



Autotrophic denitrification supported by biotite dissolution in crystalline aquifers: (2) transient mixing and denitrification dynamic during long-term pumping



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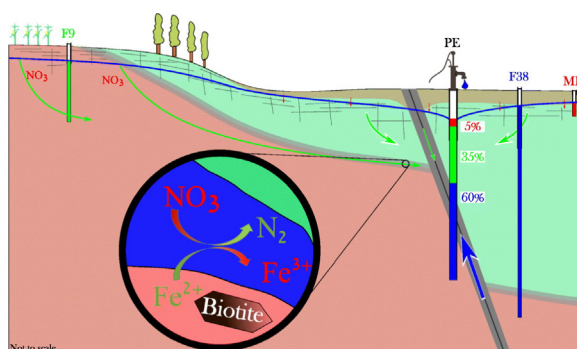
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HIGHLIGHTS

- Pumping induces a thorough reorganization of fluxes and mixing at long-term time scales.
- Mixing of groundwaters due to pumping enhances denitrification processes.
- Biotite plays a key role of electron donor in the reduction of nitrate.
- Crystalline aquifers act as sustainable bioreactors for reducing nitrate over long-term operations.

GRAPHICAL ABSTRACT



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ABSTRACT

We investigated the mixing and dynamic of denitrification processes induced by long-term pumping in the crystalline aquifer of Ploemeur (Brittany, France). Hydrological and geochemical parameters have been continuously recorded over 15 boreholes in 5 km² on a 25-year period. This extensive spatial and temporal monitoring of conservative as well as reactive compounds is a key opportunity to identify aquifer-scale transport and reactive processes in crystalline aquifers. Time series analysis of the conservative elements recorded at the pumped well were used to determine mixing fractions from different compartments of the aquifer on the basis of a Principal Component Analysis approach coupled with an end-member mixing analysis. We could reveal that pumping thus induces a thorough reorganization of fluxes known as capture, favoring infiltration and vertical fluxes in the recharge zone, and upwelling of deep and distant water at long-term time scales. These mixing fractions were then used to quantify the extent of denitrification linked to pumping. Based on the results from batch experiments described in a companion paper, our computations revealed that *i*) autotrophic denitrification processes are dominant in this context where carbon sources are limited, that *ii*) nitrate reduction does not only come from the oxidation of pyrite as classically described in previous studies analyzing denitrification processes in

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similar contexts, and that *iii*) biotite plays a critical role in sustaining the nitrate reduction process. Both nitrate reduction, sulfate production as well as fluor release ratios support the hypothesis that biotite plays a key role of electron donor in this context. The batch-to-site similarities support biotite availability and the role by bacterial communities as key controls of nitrate removal in such crystalline aquifers. However, the long term data monitoring also indicates that mixing and reactive processes evolve extremely slowly at the scale of the decade.

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1. Introduction

Although naturally present in the environment as part of the nitrogen cycle, nitrate is introduced in the subsurface by anthropogenic activities and is considered as one of the major contaminant in most parts of the world (Rivett et al., 2008). High concentrations of nitrate in water have severe health implications (methaemoglobinaemia and cancer) and environmental impacts (eutrophication of surface water). The European Union defined a standard limit of 50 mg/L for nitrate concentration in drinking water. This directive led to drastic consequences in terms of water supply strategies. Numerous wells are abandoned each year due to high concentration of nitrate. Water treatment processes used to remove nitrate are very expensive, as is the drilling of additional deeper boreholes in the expectation of finding safer groundwater.

For energy supply, bacteria mediate chemical reactions typically involving inter-compound electron transfer (Rivett et al., 2008). Denitrification is part of the nitrogen cycle. Through denitrification, nitrate is reduced to nitrous oxide (N₂O) or nitrogen gas (N₂), depending on the progress of the reaction, while another chemical compound is oxidized. In groundwater, these bacteria obtain energy through the oxidation of both organic carbon sources (heterotrophic) and inorganic chemical sources (autotrophic) as electron donors while nitrate serves as electron acceptor (Korom, 1992). Subsurface constitutes an efficient bioreactor for denitrification, as long as the environmental drivers required for the reactions are present: anaerobic conditions, availability of organic and/or mineral sources, presence of microbial communities, and sufficient nitrate concentrations (Böhlke, 2002; Pinay et al., 2015).

Aquifers in crystalline basements (plutonic and metamorphic rocks) contain low organic carbon compared to sedimentary ones, implying that autotrophic denitrification is generally dominant. Electron donors have various origins, reduced iron (Eq. (1)) and sulphur (Eq. (2)) being classically described as the main drivers for the reaction (Engesgaard and Kipp, 1992).



Dissolved iron may come from the oxidation of iron sulphide - Pyrite mineral FeS₂ - (Eq. (2)) or from the dissolution of silicate minerals such as biotite, pyroxenes and amphiboles. Manganese sulphide (MnS) can also play an important role in the reaction (Rivett et al., 2008). Oxidation of sulphur, such as pyrite, is commonly attributed to *Thiobacillus denitrificans* (Kölle et al., 1987). In crystalline rock basements, water infiltrates and circulates in the subsurface mainly through fractures, faults and other geological discontinuities. This intrinsic heterogeneity offers a high variability of flow paths for the contaminant transport (Kolbe et al., 2016; Marçais et al., 2015; Roques et al., 2014). Residence times of solutes, as well as chemical conditions (i.e. oxidation states), are highly variable in both space and time within a single aquifer. Nitrate can be transferred within the watershed through rapid and superficial flow paths. It can also travel through low-velocity flow paths deeper in the bedrock (Aquilina et al., 2012). Pumping in compartmented aquifers can induce mixing of different types of water and modify apparent

reactivity kinetics, thereby challenging the identification of degradation pathways and kinetics essential for building prediction scenarios.

Few studies have examined the long-term dynamics of denitrification in the context of operated groundwater system. Tarits et al. (2006) have analyzed the early part of the same dataset as in this study, i.e. from the Ploemeur site. They concluded that an autotrophic denitrification process was occurring in pyrite-bearing fractures during pumping. Roques et al. (2014) analyzed induced-denitrification processes during a two-month pumping test performed in a neighbored crystalline aquifer located at Saint-Brice en Coglès. Based on the results of a chemical mixing model, they demonstrated that the stoichiometry of the autotrophic reaction involving pyrite as electron donor was not respected throughout the pumping. They concluded that other minerals were involved, or additional dissolution/precipitation processes were occurring.

Some studies also analyzed denitrification kinetics in the context of controlled injection experiments. Boisson et al. (2013) successfully modeled the chain reaction kinetics of on-going autotrophic denitrification during a 12-h push-pull experiment. The authors could simulate their experimental results as a sequence of first-order reactions. Recently, Rodríguez-Escalaes et al. (2016) developed a 2D reactive transport model to simulate an enhanced in situ biodenitrification experiment previously performed in a fractured aquifer, using ethanol as an added source of carbon. However, the capability of aquifers to act as efficient bioreactors under long-term pumping remains undocumented. It is unclear whether long-term pumping enhances or reduces nitrate concentrations by mixing/dilution processes or because of biochemical removal. If reducing processes are occurring, it is also unclear which source of electron donors sustains the reaction and if the reaction rate is modified by pumping. Identifying the origin of concentration reduction is key for building predictive scenarios as net removal through biochemical processes will reduce nitrate load and legacy where dilution would only delay nitrate breakthrough and postpone remediation.

The aim of this study is to specifically give new insights about the dynamics of nitrate concentrations induced by long-term pumping and the share of dilution and reactivity in concentration evolutions. We used time series of geochemical data recorded in the now well-described Ploemeur site (Brittany, France) where a crystalline aquifer has been operated for water supply for the last 25 yrs at a rate of ~1Mm³/yr. In a companion paper (Aquilina et al., 2017), we have investigated the local denitrification mechanisms in more detail through batch experiments, using crushed rocks and groundwater from the Ploemeur site. From elements released and consumed and chemical characterization of minerals, we have determined the mineral source for the Fe(II) effectively used during denitrification. In this paper, we seek to quantify the temporal variability of reactivity induced by transient mixing of the different groundwater types present in the aquifer at the time scale of the pumping monitoring (25 yrs). Through characterization of mixing, we identify the type of denitrification induced, and further support our discussion by comparing our results to the ones obtained through batch experiments of the companion paper.

2. Context: the Ploemeur site

The Ploemeur site is located south of Brittany in France (Fig. 1). The site is implemented at the epimetamorphic zone of a large granitic

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