

Natural tracers to quantify seasonal variations of groundwater mixing in a complex alluvial aquifer (Pfywald, Switzerland)

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Abstract Dissolved sulphate, oxygen-18, deuterium and tritium have been used to quantify seasonal variations of groundwater mixing in a complex alluvial aquifer in the upper Rhone valley (Pfywald, Wallis, Switzerland). The concentration of these four natural tracers reflects spatial and seasonal chemical variations of the alluvial Rhone aquifer. Further they represent mixing rates between weakly mineralized infiltrated Rhone River water and SO₄-rich water flowing from the south valley side. The δ¹⁸O composition decreases from -14.03‰ at the south valley side to -14.85‰ near the Rhone River and follows the general groundwater flow pattern as well as the observed dissolved sulphate distribution. A positive correlation exists between the δ¹⁸O values and sulphate concentrations and can be represented by a linear regression. A two-component model has been applied to tritium concentrations to calculate groundwater mixing rates during high and low water-level periods.

INTRODUCTION

In the Pfywald area situated east of the town of Sion in the upper Rhone valley southern Switzerland (Fig. 1), the unconfined Rhone alluvial aquifer, composed of superficial glacial outwash deposits, is an important source of groundwater. This heterogeneous aquifer with an average hydraulic conductivity of 10⁻² m s⁻¹ yields large amounts of water suitable for drinking water or agricultural supply, but is also vulnerable to contamination. The alluvial aquifer is subject to numerous environmental impacts: industrial and agricultural activities, gravel pits, dumping sites, roads and a future national highway.

Since April 1996, hydrogeological, hydrochemical and geophysical methods have been applied in order to obtain hydraulic and mass transport parameters in the complex porous aquifer of the Pfywald area (Schürch *et al.*, 2000). At the research site, on a monthly basis, groundwater heads have been measured and various water types sampled for chemical analyses (Schürch & Vuataz, 2000).

METHODOLOGY

For most shallow wells one single sample representing the mean water composition has been collected using a suction pump at a flow rate of 30 l min⁻¹. Major species were analysed by ion chromatography at the GEA laboratory, University of Neuchâtel.

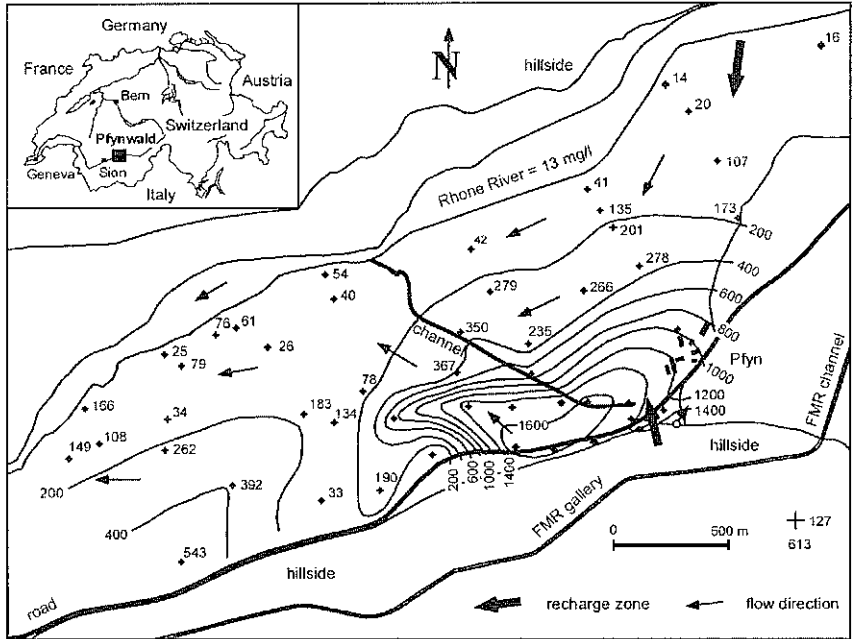


Fig. 1 Distribution map of dissolved sulphate concentrations in mg l^{-1} , groundwater flow direction and recharge zones in August 1996.

Deuterium and oxygen-18 analyses were performed at the Hydroisotop laboratory in Schweitenkirchen, Germany. About 22 samples were analysed for deuterium and oxygen-18 during the high water period of 1996, and 12 monthly values were obtained for three wells, one spring and the Rhone River. The error bar attains $\pm 0.15\text{‰}$ for $\delta^{18}\text{O}$ and $\pm 1.5\text{‰}$ for δD . Finally, the tritium analyses were carried out by the Radioactivity Monitoring Office in Fribourg, Switzerland. The uncertainty of a tritium analysis is one standard deviation.

SPATIAL DISTRIBUTION OF SULPHATE CONTENT

Groundwater recharge of the alluvial Rhone aquifer occurs in two areas during the high water period (Fig. 1). Towards the northeastern limit of the studied area, the aquifer is strongly recharged by weakly mineralized Rhone River water. The second recharge area brings SO_4 -rich groundwater flowing from gypsum, anhydrite and carbonate rocks on the south valley hillside. A computer simulation of the groundwater flow during the high water period of August 1996 indicates that 75% of the aquifer recharge is Rhone River water, and 25% is SO_4 -rich groundwater (Schürch *et al.*, 1999).

Figure 1 shows the spatial variation of the sulphate content in groundwater in August 1996. The observed sulphate content decreases from over 1500 mg l^{-1} , close to the southern valley side, to concentrations of less than 50 mg l^{-1} towards the Rhone River itself. Dissolved sulphate, showing a strong correlation with total groundwater mineralization, is considered as a conservative natural tracer for representing the

mixing processes in the oxygenated environment of the alluvial Rhone aquifer. The SO₄-rich groundwater from the southern valley side flows in different directions into the alluvial aquifer (Fig. 1), before it is directed westward by the strong groundwater flow originating from the Rhone River recharge area in the northeast.

OXYGEN-18 AND DEUTERIUM IN GROUNDWATER

Figure 2 presents the spatial distribution of δ¹⁸O composition in groundwater during a high water period. The observed oxygen-18 content varies between -13.41 and -14.85‰. The δ¹⁸O content decreases from the southern valley side to the Rhone River and follows the general groundwater flow pattern as well as the observed dissolved sulphate distribution visible in Fig. 1.

When the δ¹⁸O values are plotted in relation to deuterium composition, all these isotopic values range between the world meteoric water line ($\delta D(\text{‰}) = 8.2 \times \delta^{18}\text{O}(\text{‰}) + 10.8$; Yurtsever & Gat, 1981) and the line validated for the north and central Switzerland ($\delta D(\text{‰}) = 7.55 \times \delta^{18}\text{O}(\text{‰}) + 4.8$; Kullin & Schmassmann, 1991). The world meteoric water line represents the regression line of continental precipitation samples. Deviations from this line can be interpreted as being caused by precipitation that occurred under different climatic conditions or as changes due to geochemical processes. The isotopic values of the Rhone River mostly follow the north and central Switzerland line, which represents the regression line of precipitation samples mostly from the Swiss Molasse basin.

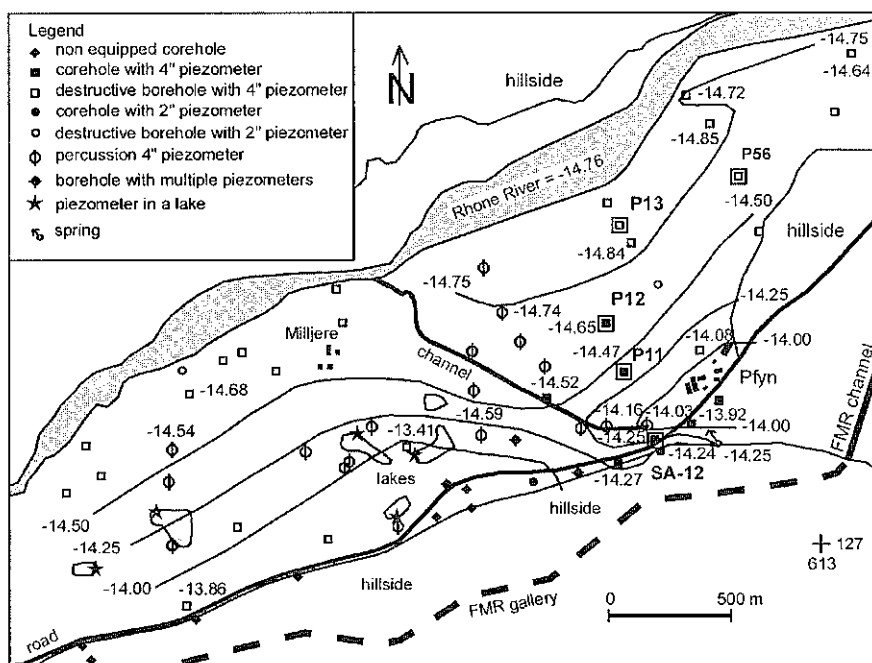


Fig. 2 Distribution map of δ¹⁸O (‰) concentrations in groundwater during the high water period (August 1996). Double squares show the observation points of tritium concentrations presented in Table 1.

SO₄ AND δ¹⁸O RELATIONSHIP

The relationship between the δ¹⁸O values and the sulphate content shows that, during a high water period, the groundwater mostly represents various stages of mixing of SO₄-rich water with the weakly mineralized Rhone River water (Fig. 3). The positive correlation existing between the δ¹⁸O values and the sulphate concentrations can be represented by a regression line with the following equation:

$$\delta^{18}\text{O}(\text{‰}) = 0.0004 \times \text{SO}_4 \text{ (mg l}^{-1}\text{)} - 14.66$$

This equation allows extrapolation of the oxygen isotope value of -13.95‰ for a SO₄-rich fluid containing a maximum of 1781 mg l⁻¹ of sulphate. The high δ¹⁸O value of -13.41‰ situated between the lakes in the southwest of the study area characterizes a local silty-sandy aquifer with a hydraulic conductivity of 10⁻⁴ m s⁻¹ and indicates infiltration from the lakes (Fig. 2). During summer, the lake water undergoes strong evaporation and is enriched in oxygen-18.

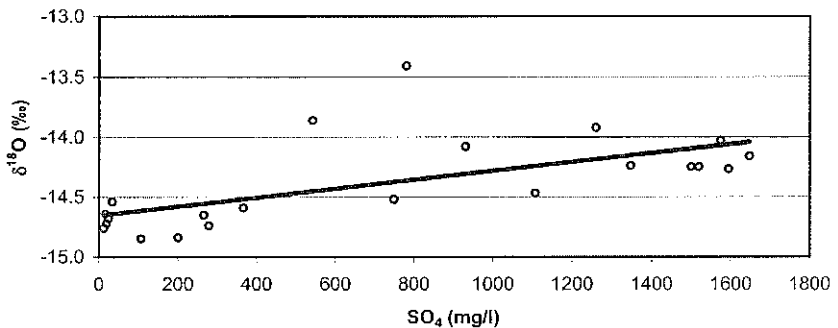


Fig. 3 Relationship between oxygen-18 and dissolved sulphate in groundwater during the high water period (August 1996). The calculated linear regression shows a positive correlation.

SEASONAL VARIATIONS

Temporal changes in groundwater chemistry and groundwater levels reflect seasonal variations of the different groundwater recharge contributions (Schürch & Vuataz, 2000). The seasonal evolution of the stable isotopes confirms the rapid dilution processes of the groundwater by the Rhone River recharge. The groundwater in the alluvial Rhone aquifer follows the isotopic variations of the Rhone River. During the high water period, stable isotopes show an increase of the average recharge elevation (Rhone River basin), which corresponds simultaneously to a decrease of the groundwater mineralization. Temporal variation of the groundwater isotopes is less pronounced than for the Rhone River because of mixing processes. The reaction delay in the aquifer is also longer. The isotopic cycle of the groundwater in the middle of the alluvial Rhone plain is retarded by seven weeks compared to groundwater near the Rhone River.

TRITIUM

Tritium, the unique radioactive hydrogen isotope, allows quantification of the recharge rates of the alluvial Rhone aquifer and of the SO₄-rich water. A two-component model has been applied to calculate groundwater mixing rates for high- and low-water periods (Table 1). This two-component model can only be applied to wells which are entirely located within the alluvial Rhone aquifer. Wells which also penetrate other geological units were not considered, because they often present mixing processes between more than two groundwater components. The uncertainty of a tritium analysis is one standard deviation and therefore the uncertainty in mixing proportions is situated between 20 and 30%.

The mixing proportion of the alluvial Rhone aquifer water increases from the southern valley side to the infiltration zone of the Rhone River in the northeast. Most of the alluvial aquifer is dominated by infiltration of Rhone River water except in its southern part, which is strongly recharged by SO₄-rich water flowing from the southern hillside. Finally, well P56 located near the infiltration zone of the Rhone River in the northeast is dry during low water periods (Fig. 2), because of the marked difference in groundwater levels between high- and low-water conditions (>5 m). The tritium contents of the groundwater show only small seasonal fluctuations in the alluvial Rhone aquifer.

Table 1 Calculated groundwater mixing rates based on tritium concentrations.

Name	Distance from the Rhone River infiltration zone (m)	Tritium (TU)	% alluvial Rhone aquifer	% SO ₄ -rich water
High water period (July 1998)				
P56	510	13.6	100	0
P13	810	12.8	92	8
P12	1250	8.8	54	46
P11	1440	4.8	15	85
SA-12	1660	3.2	0	100
Low water period (February 1998)				
P13	810	13.6	100	0
P12	1250	12.0	82	18
P11	1440	6.4	18	82
SA-12	1660	4.8	0	100

CONCLUSION

Oxygen-18, deuterium and tritium are the only natural tracers for which the tracer transit time is equal to the transit time of the groundwater. The contents of these natural tracers allow determination of the relationships between surface water and groundwater. Further, they reflect groundwater mixing rates.

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