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Physical, biogeochemical and isotopic processes related to heterogeneity of a shallow crystalline rock aquifer

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Abstract This study deals with the chemical characterization of the biogeochemical processes occurring in a shallow aquifer in crystalline rocks. The influence of rock heterogeneity and the related physical processes on the aquifer biogeochemistry have been investigated. A hydrochemical survey (major anion and cation analysis) shows that rock heterogeneity leads to a stronger spatial than temporal variability. Some rapidly recharged and low- mineralized waters are present at the soil/rock interface. However the pumped well intersects a preferential flow path and pumps nitrate-rich water. Sulfur and oxygen isotope data from sulfates in the pumped water clearly show sulfide oxidation with only 20–30% of the oxygen atoms in sulfates formed by sulfide oxidation coming from atmospheric oxygen. This low contribution of molecular oxygen in sulfide oxidation, associated with the drastic decrease in nitrate concentration, involves a marked relationship between the nitrogen and sulfur cycles through denitrification, coupled with sulfide oxidation. Conversely, for rapidly recharged waters, the rock physical heterogeneity allows sulfide oxidation by molecular oxygen indicated by a contribution of atmospheric oxygen of nearly 70% in the newly formed sulfate. As the aquifer biogeochemistry is controlled by the physical characteristics of the rocks, pumping may overcome the natural flux pattern described previously. This anthropogenic disturbance leads to a modification of water pathways (spatial mixing or relative contribution of the fracture/matrix waters to the global fluxes) and, consequently, to a modification of the physical and biogeochemical processes occurring in the aquifer.

Keywords Groundwater · Isotopic analyses · Rock physical heterogeneity · Denitrification

Introduction

Crystalline rock aquifers are considered as highly heterogeneous since their porosity is unevenly distributed through fissures and fractures. Distribution of the fracture characteristics (length and fracture center correlation patterns) controlling heterogeneity has been shown to have no

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characteristic length scale. Consequently, classical equivalent porous medium hydrogeologic models cannot be applied to many of these aquifers (Berkowitz 2002; Bonnet et al. 2001; de Dreuzy et al. 2004). In fractured rocks, heterogeneous water flow paths and channeling effects have been demonstrated (Berkowitz 2002; de Dreuzy et al. 2004). At a regional scale, heterogeneity has been investigated in relation with regional flow paths, discharge, geology or agricultural practices (Chen et al. 2004; Grassi and Cortecci 2005; Shapiro et al. 1998; Weissmann et al. 2002). At the kilometer scale, heterogeneity has been related to flow-rate in fractures and biogeochemical processes or solute cycling (Martin et al. 2004; Tarits et al. 2006). Moreover, heterogeneity has also been observed at a local scale in the order of one meter or less (Kelly 1997; Montoroi et al. 2001; Stutter et al. 2005). Studies on soil heterogeneity have demonstrated the existence of local microsites and chemical heterogeneity (Bennet et al. 2000; Little et al. 1997; Luo et al. 1999; Parkin 1987; Schramm 2003). Soil heterogeneity is often considered to be buffered with upscaling (Cacas et al. 1990; Clauser 1992; Legout et al. 2005) although this assumption is not valid at all scales for a detailed process characterization (Molénat et al. 1999; Molénat and Gascuel Odoux 2002; Rosenberry 2003; Wyns et al. 2004).

Surface aquifers develop in the upper weathered section of these crystalline formations. Brittany is an agricultural French area where intensive pig farming leads to nitrate diffuse pollution of surface and ground waters. Due to the relatively low carbon contents of crystalline rocks, the observed decrease in ground-water nitrate concentration is attributed to autotrophic denitrification. In this biogeochemical reaction (enhanced by the presence of bacteria like *Thiobacillus denitrificans*), nitrates are reduced by sulfur-bearing minerals (like sulfide). In turn, the oxidation of sulfide by nitrate leads to an increasing sulfate concentration (Frind et al. 1990; Mariotti 1986; Pauwels et al. 2000, 2001; Postma et al. 1991; Stumm and Morgan 1996; Tarits et al. 2006).

The autotrophic denitrification involves liquid (water) and solid (mineral) phases. This biogeochemical reaction must be affected by rock fracturation and related water fluxes. Both the influence of the channeling effect induced by rock heterogeneity and the influence of variations in the heterogeneity properties induced by an anthropic disturbance on biogeochemistry in the shallow part of these aquifers have yet to be investigated.

In this study, water chemistry variability, biogeochemical processes and residence times have been characterized at a local scale (60 ha) in a small crystalline aquifer (2,200 ha) pumped for water supply. The chemical variations related to the rock physical heterogeneity and the relationships between the variation in the physical parameters of the water transfer and the biogeochemical evolution have been investigated.

Background and methods

Site description

The water plant of Vau-Reuzé is located 10 km north of Rennes, in Brittany, North West France (Fig. 1). Water is pumped from a shallow well 8 m deep (modified natural spring) located in a steep slope of approximately 9%. To characterize the site hydrogeology, four piezometers were built: Pz1 near a stream in a wetland, Pz2, Pz3 and Pz4 upstream in woodlands (Fig. 1, Table 1). These wells were drilled in altered Brioverian schists. Brioverian schists are made of alternating centimeter-thick layers of 1/sandstones with a quartz and chlorite matrix and quartz and feldspar allochems, and 2/silt and clay-rich layers showing parallel laminae. The sedimentological environment is characteristic of distal turbidites (Trautmann et al. 2000). Sulfide deposits are commonly observed in rock fractures and fissures. Generally, alteration of crystalline rocks leads to the formation of an unconsolidated alterite, several tens of meters in depth (Wyns et al. 2004). Information collected during drilling indicates a thin soil layer over loamy altered schist. A 1–2 m-thick peat limited by a layer of clayey glacial tills can be found locally near the stream.

By 2001, nitrate concentration exceeded the drinking water safety limit in the pumped well

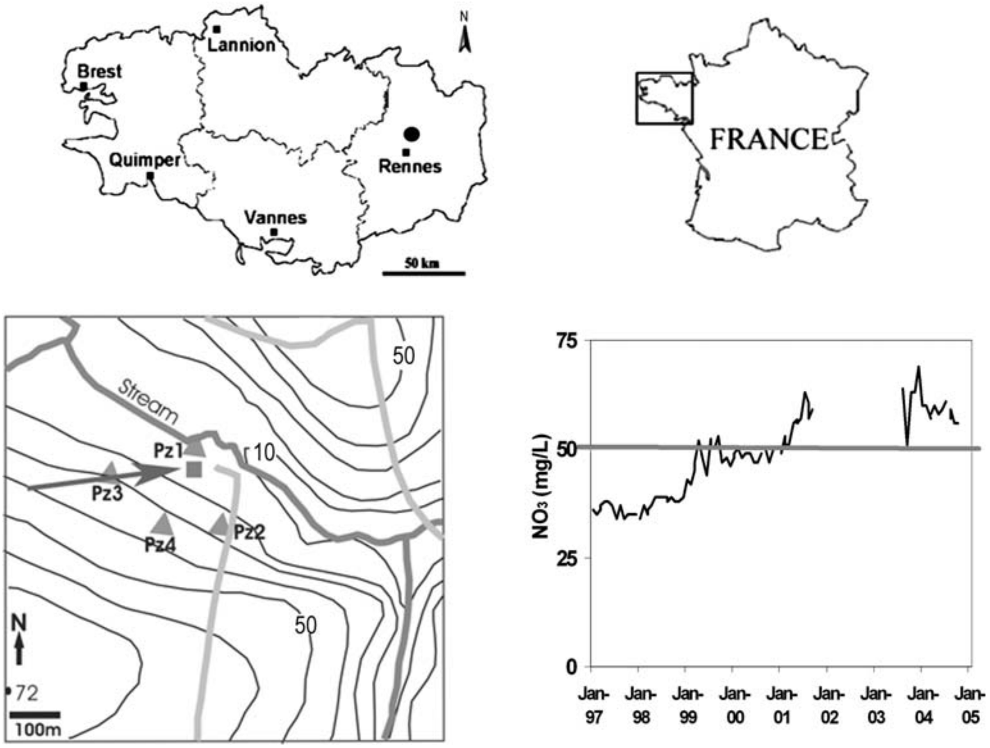

Fig. 1 Geographical setting (black spot) of the Vau Reuzé site in Brittany (France) and spatial location of wells in the study site. Square represents the exploited well and triangles the observation wells. Numbers refer to the altitude (m). Grey arrow represents the preferential flow path. Evolution of nitrate concentration versus time is indicated for the shallow pumped well (blank corresponds to the period without exploitation)

Table 1 Technical characteristics of wells

Well	Distance from pumped well (m)	Depth (m)	Screen (m)	Water inflow (m)	Geology
Pz1	31	7	3–7	4	Clayey schists
Pz2	118	13	5–13	10	Black clayey schists
Pz3	122	13	15–13	10	Black clayey schists
Pz4	112	16	7.5–16	13	Black clayey schists

(modified spring). The town council decided to search for non-polluted water deeper in the aquifer. A new well was drilled near the original spring. This well is 109 m deep and reaches the fractured part of the aquifer. Pumping was resumed in April 2004, and the drinking water obtained was a mixture of waters resulting from water pumped in both shallow and deep wells. Water from each well (whether deep or shallow) can be sampled separately. In the following text, ‘‘pumped water’’ or ‘‘pumped well’’ refers to the water sampled in the shallow pumped well.

Sample collection and geochemical analyses

Three complete geochemical surveys were carried out in December 2003, April 2004 and October 2004. The sampled water was tested for anions, cations and trace elements. Two additional samplings were carried out in June 2004 and February 2005 for anion analysis. Water was sampled using a two-holed automatic groundwater sampler (open tube that can be closed at a determined depth based on the Niskin® bottle principle—Ayraud 2006) except for the pumped well (sampled at pump tap). Conductivity, pH and Eh were measured directly in the field. A Combined SenTix 50 electrode calibrated with WTW standards was used for pH. Redox potential was measured using a platinum Ag/AgCl electrode (Mettler Pt 4805). No dissolved oxygen data is available for this site. As regards anion and cation analyses, the water was filtered through a 0.2 μm cellulose acetate mesh sieve and stored in PTFE bottles, rinsed twice with bi-distilled acid and then with ultrapure water. Bottles for cation analysis were acidified with 7 N ultrapure HNO_3. All bottles were stored at 4°C in the dark and were analyzed within a week for anions. NO_3, Cl, SO_4 and Br were analyzed using ion chromatography (Dionex DX-100). Ca, Na, Mg, K, Si and Sr were measured using an ICP-MS HP 4500 following laboratory standard methods (Bouhnik-Le Coz et al. 2001). The analytical uncertainty was about 5% for major anions and cations. All analyses were performed at the Geosciences Rennes Laboratory.

Isotopic analyses

Two field studies were carried out: the first one in April 2004 before pumping was resumed, and the second one in march 2005 in Pz4, Pz1 and in the pumping well, approximately 1 year after the pumping was resumed. The $\delta^{34}S_{\text{-}SO_4}$ of sulfates was measured from SO_2 obtained from CdS precipitated after sulfate reduction. Isotopic compositions were reported using the usual δ-scale in ‰ according to δ_{sample} (‰) = $\{R_{\text{sample}} - R_{\text{standard}}/R_{\text{standard}}\} \times 1{,}000$, where R is the $^{34}S/^{32}S$ atom ratio. The Canon Diablo Troilite standard was used for S isotopes. $\delta^{18}O_{\text{-}SO_4}$ was determined from the CO_2 produced by the reaction of $BaSO_4$ with C at 1,050°C, and reported using the usual δ-scale with the V-SMOW standard. The uncertainty for these two analyses was about ± 0.3‰. Analyses were performed in the BRGM laboratory.

CFC analyses

Chlorofluorocarbons (CFCs) are man-made compounds, produced since the 1930s and used as refrigerants, solvents, propellants and blowing agents (Plummer and Busenberg 2000). The CFC concentration in groundwater was converted into equivalent atmospheric concentration using Henry's law (Bu and Warner 1995; Warner and Weiss 1985). Atmospheric CFC concentrations obtained in this study were compared to the atmospheric evolution curve, to determine the date of recharge and thus the groundwater residence time (see Plummer and Busenberg 2000; Höhener et al. 2003 for a review). The CFC analytical methodology was adapted from Pruvost et al. 1999. CFC concentrations were obtained by degassing water samples by N_2 stripping. Gases were trapped in a stainless-steel tube filled with Porasil C and maintained at – 100°C in an ethanol bath. After 15 min of preconcentration, gases were injected into a gas chromatograph equipped with an electron capture detector (GC-ECD) by plunging the trap into boiling water. The analytical uncertainty was about 1 year for CFC-11 and CFC-12, and about 2 years for CFC-113 (Labasque 2006). Two hundred and fifty CFC analyses were carried out in the Geosciences Laboratory, and 70% of the groundwater samples were dated with at least two CFC species (with some samples possibly contaminated by one or two CFCs, or CFC-11 being unusable due to bacterial degradation in reducing conditions). For these samples, the mean observed standard deviation was 1.7 year. The global uncertainty on age, including sampling, analysis, selection of the recharge temperature in Henry's law, and dispersion–adsorption effects, was estimated to ± 2 years from these results. Nevertheless, groundwater age obtained through CFC analyses is an apparent age that may differ from the true mean groundwater age in the case of mixing processes (Weissmann et al. 2002).

Results

Hydrogeology

A pumping test was carried out during autumn 2000 to characterize the recharge area around the pumped well. The pumping rate was about 20 $m^3\ h^{-1}$ and was maintained for 2 days. Evolution of the water table from monitored wells is shown in Fig. 2. Both wells Pz3 and Pz1 strongly reacted to the pumping. Pz4 and Pz2 did not seem to be influenced by pumping in the pumped well. A preferential flux zone was drawn from the pumping test results. This zone is oriented North 60 and intersects Pz3, Pz1 and the pumped well (Fig. 1). In the area, geology indicates curve faults oriented N70–N90°E. These faults are interpreted as conjugate structures of a major shear zone (North Armorican shear zone—see Chantraine et al. 2001 for precise geological context) (Trautmann et al. 2000). Despite the absence of clear evidence, this preferential flow path has been related to the existence of a fault in the bedrock (Geoarmor 2000, 2002).

Groundwater geochemistry

For each well, most chemical species remain relatively stable with time with a variation range generally lower than 10% (Table 2). Only nitrate and sulfate present extremely high variations with time within some wells (Pz1, Pz4, and Pz2). They will thus be investigated separately. However, the highest element concentration differences are observed between wells (nearly 60% in some cases for stable species). This indicates that spatial variations are more important than temporal ones. The three wells located along the preferential flow path (Pz1, Pz3 and the pumped well—Fig. 1) exhibit a similar geochemistry for relatively conservative elements (Cl and cations) (Table 2). The Pz4 well, located upstream, shows the lowest mineralization. Concentrations in Pz2 are intermediate between Pz4 and the other three wells (Fig. 3).

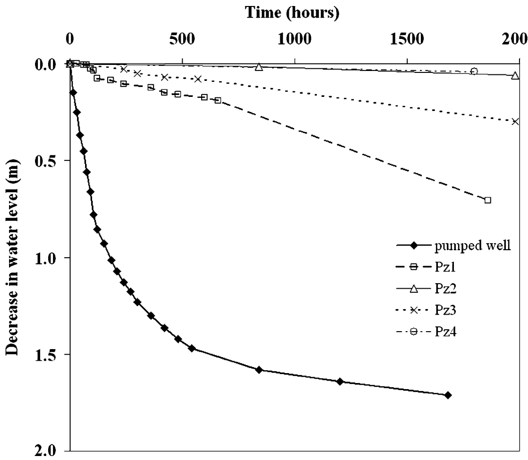

Fig. 2 Evolution of the water level during the 2-day pumping test (November 2000). The last points were measured at the end of pumping test (data from Geoarmor 2000)

Regarding the reactive species (nitrate and sulfate), a strong variability is observed not only in space but also in time (Fig. 4, Table 2). Pz1 shows the highest variability with sulfate decrease and nitrate increase as the water level decreases. To a lesser extent, in Pz4, the nitrate concentration increases and the sulfate concentration decreases during the investigated period. On the contrary, Pz3 and the pumped well present stable (like conservative elements) high nitrate and low sulfate concentrations.

Sulfate isotopic analyses show two clear trends: (1) δ^{34}S increases with increasing nitrate concentration and decreases with increasing sulfate concentration (Fig. 5a, b), and (2) a positive correlation is observed between the studied S and O isotopic ratios of sulfate (Fig. 5c). Whereas the pumped well presents little isotopic variations between the two sampling periods, Pz1 and Pz4 develop in an opposite way, even though these two wells present increasing nitrate concentrations. For Pz1, $\delta^{34}\text{S}_{\text{-SO}_4}$ and $\delta^{18}\text{O}_{\text{-SO4}}$ increase (by about 3‰) between the first and the second sampling dates while a limited decrease in $\delta^{34}\text{S}_{\text{-SO}_4}$ is observed in Pz4 (by about 1‰, close to the analytical uncertainty) and $\delta^{18}\text{O}_{\text{-SO}_4}$ decreases by nearly 2‰.

Groundwater apparent age

Groundwater apparent residence times obtained through CFC analyses are given in Table 3. These analyses were carried out during a low water table period. Data from the CFC-12 analysis were not used for the Pz2 and Pz4 apparent age determination because of concentrations exceeding equilibrium with present atmospheric concentrations. For these two wells, CFC-11 and CFC-113 indicate a recharge date between 1977 and 1982, i.e. a groundwater apparent age of about 25 ± 2 years prior to pumping. After pumping initiation, the CFC-113 analysis in Pz4 indicates an earlier recharge date (apparent age near 19 ± 2 years). Water in Pz3 has been recharged

Table 2 Data collection

Piezo	Date	Water table (m)	Conductivity (μS cm^2)	pH	O_2 (mg/l)	Eh (mV)	DOC	Cl (mg/l)	NO_3 (mg/l)	SO_4 (mg/l)	Si (mg/l)	Br (mg/l)	K (mg/l)	Ca (mg/l)	Na (mg/l)	Mg (mg/l)	Sr (ppb)	d^{34}S-SO_4 (‰)	d^{18}O-SO_4 (‰)
Pumped well	Dec-03	n.a.	420	6.9			< d. l.	50.95	62.63	18.06	5.57	0.15	2.20	37.20	24.76	17.07	107.20	11.3	4.6
	Apr-04	n.a.	394	6.3				49.74	59.09	17.30	5.44	0.12	1.65	30.02	22.25	14.77	100.65		
	Jun-04	n.a.	415	6.6		102		50.60	59.63	18.43		0.13							
	Sep-04	n.a.						50.91	60.22	18.33		0.10							
	Feb-05	n.a.	411					50.39	55.45	20.04		0.13							
	Apr-05	n.a.																11.0	4.4
Pz1	Dec-03	1.34	385	6.3			< d. l.	49.54	6.88	63.37	5.28	0.13	2.17	28.04	24.45	14.19	86.59	5.1	0.9
	Apr-04	n.a.	379	5.9		210		49.68	8.60	63.33	5.58	0.13	2.04	25.74	22.07	12.34	99.65		
	Jun-04	3.45	393	6.5	3.7	119		49.85	41.09	38.60		0.14							
	Oct-04	3.75	391	6.0				48.24	48.38	31.02	5.62		2.74	26.83	22.52	13.12	94.47		
	Feb-05	3.34	380					48.46	43.72	32.89		0.13							
	Apr-05	n.a.																7.2	4.0
Pz2	Dec-03	6.36	345	6.4			< d.l.	40.46	18.37	42.48	7.18	0.09	4.38	17.57	23.96	10.21	53.41	7.7	2.9
	Apr-04	n.a.	335	5.9		170		41.98	7.76	50.57	7.06	0.12	3.84	15.95	20.64	8.07	57.37		
	Jun-04	6.12	330	5.8	2.8	128		41.88	8.51	49.04		0.10							
	Oct-04	6.43	353	6.0				41.98	10.19	44.32	7.53		3.86	16.25	23.39	9.08	55.17		
	Feb-05	6.3	328					41.70	14.07	40.60		0.11							
Pz3	Dec-03	6.8	408	6.3			< d.l.	51.98	63.31	19.17	5.39	0.12	1.58	28.14	24.12	16.96	86.93		
	Apr-04	n.a.	400	6.1		220		51.23	59.93	19.27	6.24	0.12	1.58	26.68	23.85	15.67	90.75		
	Jun-04	7.41	330	6.2	6.9	129			58.31	19.03		0.12							
	Oct-04	8.18	376	6.1				54.88	49.80	17.23	5.32	0.11	1.47	22.38	22.70	13.55	78.82		
	Feb-05	7.51	391					52.46	54.10	18.61									
Pz4	Dec-03	9.85	276	6.6			< d.l.	25.87	11.08	25.28	8.11	0.08	2.11	14.81	20.13	8.33	40.00	9.6	6.1
	Apr-04	n.a.	297	6.3				31.73	23.20	17.15	7.89		2.57	14.73	19.97	8.18	44.82		
	Jun-04	9.31	301	6.7	4.8	126		34.82	29.30	15.29		0.08							
	Oct-04	9.73	306	6.1				36.31	30.28	14.87	6.62		2.25	14.84	20.24	8.27	45.51		
	Feb-05	9.6	297					33.65	25.14	18.27		0.10							
	Apr-05	9.52																8.9	4.4

between 1981 and 1987, which leads to an apparent age of 21 ± 3 years. The pumped water is geochemically similar to the Pz3 water and has been recharged between 1983 and 1987, indicating an apparent age of 20 ± 2 years according to the three CFC measurements. All CFC concentrations in Pz1 are in agreement with a recharge date in the 1980s but with a large variation. Integration of the three CFC data indicates a recharge date between 1980 and 1989 with an apparent age of 20 ± 5 years for this well. Low nitrate concentrations indicate existence of denitrification processes that can be coupled with CFC-11 degradation. In this case, CFC-11 data must have a greater uncertainty. When the CFC-11 concentration is not taken into account, the CFC analysis indicates a recharge between 1985 and 1989 with an apparent age for Pz1 of 18 ± 2 years.

Groundwater apparent age can be modified by processes such as matrix diffusion (Cook et al. 2005) or mixing of waters of different ages (Weissmann et al. 2002). In this study, however, the CFC data clearly indicate that (1) these waters contain a significant fraction of modern water (recharged after 1950), (2) the apparent age of waters flowing in the preferential flow zone (Pz3, Pz1, and the pumped well) is slightly younger than waters outside this zone (Pz4 and Pz2), and (3) the apparent age in all samples is not significantly different after several months of pumping (though it may have been prior to pumping, for example in Pz4).

Discussion

Physical processes and water composition

Although the investigated area is small and all the wells were drilled in the same geological weathered formation, the geochemical results show a high spatial variability. Cl and cations present an almost 2-fold concentration increase between the Pz4 low-mineralized water and the preferential flow path waters (Pz1, Pz3 and the pumped well) (Fig. 3). An explanation for the spatial heterogeneity was searched for in the initial groundwater chemistry acquisition (evapotranspiration processes) as well as in mixing mechanisms.

Water chemistry acquisition and evapotranspiration

Groundwater solutes are the result of rainwater concentration in soil through evapotranspiration and input of elements through rock weathering and clay exchange and/or anthropogenic activities. A large range of chloride concentrations is observed in the site, from 25–52 mg/l for example for a unique sampling date. Concentrations

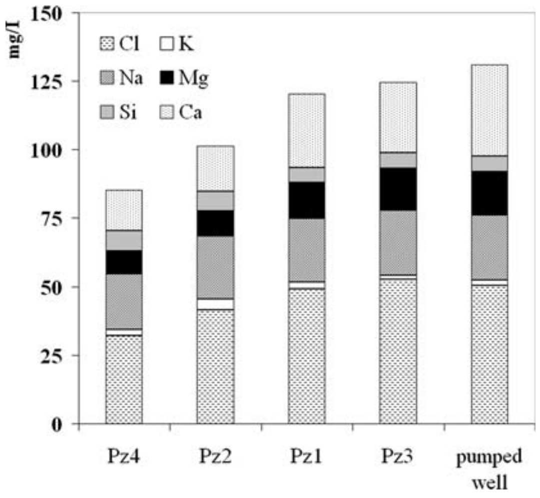

Fig. 3 Comparison of the December 2003 concentrations for site groundwaters

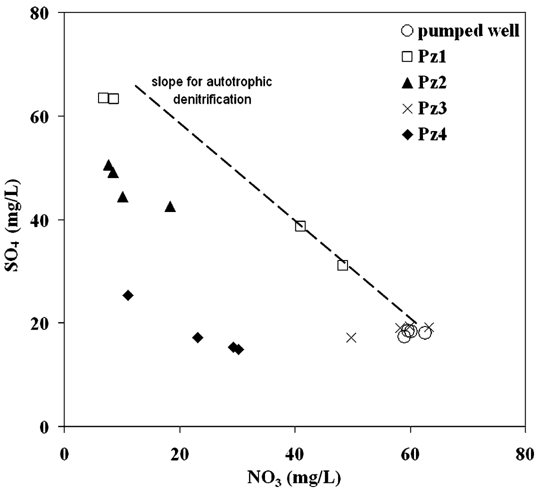

Fig. 4 NO_3 vs. SO_4 diagram

observed in Pz3 and the pumped well reflect commonly observed concentrations in rural areas where agricultural activity is intensive (Honisch et al. 2002; Whitehead et al. 2002). Agricultural inputs are homogeneous at the scale of the investigated site and cannot explain the lower concentrations observed in Pz4 well. Different hypotheses can explain the differences observed in water mineralization during the December 2003 campaign:

(1) In Britanny, the temperate climate leads to evapotranspiration rates that range from 50 to 60% of the precipitations. With annual mean Cl concentrations in rainwater ranging from 10 to 16 mg/l (Clément et al. 2003; Legout 2006; Martin et al. 2004), chloride concentrations between 20 and 40 mg/l can be expected. When evapotranspiration occurs, the proportion between conservative ions remains stable and merges with the evaporation line in a graph. Br/Cl and Na/Cl ratios are presented in Fig. 6a, b. As shown, the ratios differ for each well, which indicates that the range of mineralization cannot result from a variation in evapotranspiration intensity in the site.

(2) In some cases, a mixture of pre-1950 waters (CFC-free) and recent waters can lead to differences between apparent and true ages (Plummer et al. 2001). For water from the preferential flow path, nitrate concentration and its evolution with time in the pumped well (Fig. 1) are in agreement with the apparent age (no mixing): agricultural intensification in Brittany began during the 80s and was accompanied by high nitrate loads. For Pz2 and Pz4, the low nitrate concentration in an agricultural area can be surprising and can be interpreted as a mixture between old and more recent waters. In this case the apparent age will differ from the true mean age of water. Whereas CFC concentrations can be modified by mixing (diluted), CFC ratios are not modified by mixing and allow in a binary mixture to determine the age of the young water (Plummer et al. 2001). The CFC-11/CFC-113 ratio in Pz4 and Pz2 agrees with a

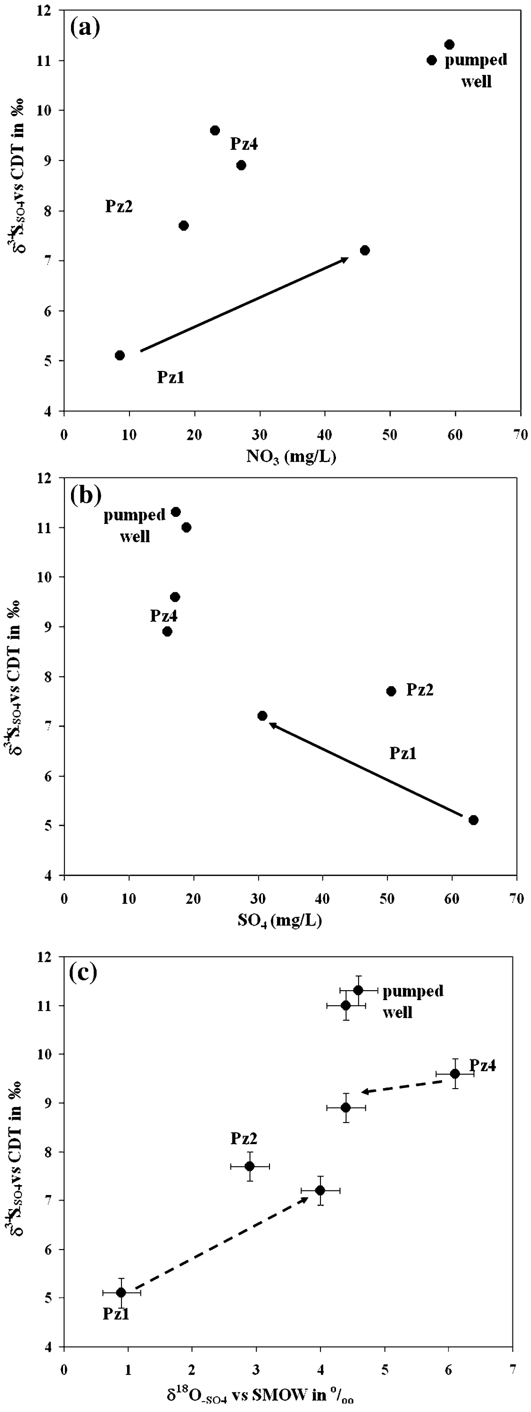

Fig. 5 Isotopic results: (**a**) $\delta^{34}S_{-SO_4}$ vs. NO_3, (**b**) $\delta^{34}S_{-SO_4}$ vs. SO_4 and (**c**) $\delta^{34}S_{-SO_4}$ vs. $\delta^{18}O_{-SO_4}$ (error bars represent analytical uncertainty) diagrams. Arrows represent the evolution of Pz4 and Pz1 between the April 2004 sampling and the March 2005 sampling

Table 3 Results of chlorofluorocarbon analyses (pptv is obtained by converting water concentration using Henry's law for a recharge temperature of 12°C)

Well	Date	CFC-12		CFC-11		CFC-113	
		pptv*	Date	pptv*	Date	pptv*	Date
pz4	18/11/2004	736	c	144	1977	28.6	1982
	18/11/2004	708	c	149	1978	29.1	1982
	28/04/2005	895	c	162	1979	49.9	1986
pz2	18/11/2004	792	c	138	1977	28.1	1982
	18/11/2004	778	c	143	1977	32.2	1983
	14/01/2005	861	c	140	1977	25.7	1982
	14/01/2005	768	c	134	1977	22.3	1981
pz3	18/11/2004	347	1982	171	1980	50.9	1987
	18/11/2004	362	1983	179	1981	42.8	1985
Pumped well	13/01/2005	442	1987	202	1983	47.6	1986
pzl	02/02/2005	472	1989	168	1980	42.0	1985

"c" indicates contaminated water (concentration exceeding equilibrium with atmosphere)

* pptv = parts solute per trillon parts solution by volume

20–25 years old water (ratio ranging from 4.9 to 5.0 for a theoretical value from 1984 to 1986 between 4 and 6) and does not indicate occurrence of mixing in this well. Low-mineralized waters observed in Pz4 and Pz2 do not result from a mixing between an old low-mineralized and a recent high-mineralized water.

(3) Low-mineralized waters can represent either old or young waters that might be less influenced by agricultural loads. According to CFC analyses, the Pz4 water is 5 years older than the Pz3 and pumped well waters (i.e. preferential flow path), and may represent the signature of agricultural activities of the early 1980s. Agricultural practices have remained intensive over the past decades and a 5-year difference cannot explain a difference of 30 and 20 mg/l in nitrate and chloride concentrations, respectively.

(4) The Pz4 mineralization can be representative of the water flow path heterogeneity in the vadose zone. In heterogeneous soils, water can bypass most parts of the profile, flowing along fissures and cracks (Beven and Germannn 1982). Water often gets its solutes while percolating in the first few meters of soil. The bypass of the soil and unsaturated zone results in low-mineralized water (Legout et al. in prep in Legout 2006). The interface between the weathered part and the fractured part of the aquifer constitutes a permeability barrier where this rapidly recharged and low-mineralized water is stored before moving laterally or infiltrating downward into the fractured part.

The difference between the investigated wells results from a higher influence of agricultural loads, related to the influence of slower recharge processes in a zone that has been identified as a preferential flow path from hydrogeological investigations. The residence time difference, induced by these two hydrological contexts related to the aquifer heterogeneity, is 5 years.

Mixing processes

The Pz2 water often presents low concentrations intermediate between those observed in the Pz4 and Pz3 waters. The variation in the evapotranspiration degree cannot be the only explanation for these concentrations in Pz2 (Fig. 6). The possibility that Pz2 may result from a mixing between Pz3 and Pz4 waters was tested according to Eq. 1:

$$[\mathrm{Pz2}] = x[\mathrm{Pz3}] + (1-x)[\mathrm{Pz4}] \tag{1}$$

where x represents the mixing ratio.

Results (Table 4) show a relatively good agreement between chloride and bromide, which indicates that the mixing hypothesis is valid.

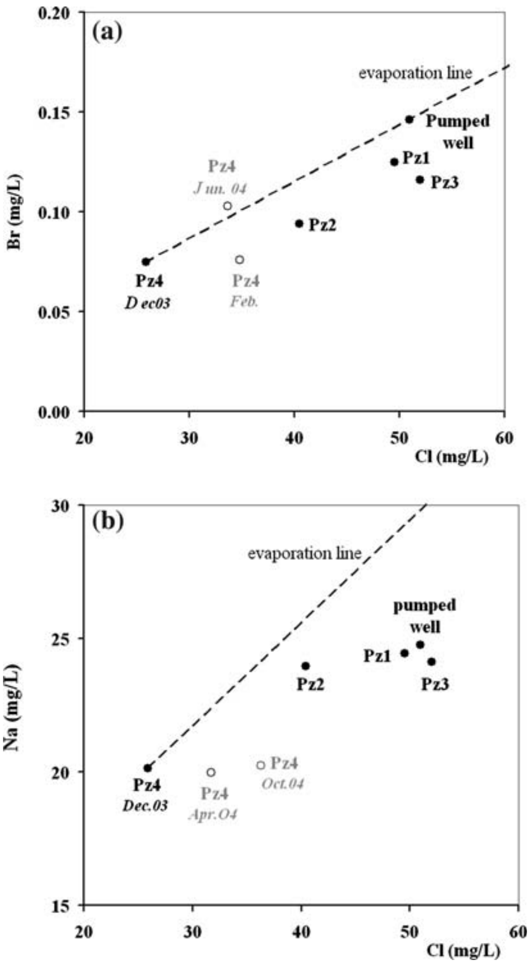

Fig. 6 (**a**) Br/Cl and (**b**) Na/Cl diagrams. The dashed line represents the effect of evaporation on the Pz4 water chemistry (the nearest to rainfall)

According to the most conservative anions (Cl and Br), Pz2 always includes at least 50% of the Pz4 water before pumping initiation (December 2003 and April 2004). The influence of Pz4 in the Pz2 water chemistry is also shown by the CFC-12 analysis, which shows high concentrations in both wells.

Physical parameters are of critical importance in the control of aquifer hydrochemistry. The water chemical composition is the result of three major components: (1) surface loadings from precipitation or anthropogenic activities, (2) evapotranspiration processes in the root zone and (3) transfer into the vadose zone. All these processes are spatially variable. However, water–rock interaction parameters (for example, reaction time and reactional surface) are stable with time as long as the aquifer properties do not change. Within the aquifer, channeling effects lead to highly contrasted chemical compositions that are spatially very close. The mixing processes related to the heterogeneity structure then also become a controlling parameter. However, evapotranspiration and mixing processes cannot explain the great variability observed in wells especially for reactive species like nitrate and sulfate.

Denitrification and sulfide oxidation, major biogeochemical processes before pumping initiation

Pz1 is located in a wetland and intercepts water flowing below and through this area. This well has a chemical composition similar to that of Pz3 and the pumped well, indicating a common origin, but it presents a high variability in sulfate and nitrate concentrations (Fig. 4, Table 2). In December 2003, the water table was high and the zone was flooded (Table 2). A 90% decrease in the nitrate content is observed between Pz3 and Pz1. Underneath the wetland, the aquifer becomes captive and denitrification develops in relation to the redox sequence (Stumm and Morgan 1996). In absence of molecular oxygen, nitrate becomes the major oxidant of organic mater according to the heterotrophic denitrification process (Eq. 2)

$$4NO_3^- + 5CH_2O + 4H^+ \rightarrow 2N_2 + 5CO_2 + 7H_2O. \quad (2)$$

Heterotrophic denitrification implies organic carbon availability. In Pz1, however, dissolved organic carbon analyses show concentrations below the detection limit (< 1 mg/l—Table 2). The sulfate concentration is relatively high in Pz1 (three times higher than in Pz3). A high sulfate concentration associated with a low nitrate concentration is often attributed to the autotrophic denitrification process (Eq. 3) (Kölle et al. 1985; Pauwels et al. 2000; Pauwels et al. 2001; Tarits et al. 2006). In crystalline rocks, sulfides can be

Table 4 Data used for the determination of the mixing ratio (x) in Pz2

	Date	Pz4	Pz3	Pz2	x
Cl	Dec-03	25.87	51.98	40.46	0.56
	Apr-04	31.73	51.23	41.98	0.53
	Oct-04	36.31	54.88	41.98	0.31
	Feb-05	33.65	52.46	41.70	0.43
Br	Dec-03	0.08	0.12	0.09	0.46
	Jun-04	0.08	0.12	0.10	0.65

widely distributed in fractures and in the rock matrix. These minerals can react with nitrate in an oxido-reduction process when oxygen concentration becomes very low. This process leads to a great interaction between the biogeochemical cycles of the two elements (N and S)

$$5FeS_2 + 14NO_3^- + 4H^+ \rightarrow 7N_2 + 10SO_4^{2-} + 5Fe^{2+} + 2H_2O. \quad (3)$$

This biologically catalyzed chemical reaction might induce a slight fractionation process of sulfur and oxygen. However, $\delta^{34}S\text{-}_{SO_4}$ of the produced sulfate is close to that of the original sulfur (Clark and Fritz 1997; Feast et al. 1997; Strebel et al. 1990; Toran and Harris 1989). Furthermore, $\delta^{34}S\text{-}_{FeS_2}$ in crystalline rocks is usually low although the range of observed values may vary (between − 13 and + 6.9‰ in Brittany—Durand 2005; Pauwels et al. 2000) and the sulfates produced from pyrite dissolution can be expected to present negative or low $\delta^{34}S\text{-}_{SO_4}$. $\delta^{34}S\text{-}_{SO_4}$ in Pz1 is the lowest value observed in the aquifer, which is in agreement with a sulfide oxidation.

According to Eq. 4, $\delta^{18}O\text{-}_{SO_4}$ of the sulfate produced by atmospheric oxidation will depend on the contribution of two oxygen sources (water or atmospheric oxygen) (Van Everdingen and Krouse 1985)

$$\delta^{18}O\text{-}_{SO_4} = f_{H_2O}(\delta^{18}O\text{-}_{H_2O} + \varepsilon^{18}O_{SO_4-H_2O}) + f_{O_2}\left[0.825(\delta^{18}O\text{-}_{O_2} + \varepsilon^{18}O_{SO_4-O_2}) + 0.125(\delta^{18}O\text{-}_{H_2O} + \varepsilon^{18}O_{SO_4-H_2O})\right] \quad (4)$$

In Pz1, the strict application of Eq. 4 indicates an atmospheric oxygen contribution close to 20–30%, larger than expected in an anaerobic medium. Atmospheric oxygen does not seem to be the sulfide oxidant in Pz1. In the case of an oxidation coupled with denitrification in an anaerobic medium, atmospheric oxygen will be replaced by nitrate oxygen. Equation 4 must be modified and $\delta^{18}O\text{-}_{NO_3}$ and $\varepsilon^{18}O_{SO_4-NO_3}$ must be known. Whereas $\delta^{18}O\text{-}_{NO_3}$ can be evaluated with data from other studies, the enrichment factor ($\varepsilon^{18}O_{SO_4-NO_3}$) is unknown. The contribution of nitrate to sulfide oxidation and the absolute evidence of autotrophic denitrification cannot be obtained.

Autotrophic denitrification involves a relationship between sulfur and nitrogen cycles developing in the aquifer. According to the Eq. 3 stoichiometry, the excess of sulfate and the lack of nitrate must be correlated. For December 2003, sulfate concentrations exceeded expected concentrations through evapotranspiration processes by 45 mg/l only. This can be explained by an autotrophic denitrification leading to a decrease of about 40 mg/l of nitrate in Pz1 as compared to the Pz3 nitrate concentration. However, the difference between Pz3 and Pz1 is higher than this value and some nitrate (approximately 15 mg/l) must have been depleted through another process. Dilution by nitrate-free water coming from the upper wetland or heterotrophic denitrification might explain such differences. Whereas isotopic data suggest an autotrophic denitrification, chemical data confirm this process in Pz1.

Nitrate and sulfate concentrations in Pz2 before pumping initiation (December 2003 and April 2004) cannot only be the result of a mixing between Pz4 and Pz3, as the sulfate concentration exceeds the concentration of the two end-members and the nitrate concentration is the lowest one (Fig. 4, Table 2). According to the low dissolved carbon concentration (below the detection limit), heterotrophic denitrification cannot explain the low nitrate concentration. As for Pz1, relatively low isotopic values also support an autotrophic denitrification process (Fig. 5). Actually, the sulfate concentration is close to the one expected for an autotrophic denitrification of water obtained by the mixing of Pz4 and Pz3 in the 50/50 proportion (for the December 2003 concentrations).

The Pz4 low nitrate concentration is explained by fast transfer through the vadose zone and there is no evidence of denitrification in this well. However, δ^{18}O-$_{\mathrm{SO_4}}$ is the highest value observed in the site. In this well, the sulfur cycle must be controlled by a specific biogeochemical process. However, the δ^{18}O-$_{\mathrm{SO_4}}$ value is mainly controlled by the biogeochemical process leading to the sulfate production and the available oxygen source. Water flowing in Pz4 has been interpreted as rapidly recharged water. In this case, atmospheric oxygen can move deeper into the soil profile than in the case of piston flow (transfer time is not sufficient for a total oxygen consumption). In an aerobic medium, sulfides can be oxidized by atmospheric oxygen (Moses et al. 1987):

$$\mathrm{FeS_2} + 7/2\mathrm{O_2} + \mathrm{H_2O} \rightarrow \mathrm{Fe^{2+}} + 2\mathrm{SO_4^{2-}} + 2\mathrm{H^+}. \tag{5}$$

According to Eq. 4, molecular oxygen, with δ^{18}O-$_{\mathrm{SO_4}}$ near + 23‰, can oxidize rock sulfides and produce sulfate with high δ^{18}O-$_{\mathrm{SO_4}}$ values. In this case, the calculated atmospheric oxygen contribution is around 70% in the newly formed sulfate. Usually, sulfide oxidation is accompanied by a decrease in δ^{34}S-$_{\mathrm{SO_4}}$. In Pz4, this decrease can be masked by natural variations in sulfide isotopic values or by the mixing of sulfates from different origins. The Pz4 sulfate isotopic ratios before pumping initiation are interpreted as the result of the aerobic oxidation of sulfide-bearing minerals.

Pumping, a disturbance of the biogeochemical processes

Pumping, which induces a change in water flux velocity and pathway, constitutes an interesting disturbance of the initial physical parameters. In the investigated site, the chemical evolution of water after pumping initiation has been monitored in order to relate chemical evolution to physical parameters.

As soon as pumping starts, the Pz4 water chemistry evolves towards pumped well-type waters (Figs. 4, 5). A mixing of the Pz4 low-mineralized water with more concentrated waters seems to be enhanced by pumping. Waters influenced by anthropogenic activities like in Pz3 and the pumped well, not only flow along the fault-zone but also in the weathered part of the aquifer as indicated by the existence of mixing in Pz2 prior to pumping. This water seems stimulated by pumping and invades all the weathered part of the aquifer (and not only Pz2), in turn mixing with pre-existing waters. The chemical data in Pz4 clearly support the existence of a mixing process. The isotopic data cannot be explained only by mixing, thus indicating the existence of biogeochemical processes affecting the sulfate concentration. While δ^{34}S-$_{\mathrm{SO_4}}$ remains almost constant (mineralogically influenced), δ^{18}O-$_{\mathrm{SO_4}}$ presents a different value closer to anthropogenic influenced waters before and after pumping initiation (Fig. 5c). The decrease in δ^{18}O-$_{\mathrm{SO_4}}$ indicates a change in O-donors in the sulfide oxidation process. Before pumping, molecular oxygen is the sulfide oxidant, and when pumping starts, mixing is enhanced and nitrate concentration increases. Oxidation of sulfides by nitrates explains the shift in δ^{18}O-$_{\mathrm{SO_4}}$.

Since pumping starts, nitrate concentration increases and sulfate concentration and water level decrease (Table 2). The evolution of the groundwater chemistry can be explained by two processes: (1) influence of a pumping-induced mixing and/or (2) classical wetland chemistry evolution that leads to reduced biogeochemical processes with a low water table.1

(1) Pz1 is strongly related to the pumped well (Fig. 2). As pumping enhanced the mixing with anthropogenic waters in Pz4, the same process can be expected to occur in Pz1. According to this hypothesis, observed nitrate and sulfate concentrations after pumping initiation are the results of a mixing between anthropogenic nitrate-rich

waters of the preferential flow path and denitrified water. Whereas the chemical data (sulfate and nitrate) are in agreement with a 30/70 mixing between denitrified and anthropogenic waters, the isotopic data do not confirm this hypothesis. Without any biogeochemical process, isotopic compositions mix conservatively (Kendall and Caldwell 1998). The calculation of mixing with $\delta^{18}O_{\text{-}SO_4}$ or $\delta^{34}S_{\text{-}SO_4}$ indicates inconsistent proportions of denitrified water: near 16% with $\delta^{18}O_{\text{-}SO_4}$ and 66% with $\delta^{34}S_{\text{-}SO_4}$. Mixing cannot be the only process explaining changes in the Pz1 water chemistry.

(2) In wetlands, denitrification processes have been shown to be related to the water level: carbon availability is maximal in the upper part of soils, so when the water table is lowered heterotrophic denitrification is reduced (Burt et al. 1999; Clément et al. 2002; Hill et al. 2004; Sanchez-Peres and Tremolieres 2003). Increasing nitrate concentrations with lowering water table may be attributed to a reduced carbon availability with depth leading to a reduction in the heterotrophic denitrification processes. However, the isotopic data indicate the autotrophic nature of denitrification in the site but evolution with time of nitrate and sulfate concentrations do not follow the theoretical slope for the autotrophic denitrification only. Occurrence of heterotrophic and autotrophic denitrifications in Pz1 might explain the slope of the nitrate–sulfate relationship observed (Fig. 4) is slightly different from the slope expected for autotrophic denitrification only as regards the Eq. 3 stoichiometry. Part of the nitrate increase can be attributed directly to a reduced heterotrophic denitrification due to low carbon availability. The decrease in sulfate concentration and the increase in $\delta^{34}S_{\text{-}SO_4}$ and $\delta^{18}O_{\text{-}SO_4}$ after pumping is resumed indicate that the autotrophic denitrification process is also limited. Denitrification (autotrophic as well as heterotrophic) implies anaerobic conditions to develop. When the water table is low, the unsaturated zone dries out and bacterial communities die. Without bacteria in the upper part of the soil, atmospheric O_2 can penetrate deeper in the unsaturated zone, reach the water table and diffuse in groundwater. Because of the more oxidant power of oxygen compared to nitrate, the autotrophic denitrification processes are stopped and nitrate concentrations increase.

Pz1 is the well closest to the pumped well, and the lowering of the water table can be either attributed to seasonal variations or to pumping initiation. If pumping is the origin of the water table lowering, the latter might remain low as long as pumping is active, preventing denitrification.

Whereas pumping initiation enhances mixing in all the area between anthropogenic (nitrate-rich) waters and pre-existing water, this physical process cannot explain all the observed changes in water chemistry.

Influence of the rock physical heterogeneity on the biogeochemical processes

In all cases, the denitrification process is never complete. This phenomenon can be attributed to the non-linearity of the denitrification process. Usually assumed first-order kinetics (Frind et al. 1990; Pauwels et al. 1998; Schürmann et al. 2003) leads to a strong lowering of the reaction after a few days (Tarits et al. 2006). The incomplete denitrification process may indicate that, although the apparent groundwater residence time in this site is in the order of 20 years, the contact time at the water/mineral-bacteria interface ranges from a few days to a few weeks.

In heterogeneous crystalline aquifers, porosity ranges from large fractures to matrix microporosity (fissures, cracks, grain joints,...) (Aquilina et al. 2004; Bonnet et al. 2001; Bour et al. 2002; Segall and Pollard 1983). Biogeochemical reactions need precise conditions to develop but may take place in microsites (Luo et al. 1999): in a global oxidizing medium, reducing conditions may develop in dead-end pores where water velocity is low. Autotrophic denitrification processes, which involve a reaction between minerals and water, need a large water–rock surface to develop. In fractured rocks, the high velocity associated with fractures and preferential fluxes leads to a simple transfer of water through the reservoir without any significant biogeochemical changes. However, the slow circulation in the matrix allows biogeochemical processes, such as denitrification, to exist, which can drastically modify hydrochemistry (Berkowitz 2002; Gouze et al. 2003; Neuman 2005; Tsang and Neretnieks 1998). The groundwater chemical composition in a well is determined by the contribution of these two types of porosity to the global water flux. The result is the mixing between water denitrified during circulation in the matrix and nitrate-rich water transferred through the fracture.

When pumping starts, the natural equilibrium is modified as indicated by changes in hydrochemistry. Pumping implies (1) a flux redistribution in fractures and favored changes in the relative contribution of each part of the fracture (the fracture itself or the matrix without any change in the water chemistry of each end-member) and /or (2) a change in water velocity leading to a lower time of contact between minerals and water, which implies less denitrified water flowing in the matrix. Whereas the mixing previously suspected in the paper (between anthropogenic and pre-existent waters) is at the site scale, the mixing between fracture and matrix waters is at a scale smaller than 1 m. For instance in Pz1, assuming that denitrification is still active in the matrix and that the proportion of fracture/matrix water is still similar, mixing at the site scale would have led to a conservative behavior of isotope ($\delta^{34}S_{\text{-}SO_4}$). Observed isotopic values, however, indicate that whereas a mixing at the site scale may also exist, the change in the Pz1 water chemistry can be explained by (1) a reduced contribution of the matrix (denitrified water) to the global flux or (2) a denitrification shutdown in the matrix.

Conclusion

Hydrogeological, chemical and isotopic studies of a superficial aquifer in crystalline rocks in Brittany allowed us to characterize the physical and biogeochemical processes enhanced by the rock physical heterogeneity, as well as the influence of an anthropic disturbance (like a pumping) on these processes.

Water channeling in the weathered part of the aquifer induces variable pathways in the unsaturated zone leading to the close presence of low- and high-mineralized waters (anthropogenic influenced waters) and contrasted redox conditions resulting in different biogeochemical processes. In rapidly recharged areas (Pz4), the presence of molecular oxygen in depth allows sulfide oxidation processes (70% of the oxygen atoms of the produced sulfate). In high-mineralized water, the observed biogeochemical processes are characterized by a strong interaction between nitrogen and sulfur cycles indicated by (1) an inverse correlation between the concentration of the two anions and (2) an atmospheric oxygen contribution, estimated by isotopic data, lower than 30% in sulfates produced by sulfur oxidation. Rock fracturation leads to an enhanced sulfide availability for a potential reaction with water as autotrophic denitrification. Whereas fracture water fluxes are often rapid, the transition layer, and its high porosity, represents the optimal microsite where biogeochemical processes coupled with minerals can develop.

The physical disturbance of water fluxes leads to a drastic modification of the groundwater chemistry. Mixing is enhanced in the site with an anthropogenic-water invasion in the low-mineralized area. Biogeochemical processes are also modified by pumping initiation: denitrification coupled or not with sulphide oxidation no longer occurs in the site. When pumping starts, the natural equilibrium is modified as indicated by changes in hydrochemistry. The pumping implies flux redistribution leading to a reduced contribution of the matrix reservoir or to less active biogeochemical processes in the matrix due to the change in the residence time of water in such a compartment.

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References

Aquilina L, de Dreuzy JR, Bour O, Davy P (2004) Porosity and fluid velocities in the upper continental crust (2 to 4 km) inferred from the injection tests at the Soultz-sous-Forêts geothermal site. Geochim Cosmochim Acta 68:2405–2415

Ayraud V (2006) Détermination du temps de résidence des eaux souterraines: application au transfert d'azote dans les aquifères fracturés hétérogènes. Memoires du CAREN n° 14, Rennes

Bennet PC, Hiebert FK, Robert Rogers J (2000) Microbial control of mineral-groundwater equilibria: macroscale to microscale. Hydrolgeol J 8:47–62

Berkowitz B (2002) Characterizing flow and transport in fractured geological media: a review. Adv Water Resour 25:861–884

Beven KJ, Germannn P (1982) Macropores and water flow in soils. Water Resour Res 18:1311–1325

Bonnet E, Bour O, Odling NE, Davy P, Main I, Cowie P, Berkowitz B (2001) Scaling of fracture system in geologic media. Rev Geophys 39:347–383

Bouhnik-Le Coz M, Petitjean P, Serrat E, Gruau G (2001) Validation d'un protocole permettant le dosage simultané des cations majeurs et traces dans les eaux douces naturelles par ICP-MS. Géosciences Rennes, Rennes

Bour O, Davy P, Darcel C, Odling NE (2002) A statistical scaling model for fracture network geometry, with validation on a multiscale mapping of a joint network (Hornelen Basin, Norway). J Geophys Res 107:2113. DOI 2110.2129/2001JB000176

Bu X, Warner MJ (1995) Solubility of chlorofluorocarbon 113 in water and seawater. Deep-Sea Res Pt I 42:1151–1161

Burt TP, Matchett LS, Goulding KWT, Webster CPH, Hancock NE (1999) Denitrification in riparian buffer zones: the role of floodplain hydrology. Hydrol Process 13:1451–1463

Cacas MC, Ledoux E, de Marsily G, Tillie B, Barbeau A, Durand E, Feuga B, Peaudecerf P (1990) Modelling fracture flow with a stochastic discrete fracture network: calibration and validation. Water Resour Res 26:479–489

Chantraine J, Egal E, Thiéblemont D, Le Goff E, Guerrot C, Ballèvre M, Guennoc P (2001) The cadomian active margin (North Armorican Massif, France): a segment of the North Atlantic Panafrican belt. Tectonophysics 331:1–18

Chen JY, Tang CY, Sakura Y, Kondoh A, Yu JJ, Shimada J, Tanaka T (2004) Spatial geochemical and isotopic characteristics associated with groundwater flow in the North China plain. Hydrol Process 18:3133–3146

Clark DI, Fritz P (1997) Environmental isotopes in hydrogeology. Lewis publishers, New York

Clauser C (1992) Permeability of crystalline rocks. Eos Trans Am Geophys Union 73:237–238

Clément J-C, Pinay G, Marmonier P (2002) Seasonal dynamics of denitrification along topohydrosequences in three different riparian wetlands. J Environ Qual 31:1025–1037

Clément J-C, Aquilina L, Bour O, Plaine K, Burt TP, Pinay G (2003) Hydrogeological flowpaths and NO_3^- removal rates within a riparian floodplain along fourth-order stream in Brittany (France). Hydrol Process 17:1177–1195

Cook PG, Love AJ, Robinson NI, Simmons CT (2005) Groundwater ages in fractured rock aquifers. J Hydrol 308:284–301

de Dreuzy JR, Darcel C, Davy P, Bour O (2004) Influence of spatial correlation of fracture centers on the permeability of two-dimensional fracture networks following a power law length distribution. Water Resour Res. W01502: DOI 10.1029/2003WR002260

Durand V (2005) Recherche multidisciplinaire pour caractériser deux aquifères fracturés : les eaux minérales de Plancoët en contexte métamorphique, et de Quézac en milieu carbonaté. Sciences de la Terre. Université de Pierre et Marie Curie – Paris VI

Feast NA, Hiscock KM, Dennis PF, Bottrell SH (1997) Controls on stable isotope profiles in the Chalk aquifer of north-east Norfolk, UK, with special reference to dissolved sulphate. Appl Geochem 12:803–812

Frind EO, Duynisveld WHM, Strebel O, Böttcher J (1990) Modeling of multicomponent transport with microbial transformation in groundwater: the Furhberg case. Water Resour Res 26:1707–1719

Geoarmor (2000) Etude hydrogéologique: relation captage/ruisseau de Quincampoix (report n° BL/GG-GR/00R1839). SIAEP de la région nord de Rennes

Geoarmor (2002) Etude de l'origine des chlorures présents dans l'eau du forage (report n° GG-FD/R2550). SIAEP de la Région Nord de Rennes, Betton

Gouze P, Noiriel C, Bruderer C, Loggia D, Leprovost R (2003) X-ray tomography characterization of fracture surfaces during dissolution. Geophys Res Lett 30:1267. DOI 1029/2002GL016755

Grassi S, Cortecci G (2005) Hydrogeology and geochemistry of the multilayered confined aquifer of the Pisa plain (Tuscany – central Italy). Appl Geochem 20:41–54

Hill AR, Vidon P, Langat J (2004) Denitrification potential in relation to lithology in five headwater riparian zones. J Environ Qual 33:911–919

Höhener P, Werner D, Balsiger C, Pasteris G (2003) Worldwide occurence and fate of chlorofluorocarbons in groundwater. Crit Rev Environ Sci Technol 33:1–29

Honisch M, Hellmeier C, Weiss K (2002) Response of surface and subsurface water quality to land use changes. Geoderma 105:277–298

Kelly WR (1997) Heterogeneities in ground-water geochemistry in a sand aquifer beneath and irrigated field. J Hydrol 198:15–176

Kendall C, Caldwell EA (1998) Fundamentals of isotope geochemistry. In: Kendall C, McDonnell JJ (eds) Isotope tracers in catchment hydrology. Elsevier Science B.V., Amsterdam, pp 51–86

Kölle W, Strebel O, Böttcher J (1985) Formation of sulphate by microbial denitrification in a reducing aquifer. Water Supply 3:35–40

Labasque T (2006) Analyse des CFC dans les eaux souterraines. Géosciences Rennes, Cahiers techniques de Géosciences Rennes, Rennes

Legout C (2006) Etude des mécanismes hydrogéologiques et biogéochimiques de la recharge des nappes libres. Mémoires du CAREN n° 16, Rennes

Legout C, Molénat J, Aquilina L, Gascuel Odoux C, Faucheux M, Fauvel Y, Bariac T (in prep) Solute transport in soil and weathered granite with fluctuating water table

Legout C, Molénat J, Lefebvre S, Marmonier P, Aquilina L (2005) Investigation of biogeochemical activities in the soil and unsaturated zone of weathered granite. Biogeochemistry 75:329–350

Little BJ, Wagner PA, Lewandowski Z (1997) Spatial relationships between bacteria and mineral surfaces. In: Banfield JF, Nealson KH (eds) Geomicrobiology: interaction between microbes and minerals. Mineralogical society of America, Washington, pp 5–31

Luo J, Tillman RW, Ball PR (1999) Factors regulating denitrification in a soil under pasture. Soil Biol Biochem 31:913–927

Mariotti A (1986) La dénitrification dans les eaux souterraines, principes et méthodes de son identification: une revue. J Hydrol 88:1–23

Martin C, Aquilina L, Gascuel Odoux C, Molénat J, Faucheux M, Ruiz L (2004) Seasonal and interannual variation of nitrate and chloride in stream water related to spatial and temporal patterns of groundwater concentrations in agricultural catchments. Hydrol Process 18:1237–1254

Molénat J, Gascuel Odoux C (2002) Modelling flow and nitrate transport in groundwater for the prediction of water travel times and of consequences of land use evolution on water chemistry. Hydrol Process 16:479–492

Molénat J, Davy P, Gascuel Odoux C, Durand P (1999) Study of three subsurface hydrologic systems based on spectral and cross-spectral analysis of time series. J Hydrol 222:152–164

Montoroi J-P, Robain H, Schmutz M, Martin C, Molénat J, Ruiz L (2001) Analyse d'un réseau piezométrique par imagerie électrique multi-électrodes (Bassin versant de Kerbernez, Bretagne). 3ème colloque GEOFCAN, Orléans

Moses CO, Nordstrom DK, Herman JS, Mills AL (1987) Aqueous pyrite oxidation by dissolved oxygen and by ferric iron. Geochim Cosmochim Acta 51:1561–1571

Neuman SP (2005) Trends, prospects and challenges in quantifying flow and transport trough fractured rocks. Hydrolgeol J 13:124–147

Parkin T (1987) Soil microsite as a source of denitrification variability. Soil Sci Soc Am J 51:1194–1199

Pauwels H, Kloppmann W, Foucher JC, Martelat A, Fritsche V (1998) Field tracer test for denitrification in a pyrite-bearing schist aquifer. Appl Geochem 13:767–778

Pauwels H, Foucher JC, Kloppmann W (2000) Denitrification and mixing in a schist aquifer: influence on water chemistry and isotopes. Chem Geol 168:307–324

Pauwels H, Lachassagne P, Bordenave P, Foucher JC, Martelat A (2001) Temporal variability of nitrate concentration in a schist aquifer and transfer to surface waters. Appl Geochem 16:583–596

Plummer LN, Busenberg E (2000) Chlorofluorocarbons. In: Cook PG, Herczeg AL (eds) Environmental tracers in subsurface hydrology. Kluwer Academic Publishers, Boston, pp 441–478

Plummer LN, Busenberg E, Böhlke JK, Nelms DL, Michel RL, Schlosser P (2001) Groundwater residence times in Shenandoah National Park, Blue Ridge Mountains, Virginia, USA: a multi-tracer approach. Chem Geol 179:93–111

Postma D, Boesen C, Kristiansen H, Larsen F (1991) Nitrate reduction in an unconfined sandy aquifer: water chemistry, reduction processes, and geochemical modeling. Water Resour Res 27(8):2027–2045

Pruvost J, Connan O, Marty Y, Le Corre P (1999) A sampling device for collection and analysis of volatile halocarbons in coastal and oceanic water. Analyst 124:1389–1394

Rosenberry DO (2003) The significance of ground water in small watershed studies. Ground Water 41:881–882

Sanchez-Peres JM, Tremolieres M (2003) Change in groundwater chemistry as a consequence of suppression of floods: the case of the Rhine flooplain. J Hydrol 270:89–104

Schramm A (2003) In situ analysis of structure and activity of the nitrifying community in biofilms, agregates and sediments. Geomicrobiol J 20:313–333. DOI 310.1080/01290450390241026

Schürmann A, Schroth MH, Saurer M, Bernasconi SM, Zeyer J (2003) Nitrate-consuming processes in a petroleum-contamined aquifer quantified using push-pull tests combined with 15N isotope and acetylene-inhibition methods. J Contam Hydrol 66:59–77

Segall P, Pollard D (1983) Joint formation in granitic rock of the Sierra Nevada. Geol Soc Am Bull 94:563–575

Shapiro SD, Rowe G, Schlosser P, Ludin A, Stute M (1998) Tritium-helium 3 dating under complex conditions in hydraulically stressed areas of a buried-valley aquifer. Water Resour Res 34:1165–1180

Strebel O, Böttcher J, Fritz P (1990) Use of isotope fractionation of sulfate-sulfur and sulfate-oxygen to assess bacterial desulfurication in a sandy aquifer. J Hydrol 121:155–172

Stumm W, Morgan JJ (1996) Aquatic chemistry: chemical equilibria and rates in natural waters. John Wiley and sons, New-York

Stutter MI, Deeks LK, Billett MF (2005) Transport of conservative and reactive tracers through naturally structured upland podzol field lysimeter. J Hydrol 300:1–19

Tarits C, Aquilina L, Ayraud V, Pauwels H, Davy P, Touchard F, Bour O (2006) Oxido-reduction sequence related to flux variations of groundwater from a fractured basement aquifer (Ploemeur area, France). Appl Geochem 21:29

Toran L, Harris RF (1989) Interpretation of sulfur and oxygen isotopes in biological and abiological sulfide oxidation. Geochim Cosmochim Acta 53:2341–2348

Trautmann F, Paris F, Carn A (2000) Carte géologique de la France au 1/50000. Feuille de Rennes no 317. BRGM, Orléans

Tsang C-F, Neretnieks I (1998) Flow channelling in heterogeneous fractured rocks. Rev Geophys 36:257–298

Van Everdingen RO, Krouse HR (1985) Isotope composition of sulphates generated by bacterial and abiological oxidation. Nature 315:395–396

Warner MJ, Weiss RF (1985) Solubilities of chlorofluorocarbons 11 et 12 in water and seawater. Deep-Sea Res 32:1485–1497

Weissmann GS, Zhang Y, LaBolle EM, Fogg GE (2002) Dispersion of groundwater age in an alluvial aquifer system. Water Resour Res 38:16-11–16-13

Whitehead PJ, Johnes PJ, Butterfield D (2002) Steady state and dynamics modelling of nitrogen in the river Kennet: impacts of land use change since the 1930's. Sci Total Environ 282–283:417–434

Wyns R, Baltassat J-M, Lachassagne P, Legchenko A, Vairon J, Mathieu F (2004) Application of magnetic resonance soundings to groundwater reserve mapping in weathered basement rocks (Brittany, France). Bull Soc géol Fr 175:21–34