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# Need for Direct Measurements of Coupled Microbiological and Hydrological Processes at Different Scales in Porous Media Systems

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**Abstract:** Reactive transport models contain terms describing microbiological and hydrological processes that control fate and transport of contaminants in porous media. Most models assume that microbial reaction rate is independent of microbial biomass distribution or that biomass is uniformly distributed across media surfaces in a manner that mass transport does not limit reaction rate. Experimental data, as well as some computational models, however, suggest otherwise, indicating a need to experimentally establish how the coupling of microbial biomass and flow distribution influence microbial reaction rates. Nuclear magnetic resonance techniques offer the opportunity to quantify in three dimensions the coupling of microbial biomass and flow velocity distribution in opaque porous media at multiple scales in a noninvasive manner. Experimental data obtained with these techniques can be used to improve the accuracy of boundary conditions used by reactive transport models to predict contaminant fate and transport at the pore and core scales. Further improvements in surface and subsurface magnetic resonance techniques may allow future detection and measurement of microbial biomass distribution in the subsurface at the field scale.

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## Introduction

The demand for energy, potable water, and minerals is expected to increase dramatically over the next 50 years. Efficient exploitation of these resources requires an understanding of the physical, geological, hydrological, chemical, and biological processes that occur in Earth's deep subsurface environment. Currently, we depend on computational models to monitor and manage these resources. However, today's best models often fail to accurately predict subsurface processes at the field scale. This is due to our inadequate understanding of these processes and the parameters controlling them. We lack experimentally derived data sets for model calibration and validation, and appropriate techniques for characterizing subsurface properties and heterogeneities that control processes of interest.

The data sets currently used to model subsurface behavior have been obtained under experimental conditions that often fail to couple those geological, hydrological, chemical, and biological processes that operate at the field scale. For example, chemical adsorption, precipitation, ion exchange, oxidation/reduction, and

complexation/chelation reactions, colloid formation, and microbiologically-mediated transformations in porous media have not been rigorously defined in terms of hydrodynamic parameters in spite of the fact that all these processes are controlled by mass transport (Fig. 1). Microbial processes, due of their complexity, have been particularly challenging to couple to geological, hydrological, and chemical phenomena, even in highly simplified experimental systems. Nevertheless, the growing awareness that many abiotic processes in the subsurface are coupled to microbial activities has led to significant advances in our understanding of not only mineral transformations, but also microbial metabolism of geological material (Chapelle 2000; Lovley and Anderson 2000). For example, we are presently at the threshold of understanding how bacteria transfer electrons to solid phase minerals; a milestone in microbial physiology and a key to understanding mineral transformations.

An anticipated practical outcome of this knowledge is the application of microbial metabolism to control subsurface contaminant transport and remediate difficult to access subsurface sites contaminated with toxic organic solvents, heavy metals, and radionuclides (Dutta et al. 2005; Fredrickson et al. 1990; Miller et al. 2001; Turick et al. 1996; Wobber 1990). The science resulting from this interdisciplinary research has led to the establishment of several recent field-scale projects that demonstrated the feasibility of in situ microbially-mediated immobilization of uranium (Anderson et al. 2003; Istok et al. 2004; Wu et al. 2006a,b) and strontium (Fujita et al. 2004, 2003), and the retardation of methyl tertiary butyl ether (MTBE) and nitrate transport in aquifers (Dutta et al. 2005; Miller et al. 2001). While the feasibility of exploiting specific microbial activities in the deep subsurface to mediate or facilitate a desired geochemical process has now been clearly established, significant knowledge gaps still exist that compromise our ability to maintain the desired level of control over the processes. The knowledge gaps include understanding

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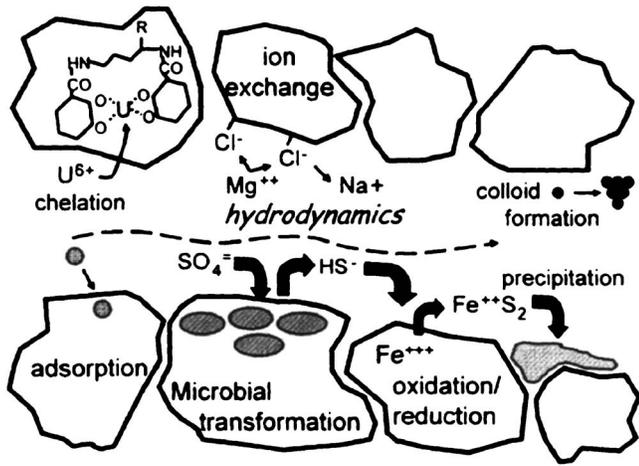


Fig. 1. Relationship between hydrological, geochemical, and microbiological processes in porous media

what controls fate and transport behavior in the subsurface, and how those controlling parameters can be measured at the appropriate scales (National Research Council 2000).

In this paper, we review benchmarks in understanding and modeling microbial processes that are coupled to physical and hydrological properties of porous media systems. We identify model assumptions that need to be tested through experimentation, and describe experimental approaches that should yield data sets that can be used to test and improve the models. Specifically, we describe the potential for nuclear magnetic resonance techniques to couple microbial biomass distribution to flow distribution at different scales, and how experimental data produced with these techniques at the laboratory scale may, in the future, reduce uncertainties of boundary conditions used by current models to predict contaminant fate and transport at the field scale.

### Microbial Behavior in Porous Media

Microorganisms have long been known to influence the fate and transport of organic matter in soils through their enzymatically-catalyzed biodegradative activities (McNabb and Dunlap 1975). Various expressions based on Monod kinetics have been used to model rates of microbiologically mediated reactions (Boethling and Alexander 1979; Williamson and McCarty 1976). Reactive transport models have incorporated parameters based on Monod kinetics to account for biological impacts on contaminant fate and transport in the subsurface (Baveye and Valocchi 1989; Bower and McCarty 1984; Ginn et al. 1995; Harvey et al. 1989; McCarty et al. 1984; Molz et al. 1986; Rittmann et al. 1980; Wood et al. 1994).

Fixed-bed column reactors containing various types of porous media are commonly used to generate experimental data on coupled hydrological, geophysical, and geochemical, processes for testing and calibrating various reactive transport models. Column reactors containing intact core material have provided useful data on coupled processes that have been scaled up to the field (Brooks and Carroll 2002; Pace et al. 2003; Sanchez-Martin et al. 2001; Winfred et al. 2006). Fixed-bed column reactors have also been used to obtain data on bacterial cell transport as well as solute consumption or degradation by microorganisms in porous media (DeFlaun et al. 1997; Hornberger et al. 1992; Murphy et al. 1997; Smith et al. 1985). Fixed-bed columns of undisturbed core

material have served to relate transport of bacteria and colloids to hydrodynamic and physical features of geological media (Fisk et al. 1999; Smith et al. 1985; van Elsas et al. 1990; White 1985), and to obtain rates of biogeochemical transformations in porous geological media under dynamic flow conditions (Benner et al. 2002; Gu et al. 2005; Hansel et al. 2003, 2004; Roden et al. 2000).

### Porous Media-Associated Biomass

Porous media provides a large surface area for colonization by microorganisms, and there is growing evidence that a portion of the microbial biomass in the subsurface is associated with the surfaces of geological media (Cunningham et al. 1991; Harvey et al. 1984; Lehman et al. 2001; Lehman and O'Connell 2002; Lehman et al. 2004; McNabb and Dunlap 1975; Taylor and Jaffe 1990c). Bacteria associate with geological media to access nutrients and/or contaminants adsorbed to solid surfaces and to maximize access to these solute molecules when they are dissolved in pore water flowing across media surfaces. Expressions for bacterial attachment to porous media particle surfaces, surface-associated biomass accumulation, and detachment have been developed and incorporated into reactive transport models (Characklis et al. 1987; Johnson et al. 1995; Murphy and Ginn 2000; Peyton and Characklis 1993; Taylor and Jaffe 1990c). The amount of biomass produced during consumption of a soluble substrate flowing through a fixed-bed reactor is used to calculate specific reaction rate and yield coefficient (Murphy et al. 1997). Conventional biomass assays, such as direct microscopic cell counts, protein, lipid, or total organic carbon require the recovery of a portion of the porous medium for each analysis, which requires interruption of flow, disassembly of the column, and destruction of bed integrity (Chen et al. 1992). This precludes the opportunity to monitor changes in "fixed" biomass associated with the porous media during an experiment. Thus, the fixed biomass is usually only determined following termination of an experiment.

Rittmann and McCarty (1980a,b) presented a model for relating fixed biomass to substrate consumption that uses the measured thickness and mass density of the fixed biomass to quantify biomass accumulation under steady-state conditions. They further suggested that fixed biomass under these conditions could be calculated from a normalized rate of substrate loading at colonized porous media surfaces, a parameter that could be computed from overall substrate consumption within the column. Modeling substrate flux in this manner is based on the assumption that mass transport limitation does not occur within the biomass associated with porous media (Rittmann 1993). While this assumption may be justified in some subsurface environments where availability of energy limits the formation of multiple bacterial cell layers on porous media surfaces, it remains to be rigorously tested for subsurface systems receiving significant inputs of nutrients to stimulate growth or activity of surface-associated microbial biomass to enhance contaminant removal or transformation.

### Microbial Distribution in Porous Media Systems

Reactive transport models may fail to accurately predict biodegradation of a subsurface contaminant in the field as a result of assigning unrealistic boundary conditions due to poor understanding of heterogeneities within the system (LaViolette et al. 1999; Madsen 1991; Vermeulen et al. 2006; Zhang et al. 2006). Assignment of accurate boundary conditions for microbial reaction rates

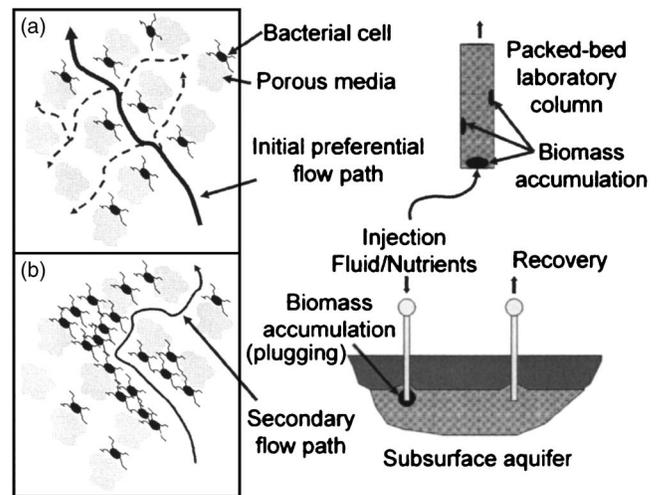
in reactive transport models begins with an understanding of how microbial biomass is distributed within flow paths. At the pore scale, some investigators suggest that the biomass is patchy (Vandevivere and Baveye 1992a,b), while others assume that it is distributed as a continuous biofilm across the particle surface (Cunningham et al. 1991; Taylor and Jaffe 1990c). Rittmann (1993) suggested that as long as mass transport is not limiting, reaction rate is independent of biomass distribution, and can be calculated from substrate utilization.

More recent modeling efforts indicate that biomass distribution does influence overall reaction kinetics of the system. LaViolette et al. (1999) used a simple mathematical model to demonstrate that spatial disorder in the distribution of microorganisms degrading a contaminant even across small distances that separate microbial aggregates induces a wide range of times to achieve degradation to an arbitrary limit. This suggests that mass transport limitations do exist, and models that employ an ensemble of biomass distributions that reflect these limitations rather than a single spatial averaged distribution free of mass transport limitations can provide reasonable bounds on the range of expected behavior and transformation of substrate. Studies are needed to determine under what microbial biomass distributions, pore geometry, hydrodynamics, and aqueous phase chemistry mass transport limitations control microbial reaction rates, and new techniques are needed to measure these parameters in porous media systems.

### Coupling Microbial Processes to Subsurface Heterogeneities

There is abundant evidence that the distribution of microbial activity and biomass in the subsurface is heterogeneous (Balkwill 1989; Becker et al. 2006; Francis et al. 1989; Hadleman and Amy 1993; Nunan et al. 2002; Pedersen and Ekendahl 1990; Sinclair and Ghiorse 1989). Heterogeneity of microbial distribution and activity appears to be linked to physical, geological, geochemical, and hydrological heterogeneities in porous media systems (Fisk et al. 1999; Kolbel-Boelke et al. 1988; Schryver et al. 2006; Smith et al. 1986; Zhou et al. 2002). When the limiting nutrient exists as a solute in the aqueous phase, solid phase-associated microbial activity and growth are controlled by the flux of solute to the surface of the solid phase, which in porous media is controlled by head pressure and hydraulic conductivity of the media (Characklis et al. 1990). This is supported by evidence that greater microbial biomass and activity is detected in fractures with high hydraulic conductivity than in low permeability clay layers, where water flux is controlled by diffusion (Kieft et al. 1997; Sinclair and Ghiorse 1989). Reactive transport models have incorporated terms that couple metabolic activity and growth of microorganisms to variations in hydraulic conductivity caused by clastic heterogeneities (Murphy et al. 1997).

Subsurface physical and geological heterogeneities vary with scale. Little is known of the distribution and organization of microorganisms at different scales in the subsurface, particularly at the field scale, where we depend upon their activities and function to remediate contaminated zones or form barriers to impede contaminant transport. A key unanswered question is at what scale are heterogeneities in microbial biomass distribution important determinants of subsurface processes, such as contaminant fate and transport? One study found that bacteria were distributed in a heterogeneous manner in a subsoil system at the centimeter and <0.5 millimeter scales, but not at the millimeter scale, sug-



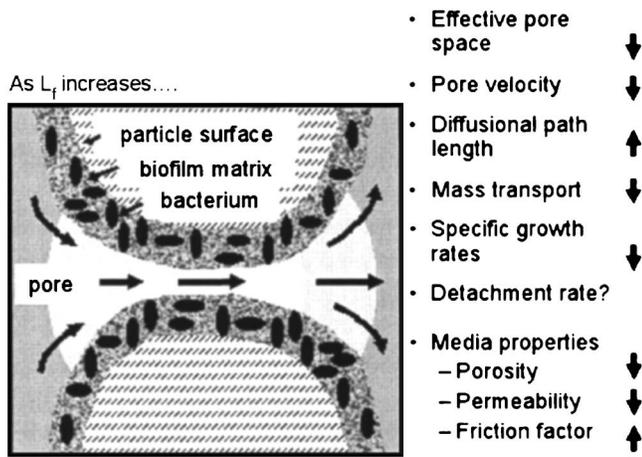
**Fig. 2.** Influence of accumulation of fixed microbial biomass on flow in porous media: (a) initial biomass and flow distribution; (b) biomass and flow distribution after surface-associated cell growth.

gesting that factors affecting development of bacterial distribution operate at different scales (Nunan et al. 2002). Differences in nutrient transport controlled by physical features of the system were proposed as a possible structuring agent for the centimeter-scale spatial patterns that were observed.

Few reactive transport models effectively accommodate scale-dependent heterogeneities. Recently, Seeboonruang and Ginn (2006a,b) presented nonreactive tracer models that utilized solute flux distributions as a signature of solid phase heterogeneity at different scales. It may be possible to combine this modeling approach with that described by LaViolette et al. (1999) to link both physical and microbiological scale-dependent heterogeneities to solute flux and biodegradation.

### Feedbacks: Microbial Activities That Cause Physical and Hydrological Heterogeneity

Microbial activities can also promote the establishment of physical and hydrological heterogeneities in porous media systems. One of the most studied processes involving microorganisms in porous media is the coupling of microbial growth to system permeability. When a porous media system is perfused with an aqueous phase containing dissolved nutrients that support microbial growth, the newly formed microbial biomass typically accumulates in the pores (Baveye et al. 1998; Characklis et al. 1987; Cunningham et al. 1991; Taylor and Jaffe 1990c). Much of the newly formed biomass becomes fixed to the pore walls via extracellular polymeric substances (EPSs) to increase access to the nutrients in the flowing aqueous phase (Fig. 2) (Allison 1947; Characklis et al. 1987; McCalla 1946; Nevo and Mitchell 1967). As biomass and EPS accumulate in the pore space, flow becomes restricted, limiting mass transport of nutrients to the cells (Taylor and Jaffe 1990c; Vandevivere and Baveye 1992a; b). Biomass often accumulates most rapidly in pores near the site of inoculation of microorganisms and nutrient introduction, contributing to heterogeneity in biomass distribution in the system (Fig. 2) (Geesey et al. 1987; Seymour et al. 2004a; Shaw et al. 1985). The unfavorable conditions created by mass transport limitation promotes detachment of cells and cell aggregates, which can become trapped in pores and impede flow further downstream (Hunt et al. 2004). Biomass and EPS may eventually fill and block flow



**Fig. 3.** Relationship between particle-associated biofilm thickness ( $L_f$ ) and microbiological, hydrological, and physical properties of a porous media system

through primary pathways, and force flow diversion to secondary pathways to initiate a new cycle of biomass accumulation in a different region of the system (Fig. 2).

The coupling of microbial biomass accumulation to hydrology at the pore scale has been shown to influence or control larger scale system behavior. Injection of nutrient-containing water into an oil bearing formation to enhance oil recovery often leads to microbially-mediated formation plugging at the water injection site (Cerini et al. 1946; Clementz et al. 1982). Intentional stimulation of microbial growth at specific subsurface locations is the basis of in situ formation of biobarriers to impede subsurface flow as a means of retarding the transport of contaminants dissolved in groundwater (Sharp et al. 1999). Intentional stimulation of microbial biomass production has also been used to plug fractures in aquifers (Ross and Bickerton 2002), and to plug preferential flow paths (thief zones) for water in oil formations during secondary oil recovery (Cusack et al. 1992; Lappin-Scott et al. 1988; MacLeod et al. 1988).

A number of approaches have been used to model relationships between accumulation of microbial biomass and hydraulic conductivity in porous media. Taylor and Jaffe (1990a) showed that computational results for cut-and-random-rejoin type pore models were in good agreement with experimental results obtained for a porous medium composed of sand with a grain size ranging from 0.59–0.84 mm in diameter. The model assumes that the biomass is distributed as a uniformly thin biofilm, a feature that was not verified experimentally in the packed-bed sand columns used in the study. These same investigators went on to establish relationships between biomass accumulation and dispersivity in the same porous media (Taylor and Jaffe 1990b). Their results indicated that dispersivity caused by biofilm growth in the porous medium dominated solute transport.

Cunningham et al. (1991) used a noninvasive optical method to measure changes in average biofilm thickness and density in a fixed-bed column reactor containing glass spheres to define the relationship between biomass accumulation and permeability. The amount of biomass that accumulated on the spheres over a ten-day period of nutrient infusion varied with distance from the inlet in an unpredictable manner. Larger pore sizes resulted in greater biofilm thickness. As biofilm thickness increased, porosity and permeability decreased, while diffusional path length and friction factor increased (Fig. 3). They suggested that porosity,

permeability and friction factor may be predicted from substrate consumption according to Rittmann and McCarty (1980a,b), or that biomass thickness may be computed from knowledge of porosity (Cunningham et al. 1991). These relationships are based on the untested assumption that biomass is uniformly distributed across the surface of the spheres throughout the column.

Chen-Charpentier and Kojouharov (2000) developed a Eulerian-Lagrangian numerical simulator to solve one-dimensional, transient convective-dispersive transport equations with nonlinear reaction terms involving bacterial growth and contaminant biodegradation in the subsurface. The simulation deviated from experimental results in the influence of particle size on the relationship between porosity and biomass accumulation. This was attributed to the fact that no detachment term was included in the model, and a biofilm concentration parameter was substituted for biofilm thickness to avoid making assumptions on the biomass distribution, for which no data were collected.

### **Need for Experimental Data to Test Model Assumptions**

While much progress has been made in modeling the relationships between hydraulic conductivity and accumulation of microbial biomass in porous media, the assumption of a uniform distribution of biomass on which the above models are based still needs to be experimentally verified at the pore scale (Baveye et al. 1998; Rockhold et al. 2004). Thus, a key unresolved question that needs to be answered is how is microbial biomass distributed at different scales in porous media systems? Flat-plate channel-flow reactor systems, which permit more precise control over pore structure and flow rate while allowing determination of spatially resolvable microbial biomass and activity, may be better suited than packed-bed column reactors for establishing relationships between flow, biomass accumulation at surfaces, and substrate conversion rate (Baty et al. 2000; Gonzalez-Gil et al. 2005; Stoodley et al. 2002, 1994, 2001).

In addition, the assumption that growth and activity of microorganisms associated with porous media surfaces are not transport limited needs to be experimentally verified over a range of subsurface conditions. Are there regions of a porous media system in which microbial reactions are transport limited? The answer to this question requires experimental measurement of spatial distributions of flow velocity, biomass, and substrate utilization or transformation under different flow rates, substrate concentrations, and pore structures. A variety of reactors and experimental systems have been used to characterize flow within and around biomass that has accumulated at solid surfaces (deBeer et al. 1994; Stoodley et al. 1994; van As and Lens 2001; Xia et al. 1998). However, these approaches cannot provide the quantitative velocity distributions that influence and are influenced by accumulation of biomass in three-dimensional media due to sample opacity.

### **Nuclear Magnetic Resonance Techniques**

Nuclear magnetic resonance (NMR) techniques have been used to define water behavior and movement through saturated and unsaturated complex heterogeneous porous media over a wide range of scales (Anadon et al. 2006; Brown et al. 1998; Callaghan 1991; Dijk et al. 1999; Sederman et al. 2003). The techniques are based on the relaxation rate of protons in water molecules following exposure to an induced magnetic field. The magnetiza-

tion response is sensitive to any condition that affects the translational or rotational motion of water molecules, such as proximity to surfaces, solution viscosity, or interactions with colloids or polymer gel structures. The approach can identify regions of a porous media in which water movement is diffusion or advection controlled, based on velocity fields, and diffusion coefficients can be calculated from proton magnetization evolution (Callaghan 1991).

### **Magnetic Resonance Imaging**

Magnetic resonance imaging (MRI) offers the opportunity to measure and thereby link flow and biomass distribution in opaque porous media in multiple dimensions in a noninvasive manner at the pore and core scales. Potter et al. (1996) were among the first to use pulsed-field-gradient spin-echo (PGSE) technique to spatially map noninvasively the distribution of bacteria within water-saturated quartz sand packs. They found that high gradient values were effective filters of extracellular water and sand grains allowing specific quantification of suspended bacterial biomass. Hoskins et al. (1999) compared light microscopic images of biofilm biomass formed in glass bead-filled flow reactors with longitudinal  $T_1$ -weighted and transverse  $T_2$ -sorted proton relaxation time-derived magnetic resonance images. Both the  $T_1$ -weighted magnetic resonance images and optical images detected biomass in the same volume of porous media for 77.9% of the locations with a net error of 8.1% false negative locations. The results indicated optical imaging underestimated, whereas magnetic resonance imaging overestimated the actual volume occupied by biomass in the system.  $T_2$  relaxation data could not distinguish between the fluid in the bulk aqueous phase and fluid associated with the biomass phase due to the influence of pore surfaces and biomass surfaces on proton relaxation.

A strength of magnetic resonance methods for the characterization of complex flow patterns in porous media is the ability to spatially resolve velocity and statistically characterize the dynamics by measurement of the propagator or displacement conditional probability using the PGSE approach. Seymour et al. (2004a) used a spatially resolved multiecho Carr-Purcell-Meiboom-Gill method to resolve secondary flow caused by biomass accumulation in primary flow channels (1 mm<sup>2</sup> glass capillaries) using  $T_2$  maps of flow fields with length scales between 10 nm and 100  $\mu\text{m}$  (microhydrodynamics). Quantitative measurement of these secondary flows is required to model transport across the bulk fluid-biomass boundary and within the fixed biomass. The mechanism for initiation of secondary flows is the irregular spatial distribution of the viscoelastic fixed biomass as a boundary condition on the flowing aqueous phase (Seymour et al. 2004a). The propagator produced from experimental velocity data obtained in the presence of biomass deviated in a predictable manner from both experimentally-derived data and that produced by a theoretical model of velocity distributions in the absence of biomass. The data revealed that the velocity was zero within the volume occupied by cell clusters and only slightly higher within the extracellular polymeric hydrogel produced by and enveloping the immobilized cells. This suggests that volumes occupied by fixed biomass have low permeability, indicating that transport is likely to be diffusion controlled. The establishment of low velocity flow in regions of fixed biomass also resulted in higher velocity flow in biomass-free regions of the primary flow path, compared to media that had not been inoculated with bacteria.

Biomass accumulation also induced anomalous fluid transport

in porous media systems. Seymour et al. (2004b) used magnetic resonance microscopic imaging (MRM) to study the impact of microbial biomass accumulation in porous media constructed of 241  $\mu\text{m}$  diameter monodisperse polystyrene beads on scale dependent dispersion dynamics over a 7–10 day timeframe. Velocity maps were obtained under flow conditions while  $T_2$  maps were obtained in the absence of flow. Spatial resolution was 54.7 mm/pixel in plane over a 1,000  $\mu\text{m}$  slice for velocity and a 200  $\mu\text{m}$  slice for  $T_2$  maps. The growth of microorganisms associated with the solid phase altered the distribution of flow velocities toward smaller displacements due to entrainment of fluid within the biomass growing in the pore space and trapped in biomass-clogged dead-end flow paths, as well as toward larger displacements in high permeability pores not yet impacted by biomass accumulation. These investigators found that biomass accumulation in porous media generated a transition in the hydrodynamic dispersion dynamics that could be modeled as a transition from normal to anomalous transport using a fractional advection diffusion equation. This modification to the advection diffusion equation accommodates the separation of scales, which occurs in the development of Brownian motion theory, and causes failure of the conventional advection diffusion equation to model macroscopic transport in systems with heterogeneity over multiple scales (Seymour et al. 2004b). The data revealed strong coupling between biomass accumulation-induced evolution of the propagator and stretched exponential scaling in  $q$  space, which is amenable to investigations of time and space coupling in continuous time random walk models. Thus, MRM can be used to resolve long-standing questions and uncertainties about biomass distribution and mass transport limitations on microbiological contaminant degradation or transformation over time periods in which microorganisms respond to changes in their environment at the pore and core scales.

The quantitative nature of the experimental data obtained by NMR imaging techniques makes them useful for testing and refining expressions describing the coupling of microbiological and hydrological processes in computational models. This approach now needs to be used to map microbial biomass and flow distribution in engineered heterogeneous geological media with different pore structures and flow regimes. The ability of MRI to monitor microbial growth and distribution as well as flow distribution at multiple scales within packed-bed laboratory columns provides a critical link to scaling microbial contaminant biodegradation or biobarrier performance to the field scale (Potter et al. 1996). In the future, it may be possible to make in situ measurements of microbial distribution in the field using NMR well-logging equipment (Kleinberg et al. 1992; Taicher et al. 1994).

### **Surface Nuclear Magnetic Resonance**

Alternatively, subsurface microbial biomass distribution may someday be measurable using surface nuclear magnetic resonance (SNMR), another relatively new NMR imaging technology that has passed the experimental stage to become a useful geophysical tool for detecting and characterizing water in the subsurface. It directly detects and assesses subsurface water based on above-ground surface measurements, providing quantitative information of mobile water content and pore structure parameters leading to hydraulic conductivities [Legchenko et al. "A device for measurement of subsurface water saturated layer parameters," USSR Patent No. 1540515 (in Russian) (1990)]. It is used at the field scale to describe the distribution and transport of water across fractures and low permeability zones (Brown et al. 1998; Dijk

et al. 1999), and to quantify and characterize subsurface water in different geological formations (Legchenko et al. 2002; Roy and Lubczynski 2003; Yaramanci 2004). It is also used to determine nonaqueous phase liquids source zone architectures during surfactant enhanced nonaqueous phase liquid dissolution in aquifers containing three-dimensional correlated heterogeneous permeability fields, and surfactant flow paths by imaging the breakthrough of a paramagnetic tracer (Werth and Zhang 2005).

SNMR measurements are conducted using a  $\sim 100$  m loop laid out in a circular or rectangular pattern through which pulses of alternating current are passed. When the current is switched off, a voltage  $e(t)$  with frequency  $\varphi_L$  and decaying amplitude  $E_{0d}$  is induced in the loop by the relaxation of protons of water in a volume extending  $\sim 100$ – $170$  m beneath the loop, depending on the strength of the local geomagnetic field and electrical conductivity of the surrounding rock (Legchenko et al. 2002). The envelope of this voltage is directly related to the water content and to the decay time of every volume element in the subsurface contributing to the signal. The signal amplitude  $E_{0d}$ , along with the recorded decay time  $T$  described by the relaxation time constant  $T_2^*$ , are used to extrapolate free water content as a function of depth (Schirov et al. 1991; Yaramanci et al. 1999).  $T_2^*$  inversion is used to determine mean pore size and, thus, grain size as well as hydraulic conductivity as a function of depth. The phase  $\varphi_{0d}$  correlates with the electrical conductivity of the surrounding rock, but is not used for SNMR data interpretation. Recently, Weichman et al. (2000) presented a formula that includes the full complex NMR response, including the imaginary part, which had not been previously modeled, and showed that the diffusive long time tail of the signal may be used to infer the distribution of time constants  $T_1$ , normally not measurable in geophysical applications. In the future, it may be possible to resolve at the field scale microbial biomass distribution through  $T_1$  methods, developed as described above, at the pore and core scales.

## Summary and Conclusions

Recognition that microorganisms colonize the surfaces of porous media in systems ranging from fixed bed reactors to subsurface environments has led to improvements in the ability of reactive transport models to predict rates of contaminant biodegradation or biotransformation. However, most reactive transport models still assume that this fixed microbial biomass is uniformly distributed across the surface of particles and throughout a porous media system, and that the fixed biomass does not limit mass transport of a solute dissolved in the bulk aqueous phase to all biocatalytic sites in the system. Nevertheless, experimental studies have shown that biomass is heterogeneously distributed, and that mass transport limitations exist in porous media systems. Thus, reactive transport models need to be modified to account for the effect these phenomena have on coupled processes such as solute degradation and pore plugging. NMR techniques offer the opportunity to experimentally couple microbial biomass and flow distribution in porous media in three dimensions at different scales in a noninvasive manner. Surface nuclear magnetic resonance may someday provide information on the distribution of microbial biomass in the subsurface at the field scale. This information should improve the accuracy of boundary conditions assigned to reactive transport models, resulting in better predictions of subsurface contaminant transport and transformation rates in the field.

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