UPPSALA
UNIVERSITET

<http://uu.diva-portal.org>

This is an author produced version of a paper published in *Journal of Contaminant Hydrology*. This paper has been peer-reviewed but does not include the final publisher proof-corrections or journal pagination.

Citation for the published version:

Roger B. Herbert Jr.

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

Journal of Contaminant Hydrology, 2010, Vol. 123, Issue 1-2, pp. 30-39

URL: <http://dx.doi.org/10.1016/j.jconhyd.2010.12.004>

Access to the published version may require subscription.

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

Roger B. Herbert Jr.*
Department of Earth Sciences
Uppsala University
75236 Uppsala, Sweden

E-mail: Roger.Herbert@geo.uu.se

Fax: +46 - 18 - 55 11 24

* Corresponding author

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.

Keywords: dual porosity, heterogeneity, tracer, diffusion, dispersivity, CXTFIT

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 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 Wierenga, 1976; van Genuchten and Wagenet, 1989).

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 x 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 – 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 compounds in the substrate. Column experiments were conducted at three different discharge rates: ~150 mL day⁻¹, ~360 mL day⁻¹, and ~750 mL day⁻¹. These discharge rates correspond to theoretical hydraulic residence times of 2.8, 1.2, and 0.56 days, assuming that the total porosity consists entirely of mobile water. Throughout the course of the experiment, nitrate and ammonium concentrations in the column effluent were measured at regular intervals, while discharge pH, hydrogen sulfide concentrations, total organic carbon (TOC) concentrations, and alkalinity were measured on several occasions. Note that no ammonium was added to the column input; all ammonium discharging from the column was present or produced in the material (see section 3.2).

2.2 Displacement tests and dual porosity model

Displacement tests were conducted using the two columns in order to investigate non-reactive solute transport in dual porosity media, and to determine the transport parameters for a subsequent field application. For the displacement tests, chloride (as KCl) was used as a tracer for conservative transport through the column matrix. For the period of the tests, chloride was added to the input solution (also containing nitrate and sulfate) for an initial concentration (C_0) of 150 mg L⁻¹ Cl⁻. Since there was chloride present in the column pore water prior to the start of the tracer experiments ($C_i \approx 40 - 50$ mg L⁻¹ Cl⁻), chloride concentrations in breakthrough curves are presented as $(C - C_i)/(C_0 - C_i)$. This initial chloride concentration was derived from impurities in the *purum*-grade KNO₃ reagent, and was constant over the course of the experiment. For each displacement test, the chloride input solution was added as a step input when the chloride concentration in the column discharge was stable at the background level. Upon completion of each displacement test, the chloride-nitrate-sulfate solution was removed from the column input and replaced with the nitrate-sulfate solution.

Breakthrough curves from the displacement tests are fitted with an analytical solution of a two region (i.e. dual porosity) adaption of the ADE, described in van Genuchten and Wagenet

(1989). In this formulation, advective-dispersive transport is confined to a mobile liquid region (identified with subscript m), while the presence of a solute in an immobile region (subscript im) within an aggregate is dependent on diffusion from the mobile to the immobile liquid (van Genuchten and Wagenet, 1989). The steady-state flow, two region transport model is expressed as follows (zero-order production, first-order decay and adsorption are not considered, although these processes can be considered in the model):

$$\theta_m \frac{\delta c_m}{\delta t} = \theta_m D_m \frac{\delta^2 c_m}{\delta x^2} - q \frac{\delta c_m}{\delta x} - \alpha(c_m - c_{im}) \quad (1)$$

$$\theta_{im} \frac{\delta c_{im}}{\delta t} = \alpha(c_m - c_{im}) \quad (2)$$

where

θ_m, θ_{im} = volumetric water content of mobile and immobile liquid phase

c_m, c_{im} = concentration in mobile and immobile phases

D_m = dispersion coefficient of mobile phase

v_m = pore water velocity of mobile phase

$q = v_m \theta_m$ = volumetric flux density (Darcy velocity)

α = first-order mass transfer coefficient

Note that, for the two-region model, $v = \theta_m v_m / \theta$ and $D = \theta_m D_m / \theta$. The computer code CXTFIT (Toride et al., 1999) is used for parameter estimation from breakthrough curves. CXTFIT is used to estimate the parameters v , D , β and ω by fitting the parameters in an analytical solution to the two region advection-dispersion equation (cf. equations 1 and 2), applying appropriate boundary conditions and initial values, using a non-linear least squares inversion approach. The parameters β and ω are dimensionless expressions of the fraction of mobile water and the mass transfer coefficient, respectively:

$$\beta = \frac{\theta_m}{\theta} \quad (3)$$

$$\omega = \frac{\alpha L}{\theta v} \quad (4)$$

where θ is the total porosity ($\theta_m + \theta_{im}$) and L is the characteristic length of the studied system (column length). For this experimental set-up, flux-type inlet conditions and flux-averaged outlet conditions have been used as boundary conditions (van Genuchten and Parker, 1984).

The parameter β represents the fraction of solute present in the mobile region under equilibrium conditions while ω represents the ratio between hydrodynamic residence time and a characteristic time of solute movement in the immobile region. The two region model simplifies to a one region, one porosity model when $\beta = 1$. Solute concentrations in the mobile and immobile phases are in equilibrium for high values of ω ($\omega > 100$), while mass transfer between mobile and immobile phases becomes insignificant at very low values of ω ($\omega \approx 0$; i.e. $\alpha \approx 0$).

In the determination of transport parameters with CXTFIT, initial parameter estimates need to be provided. In addition, it is desirable that parameter ranges are constrained as much as possible so as to obtain unique estimations. For this study, initial parameter values and constraints have been defined for an estimated fraction of mobile water (β_{est}), an estimated pore water velocity (v_{est}), a dispersion coefficient (D_{est}), and an estimated dimensionless mass transfer coefficient (ω_{est}). As an initial estimate, the parameter β_{est} is assigned a value of 0.5, equal to the pore fraction occupied by sawdust, under the simple assumption that mobile water occurs in the sawdust and not in the sludge. The initial estimate for pore water velocity (v_{est}) was set equal to the Darcy velocity q divided by the porosity ($q = Q/A$; A is column cross-sectional area; cf. Seifert and Engesgaard, 2007). The total porosity (θ) of the porous medium was determined by completely drying an initially water-saturated column at 80°C; a value of 0.40 was obtained. The initial estimate for the dispersion coefficient (D_{est}) is based on the relationship $D = v\lambda$ (λ = longitudinal dispersivity; Domenico and Schwartz, 1998) and an initial estimate of 1 cm for λ . The minimum and maximum values imposed on v_{est} and D_{est} are based on the uncertainty in these estimates; the uncertainty in v_{est} is estimated to $\pm 50\%$, while the upper limit on D_{est} is based on an estimated upper limit on λ of 3 cm. This upper limit is rather arbitrary, but the scale of the system is 21 cm, and the longitudinal dispersivity should only be a fraction of the scale of observation. Although there are no general rules for the magnitude of dispersivities in laboratory – scale systems, Gelhar et al. (1992) demonstrated that field-scale and aquifer-scale dispersivities generally increase with the scale of observation and are on the order of two orders-of-magnitude smaller than the scale of study.

The initial estimate for the dimensionless mass transfer coefficient (ω_{est}) is calculated from equation 4, with α determined as follows (Parker and Valocchi, 1986; Seifert and Engesgaard, 2007):

$$\alpha = \frac{15D_e\theta_{im}}{l^2} \quad (5)$$

where D_e is the effective diffusion coefficient of chloride in water, 15 is a shape factor for diffusion into spherical aggregates, and l is the length of diffusion. It is assumed that the sludge aggregates are 2 cm spherical particles, and l is therefore the radius of the aggregates. The sawdust is much smaller in size (ca. 0.1 - 1 mm flakes), and is assumed to function as a typical porous medium.

The initial parameter estimates and constraints are presented in Table 1. In addition to the fitted parameters, breakthrough time (t_b) and effective porosity (θ_e) were calculated from the chloride breakthrough curves. The breakthrough time is defined as the time when $(C-C_i)/(C_0-C_i)$ equals 0.5 in the column discharge (cf. Domenico and Schwartz, 1998), and the effective porosity is defined as Qt_b/V , where Q is the flow rate through the column (mL d^{-1}) and V is the column volume (mL). The theoretical hydraulic residence time (t_{Rt}) is calculated from known parameters as $L\theta/q$ (Table 1). Since breakthrough curves for dual porosity media are asymmetrical, the t_b parameter lacks its traditional definition because of significant tailing and can differ significantly from t_{Rt} . 2.3 Analyses

Nitrate was determined using an ion selective electrode (Orion™ 97-07) on samples preserved with boric acid. Prior to analysis, samples were treated by adjusting the ionic strength and precipitating interfering agents (hydrogen sulfide, chloride, humic substances) with Orion™ interference suppression solution. Electrode readings were recalculated to concentrations using a multipoint calibration curve constructed for the relevant range of analytical results. Ammonium was determined using a Hitachi UV/vis-spectrophotometer and the phenol – hypochlorite – nitroprusside method. Chloride and hydrogen sulfide concentrations were measured by potentiometric titration against a silver/sulfide ion selective electrode (Orion™ 96-16). Total organic carbon (TOC) was determined on a Shimadzu TOC-5000 analyzer.

3. Results and discussion

3.1 Hydraulic properties with single porosity model

The displacement tests were conducted at three different flow rates: $\sim 150 \text{ mL day}^{-1}$ (“low flow”), $\sim 360 \text{ mL day}^{-1}$ (“medium flow”) and $\sim 750 \text{ mL day}^{-1}$ (“high flow”), corresponding to Darcy velocities of $\sim 3 \text{ cm d}^{-1}$, $\sim 7 \text{ cm d}^{-1}$ and $\sim 15 \text{ cm d}^{-1}$, respectively. While displacement

tests were conducted on both columns at medium and high flow rates, only column 1 was studied under low flow conditions. In order to motivate the use of the dual porosity model on the resultant chloride breakthrough curves, parameter estimates were first provided using a single porosity model. In this approach, the initial parameter estimates shown in Table 1 were used, but no parameter constraints were applied. In the single porosity case, β and ω were assigned fixed values of 0.99 and 100, respectively, implying that the mobile porosity approximately equals total porosity and exchange between mobile and immobile water is rapid.

Data from representative chloride breakthrough curves are presented in Figures 1a and 1b, along with the fitted breakthrough curves from CXTFIT; the fitted parameters v and D are shown in Table 2. While the fitted pore water velocities are similar to the initial parameter estimates, the fitted dispersion coefficients are large and the matrix dispersivities are consequently large. Indeed, dispersivities for the medium and high flow cases are at the same scale or exceed the scale of the system. Although λ for the low flow case (5.6 cm) may be considered acceptable if only low flow was considered, the λ values at higher flow rates are unreasonably large. The large longitudinal dispersivities, combined with λ values that increase with flow rate, indicate an inadequate model of solute transport in the system and support the assumption that a single porosity model is generally not applicable to the reactive media used in this study. Furthermore, inspection of the fitted chloride breakthrough curves (Figure 1) indicates a poor fit in regions where tailing is expected (i.e. where $t \ll t_b$ and $t \gg t_b$). Hence, only the dual porosity model will be considered in this study.

3.2 Hydraulic properties with dual porosity model

Hydraulic parameters estimated by CXTFIT from the best fit to experimental data are tabulated in Table 3. In addition to previously-defined parameters in Table 3, hydraulic residence time (t_R) has been calculated from the velocity of the mobile water (L/v_m). Data from representative chloride breakthrough curves are presented in Figures 2a and 2b, along with the fitted breakthrough curves from the CXTFIT non-equilibrium dual porosity model. Initial CXTFIT simulations for parameter estimation converged to pore water velocities that did not greatly differ from the original estimates, with β values in a range from 0.09 to 0.34 and α values from 0.14 to 2.1 d⁻¹ (see Table 3). Since β and α are considered intrinsic material properties and should be similar for all experiments, this degree of variation was too large. However, three of the experiments (column 2 at medium and high flow and column 1 at

high flow; Table 3) could be fitted with similar β values and α values of the same magnitude, which suggested that the remaining two experiments (column 1 at low and medium flow) may have converged to a local minimum of the objective function in the least squares optimization procedure. This possibility was investigated by running multiple simulations with CXTFIT using the parameter estimates and constraints shown in Table 1, but with β fixed at specific values. The mean square error (MSE) reported by CXTFIT was used as a measure of the goodness-of-fit of the analytical solution to the chloride breakthrough curves. As shown in Figure 3, both of the columns at different flow rates exhibit MSE minima where $\beta = 0.2$ to 0.3 . For the two experiments (column 1 at low and medium flow) that originally converged with β values outside this range, parameter estimates were instead obtained for a fixed β at the MSE minimum (“final” values in Table 3).

As expected, the results of the displacement tests (Table 3) show increasing pore water velocities of mobile water (v_m) and decreasing hydraulic residence times (t_R) with increasing flow rates. The dispersion coefficient of the mobile phase (D_m) increases with increasing v_m , as expected for the relationship $D = \lambda v$, but it should be noted that CXTFIT converged using the upper limit constraint for D_{est} for each case except for column 2 at medium flow. This suggests that CXTFIT may have converged to greater D_m values if the upper limit was increased, but this would have resulted in longitudinal dispersivities (λ) that approached the scale of the system, which would be unreasonable. For the simulation results (Table 3), the calculated values for λ are moderate, with a mean value of 2.3 cm. As the longitudinal dispersivity is assumed to be an intrinsic property for saturated flow (Toride et al., 2003), the λ values for all experiments should be similar, which appears to be the case in this study. These are relatively large dispersivities for laboratory – scale systems, where dispersivities are often determined as one to two orders-of-magnitude lower for porous media in the sand and silt fractions (e.g. Toride et al., 2003). However, relatively large dispersivities have been measured in other laboratory column studies as well where a heterogeneous and fibrous substrate was studied (e.g. compost, $\lambda \approx 2$ cm; Waybrant et al., 2002) or where decreases in θ_m due to biomass production occurred ($\lambda = 0.2 - 2$ cm; Seifert and Engesgaard, 2007).

The fraction of the porosity consisting of mobile water (β) is fairly consistent for all the experiments, lying in the range 0.23 to 0.30, with an average value of 0.27. This value is less than the estimated initial value for β (0.5), and suggests that not only does sludge pore space contain immobile water, but a significant fraction of the sawdust pore space must also contain

immobile water. The mass transfer coefficient α , determined from the fitted parameter ω , is in the range of $0.14 - 0.83 \text{ d}^{-1}$, with an average value of 0.42 d^{-1} . The fitted ω values are much smaller than the estimated values ($\omega_{\text{est}} \approx 11$ to 54), which can be attributed to large uncertainties in the shape factor (spherical aggregate assumption) and diffusion length (i.e. aggregate size). The ω values determined by CXTFIT are low, and imply that diffusive mass transfer between regions of mobile and immobile water is slow but not insignificant over the length of the column. Because of diffusive exchange between immobile and mobile water, simulated chloride concentrations (Figure 2) in the immobile phase lag behind concentration increases in the mobile phase. For systems where contaminant treatment (e.g. by denitrification, see below) is expected to primarily occur in the immobile phase, this implies that reaction rates must be faster than diffusion into the immobile phase, which in turn must be faster than the hydraulic residence time. If mass transfer is too slow for efficient treatment, one method for increasing mass transfer coefficients would be to decrease the size of aggregates that contain immobile water (cf. Equation 5).

The dual porosity model provides a much improved representation of solute transport in the investigated heterogeneous system compared with the single porosity model, as indicated by a better fit to experimental data and the relatively consistent parameters estimated for α , β and λ over a range of flow rates. However, the estimated parameters are not identical for the different flow rates, suggesting that the actual flow system is more complex than simulated with a dual porosity model. The dual porosity model is limited to the consideration of two pore regions that interact by exchanging solutes in response to concentration gradients. At a macroscopic level, two solute concentrations and two flow velocities characterize the system at any point in time and space. A better representation of the system may require the consideration of additional pore regions with contrasting properties (e.g. permeability), spatial variability in pore water velocity, and/or multi-domain behavior.

3.2 Denitrification experiment

The nitrate and ammonium concentrations in the column discharge are depicted in Figure 4. Nitrate concentrations in the column discharge are low throughout the experiment, except at the highest flow rate (i.e. shortest residence time). Average nitrate concentration is $0.4 - 0.5 \text{ mg N L}^{-1}$ at low and medium flow and is 7.8 mg N L^{-1} at high flow, where the lower concentrations are most likely rate-limiting. In terms of nitrate removal, the column system removes $>95\%$ of influent nitrate at low and medium flow, but only $50 - 75\%$ of influent

nitrate at high flow. For this experiment, apparent denitrification rates can be calculated from the amount of nitrate removed by denitrification ($C_0 - C$), divided by the hydraulic residence time (t_R). These rates are considered “apparent” since the resident concentration profiles in the columns are not known and the calculations assume a linear decrease in concentration over the length of the column. Indeed, for the low and medium flow experiments, these are minimum denitrification rates since nitrate is almost completely consumed in the columns by denitrification; rapid denitrification over a shorter distance than the length of the column would result in a larger denitrification rate. Calculations yield apparent denitrification rates of 38 - 102 mg N L⁻¹ d⁻¹ for the various experiments, but if the rates from only the high flow experiment are considered, then rates of 102 and 98 mg N L⁻¹ d⁻¹ are determined for columns 1 and 2, respectively.

The pH of the column effluent was initially ~6.8, but increased to ~7.4 over the course of the experiment. Average total alkalinity from several measurements was 195 mg HCO₃⁻ L⁻¹ and 239 mg HCO₃⁻ L⁻¹ from columns 1 and 2, respectively. The increase in pH is attributed to the increase in carbonate alkalinity (mainly HCO₃⁻) that is associated with heterotrophic denitrification and carbonate equilibrium:

After the onset of the column experiment, the production of hydrogen sulfide in the columns was detected by its distinct smell in the column discharge. One measurement on day 226 yielded concentrations of 24 and 20 mg HS⁻ L⁻¹ from columns 1 and 2, respectively.

Hydrogen sulfide is derived from microbial sulfate reduction in the column substrate. At the start of the experiment, the TOC concentration was initially ca. 15 mg C L⁻¹ in the column effluent from column 2 (column 1 not measured), but decreased rapidly to ca 8 mg C L⁻¹ and stabilized at this level.

Ammonium concentrations are initially elevated in the discharge solution but decrease gradually over the course of the experiment, approaching a stable concentration of ca. 0.6 mg N L⁻¹ after 90 days. As ammonium is present in the column discharge prior to the addition of nitrate to the column input, the ammonium is most likely present in the sludge pore water at the start of the experiment (i.e. immobile water), diffusing into the mobile region along a concentration gradient at the start of the experiment. However, it is not likely that the slow decline in ammonium concentrations in the effluent is solely due to residual ammonium in the immobile water. A CXTFIT simulation of the leaching of a conservative compound from the

column pore space (Figure 4, “modeled NH_4^{+} ”), using the fitted parameters shown in Table 3, indicates that normalized concentrations (C/C_0) of such a compound would decline to less than 0.01 after six days; this period is much longer in the column experiment. There must therefore be another source of ammonium in the reactive substrate. Low ammonium concentrations may also be the result of 1) dissimilatory nitrate reduction to ammonium (DNRA), 2) cation exchange with Na^+ and K^+ present in the column input solution, and 3) organic matter degradation by aerobic respiration close to the column input. In terms of DNRA and cation exchange, these processes are probably of minor quantitative importance under these specific experimental conditions. Aerobic respiration, on the other hand, will provide a continual source of ammonium to the pore water as proteinaceous material in the reactive substrate is oxidized by dissolved oxygen in the influent water. Slowly declining ammonium concentrations probably indicate the consumption of highly labile organic compounds in the reactive substrate; after ca. 80 days from $t=0$, the reactivity of this fraction appears to have greatly decreased. The concept of organic matter composed of fractions with varying reactivity is consistent with previously proposed models (Westrich and Berner, 1984; Boudreau and Ruddick, 1991) and declining microbial reaction rates in reactive barriers (e.g. Benner et al., 2002). Over the short time scale and low flow rates of the experiment, the oxidation of organic matter is not expected to affect the hydraulic properties of the reactive substrate.

Although the simulation of biogeochemical processes in the column system is beyond the scope of this study, the processes that should be considered in such a simulation are aerobic respiration, denitrification, and sulfate reduction. Each of these heterotrophic processes is coupled to the oxidation of organic matter composed of fractions with different reactivities (see above); reaction rates are expressed using Monod-type kinetics. As the experiment is conducted under steady-state flow conditions, a relatively simple one-dimensional reactive transport model incorporating a dual porosity system can be used, such as PHREEQC (Parkhurst and Appelo, 1999).

4. Implications for barrier systems

The results of these column experiments have several implications for field-scale barrier systems. Firstly, the study demonstrates that the dual porosity formulation in CXTFIT can be implemented in explaining solute transport in a mixture of substrates relevant for barrier systems. At shorter residence times, a dual porosity model is needed to explain the tailing (cf.

Figure 2) that is observed in displacement tests. However, in a system where t_R is long, allowing for solute equilibrium between mobile and immobile water, a single porosity formulation may be adequate for describing solute transport. Indeed, considering the nature of the porous media used in this study (i.e. highly contrasting permeabilities, compressible material, additional levels of porosity), it is possible that more complex models are needed to fully explain system behavior (e.g. continuous time random walk formulations; Berkowitz et al., 2006).

In this study, decreases in hydraulic residence time coincide with decreases in the degree of nitrate removal, suggesting that the diffusive mass transfer rate is limiting the degree of treatment at lower t_R (i.e. higher flow rates). This is supported by the estimated average mass transfer time ($\alpha^{-1} = 2.4$ days; cf. Table 3), which is somewhat greater than the hydraulic residence times (0.57, 0.37, 0.13 days). Furthermore, denitrification kinetics may also be limiting treatment at high t_R , but an accurate estimate of an intrinsic denitrification rate is not available with the present data set. In order to optimize treatment with a dual porosity substrate, t_R in the mobile region should exceed the diffusive mass transfer time (α^{-1}). As previously mentioned, α can be increased (α^{-1} decreased) by decreasing the size of aggregates containing bioreactive zones. However, in field-scale barrier systems, small aggregate sizes may not be easily maintained during material processing. Instead, t_R will need to be increased by, for example, increasing the flowpath length through a permeable reactive barrier.

A word of caution needs to be raised about the extrapolation of parameter values from laboratory-scale to field-scale experiments. A primary assumption enabling such an extrapolation is that the degree of heterogeneity is the same at both scales. This is most likely not true, as larger-scale heterogeneities often arise in larger-scale systems. The simulation of solute transport in a field-scale system may therefore need to consider large scale heterogeneities and their impact on residence time and contaminant removal (i.e. in permeable reactive barriers).

As a final note, it should be remarked that many permeable reactive barriers containing an organic substrate have hydraulic residence times that are much longer than the residence times used in this study (see e.g. Blowes et al., 2000; Benner et al., 2002). This results in dual porosity systems where hydraulic residence times are greater than the diffusive mass transfer times, and treatment in microenvironments containing immobile water is thus feasible. 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.

5. Acknowledgments

This project has been financed by VINNOVA, through the program *Strategiskt gruvforskningsprogram*. Robin Djursäter is thanked for his assistance in the laboratory. Two anonymous reviewers have provided substantial comments that have greatly improved the quality of this manuscript.

6. References

- Benner, S.G., Blowes, D.W., Ptacek, C.J., Mayer, K.U., 2002. Rates of sulfate reduction and metal sulfide precipitation in a permeable reactive barrier. *Appl. Geochem.* 17, 301–320.
- Berkowitz, B., Cortis, A., Dentz, M., Scher, H. 2006. Modeling non-Fickian transport in geological formations as a continuous time random walk, *Rev. Geophys.*, 44, RG2003, doi:10.1029/2005RG000178.
- Blowes, D.W., Robertson, W.D., Ptacek, C.J., Merkley, C., 1994. Removal of agricultural nitrate from tile-drainage effluent water using in-line bioreactors. *J. Contam. Hydrol.* 15, 207 – 221.
- Blowes, D.W., Ptacek, C.J., Benner, S.G., McRae, C.W.T., Bennet, T., Puls, R., 2000. Treatment of inorganic contaminants using permeable reactive barriers. *J. Contam. Hydrol.* 45, 123 – 137.
- Boudreau, B.P., Ruddick, B.R., 1991. On a continuum representation of organic matter diagenesis. *Am. J. Sci.* 291, 507–538.
- Domenico, P.A., Schwarz, F.W., 1998. *Physical and Chemical Hydrogeology*, John Wiley & Sons, New York, 506 p.
- Gavaskar, A.R., Gupta, N., Sass, B.M., Janosy, R.J, O'Sullivan, D. (1998) *Permeable barriers for groundwater remediation*. Battelle Press, Columbus, 176 p.
- Gelhar, L.W., Welty, C., Rehfeldt, K.R., 1992. A critical review of data on field-scale dispersion in aquifers. *Water Resour. Res.* 28, 1955 – 1974.

Herbert, R.B., 2003. Zinc immobilization by zerovalent Fe: Surface chemistry and mineralogy of reaction products. *Min. Mag.* 67, 1285–1298.

Herbert, R.B., Björnström, J. 2009. Barrier system for the treatment of nitrogen effluents from the Malmberget iron mine. In: *Proceedings, Securing the Future and 8th ICARD*, June 22 – 26, 2009, Skellefteå, Sweden.

Kamolpornwijita, W., Liang, L., Westa, O.R., Molinea, G.R., Sullivan, A.B., 2003. Preferential flow path development and its influence on long-term PRB performance: Column study. *J. Contam. Hydrol.* 66, 161-178.

Mayer, K.U., Blowes, D.W., Frind, E.O., 2001. Reactive Transport Modeling of an in Situ Reactive Barrier for the Treatment of Hexavalent Chromium and Trichloroethylene in Groundwater. *Water Resour. Res.* 37, 3091–3103.

Mayer, K.U., Benner, S.G., Blowes, D.W., 2006. Process-based reactive transport modeling of a permeable reactive barrier for the treatment of mine drainage. *J. Contam. Hydrol.* 85, 195–211.

Mackenzie, P.D., Horney, D.P. Sivavec, T.M., 1999. Mineral precipitation and porosity losses in granular iron columns. *J. Haz. Mat.* 68, 1 –17.

Parker, J.C., Valocchi, A.J., 1986. Constraints on the validity of equilibrium and first-order kinetic transport models in structured soils. *Water Resour. Res.* 22, 399 - 407.

Parkhurst, D.L., Appelo, C.A.J., 1999. User's Guide to PHREEQC (Version 2) — a Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. U.S. Geological Survey Water-Resources Investigations Report, vol. 99-4259.

Robertson, W.D., Vogan, J.L., Lombardo, P.S. 2008. Nitrate removal rates in a 15-year-old permeable reactive barrier treating septic system nitrate. *Ground Water Monit. Remed.* 28, 65 – 72.

Schipper, L.A., Barkle, J.F., Hadfield, J.C., Vojvodic-Vukovic, M., Burgess, C.P., 2004. Hydraulic constraints on the performance of a groundwater denitrification wall for nitrate removal from shallow groundwater. *J. Contam. Hydrol.* 69, 263– 279

- Seifert, D., Engesgaard, P., 2007. Use of tracer tests to investigate changes in flow and transport properties due to bioclogging of porous media. *J. Contam. Hydrol.* 93, 58 – 71.
- Toride, N., Inoue, N., Leij, F., 2003. Hydrodynamic dispersion in an unsaturated dune sand. *Soil Sci. Soc. Am. J.* 67, 703 – 712.
- Toride, N., Leij, F.J., van Genuchten, M.Th., 1999. The CXTFIT code for estimating transport parameters from laboratory or field tracer experiments, Version 2.1, Research Report No. 137, U.S. Salinity Laboratory, Agricultural Research Service, U.S. Department of Agriculture, Riverside, California, USA.
- van Genuchten, M.Th., Parker, J.C., 1984. Boundary conditions for displacement experiments through short laboratory columns. *Soil Sci. Soc. Am. J.* 48, 703 – 708.
- van Genuchten, M. Th., Wagenet, R.J., 1989. Two-site/two-region models for pesticide transport and degradation: Theoretical development and analytical solutions. *Soil Sci. Soc. Am. J.* 53, 1303 - 1310.
- van Genuchten, M. Th., Wierenga, P.J., 1976. Mass transfer studies in sorbing porous media. I. Analytical solutions, *Soil Sci. Soc. Am. J.* 40, 473 – 480.
- Waybrant, K.R., Ptacek, C.J., Blowes, D.W., 2002. Treatment of mine drainage using permeable reactive barriers: Column experiments. *Environ. Sci. Technol.* 36, 1349-1356.
- Westrich, J.T., Berner, R.A., 1984. The role of sedimentary organic matter in bacterial sulfate reduction: the G model tested. *Limnol. Oceanogr.* 29, 236–249.

Figure captions:

Figure 1: Chloride breakthrough curves from displacement tests at medium flow (a) and high flow (b). The fitted curves from CXTFIT are based on best fits from a single porosity model ($\beta = 0.99$, $\omega = 100$). No parameter constraints are imposed. Note that the x-axis has a logarithmic scale.

Figure 2: Chloride breakthrough curves from displacement tests at medium flow (a) and high flow (b). The fitted curves from CXTFIT are based on best fits from a dual porosity model using the constraints shown in Table 1. Note that the x-axis has a logarithmic scale.

Figure 3: Mean square errors as a function of β for multiple CXTFIT simulations. For each simulation, β was fixed at the value along the x-axis but with constraints on ν , D and ω as shown in Table 1.

Figure 4: Concentrations of nitrate and ammonium (as N concentration) in column effluent, along with simulated NH_4^+ concentrations assuming an initial source that diffuses from the immobile water. Changes in flow rates are demarked with vertical lines. Day 0 marks the change from deionized water in the column input to a nitrate-sulfate solution.

Table 1: Initial estimates and constraints on transport parameters ν , D , β , and ω fitted by CXTFIT.

Parameter	Units	Initial value	Upper limit	Lower limit
ν	cm d^{-1}	$\nu_{\text{est}} = q / \theta$	$1.5 \nu_{\text{est}}$	$0.5 \nu_{\text{est}}$
D	$\text{cm}^2 \text{d}^{-1}$	$D_{\text{est}} = \nu_{\text{est}} \times 1\text{cm}$	$3 D_{\text{est}}$	$0.5 D_{\text{est}}$
β	–	$\beta_{\text{est}} = 0.5$	0.99	0.01
ω	–	$\omega_{\text{est}}^{\dagger}$	100	0.01

$\dagger$ see equation 4

Table 2: Hydraulic parameters determined directly from chloride breakthrough data (t_b , θ_e) and estimated by CXTFIT (ν , D) using single porosity model ($\beta=0.99$, $\omega=100$). λ is calculated from D/ν . No limits are imposed on estimated parameters. Definitions: q = Darcy velocity; t_b = breakthrough time when $(C-C_i)/(C_0-C_i)=0.5$; t_{Rt} = theoretical hydraulic residence time = $L\theta/q$; θ = total porosity, θ_e = effective porosity (see text).

							CXTFIT		
							fitting parameters		
	Flow, Q (mL d^{-1})	q (cm d^{-1})	θ	θ_e	t_b (d)	t_{Rt} (d)	ν (cm d^{-1})	D ($\text{cm}^2 \text{d}^{-1}$)	λ (cm)
<i>Low flow</i>									
Column 1	153.0	3.0	0.40	0.24	1.7	2.8	11.0	60.9	5.6
<i>Medium flow</i>									
Column 1	357.6	7.1	0.40	0.24	0.72	1.2	16.1	290.8	18.1
Column 2	364.8	7.3	0.40	0.22	0.64	1.2	17.2	346.4	20.2
<i>High flow</i>									
Column 1	745.1	14.8	0.40	0.12	0.17	0.57	43.4	1535	35.4
Column 2	733.7	14.6	0.40	0.12	0.17	0.58	51.1	1460	28.6

Table 3: Hydraulic parameters estimated by CXTFIT (v_m , D_m , β , ω). α is calculated from equation 4, v_m and D_m are calculated from v , D and β . $\lambda = D_m/v_m$. Hydraulic residence time (t_R) calculated as L/v_m . Hydraulic conditions are presented in Table 2.

	CXTFIT fitting parameters				λ (cm)	α (d ⁻¹)	t_R (d)
	v_m	D_m	β	ω			
	(cm d ⁻¹)	(cm ² d ⁻¹)					
<i>Low flow</i>							
Column 1(initial)	128.3	262.7	0.087	7.07	2.1	1.50	0.16
Column 1 (final) [†]	36.9	76.0	0.30	3.95	2.1	0.83	0.57
<i>Medium flow</i>							
Column 1 (initial)	49.4	157.5	0.34	0.79	3.2	0.25	0.42
Column 1 (final) [†]	68.6	119.5	0.25	0.85	1.7	0.28	0.31
Column 2	48.7	81.8	0.30	0.50	1.7	0.14	0.43
<i>High flow</i>							
Column 1	157.2	475.2	0.23	0.62	3.0	0.43	0.13
Column 2	156.5	431.1	0.25	0.55	2.8	0.41	0.13
Average	--	--	0.27	--	2.3	0.42	--

[†] Parameters estimated by constraining β and selecting parameters with lowest mean square error for fit (see Fig. 3)

Figure 1

Figure 2

Figure 3

Figure 4