Groundwater components in the alluvial aquifer of the alpine Rhone River valley, Bois de Finges area, Wallis Canton, Switzerland

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Abstract Source, type, and quantity of various components of groundwater, as well as their spatial and temporal variations were determined by different hydrochemical methods in the alluvial aquifer of the upper Rhone River valley, Bois de Finges, Wallis Canton, Switzerland. The methods used are hydrochemical modeling, stable-isotope analysis, and chemical analysis of surface water and groundwater. Sampling during high- and low-water periods determined the spatial distribution of the water chemistry, whereas monthly sampling over three years provided a basis for understanding seasonal variability. The physico-chemical parameters of the groundwater have spatial and seasonal variations. The groundwater chemical composition of the Rhone alluvial aquifer indicates a mixing of weakly mineralized Rhone River water and SO_4-rich water entering from the south side of the valley. Temporal changes in groundwater chemistry and in groundwater levels reflect the seasonal variations of the different contributors to groundwater recharge. The Rhone River recharges the alluvial aquifer only during the summer high-water period.

Résumé Origine, type et quantité de nombreux composants d'eau de l'aquifère alluvial dans la vallée supérieure du Rhône, Bois de Finges, Valais, Suisse, ainsi que leurs variations spatiales et temporelles ont été déterminés par différentes méthodes hydrochimiques. Les méthodes utilisées sont la modélisation hydrochimique, les isotopes stables, ainsi que l'échantillonnage en période de hautes eaux et de basses eaux pour étudier la distribution spatiale de la composition chimique, alors qu'un échantillonnage mensuel pendant trois ans sert à comprendre les processus de la variabilité saisonnière. Les paramètres physico-chimiques des eaux souterraines montrent des variations spatiales et saisonnières. La composition chimique de l'aquifère alluvial du Rhône indique un mélange entre une eau peu minéralisée venant du Rhône et une eau sulfatée s'écoulant du versant sud. La modification temporelle des paramètres chimiques des eaux souterraines et de la piézométrie reflètent les variations saisonnières des apports d'eau de la nappe souterraine. En période de hautes eaux durant l'été, seul le Rhône recharge l'aquifère alluvial.

Resumen Se ha determinado el origen, tipo y cantidad de diversos elementos de las aguas subterráneas en el acuífero aluvial del valle superior del río Ródano (Bois de Finges, Cantón de Wallis, Suiza), así como sus variaciones espaciales y temporales, mediante métodos hidroquímicos. Entre las herramientas utilizadas, se incluye la modelación hidroquímica, el análisis de isótopos estables y el análisis químico de aguas superficiales y subterráneas. El muestreo en épocas de estiaje y lluvias sirvió para determinar la distribución espacial de la química del agua, mientras que la variabilidad estacional fue caracterizada por medio de muestreos mensuales durante un período de tres años. Los parámetros físicoquímicos de las aguas subterráneas muestran variaciones espaciales y estacionales. La composición química de las aguas subterráneas del acuífero aluvial del río Ródano indica que hay mezcla entre las aguas débilmente mineralizadas del río y las aguas cargadas en sulfato (SO_4^{-2}) que proceden de la parte meridional de valle. Los cambios temporales en la química de las aguas subterráneas y en los niveles piezométricos reflejan las variaciones estacionales de las diferentes contribuciones de la recarga. El río Ródano recarga al acuífero aluvial únicamente durante el período estival, cuando el caudal es elevado.

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Introduction

The Bois de Finges/Pfynwald is situated in the upper Rhone River valley, 20 km east of the town of Sion, Wallis Canton, Switzerland. Locations are shown in Fig. 1. Because the line of demarcation in the usage of the French and German languages is here, two names appear on the maps of this area, but only the French names are used in this paper. In the geographic Bois de Finges area, the unconfined alluvial aquifer of the Rhone River valley is an important source of groundwater in the upper part of the valley. The aquifer is composed of surficial glacial outwash deposits. This aquifer yields large amounts of water suitable for drinking water or agricultural supply, but it is also vulnerable to contamination. Moreover, the alluvial aquifer is subject to numerous possible environmental contaminants from various sources, including the town of Sierre, industrial and agricultural activities, gravel

pits, dump sites, roads, and a planned national highway.

The objective of this research is to identify the source, type, and quantity of various components of groundwater, and to describe their spatial and temporal variations, by utilizing various hydrochemical, hydrogeological, and geophysical methods. The hydrochemical and hydrogeological studies were carried out at the Centre of Hydrogeology, University of Neuchâtel, whereas the geophysical research was carried out by the Institute of Geophysics, University of Lausanne. In this paper the results obtained from the different hydrochemical methods are presented and discussed, whereas those obtained by the geophysical borehole and surface measurements are described in Monnet et al. (2000) and Monnet and Chapellier (2000).

Since April 1996, hydrogeological and hydrochemical investigations have been undertaken in the Bois de

Fig. 1 Location and schematic geologic map of the Bois de Finges area, Canton Wallis, Switzerland
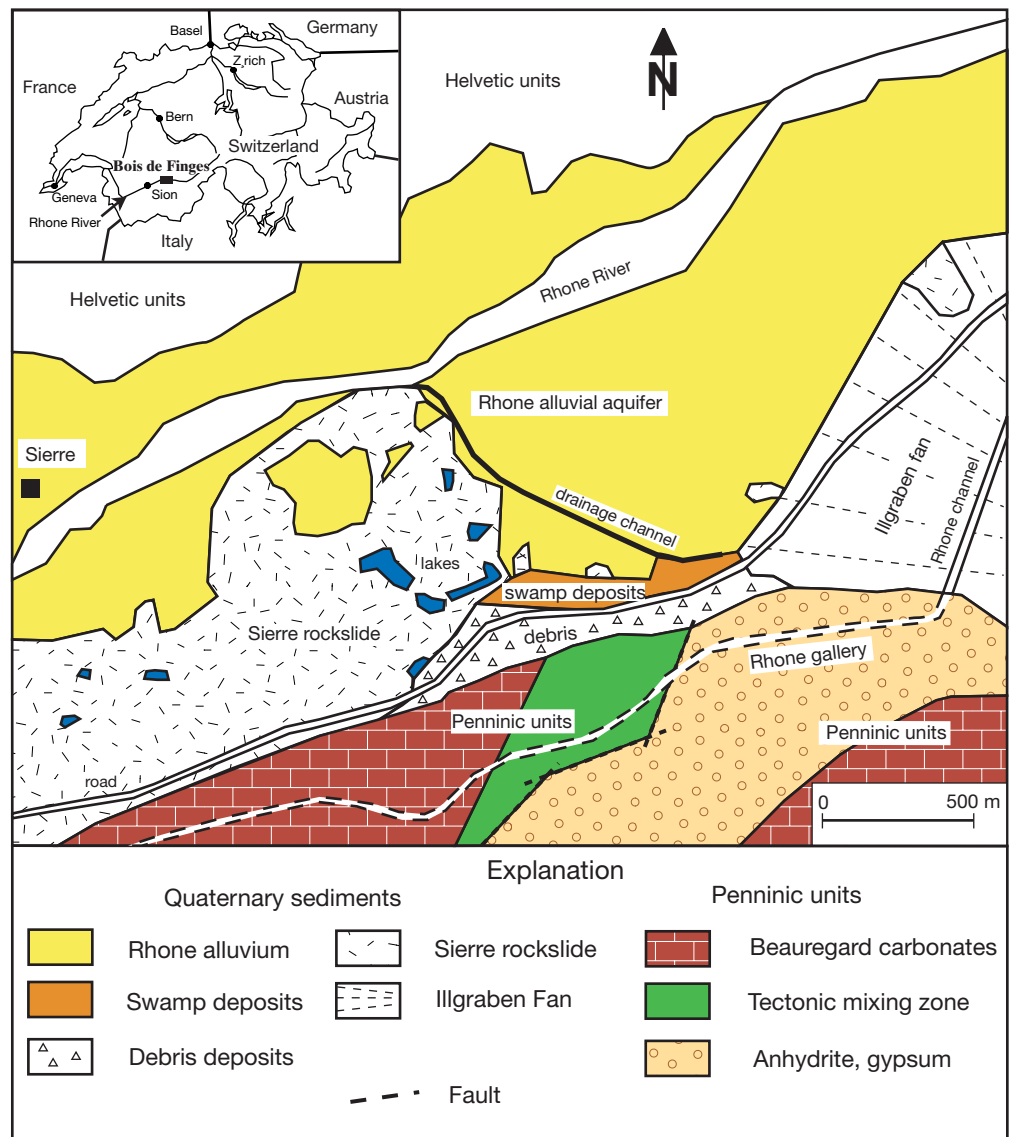
Finges area. On the research site, the groundwater head was measured and the water sampled monthly for chemical constituents. The observation network includes 58 piezometers and boreholes, as well as a spring and the Rhone River. The average depth of the piezometers is 10 m; five boreholes are 20–30 m deep (Berthod 1995). To understand how change in groundwater chemistry is a function of time and space, investigation of the chemical composition of the groundwater at various depths and locations, as well as that of surface waters, was carried out monthly.

Water exchange between the river and the aquifer is a function of the difference in potential, the leakage factor, and the section of the river–aquifer interface (Edmunds et al. 1976; Hötzel and Reichert 1992; Briechle 1997). In the Bois de Finges area, the Rhone River decreases 88 m in altitude along its 7-km course. The steepness of the slope of the Rhone River bed, which ranges from 6–12%, favours the deposition of coarse material with a high hydraulic conductivity, which promotes surface-groundwater exchange. The bed of the river is 2–8 m above the water table. With an annual average precipitation of 587 mm, the Bois de Finges area is one of the driest regions of Switzerland.

Geology

The geology of the Bois de Finges area consists of Helvetic units on the north side of the Rhone River valley, dominated by marly limestone of Jurassic age, and of Penninic units on the south side (Fig. 1). The Penninic units are composed of anhydrite, porous calco-dolomite, and marl of Triassic age; quartzite, sandstone, and conglomerate of Permo-Triassic age; and schist and arkose of Permo-Carboniferous age (Escher 1988).

The Quaternary sediments consist of alluvial sandy gravel which fills the Rhone trough; alluvial deposits of the Illgraben fan; the Sierre rockslide, which includes only Helvetic rocks; debris deposits dominated by Penninic rocks; and swamp deposits (Fig. 1). The Illgraben fan in the eastern part of the area has diverted the Rhone River bed to the northern side of the valley. The fan consists of a silty and sandy upper part and sandy gravel below. Lakes and hills form most of the surface of the Sierre rockslide. This gigantic rockslide (about 1 km³) occurred at the end of the last glaciation, about 10,000 years ago, when the mountain sides became unstable after the retreat of the Rhone glacier (Burri 1997).

Fig. 2 Geologic section through alluvial deposits of the Rhone River valley, showing sample localities. *P* Piezometer; *SA* cored drill hole; *Q* spring. Line of section and location of sample localities are shown in Fig. 3
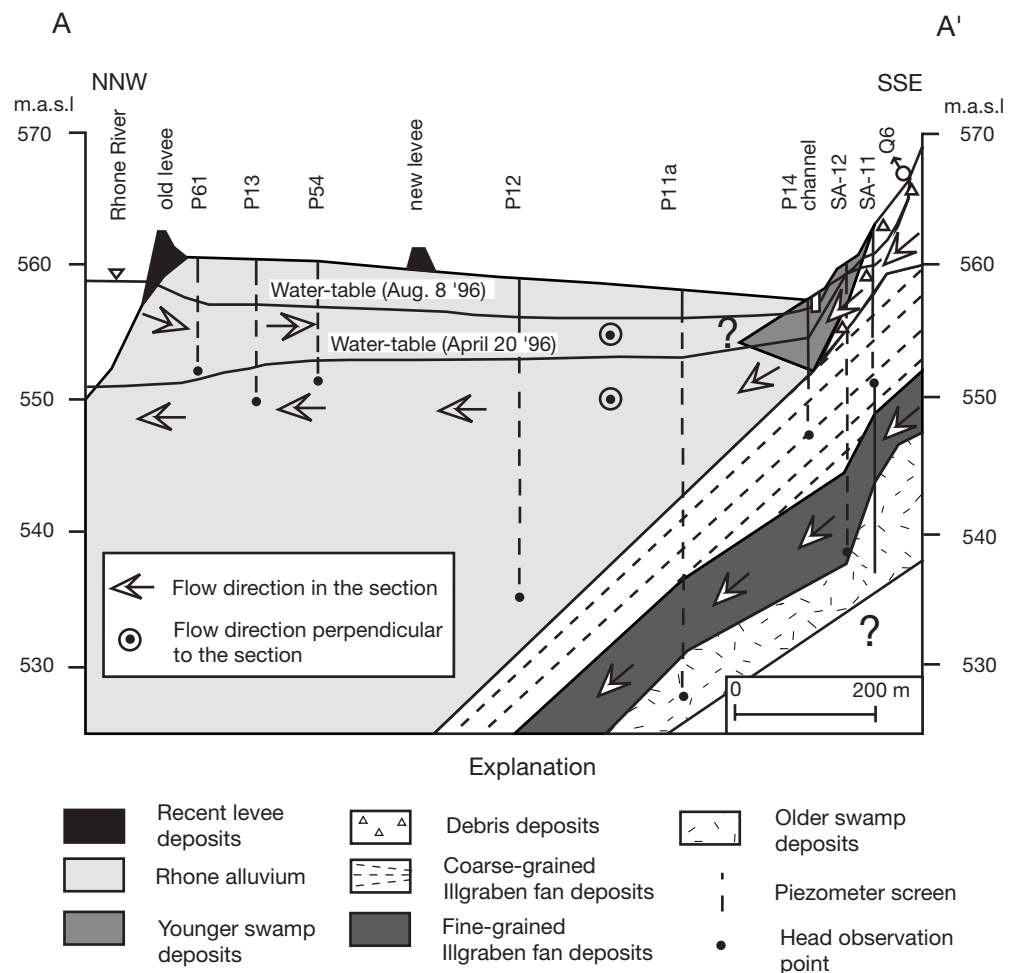
The heterogeneous Rhone alluvial sediments are the major aquifer in the Bois de Finges area. Locally, on the south side of the valley, Illgraben fan deposits and debris deposits are intercalated with Rhone alluvial sediments, as shown in the section of Fig. 2. The alluvial fan has a 5% slope to the northwest and dips under the Rhone sediments; a depth of 15.20 m to the top of the fan deposits was measured in borehole P11a (Fig. 2).

Hydrogeology

A general view of the spatial aspects of groundwater circulation in the southern part of the Bois de Finges area is shown on the contour map of the potentiometric surface on 8 August 1996 (Fig. 3). This was a time of high water, when groundwater recharge to the Rhone alluvial aquifer occurred in two main areas. At the northeastern limit of the study area, surface water moved from the Rhone River bed, on a broad front about 700 m wide, southward into the alluvium; the

water then followed a path through the alluvium toward the drainage channel across the center of the area (Fig. 3). The second recharge area is at the base of Gorwetsch Mountain in the east-central part of the area, where subsurface flow enters the Rhone alluvium and underlying units (Fig. 3). This recharge flow is along a front about 800 m wide perpendicular to the main groundwater flow in the aquifer.

The contour map (Fig. 3) was also used for flow-simulation experiments after the model of Schürch et al. (1999). These experiments show that 75% of the total recharge originates from the Rhone River and 25% from the sulphate-rich water source. In this model, the Gorwetsch Mountain runoff is incorporated in the sulphate recharge. On the other hand, the Illgraben fan does not contribute recharge to the valley aquifer, especially in this area of low annual precipitation.

An average groundwater velocity and the porosity of the Rhone aquifer were determined by tracer tests in borehole P11a (Kennedy et al. 1998). Hydraulic conductivity was determined from pumping tests and piezometric readings in the boreholes (Jawecki 1996). The average groundwater flow velocity in the Rhone aquifer is about 110 m/d, and the average hydraulic conductivity is 10^{-3} m/s. A similar high flow velocity has also been determined for alluvial sediments of the

Fig. 3 Configuration of water table in early August 1996 during high flow on the Rhone River. Cross section *A-A'* is shown in Fig. 2 and *I-I'* in Fig. 7
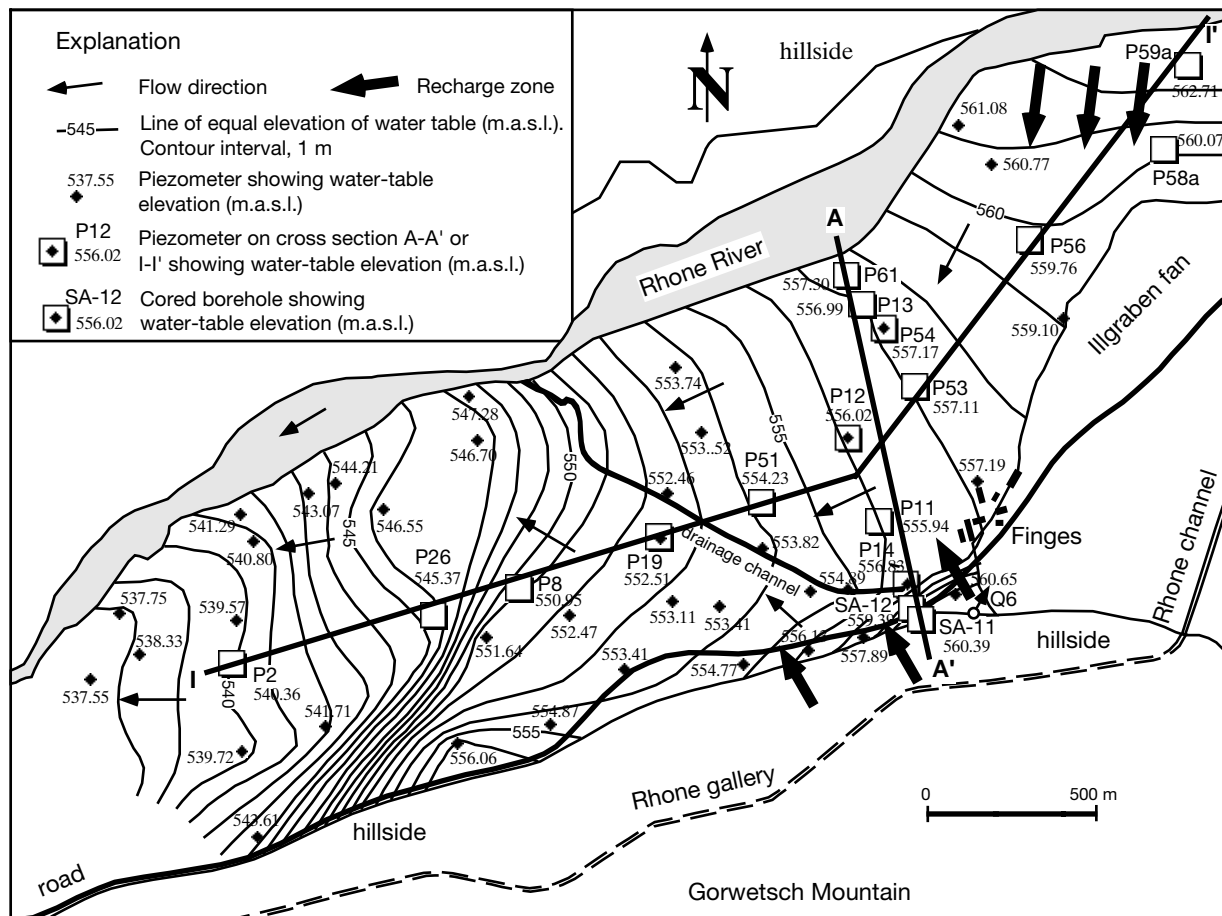
Aar River valley in central Switzerland (Rossi et al. 1994). In the Sierre rockslide, situated down the valley from the drainage channel, flow velocity is only a few meters per day; hydraulic conductivity ranges from 10^{-6} to 10^{-4} m/s. The swamp deposits and debris deposits have hydraulic conductivities of 10^{-5} and 10^{-3} m/s, respectively. The water level of most of the lakes in the Sierre rockslide zone is in equilibrium with the water table. However, the relationship between the lakes and groundwater inflow is not yet clear, particularly when the lakes are used as reservoirs for irrigation (Berthod 1995).

Methods

The groundwater mineralization of the Rhone aquifer varies not only spatially but also temporally. Fifty-eight water samples were collected during high and low water periods to determine the spatial distribution, and monthly water samples were taken from ten selected boreholes over a 3-year period to determine seasonal variations in mineralization. For most shallow piezometers and boreholes, one single sample representing the mean water composition was taken with the help of a suction pump at a flow rate of 30 L/min under stable conditions.

Field measurements for water temperature, electrical conductivity, dissolved oxygen, redox potential (Eh), and pH were made, and samples were collected from a spring, boreholes, piezometers, and the river for analysis of major cations and anions. All samples, except those for isotope analyses, were filtered in the field at 0.45 µm. The discharge of the spring was measured with a 10-L bucket and a chronometer.

The laboratory analysis program comprised the following: bicarbonate was analysed by titration less than 12 h after sampling, whereas calcium and magnesium were determined by titration not later than 48 h after sampling. Analyses of sodium, potassium, strontium, sulphate, chloride, and nitrate were carried out 3–4 weeks after sampling by ion chromatography at the GEA laboratory, University of Neuchâtel. Deuterium and oxygen-18 analyses were performed by the HYDROISOTOP laboratory, Schweitenkirchen, Germany. Between November 1996 and October 1997, water samples were collected monthly for deuterium and oxygen-18 values from piezometers P12, P13, and P52, and from the spring Q6. The Rhone River was sampled for deuterium and oxygen-18 on a monthly basis from April 1998 to March 1999. During low-water periods, when the Rhone River bed was dry, samples were taken in the Rhone channel (Fig. 1).

The saturation indexes for gypsum and calcite reported in this article were calculated with the hydrochemical computer code PHREEQE (Parkhurst et al. 1993). A two-component model was used to calculate the groundwater mixing rate of the weakly mineralized water of the aquifer, infiltrated from the Rhone River, with the SO_4-rich water flowing into the aquifer from the south side of the valley. Using the geochemical code PHREEQCI (Charlton et al. 1997), the SO_4-rich water was continually mixed in 10% increments, and it was assumed that no physical and chemical reactions took place in the aquifer.

Groundwater Chemistry

Spatial Distribution of Water Types

The spatial variation of the sulphate content of the groundwater in the aquifer during the high-water period of August 1996 is shown in Fig. 4. The distribution of the sulphate content follows the general groundwater flow pattern shown in Fig. 3. The measured sulphate content of groundwater in the Rhone alluvium decreases from about 1600 mg/L close to the south valley side to concentrations of about 50 mg/L toward the Rhone River. A maximum sulphate concentration of 1781 mg/L occurs locally in debris deposits on the south hillside (sample point SA-8). Table 1 contains physico-chemical analyses of groundwater samples from selected boreholes taken during the high-water period of August 1996, as well as during the low-water period of March 1997.

The relation between various chemical parameters and sulphate in groundwater and surface water of the Bois de Finges area is presented on Fig. 5, based on 58 sample sites (55 piezometers and boreholes, a spring, the drainage channel, and the Rhone River) sampled during the high-water period of August 1996. The concentrations of calcium, magnesium, and strontium show a positive linear correlation with respect to measured concentrations of sulphate. In the highly permeable Rhone aquifer, these correlations with sulphate and the saturation index of gypsum suggest a mixing process between low-mineralized Rhone River water and SO_4-rich water from anhydrite- and gypsum-bearing rocks of Triassic age on the south side of the valley (Fig. 1). X-ray analyses of Rhone alluvial sediments did not detect the presence of evaporites, which therefore excludes gypsum dissolution process, in the alluvial Rhone aquifer (Schürch 2000). Most diluted groundwater in the Rhone alluvium plots above the line of the molar Ca/SO_4 ratio=1, whereas SO_4-rich water plots below this line due to the loss of calcium by calcite precipitation.

The concentrations of sodium, chloride, bicarbonate, and nitrate do not show clear correlations with the sulphate content of the groundwater (Fig. 5). The sodium and chloride concentrations reflect a very low natural background (Table 1). The chloride concentration of groundwater along the road at the south valley side is affected by salt for road deicing during the winter (sample P52). The nitrate concentration is normally less than 5 mg/L, except in zones of concentrated agricultural activities, which are mostly located on the southeastern part of the Rhone alluvium and
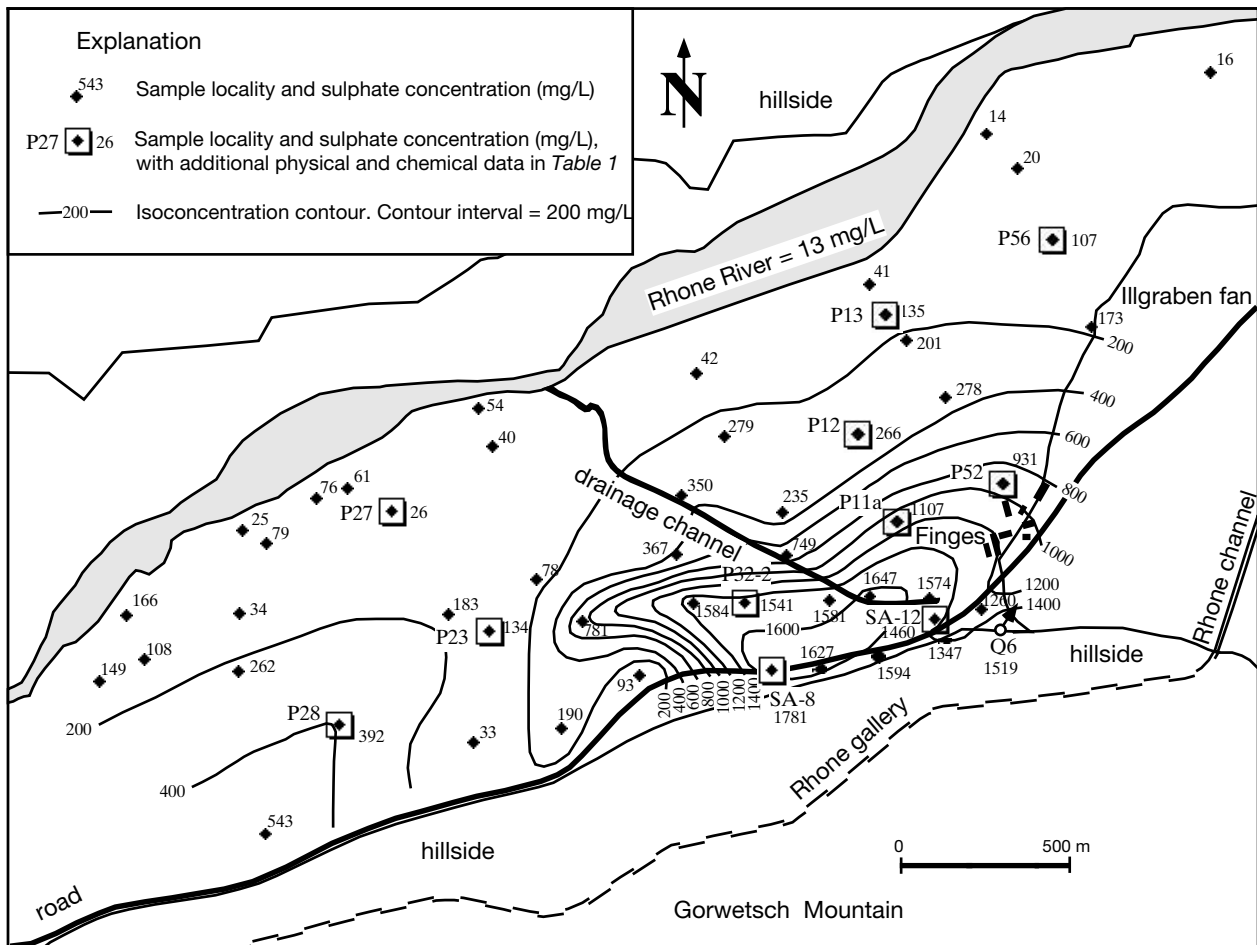
Fig. 4 Distribution of dissolved sulphate concentrations in early August 1996 during high flow on the Rhone River

on the Illgraben fan near Finges (Fig. 3). Furthermore, the saturation index of calcite is generally greater than zero.

Hydrochemical Typology

The spatial distribution of groundwater chemistry combined with the spatial distribution of rock types (Figs. 1 and 5) allow several water types to be identified. The typology of the different waters and their representative sampling point, hydrochemical character, and geological setting are given in Table 2, and their ionic composition is represented in Fig. 6. The range of variation in total dissolved solids (TDS) between periods of high water and low water in the Rhone River is indicated in Table 2 for most sampling points.

The chemical water types are classified by the cations and anions that compose $\geq 20\%$ of the TDS. During high-water period, the Rhone River water that recharges the Rhone aquifer on the northeastern border of the studied area is a Ca–Mg–HCO$_3$–SO$_4$ water

type and includes only 77 mg/L TDS. Although fairly close to the river, the chemistry of the groundwater at sample point P56 (Ca–Mg–SO$_4$–HCO$_3$) reflects the northward incursion of sulphate-rich water in the alluvial aquifer (Fig. 4). The spatial and temporal evolution of groundwater chemistry along the principal groundwater flow path from the infiltration zone at the Rhone River in the northeast into the Sierre rockslide in the southwest is shown in Fig. 7.

Groundwater TDS values are normally lower during high water on the Rhone River. However, at sample localities P12 and P53 (Fig. 3), the TDS values are inverted, which reflects a local change in the lithology of the alluvial fill from gravel to silty sand. The groundwater of the Sierre rockslide is a Mg–Ca–SO$_4$ water type (sample point P23) at the eastern part and a Ca–Mg–SO$_4$–HCO$_3$ type (sample point P28) in the center part (see Fig. 4 for sample locations). These spatial variations in groundwater chemistry in the Sierre rockslide are due to its heterogeneous lithologic composition, which is dominated by silty and sandy limestone debris of Helvetic origin, but includes swamp deposits in depressions between hills. On the other hand, the Sierre rockslide aquifer is also recharged along the south hillside (sample point P28). Therefore, it cannot be excluded that the different

Fig. 5 Relation between (1) major ions, pH, and saturation indexes for calcite and gypsum and (2) dissolved sulphate concentration in groundwater. Samples collected during high flow on the Rhone River in early August 1996. Selected chemical analyses are shown in Table 1 and selected saturation indexes in Table 2
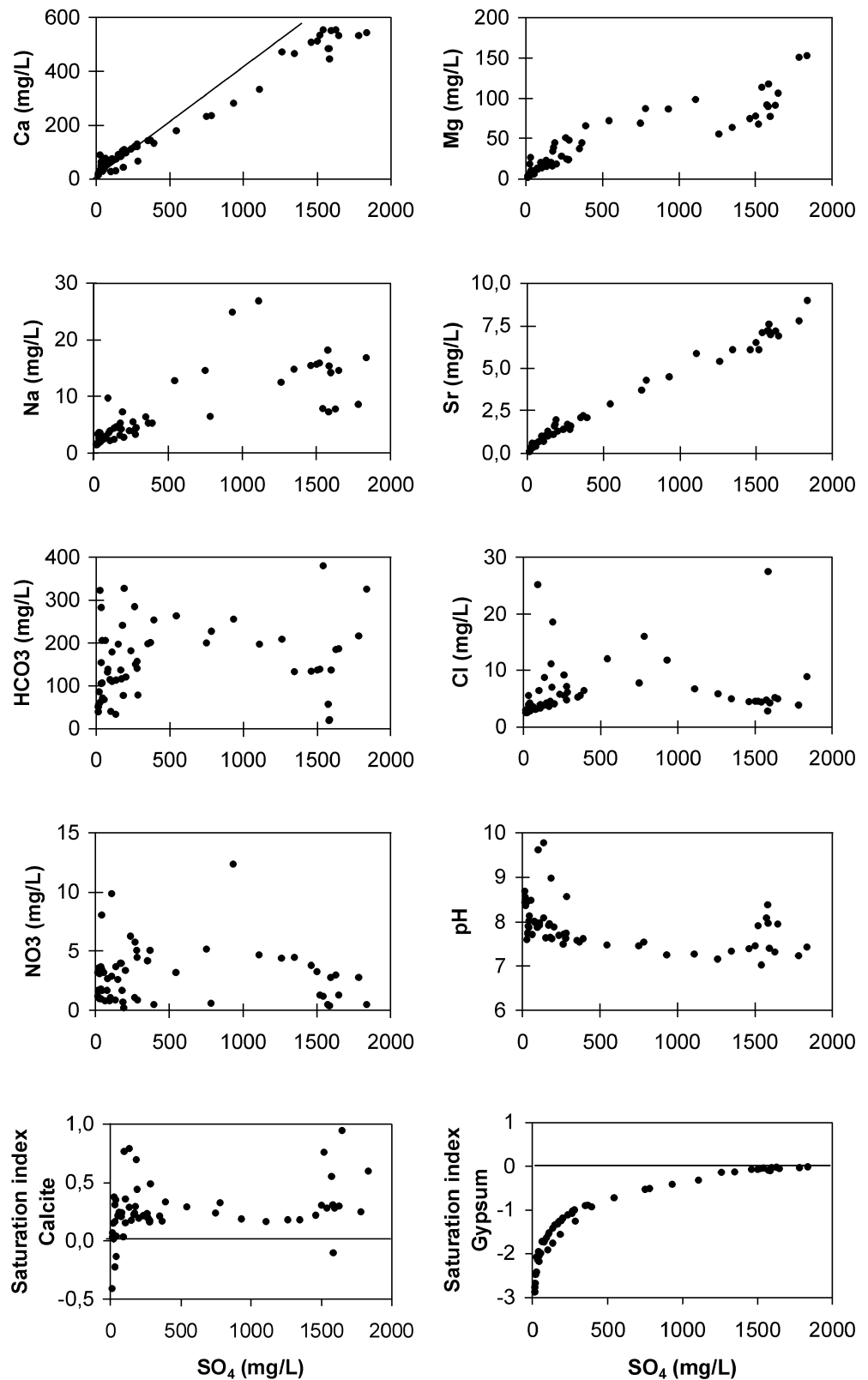
types of water in the Sierre rockslide represent mixtures of SO_4-rich water and Ca–HCO_3 water from areas of lower mineralization to the northeast (sample point P27; Fig. 4).

The groundwater chemistry of borehole SA-8 (Table 1) represents the high end member of SO_4-rich water from anhydrite- and gypsum-bearing rocks along the south side of the valley, because this groundwater

Table 1 Physical and chemical analyses of groundwater from selected boreholes and spring Q6, and water from the Rhone River, collected during high-water flow on the river, 5–15 August 1996, and during a low-water period, 10–18 March 1997. Location of boreholes shown in Fig. 4. SA Cored borehole; P piezometer; Q spring; EC electrical conductivity at 25 °C; Eh redox potential; TDS total dissolved solids; Bal. ionic balance =[(Σ cation+Σ anion)/(Σ cation−Σ anion)]×100(%)

Sample point	Date	Temp. (°C)	EC (µS/cm)	pH	Eh (mV)	O_2 (mg/L)	Altitude of water table (m a.s.l.)	TDS (mg/L)	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	Sr (mg/L)	SO_4 (mg/L)	HCO_3 (mg/L)	Cl (mg/L)	NO_3 (mg/L)	Bal. (%)
High-water flow																		
SA-8	15 Aug 1996	12.7	2940	7.23	132	1.3	554.77	2702	533.2	151.0	8.6	4.8	7.8	1781	216.6	3.9	2.8	−1.6
P32-2	9 Aug 1996	9.0	2790	7.03	−115	1.5	553.41	2614	554.4	113.8	7.9	3.7	7.1	1541	380.5	4.4	1.2	−1.1
Q6	5 Aug 1996	12.8	2470	7.91	485	9.0	-	2292	534.4	68.1	15.9	3.3	6.1	1519	139.5	4.6	1.3	−1.4
SA-12	5 Aug 1996	13.1	2460	7.46	481	8.7	559.39	2263	513.6	78.1	15.7	3.7	6.5	1500	137.3	4.6	3.3	−1.1
P11a	8 Aug 1996	14.8	2090	7.27	410	5.8	555.94	1786	333.2	98.5	26.9	5.2	5.9	1107	197.5	6.8	4.7	−0.9
P52	6 Aug 1996	13.1	1830	7.25	459	6.5	557.19	1616	282.8	86.6	24.9	6.1	4.5	931	256.2	11.9	12.4	−3.4
P28	13 Aug 1996	12.1	1081	7.62	428	5.4	541.71	862	134.0	65.9	5.3	2.2	2.1	392	253.6	6.5	0.5	−0.6
P12	6 Aug 1996	9.8	774	7.72	447	8.0	556.02	583	122.8	24.6	3.8	3.8	1.5	266	151.0	5.6	5.8	1.0
P27	12 Aug 1996	11.3	559	7.60	371	9.9	546.55	468	89.2	18.5	3.4	3.5	0.3	26	323.3	3.1	1.0	2.2
P13	6 Aug 1996	9.4	482	8.09	458	9.4	556.99	352	74.8	15.3	2.4	2.2	1.0	135	113.6	3.9	3.7	3.2
P56	6 Aug 1996	10.5	446	7.98	452	9.6	559.76	317	67.2	14.1	2.2	2.4	0.7	107	110.5	3.4	9.9	4.2
P23	12 Aug 1996	10.2	392	9.78	69	4.0	551.64	241	31.6	23.1	4.4	3.0	1.3	134	33.6	8.8	0.9	2.3
Rhone River	7 Aug 1996	7.1	104	8.44	485	11.5	-	77	15.2	2.2	1.6	1.1	0.1	13	39.7	3.0	1.2	0.9
Low-water flow																		
SA-8	18 Mar 1997	11.3	2920	7.34	131	1.6	554.39	2672	514.8	152.4	13.3	5.1	8.6	1808	168.5	9.4	0.1	−2.2
P32-2	14 Mar 1997	9.2	2780	7.05	−125	0.0	552.76	2672	552.0	120.3	10.8	3.7	8.1	1621	351.5	12.9	0.2	−2.4
Q6	10 Mar 1997	13.5	2565	7.50	484	9.2	-	2350	522.0	87.5	21.0	3.8	7.3	1541	158.6	14.2	1.4	−1.2
SA-12	10 Mar 1997	12.3	2500	7.44	436	8.2	559.05	2267	517.2	80.2	18.5	4.3	7.0	1492	136.5	14.6	3.2	−0.7
P11a	13 Mar 1997	12.1	2190	7.32	372	6.2	553.40	1861	363.6	105.0	24.0	4.6	6.7	1160	181.5	15.5	6.5	0.5
P52	11 Mar 1997	12.9	1886	7.34	490	7.0	553.93	1607	286.8	94.1	25.1	4.9	5.8	945	223.4	17.4	10.2	−1.5
P13	11 Mar 1997	8.7	765	8.05	489	8.5	553.52	552	121.6	23.6	3.2	2.5	1.8	283	105.3	8.0	4.5	1.8
P12	11 Mar 1997	8.5	581	7.95	480	8.6	553.36	403	85.6	18.0	3.5	2.8	1.3	149	129.6	8.7	5.4	3.6
P27	17 Mar 1997	10.7	557	7.69	412	9.3	545.53	446	86.4	18.5	3.5	3.4	0.3	31	297.4	4.5	1.7	3.4
P23	17 Mar 1997	8.3	395	9.73	22	1.5	551.34	242	31.6	25.0	4.1	2.8	1.4	127	41.2	10.0	0.0	3.8
Rhone River	10 Mar 1997	7.7	244	8.47	454	11.3	-	153	31.6	3.9	5.7	2.0	0.4	39	59.5	9.0	2.3	2.8

Table 2 Representative chemical types of groundwater and river water, and saturation indexes of selected minerals in the geological environments of the Bois de Finges area. Sample localities are shown in Fig. 4, chemical data in Table 1. *TDS* Total dissolved solids, measured during high river flow (August 1996); *Δ TDS* coefficient variation (%) between TDS value at low river flow (March 1997) (LW) and high river flow (August 1996) (HW): [(LW97–HW96)/HW96]×100; *SI* saturation index; *ND* not determined

Parameter	SA-8	P32-2	P28	P27	P23	P56	Rhone River
Chemical type	Ca–Mg SO$_4$	Ca–Mg SO$_4$–HCO$_3$	Ca–Mg SO$_4$–HCO$_3$	Ca HCO$_3$	Mg–Ca SO$_4$	Ca–Mg SO$_4$–HCO$_3$	Ca–Mg HCO$_3$–SO$_4$
TDS (mg/L)	2702	2614	862	468	241	317	77
Δ TDS (%)	1.1	2.5	ND	–4.7	1.3	ND	98.7
Lithology	Anhydrite	Sandy clay	Silty sand	Limestone	Clay	Sandy gravel	River
Geological unit	Triassic rocks	Swamp deposits	Sierre rockslide	Sierre rockslide	Sierre rockslide	Rhone alluvium	Surface water
SI calcite	0.26	0.28	0.33	0.38	0.80	0.18	–0.41
SI aragonite	0.11	0.21	0.26	0.29	0.65	0.02	–0.53
SI dolomite	0.15	0.61	1.05	0.75	1.60	–0.31	–0.97
SI strontianite	–1.05	–1.06	–0.94	–1.57	–0.03	–1.18	–2.03
SI gypsum	–0.03	–0.04	–0.92	–2.07	–1.76	–1.24	–2.87

Fig. 6 Chemical water types, arranged by increasing cation and decreasing anion content to reflect progressive calcium-sulphate enrichment of groundwater from the Rhone River toward south side of valley. Chemical data are shown in Table 1, water types in Table 2, sample locations in Fig. 4
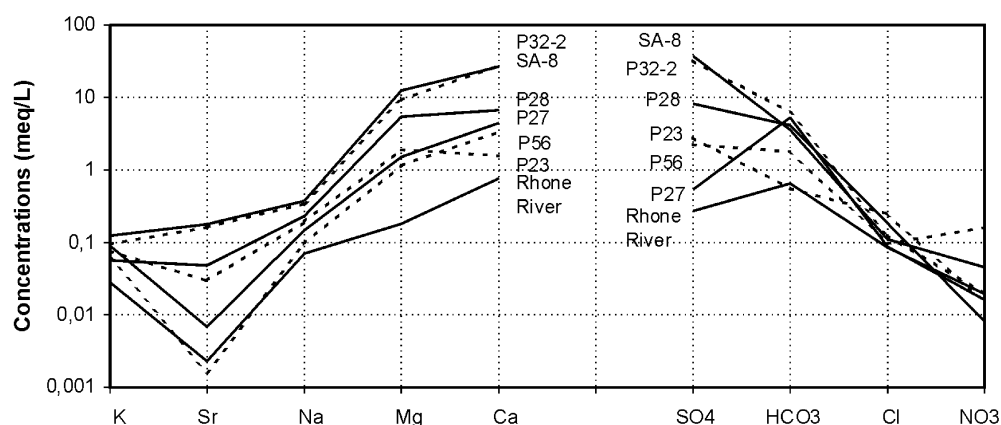
best fulfills the following conditions: (1) it is saturated with gypsum; (2) it is situated in the recharge zone of SO$_4$-rich water; (3) its chemistry excludes any recharge of weakly mineralized water from the Rhone River; and (4) there is limited seasonal hydrochemical variation. The water in SA-8 borehole is of Ca–Mg–SO$_4$-type with TDS of about 2700 mg/L. It is characterized by saturation indices of gypsum and calcite of about –0.03 and 0.26, respectively. The dissolution of anhydrite and gypsum is responsible for most of the groundwater mineralization (Table 2). Mandia (1993) has studied the various Triassic aquifers of the Canton Wallis.

Groundwater in the swamp deposits near the south valley border (sample point P32–2) is a Ca–Mg–SO$_4$–HCO$_3$ type, has TDS of 2500 mg/L, and emits a strong H$_2$S odour. The odour indicates partial sulphate reduction by oxidation of organic material in a reduced environment. The amount of dissolved oxygen originally in the recharge water has been lowered by interaction with the organic material (Eq. 1), thereby reducing the pH from 7.5 to 7.0 (Appelo and Postma 1993):

$$CH_2O + O_2 \Leftrightarrow CO_2 + H_2O \qquad (1)$$

When the redox potential is low enough, the species of sulphur appears by reduction of sulphate:

$$2\,CH_2O + SO_4^{2-} + H^+ \Leftrightarrow HS^- + 2\,H_2O + 2\,CO_2 \qquad (2)$$

The oxidation of organic material produces CO$_{2(aq)}$, which allows further calcite dissolution. The relatively high dissolved oxygen content of the P32–2 water sample and the redox potential measured (Table 1) are the result of the sampling procedure, which entailed use of a suction pump. Swamp deposits occur also in the lowermost part of some boreholes at depths of 10–30 m (Fig. 2).

Seasonal Variations

Seasonal variations in groundwater chemistry and piezometric levels reflect fluctuations in groundwater recharge. The Rhone alluvial aquifer is only recharged by the Rhone River in summer, at the time of high water. In winter, however, the Rhone River bed is dry along a 7-km reach in the study area, because as much as 60 m^3/s of flow is diverted into the Rhone channel (Fig. 1) in order to produce electricity. On the other hand, recharge of SO$_4$-rich water along the south side
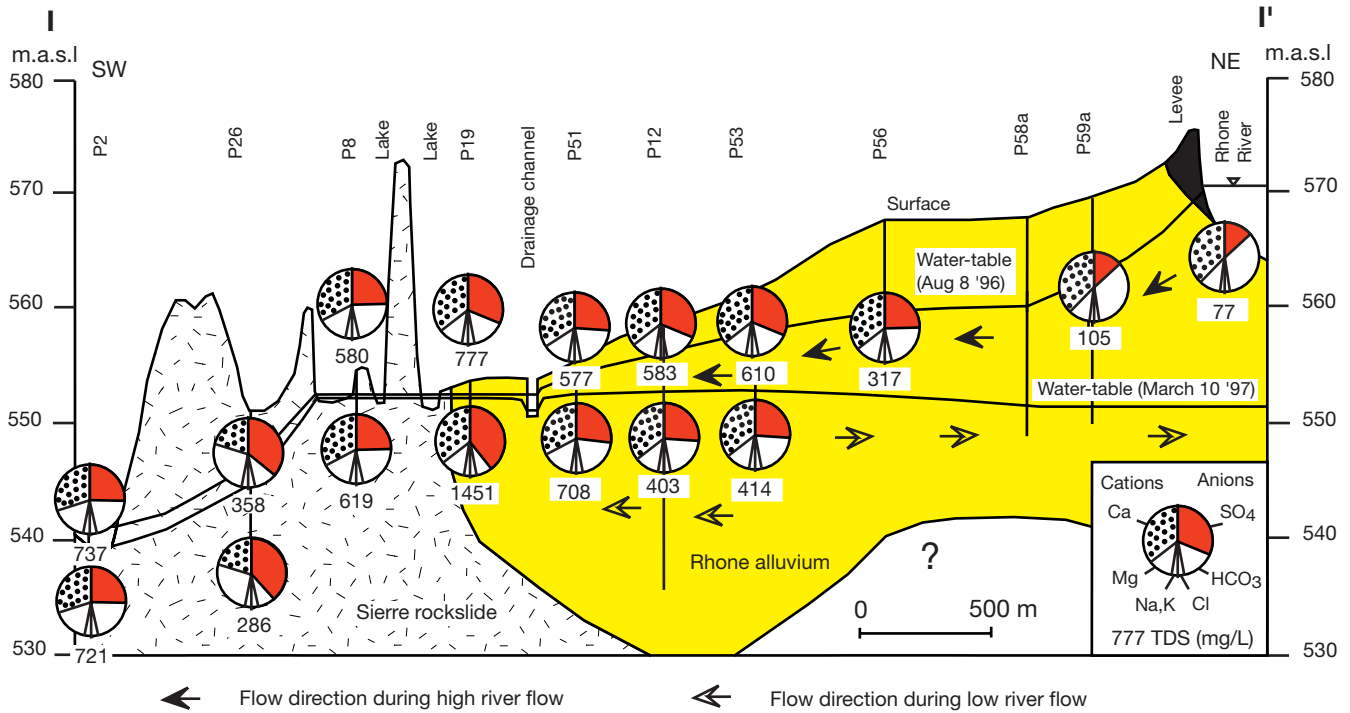
Fig. 7 Cross section I-I' along principal groundwater flow path, showing spatial and temporal evolution of water chemistry from high flow on the Rhone River, 8 August 1996 (*upper pie charts*) to low flow, 10 March 1997 (*lower pie charts*). Line of cross section and sample localities are shown in Fig. 3, chemical data in Table 1

of the valley has only minor seasonal variations. The effect of seasonal variation in recharge by the Rhone River is well exhibited by the 11-m fluctuation of the water table between high and low flow on the river at sample locality P59a, near the river recharge area. In contrast, almost no water-table fluctuations occur at sample locality SA-12, along the south side of the valley (Figs. 7 and 8).

The water-table levels and the TDS at four sample localities are compared with the seasonal variations in rainfall and Rhone River flow over a 3-year period from June 1996 to June 1999 (Fig. 8). The sample point P13 shows a continuous decrease in the water table from June 1996 almost to June 1997 and an initial decrease in TDS at that point, followed by a slight increase in TDS from January 1997 to June 1997 (Figs. 8c, d).

The water-table level in piezometer P52 (Fig. 8c), which penetrates 6 m of Rhone alluvium and another 4 m of Illgraben fan deposits, reflects seasonal fluctuations of the Rhone River. During the low-water period, the Rhone alluvium of the piezometer P52 is completely unsaturated, because the water-table level is about 7.50 m deep. A computer simulation of the groundwater flow during the high-water period of August 1996 (Schürch et al. 1999) shows that water infiltrating from the Rhone River in the northeastern

part of the study area takes almost 6 weeks to reach piezometer P52, a distance of 1270 m from the river. This groundwater flow velocity of 28 m/d is less by a factor of 4 than the average flow velocity calculated for the Rhone alluvium at borehole P11a.

Interpretation of the chemical and isotopic data for piezometer P52 (Table 1) indicates a three-component system in this part of the study area: (1) water infiltrates from the Rhone River into the Rhone alluvium; (2) SO_4-rich water, originating along the south side of the valley, flows into the Illgraben fan deposits; (3) local recharge of oxygenated bicarbonate water originating from precipitation on the Illgraben fan and the debris deposits. This third recharge component is present only in the boreholes along the south side of the valley (sample points P52 and SA-12, Fig. 8c, d) as the response to rain storms (November 1996) and snow melting (May 1998). The response time of piezometer P52 is 1 month, whereas that of piezometer SA-12 is 2 months.

Mixing Processes

In general, the groundwater composition of the highly permeable Rhone alluvial aquifer is a mixture of weakly mineralized water infiltrated from the Rhone River and SO_4-rich water originating from evaporitic-bearing rocks on the south side of the valley. A two-component model was used to calculate the different mixing rates of the weakly mineralized water (sample point P56) and the SO_4-rich water (sample SA-8). Using the PHREEQCI code, running the PHREEQC thermodynamic database (Charlton et al. 1997), SO_4-rich water was progressively mixed in 10% incre-

Fig. 8 Relation of precipitation, Rhone River level, water-table elevation, and total dissolved solids in groundwater, Bois de Finges area. **a** Precipitation, 1 June 1996 to 1 June 1999. Measured at Sierre, station no. 7360, Swiss Institute of Meteorology. **b** Rhone River level, 1 June 1996 to 4 June 1999. Measured at Sion station, National Hydrological and Geological Survey, 20 km downstream from study area. **c** Hydrographs of water table in Rhone alluvial aquifer. Measured monthly in four selected boreholes, 1 June 1996 to 4 June 1999. (Location of boreholes is shown in Fig. 4.) **d** Total dissolved solids in groundwater from four selected boreholes and the Rhone River. Sampled monthly, 1 June 1996 to 4 June 1999. Location of boreholes is shown in Fig. 4
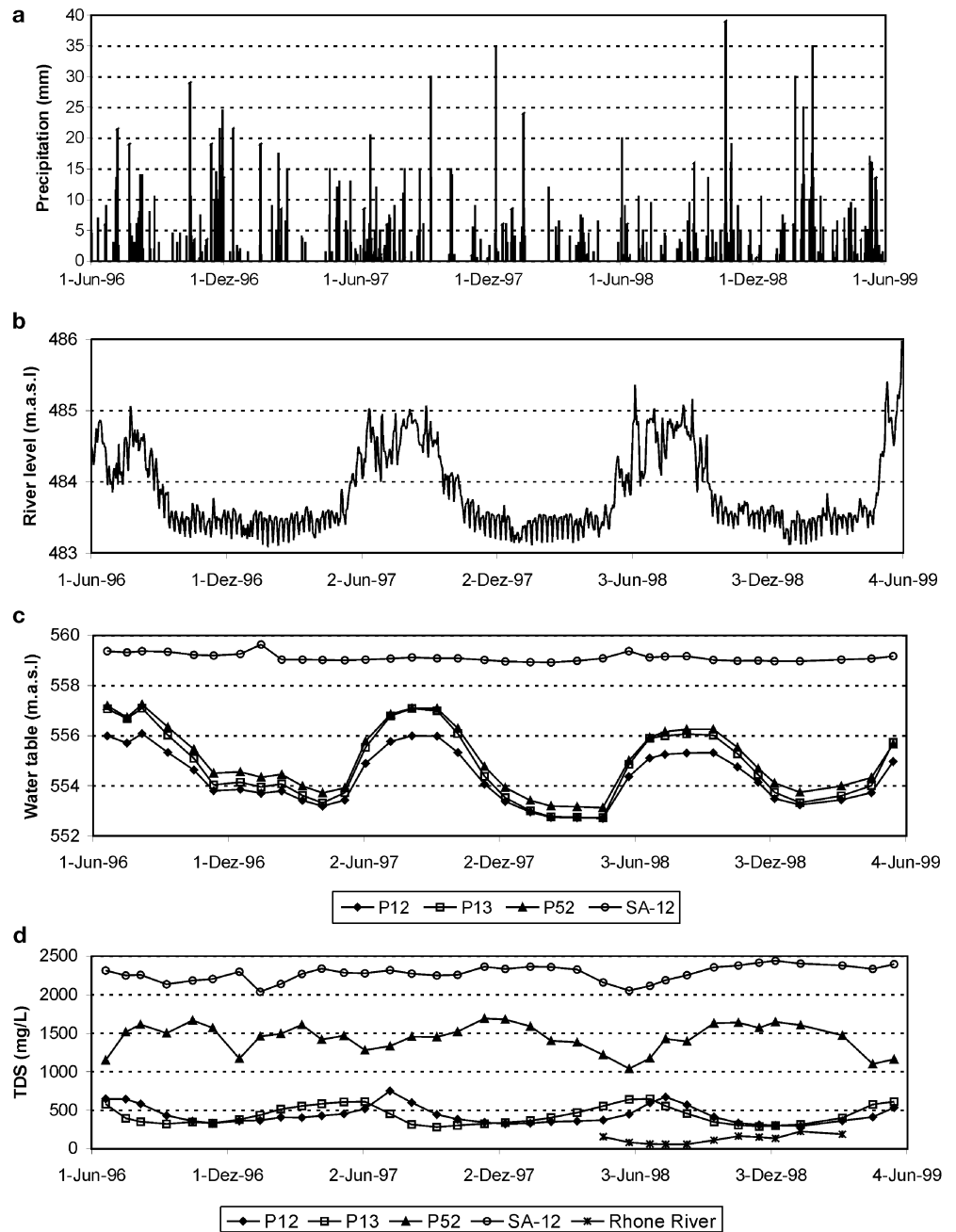
ments with weakly mineralized water from 10–90%. The input data were the water analyses of SA-8, corresponding to 0% and P56, corresponding to 100% (Table 1). The P56 analysis was considered the standard for weakly mineralized water, even though it contains some sulphate. The model discounts any physical and chemical reactions in the aquifer. The code calculated the speciation of the dissolved chemical components, as well as the saturation index of calcite, aragonite, dolomite, strontianite, gypsum, and anhydrite for each 10% increment (11 simulation points).

The simulated mixing progression was compared with selected chemical constituents of the analysed groundwater samples (Table 1), namely concentrations of calcium and magnesium. Sulphate content and the saturation index of calcite and gypsum are plotted in Fig. 9. The Ca–SO$_4$ plot (Fig. 9a) shows that most of the analysed groundwater samples from the Rhone alluvium fit very well with the simulated mixing line. On the other hand, groundwater of the Rhone alluvium is enriched with magnesium (Fig. 9b). The simulated values of the saturation index of calcite (Fig. 9c) do not correspond to those calculated for the field samples (Fig. 5). The calculation of the saturation index of calcite depends strongly on the pH, which was measured in the field. Degassing of CO$_2$
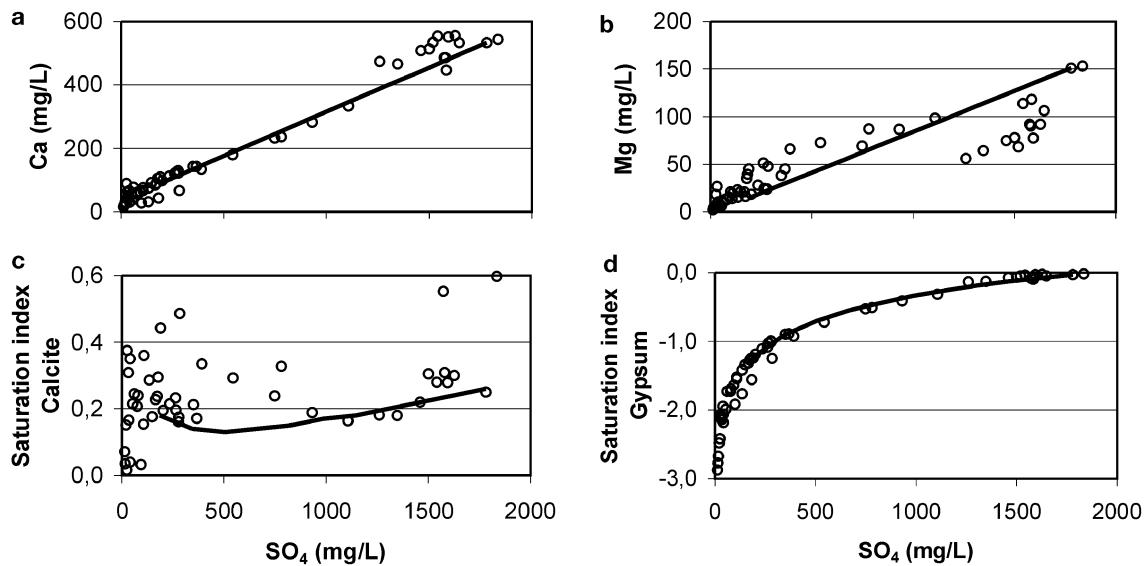
Fig. 9 Relation between (1) calcium and magnesium concentrations and saturation indexes for calcite and gypsum, and (2) dissolved sulphate concentration in groundwater. Also shown is model-derived simulated progressive mixing rate (*thick line*) of weakly mineralized groundwater near the Rhone River (sample locality P56) and SO_4-rich water (sample locality SA-8) at south valley side. Samples collected 5–15 August 1996 during high river flow. Chemical data are shown in Tables 1 and 2, sample localities in Fig. 4

during groundwater sampling with the help of a suction pump normally results in pH values that are too high. On the other hand, the simulated values of the saturation index of gypsum (Fig. 9d) correspond closely to those calculated for the field samples. This confirms that, as a first approximation, groundwater-sulphate content can be considered as a conservative estimation of the degree of mixing in the oxygenated environment of the Rhone alluvial aquifer. Moreover, the calculated saturation index of gypsum ranges from –2.5 to –0.03, which precludes any precipitation of evaporates (Fig. 5).

Oxygen-18 and Deuterium in Groundwater

Relation Between $\delta^{18}O$ and δD

The study of stable isotopes is based on the tendency of some pairs of isotopes to fractionate or separate into light and heavy fractions. Results are expressed as deviation in parts per thousand (Fritz and Fontes 1980). The $\delta^{18}O$ values plotted against the δD values of water samples collected monthly from piezometers P12, P13, and P52 in the Rhone alluvial aquifer, the spring Q6, and the Rhone River are shown in Fig. 10. The $\delta^{18}O$ values of water in the Rhone alluvial aquifer range from –14.39 to –14.70‰. The highest values of –13.80 to –14.29‰ were for the groundwater from the P52 piezometer near the intersection of Rhone

alluvium and Illgraben fan deposits (Fig. 4). The $\delta^{18}O$ values of the gypsum-saturated spring Q6 range from –14.02 to –14.12‰. Water from the Rhone River had a $\delta^{18}O$ value of –15.94 in May 1998 and –13.98‰ in December 1998. Except for most analyses of P52 and the Rhone River samples, all values were within the error bar, which is ±0.15‰ for $\delta^{18}O$ and ±1.5‰ for δD.

All these isotopic values plot between the world meteoric water line (Yurtsever and Gat 1981; Eq. 3) and the north and central Switzerland line (Kullin and Schmassmann 1991; Eq. 4), with the exception of the P52 and Rhone River samples. The world meteoric water line, representing the regression line of continental precipitation samples, has the following equation (Yurtsever and Gat 1981):

$$\delta D \ (‰) = 8.2 \times \delta^{18}O \ (‰) + 10.8 \tag{3}$$

Deviation from the world meteoric water line represents precipitation that occurred under different local or regional climatic conditions or that has undergone geochemical change.

The $\delta^{18}O$ values of the Rhone River water mostly follow the north and central Switzerland line (Fig. 10), which represents the regression line of precipitation samples on the Swiss Plateau and which has the following equation (Kullin and Schmassmann 1991):

$$\delta D \ (‰) = 7.55 \times \delta^{18}O \ (‰) + 4.8 \tag{4}$$

These $\delta^{18}O$ values of the Rhone River water, which mostly follow the north and central Switzerland line, indicate that the recharge area of the Rhone River system is much larger than the local infiltration zone that influences the Bois de Finges aquifer.

Seasonal Variations

During the high-water period on the Rhone River in the summer, the river water decreases in $\delta^{18}O$, which

Fig. 10 Relation between oxygen-18 and deuterium in groundwater from three boreholes, an SO$_4$-rich spring Q6, and Rhone River water. Samples were collected monthly over a hydrological year. Sample locations are shown in Fig. 3. *Error bars* for oxygen-18 and deuterium are ±0.15 and ±1.5‰, respectively
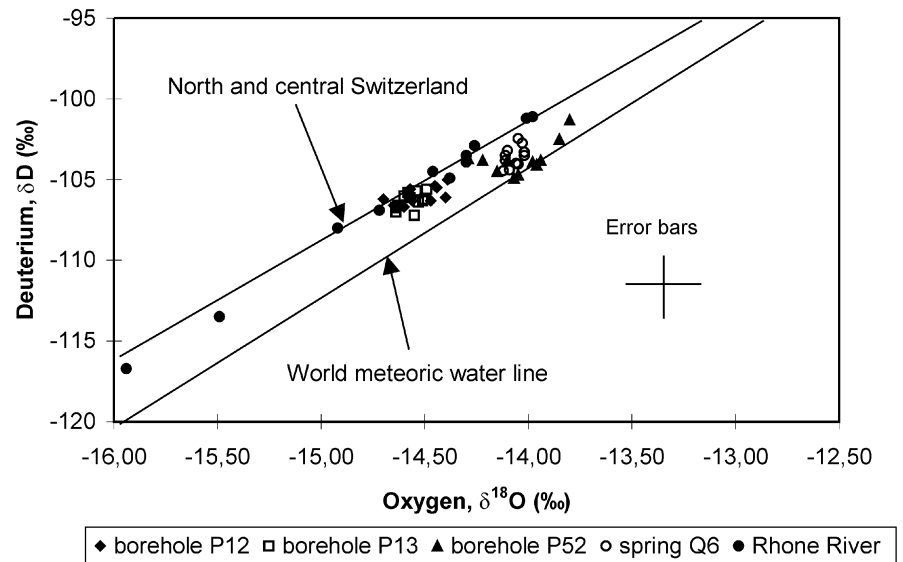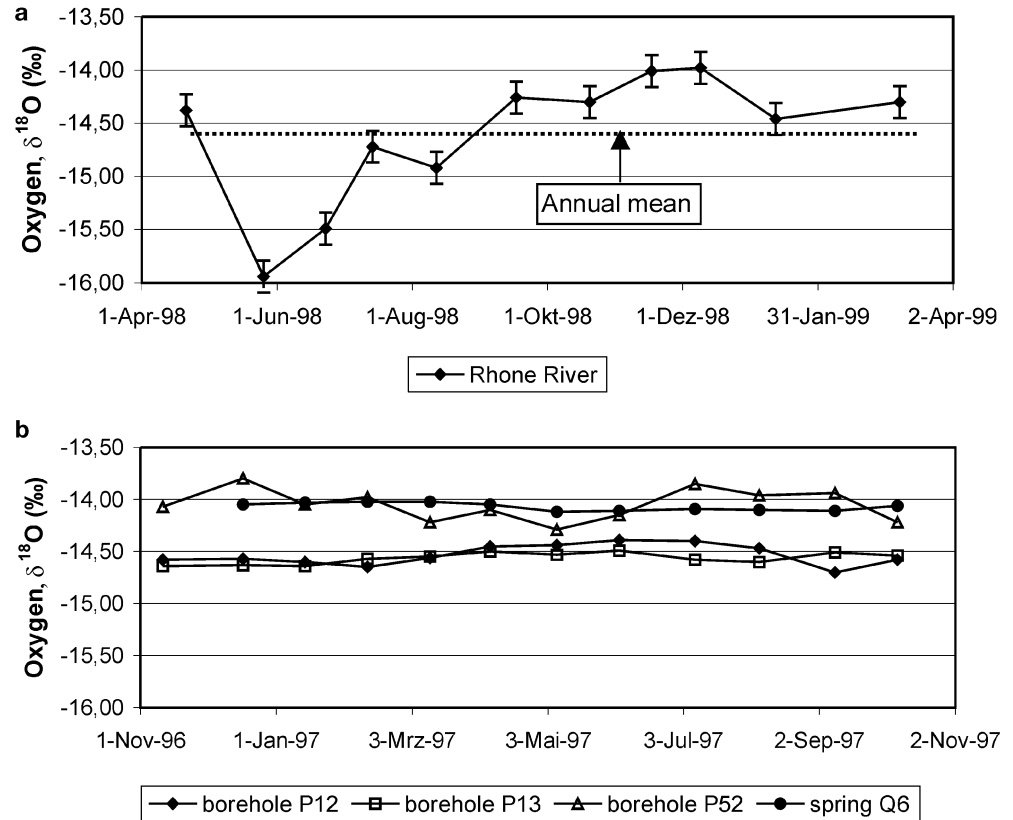
Fig. 11 Seasonal variation in oxygen-18 values in groundwater of the Rhone aquifer, a spring, and Rhone River water. **a** Monthly oxygen-18 values of Rhone River water, April 1998 to March 1999. **b** Monthly oxygen-18 values of groundwater from three boreholes and a spring, November 1996 to October 1997

reflects the $\delta^{18}O$ content of the snow meltwater from the higher altitudes in the Rhone River basin. Variations in the $\delta^{18}O$ composition of the Rhone River in the Bois de Finges area also strongly reflect the seasonal hydroelectric generation in the upper Rhone River basin, which controls the release of river water. In the Bois de Finges area, the annual mean value of $\delta^{18}O$ of the Rhone River water is –14.60‰. However,

the cycle of $\delta^{18}O$ variation of the river water is very different from the normal isotopic cycle of precipitation that has minimum $\delta^{18}O$ values in the winter and maximum values in the summer (Schotterer et al. 1995).

Although the seasonal variations of the $\delta^{18}O$ isotope are less pronounced than the error bar, the variations seem to confirm the rapid dilution of P13

groundwater by recharge from the nearby Rhone River, and, as would be expected, the P13 variations follow those of the Rhone River. However, delays in changes in the $\delta^{18}O$ composition of the groundwater from that of the Rhone River are related to distance from the river recharge area and local variations in the hydraulic conductivity of the aquifer. The seasonal variations of $\delta^{18}O$ in the Rhone River water are shown in Fig. 11a, whereas those in the groundwater at three borehole localities and the spring Q6 are shown in Fig. 11b.

The isotopic composition of groundwater at sample point P52, which is close to the south side of the valley, is influenced by the seasonal rainfall, as well as the mixing of Rhone River water and SO_4-rich recharge water.

Conclusions

Groundwater flow within the Rhone alluvial aquifer in the Bois de Finges area is in a shallow system that is recharged by weakly mineralized Rhone River water along the northeastern edge of the study area and by SO_4-rich water from the south valley side. The groundwater circulates rather rapidly through the system along highly permeable zones. Recharge from the Rhone River is only during summer, a high-water period. In winter, the riverbed is dry over a distance of 7 km.

The spatial distribution of groundwater chemistry combined with the spatial distribution of rock types allow several water types to be identified. During high-water period, the Rhone River water that recharges the Rhone aquifer on the northeastern border of the area is a $Ca–Mg–HCO_3–SO_4$ water type and has only 77 mg/L TDS. Groundwater TDS values in the Rhone alluvium are normally lower during high water on the Rhone River, reflecting groundwater dilution by infiltrating river water. The water from evaporitic-bearing rocks on the southern side of the valley is of $Ca–Mg–SO_4$ type with TDS of about 2,700 mg/L. In general, the groundwater composition of the highly permeable Rhone alluvial aquifer is a mixture of weakly mineralized water infiltrated from the Rhone River and SO_4-rich water from the south side. A two-component model was used to calculate the different mixing rates. The simulated values of the saturation index of gypsum correspond closely to those calculated for the field samples. This result confirms that, as a first approximation, groundwater sulphate content can be considered as a conservative estimate of the degree of mixing in the oxygenated environment of the Rhone alluvial aquifer. The groundwater of the Sierre rockslide is an $Mg–Ca–SO_4$ water type at the eastern part and a $Ca–Mg–SO_4–HCO_3$ type in the center part. These spatial chemical variations in groundwater in the Sierre rockslide are due to its heterogeneous lithologic composition, which is dominated by silty and sandy limestone debris of Helvetic origin but includes swamp deposits in depressions between hills.

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