



Multiple isotope approach to the determination of the natural attenuation potential of a high-alpine karst system

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SUMMARY

³H, ^δ¹⁸O and ^δ²H measurements on groundwater and chemical and isotope analyses on groundwater sulfate were used to determine the origin and mean transit times of groundwater and the sources affecting groundwater sulfate in a high-alpine karstic catchment area in southern Germany.

Modelling results using a lumped parameter approach yielded mean transit times of water between 4 and 12 years for different karst springs. However, results obtained from ^δ¹⁸O and ^δ²H measurements on groundwater showed that a calculated mean transit time of 12 years for groundwater flow in one karst system can only be explained by mixing of young and old tritium-free ice and snowmelt water.

Groundwater sulfate characterized by ^δ³⁴S values of around 20‰ and ^δ¹⁸O values of ca. 12‰ in concert with sulfate concentrations of approximately 11 mg/L are probably affected by evaporites. In contrast, ^δ³⁴S values of around 6‰ and ^δ¹⁸O values up to 9.4‰ in concert with sulfate concentrations between 1 and 7 mg/L mainly derive from atmospheric deposition. However, a ^δ³⁴S value of −7.3‰ identified for one of the karst springs demonstrates that the oxidation of sulfide-containing minerals must be considered as an additional source, affecting sulfate concentrations in groundwater. The estimated transit time distribution of groundwater shows relatively high mean transit times between 2 and 5 years with a low contribution of very short transit times of less than 1 year. The high contribution of long mean transit times of groundwater in the alpine karst system, which represents an important drinking water resource, is an important function for drinking water supplies.

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Introduction

Alpine catchment areas represent important drinking water resources in Europe and therefore fulfill an important function for future drinking water supply. Numerous water utilities such as the cities of Vienna, Innsbruck and Grenoble operate reservoir systems in alpine catchment areas. However, increasing concentrations of anthropogenic pollutants such as PAHs (polycyclic aromatic hydrocarbons), metals such as platinum and palladium, and nitrogen in precipitation, and increased tourist activity may affect groundwater quality in high-alpine catchment areas (Gocht et al., 2007; Barbante et al., 2001; Galloway, 1995). Furthermore, future climate conditions and meteorological variables such as temperature and precipitation, and change in air pollution emissions may also affect groundwater quality in elevated catchment areas (Kinney, 2008).

Einsiedl and Mayer (2005) reported that, on the one hand, mixing processes between young and old groundwater, the latter being stored in the rock matrix, and on the other hand, microbial degra-

ation of pollutions represent important mechanisms for natural attenuation of groundwater in karst aquifers having sufficient rock matrix porosity (Einsiedl and Mayer, 2006). However, the natural attenuation potential of karst groundwater systems without matrix porosity is probably lower. Therefore, it is particularly important to better understand the hydrodynamic processes of high-alpine karstic catchment areas with high vulnerability to contamination to save these groundwater systems as future drinking water resources.

Environmental isotopes such as ³H, ^δ¹⁸O and ^δ²H represent powerful tools to estimate the vulnerability of karstic catchments (Einsiedl, 2005; Maloszewski et al., 2002; Katz et al., 2001). For example Zuber and Motyka (1998) combined the lumped parameter approach with ³H data in groundwater and precipitation to identify the mean transit time of water and the vulnerability of karst groundwater systems to pollution.

In the present study we estimated the transit time distribution of water in a complex, high-alpine karst system. To reach this goal we used an extended long-time ³H data set. The long time ³H data set was obtained during different sampling campaigns performed between 1988 and 2007 in the Wimbach karst groundwater. Six karst springs and one river were repeatedly sampled during low flow conditions and during high groundwater recharge periods.

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Estimation of the mean transit times (MTT) of groundwater was accomplished using the tritium method linked to a dispersion model to compare our data to an earlier study with a tritium record of 4 years (Maloszewski et al., 1992). Moreover, we interpreted our modelling results obtained by the tritium method in combination with $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of groundwater to explain the calculated long mean transit times of water in this complex karstic groundwater system. Furthermore, the stable isotopes of sulfate were used to understand the broad range of sulfate concentrations between 1 and 12 mg/L in the karst groundwater system. Using these data, we get an improved understanding of the origin, pathways, transit times of groundwater, and the chemical history of sulfate in alpine karstic systems of the Wimbach catchment.

Materials and methods

Study site

The Wimbach catchment area investigated in this study is located approximately 100 km southeaster of Munich in the Berchtesgaden National Park, southern Germany (Fig. 1). The catchment area is approximately 33 km² extending from 636 to 2713 m a.s.l. The average altitude of this area is around 1520 m. The bedrock is composed of karstified Triassic Dachstein limestones and Triassic Ramsau dolomites. The Wimbachgries formed by glacial erosion of the dolomites is up to 300 m thick and fills up the valley of the Wimbach catchment area. The hydrogeology is characterized by many karst springs discharging at the base of the limestone unit.

Annual precipitation is approximately 2.5 m/a. Water balance estimates suggest an annual evapotranspiration of approximately 0.8 m/a and the average groundwater recharge for the Wimbach valley is around 1.7 m/a (Maloszewski et al., 1992).

Sampling

To investigate the hydrogeology in the alpine karst aquifer of Wimbach catchment, samples from Wimbach River (WR1, WR2) and groundwater discharging from six springs (site S1–S6) were collected during groundwater recharge conditions (November 2006 and March 2007) and during a short rain event at low flow conditions in summer (July 2007) (Fig. 1).

Groundwater samples for chemical and stable isotope analyses ($\delta^{18}\text{O}$, $\delta^2\text{H}$) were collected in November 2006 and March and July 2007, whereas tritium samples were only collected in March 2007. Groundwater for stable isotope analyses on sulfate were collected in March (WR1, S1–S4) and July 2007 (WR1, S2–S6) which are the times of high groundwater recharge and low flow conditions, respectively. Up to 5 L of groundwater were sampled to provide enough sulfate for isotope analyses.

Methods

Water samples from the springs were measured by ion chromatography for concentrations of major cations and anions (Dionex DX 100) with analytical uncertainties of $\pm 3\%$ estimated from duplicate analyses. DOC concentrations were determined with a SHIMA-

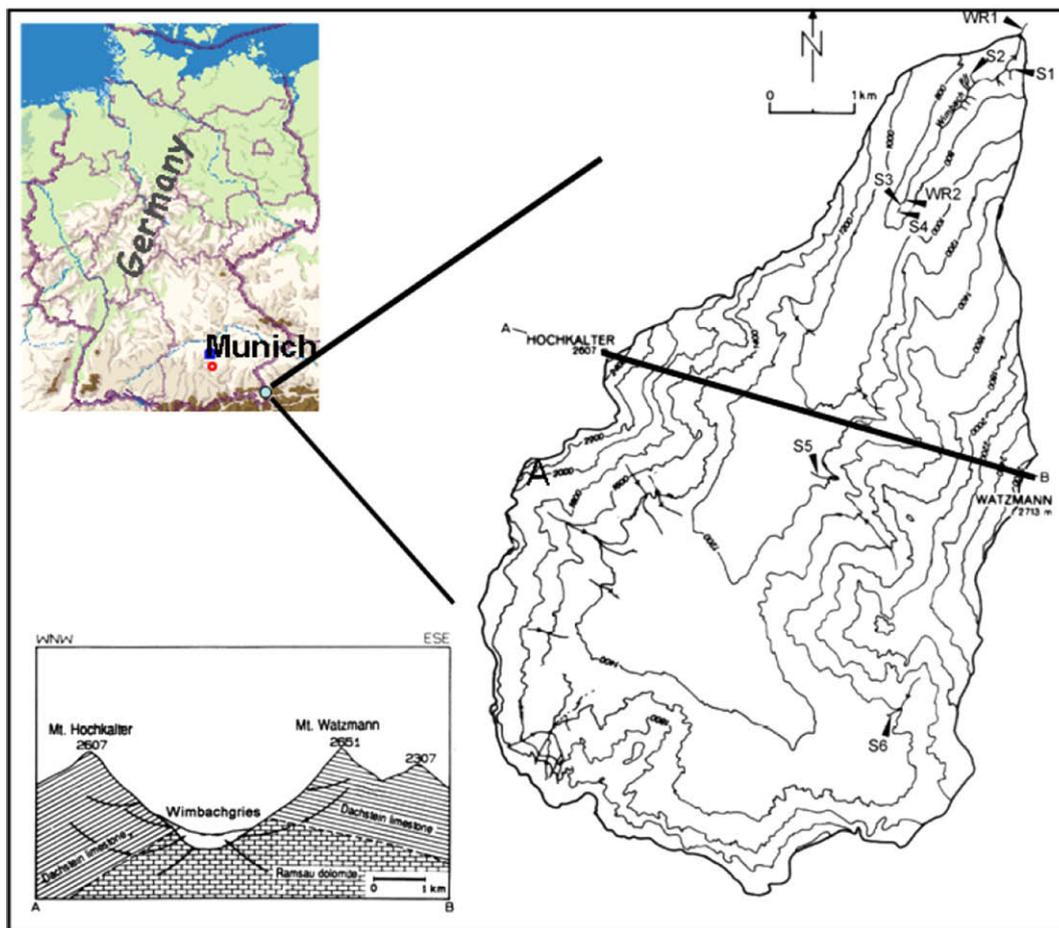


Fig. 1. Karstic catchment area of the Wimbach valley (right) and a cross-section from the Hochkalter (A) to the Watzmann massif (B) (left).

DZU TOC- V_{CPH} . The detection limit was 0.1 mg/L DOC with an analytical uncertainty of ± 0.1 mg/L.

Sulfur and oxygen isotope ratios of sulfate in groundwater were determined using a technique similar to that described by Silva et al. (2000). Sulfate was removed from the water as described by Einsiedl and Mayer, 2005, 2006. Approximately 5 L of groundwater were passed through cation (Biorad AG 50 W-X4, H⁺-form) and anion exchange resin columns (Biorad AG 1X-8) to exchange cations with H⁺ and to retain the anions. Sulfate, nitrate and phosphate were eluted from the anion exchange columns with 15 mL 3M HCl. Circa 5 mL of 0.2 M BaCl₂ solution was added to precipitate BaSO₄ and Ba₃(PO₄)₂, which were removed by filtration. Excess Ba²⁺ was subsequently removed by passing the sample through another anion exchange resin (Biorad AG 50W-X4, Cl⁻-form). For sulfur, V₂O₅ was added to the tin cups. These cups were thermally decomposed in an elemental analyser and the resultant e.g. N₂ was analysed by isotope ratio mass spectrometry in continuous-flow mode. Oxygen isotope ratios of SO₄²⁻ were determined on CO generated by pyrolysis of high purity silver cups containing 400 µg of BaSO₄, respectively using a TC/EA reactor (1350 °C) coupled to a Finnegan 253 isotope ratio mass spectrometer in continuous-flow mode. The accuracy and precision of the measurements was assured by repeated analyses of lab internal and international reference materials (IAEA S1, S2, SO5, NBS 127).

Results are reported as parts per thousand (‰) using the usual delta notation:

$$\delta_{\text{sample}} (\text{‰}) = [(R_{\text{sample}} - R_{\text{standard}}) / R_{\text{standard}}] * 1000 \quad (1)$$

where R is the ³⁴S/³²S or the ¹⁸O/¹⁶O ratio of the sample and the standard, respectively. $\delta^{34}\text{S}$ values with respect to Canon Diablo Troilite (V-CDT) and $\delta^{18}\text{O}$ values of sulfate relative to Vienna Standard Mean Ocean Water (V-SMOW). $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values are reported with an overall analytical precision of $\pm 0.2\text{‰}$ and $\pm 0.4\text{‰}$, respectively.

Tritium measurements were performed by liquid scintillation counting of water after electrolytic enrichment of ³H (Eichinger et al., 1980). The detection limit of this method is 0.7 TU. Samples for the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ determination were collected in 10 mL glass bottles and analysed for $\delta^{18}\text{O}$ by the CO₂ equilibrium method using mass spectrometry. Deuterium determination was performed via mass spectrometry, following uranium reduction. The standard deviation was approximately $\pm 0.1\text{‰}$ for $\delta^{18}\text{O}$ and $\pm 2\text{‰}$ for $\delta^2\text{H}$ in water, respectively.

Estimation of system parameters by modelling of environmental tritium series

The quantitative evaluation of the environmental tracer data is based mostly on using the lumped-parameter models (Maloszewski and Zuber, 1982, 1985, 1996). The main advantage of those models is the fact that they require only knowledge of tracer concentrations in the recharge area (input function) and some records of tracer data at the observation site (output). In spite of their simplicity, lumped-parameter-models can yield useful information on regional hydrogeological phenomena such as the transit time of groundwater. The basic principles of these models are well described in the literature (Maloszewski and Zuber, 1982, 1985, 1996), while their applications have been shown in several studies (e.g. Dewalle et al., 1997; Maloszewski et al., 1983, 1992, 2002). Each lumped-parameter model is characterized by its own transit time distribution function. The form of that function must be known or assumed based on hydrological information about the system under consideration (Maloszewski and Zuber, 1982; Maloszewski et al., 2004). Generally, the transit time distribution function has one or two unknown (fitting) parameters. To determine

values of model parameter(s), the temporal variation of input (recharge water) concentration, $C_{in}(t)$, is used to fit the theoretical output concentration, $C_{out}(t)$, to the concentrations measured in the output of the system (spring, pumping well, stream). The input concentration of environmental tracer can be directly measured or has to be calculated from known hydrological and isotope data (e.g. Grabczak et al., 1984; Maloszewski and Zuber, 1982; McGuire et al., 2002). The relationship between input and output concentrations is described by the convolution integral (Maloszewski and Zuber, 1982):

$$C_{out}(t) = \int_0^\infty C_{in}(t - \tau)g(\tau) \exp(-\lambda\tau)d\tau \quad (2)$$

where λ represents the decay constant of the radioactive tracers, while $g(\tau)$ is the transit time distribution function.

Generally, karst aquifers are considered as triple-porous systems (Maloszewski et al., 2002) which include (1) conduits connecting the sinkholes directly to the karst springs and (2) the fissured-porous karst which is characterized by a double-porous system of mobile fracture water and more immobile water in the micro-porous rock matrix. The water flow velocities in the conduits are in the range of meters to kilometers/day, while the water transport in the fissured-porous system which has a sufficient rock matrix is up to decades (e.g. Einsiedl, 2005; Einsiedl and Mayer, 2005). During the field campaign water samples were collected during low flow conditions. Therefore, only groundwater stemming from the fissured-porous system (without any conduit flow) was sampled. In that case Maloszewski and Zuber (1985) and Maloszewski (1994) found, when the tracer flows sufficiently long through the fissured-porous karst system, the transit time of tracer particles has the same shape as those obtained by an ordinary dispersion model which is used for simple mono-porous systems (without rock matrix porosity). Physically, this means for large transit times of mobile water that the tracer can completely diffuse into the more immobile water of the rock matrix and steady state conditions may be assumed. In this case the distribution of conservative tracer in the mobile and more immobile water system only depends on the ratio of water volumes in both, the mobile and more immobile water system. Consequently, the tracer concentration which is observed in the spring water of the karst system behaves as tracer transport in an apparently mono-porous system which is characterized by a larger volume of water (sum of mobile and immobile water). As a result the distribution of the tracer transit (residence) time in such a system is retarded compared to the transit time distribution of mobile water, because of the diffusion of tracer into the more immobile rock matrix. Maloszewski (1994) and Maloszewski et al. (2004) have found that the ordinary dispersion model is applicable in karst aquifers with a double-porous system, when the mean transit time of mobile water (T) is larger than 2–3 years, which is fulfilled in the catchment areas of the study area. Then the dispersive transit time distribution function reads as

$$g(\tau) = \frac{1}{\sqrt{4\pi P_D^* \tau / T^*}} \frac{1}{\tau} \exp \left[-\frac{(1 - \tau/T^*)^2}{4P_D^* \tau / T^*} \right] \quad (3)$$

with τ being the transit time of single tracer particle through the system, P_D^* – apparent dispersion parameter (Maloszewski et al., 2004) and T^* – the mean transit time of tracer which is related to the transit time of water (T) by the following equation:

$$T^* = \left(\frac{n_m + n_{im}}{n_m} \right) \times T = \frac{n_{total}}{n_m} \times T = RT \quad (4)$$

where T is the mean transit time of mobile water through the system (defined as V_m/Q), n_m and n_{im} are the fracture (mobile) and the matrix (stagnant) porosities, respectively, n_{total} is the total saturated

rock porosity ($n_{im} + n_m$) and R (n_{total}/n_m) is the retardation factor resulting from the diffusion of tracer into the stagnant water.

Generally, modelling environmental tracer data yields the form of the transit time distribution function (type of model) and its parameters. Here, the value of parameter T^* , found by applying (Eq. (3)) enables the volume of water in the whole system (V), i.e. the sum of mobile (V_m) and stagnant (V_{im}) to be calculated

$$QT^* = RTQ = \left(\frac{n_m + n_{im}}{n_m} \right) \times TQ = V_m + V_{im} = V \quad (5)$$

In groundwater systems, where the volume of stagnant water is negligibly small, there is little retardation due to diffusion ($R \approx 1$) and then the mean transit time of tracer (T^*) is directly equal to the mean transit time of water (T). In such a case Eq. (5) yields directly the volume of mobile water in the system. The transit time distribution function (Eq. (3)) with its parameters can also be used to find some additional information for the water managers. For example one can estimate the contribution of water $p(T_i)$ flowing out from the system with the turnover times (τ) being below defined transit time (T_i), (i.e. between 0 and T_i) which can be calculated as follows:

$$p(T_i) = \int_0^{T_i} g(\tau) d\tau \times [100\%] \quad (6)$$

Results

Water chemistry

Table 1 summarizes chemical data for groundwater from the karst springs from sites S1–S6 and the Wimbach River WR1 sampled during groundwater recharge conditions (November 2006 and March 2007) and low flow (July 2007). The groundwater and river water WR1 was characterized by pH values between 6.7 and 8.6 and a temperature of about 8 °C. The electrical conductivity varied between 125 and 343 $\mu\text{S}/\text{cm}$. During groundwater recharge all groundwater samples are of the $\text{Ca}^{2+}/\text{Mg}^{2+}-\text{HCO}_3^-$ type characteristic for carbonate aquifers. Chloride concentrations in the high-alpine karst system are, as expected, below the detection lim-

it of 2.5 mg/L. The calculated Ca/Mg ratios in the karst water are between approximately 2 and 2.6, which may suggest that the groundwater flow is through the Triassic Dachstein limestones. Nitrate concentrations in spring water and in the Wimbach River WR1 were between 1.4 and 4.6 mg/L and sulfate concentrations varied between 1.1 and 12.8 mg/L. DOC concentrations in karst water ranged from 0.3 to 1.4 mg. During low flow conditions (July 2007) and groundwater recharge chemical and physical parameters were fairly constant.

Tritium data

The ^3H input function was obtained from the German precipitation station Jettenberg (1970–2007) located close to the catchment area. The data set was completed using the IAEA records from Ottawa and Vienna (1962–1969) because no other IAEA stations reported ^3H data prior to 1969.

Additional tritium measurements from spring water S1–S6 and from Wimbach River WR1 and WR2 were included in this study sampled between 1988 and 1991 (Maloszewski et al., 1992). Therefore, long-term tritium data sets from groundwater between 1988 and 2007 were used for modelling. Tritium contents in groundwater obtained from sites WR1 and WR2 and S1 to S6 ranged from 7 to 9 TU. Throughout the last 19 years tritium contents in groundwater decreased from around 27 TU in 1988 to 10 TU in all springs.

$\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ of groundwater sulfate

During groundwater recharge $\delta^{34}\text{S}$ values ranged between 5.5‰ and 21‰ and the $\delta^{18}\text{O}$ values of sulfate were between 4.8‰ and 12‰. At low flow conditions $\delta^{34}\text{S}$ values ranged between –7.2‰ and 20‰ and the $\delta^{18}\text{O}$ values of sulfate were between 4.7‰ and 13‰. All isotope data are summarized in Table 1 and Fig. 2.

Stable isotopes of water

Stable isotopes of water were measured for all sampling campaigns ($n = 3$) performed in November 2006 and March (WR1,

Table 1
Concentrations of major dissolved species in groundwater shown as mean concentrations and standard deviation ($\pm 1\sigma$) and isotopic composition of groundwater sulfate of the sampling intervals between 2006 and 2007 during groundwater recharge (GR) and low flow conditions (LF).

Spring	WR1	$\pm 1\sigma$	S1	$\pm 1\sigma$	S2	$\pm 1\sigma$	S3	$\pm 1\sigma$	S4	$\pm 1\sigma$	S5	S6
pH (GR)	7.4	–	7.6	–	8.1	–	7.5	–	7.4	–	7.6	–
pH (LF)	6.7	–	–	–	8.6	–	7.9	–	8.2	–	8.5	8.4
Conductivity ($\mu\text{S}/\text{cm}$) (GR)	235	–	220	–	330	–	220	–	225	–	125	133
Conductivity ($\mu\text{S}/\text{cm}$) (LF)	229	–	–	–	343	–	235	–	217	–	138	149
O_2 (mg/L) (GR)	–	–	–	–	–	–	–	–	–	–	–	–
O_2 (mg/L) (LF)	10.9	–	–	–	10.3	–	11.2	–	11.0	–	10.5	9.9
Na^+ (mg/L) (GR)	0.9	0.4	2.3	1.02	1.6	–	0.9	–	0.6	0.1	1.9	<0.5
Na^+ (mg/L) (LF)	0.7	–	–	–	0.7	–	0.5	–	0.6	–	0.9	<0.5
NH_4^+ (mg/L) (GR)	<0.05	–	<0.05	–	<0.05	–	<0.05	–	<0.05	–	<0.05	<0.05
NH_4^+ (mg/L) (LF)	<0.05	–	–	–	0.08	–	<0.05	–	<0.05	–	1.45	<0.05
K^+ (mg/L) (GR)	<0.25	–	0.3	–	0.3	–	<0.25	–	<0.25	–	<0.25	<0.25
K^+ (mg/L) (LF)	<0.25	–	–	–	<0.25	–	<0.25	–	<0.25	–	–	<0.25
Ca^{2+} (mg/L) (GR)	29.9	0.3	29.6	0.5	38.8	6.7	29.6	1.4	30.8	9.8	20.8	20.9
Ca^{2+} (mg/L) (LF)	30.3	–	–	–	48.0	–	28.9	–	28.7	–	21.3	19.8
Mg^{2+} (mg/L) (GR)	12.8	0.2	12.3	0.8	15.9	3.12	12.4	0.4	14.1	4.4	10.4	8.8
Mg^{2+} (mg/L) (LF)	12.3	–	–	–	18.4	–	12.7	–	12.8	–	10.0	8.9
Cl^- (mg/L) (GR)	<2.5	–	<2.5	–	<2.5	–	<2.5	–	<2.5	–	<2.5	<2.5
Cl^- (mg/L) (LF)	<2.5	–	<2.5	–	<2.5	–	<2.5	–	<2.5	–	<2.5	<2.5
SO_4^{2-} (mg/L) (GR)	12.8	0.1	10.0	0.1	10.1	4.2	11.2	0.5	6.7	0.5	<5	<5
SO_4^{2-} (mg/L) (LF)	12.5	–	–	–	6.0	–	12.3	–	8.7	–	1.1	1.7
NO_3^- (mg/L) (GR)	1.9	0.2	2.3	0.5	3.5	1.6	1.9	0.1	3.0	1.9	1.9	1.5
NO_3^- (mg/L) (LF)	2.0	–	–	–	4.6	–	1.7	–	1.7	–	1.8	1.4
DOC (mg/L)	1.1	0.3	0.6	–	0.8	–	0.4	–	0.4	–	0.8	1.4
$\delta^{34}\text{S}/\delta^{18}\text{O}$ (GR)	19.1/11.4	–	21.0/11.4	–	20.0/11.1	–	20.2/12.3	–	5.5/4.8	–	–	–
$\delta^{34}\text{S}/\delta^{18}\text{O}$ (LF)	20.6/12.7	–	–	–	6.2/6.8	–	21.6/12.6	–	-/-	–	4.2/9.4	-7.3/4.7

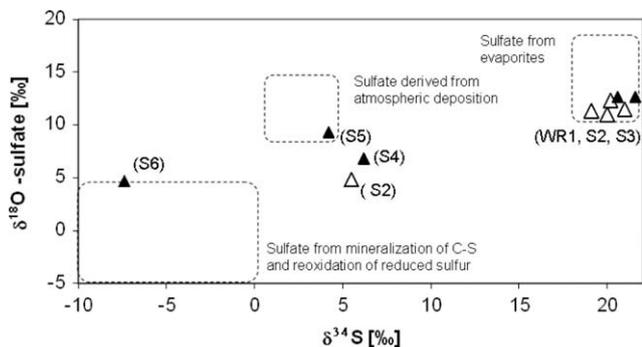


Fig. 2. $\delta^{34}\text{S}$ against $\delta^{18}\text{O}$ values of groundwater sulfate (triangles) and different fingerprints of sulfate during groundwater recharge (open symbols) and low flow conditions (filled symbols).

S1–S4) and July 2007 (WR1, S1–S6). During times of higher groundwater recharge (November and March) the $\delta^{18}\text{O}$ values from sites S1–S6 and from WR1 ranged from -12.5‰ to -10.8‰ and the $\delta^2\text{H}$ values were between -90.3‰ and -78.2‰ (Fig. 3).

During low flow (July 2007) $\delta^{18}\text{O}$ values were between -12.3‰ and -10.6‰ and $\delta^2\text{H}$ ranged from -88.8‰ to -77.7‰ and were similar compared to those observed during the sampling campaigns in 2006 representing groundwater recharge conditions.

Discussion

To estimate the vulnerability of groundwater in a fairly high-velocity, high-alpine karst system we calculated the mean transit time of ^3H in groundwater using a dispersion model and long term ^3H records for precipitation and for ^3H data in groundwater sampled between 1988 and 2006. Moreover, we determined the contribution of water, $p(T)$, flowing out in different sampling sites as a function of defined transit time periods to estimate the vulnerability of drinking water supplies to pollution.

Furthermore, to identify biogeochemical reactions regulating sulfate concentrations in the karstic groundwater system we used chemical and isotopic techniques.

Estimation of transit time distribution of water

The results of modelling tritium data observed for three sampling sites in the Wimbach catchment are shown in Fig. 4, while the values of fitting parameters for all sites are summarized in Ta-

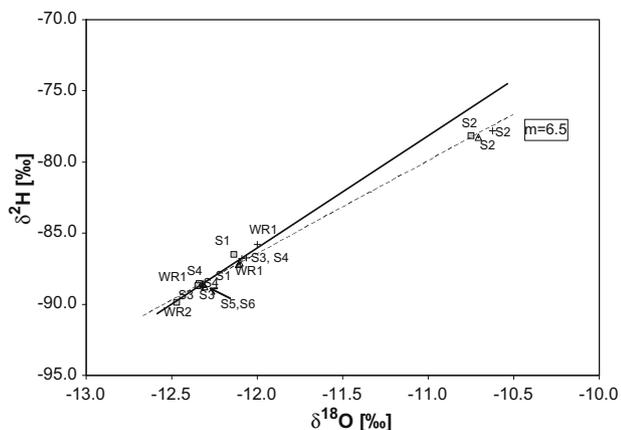


Fig. 3. $\delta^{18}\text{O}$ against $\delta^2\text{H}$ for site S1 to S6 and WR1 and WR2 for different sampling campaigns (triangles: November 2006, circles: December 2006, squares: March 2007, drawn line: Mean water ocean line (MWL), dotted line: regression line with a slope m of 6.5.

ble 2. The calculations were performed using the FLOWPC software described in detail in Maloszewski and Zuber (1996). The gauging station installed on the Wimbach River (WR1, Fig. 1) collects the total outflow from the catchment with a mean discharge of about $Q = 1.75 \text{ m}^3/\text{s}$. The sampling site WR2 is installed where the underground stream, which later becomes the Wimbach River, appears on the ground surface. The karst springs (S1–S6) are characterized by different discharges. The main spring (S3) collects 80% of water flowing out from the catchment, while two other springs (S2 and S5) have relatively low discharges (about 2 L/s). The springs S1, S4 and S6 have still lower discharges and are estimated to $< 1 \text{ L/s}$. The mean transit time of tritium for the whole catchment, estimated in gauging station (WR1) was equal to 4.5 years. Springs S3 and S4, as well as the sampling station (WR2), have nearly the same mean transit times (4.2–4.5 years) (Table 2). Both springs and the stream (WR2) are situated in the same region of the valley, where the groundwater discharge emerges at the surface (Fig. 1). This means that the transit time from that area to the gauging station (WR1) is insignificantly small. Spring S5 ($Q = 2.5 \text{ L/s}$) drains the subcatchment area which has the largest topographic relief in the Wimbach valley with a range of 1500 m (i.e., from the bottom of the valley to the Watzmann Peak). Since this subcatchment has the thickest unsaturated zone in the catchment area, a larger mean transit time of about 7 years compared to springs S1, S3, S4 and S6 (MTT ≈ 4 years) seems likely. Maloszewski and Zuber (1985) showed for lumped-parameter models that a long data record for tritium in groundwater is accompanied by a decrease in the uncertainty of the calculated mean transit times. In our case we estimate the uncertainty of the estimated transit times of approximately ± 1 year. The largest transit time (12 years) was found in the small spring S2 ($Q = 2 \text{ L/s}$). The modelling results summarized in Table 2 are in line with the results of an earlier study (Maloszewski et al., 1992) with a tritium record of 4 years compared to our study using a extend ^3H record of approximately 20 years.

From simple hydrogeological calculations (groundwater recharge, thickness of the aquifer and the unsaturated zone, rock porosity) and based on our results for springs S1 and S3–S6 a mean transit time of groundwater of up to some years can be expected. To explain the long mean transit time of 12 years it is hypothesized that mixing of young and old groundwater controls the modelled long mean transit times for spring S2. The stable isotopes of water ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) were used to identify different water sources in the karst groundwater springs (S1–S6). Generally, $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values in precipitation in such high-alpine catchments are in the range of -12‰ and -90‰ , respectively, as observed in springs S1, S3, S4, S5 and S6 and the Wimbach River WR1 and WR2. The increase of the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values up to approximately -10.8‰ and -80‰ , respectively, in spring S2 indicates the mixing of young karst groundwater with water enriched in the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ (Fig. 3). Based on our results for springs S1 and S3–S6 for spring S2 it is suggested that young groundwater containing tritium with mean transit times of approximately 4 years mixes with old ice and snow melt water from the Hochkalter (Fig. 1). The latter is enriched in $\delta^{18}\text{O}$ and $\delta^2\text{H}$ by evaporation processes compared to those of recent precipitation values (Stichler and Aermann, 1978), whereas only the ice melt water is more or less tritium free ($< 0.7 \text{ TU}$) leading to higher mean transit times in the groundwater of spring S2. However, since the contribution of old ice and snow melt water to the total discharge of the spring is unknown, numerous interpretations focusing on the transit time of groundwater at spring S2 are likely.

The yielded mean transit times enabled to calculate the mean water volume (Eq. (5)) in different parts of the catchment. The whole volume of water (V_{total}) in the Wimbach catchment, estimated based on the parameters found for the gauging station

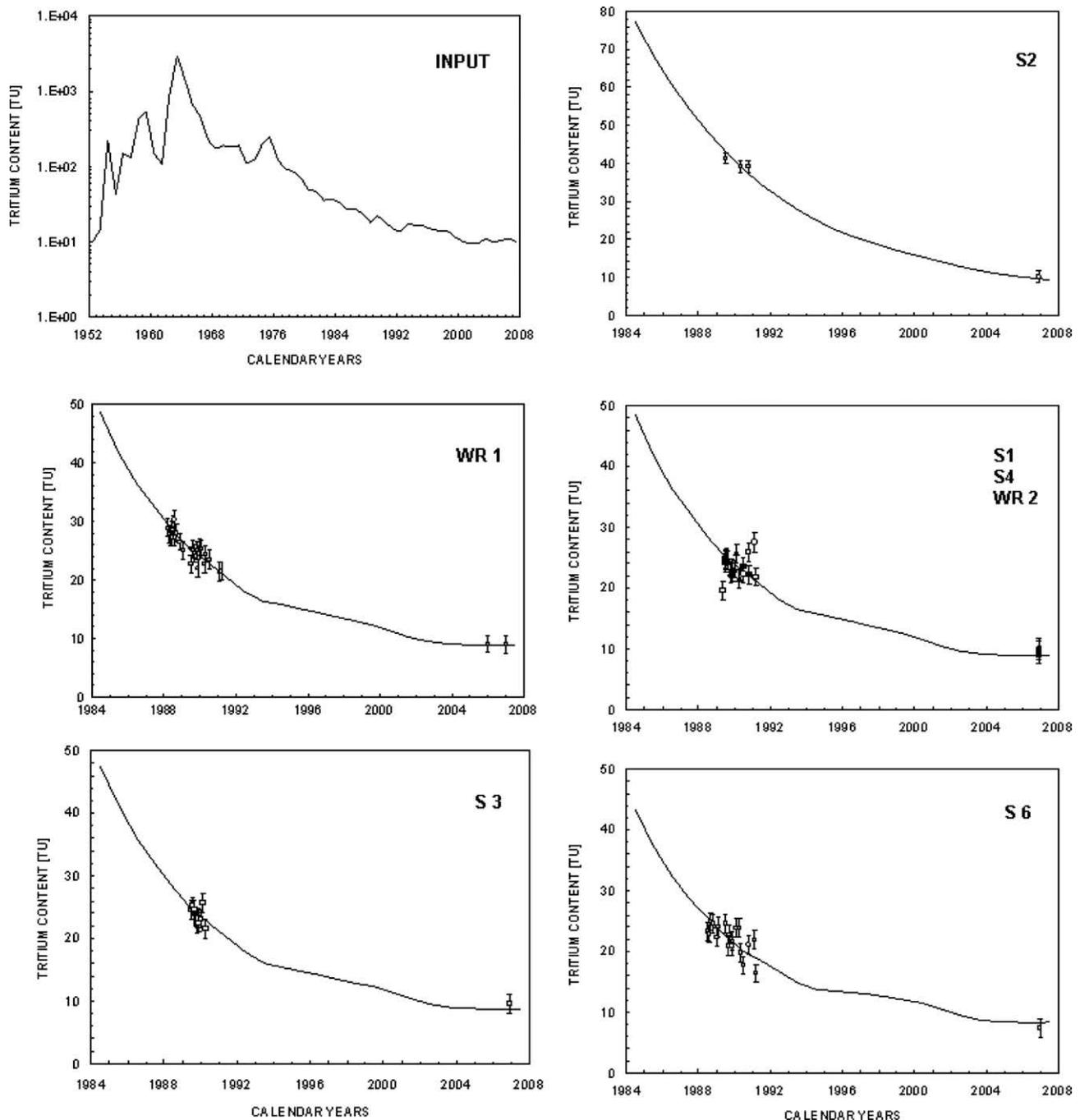


Fig. 4. Results of modelling tritium data observed in the WR1, WR2-gauging stations and the karst springs S1–S4, and S6. In the upper part the tritium input function (weighted yearly means for Wimbach catchment), is also shown.

(WR1) is about $250 \times 10^6 \text{ m}^3$. For the complete catchment surface of 33.4 km^2 this corresponds to about 7.5 m thick water equivalent (column) as an average.

The Wimbach catchment is filled in the valley with porous sedimentary material (Wimbachgries) having a volume of about 10^9 m^3 and a porosity of about $n_{total} = 0.3$. These data indicate that the potential water storage (V_{WG}) of the Wimbachgries is about $3 \times 10^8 \text{ m}^3$. This might suggest that the whole water ($V_{total} = 250 \times 10^6 \text{ m}^3$) in the catchment is stored only in the clastic material filling the valley ($V_{WG} = 3 \times 10^8 \text{ m}^3$). However, first geophysical investigations have shown that less than 1/3 of Wimbachgries is filled with water, whereas 2/3 of Wimbachgries represent the unsaturated zone. It finally yields the possible water volume which could be stored there to be of about $100 \times 10^6 \text{ m}^3$.

Taking this into account one obtains the volume of water stored in the rest of the catchment (in the mountain slopes) being of about $150 \times 10^6 \text{ m}^3$. For the surface of the slope being of about 25 km^2 it yields the average water equivalent of about 6 m. The mean recharge in the catchment was estimated to be of about $q = 1.65 \text{ m/year}$ (Maloszewski et al., 1992). Assuming that infiltration is equally distributed on the catchment slope it yields the mean transit time through this part of about 3.5 years. This value fits well the transit times between 2.5 and 5.3 years found by Maloszewski et al. (1992) when applying a dispersion model to environmental isotope data observed in different small springs at the slope of the Wimbach catchment.

By applying Eq. (6), one can construct diagrams revealing the portion of water, $p(T)$, flowing out in different sampling sites as a

Table 2

Model parameters (T^* , P_D^*) found by calibrating the Dispersion Model to the tritium data observed in different sampling sites in the Wimbach catchment area and derived volumes of water (WR1 is the gauging station on the Wimbach River, S3 is the main karst spring from which the water discharges to the Wimbach River 1 km below the sampling site WR2, Fig. 1).

Sampling site	Type	Discharge, Q (L/s)	Transit time, T^* (years)	Dis. par., P_D^* (-)	Volume of water, V (m ³)
WR1	River	1750	4.5	0.5	248×10^6
WR2	Stream	n.d.	4.2	0.5	–
S1	Spring	n.d.	4.8	0.5	–
S2	Spring	ca. 2	12.0	0.5	0.8×10^6
S3	Spring	1400	4.4	0.4	194×10^6
S4	Spring	n.d.	4.5	0.5	–
S5	Spring	ca. 2.5	7.1	0.3	0.5×10^6
S6	Spring	n.d.	4.2	0.5	–

function of defined transit time periods (always between 0 and T). Such diagrams may be used to estimate the vulnerability of drinking water supplies for pollutions. Fig. 5 demonstrates such a diagram for the gauging station (WR1) and main karst spring (S3). Table 3 summarizes the results for selected sampling sites. The results obtained for the main karst spring (S3) and the gauging station (WR1, being simultaneously drinking water supply for the city) clearly demonstrate that only 9% of groundwater shows transit times up to one year and more than 90% of the groundwater is characterized by transit times between 1 and > 10 years. Two other springs are characterized by a contribution of water with short and longer transit times of 5% and 20% and by 1% and 40%, for S5 and S1, respectively.

Water chemistry and isotopic composition of groundwater sulfate

Different studies have shown that sulfate-reducing microorganisms and denitrifiers contribute extensively to the degradation of organic contaminants in porous aquifers and fractured rocks (e.g. Meckenstock et al., 2004; Spence et al., 2005). Furthermore, (Einsiedl and Mayer, 2005; Einsiedl and Mayer, 2006) reported that sulfate reduction and denitrification have occurred in a fissured-porous karst aquifer using hydrochemical and isotopic data. Therefore, it is of interest to understand sources and processes affecting groundwater sulfate and nitrate in a high-alpine karstic catchment area, implying the importance of microbial processes for biogeochemical processes in karst groundwater. All groundwater samples (S1–S6) and water samples from the Wimbach River WR1 sites

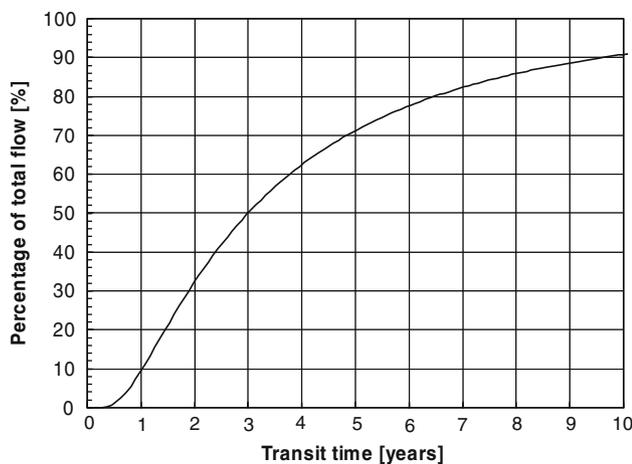


Fig. 5. Cumulative diagram showing the percentage of discharge as a function of transit time calculated for the Wimbach gauging station (WR1) and karst spring: S3.

Table 3

Portions of discharged water characterized by transit times with values in different time intervals calculated for selected sampling sites.

Transit time intervals (years)	Contribution of water flow p (%)		
	WR1/S3	S5	S1
0 < T < 1	9	5	1
0 < T < 2	32	7	5
0 < T < 3	50	20	13
0 < T < 4	63	34	21
0 < T < 5	71	46	30
5 < T < 10	20	34	30
T > 10	9	20	40

showed low nitrate concentrations in the range between 1 and 5 mg/L. Furthermore, during low flow, ammonium concentrations of 0.08 and 1.5 mg/L were found in springs S2 and S5, respectively. Nitrate and ammonium concentrations in atmospheric deposition are typically < 1 and around 1 mg/L in this catchment area, respectively. Therefore, such low nitrate concentrations in groundwater suggest that nitrogen is derived from atmospheric deposition.

Sulfate concentrations in atmospheric deposition are around 1 mg/L in this catchment area (Staatsministerium flUF, 2005) with sulfate enrichment in groundwater due to evaporation by a factor of 2. Furthermore, a somewhat higher sulfate concentration in groundwater in forested areas compared to open field deposition can be expected (Draaijers et al., 1997). Samples from springs S1–S6 and WR1 from the Wimbach River showed sulfate concentrations in the range of 1 and 12 mg/L. Therefore, we hypothesize that sulfate concentrations in groundwater of the Wimbach catchment of more than 10 mg/L may be regulated by geogenic sulfate sources such as evaporites in Triassic limestones (WR1, S1–S3). Sulfate concentrations in the forested catchment area of spring S4 of around 6 mg/L are probably somewhat higher as expected for groundwater sulfate derived from atmospheric deposition in southern Germany and may stem from mixing processes between sulfate derived from atmospheric deposition and sulfate stemming from evaporites, whereas sulfate concentrations of around 1 mg/L (S5, S6) may be controlled by atmospheric sulfate or by bacterial sulfate reduction. Stable isotopes are a powerful tool to determine the sources and processes affecting the range of sulfate concentrations in the karst system.

During groundwater recharge the isotopic composition of groundwater sulfate ranged between 5.5 and 21‰ for $\delta^{34}\text{S}$ (S1 to S4, WR1) and was around 11‰ for the $\delta^{18}\text{O}$ from sites S1 to S3 and WR1 (Fig. 2). However, the $\delta^{18}\text{O}$ value of groundwater sulfate from the forested site S4 was depleted up to several per mil compared to all other sampled sites. For springs S5 and S6 no sampling was performed.

During low flow $\delta^{34}\text{S}$ values were similar to those observed during groundwater recharge at Wimbach River WR1 and at spring S3, whereas at sampling site S2 $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values of groundwater sulfate showed a decrease up to several per mil in concert with decreasing sulfate concentrations, compared to those observed during groundwater recharge conditions. For springs S5 and S6 with sulfate concentrations of around 1 mg/L $\delta^{18}\text{O}$ values were 9.4 and 4.7‰, respectively. Moreover, $\delta^{34}\text{S}$ values for springs S5 and S6 were 4.2 and –7.3‰, respectively.

$\delta^{34}\text{S}$ values of groundwater sulfate (S1–S3, WR1) with $\delta^{34}\text{S}$ values of around 20‰ accompanied by $\delta^{18}\text{O}$ values of around 11‰ and sulfate concentrations between 10 and 13 mg/L are characteristic of sulfate formed by the solution of evaporites in groundwater. In contrast, $\delta^{34}\text{S}$ values of around 4‰ (S5) in concert with $\delta^{18}\text{O}$ values of ca. 10‰ and groundwater sulfate concentrations of about 1 mg/L may derive from atmospheric deposition. Cortecchi et al. (1981) provided evidence that evaporites have $\delta^{34}\text{S}$ values of

around 20‰ while $\delta^{18}\text{O}$ values are believed to range between 10‰ and 18‰ and are similar to those observed in our study. In addition, (Pichlmayer and Blochberger, 1994) found $\delta^{34}\text{S}$ values from sulfate derived from atmospheric deposition between 0‰ and 5‰ with an arithmetic mean of 3‰ for the last 150 years in Germany. Furthermore, Mayer et al. (1995) and Einsiedl et al. (2007) reported that $\delta^{18}\text{O}$ values of sulfate derived from atmospheric deposition are between 8‰ and 16‰ in southern Germany. The $\delta^{34}\text{S}$ values of groundwater sulfate for S2 and S4 accompanied by sulfate concentrations of up to 7 mg/L are somewhat higher than that reported by Pichlmayer and Blochberger (1994) and may be explained by some influence of evaporites at this groundwater site.

The observed negative $\delta^{34}\text{S}$ value of groundwater sulfate at sampling site S6 is in line with the interpretation that sulfide-containing minerals such as FeS or FeS₂ are oxidized in the karst system. However, sulfate concentrations of around 1 mg/L in groundwater S6, which are similar to those derived from atmospheric deposition (S5) may be explained by mixing of two different sulfur sources. However, the karst water characterized by depleted $\delta^{34}\text{S}$ values (S6) may be contributed to less degree. The $\delta^{18}\text{O}$ values of groundwater sulfate from sites S2 (low flow), S4 (groundwater recharge) and S6 (low flow) are depleted by several per mil ($\delta^{18}\text{O}_{\text{sulfate}} \sim 5\text{‰}$) as compared to sulfate derived from atmospheric deposition ($\sim 10\text{‰}$) and from evaporites. Generally, sulfate is cycled through the organic sulfur pool during transport through the mineral soil where four oxygen molecules with water oxygen (-10‰) and molecular oxygen (23.5‰) are incorporated in the newly formed sulfate (Einsiedl and Mayer, 2005). Furthermore, oxidation of sulfide-containing minerals is also in concert with an incorporation of water oxygen and molecular oxygen (Balci et al., 2007). These processes probably shift the isotopic value of $\delta^{18}\text{O}$ in groundwater sulfate at sites S2, S4 and S6 to lower values and SO_4^{2-} formed by mineralization of carbon-bonded S or reoxidation of sulfide-containing minerals is expected to have $\delta^{18}\text{O}$ values between 0‰ and around 4‰ (Mayer et al., 1995; Einsiedl and Mayer, 2005; Balci et al., 2007). The somewhat higher $\delta^{18}\text{O}$ values in groundwater sulfate (S2, S4) may be, as expected, in line with the interpretation that the solution of evaporites with $\delta^{18}\text{O}$ values of around 15‰ also masks the isotopic composition of groundwater sulfate formed by mineralization. Moreover, the variations in the $\delta^{18}\text{O}$ values of groundwater sulfate during different flow conditions (S2) accompanied by variation of sulfate concentrations may also be explained by mixing of different sulfate sources. Sulfate derived from precipitation which is cycled through the organic carbon pool and characterized by low $\delta^{18}\text{O}$ values leads to decreasing $\delta^{18}\text{O}$ values in groundwater sulfate (S2), whereas sulfate stemming from the solution of evaporites with $\delta^{18}\text{O}$ values of around 15‰ caused increasing $\delta^{18}\text{O}$ with increasing sulfate concentrations as observed in spring S2. These results show that the groundwater quality from this high-alpine karstic catchment area is controlled mainly by atmospheric transport of nitrate and ammonium and the solution of evaporites and sulfide-containing minerals.

Conclusions

With respect to the high vulnerability of karst systems relatively high mean transit times of water of around 4 years with a low contribution of very short transit times (<1 year) is an important characteristic to save the future drinking water resource in the Wimbach catchment. Based on our modelling results, we suggest that a high contribution of groundwater in the catchment has transit times between 2 and >10 years. The mixing of groundwater with event water, which can be affected by pollutants in precipitation, probably regulates the natural attenuation process of such

groundwater systems through dilution and dispersion. The results of this study also demonstrate that the estimation of the transit time distribution for karst springs fulfill an important tool for water suppliers and that simple box model approaches can be used to investigate critical parameters for groundwater management.

In this study we also have measured the stable isotopes of water and groundwater sulfate in a high-altitude alpine catchment area to investigate groundwater flow and transport processes and to identify the biogeochemical reactions affecting sulfate and its origin. The link between calculated transit times using tritium and a lumped parameter approach and the results of stable isotopes in groundwater show that mean transit times of up to 12 years (S2) can be explained by mixing of different water sources. Furthermore, we found that different sulfur sources such as evaporites and pyrite oxidation affect sulfate in groundwater. However, we found no isotopic evidence that bacterial sulfate reduction has occurred in the groundwater system to explain the broad range of sulfate concentrations in different karst springs of the Wimbach valley.

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