ELSEVIER

Available online at www.sciencedirect.com

SCIENCE DIRECT®

Applied Geochemistry 20 (2005) 701–712

Applied Geochemistry

www.elsevier.com/locate/apgeochem

# Assessing river–groundwater exchange in the regulated Rhone River (Switzerland) using stable isotopes and geochemical tracers

M. Fette [a,*], R. Kipfer [b,c], C.J. Schubert [a], E. Hoehn [b], B. Wehrli [a]

[a] *Limnological Research Center, Swiss Federal Institute of Environmental Science and Technology (EAWAG) and Swiss Federal Institute of Technology (ETH), Seestrasse 79, CH-6047 Kastanienbaum, Switzerland*

[b] *Water Resources and Drinking Water, Swiss Federal Institute of Environmental Science and Technology (EAWAG), Überlandstrasse 133, CH-8600 Dübendorf, Switzerland*

[c] *Isotope Geology, Swiss Federal Institute of Technology (ETH), CH-8902 Zürich, Switzerland*

## Abstract

Modern flood protection projects are often combined with measures for river restoration, which enlarge the river bed to improve the flow capacity during peak discharge. For the planning of such projects it is essential to quantify the river–groundwater exchange. To address this question in the highly regulated upper Rhone River basin, a combination of stable isotope techniques with geochemical and transient tracers has been used. The $\delta^{18}O$ signal in precipitation decreases towards more negative values with a slope of 0.34‰ per 100 m altitude, precipitation during winter was about 5.5‰ more negative than in summer. Since in winter about 55% of the water in the River Rhone comes from high alpine hydropower reservoirs with a known $\delta^{18}O$ value, this isotopic signature provides direct information of the source region and the seasonality in samples from groundwater wells. On a spatial scale $SO_4^{2-}$ measurements help to constrain groundwater components, because the tributaries and groundwater sources south of the Rhone are rich in $SO_4^{2-}$ with concentrations of more than 12 mM in spring water. In winter the Rhone water reaches concentrations of up to 1.5 mM, and during snowmelt in summer, this value drops below 0.5 mM. Finally the transient tracer $^3H/^3He$ is used to estimate groundwater inflow in deep gravel pits and to calculate an average travel velocity in the alluvial aquifer of about 1.7 km $a^{-1}$.


## 1. Introduction

Alpine rivers are in the midst of a major transition. Over the last two centuries most river systems in Central Europe have been regulated to improve flood protection. About 50 a ago, large hydropower schemes were developed in the Alps, Scandinavia, the Pacific Northwest and in other mountain regions, which strongly modified the hydrological regimes (Johnson et al., 2001; Gleick, 2003; Bratrich et al., 2004). Today, the signs that global warming affects the water storage capacity of mountain glaciers (Haeberli et al., 1999), the seasonal precipitation patterns (Schmidli et al., 2002) and the frequency of extreme events (Frei and Schär, 2001) demand a re-evaluation of flood protection designs. In addition, the environmental impacts of hydropower use have received intense public attention.

* Corresponding author. Fax: +41 41 349 2168.
*E-mail address:* markus.fette@eawag.ch (M. Fette).

0883-2927/$ - see front matter 
doi:10.1016/j.apgeochem.2004.11.006

As a consequence, the upgrading and renewal of flood protection dykes in the lowlands is now often combined with river restoration projects, which should allow for a more natural morphology and provide habitats for riparian ecosystems (Naiman et al., 1992). Because river restoration often involves removing or dislocating dams and dykes, the planning and design of such projects under the boundary conditions of both flood protection and hydropower schemes should be based on a detailed knowledge of river–groundwater interactions. In this work, the authors test and apply a combination of different tracer methods to track river–groundwater interactions in the canalized Rhone River receiving the outflow of several large hydropower reservoirs.

Located in the central Alps of south-western Switzerland, the Rhone River originates from the Rhone glacier at an altitude of 1763 m above sea level (ASL) and drains the catchment of the Canton Valais into Lake Geneva. The basin area is 5220 $km^2$ and consists of 38% rocks and glaciers, 46% forest and pasture and 16% agricultural land. Seasonal discharge in the Rhone River is controlled by upstream glaciers with low flows during the winter and high flows starting in May and ending with the high altitude freeze in October (Loizeau and Dominik, 2000).

Valais is ideally suited for the operation of hydroelectric power plants due to its topographical characteristics. Over the last century, several large projects were realized, among them is the largest hydroelectric power plant in Switzerland, Cleuson-Dixence with a reservoir volume of 0.4 $km^3$ and a total annual energy production of 2100 GW h. At present, the major Valais reservoirs can hold about 1.2 $km^3$ of water in total, which represents about 20% of the total annual river flow. When hydropower operation started in the 1950s, the winter discharge increased drastically, with average values ranging between 50 and 60 $m^3 s^{-1}$ before 1950 and reaching 120 $m^3 s^{-1}$ in the 1980s (Loizeau and Dominik, 2000). On average, about 55% of the total discharge in winter is due to the hydropower plants. In summer, 78% of the average discharge of 300 $m^3 s^{-1}$ comes from natural sources with the hydropower plants adding the remaining 22% (Loizeau and Dominik, 2000).

Water from high alpine catchments from altitudes of more than 4000 m ASL down to about 1700 m ASL is collected in centralized reservoirs. The tributaries and aquifers discharging to the main river in the lowland are mainly fed by precipitation below the hydropower reservoirs. This creates two separated hydrological cycles.

During the winter months, most of the reservoir water is released by the hydropower plants. This significantly increases the winter discharge of the Rhone River. The storage of the discharge from high-altitude catchments leads to a reduced summer runoff of the Rhone and to a decrease in the number and intensity of flood events, favouring clogging tendencies of the river bed.

After a dramatic flood in 1860, the Rhone River was regulated with dykes for flood protection along the whole valley floor. During the first (1863–1928) and the second (1930–1960) phases of regulation of the Rhone, the main river reaches were canalized. More recent catastrophic floods, such as in October 2000, revealed the risk of future levee breaches and hence triggered the planning of a third correction phase. The engineers of the "Third Rhone River Regulation" emphasize integrated planning, considering not only economic, social and political aspects, but also explicitly including ecological demands (Canton du Valais, 2000). In contrast to the past efforts, the new project aims to enlarge the narrow river corridor, giving the river more space. Due to the infrastructural pressure in the floodplain, however, these enlargements will also be surrounded by levee structures for flood protection.

For the "Third Rhone River Regulation" it is important to analyze and quantify the exchange between the Rhone and the adjacent groundwater. Due to flood protection measures, partial clogging of the river bed and a network of drainage channels in the floodplain, the groundwater level is much lower than the average Rhone level (Canton du Valais, 1996). The planned river enlargement could therefore lead to a significant increase of the groundwater level potentially endangering buildings and infrastructure, as well as the quality of drinking water in pumping stations located near the river.

This paper reports the results of an interdisciplinary study to qualitatively trace the water masses of the artificial high - altitude hydrological cycle from the reservoir to the river and further into the groundwater. The alpine environment as well as the geological situation in the Rhone valley is well suited for applying a combination of stable isotope analysis with geochemical measurements ($SO_4^{2-}$) and transient tracer techniques ($^3H/^3He$) to address the following questions:

(1) Can the seasonality of $\delta^{18}O$ and $SO_4^{2-}$ concentration in the Rhone River be used to separate the hydrological cycles above and below 1700 m ASL?
(2) Can lateral groundwater sources be identified and river–groundwater exchange in the alluvial aquifer be quantified?

The approach should support further risk assessments of changing river–groundwater interactions during restoration projects in heavily regulated Alpine river systems with hydropower schemes.

## 2. Methods and study site

The investigation is based on sampling of precipitation, spring water, surface water and groundwater from

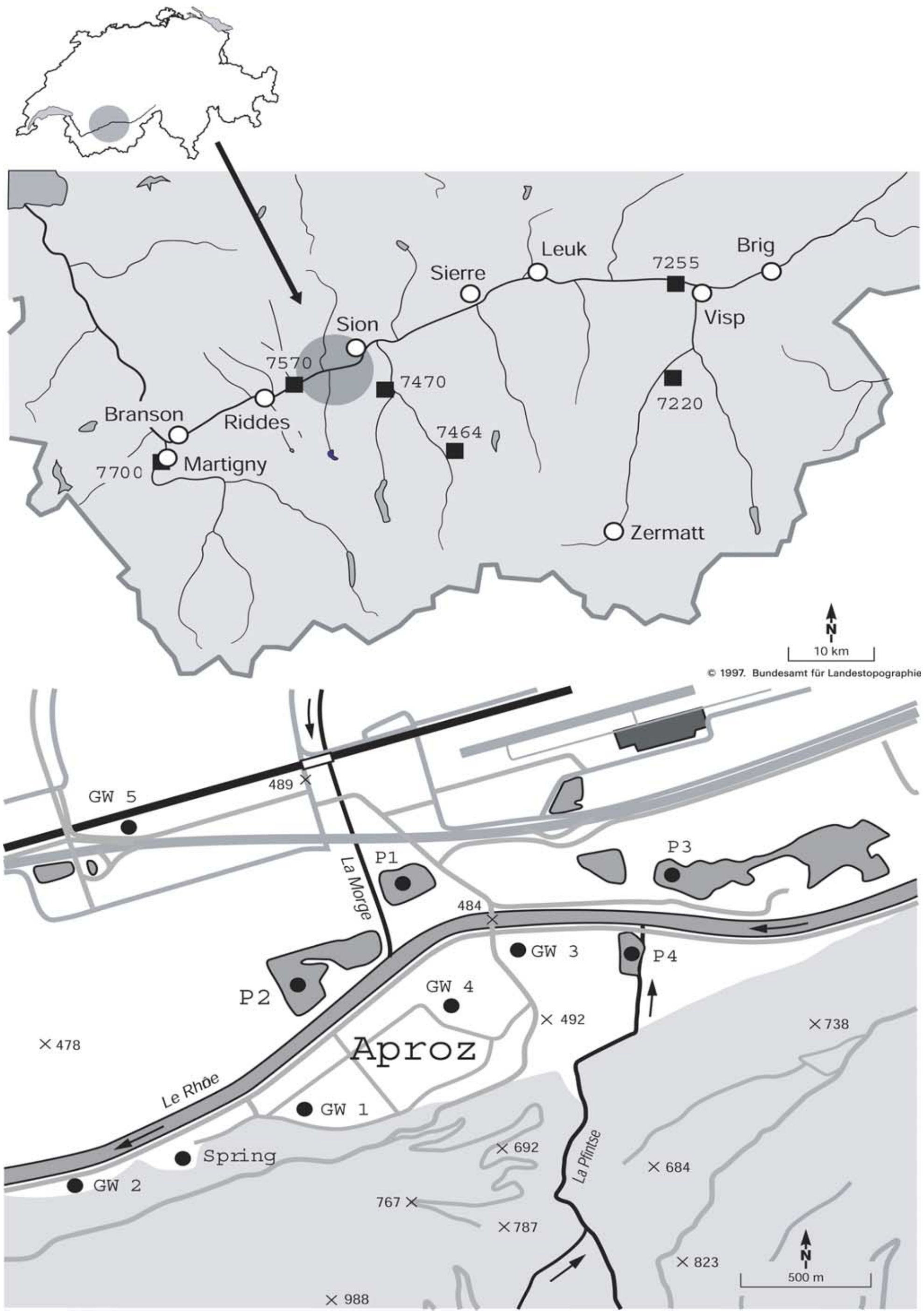


Fig. 1. Area of investigation between the towns of Sion and Martigny in the Canton Valais (Switzerland). The rain gauges were located at different altitudes: 471 m (Martigny, SMA No. 7700), 640 m (Visp, SMA No. 7255), 737 m (Fey, SMA No. 7570), 1260 m (Hérémence, SMA No.7470), 1617 m (Grächen, SMA No.7220), 1825 m (Evolène, SMA No. 7454).

2001 to 2003. These campaigns combined isotopic tracers ($\delta^{18}O$, $\delta D$, $^{3}H/^{3}He$) with standard geochemical parameters (e.g., $SO_4^{2-}$, $Cl^-$, specific conductance).

Data for the Local Meteoric Water Line (LMWL) were collected monthly between February 2002 and 2003. In collaboration with the Meteorological Survey

of Switzerland (SMA), composite samples representing monthly averages were collected, using standard rain gauges according to specifications of the World Meteorological Organization (WMO). The rain gauges were located at different altitudes: 471 m (Martigny), 640 m (Visp), 737 m (Fey), 1260 m (Hérémence), 1617 m (Grächen), 1825 m (Evolène) – all on the southern mountain range of the Rhone valley. The rain samples, stored in polyethylene (PE) bottles and cooled to 4 °C were analyzed for $\delta^{18}O$ and $\delta D$. Isotopic compositions at higher altitudes were calculated from extrapolation of the LMWL to the respective altitude.

Surface water was collected in July 2001 and December 2001, surface water and groundwater in April 2002, August 2002, April 2003 and May 2003. Groundwater was pumped from 2'' and 4'' bores with a submersible groundwater pump (Grundfos MP1). A pumping time equivalent to the displacement of 3 borehole volumes resulted in a constant value for specific conductance.

Samples were analyzed at the EAWAG Kastanienbaum for $^{18}O/^{16}O$ and $^{2}H/H$ ratios by a Micromass Isoprime isotope ratio mass spectrometer (IRMS) in continuous flow mode. The $\delta^{18}O$ and $\delta D$ isotope compositions of the water samples are conventionally expressed as a permil deviation from Vienna Standard Mean Ocean Water (VSMOW). The overall analytical errors are 0.2‰ and 2‰ for $\delta^{18}O$ and $\delta D$, respectively. Prior to analysis, the samples were equilibrated with a $CO_2$–He and $H_2$–He mixture, respectively, at 40 °C for at least 12 h. Anions ($Cl^-$, $SO_4^{2-}$) were analyzed by means of a Metrohm ion chromatograph, model 761. The detection limit was 5.0 mg/L for $SO_4^{2-}$ and 0.5 mg/L for $Cl^-$.

For the determination of water ages younger than 50 a, the $^{3}H/^{3}He$ dating method offers a direct measure for the time since groundwater had its last gas exchange with the atmosphere and provides quantitative groundwater residence times (Beyerle et al., 1999). The mass spectrometric measurements of $^{3}H/^{3}He$ were performed at ETH Zürich according to analytical protocols described by Beyerle et al. (2000). All analyzed water samples were corrected for excess air being determined by the analysis of all atmospheric noble gases (Aeschbach-Hertig et al., 1999).

To investigate the water exchange between the river and the groundwater, the research focuses on the Rhone River between Sion and Martigny as well as on a region about 5 km downstream of Sion (Fig. 1).

The mountains north of this river reach consist of sedimentary rocks of the Helvetic Nappes, mainly formed of limestone (GéoVal, 1986). South of the river the Penninic Nappes with limestone and schistose marls prevail. The Triassic "Zone Houillère" at the bases of the Penninic Nappes contains anhydrite, gypsum, and dolomite. This formation is impermeable and has a draining effect. It crops out SW of the village of Aproz, feeding mineral sources and springs with $SO_4^{2-}$-rich water (Cadisch, 1953; Labhart, 2001; GéoVal, 1986). Hence, $SO_4^{2-}$-rich groundwater is expected to provide an excellent geochemical tracer for water influx from the southern mountain range.

The floodplain of the valley floor is filled with alluvial sand and gravel housing the main unconfined aquifer. Laterally, it extends over the whole valley floor up to the rising edges of the rocky valley sides. The base of the aquifer lies at approximately 30–35 m where fluvio-lacustrine deposits occur. Different pumping test in this area showed a hydraulic conductivity between $1.4 \times 10^{-2}$ and $1.5 \times 10^{-4}$ m s$^{-1}$ (GéoVal, 1986) yielding porosities up to 30% (Hölting, 1996). Together with the hydraulic gradient of around 1‰ in the investigated aquifer (GéoVal, 1986), average flow velocities up to 1.5 km a$^{-1}$ are possible.

In this region, gravel excavation has created several small artificial ponds (Fig. 1). P1 covers around 30,000 m$^2$, with a maximum depth of approximately 30 m and has an estimated volume of around 440,000 m$^3$. P2 is about twice this size and has maximum depth of around 40 m. The ponds have no visible surface inflow or outflow. Both ponds are still in use for gravel production and cut therefore also in the deeper aquifer strata. In addition, observation wells GW1, GW2, GW3, GW4 and GW5, which all reach down to a maximum depth of 10 m were sampled (Table 4).

## 3. Results

### 3.1. Seasonality of isotopic signature in precipitation

A LMWL for the area of investigation was established and the seasonality of isotopic composition of water was studied in the precipitation, the reservoirs and the discharge of the Rhone River (Dansgaard, 1964; Schotterer et al., 2000). Based on the monitoring of the isotopic signature of precipitation at different altitudes, a $\delta^{18}O$/altitude relationship was calculated. Plotting the isotopic signature versus the sampling altitude (Fig. 2) enables determination of the geographical altitude of origin of the water sample (Siegenthaler and Oeschger, 1980).

The mathematical regression of the LMWL data for the upper Rhone valley, defined by the least-squares fit of precipitation data ($\delta D = 7.58\,\delta^{18}O + 5.2$), matches very closely the local meteoric water line for Northern Switzerland: $\delta D = 7.55\,\delta^{18}O + 4.8$ (Pearson et al., 1991). In addition to this altitude effect, the $\delta^{18}O$ and $\delta D$ values of precipitation are also controlled by temperature, humidity and water vapor. Because of the higher temperature difference in winter between the source of air–vapour and the area of precipitation, more water vapour can be removed from the air masses on their trajectory, making the high alpine precipitation isotopically

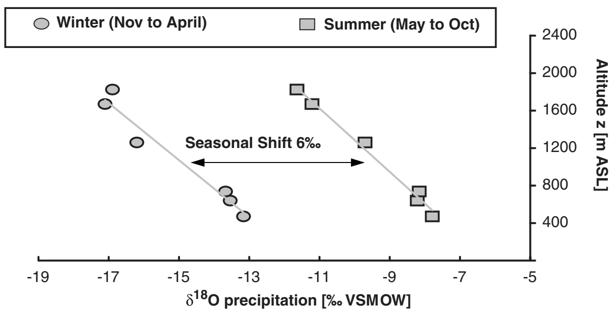


Fig. 2. Relation between altitude and $\delta^{18}O$ in precipitation in the hydrological summer from May to October ($z = -297.95 * \delta^{18}O - 3406.1$, $r^2 = 0.9502$) and in the hydrological winter from November to April ($z = -285.33 * \delta^{18}O - 1648.2$, $r^2 = 0.669$). The seasonal shift is up to 6‰.

depleted in D and $^{18}O$ in winter (Kendall and Coplen, 2001; Schotterer et al., 2000). This means that in general, the $\delta$ values are higher in summer and lower in winter.

Averaging surface water samples from different seasons might lead to erroneous altitude estimates because doing so neglects the seasonal variations in the stable isotope compositions. The average seasonal variation in Switzerland reaches up to 4‰–6‰(Schotterer et al., 2000). In the present case, a variation in $\delta^{18}O$ of precipitation up to 6‰ between summer and winter was observed (Fig. 2).

### 3.2. Seasonality in river water

The stable isotope information in precipitation should also be seen in the receiving river. To assess the seasonal changes of the isotopic composition, the Rhone River and its tributaries were sampled during a 48 h period in July 2001 and again in December 2001. The data in Fig. 3 compare the river signature for $SO_4^{2-}$ and $\delta^{18}O$ in July and December at the hydrometric stations of Sion and Branson. There is a distance of about 25 km between the two hydrometric stations, with two of the most powerful hydropower plants of Switzerland discharging within this area. The $\delta^{18}O$ winter values in the river (−13.3‰to −14.2‰) are larger than in summer (−15.2‰ to −14.4‰), with variations in $\delta^{18}O$ of up to 0.8‰. The most depleted $\delta^{18}O$ value is slightly more negative than the average $\delta^{18}O$ values measured in August 2002 in the two large reservoirs in the high alpine region (Grande Dixence and Mauvoisin: $\delta^{18}O = -14.9$‰). This means that the seasonality in the river water (more negative values in summer than in winter) is reversed in comparison to the seasonality in precipitation (more negative in winter than in summer).

Plotting the summer and winter $SO_4^{2-}$ concentration against the sampling time in Fig. 4 shows that the

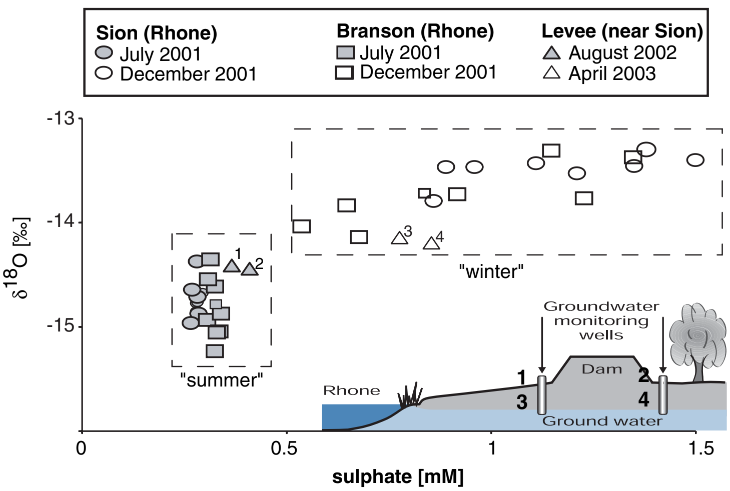


Fig. 3. Seasonal geochemical variation of the Rhone River near Sion and Branson during a 48 h sampling campaign in July and December 2001. July and December values cover distinct fields. The inset shows schematically the dyke structure. The numbers in the main graph and the inset indicate the distance of the wells to the Rhone River and the period of time of sampling.

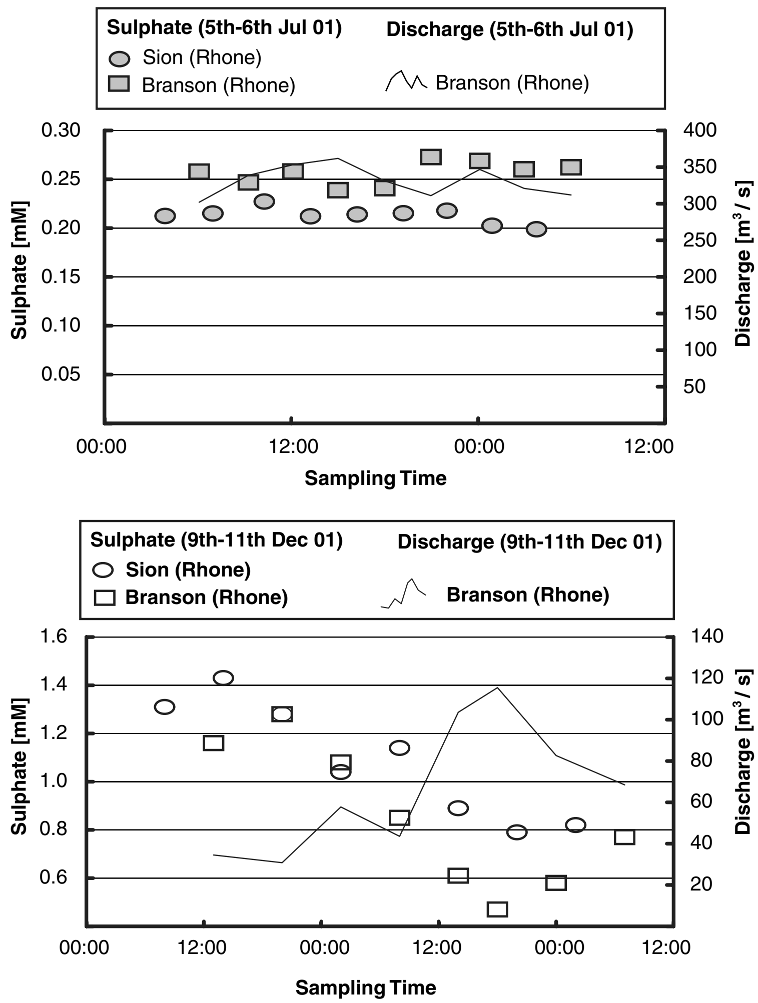


Fig. 4. Evolution of $SO_4^{2-}$ concentration over time in the Rhone in summer (top) and in winter (bottom) in comparison to the low mineralized discharge of the hydropower plants. Dilution effects can be observed especially in the winter readings, showing a decrease in $SO_4^{2-}$ concentration with increasing Rhone discharge due to the influence of the hydropower plants.

Table 1
$\delta^{18}O$ signature in the reservoirs Grande Dixence and Mauvoisin

| | July 2001 $\delta^{18}O$ (‰) | August 2002 $\delta^{18}O$ (‰) | November 2001 | | December 2001 $\delta^{18}O$ (‰) |
|---|---|---|---|---|---|
| | | | $\delta^{18}O$ (‰) | $SO_4^{2-}$ (mM) | |
| Grande Dixence 2365m ASL | −15.1 | −15.0 | −14.3 | 0.084 | −14.3 |
| Mauvoisin 1975m ASL | −15.4 | −14.8 | −14.0 | 0.072 | −13.8 |
| AVERAGE | −15.3 | −14.9 | −14.2 | 0.078 | −14.1 |

Sampling in July 01 and December 01 was done in the valley outflow of the power plants whereas in August 2002 and November 2001 the sampling was done directly in the reservoirs. $SO_4^{2-}$ concentrations were only measured in November 2001.

discharge of the hydropower plants, characterized by an overall very low mineralization (Table 1), dilutes the $SO_4^{2-}$ concentration in winter, but has only a marginal effect during melt water discharge in summer. This provides the possibility of assessing the river–groundwater interactions in more detail.

### *3.3. River–groundwater interactions*

Most of the groundwater wells and gravel ponds sampled during the campaigns follow the LMWL quite closely. Only P3 shows clear signs of evaporative loss and was therefore excluded from further analysis (Fig.

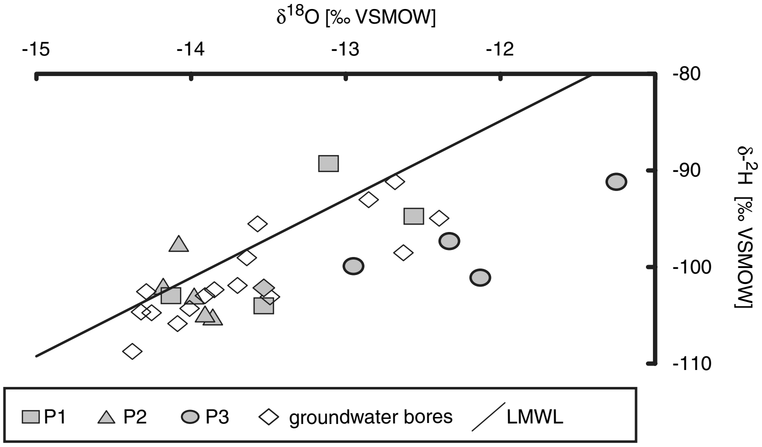


Fig. 5. Local meteoric water line (LMWL) for the upper Rhone valley compared to sampling results in groundwater wells and gravel ponds. The well samples and P1 and P2 scatter slightly below the LMWL. The data from P3 are characterized by a smaller slope giving a strong indication of evaporation.

5). In the following, the authors first analyze the possible groundwater contribution based on the time-series in the Rhone River, and then document the $\delta^{18}O$ and $SO_4^{2-}$ data in the network of groundwater wells (Fig. 1).

The river water in comparison to the groundwater is virtually devoid of $SO_4^{2-}$. For that reason, the seasonality of the $SO_4^{2-}$ signal can be used to obtain qualitative and quantitative information about the diffuse exfiltration of aquifer water in the river and the discharge of the channels draining the alluvial floodplain. The $SO_4^{2-}$ concentration in the Rhone in winter is in general higher upstream (Sion) than downstream (Branson), producing a strong $SO_4^{2-}$ ion gradient between 0.5 and 1.5 mM. In summer, the $SO_4^{2-}$ concentration is significantly lower at a nearly constant value around 0.3 mM and with slightly higher $SO_4^{2-}$ concentration downstream than upstream.

The clear seasonality in $SO_4^{2-}$ concentrations is caused by an augmented $SO_4^{2-}$ load during winter by the drainage of $SO_4^{2-}$ rich ground water from the floodplain. The strong ion gradient can be interpreted as dilution of river water by $SO_4^{2-}$-poor outflow from hydropower plants (Fig. 4). Groundwater drainage can be estimated by comparing the $SO_4^{2-}$ flux at the upstream (Sion) and downstream Branson stations: the $SO_4^{2-}$ flux increases between the two stations from 64 to 85 mol $s^{-1}$ during summer and from 41 to 52 moles $s^{-1}$ during winter. The increase in winter $SO_4^{2-}$ flux is due to the tributaries (1.8 mol $s^{-1}$), drainage channels (1.9 mol $s^{-1}$), hydropower plants (2.0 mol $s^{-1}$) and exfiltrating groundwater which can be calculated as 7.3 mol $s^{-1}$. This means that 51% of the increase in winter $SO_4^{2-}$ flux must be due to diffuse exfiltration from the aquifer to the river.

The seasonality of geochemistry can also be detected in the groundwater samples from wells within the dam structure (Fig. 3, inset). The samples taken in April 2003 exhibit the winter signature of the river whereas the levee samples taken in August 2002 follow the summer signature. While the stable isotope signature of the groundwater is similar in winter and in summer, the well further away from the Rhone river (samples 2 and 4) shows higher $SO_4^{2-}$ concentrations than the well right next to the river (samples 1 and 3). These observations provide first qualitative evidence for the infiltration of river water to the floodplain via the levee structures.

In Fig. 6, the $SO_4^{2-}$ concentration is plotted against $\delta^{18}O$. The waters can be interpreted as mixtures of 3 distinct geochemical end-members or water components. The first component is represented by spring water, originating from the "Zone Houillère". This highly mineralized water is characterized by a very high $SO_4^{2-}$ content (≈12.5 mM) and an isotopic signature of $\delta^{18}O = -13.7‰$. The water is exploited for production of mineral water and commercialized under the brand name "Aproz". It is known for its high mineralization due to the high $SO_4^{2-}$ content.

GW1 is directly influenced by water of the same origin as the spring. This well is located in the southern floodplain just at the outcrop of the Zone Houillère. The high $SO_4^{2-}$ concentration in May decreases in August, indicating a dilution effect with infiltrating Rhone water during the high flow season.

The second end-member is represented by the groundwater in wells GW2, GW3 and GW4, which are influenced by the Rhone River and characterized by low $SO_4^{2-}$ concentrations and $\delta^{18}O$ signatures varying between $-13.5‰$ and $-14.4‰$. These wells seem to be only influenced to a minor extent by $SO_4^{2-}$-rich mountain water, as the isotopic compositions of these groundwaters coincide with the River Rhone and are

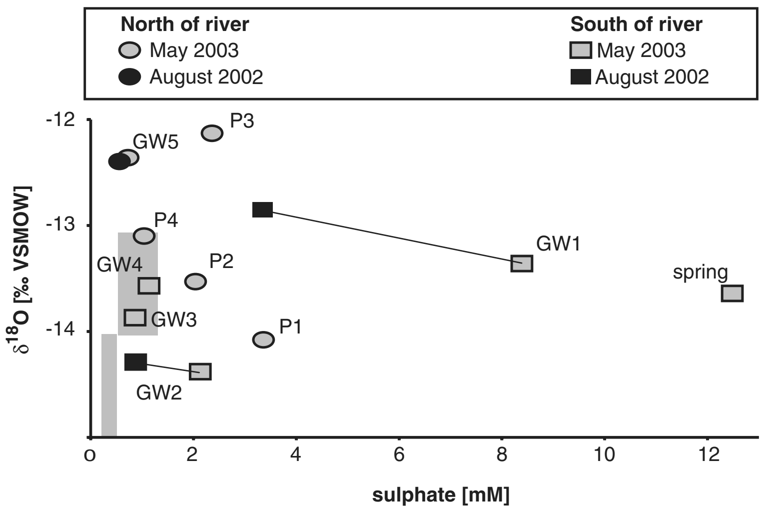


Fig. 6. $\delta^{18}O$ and $SO_4^{2-}$ concentration from selected groundwater samples (GW) and in gravel ponds (P). The grey area represents the range of values of the Rhone River in summer and in winter (compare Fig. 3). The waters can be interpreted as mixtures of 3 distinct geochemical end-members: (1) spring, (2) GW5 and (3) Rhone (see text).

characterized by low $SO_4^{2-}$ concentrations (Fig. 6). The August reading of GW1 and GW2 shows an especially strong influence of Rhone water.

The third end-member is represented by GW5 and is characterized by low $SO_4^{2-}$ concentrations and $^{18}O$-enriched $\delta^{18}O$ values that are characteristic for mountain water originating from the northern slope of the Valais valley.

## 4. Discussion

### 4.1. Seasonality of tracer signals

The catchments of the hydropower schemes reach down to altitudes of about 1700 m ASL. This "border" separates the high altitude water from the undisturbed drainage basins.

The discharge of glaciated basins shows distinctive annual variation, since water is stored as snow in winter and released by melting in early summer (Klok et al., 2001) and precipitation is dominated by rainfall in late summer and autumn. During the snow melt period, the $\delta^{18}O$ signature of melt water becomes enriched in $^{18}O$ until the snow-pack is completely melted. Taylor et al. (2001) showed that the isotopic change during a melting event is typically 3 to 5‰. This seasonal trend can also be followed in the isotopic signature of Grande Dixence and Mauvoisin (Table 1). The average isotopic signature in the reservoirs increases on average from −15.3‰ in July to −14.1‰ in December.

In the valley floor, the $\delta^{18}O$ of the Rhone River tends to follow the seasonality of the reservoirs (Fig. 3, Table 1), but river water is more enriched in $\delta^{18}O$. Evaporation can be excluded as the cause of enrichment, because Rhone water samples from August 2002 plot nearly perfectly on the LMWL. Rozanski et al. (2001) report that the O and H isotopic composition of most of the world rivers were close to the LMWL indicating that evaporative fractionation of $\delta^{18}O$ of riverine water can usually be neglected.

Based on the known hydropower release rates, the isotopic signature of the "natural" component (N) in the river can be estimated, using the observed variation in $\delta^{18}O$. The isotopically more positive signature of the Rhone water (R) in comparison to the water in the reservoirs (H) reflects the contribution of the "natural" components (groundwater and surface runoff) of the river water. July water from the reservoirs contributes 22% to the total discharge of the Rhone with $\delta^{18}O_{\text{H-July}} = -15.3‰$ (Table 1), whereas the water in the Rhone shows an isotopic signature of $\delta^{18}O_{\text{R-July}} = -14.8‰$. The remaining 78% of the total discharge is of "natural" origin with an unknown isotopic signature (Loizeau and Dominik, 2000).

A simple mass balance for $\delta^{18}O$ reveals the isotopic composition of this "natural" component of the river water $\delta^{18}O_{\text{N-July}}$

$$\delta^{18}O_{\text{N-July}} = \frac{\delta^{18}O_{\text{R-July}} - (0.22 \cdot \delta^{18}O_{\text{H-July}})}{0.78} = -14.7‰.$$

In winter, a similar calculation (55% of discharge in the Rhone River from the hydropower plants, 45% of "natural" origin) yields a stable isotope composition for the natural component of $\delta^{18}O_{\text{N-December}} = -13.2‰$ (Table 1).

Table 2
Equations for calculation of altitudes of water origin in the Rhone River catchment during the two hydrological seasons

| | Equation ($^{18}$O) | $\delta^{18}$O-range (‰) |
|---|---|---|
| Hydrological year 2001–2002 | $z = -311.67 \times -2906.5$ | – |
| Hydrological winter November to April | $z = -297.95 \times -3406.1$ | −15.24 to −14.36 mean ≈ −14.8 |
| Hydrological summer May to October | $z = -285.33 \times -1648.2$ | −14.15 to −13.25 mean ≈ −13.7 |

$z$ = altitude (m ASL), $x = \delta^{18}$O (‰). See text for explanation. Measured $\delta^{18}$O data from Fig. 2.

### 4.2. $\delta^{18}O$ as a tracer for the altitude of water origin

The average altitude of origin of the discharge water can be estimated from the $\delta^{18}$O-altitude relationship (Fig. 2 and Table 2). Due to the extrapolation above the calibrated altitude range, it is not possible to obtain reliable altitude calculations for the water stored in the large reservoirs. The quantitative relation between precipitation and accumulated reservoir water is quite complex. Enrichment of the snow-pack by evaporation and snow–atmosphere exchange produces a mean isotope content of the melt water, which is normally higher than that of the original precipitation (Kendall and McDonnell, 1998). As a consequence, the average $\delta^{18}$O in the hydropower reservoirs Grande Dixence and Mauvoisin (Table 1) is more positive than expected for the average altitude of their catchments, which is around 3000 m ASL.

Two pathways from precipitation to groundwater discharge should be considered: One part of the precipitation falling below the lower limit of the reservoir catchments drains directly to the stream by tributaries. A large fraction of the water, however, is retained in soils and aquifers and slowly percolates towards the valley ground. Thus, while snowmelt is clearly responsible for a drastic increase in the volumetric discharge in spring, less than half of that melt water runs off directly to the river in the valley and the remaining infiltrates and forces previously stored groundwater to discharge (Martinec et al., 1982). This piston effect is responsible for the seasonal change of $\delta^{18}$O of the natural component of the Rhone water. This means that the more positive $\delta^{18}$O values of summer precipitation appear as the natural component in the river in winter (Schotterer et al., 2000), whereas the more negative isotopic composition of the winter precipitation arrives with the snowmelt in the summer months (Fig. 3).

The seasonally varying recharge altitudes of the "natural component" of the water in the Rhone River can be determined. This leads to a calculated recharge altitude for the natural summer discharge ($\delta^{18}O_{N\text{-July}} = -14.7$‰) in the Rhone of 1675 m ASL and for the natural winter discharge ($\delta_{18}O_{N\text{-December}} = -13.2$‰) of 1208 m ASL. The estimated altitude range corresponds very well with the concept of two separated hydrological water sources, one above and one below the main hydropower reservoirs. The difference between winter and summer is related to the fact that the higher snowline in summer increases the altitude from where surface runoff is possible.

### 4.3. Identification of lateral groundwater sources in the alluvial floodplain

To test the hypothesis of an important groundwater contribution in the natural runoff of the Rhone, 5 groundwater wells in the area SW of Sion were sampled in April 2002, August 2002, April and May 2003. The chemical composition of the groundwater wells is summarized in Fig. 6.

GW1 is located in the valley floor south of the Rhone and is strongly influenced by lateral inflow from $SO_4^{2-}$-rich water drained and mineralized by the "Zone Houillère". Only during high Rhone water levels in August were the $SO_4^{2-}$ contents in this well significantly diluted by low mineralized Rhone water.

GW2 is located outside of the levee structure of the Rhone on the southern border of the river and at the edge of the mountain slope. Geographically it is comparable to GW1, but the chemical signature differs significantly. In April, during the low water season, this well is affected by water with a high $SO_4^{2-}$ concentration – but to a much lower extent than GW1. In August, during high water levels of the Rhone, GW1 is significantly affected by admixing of riverine water.

Groundwater wells GW3 and GW4 are also strongly affected by Rhone water during the low water season in winter. These are plotted in the grey area in Fig. 6 and show little geochemical evidence for sources other than the Rhone.

The observed evolution of the groundwater chemistry is conceptually easy to understand in terms of mixing. GW1 is located directly in the middle of the high mineralized water originating from the "Zone Houillère". The location of GW2, GW3 and GW4 is geometrically sheltered from the direct influence of the $SO_4^{2-}$ rich hang water and therefore more influenced by the Rhone River. This is shown by a very constant $SO_4^{2-}$ and $\delta^{18}$O composition. Regardless of the high or low water season, GW5 seems neither affected by the Rhone River nor by the $SO_4^{2-}$ plume of the water originating from the "Zone Houillère" and hence seems to represent a different geochemical component defining the groundwater on the northern side of the Rhone valley.

Table 3
Water ages determined by $^{3}H$–$^{3}He$ dating allows determination of the average flow velocity within the valley aquifer

| Sampling well | Distance from P1 (km) | Water age (a) | GW-flow velocity ($km\ a^{-1}$) |
|---|---|---|---|
| P1 | 0 | ~3 | 2.3 |
| North-East Riddes | ~4.5 | ~5 | 1.1 |
| North-East Branson | ~15.7 | ~15 | |

The comparison of the different wells reveals a rather heterogeneous aquifer that can be geochemically separated into zones with infiltration of river water over short distances and input from the lateral slopes. Close to the river, the groundwater in the valley floor is diluted with low mineralized riverine water during high discharge in summer.

With a depth of around 30 and 40 m, respectively, the ponds integrate over the whole depth of the aquifer, whereas the shallow wells (<10 m depth) receive the water of the uppermost level of the aquifer. The deeper part of the aquifer is less affected by the input of river water and hence river driven dilution effects are of minor importance in the ponds. P1 and P2 are located between the Rhone and the northern mountain slope. On the $SO_4^{2-}/\delta^{18}O$ graph, the values from the ponds can be interpreted as a binary mixture of riverine water and $SO_4^{2-}$-rich "spring" water from the southern mountain slope (Fig. 1). The pronounced high $SO_4^{2-}$ concentrations especially indicate significant water input from the south and give direct evidence that groundwater has to flow under the river in order to find its way into the ponds.

Temperature and conductivity profiles as well as groundwater age ($^{3}H$–$^{3}He$ method, Beyerle et al., 2000) were obtained in P1 in April 2003 and May 2003. Concentration–temperature–depth (CTD)-profiles of physical properties of the water column show the onset of stratification in temperature as well as in specific conductance. In April, the temperature in the deep water body at 30 m was 8.4 °C. Within the following 30 days, the deep water body warmed up about 3 °C to reach finally 11.5 °C. Such dramatic increase of deep water temperature of a stratified water column is very unusual and cannot be caused by solar radiation as a simple calculation with Bears law, taken from Cole and Buchak (1995) shows: in 5 m (depth of the metalimnion of the water column in the gravel pond), the initial estimated solar radiation of 1000 $kW\,h\,(m^2\,a)^{-1}$ at the surface is reduced by extinction to ~220 $kW\,h\,(m^2\,a)^{-1}$ at 5 m depth. Dividing this remaining warming energy by the heat capacity of water (4.1 $kJ\,(kg\,K)^{-1}$) and applying that on the remaining 25 m of the epilimnion of the water column leads to a maximum possible theoretical increase in temperature of ~0.6 °C within a 30 day period. Also it has to be noted that the stability of the water column would strongly increase due to heating of the surface water causing a further reduction of warming of the deep water below the thermocline. The rapid temperature increase in the stratified deep water therefore points to a high groundwater exchange.

### *4.4. What is the longitudinal travel velocity of the groundwater?*

The change in $^{3}H$–$^{3}He$ in the deep water of P1 provides a second, independent argument of the rapid exchange of the deep water. In April, after the maximum extent of winter mixing, the pond water has already remarkably high water ages (1.3 a). The starting stratification in the lake prevents He from degassing out of the water body. Inflow of groundwater to the pond, which already has a significant residence time underground, increases the water age in the lake by about 3 a in a very short time. The only explanation is a complete exchange of water in the lake.

The isotopic analyses confirm that the gravel ponds are part of the flowing groundwater. Fig. 5 shows that the sampling values of P1 and P2 scatter around the LMWL in the same manner. Only P3 shows a lower slope indicating stagnating water affected by evaporation. P3 is no longer used for gravel excavation. The groundwater exchange is slowed down by clogging of the lake bottom by organic and/or inorganic sediments (Yehdegho et al., 1997). In contrast, P1 and P2 are still in use for gravel production that slows down clogging by regularly allowing "flowing" conditions in the ponds.

In a longitudinal sense, $^{3}H$–$^{3}He$ dating allows determining the average flow velocity within the valley aquifer (Table 3). Measurements done between Sion and

Table 4
Tracer data for GW1 to GW5

| | Sulfate (mM) | | $\delta^{18}O$ (‰) | | Distance to river (m) | Depth (m) |
|---|---|---|---|---|---|---|
| | May 03 | August 02 | May 03 | August 02 | | |
| GW1 | 8.39 | 3.34 | −13.36 | −12.85 | 150 | 9.7 |
| GW2 | 2.13 | 0.88 | −14.38 | −14.29 | 30 | 6.5 |
| GW3 | 0.86 | – | −13.87 | – | 35 | 7.2 |
| GW4 | 1.13 | – | −13.57 | – | 125 | 6.1 |
| GW5 | 0.73 | 0.56 | −12.36 | −12.40 | 1000 | 6.2 |

Branson in shallow groundwater bores as well as in the ponds already discussed yield an estimated average flow velocity within the aquifer of between 1.1 and 2.3 km $a^{-1}$ which agrees well with the hydraulic estimates made in the methods section.

## 5. Conclusions

Summarizing all the data, the introductory questions can be answered as follows:

1. Can the seasonality of $\delta^{18}O$ and $SO_4^{2-}$ concentration in the River Rhone be used to separate the hydrological cycles above and below 1700 m ASL?

A local meteoric water line for the area of investigation was established as well as the seasonality of isotopic composition in precipitation, in the reservoirs and in the discharge of the Rhone River. The results show, that $\delta^{18}O$ values in precipitation are higher in summer and more negative in winter. In the present case, a variation in $\delta^{18}O$ of precipitation up to 6‰ between the different seasons was observed. In the receiving river, however, the water is more enriched in $\delta^{18}O$ and its seasonality is reversed in comparison to the precipitation data. The seasonal shift of $\delta^{18}O$ in river water shows here a variation of up to 1.5‰ with more positive $\delta^{18}O$ values in winter than in summer.

The average altitude of origin of the natural component of the discharge water can be estimated from the $\delta^{18}O$-altitude relationship to altitudes between 1675 m ASL (summer) and 1208 m ASL (winter). This altitude range corresponds very well with the concept of two separated hydrological water sources, one above and one below the main hydropower reservoirs.

2. Can we identify lateral groundwater sources and quantify river–groundwater exchange in the alluvial aquifer?

Sulfate-rich groundwater is an excellent geochemical tracer for water influx from the southern mountain range and can be used for identification of lateral groundwater sources in the area of investigation. Low $SO_4^{2-}$ concentrations in sampling station GW3 and GW4 indicate, that the groundwater here is mainly affected by river water. They are characterized by an averaged signature of the Rhone. The deep ground water is chemically affected by inputs from the slopes of the southern mountain ranges and is characterized by high $SO_4^{2-}$ concentrations. Sampling of P1 as well as GW2 shows clear signs of a southern groundwater component which flows under the riverbed. GW5 represents the northern side of the shallow valley aquifer, characterized by significantly more positive delta values and lower $SO_4^{2-}$ concentration, characteristic for the northern slopes. The aquifer seems to be mainly recharged upstream of the test site. This is indicated by the low groundwater ages in the area of investigation. Looking at the continuously increasing water ages towards Branson, a rather large groundwater velocity within the aquifer of 1.7 km $a^{-1}$ can be calculated as an upper limit.

Sulfate flux in the river is a valuable tracer to quantify the river groundwater interaction. Diffuse groundwater drainage can be estimated by comparing the $SO_4^{2-}$ flux at the upstream (Sion) and downstream station (Branson). A simple mass balance shows that 51% of the total increase in $SO_4^{2-}$ flux in the area of investigation must be due to exfiltrating groundwater. River water infiltrating in the aquifer mainly takes place during the summer month.

## Acknowledgements

We thank the following individuals for their help with sampling campaigns and access to existing data: M. Richard (Aproz SA), R. Décorvet (BEG), P. Ornstein (CREALP), M. Brögli, S. Klump, D. McGinnis, M. Schurter (EAWAG), M. Darioli, M.Hagin (EOS), M. Evequoz (Evequoz SA), B. Schädler, R. Kozel, D. Streit (FOWG), O. Ménétrey (Commune Nendaz), B. Bezola, M. Dösegger (SMA), T.Arborino, D. Bérod, A. Vogel (Canton Valais). This work is financially supported by the Rhone-Thur project (www.rhone-thur.eawag.ch).

## References

Aeschbach-Hertig, W., Peeters, F., Beyerle, U., Kipfer, R., 1999. Interpretation of dissolved atmospheric noble gases in natural waters. Water Resour. Res. 35, 2779–2792.

Beyerle, U., Aeschbach-Hertig, W., Hofer, M., Imboden, D.M., Baur, H., Kipfer, R., 1999. Infiltration of river water to a shallow aquifer investigated with $^3H/^3He$, noble gases and CFCs. J. Hydrol. 220, 169–185.

Beyerle, U., Aeschbach-Hertig, W., Imboden, D.M., Baur, H., Graf, T., 2000. A mass spectrometric system for the analysis of noble gases and tritium from water samples. Environ. Sci. Technol. 34, 2042–2050.

Bratrich, C., Jorde, K., Meier, W., Peter, A., Schneider, M., Truffer, B., Wehrli B, 2004. Green Hydropower: a new assessment procedure for river management. River Res. Appl. 20, 1–18.

Cadisch, J., 1953. Geologie der Schweizer Alpen. Wepf & Co Verlag, Basel.

Canton du Valais, 1996. Concept Global de Revalorisation du Rhône Valaisan. Rapport de Synthèse.

Canton du Valais, 2000. Synthesebericht zur 3. Rhonekorrektion.

Cole, T.M., Buchak, E.M., 1995. CE-QUAL-W2: A Two Dimensional, Laterally Averaged, Hydrodynamic and Water Quality Model, Version 2.0, Instruction Report EL-95-, US Army Engineer Waterways Experiment Station, Vicksburg MS.

Dansgaard, W., 1964. Stable isotopes in precipitation. Tellus XVI, 436–468.

Frei, C., Schär, C., 2001. Detection probability of trends in rare events. Theory and application to heavy precipitation in the Alpine region. J. Climate 14, 1568–1584.

GéoVal, 1986. Projet Hydro Rhône. Rapport après 3 ans d'observation. GeoVal No: GEO3/05.

Gleick, P.H., 2003. Global freshwater resources: soft-path solutions for the 21st century. Science 302, 1524–1528.

Haeberli, W., Frauenfelder, R., Hoelzle, M., Maisch, M., 1999. On rates and acceleration trends of global glacier mass changes. Geografiska Annaler: Ser. A, Phys. Geogr. 81, 585–591.

Hölting, B., 1996. Hydrogeologie: Einführung in die allgemeine und angewandte Hydrogeologie. Enke Verlag, Stuttgart.

Johnson, N., Revenga, C., Echeverria, J., 2001. Managing water for people and nature. Science 292, 1071–1072.

Kendall, C., Coplen, B., 2001. Distribution of oxygen-18 and deuterium in river waters across the United States. Hydrol. Proc. 15, 1363–1393.

Kendall, C., McDonnell, J.J. (Eds.), 1998. Isotope Tracers in Catchment Hydrology. Elsevier, Amsterdam.

Klok, E.J., Jasper, K., Roelofsma, K.P., Gurtz, J., Badoux, A., 2001. Distributed hydrological modelling of a heavily glaciated Alpine river basin. Hydrol. Sci. J. 46, 553–570.

Labhart, T., 2001. Geologie der Schweiz. Ott Verlag, Thun.

Loizeau, J.L., Dominik, J., 2000. Evolution of the Upper Rhone river discharge and suspended sediment load during the last 80 years and some implications for Lake Geneva. Aquat. Sci. 62, 54–67.

Martinec, J., Oeschger, H., Schotterer, U., Siegenthaler, U., 1982. Snowmelt and groundwater storage in an Alpine basin. In: Proc. Exeter Symp., July 1982. IAHS Publication, 138.

Naiman, R.J., Beechie, T.J., Benda, L.E., Berg, D.R., Bisson, L.H., MacDonald, L.H., O'Connor, M.D., Olson, P.L., 1992. Fundamental elements of ecologically healthy watersheds in the Pacific Northwest coastal ecoregion. In: Naiman, R.J. (Ed.), Watershed Management: Balancing Sustainability and Environmental Change. Springer, New York, pp. 127–187.

Pearson, F.J., Balderer, W., Loosli, H.H., Lehmann, B.E., Matter, A., Peters, T., Schmassmann, H., Gautschi, A., 1991. Applied isotope hydrogeology – a case study in Northern Switzerland. Nagra Technical Report 88-01.

Rozanski, K., Froehlich, K., Mook, W., Stichler, W., 2001. Volume III: Surface waters. In: NAPC Isotope Hydrology Section. Environmental Isotopes in the Hydrological Cycle. Principles and Applications. Available from: <http://www.iaea.org/programmes/ripc/ih/volumes/volume3.htm> (accessed 04.07.03.).

Schotterer, U., Stocker, T., Bürki, H., Hunziker, J., Kozel, R., Grasso, D.A., Tripet, J.P., 2000. Das Schweizer Isotopenmessnetz – Trends 1992–1999. Gas-Wasser-Abwasser 80, 3–11.

Schmidli, J., Schmutz, C., Frei, C., Wanner, H., Schär, C., 2002. Mesoscale precipitation variability in the Alpine region during the 20th century. Internat. J. Climatol. 22, 1049–1074.

Siegenthaler, U., Oeschger, H., 1980. Correlation of $^{18}O$ in precipitation with temperature and altitude. Nature 285, 314–317.

Taylor, S., Feng, X., Williams, M., McNamara, J., 2001. How isotopic fractionation of snowmelt affects hydrograph separation. In: Conf. Proc. 59th Eastern Snow Conference in Stowe, Vermont.

Yehdegho, B., Rozanski, K., Zojer, H., Stichler, W., 1997. Interaction of dredging lakes with the adjacent groundwater field: an isotopic study. J. Hydrol. 192, 247–270.