

Denitrification processes in a schist aquifer: multi-isotope constraint applied to a field tracer test

Emmanuelle Petelet-Giraud^a, Marie Pettenati^b, Luc Aquilina^c, H el ene Pauwels^d, Wolfram Kloppmann^a, Alexandre Boisson^b, Eliot Chatton^c, Fr ed eric Mathurin^b

^a BRGM (French Geological Survey), Laboratory Division, BP 36009, 45060 Orleans, France;

^b BRGM (French Geological Survey), Water Environment and Ecotechnologies Division, BP 36009, 45060 Orleans, France

^c G eosciences Rennes, Universit e Rennes 1-CNRS, UMR 6118, 263 av du g en eral Leclerc, bat 15, 35042 Rennes Cedex, France

^d BRGM (French Geological Survey), Development Division, BP 36009, 45060 Orleans, France

Abstract

In low-permeability environments, the solutions of heat storage are still limited to the capacities of geothermal borehole heat exchangers. To optimize the performance of classical borehole heat exchangers, the possibilities of periodic storage of sensitive heat in "semi-open circulation" in a low-permeability environment is studied. In this paper we characterize the impact of water-rock interaction on water quality in the case of NO₃-rich water circulation in the hard rock aquifer of Naizin (Brittany) for heat storage purposes. This includes tracer tests experiment by injecting conservative and reactive tracers in the schist aquifer of Naizin in Brittany combined with a multi-isotopic approach in order to identify denitrification process.

Introduction

This study is part of a research project exploring the thermal aptitudes of permanent semi-open circulation wells for energy storage in a low-permeability environment such as hard rock. One aspect is to study the water-rock interactions that can modify the heat-exchange surface between water and rock over time thus changing the energy performance of the component. The hard-rock aquifer of Naizin with NO₃-rich water has been selected to characterize water-rock interaction during water circulation tests.

Intensive agricultural activities have significantly altered the pools and fluxes of nutrients, especially regarding Nitrogen, resulting in strong water quality degradation of both surface- and groundwater resources. Nitrates (NO₃) in groundwater are one of the major causes of water quality degradation. Once nitrates are introduced into the aquifer system, the only way to recover a good water quality is by reducing NO₃ amounts through denitrification, i.e. the transformation of NO₃ into gaseous N₂ (or N₂O). This transformation involves several intermediate N-species (NO₂, NH₄, NO) through various reactions. The denitrification process within aquifers is generally biologically mediated by bacteria (autotrophic or heterotrophic), while hydrogen, hydrogen sulfide, methane, organic carbon, dissolved iron (Fe²⁺), Fe-silicates and sulfide minerals are the potential electron donors.

The objective of this study, through a tracer test experiment, is to better constrain the denitrification process within a schist aquifer where such reactions have already been observed. Preliminary results of a multi-isotopic approach ($\delta^{15}\text{N}$ - $\delta^{18}\text{O}$ of nitrates, $\delta^{34}\text{S}$ - $\delta^{18}\text{O}$ of sulfates and $^{87}\text{Sr}/^{86}\text{Sr}$ of strontium) are presented.

Study site

The geology of the Naizin site (Brittany, France, Fig.1) mainly consists of Brioverian pyrite-bearing schist (530 Ma). Overlaying layers comprise weathered facies. The upper compartment, weathered facies, has a storage role, whereas the lower compartment (schist) presents fissure and fracture porosity and has a transmissive role. Connections between the two compartments were evidenced through piezometric and chemical monitoring with and upward exchanges, even if they remain rather poor (Pauwels et al., 2000). Groundwater presents distinct chemical compositions between the weathered part and the fissured part of the aquifer, especially regarding nitrates concentrations. The upper compartment (the first few meters below the water table) presents NO₃ concentration up to 200 mg.L⁻¹ in relation with intensive agriculture in the catchment (indoor pig-stock breeding, maize and wheat farming). In the lower compartment, where water circulates in the fissured zone, NO₃ concentrations decrease to below the detection limit. Previous studies in the catchment attributed at least part of this decrease to a denitrification process, transforming NO₃ into gaseous species N₂ or N₂O (Pauwels et al., 1998; 2000).

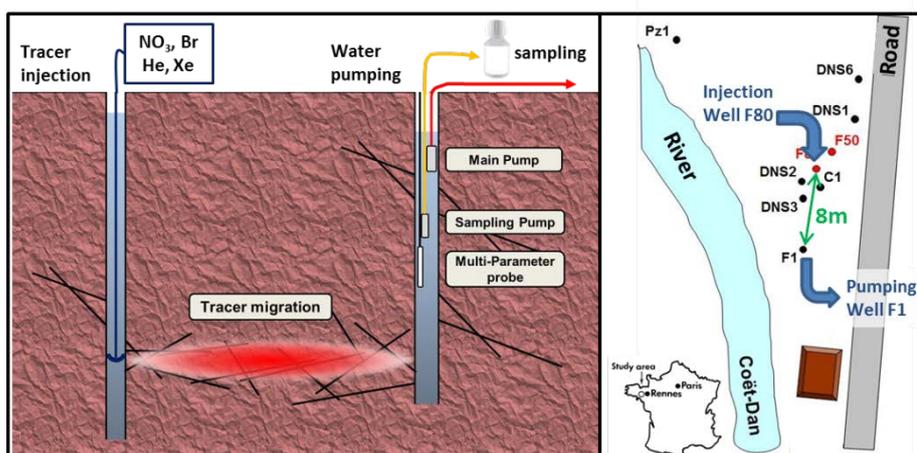


Fig. 1. Location of the study area: Naizin site in Brittany (France). Tracer experiment scheme with injection in F80 well and pumping in F1.

Methods

The tracer test experiment has been performed between two wells: injection in F80 and pumping in F1, distance between the two wells is 8 m (Fig.1). The test consists in the injection of a mixture of tracers (conservative and reactive) within the fissured part of the aquifer. A fracture was previously identified in the F80 well. A total of 110 L of tracer was injected in 20 min ($W=5.5 \text{ L}\cdot\text{min}^{-1}$), the water injected is composed of the F1 well water doped with KBr and NaNO_3 , as well as Xe, He and O_2 . The pumping rate in F1 was $0.947 \text{ m}^3\cdot\text{h}^{-1}$ over 5 days (120 hours). A total of 34 samples were sampled in the F1 well during the pumping period. Major and trace elements were analyzed on all the samples collected, whereas the isotopes ($\delta^{15}\text{N}\text{-NO}_3$ and $\delta^{18}\text{O}\text{-NO}_3$, $\delta^{34}\text{S}\text{-SO}_4$ and $\delta^{18}\text{O}\text{-SO}_4$, and $^{87}\text{Sr}/^{86}\text{Sr}$ of strontium) were analyzed on 11 samples according to the NO_3 evolution in the restitution curve.

Results and discussion

Figure 2 illustrates the evolution of dissolved nitrogen species during the tracer test compared to Bromide (note that gaseous species are not reported).

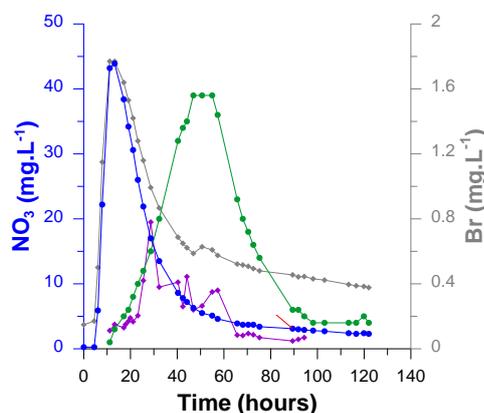


Fig. 2. Evolution of dissolved nitrogen species in the F1 pumping well compared to Bromide

The nitrates concentration in the F1 well before the tracer injection was below the detection limit. NO_3 appears only 6 hours after the beginning of the tracer test, reflecting a very rapid transfer time, and reached its maximum at 13 hours simultaneously with bromide. The NO_3 concentrations then rapidly drop down to 2.3 mg/l at 120 hours. Small but significant amounts of NO_2 and NH_4 , that were not present initially, appear in solution before the NO_3 pic.

Compared to Br, NO_3 concentrations decrease much more rapidly (Fig. 2) and assuming a conservative behavior of Br and similar transport mechanisms for NO_3 and Br, the comparison between both dissolved species concentrations allows estimating the quantity of NO_3 removed by denitrification. At this stage, we use the NO_3/Br ratio at the pic of the restitution curve (i.e. 32 molar ratio) as the reference. If no denitrification

occurs this ratio would remain the same and $[\text{NO}_3^-]$ would be expressed as $[\text{Br}] \times 32$. The difference between this theoretical value and the measured one would represent the missing part of NO_3^- , reflected the reduced part of NO_3^- . Figure 3 represents the $\delta^{15}\text{N}-\text{NO}_3^-$ versus the relative residual fraction of NO_3^- (i.e. the reverse of the relative amount of reduced NO_3^- calculated above), allowing to avoid the dilution effect all along the tracer test experiment

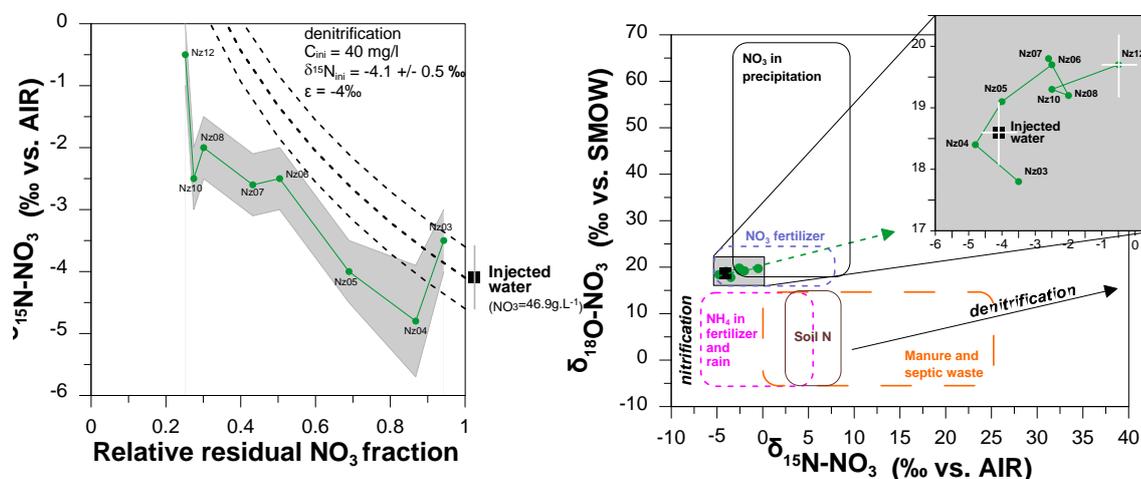


Fig. 3. $\delta^{15}\text{N}-\text{NO}_3^-$ vs. the relative residual fraction of NO_3^- (left). $\delta^{15}\text{N}-\text{NO}_3^-$ vs. $\delta^{18}\text{O}-\text{NO}_3^-$ with reference boxes from Kendall (1998) (right).

The isotopic composition of nitrogen provides information on denitrification process as denitrification leads to an enrichment of the residual NO_3^- , this isotopic evolution can be described by a Rayleigh distillation process. At the pic nitrates, the $\delta^{15}\text{N}-\text{NO}_3^-$ is not modified from the signature of the injected water ($\delta^{15}\text{N} = -4.1 \text{ ‰}$; $\delta^{18}\text{O} = 18.6 \text{ ‰}$, typical of synthetic NaNO_3 used in the injected water), there is thus no denitrification at the NO_3^- pic. During the tracer experiment, the NO_3^- concentrations decrease while the $\delta^{15}\text{N}-\text{NO}_3^-$ values increase from -4.1 to $+0.5 \text{ ‰}$. This evolution is relatively well reproduced using a Rayleigh distillation model with an initial $\delta^{15}\text{N}-\text{NO}_3^- = -4.1 \text{ ‰}$, an initial concentration of $\text{NO}_3^- = 40 \text{ mg.L}^{-1}$, and an enrichment factor $\epsilon = -4 \text{ ‰}$. This low ϵ value is in agreement with what was observed by Pauwels et al. (2000) in the deep aquifer, and suggest relatively rapid denitrification process (Mariotti et al., 1988) in full agreement with results from Pauwels et al. (1998) in the same area. Coupling $\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{18}\text{O}-\text{NO}_3^-$ confirms the denitrification with an observed increase in both $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of the residual nitrate (Fig. 3, right) and a ratio of enrichment of oxygen to nitrogen close to 1:2 (Kendall, 1998).

In the previous studies on the deep part of the aquifer, denitrification through pyrite oxidation (denitrification during the chemo-autotrophic respiration of *Thiobacillus denitrificans*, which oxidizes sulfur) was identified as a potential important way of denitrification, pyrite being abundant in the schist aquifer (Pauwels et al., 2000): $14 \text{ NO}_3^- + 5 \text{ FeS}_2 + 4 \text{ H}^+ \rightarrow 7 \text{ N}_2 + 10 \text{ SO}_4^{2-} + 5 \text{ Fe}^{2+} + 2 \text{ H}_2\text{O}$. Pyrite oxidation releases dissolved sulfates in solution and thus this could be traced through the $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ signatures of sulfates. Variation of the dissolved sulfate concentration is limited during the tracer test experiment ($+10 \%$) as well as the $\delta^{34}\text{S}-\text{SO}_4$ evolution (Fig. 4). Nevertheless the trend observed, with decreasing $\delta^{34}\text{S}-\text{SO}_4$ values while SO_4 concentrations increase, suggest a sulfate input from oxidation of sulfur minerals. Pyrite (FeS_2) was analyzed in the local Brioverian schists, giving $\delta^{34}\text{S} = +4 \text{ ‰}$ and $+6.9 \text{ ‰}$ (Pauwels et al., 2000). The amount of NO_3^- reduced cannot only be explained by pyrite oxidation, even if secondary sulfate minerals may precipitate locally and thus control the amount of sulfate in solution.

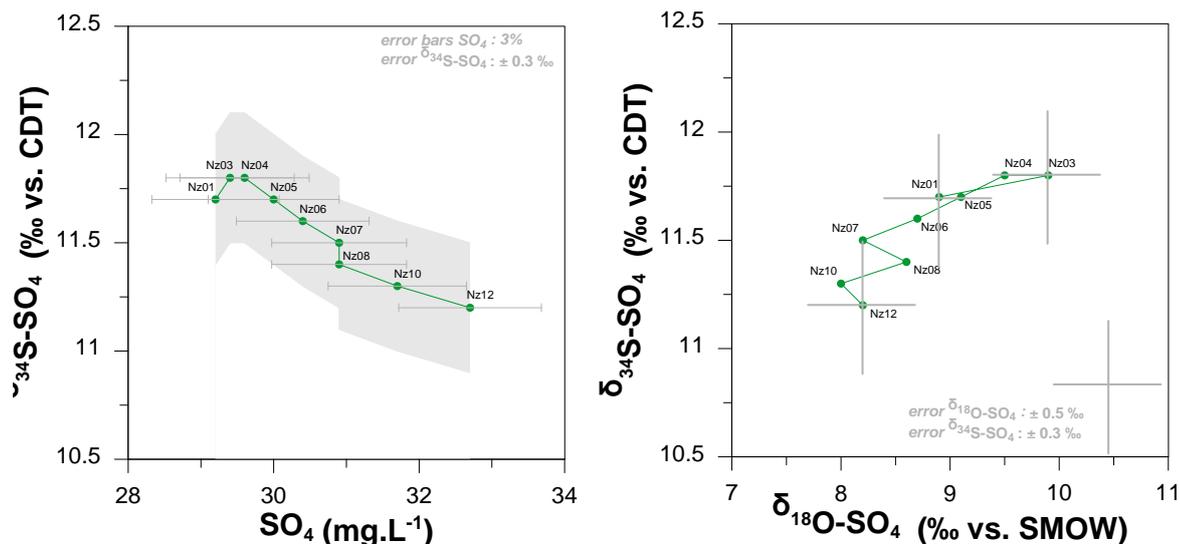


Fig. 4. $\delta^{34}\text{S-SO}_4$ vs. SO_4 concentration (left). $\delta^{34}\text{S-SO}_4$ vs. $\delta^{18}\text{O-SO}_4$ (right).

Other electron donors may also contribute to the denitrification process. Benzine et al., (2013) suggested autotrophic denitrification using biotite as a source of Fe(II) in the denitrification processes. Biotite being abundant in the Brioverian schists, we tried to test this hypothesis by analyzing Strontium isotopes all along the tracer test. If biotite is preferentially dissolved, the released Sr in solution should be more radiogenic and thus lead to an increase of the $^{87}\text{Sr}/^{86}\text{Sr}$ in solution. The Sr concentration increases at the first stage of the tracer experiment, up to concentration higher than those measured in the aquifer before the tracer test, but also higher than the concentration in the injected water. This reflects Sr input through water rock interaction (this is also the case for Ca). Nevertheless, $^{87}\text{Sr}/^{86}\text{Sr}$ signatures remain stable all along the tracer test experiment ($^{87}\text{Sr}/^{86}\text{Sr} \sim 0.71594$) suggesting that if biotite dissolution occurs the Sr amount released from biotite dissolution is not important enough compared to the total Sr mass balance.

The preliminary results of this tracer test experiment based on conservative and reactive tracers has allowed to point out that denitrification processes are taking place in the fractured Brioverian schists of the Naizin site. Denitrification almost starts immediately after the tracer test injection and is clearly visible over a very short distance (8 m between injection and pumping wells) and time (120 hours), this rapid denitrification is confirmed by a low enrichment factor for $\delta^{15}\text{N-NO}_3$. Pyrite oxidation was evidenced through sulfate isotopes but cannot explain alone all the reduced NO_3 , and biotite dissolution was not evidence through $^{87}\text{Sr}/^{86}\text{Sr}$ isotopes. The processes involved in the denitrification (i.e. the origin of electron donors) are still need to be better constrained and quantified, in the next steps, precise N mass balance as well as other dissolved species involved in the denitrification process will be modeled and confronted to the isotopic approach.

This study is part of the ANR Stock-en-Socle project (ANR-13-SEED-0009), that examines heat-energy storage through semi-opened circulation into low-permeability hard-rock aquifers.

References

- Benzine J, Shelobolina E, Xiong MY, Kennedy DW, McKinley JP, Lin X and Roden EE (2013) Fe-phyllsilicate redox cycling organisms from a redox transition zone in Hanford 300 Area sediments. *Front. Microbiol.* 4:388. doi: 10.3389/fmicb.2013.00388
- Kendall, C., 1998. Tracing nitrogen sources and cycling in catchments, in: *Isotope Tracers in Catchment Hydrology*, C. Kendall and J. J. McDonnell (Eds.). Elsevier Science B.V., Amsterdam. pp. 519-576.
- Mariotti, A., Landreau, A., Simon, B., 1988. ^{15}N isotope biogeochemistry and natural denitrification process in groundwater: application to the chalk aquifer of northern France. *Geochim. Cosmochim. Acta* 52, 1869–1878.
- Pauwels, H., Kloppmann, W., Foucher, J.-C., Martelat, A., Fritsche, V., 1998. Field tracer test for denitrification in a pyrite-bearing schist aquifer. *Appl. Geochem.* 13(6), 767–778.
- Pauwels, H., Foucher, J.-C., Kloppmann, W., 2000. Denitrification and mixing in a schist aquifer: influence on water chemistry and isotopes. *Chemical Geology*, 168, 307–324.