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Modeling long term Enhanced *in situ* Biodenitrification and induced heterogeneity in column experiments under different feeding strategies

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SUMMARY

Enhanced *In situ* Biodenitrification (EIB) is a capable technology for nitrate removal in subsurface water resources. Optimizing the performance of EIB implies devising an appropriate feeding strategy involving two design parameters: carbon injection frequency and C:N ratio of the organic substrate nitrate mixture. Here we model data on the spatial and temporal evolution of nitrate (up to 1.2 mM), organic carbon (ethanol), and biomass measured during a 342 day-long laboratory column experiment (published in Vidal-Gavilan et al., 2014). Effective porosity was 3% lower and dispersivity had a sevenfold increase at the end of the experiment as compared to those at the beginning. These changes in transport parameters were attributed to the development of a biofilm. A reactive transport model explored the EIB performance in response to daily and weekly feeding strategies. The latter resulted in significant temporal variation in nitrate and ethanol concentrations at the outlet of the column. On the contrary, a daily feeding strategy resulted in quite stable and low concentrations at the outlet and complete denitrification. At intermediate times (six months of experiment), it was possible to reduce the carbon load and consequently the C:N ratio (from 2.5 to 1), partly because biomass decay acted as endogenous carbon to respiration, keeping the denitrification rates, and partly due to the induced dispersivity caused by the well-developed biofilm, resulting in enhancement of mixing between the ethanol and nitrate and the corresponding improvement of denitrification rates. The inclusion of a dual-domain model improved the fit at the last days of the experiment as well as in the tracer test performed at day 342, demonstrating a potential transition to anomalous transport that may be caused by the development of biofilm. This modeling work is a step forward to devising optimal injection conditions and substrate rates to enhance EIB performance by minimizing the overall supply of electron donor, and thus the cost of the remediation strategy.

1. Introduction

Nitrate is a priority environmental pollutant in many countries due to the combination of high toxicity and widespread presence (European Environment Agency, 2007; Organisation for Economic Co-operation and Development, 2008). Agricultural leaching has been identified as the primary source of groundwater nitrate contamination (Böhlke, 2002; Jahangir et al., 2012). Additional sources of nitrate pollution include landfill leachate, leaking septic tanks, and municipal storm water runoff (Hiscock et al., 1991; Panno et al., 2008).

Different options to reduce the high nitrate concentration levels in groundwater are available, including improved farming practices, delineation of aquifer protection zones, or dilution with low-nitrate water sources. However, these options are seldom available due to legal, logistic, or economical constraints. Thus, groundwater remediation technologies, such as ion exchange, reverse osmosis, electrodialysis, and Enhanced *In situ*

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Biodenitrification (EIB) (Haugen et al., 2002), are often the only practical options left to deal with nitrate-contaminated aquifers.

EIB holds environmental and economic advantages over the other remediation methods mentioned, because it is simple, selective, and cost efficient (Smith et al., 2001). The technology is based on the reduction of nitrate to dinitrogen gas by anaerobic heterotrophic facultative bacteria that use nitrate as electron acceptor. Such bacteria are ubiquitous in soil and groundwater (Beauchamp et al., 1989). EIB is feasible anywhere bacteria may thrive, organic electron donors can be supplied, and oxygen levels are below 1–2 mg/L (Korom, 1992). In natural aquifer conditions, a major limiting factor for biodenitrification is organic matter. Therefore, the main idea behind EIB is the addition of an organic carbon source (acting as electron donor for nitrate reduction and as a carbon source for biomass growth), while controlling a suite of environmental parameters such as the concentrations of other oxidants (e.g. O_2), pH, and nutrient levels (e.g. phosphorous or oligo-elements). Optimal configuration of EIB, involving the presence of one or more injection and extraction wells, is site specific, depending on pumping rate, groundwater flow velocity, and residence time of nitrate in the system (Khan and Spalding, 2004).

The injection of organic carbon during EIB creates a bioactive zone, characterized by the growth of denitrifier biomass, heterogeneously distributed throughout the porous media depending on nutrient availability. Biomass can be found either as suspended matter or as biofilms attached to the solid matrix. Biofilms occur as micro-colonies or aggregates composed by denitrifier microorganisms, extracellular polymeric or proteinic substances (EPS), and potentially trapped dinitrogen gas formed during denitrification (Dupin and McCarty, 2000; Hand et al., 2008; Rittmann, 1993; Vandevivere and Baveye, 1992).

As biofilm develops and the pore space is occupied, partial bioclogging might take place, affecting a number of hydraulic properties. In addition to bioclogging, a reduction of hydraulic conductivity can be associated with the presence of trapped N_2 gas (Amos and Mayer, 2006; Jarsjö and Destouni, 2000). While the word clogging is traditionally defined in terms of the overall reduction in hydraulic conductivity (Vandevivere and Baveye, 1992), the decrease in effective pore volume caused by biofilm growth also changes porosity. Due to the variation of these two hydraulic parameters, changes in groundwater velocity might be recorded (Pavelic et al., 2007; Taylor and Jaffé, 1990; Taylor et al., 1990), changing residence time between injection and extraction wells, thus influencing the overall capacity for biodenitrification. Furthermore, the spatial heterogeneity of hydraulic properties caused by the inhomogeneous distribution of biofilm throughout the porous media also promotes changes in dispersivity (Seifert and Engesgaard, 2007). Dispersivity is an important parameter as it affects the mixing of nitrate with injected organic substrate, and it is sometimes the limiting factor for the reaction processes (Dentz et al., 2011).

Thus, the amount of biomass and the way it grows significantly affect the performance of EIB facilities. Biomass growth is driven among other things by the feeding strategy, i.e., the frequency of injection, the total carbon supplied, and the resulting carbon–nitrogen ratio (C:N). With the objective of limiting the biomass growth, some authors suggested injecting the electron donor in discrete pulses rather than as a continuous supply (Franzen et al., 1997; Gierczak et al., 2007; Peyton, 1996; Semprini et al., 1991, 1990; Shouche et al., 1993). Nevertheless, little is known about how the frequency of injection pulses affects biomass growth and nitrate degradation. Regarding the C:N ratio, Vidal-Gavilan et al. (2014) observed that even working with low C:N ratios (C:N = 1; below the stoichiometric one: C:N = 2.5), high denitrification rates were achieved after biofilm development. The authors attributed this to the occurrence of endogenous bacterial decay.

Proper understanding of processes occurring during EIB involves the need for multispecies reactive transport modeling (RTM) (Chen and MacQuarrie, 2004; Lee et al., 2006; Rodríguez-Escales et al., 2016). Such models can facilitate exploring a variety of remediation strategies such as injection duration and rate, and concentration of reactants. Nevertheless, there is a need to develop specific models to evaluate how different feeding strategies interact with transport processes.

The present work is aimed at developing a model capable of reproducing different feeding injection frequencies (from weekly to daily) with different C:N ratios in a long term column experiment of Enhanced *in situ* Biodenitrification, lasting 342 days (Vidal-Gavilan et al., 2014). This modeling study focusses on the EIB performance in response to the frequency of organic substrate addition as well as the changes in hydraulic and transport properties promoted by the growth of biofilm. Proper understanding of the processes taking place allow defining the optimal injection strategy (frequency and rate) capable of enhancing EIB performance (high performance at low cost) by minimizing the overall supply of labile organic carbon substrate.

2. Materials and methods

2.1. Description of the experiment and data set

A full description of the experiment is provided in Vidal-Gavilan et al. (2014), and sketched here in Fig. 1 for completeness. It consisted of a glass cylindrical column (70 cm length, 8 cm inner diameter) filled with unconsolidated sediment from a sandy alluvial aquifer (located in Argentona, NE Spain). The sediment was composed by medium and coarse-grained sand mainly made up of quartz and feldspar and with a small silt content, the organic matter content in the sediment was negligible (Vidal-Gavilan et al., 2014). Water was forced to flow from the bottom to the top of the column with a pump-controlled average flow-rate of 180 mL/d resulting in a residence time in the column of about 6.4 days. A total of eight sampling ports were installed: one at the inflow reservoir, six along the column (at 6, 16, 26, 36, 46 and 56 cm from inlet), and one at the outflow, allowing the delineation of aqueous compounds and suspended biomass profiles at different predefined times. The data set provided in Vidal-Gavilan et al. (2014) and used in the modeling effort includes aqueous concentrations of ethanol, nitrate, and biomass at selected times at the sampling ports placed within the column. A control experiment without carbon substrate addition ran for 2 months, and natural denitrification was not observed, as changes in nitrate along the column were lower than 1% (Vidal-Gavilan et al., 2014).

The water used in the experiment was obtained from an existing large-diameter well located at the site. Three 25-L containers were used to store the input water for the experiment, filled up at different days (August 2011, December 2011, and April 2012). The well was always purged prior to sampling. No forced deoxygenation took place, so that the input water (see Table 1) was oxic and saturated with oxygen. The experiment ran for 342 days at aquifer temperature (15 °C). Ethanol was added as an external organic carbon source by means of four injectors located 16 cm from the inlet (see Fig. 1). It was added by mixing it with the input water previous to injection (Table 1). Different feeding strategies were tested during the experiments (Table 2), characterized by different injection frequencies (weekly *versus* daily) and carbon to nitrogen molar ratios (from 2.5 to 1). In this ratio the amount of C is computed from the concentration of ethanol multiplied with the duration of injection (0.5 min). Feeding was twice discontinued, first between days 150 and 175 due to pump failure (no water was supplied), and then between days 286 and 311, this time to