



Implications of non-equilibrium transport in heterogeneous reactive barrier systems: Evidence from laboratory denitrification experiments

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ABSTRACT

Organic substrates in reactive barrier systems are often heterogeneous material mixtures with relatively large contrasts in hydraulic conductivity and porosity over short distances. These short-range variations in material properties imply that preferential flow paths and diffusion between regions of higher and lower hydraulic conductivity may be important for treatment efficiency. This paper presents the results of a laboratory column experiment where denitrification is investigated using a heterogeneous reactive substrate (sawdust mixed with sewage sludge). Displacement experiments with a non-reactive solute at three different flow rates are used to estimate transport parameters using a dual porosity non-equilibrium model. Parameter estimation from breakthrough curves produced relatively consistent values for the fraction of the porosity consisting of mobile water (β) and the mass transfer coefficient (α), with average values of 0.27 and 0.42 d^{-1} , respectively. The column system removes >95% of the influent nitrate at low and medium flow, but only 50–75% of the influent nitrate at high flow, suggesting that denitrification kinetics and diffusive mass transfer rates are limiting the degree of treatment at lower hydraulic residence times. Reactive barrier systems containing dual porosity media must therefore consider mass transfer times in their design; this is often most easily accommodated by adjusting flowpath length.

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1. Introduction

Groundwater remediation using subsurface reactive barrier systems is a viable option when appropriate reactive mixtures can be identified for a given groundwater composition and hydrogeological regime (see [Blowes et al., 2000](#); [Gavaskar et al., 1998](#)). As most reactive barrier systems function by promoting a change in redox state for immobilizing (e.g. heavy metals) or transforming contaminants (e.g. chlorinated solvents, nitrate), reactive materials generally consist of electron donor sources such as zerovalent iron (Fe^0) or organic carbon ([Blowes et al., 2000](#)). Organic substrates have been chosen in a variety of cases ([Benner et al., 2002](#); [Blowes et al., 1994](#); [Robertson et al., 2008](#); [Schipper et al., 2004](#)) where carbon sources are required for heterotrophic

microbial reduction of groundwater constituents (e.g. dissimilatory sulfate reduction, denitrification).

Most fine-grained organic substrates (e.g. garden compost, sawdust) used in reactive barrier systems have low hydraulic conductivities. If the hydraulic conductivity of the aquifer is greater than that of the reactive organic substrate, the organic material must be mixed with a supporting material such as sand or gravel so that the mixture's hydraulic conductivity exceeds that of the surrounding aquifer ([Blowes et al., 2000](#)). The resulting mixture of organic substrate, supporting material (e.g. gravel), and perhaps other substances is therefore a heterogeneous material with relatively large contrasts in hydraulic conductivity and porosity over short distances (<1 cm). These material properties have two major implications for a barrier system consisting of such material: 1) zones of higher and lower hydraulic conductivity (K), and thereby preferential flow, may be created in the barrier because of inadequate mixing as well as material

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segregation and settling during barrier installation; 2) solute exchange (diffusion) between regions of higher K and lower K may be important when specific biogeochemical reactions are favored in low K regions (i.e. regions of high hydraulic residence time).

The establishment of preferential flowpaths in reactive barriers by the presence of either high K pathways (Benner et al., 2002) or by pore space clogging as a result of secondary mineral formation (e.g. Herbert, 2003; Kamolpornwijita et al., 2003; Mackenzie et al., 1999; Mayer et al., 2001, 2006) has been the subject of much study, as preferential flow may lead to lower barrier performance than initially predicted. However, issues dealing with porosity decreases are generally restricted to zerovalent iron barriers (cf. Blowes et al., 2000), and not to barriers consisting of a reactive organic substrate (cf. Benner et al., 2002). In contrast, the implications of solute exchange between high K and low K regions in reactive barrier systems has received little attention, most likely because the great majority of field-scale barrier systems consist of zerovalent iron, where diffusion-controlled solute exchange is generally not a process contributing to remediation. This is not necessarily the case in organic-based barrier systems where such biogeochemical processes as sulfate reduction and denitrification may be limited to microenvironments within low K regions.

In systems where there are large contrasts in hydraulic conductivity over short distances, solute transport modeling using the advection–dispersion equation (ADE) and assuming a single porosity, homogeneous medium may not adequately describe the physical processes occurring in the system. While displacement experiments with single porosity media produce symmetrical breakthrough curves, breakthrough curves from displacement experiments using reactive mixtures with two contrasting regions are characteristically asymmetrical and exhibit “tailing” because of solute exchange between the two hydraulically distinct regions (van Genuchten and Wierenga, 1976). Modeling solute transport in such media with a single porosity model would require modeling with unrealistically large dispersion coefficients (i.e. dispersivities similar to or larger than the characteristic length of the system) and would furthermore result in a poor fit to experimental data. Instead, solute transport may be simulated using a dual porosity approach where two distinct regions are simulated, consisting of mobile and immobile water. Mass transfer between the regions is considered as a first-order process (van Genuchten and Wagenet, 1989; van Genuchten and Wierenga, 1976).

This paper presents the results of a laboratory column experiment where denitrification is investigated using a heterogeneous reactive substrate. As there are large contrasts in the hydraulic conductivities of components in the reactive mixture, the aim of this study is to determine the significance of solute exchange between high K and low K regions for transport and for denitrification rates in this system. Using displacement experiments with a non-reactive solute, transport parameters are determined in terms of a dual porosity non-equilibrium ADE. Since the reactive substrate is intended for use in a field-scale barrier system (Herbert and Björnström 2009), understanding non-equilibrium transport in this material at the laboratory scale will facilitate modeling the process at the field scale.

2. Materials and methods

2.1. Column experiment

A column experiment was conducted to study the effect of heterogeneous reactive substrate mixtures on the breakthrough of a non-reactive solute and on denitrification rates in the material. Two plexiglas columns (21 cm length \times 8 cm diameter) were constructed for upward saturated flow and operated at room temperature. These columns were identical and run as duplicates. The input solution was pumped at constant rate, using a peristaltic pump, through 1 mm (inner diameter) Teflon tubing into the center of each column base. Water discharged from the top of the column through similar tubing. The base of each column was filled with a 1 cm layer of sand (primarily quartz), followed by 19 cm reactive substrate, and finally a 1 cm layer of sand at the top, closest to the discharge point.

The reactive substrate in both columns consisted of a 4:1:1 mixture (by volume) of LECA® pellets (baked clay pellets), water-saturated sawdust, and activated sewage sludge. The sewage sludge was obtained from the Uddebo sewage treatment plant in Luleå, Sweden, while the sawdust was obtained from a local lumberyard. These reactive materials were selected as substrates for the growth of denitrifying bacteria in a field-scale barrier system (Herbert and Björnström, 2009); other denitrification studies have shown that sawdust is a suitable substrate (e.g. Robertson et al., 2008; Schipper et al., 2004), providing a long-term carbon source for the growth of heterotrophic denitrifying bacteria. The sewage sludge is included because it is a source of denitrifying bacteria and allows for the rapid establishment of a denitrifying community in the columns. The LECA® pellets (8–12 mm diameter) functioned as a supporting material and increased the hydraulic conductivity of the mixture. Prior to packing the columns, the reactive mixture was thoroughly mixed. However, because of the large differences in material properties between the LECA® pellets, water-saturated sawdust, and moist sewage sludge, it was not possible to finely disperse the sewage sludge with the sawdust and pellets. Consequently, small sludge aggregates remained in the final mixture, interspersed with sawdust and pellets. Thus, large contrasts in hydraulic conductivity existed in the reactive material at the start of the experiment, warranting the use of a dual porosity non-equilibrium model for simulating solute transport in the columns (see below). While packing the columns, distilled water was pumped from below while the column was filled, to avoid the entrapment of air bubbles in the material.

The column experiment discussed in this paper was conducted for 240 days. Two weeks prior to the start of the denitrification experiment (i.e. –14 to 0 days), deionized water was pumped into the column to establish a steady-state flow field. From 0 to 240 days, the input solution contained ca. 20 mg N L⁻¹ (as nitrate) and 350 mg SO₄²⁻ L⁻¹ (derived from KNO₃ and Na₂SO₄ reagents of *purum* and *pro analysi* grade, respectively). Sulfate was included in the input solution since the reactive substrate is intended to be used in a mining environment where sulfate is plentiful (Herbert and Björnström, 2009), and since sulfate-reducing bacteria will compete with denitrifying bacteria for labile organic

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