



Modeling biogeochemical processes and isotope fractionation of enhanced *in situ* biodenitrification in a fractured aquifer



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ABSTRACT

Enhanced *in situ* biodenitrification (EIB) is a feasible technology to clean nitrate-polluted groundwater and reach drinking water standards. Aimed at enabling a better monitoring and management of the technology at the field scale, we developed a two-dimensional reactive transport model (RTM) of a cross section (26.5 × 4 m) of a fractured aquifer composed of marls involving both biogeochemical processes and associated isotope fractionation. The RTM was based on the upscaling of a previously developed batch-scale model and on a flow model that was constructed and calibrated on *in situ* pumping and tracer tests. The RTM was validated using the experimental data provided by Vidal-Gavilan et al. (2013). The model considers several processes including (i) exogenous and endogenous microbial nitrate and sulfate respiration coupled to ethanol oxidation and linked to microbial growth and decay, and (ii) geochemical interactions (dissolution/precipitation of calcite), and (iii) isotopic fractionation of the reaction network (¹⁵N–NO₃, ¹⁸O–NO₃, ¹³C–DIC, ¹³C–ethanol, ¹³C–biomass, and ¹³C–calcite). Most of the calibrated microbiological parameter values at field scale did not change more than one order of magnitude from those obtained at batch scale, which indicates that parameters determined at the batch scale can be used as initial estimates to reproduce field observations provided that groundwater flow is well known. In contrast, the calcite precipitation rate constant increased significantly (fifty times) with respect to batch scale. The incorporation of isotope fractionation into the model allowed to confirm the overall consistency of the model and to test the practical usefulness of assessing the efficiency of EIB through the Rayleigh equation approach. The large underestimation of the Rayleigh equation of the extent of EIB (from 10 to 50%) was caused by the high value of hydrodynamic dispersion observed in this fractured aquifer together with the high reaction rates.

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1. Introduction

Nitrate is one of the most prevalent and common groundwater contaminants (European Environment Agency, 2007; Organisation for Economic Co-operation and Development, 2008; Rivett et al., 2008). Excessive ingestion of nitrates from polluted drinking water and their subsequent conversion to nitrites can induce methemoglobinemia in humans and potentially play a role in the development of cancers (Fan and Steinberg, 1996; Fewtrell, 2004; Höring and Chapman, 2004). Therefore, the European Union has established maximum concentrations of nitrate and nitrite in drinking water of 50 mg/L for nitrate and 0.5 mg/L for nitrite. The proportions of groundwater bodies at high risk of nitrate pollution (showing mean nitrate concentrations greater

than 25 mg/L) were reported as 80% in Spain, 50% in the UK, 36% in Germany, 34% in France and 32% in Italy (European Environment Agency, 2007). The high nitrate concentrations decrease the availability of water for domestic uses. Consequently, many water supply wells have been abandoned (Gierczak et al., 2007). Due to its minimal cost, the most common solution to nitrate pollution has been to mix polluted and clean groundwater. Nevertheless, this solution is extremely limited by water scarcity in Mediterranean and/or (semi-) arid countries, a situation that will become worse due to climate change (IPCC, 2007). Even in countries with no water shortage problems, there is often a lack of clean water to mix and dilute groundwater with high nitrate concentrations (Stuart et al., 2011; Veraart et al., 2014). In this context, it is necessary to implement other solutions to improve the quality of the groundwater.

Many technologies are available for treating nitrate in groundwater, such as reverse osmosis, ion exchange, electrodialysis, and chemical and biological denitrification (McAdam and Judd, 2007; Schnobrich et al.,

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2007; Ricardo et al., 2012). Most of these technologies focus on *ex situ* treatments, which are inherently more expensive than *in situ* treatments due to energy consumption and the interference with surface activities (e.g., building a treatment plant) (Della Rocca et al., 2007). Biological denitrification, which is known as Enhanced *In situ* Bionitrification (EIB), has environmental and economic advantages over other methods because it is simple, selective, and cost effective (Smith et al., 2001). EIB is defined as a process in which organic carbon is injected into the groundwater through injection wells to enhance microbial denitrification. During this process, nitrate is reduced to dinitrogen gas by anaerobic facultative bacteria that use nitrate as the electron acceptor and that are ubiquitous in surface water, soil and groundwater (Beauchamp et al., 1989). This technology is feasible for cleaning nitrate-polluted groundwater and meeting drinking water standards (Matějík et al., 1992; Khan and Spalding, 2004; Vidal-Gavilan et al., 2013).

Geochemical interactions occur between the bionitrification reactants and the porous geological medium in response to biodegradation reactions. These interactions may play a critical role in the implementation of EIB in aquifers. Because of the production of dissolved inorganic carbon (DIC) and pH alteration, carbonate mineral dissolution/precipitation is induced by changes in the initial hydrogeological and hydrochemical properties of the aquifer by heterotrophic bionitrification (Rodríguez-Escales et al., 2014). Moreover, dinitrogen gas production can lead to a modification of the hydraulic conductivity (Amos and Mayer, 2006). These changes can modify the hydrogeological characteristics of the aquifer and modify the efficiency of the groundwater treatment (Noiri et al., 2012).

Another important factor when monitoring EIB in the field is the dilution caused by hydrodynamic dispersion of nitrate rich water and water with lower nitrate levels (e.g., recharge). Even without any entrance of clean groundwater, dilution will occur in the fringe of the cleaned groundwater plume from EIB and polluted groundwater. Because of dilution, a decrease in nitrate concentration cannot always be attributed to degradation. Monitoring the changes in the nitrogen and oxygen isotope ratios of nitrate ($\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{18}\text{O}-\text{NO}_3^-$) allows the degradation to be identified (Otero et al., 2009; Puig et al., 2013; Carrey et al., 2014) and therefore nitrate transformation and dilution to be distinguished. In EIB applications, this distinction improves the characterization of the clean groundwater plume and allows nutrient injection to be optimized, reducing treatment costs. As NO_3^- is consumed, the residual NO_3^- becomes enriched in the heavy isotopes ^{15}N and ^{18}O , and the denitrification reaction follows a Rayleigh distillation process (Eq. (1)):

$$R_s = R_{s,0} f^{(\alpha-1)} \quad (1)$$

where R_s is the stable isotope ratio (i.e., $^{15}\text{N}/^{14}\text{N}$; $^{18}\text{O}/^{16}\text{O}$) of the fraction of molecules remaining, f ; $R_{s,0}$ is the initial isotopic composition of the molecule; and α is the kinetic isotopic fractionation factor of the transformation process, which is often represented as the kinetic isotopic enrichment factor ϵ (in permil, ‰), where $\epsilon = (\alpha - 1)$.

Despite that many studies have characterized the isotopic processes associated with bionitrification by using the Rayleigh equation, some of the most recent works have shown that this equation does not always give accurate results at the field scale (Abe and Hunkeler, 2006; van Breukelen, 2007; van Breukelen and Prommer, 2008; Green et al., 2010; van Breukelen and Rolle, 2012). It must be mentioned that all of these studies focused on natural attenuation processes while none on enhanced bionitrification and fractured aquifers. The differences between Rayleigh-determined and field-scale results are caused because the Rayleigh equation was developed for a closed system (van Breukelen, 2007) and does not account for hydrodynamic dispersion that tends to attenuate isotopic variations. These limitations have been addressed by incorporating isotope fractionation processes into

numerical or analytical reactive transport models that account for hydrodynamic dispersion (van Breukelen and Prommer, 2008).

In addition to nitrate isotopes, other isotopes such as carbon isotopes are also involved in EIB, and can help to quantify the reaction network (biological reactions and geochemical interactions). The inclusion of dissolved inorganic carbon isotopes ($\delta^{13}\text{C}-\text{DIC}$) into the biogeochemical model, which are involved in both direct (oxidation of organic carbon) and indirect processes (carbonate mineral interaction) of enhanced bionitrification, is expected to allow better evaluations of the consistency of the model due the central role that $\delta^{13}\text{C}-\text{DIC}$ plays in the overall reaction network (Rodríguez-Escales et al., 2014).

In this context, a field-scale reactive transport model (RTM) of EIB integrating hydrology, microbiology, geochemistry, and isotope fractionation can provide significant benefits for the planning, characterization, monitoring and optimization of this technology in field applications. The integration of all the processes allows the evaluation of their relationships with each other and the prediction of secondary processes such as induced mineral precipitations or dissolution.

Several studies have evaluated bionitrification using numerical models at different scales (Smith et al., 2001; Chen and MacQuarrie, 2004; Lee et al., 2006; André et al., 2011; Mastrocicco et al., 2011; Boisson et al., 2013). However, few studies have focused on modeling enhanced bionitrification (André et al., 2011; Mastrocicco et al., 2011; Boisson et al., 2013), and only one study has been performed at the field scale (Boisson et al., 2013). Furthermore, few studies have examined the effects of geochemical interactions on bionitrification within the aquifer matrix (Chen and MacQuarrie, 2004) and only a few have explored the potential use of isotope fractionation for monitoring bionitrification (Lehmann et al., 2003; Chen and MacQuarrie, 2004).

The models that have evaluated bionitrification at the field scale (Chen and MacQuarrie, 2004; Lee et al., 2006; Boisson et al., 2013) do not consider all of the processes involved. The most complete model, which was presented by Chen and MacQuarrie (2004), was applied to a sedimentary aquifer under natural attenuation conditions and did not take into account all of the isotopes modified by bionitrification (only $^{15}\text{N}-\text{NO}_3^-$). Furthermore, no field integrated model described flow and transport through fractured media, which are characterized by higher heterogeneity with more complex hydrological conditions. Only one model has been developed for this type of geological formation, but it concerns the simulation of push-pull test involving only microbiological processes (Boisson et al., 2013).

Because of this lack of knowledge, the aim of this paper is to develop a reactive transport model that considers microbiological processes, geochemical interactions, and complete isotope geochemistry during EIB in a fractured media at the field scale. In fractured aquifers, hydrogeological parameters such as heterogeneity, connectivity between the fracture networks, flow dynamics, and porosity differ notably from those in more extensively tested alluvial aquifers and may pose difficulty for the modeling of *in situ* technologies. The model focuses on microbiological processes, such as exogenous and endogenous nitrate and sulfate respiration coupled with microbial growth and decay, geochemical processes, such as the precipitation of calcite, nitrate isotopic fractionation, including $\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{18}\text{O}-\text{NO}_3^-$, and carbon isotope interactions. In addition, once the model was constructed, the extent of bionitrification using nitrate isotopes was also evaluated with the Rayleigh equation to assess its use from a practical perspective in EIB applications. To our knowledge, this is the first reactive field-scale model of EIB in the literature which considers microbiological, geochemical, and isotopic processes in one integrated model.

2. Materials and methods

2.1. Field site description and model code

The model aimed to simulate a slug injection experiment conducted as part of an EIB field experiment described in Vidal-Gavilan et al.

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