GEOPHYSICAL MONITORING OF GAS PRODUCTION DURING BIOSTIMULATION

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ABSTRACT

Active remediation treatments, such as in-situ chemical oxidation or bioremediation, often cause transformations in subsurface systems by altering the aqueous composition, and/or by promoting mineral dissolution/precipitation, gas generation and biofilm development. These products in turn can effect the porosity and permeability of the system, which can influence the treatment delivery and remediation efficacy. Geophysical methods including; seismic, radar, and electrical, have potential for providing information about these dynamic and coupled processes in a non-invasive and high-resolution manner. An improved ability to monitor dynamic subsurface processes that occur during remediation and over a variety of spatial scales could reduce the uncertainty currently associated with the efficacy of many remediation treatments. However, an understanding of the relative sensitivities of the geophysical attributes to the transformation products and in the presence of hydrogeological heterogeneity is necessary before using these data in a quantitative manner to monitor remediation processes.

In this study, we investigated how biogenic gas, which was generated during a controlled column-scale biostimulation experiment, influenced electromagnetic wave travel time and amplitude measurements collected using a time domain reflectometry (TDR) system. Both radar velocity and amplitude data were used to indicate the onset of denitrification in an originally water-saturated sand column. Radar velocities were used within a petrophysical mixing model to obtain spatially-and temporally variable estimates of the percent of the pore space that was replaced by N_2 gas. At the end of the experiment, the radar velocity data suggested that the average gas saturation in the column was 24.6%. This estimate agrees favorably with the estimate of 23.3%, obtained using column weight loss measurements. Hydraulic conductivity decreased during the experiment by 55% due to pore clogging by the generated gas bubbles. This experiment illustrated how radar data can be used at the laboratory scale to monitor gas evolution caused by microbial activity during biostimulation. The experiment represents a small step in our ongoing work to investigate the potential of various geophysical attributes for detecting system transformations that commonly occur during remediation over a range of spatial and temporal scales.

INTRODUCTION

Biogeochemical and hydrological processes are naturally coupled and variable over a wide range of spatial and temporal scales (e.g., Gelhar, 1993, Lovley et al., 1994 respectively). In addition to these natural variabilities under static conditions, many remediation approaches also induce *dynamic* biogeochemical and hydrological transformations in subsurface systems. It is widely accepted that effective remediation requires a better understanding of coupled processes than is currently available. Examples where strongly coupled processes play a large role in remediation success include, among others, in-situ redox manipulation for removal of chlorinated hydrocarbons, chromium, and uranium, coupled heat flow and transport for both enhanced remediation and near radioactive wastes, bioremediation, steam cleaning and air sparging. All of these methods perturb the subsurface and result in dynamic coupled process reactions. Potential alterations due to remediation treatments include, for example, dissolution and precipitation of minerals, surface complexation, gas evolution, changes in soil water and oxygen levels, sorption, attachment/detachment, oxidation and reduction (inorganic and microbially mediated), biofilm generation, and changes in permeability and porosity. Several of these parameters/processes are coupled. A lack of understanding of the coupled nature of these processes renders estimation of the parameters that control remediation difficult. For example, chemical oxidation may induce redox conditions required to remediate contaminants, but it is difficult to estimate the sustainability of these necessary conditions over time. Additionally, mineralization, gas evolution, and biofilm generation will block the pore space and reduce hydraulic conductivity, rendering it more difficult to introduce treatment into the subsurface via injection or to withdraw groundwater via pumping.

The wide range of variability and the coupled nature of the properties/processes under both static and dynamic conditions render investigations of these coupled processes extremely challenging. Further complicating the problem is the inability to collect the necessary measurements using conventional characterization tools at a high enough spatial resolution yet over a large enough volume for understanding field-scale transformations. Because of these limitations, current understanding of biogeochemical-hydrological processes and their interdependencies is limited at the laboratory scale and is rarely attempted at the field scale. As a result, prediction of transformation rates or the sustainability of desired redox and hydraulic conditions is marred with uncertainty. These limitations severely inhibit the ability to design optimal remediation schemes, to determine the subsurface treatment zone of influence, or to monitor the efficacy of a remediation treatment.

Based on our previous success at both the lab and the field scales at using geophysical data to estimate hydrogeological properties (Hubbard et al., 1997a, 1999, 2000, 2001; Chen et al. 2001), we are investigating the utility of various geophysical methods for monitoring system transformation that occur during remediation (Williams, 2002; Hubbard et al., 2002). Just as medical imaging technology provides dense information and has reduced the need for invasive surgery, geophysical methods hold promise for rapid, non-destructive, relatively inexpensive and vastly improved monitoring of coupled processes. Although geophysical methods can not sense the processes directly, they have the capability of detecting averaged physical and chemical changes that occur during remediation, such a gas evolution, precipitation, and possibly biofilm development. The geophysical data typically provide information at a scale that is between the pore-scale and the field-scale, and thus can help to bridge the information gap between these two typical measurement scales.

For this study, we conducted a controlled laboratory experiment to investigate the sensitivity of radar attributes for detecting N_2 gas generated during denitrification. We chose to investigate the potential of radar methods for this experiment primarily because field-scale radar tomographic methods have been successfully used in conjunction with biostimulation experiments already to provide very high resolution estimates of hydrogeological (Chen et al., 2001; Hubbard et al., 2001) and geochemical (Chen et al., 2003) parameters. At the DOE bacterial transport field site, the estimates obtained using radar tomographic data were very useful for predicting flow and transport (Scheibe and Chien, 2003) and for understanding field-scale bacterial transport (Mailloux et al., 2003). Additionally, as a consequence of the greater energy available from nitrate reduction, the majority of nitrate in a groundwater system is reduced prior to reduction of manganese, iron, and sulfate. Thus, the onset of denitrification is an important indicator for determining the redox state of the aquifer that is being perturbed, and advanced techniques to detect this onset and monitor associated processes in a remote and accurate manner are needed.

BACKGROUND: RADAR METHODS

Ground penetrating radar (GPR) is a geophysical technique that uses electromagnetic energy with central frequencies generally between 50 and 1200 MHz to image the subsurface. Electromagnetic energy propagates from a transmitting antenna, and is modified by subsurface contrasts in dielectric constant (κ) and magnetic permeability (μ). As most soils have negligible variation in magnetic permeability, variations in κ have the most significant impact on the recorded GPR response. By knowing the travel path length of the radar wavefront, the electromagnetic wave velocity can be estimated from the travel time of the GPR signal. For low-loss media (i.e., soils with low salinity and clay content), and at the high frequencies typically used for field radar and for TDR techniques, the velocity (v) of the soil can be related to the dielectric constant by:

$$\kappa = \left(\frac{c}{v}\right)^2, \qquad \text{(Eq. 1)}$$

where c is the known electromagnetic wave velocity in free space (Davis and Annan, 1989).

Variations in soil moisture content have the most significant effect on the subsurface dielectric constant. This is because the dielectric constant of water over the GPR frequency range is ~81, whereas the dielectric constant of air is 1, and that of most soils is between 4 and 7 (Davis and Annan, 1989). Therefore, changes in the volume percentage of water will dominate changes in the effective dielectric constant. In our experiment, we capitalize on this characteristic by assessing the change in dielectric constant as N_2 gas evolves within an originally water-saturated pore space. In order to estimate the volume of the pore space that is occupied by the two disparate fluids, a petrophysical model is required. As will be discussed in the next section, we will use an experiment-specific mixing model, based on a model described by Roth et al. (1990) for a three component system comprised of soil, water, and air. In this system, the effective dielectric constant (κ_{eff}) of a material was described by:

$$\kappa_{eff} = \left[(1-\phi)\sqrt{\kappa_s} + (\phi - \boldsymbol{VWC})\sqrt{\kappa_a} + \boldsymbol{VWC}\sqrt{\kappa_w}\right]^2, \qquad \text{(Eq. 2)}$$

where ϕ is the soil porosity, VWC is the free soil water content and κ_s, κ_a and κ_w are the dielectric constants of soil, air and water, respectively. Thus, once the dielectric constant of the electromagnetic wave is determined from analysis of the GPR velocity data and using (1), it can be used to estimate the VWC using a relationship such as (2).

The amplitude of the radar signal may also be useful for remediation monitoring. The amplitude is a complex function of both the dielectric constant and the electrical conductivity of the medium through which it travels. As shown by Davis and Annan (1989), for low electrical conductivity materials and at high frequencies used by GPR systems, the attenuation (α) of the electromagnetic wave can be approximately expressed as:

$$\alpha = \frac{194.5 * \sigma}{\sqrt{\kappa}}, \qquad \text{(Eq. 3)}$$

where conductivity is expressed in S/m and attenuation is expressed in dB/m. This expression suggests that amplitude attenuation of an electromagnetic wave is directly proportional to electrical conductivity, and inversely proportional to the dielectric constant of the material through which it travels. Since the electrical conductivity of gas is much less than that of water, the radar amplitude also may be useful for indicating pore-fluid replacement during biostimulation.

At the field scale, surface- and crosshole-based GPR systems can be used to obtain dielectric constant estimates, which can in turn be used to investigate pore fluid characteristics, such as the volume of the pore fluid that is water-filled in unsaturated systems. Examples of the use of crosshole and surface GPR velocity data for estimation of water content at the field scale are given by Hubbard et al., (1997a,b), Binley et al. (2001, 2002), Huisman et al., (2003), Grote et al. (2003), and Lunt et al. (2003). In the laboratory, measurements of dielectric constants can be made using a time domain reflectometer (TDR). TDR techniques also use electromagnetic waves to probe the subsurface, but at higher frequencies (~1 GHz) than GPR techniques. With the TDR method, the electromagnetic energy is guided along metal prongs, or waveguides, which have been inserted into the material (e.g., Topp, 1980). The wave travels down the length of the prongs and back to the detector. By knowing the signal travel time and prong length, the electromagnetic velocity can be calculated, and used with (1) to calculate the dielectric constant. As with surface or tomographic GPR data, calibration equations are necessary to convert the obtained dielectric constant measurement into estimates of the property of interest, which for this study was the percent of evolved N_2 in the pore space. Analogous to (3) the amplitude of the recorded TDR waveform is also influenced by the electrical conductivity, and thus may provide additional information about the changes in the pore fluid conductivity as discussed by (Dalton et al., 1994; White et al., 1994).

BIOSTIMULATION MONITORING USING RADAR TECHNIQUES

Microorganisms catalyze most of the redox processes that occur in aquatic sediments and groundwater systems (Lovely and Goodwin, 1988). Under anaerobic conditions, nitrate is the most thermodynamically favored electron acceptor and is used by many facultative anaerobic bacteria (Chapelle, 2001). Nitrate reduction coupled with respirative energy production is called denitrification. In a general form, biogenic reduction of nitrate (NO_3) to N_2 gas is expressed as:

$$DOC + NO_3 \Rightarrow CH_2O\ (\text{biomass}) + CO_2 + N_2\ , \qquad \text{(Eq. 4)}$$

where DOC refers to dissolved organic carbon and CH_2O is the generalized form of assimilated biomass. As a consequence of the greater energy available from nitrate reduction, the majority of nitrate in a groundwater system is reduced in advance of the less energetic reduction of manganese, iron, and sulfate. Thus, detecting the onset of denitrification is an important indicator for determining the redox state of the aquifer that is being perturbed. In addition to understanding when denitrification is occurring, the quantity of gas that is evolved is also of interest. Researchers working at the laboratory scale have recognized that permeability can be reduced by up to *three orders* of magnitude due to bacteria-related gas formation (e.g., Vandevivere and Baveye, 1995.). Reduction of permeability of this magnitude can clog the near-wellbore area, significantly reducing the ability to deliver treatment injectate to the contaminated aquifer or decrease well yields and ability to withdraw representative samples.

Experimental Design

Our goal in this study was to assess the impact of the pore fluid replacement (from water to gas) on the radar attributes and on the hydraulic conductivity during a column-scale biostimulation experiment. The key steps in the experimental design included packing and inoculating sand columns with microbes, providing a nutrient to the microbes to stimulate denitrification, and measuring the hydraulic and geophysical responses during the biostimulation experiment. Many of our experimental parameters were chosen to mimic conditions of an associated field-scale biostimulation experiment that was conducted at the DOE Bacterial Transport Site in Oyster, Virginia (Mailloux et. al., 2002). Columns having a height of 30.48-cm were packed using U.S. Silica sand F-60, which is a very fine to medium grained, poorly sorted sand. The sand was rinsed repeatedly with deionized water and then autoclaved for 21 minutes and dried at 105ºC. The sand was inoculated with a facultative

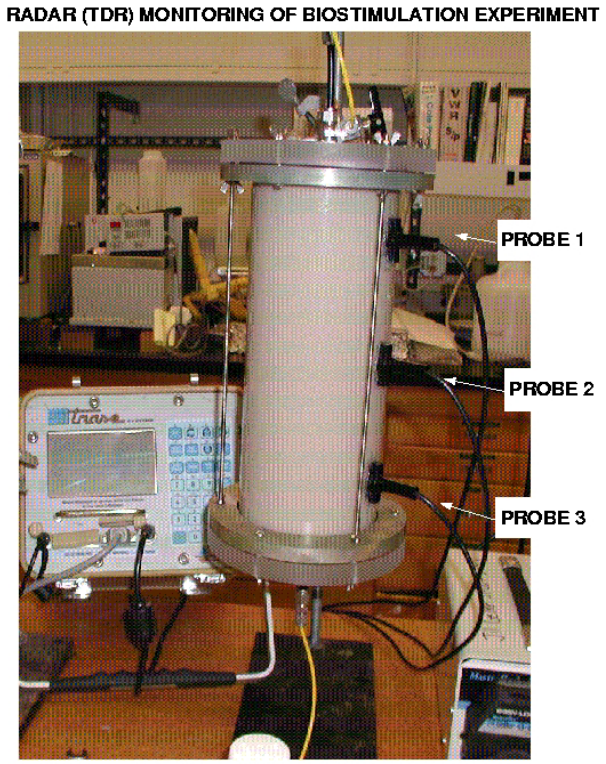

Fig. 1 Experimental column showing placement of three TDR probes and TDR recording system

nitrate- and iron-reducing microorganism *Acidovorax sp.* strain OY-107 (described in Johnson et al., 2001), which had been grown to a cell density of 10^8 cells/ml in a fluid identical to that used to saturate the sediment columns. An equivalent pore volume of the microbial suspension was added to the sediment prior to packing and allowed to affix for a period of two days. After this time, the inoculated sediments were added to each of the columns within a laminar flow hood and packed by repeatedly tapping the base of each against the surface of the flow hood. Once they were filled with sediment, each of the columns was saturated from the base upwards using a peristaltic pump and flushed with ten pore volumes of vacuum de-aired, autoclaved tap water to ensure complete saturation and the removal of any entrapped gases. Following the tap water flush, two pore volumes of a growth medium containing acetate as an electron donor and nitrate as an electron acceptor ('Medium D' as described in Williams, 2002) were passed through each column after which they were sealed. The starting concentrations for acetate and nitrate within the columns were 14.7mM and 23.5mM, respectively. An image of the sand-packed, TDR-instrumented experimental column is shown in Fig. 1.

After introduction of the growth medium, nitrate reduction began, with reactions following the form of equation (4), generating N_2 gas within the originally water-filled pore spaces. The formation of gas bubbles within the column was apparent after several days. Fifteen days after introduction of the growth medium, the pressure build-up near the top of the column due to the gas generation was sufficient enough to causing small leakage from the valve sealing the column. To relieve this pressure, the valve was opened at the top of the column for a few seconds and then closed again. This pressure relief process was initiated two more times during the experiment as gas built up, at increments of 4-5 days each.

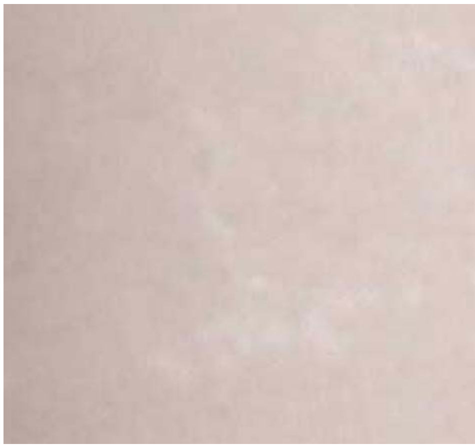

Fig. 2 Image of column wall (3-cm by 3-cm) showing 'patchy' distribution associated with the presence of evolved gasses in the pore spaces

TDR measurements were made along the length of the column from November 27th, 2001 until January 8th, 2002. Measurements for this experiment were made using three 8-cm TDR probes and a SoilMoisture Trase System, which were spaced evenly along the length of the TDR column as shown in Fig. 1. The average sample volume of each TDR probe was cylinder of approximately 75 cm^3 centered around the probes. Readings were automatically collected once per hour at each probe for the first 24 days of the experiment (and then intermittently after that) using a demultiplexer attached to the Trace System. The velocity of the electromagnetic wave traveling down the probe length and back to the TDR system was automatically detected, picked, and converted to dielectric constant using (1). The waveforms were also digitally recorded for subsequent investigation of the amplitude responses.

In addition to the geophysical measurements, hydraulic measurements were intermittently collected. The TDR column was weighed prior and subsequent to the experiment to assess any changes in bulk weight associated with gas production. Hydraulic conductivity measurements were collected from an identical column at various times during the experiment using a constant head measurement approach.

Data Analysis and Results

The dielectric constant value obtained from the TDR reading is an effective bulk dielectric value representing a volume surrounding the 8-cm prong that is filled with both the sand grains and the pore space. Following (2), we used a volumetric averaging/mixing model to represent the effective dielectric measurement (κ_{eff}) as a function the individual components that contribute to the measurement, including the dielectric constants of N_2 (κ_{N_2}), water (κ_w), and sand grain (κ_S):

$$\kappa_{eff} = [(1-\phi)\sqrt{\kappa_s} + \phi(1-S_w)\sqrt{\kappa_{N_2}} + \phi S_w\sqrt{\kappa_w}]^2, \qquad \text{(Eq. 5)}$$

where ϕ is the porosity of the material and S_w (where $Sw=VWC/\phi$) is the fraction of the pore space saturated with water. Based on laboratory measurements and values from literature, we assumed the following parameters for our analysis: ϕ=0.38, κ_w=80, κ_s=6.9, and κ_{N_2}=1. By rearranging (5), we can use the measured κ_{eff} value and assumed constants to solve for S_w:

$$S_w = \frac{\sqrt{\kappa_{eff}} - (\phi-1)\sqrt{\kappa_S} - \phi\sqrt{\kappa_{N_2}}}{\phi(\sqrt{\kappa_w} - \sqrt{\kappa_{N_2}}} \qquad \text{(Eq. 6)}$$

By assuming that the pore space is either filled with water or with the generated gas, we can estimate the percentage of the pore space that is gas-filled as 1-S_w. Using this approach with the dielectric constant measurements obtained from TDR readings during the biostimulation experiment, we estimated the percent of evolved N_2 gas in the pore space as a function of probe location and over time.

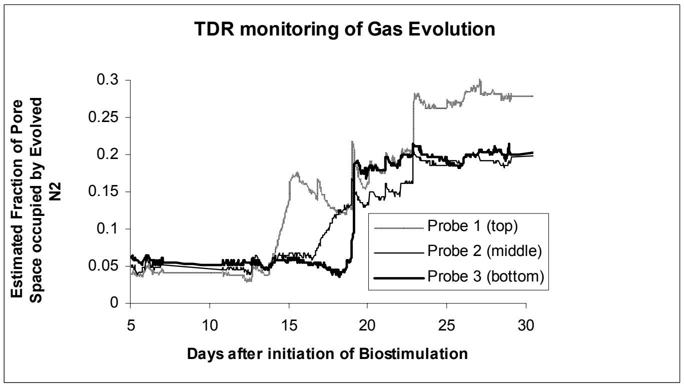

Fig. 3 Estimated fraction of the pore volume occupied by evolved N_2 gas as a function of time after initiation of biostimulation experiment using radar velocity data

Figure 3 illustrates the percent of the pore space estimated to have filled with N_2 gas as a function of time after the biostimulation experiment began. This figure illustrates how the pore water started to be significantly replaced by gas after about thirteen days. Gas was first detected by probe #1, or the top probe in the column. The apparent 'jumps' in the estimated evolved N_2 gas (e.g., at 15, 20 and 23 days for probe 1) are associated with the pressure release procedure described above. With time, all of the probes sensed the presence of a significant volume of gas. At the end of the experiment, we estimated that approximately 22% of the pore spaces were filled with N_2 gas for the bottom third of the column, about 21% of the pore spaces were filled with gas for the middle third of the column, and that 31% of the pore spaces were filled with N_2 gas at the top third of the column, yielding an average estimated gas saturation over the entire column of 24.6 % (Table I).

In addition to the travel time of the electromagnetic signal down the length of the TDR prong and back, the amplitude of the signal can also be used as an indicator of gas versus water in the pore space. Figure 3 illustrates the amplitude of the TDR waveform recorded at prong #1 at the beginning and at the end of the experiment. This image illustrates how the reflected amplitude of the later waveform (measured on December 16th, or on the 20th day of the experiment) is significantly less attenuated than the earlier waveform (measured on November 27th, or at the beginning of the experiment). The relatively small slope of the voltage rise due to the reflection from the end of the probe are characteristic signs of higher electrical conductivity (Zegelin et al., 1992). As gas has a lower electrical conductivity than water, the radar amplitude is less attenuated in a material with gas-filled pores than in the same material saturated with water following (3). Although we did not quantitatively process the TDR amplitude data to estimate gas production, the comparisons shown in Fig. 4 were consistent throughout the experiment with the information obtained using the travel time portion of the signal, and suggest that TDR amplitude data may also be a useful indicator of gas production.

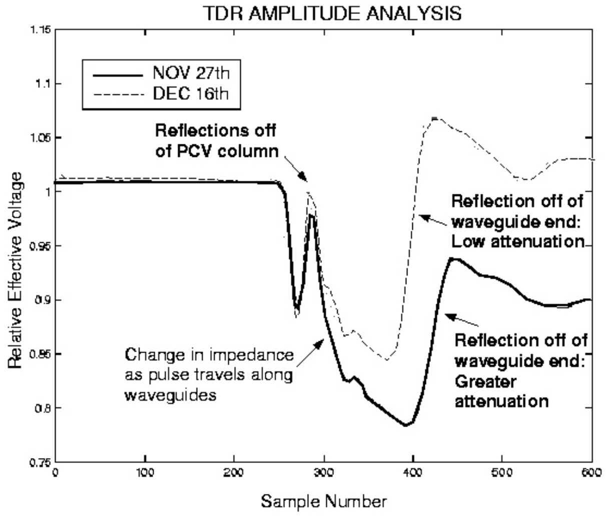

Fig. 4 Example of the increase in electromagnetic wave amplitude as gas replaces water in the pore space of the column sands

Hydrological measurements were also made in an experimental column having an identical experimental design as the TDR column. Hydraulic conductivity, measured using a constant head approach, fell more than 50% over the course of the experiment, from 0.0038 cm/s prior to the biostimulation to 0.0017 cm/s after the cessation of the experiment. The column weight varied from 7027-g at the beginning of the experiment to 6718-g at the end of the experiment. If the weight loss is attributed to the presence of gas versus water in a material with a porosity of 0.38, then the estimated volume of gas in the column at the end of the experiment is 309-mL. This corresponds to 23.3% of the available pore space being occupied by gas, which compares favorably with the 24.6% estimated using the radar velocity data. Table 1 summarizes the geophysical and hydrological measurements associated with the column-scale biostimulation experiment.

Table I Experimental geophysical and hydrological measurements and interpretations.

Investigation Approach:	**Value at beginning of experiment**	**Value at end of experiment**	**Interpretation of time-lapse changes**
Dielectric from Radar Velocity	24.8 (average)	19 (average)	24.6 % of pore space occupied by evolved N_2 gas
Column Weight	7027 g	6718 g	23.3% of pore space occupied by evolved N_2 gas.
Radar Amplitude	Low	High	Evolved gas in pore space attenuates signal less than water in pore space
Hydraulic Conductivity	0.0038 cm/s	0.0017 cm/s	55% reduction in hydraulic conductivity

CONCLUSIONS

This experiment illustrated how, at the laboratory scale and under controlled and homogeneous conditions, radar wave travel times and amplitudes were used to monitor gas evolution caused by microbial activity during biostimulation. The experiment suggested that the radar attributes may be good indicators of the onset and extent of denitrification that during biostimulation. However, in order to fully investigate the potential for geophysical data as a bioremediation monitoring tool, it is necessary to investigate the sensitivity of the geophysical responses to various electron accepting processes and under various heterogeneity conditions and spatial scales. Assessing the sensitivity and accuracy of different geophysical attributes (seismic, radar, electrical), for estimating different remediation products (gasses, precipitates and biofilms) as a function of heterogeneity and scale is the focus of our ongoing research (Williams, 2002; Hubbard, 2002).

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SELECTED REFERENCES

1 Binley, A., P. Winship, R. Middleton, M. Pokar, and J. West, High-resolution characterization of vadose zone dynamics using cross-borehole radar, *Water Resour. Res.,* 37, 2639-2652, 2001.

2 Binley, A., G. Cassiani, R. Middleton, and P. Winship, Vadose zone flow model parameterization using cross-borehole radar and resistivity imaging, *J. of Hydrolog*y, 267, 147-159, 2002.

3 Chapelle, F.H., Ground-water microbiology and geochemistry, John Wiley & Sons, New York, 2001.

4 Chen, J., S. Hubbard and Y. Rubin, Estimating Hydraulic Conductivity at the South Oyster Site from Geophysical Tomographic Data using Bayesian Techniques based on the Normal Linear Regression Model, *Water Resources Research*, 37(6), 1603-1613, 2001.

5 Chen, J., S. Hubbard, C. Murray, E. Rodin, and Y. Rubin, Estimation of Geochemical Heterogeneity using Radar Tomographic Data and an MCMC Approach, Submitted for publication in *Water Resources Research*, 2003.

6 Dalton, F. N. , W. N. Herkelrath, D. S. Rawlins, and J. D. Rhoades. 1984. Time Domain Reflectometry: Simultaneous Measurement of Soil Water Content and Electrical Conductivity with a Single Probe, *Science*, Vol. 224, June, pp. 989-990.

7 Davis, J.L., and P.A. Annan, Ground penetrating radar for high-resolution mapping of soil and rock stratigraphy: *Geophys. Props*. 37, 531-551, 1989.

8 Gelhar, L.W., *Stochastic Subsurface Hydrology*, Prentice Hall, New Jersey, 1993.

9 Grote, K., S. Hubbard, and Y. Rubin, Field-Scale Estimation of Water Content using GPR Groundwave Techniques, accepted for publication in *Water Resources Research*, 2003.

10 Hubbard, S., Peterson, J.E., Majer, E.L., Zawislanski, P.T., Roberts, J., Williams, K.H. and Wobber, F., Estimation of permeable pathways and water content using tomographic radar data, *The Leading Edge of Exploration*, 16(11), 1623-1628, 1997a.

11 Hubbard, S.S., and Y. Rubin, Saturation and Permeability measurement using radar Data, *Water Resour. Res.*, 33(5), 971-990, 1997b.

12 Hubbard, S., Rubin, Y., and Majer, E.L., Spatial correlation structure estimation using geophysical data, *Water Resources Research*, 35(6), 1809-1825, 1999.

13 Hubbard, S. and Rubin, Y., A Review of Selected Estimation techniques using Geophysical Data, *Journal of Contaminant Hydrology*, 45(2000),3-3, 2000.

14 Hubbard, S.S, J. Chen, J. Peterson, E.L. Majer, K.H. Williams, D.J. Swift, B. Mailloux and Y. Rubin, Hydrogeological characterization of the South Oyster Bacterial Transport Site using geophysical data, *Water Resources Research* 37(10), 2431-2456, 2001.

15 Hubbard. S.S., K.H. Williams, B. Mailloux, E. Majer, Monitoring Microbially-induced physical property changes using geophysical data, AGU Invited Presentation, Eos. Trans. AGU 83(19), Spring Meet. Suppl., Abs. H21A-02, 2002.

16 Huisman., S. Hubbard, S., D. Redman, P. Annan, Monitoring Soil Water Content with Ground-Penetrating Radar: A Review, accepted for publication in *Vadose Zone Journal*, 2003.

17 Johnson, W.P., P. Zhang, P.M. Gardner, M.E. Fuller, and M.F. DeFlaun, Evidence for detachment of indigenous bacteria from aquifer sediment in response to arrival of injected bacteria, *Applied and Environmental Microbiology*, 67(10), 4908-4913, 2001.

18 Lovely, D.R., F.H. Chapelle, and JC. Woodward, Use of dissolved H2 concentrations to determine distribution of microbially catalyzed redox reactions in anoxic groundwater, *ES&T,* 26(6), 1062-1067, 1994.

19 Lovley, D.R., and S. Goodwin, Hydrogen concentrations as an indicator of the predominant terminal electron-accepting reactions in aquatic sediments, *Geochimica et Cosmochimica Acta* 52: 2993-3003.

20 Lunt, I., S. Hubbard, and Y. Rubin, Estimation of volumetric water content using surface Ground Penetrating Radar Reflection travel time data, submitted to *Water Resources Research*, 2003.

21 Mailloux, B. S. Devlin, T. C. Onstott, D. Sigman, J. Hall, M. E. Fuller, M. F. DeFlaun, S. H. Streger, K. H. Williams, S. S. Hubbard, and J. McCarthy, The Fate of Nitrate During Stimulation of Coastal Plain Sediments, Eos.Trans. AGU, 83(47), Fall. Meet. Suppl., Abstract H12C-0938, 2002

22 Mailloux, B.J., M.E. Fuller, T.C. Onstott, J. Hall, H. Dong, M.F. DeFlaun, S.H. Streger, R.K. Rothmel, M. Green, D.J.P. Swift, and J. Radke, the role of physical, chemical and microbial heterogeneity on the field-scale transport and attachment of bacteria, *Water Resources Research*, 39(6), 1142, doi: 10.1029/2002WR001591, 2003.

23 Roth, K., Schulin, R., Fluhler, H., and Attinger, W., 1990, Calibration of time domain reflectometry for water content measurement using a composite dielectric approach, *Water Resources Research*, v. 26, p. 2,267-2,273.

24 Schiebe, T. and Y. Chien, An evaluation of conditioning data for solute transport prediction, *Groundwater,* 41(2), 128-141, 2003.

25 Topp, G.C., J.L. Davis, and A.P. Annan. Electromagnetic determination of soil-water content: Measurement in coaxial transmission lines. *Water Resour. Res*., v.16, 1980, pp. 574-582.

26 Vandevivere, P., P. Baveye, D. Sanchez de Lozada, and P. DeLeo, Microbial clogging of saturated soils and aquifer materials: evaluation of mathematical models, *Water Resources Research*, 31(9), 2173-2180, 1995.

27 Williams, K.H., Monitoring microbe-induced physical property changes using high-frequency acoustic waveform data: toward the development of a microbial megascope, Lawrence Berkeley National Laboratory, LBNL-50692, 2002.

28 White, I, S. J. Zegelin, G. C. Topp, and A. Fish, Effect of Bulk Electrical Conductivity on TDR Measurement of Water Content in Porous Media, Symposium and Workshop on Time Domain Reflectometry in Environmental, Infrastructure, and Mining Applications held at Northwestern University, Evanston, Illinois, September 17-19, 1994, Washington, D.C, pp. 294-308. USBM special publication SP 19-94, 1994.

29 Zegelin, S.J., I. White, and G.F. Russell, A critique of the time domain reflectometry technique for determining field soil-water content, Soil Society Science of America, Advances in Measurement of Soil Physical Properties: Bringing Theory into Practice*, SSSA Special Publication* 30, p. 187-209, 1992.