 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 nicely fits our results and supports the fact that the main mixing and storage processes to occur in the upper part of the unsaturated zone. Hydrochemical and isotope studies from various regions (Arabika Massif, New Zealand and New Mexico) demonstrate that a delay in flow caused by storage in the epikarst can range from several days to a few months (Williams, 1983; Klimchouk and Jablokova, 1989). On the other hand, seasonal variations of $\delta^{18}\text{O}$ were found to be significantly reduced after about 3.5 years of residence time in the soil and epikarst zone in the neighbouring Fränkische Alb (Stichler and Herrmann, 1983). With the current data set we are not able to determine exact

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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 water storage, whereas the soil and the epikarst have only a low storage capacity. However, Perrin (2003) stipulated that the soil and the epikarst subsystems appear to act as an important storage element of the karst system. With the current data set, a differentiation between these compartments is not possible. However, given the thickness of the vadose zone of the Blautopf Catchment (in average 100–150 m) a considerable storage can be assumed for the epikarst. In any case, the homogenisation of the isotopic composition seems to take place close to the surface. This is confirmed by other workers who found a good match between the isotopic composition of the drip and the soil water in Brazil (Cruz Jr et al., 2005).

For the saturated flow, Worthington et al. (2002) estimated hydraulic conductivities for different carbonate aquifers, amongst others one of the Schwäbische Alb. They determined average hydraulic conductivities of $8 \times 10^{-9} \text{ m s}^{-1}$. Associated slow water movement can be considered as storage. The base flow preferentially enables gravimetric flow of more easily mobilized water. However, after heavy rain events also smaller fissures become flooded and connected (Fig. 5). In such a case, the hydraulic pressure pushes the pre-event water out of the storage zone towards the larger conduits in a piston flow effect. In 1974 Mangin already stated that epikarst becomes saturated and connected during heavy rain events. The good agreement between cave seepage water and Blautopf discharge also implies that only a minor part of heavy precipitation events bypasses the epikarst and soil zone along preferential flow paths. This confirmed by the fact that high discharge seemed 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 modelling where the conductive part of the complete discharge was determined with only about 1% (Bauer and Selg, 2006). Nevertheless, during extreme events the conductive discharge during an event can be as high as 5–10% (Bauer and Selg, 2006).

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An investigation of persistent pollutants (POPs) in the same area produced similar findings with the largest amounts of POPs reaching the saturated zone shortly after high discharge events such as snow melts. This can be explained by the piston flow effect with the increasing pressure from higher precipitation amounts mobilising particles deposited in the fissures of the epikarst. 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).

4 Conclusions

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

(i) The variability of the stable isotope signal of the precipitation could not be 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 did only show little variability in its isotopic composition that 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 but 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 snow melts) because the Blautopf Spring always maintained its homogeneous isotope values. Nonetheless, other investigations showed increased mobilisation of pollutants during such times. This may be explained through involvement of the fine fracture

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system of the epikarst.

Future work should focus at 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 travelling times of subsurface water masses.

Acknowledgements. This project was funded by the Deutsche Forschungsgemeinschaft (DFG; German Research Foundation) under grants no. GR 971/20-2. We are grateful to the team of Heiner Taubald who did the isotope measurement, to Patrick Thielsch who recorded the weather data and to the Landesanstalt für Umwelt, Messungen und Naturschutz Baden-Württemberg (Karlsruhe) to provide the spring data. This work was also supported by a grant from the Ministry of Science, Research and the Arts of Baden Wuerttemberg (AZ33-7533.18-15-02/80) to Johannes Barth and Peter Grathwohl. This work was also supported by the European Integrated Project AquaTerra (GOCE 505428). The project has received research funding from the Community's Sixth Framework Programme.

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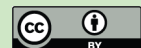
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Table 1. Selected isotope values ($\delta^{18}\text{O}$ and δD) from the precipitation, seepage water of the Laichinger Tiefenhöhle and groundwater (Blautopf Spring).

Precipitation		Seepage water (LTH)		Groundwater (BT)	
δD	$\delta^{18}\text{O}$	δD	$\delta^{18}\text{O}$	δD	$\delta^{18}\text{O}$
-38.5	-5.9	-73.2	-9.9	-71.2	-10.0
-69.3	-9.3	-72.6	-10.1	-72.4	-9.9
-61.1	-8.5	-72.4	-10.1	-72.3	-9.9
-64.2	-9.3	-72.6	-10.2	-71.6	-10.0
-53.8	-7.7	-72.4	-10.1	-70.6	-10.5
-54.7	-7.7	-72.3	-10.3	-71.0	-9.9
-15.4	-2.9	-71.9	-10.1	-70.3	-9.8
-58.9	-8.3	-72.1	-10.1	-70.2	-9.8
-18.7	-3.8	-72.5	-10.1	-67.3	-10.0
-29.8	-4.8	-72.9	-10.1	-69.4	-9.7
-52.9	-7.2	-72.7	-10.3	-71.0	-9.9
-53.1	-8.6	-72.7	-10.1	-69.5	-9.6
-41.5	-6.1	-72.6	-9.9	-69.9	-10.1
-48.9	-7.5	-71.9	-9.9	-70.2	-10.0
-66.2	-9.4	-71.1	-9.9	-70.3	-10.0
-40.4	-6.6	-70.0	-9.8	-70.4	-10.0
-52.8	-7.9	-70.5	-9.6	-70.4	-10.5
-43.6	-8.0	-70.3	-9.6		
-46.7	-7.2	-69.6	-9.7		
-81.2	-11.4	-69.3	-9.5		
-112.2	-14.9	-68.1	-9.6		
-64.5	-9.2	-69.4	-9.7		
-72.7	-11.6	-68.0	-9.8		
-124.6	-17.3	-68.3	-9.7		

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Table 1. Continued.

Precipitation		Seepage water (LTH)		Groundwater (BT)	
δD	$\delta^{18}O$	δD	$\delta^{18}O$	δD	$\delta^{18}O$
-123.5	-16.2	-71.3	-9.9		
-74.2	-10.5	-72.1	-10.6		
-96.9	-13.5	-71.4	-10.0		
-111.0	-15.3	-70.6	-10.0		
-125.0	-17.7	-72.6	-9.9		
-59.0	-10.0	-71.3	-10.3		
-111.4	-16.2				
-68.6	-9.3				
-51.2	-7.6				
-51.8	-7.5				
-32.3	-5.7				
-125.4	-16.8				
-37.5	-5.6				
-55.3	-8.4				
-37.4	-5.6				
-32.5	-5.1				
-77.5	-4.6				
-31.0	-11.2				

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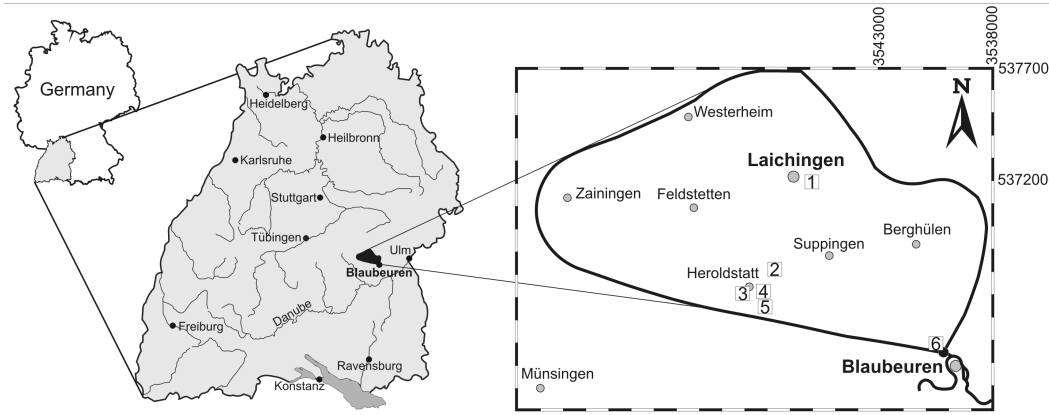


Fig. 1. The catchment area with the Blautopf Spring and the investigated caves; 1 = Laichinger Tiefenhöhle (LTH), 2 = Hawaii-Schacht (HWS), 3 = precipitation sampling point, 4 = sewage plant of Heroldstatt, 5 = Sontheimer Höhle (SH) and 6 = Blautopf.

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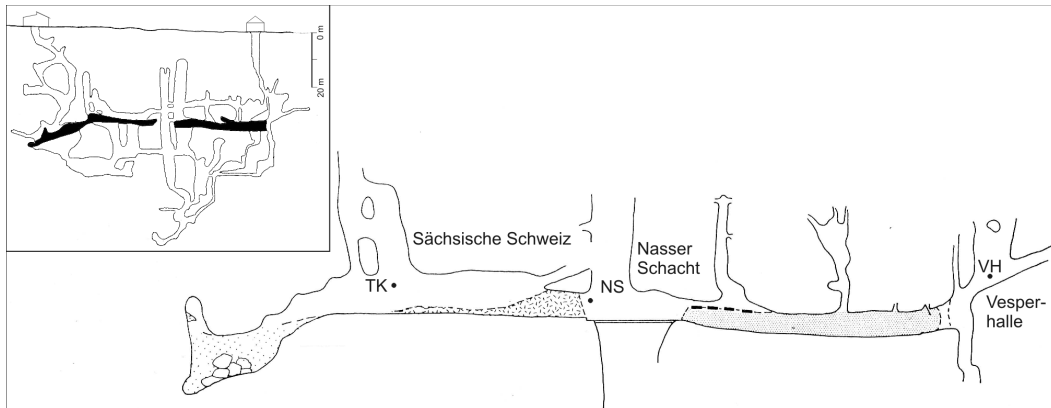


Fig. 2. Position profile of the sampling sites in the Laichinger Tiefenhöhle, TK: Sächsische Schweiz, NS: Nasser Schacht and VH: Vesperhalle (changed according to Burger et al., 1993).

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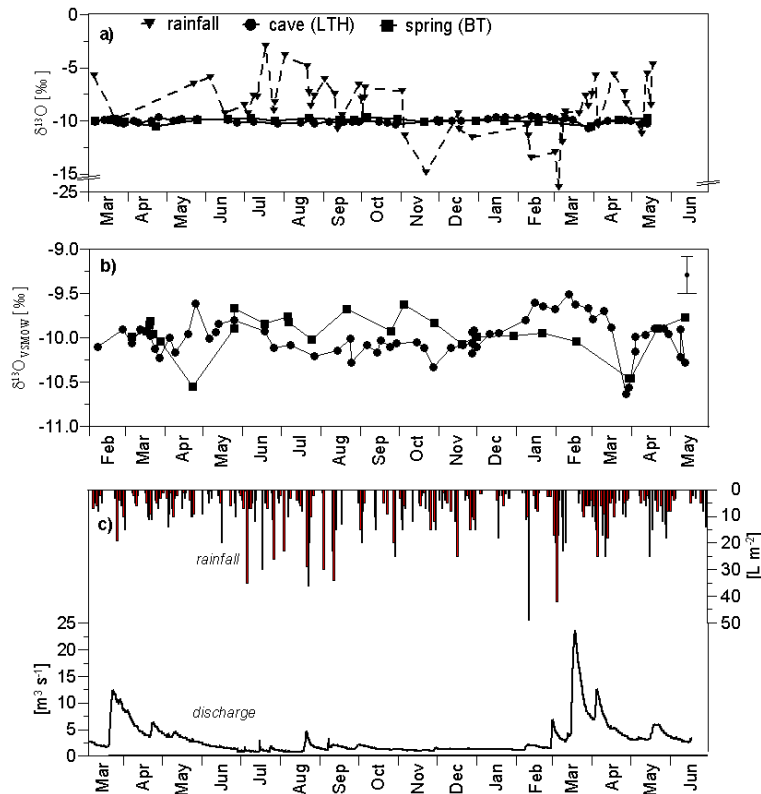


Fig. 3. Graph (a) shows the $\delta^{18}\text{O}$ composition of the rainfall (Heroldstatt), the spring (Blautopf) and the seepage water (Laichinger Tiefenhhle); (b) shows a more detailed $\delta^{18}\text{O}$ composition of the spring and the seepage water (legend see a). The lower graph (c) shows the precipitation and the discharge. Note the different scales on the y-axes. The standard deviation of the ^{18}O measurements is indicated in graph (b) top right.

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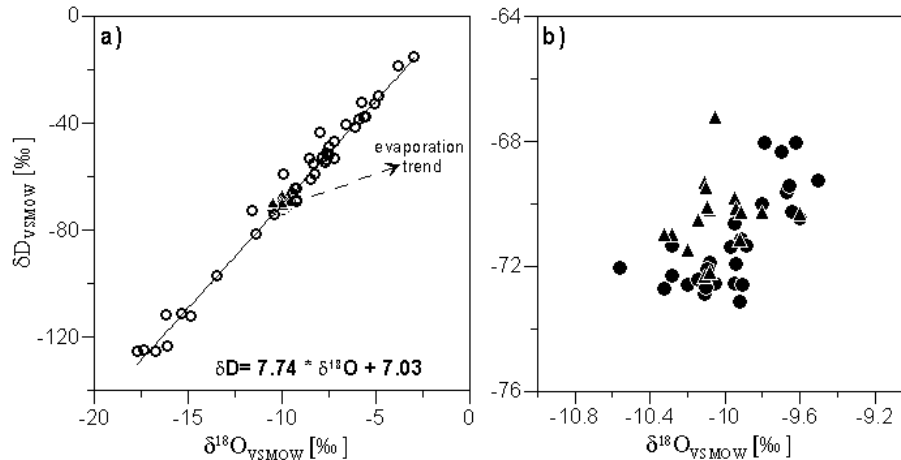


Fig. 4. (a) Local meteoric water line of the Blautopf Catchment with evaporation trend (b) Seepage and ground water in detail. Symbols: ◦ rainfall • seepage water ▲ groundwater.

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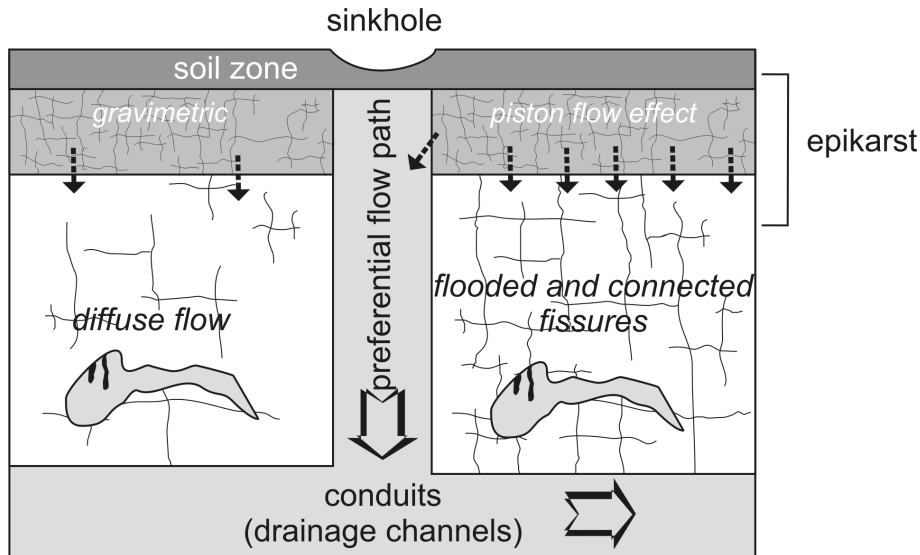


Fig. 5. Schematic representation of the different flow paths during base flow conditions (left) and high flow (right).

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