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The FY09 ERSD Overall PART charge to Lawrence Berkeley National Laboratory Environmental Geophysics Group is to ‘*test geophysical techniques that measure parameters controlling contaminant movement under field conditions in at least two distinct subsurface environments*’. In this third of four quarterly reports, *we describe progress in using geophysical methods to monitor subsurface biogeochemical processes associated with natural or engineered in situ environmental remediation.*

1. Introduction

Contaminant flow and transport, natural attenuation, and contaminant remediation efficacy are influenced by hydrogeological and biogeochemical properties. As was described in the FYQ1 and FYQ2 reports, hydrogeological properties, such as the spatial distribution of hydraulic conductivity, impact the migration and distribution of contaminant plumes. When assessing in-situ remediation efficacy, both hydrological and biogeochemical properties must be considered, because hydrological heterogeneity influences the distribution of injected amendments and biogeochemical heterogeneity influences the evolution of a subsurface plume and susceptibility to and sustainability of the remediation treatment. Examples of important biogeochemical properties for assessing plume evolution or remediation efficacy include: the characteristics of the contaminant itself (mass, distribution, decay or degradation rates, sorption affinity), aquifer sediment properties (distribution of sediment geochemistry, sorption affinity, geochemical stability), and the groundwater chemistry (EPA, 2007).

As challenging as it can be to characterize hydrogeological heterogeneity under static conditions, the complexity of subsurface hydrological and biogeochemical properties is magnified upon the introduction of plumes and remedial treatments into the subsurface, because these processes disrupt geochemical equilibrium. In-situ remediation treatments can quickly induce dramatic perturbations to subsurface system: examples of treatments that cause large subsurface perturbations include *in situ* chemical oxidation, pH manipulation, and bioremediation. Potential alterations resulting from these *in-situ* remediation treatments include the dissolution and precipitation of minerals, gas evolution, changes in pore water composition, sorption/desorption, microbial attachment and detachment, oxidation and reduction, and biofilm generation. Some of these transformations can in turn alter the hydrological properties of a system. For example, the generation of gas bubbles, biofilms, and precipitates can clog pore spaces, thereby decreasing hydraulic conductivity and rendering it difficult to introduce subsequent treatment into the subsurface.

Although *in situ* remediation strategies are frequently used in practice, the spatiotemporal distribution of associated biogeochemical transformations and the impact of transformational

end-products on hydrological characteristics on remediation efficacy are difficult to characterize. As described by Atekwana et al. (2006), the subdiscipline of biogeophysics, the use of time-lapse geophysical methods, has recently evolved as an approach to remotely monitor biogeochemical transformations. Whether for hydrogeophysical or biogeophysical applications, the main advantage of using geophysical data over conventional (wellbore based) measurements is that geophysical methods provide spatially extensive information about the subsurface in a minimally invasive manner. The greatest disadvantage is that the geophysical methods are indirect; they only provide proxy information about subsurface properties or processes relevant to contaminant remediation.

With funding from the DOE Environmental Remediation Science Program, a recent thrust of the LBNL environmental geophysical group is to advance the use of geophysical methods for monitoring biogeochemical processes. In this Q3 report, we review some of our recent advances and discuss existing challenges.

2. Monitoring Subsurface Biogeochemical Processes using Geophysical Data

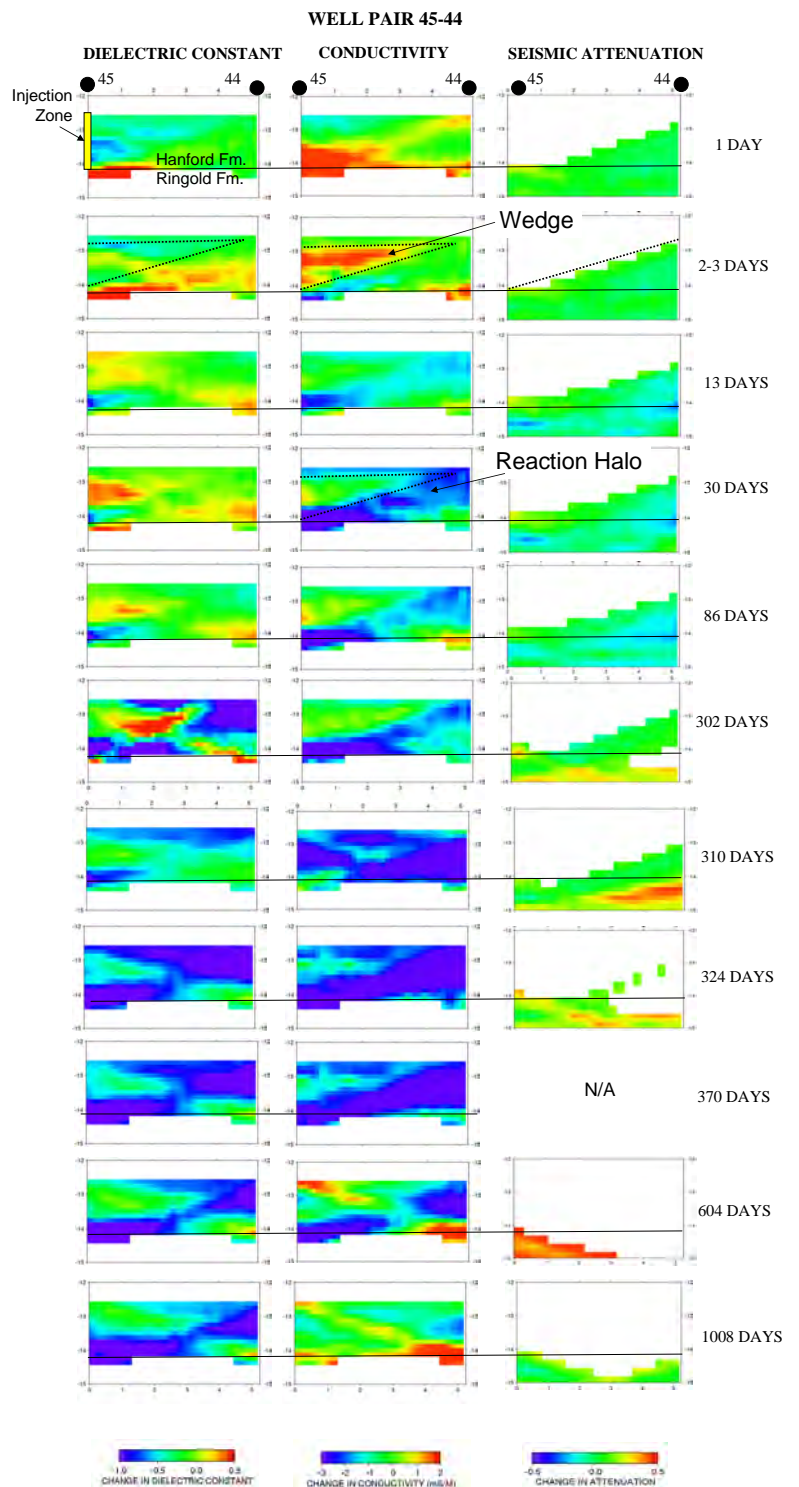
The premise of the LBNL biogeophysical effort is that some of the remediation-induced biogeochemical end-products will be detectable using geophysical methods. Here, we briefly review some recent biogeophysical research that illustrates the potential of geophysical methods for providing information about biogeochemical changes associated with natural plume evolution or remediation treatments. Examples include: (1) the use of time-lapse field-scale datasets to track transformations associated with remedial treatments at field scale; (2) controlled laboratory experiments to quantify the geophysical responses to remediation-induced end-products; and (3) development of frameworks that permit the estimation of biogeochemical parameters using time-lapse geophysical datasets. These examples illustrate both the potential and challenges associated with geophysical monitoring of biogeochemical processes.

2.1 Field-scale Inference of Biogeochemical Transformations. A field-scale geophysical monitoring study was performed as part of an effort to assess the ability to bioremediate the groundwater at the 100H area of the Department of Energy (DOE) Hanford Site, which is located ~1,000 m from the Columbia River. The contaminant of concern at this site is chromate, Cr(VI). Cr(VI) exists in strongly oxidizing environments and is very mobile and acutely toxic, while Cr(III) exists in moderately oxidizing and reducing environments and is immobile and not toxic. The pilot experiment was performed to evaluate the ability of an electron donor called Hydrogen Release Compound (HRC) to stimulate biological activity, thereby creating a reducing environment that will cause the transformation of Cr(VI) to Cr(III). HRC is a viscous, slow-release polylactate that is designed to remain near the injection region and to slowly release soluble and bioavailable lactic acid downgradient to stimulate sustained biological activity.

At the study site, hydrological wellbore and radar and seismic tomographic velocity datasets were first used within a statistical approach to estimate hydrological zonation (refer to FY2009 Q2 report). Time-lapse seismic and radar tomographic datasets were then collected during thirteen acquisition campaigns over a three year period post-HRC injection. Three different pumping campaigns were initiated during the experiment to re-stimulate activity in the injection zone. Figure 1 shows the changes in dielectric constant, electrical conductivity, and seismic attenuation obtained from inversion of the datasets and differencing from the baseline dataset.

Because we are at an early stage in understanding remediation-induced geophysical responses, a suite of batch laboratory experiments were performed to develop an understanding of the geophysical responses to key transformations that were expected to occur in the field, such as: (1) pore-water replacement by the injected electron donor; (2) gas bubble formation; (3) variations in TDS; (4) evolution, dissolution, or mineralogical alteration of solid phase constituents. Using results from the laboratory experiments and constraints offered by field-scale geochemical measurements, the field-scale geophysical monitoring datasets were used to infer the spatial distribution of: injected electron donor; the evolution of gas bubbles; variations in total dissolved solids (nitrate and sulfate) as a function of pumping activity; and the formation of precipitates and the dissolution of calcites (Hubbard et al., 2008). Although qualitative in nature, the integrated interpretation illustrated how geophysical techniques have the potential to provide a wealth of information about coupled hydrobiogeochemical responses to remedial treatments in high spatial resolution and in a minimally invasive manner. The study illustrated the advantages of using multiple lines of evidence to constrain the interpretation of a long-term, field-scale geophysical monitoring dataset and the interpretation of biogeochemical transformations as a function of hydrological heterogeneity and pumping activity.

Figure 1. Time-lapse estimates of changes in dielectric constant, electrical conductivity and seismic attenuation (right) obtained using tomographic radar and seismic methods in association with a biostimulation experiment conducted to reduce and immobilize chromate at the Hanford, WA DOE Site. Day 0 was indicates the date of amendment injection (i.e., initiation of biostimulation). Interpretation of the field geophysical monitoring data, constrained by laboratory biogeochemical experimental results and field aqueous geochemical data, permitted the spatiotemporal interpretation of amendment distribution, the evolution of gasses and precipitates, and the change in TDS associated with the biostimulation. Modified from Hubbard et al. (2008).



2.2 Laboratory Quantification of Geophysical Signatures to Remediation-Induced Transformations. The qualitative field-scale case study described in Section 2.2 illustrates the potential for monitoring some of the end-products associated with remediation treatments. It also highlights some of the challenges, including accounting for the impact of multiple and often competing remediation processes on the geophysical signature and developing an approach to honor the direct (but sparse) geochemical and the indirect (but spatially extensive) geophysical data simultaneously. Recent and ongoing LBNL research funded by ERSP is investigating how geophysical signatures change as a function of induced biotic and abiotic transformations, including the evolution of electrically conductive (FeS) and non-conductive (calcite) precipitates, gases, biofilms, TDS, and electroactive ions. Here, we focus our discussion on the geophysical signature to precipitates formed during bioremediation, because of their potential to lead to bioclogging and thus flow rerouting, which may in turn impact the efficacy and sustainability of the remediation treatment itself.

The first flow-through biogeophysical column experiments performed to assess the impact of precipitates on geophysical signatures was described by Williams et al. (2005). These column experiments were designed to examine the seismic and complex resistivity response to microbe-induced ZnS and FeS precipitation during a biostimulation experiment performed using sulfate reducing bacteria. The experimental columns were instrumented along their length with geophysical sensors, as well as with biogeochemical fluid sampling ports. The experiments were conducted under temperature-controlled conditions over a period of 78 days using five polycarbonate columns having inner diameters of 5.08 cm and lengths of 30.5 cm. Although different columns were used to collect geophysical and biogeochemical datasets and to serve as abiotic control columns, care was taken to ensure that the column packing, flow rates, and other experimental parameters were similar across the columns.

Several pore volumes of lactate were flushed through the water-saturated, sand packed columns before the experiment started, at which time *Desulfovibrio vulgaris* were introduced into the middle and the nutrients were introduced into the bottom of the upward-flowing column. From the multi-level sampling ports (spaced 3.8 cm along column length), sulfate reduction was monitored over seven weeks, as indicated by decreasing substrate and metals concentrations, increasing biomass, and visually discernable regions of metal sulfide accumulation. The region of sulfide mineral precipitation showed a shift toward the influent (bottom) portion of the column over time as a result of microbial chemotaxis towards elevated substrate concentrations at the base of the column (Figure 2a). Upon termination, the fluid sampling and geophysical measurement columns were destructively evaluated; the sediment samples were collected to determine grain-affixed biomass, extractable metals, and to provide materials for electron microscopy. Scanning electron microscope (SEM) images of retrieved samples indicated that the biostimulation led to the aggregation of sulfide-encrusted bacterial cells (Figure 2b).

Based on the co-collected biogeochemical and geophysical data from these flow-through columns, Williams et al. (2005) documented that the time-lapse geophysical signatures tracked the onset and evolution of the geochemical transformations over space and time. In particular, regions of sulfide precipitation and accumulation resulted in substantial changes in seismic and complex electrical measurements (the latter conducted over a range of 0.1-1000Hz). The high-

frequency seismic wave amplitudes were reduced by nearly 84% and significant increases in complex electrical conductivity were observed with only minimal changes in the fluid conductivity (Figure 2b and 2c, respectively). Changes in the electrical phase response and seismic attenuation were attributed to alterations in subsurface mineralogy arising from stimulated microbial activity within the pore space, including precipitation reactions, aggregation dynamics, and solid-state mineral transformations.

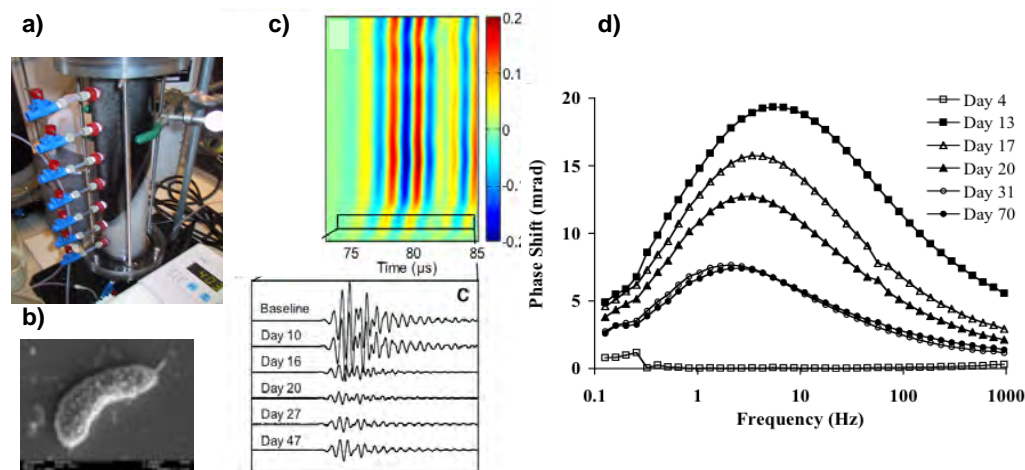


Figure 2 (a) Example experimental column illustrating how measurements are collected down the length of the column and the presence of a developed sulfide precipitation front associated with sulfate reduction. (b) TEM image illustrating the mineralized encrustation on the experimental microbe due to the formation of sulfide precipitates (scale $\sim 1\mu\text{m}$). Changes in (c) seismic amplitude (d) IP response associated with the initiation and aggregation of evolved sulfide precipitates at the laboratory scale (modified from Williams et al., 2005).

We are currently performing flow through column studies to explore the seismic, radar, and complex electrical signatures of nonconductive (i.e., calcite) precipitates (Wu et al., 2008, 2009) as well as electroactive ion concentration. As is described below, an increased understanding of the geophysical responses to various end-products, obtained through such controlled column studies, is a necessary component for geophysical quantification of biogeochemical processes.

2.3 Development of Biogeochemical Estimation frameworks using Geophysical Datasets.

In order to use the time-lapse geophysical data to quantitatively estimate biogeochemical end-products, it is necessary to develop a framework that can integrate time-lapse geophysical, geochemical, and other types of datasets with petrophysical relationships (developed, for example, using theory and laboratory experiments described in Section 2.2). To meet this objective, we have developed a state-space Bayesian approach that uses Markov Chain Markov Chain sampling methods to find the solutions. Although the framework is general (and thus can be used with a variety of collected time-lapse geophysical and geochemical datasets), we have tested the model on the laboratory dataset described above (Williams et al., 2005).

In the estimation approach, we consider characteristics of end-products of biogeochemical transformations as state vectors, which evolve under constraints of local environments through

evolution equations. We consider time-lapse geophysical data as available observations, which could be linked to the state vectors through empirical petrophysical models. We estimate the state vectors and their associated unknown parameters over time using Markov chain Monte Carlo sampling methods. To demonstrate the use of the state-space approach, we applied it to the complex resistivity data described in Section 2.2, which were collected during laboratory column biostimulation experiments that were poised to precipitate iron and zinc sulfides during sulfate reduction. We developed a petrophysical model to link the sulfide precipitate properties to the time-lapse geophysical attributes and estimate volume fraction of the sulfide precipitates, fraction of dispersed, sulfide-encrusted cells, mean radius of aggregated clusters, and permeability over the course of the experiment. In the petrophysical model, we assumed that the precipitation mechanisms varied over time, initially forming FeS and ZnS precipitates (which increased the volume fraction and specific surface area of the sample), followed by a coating of dispersed microbial cells with FeS and ZnS precipitates, finally followed by the formation of clusters of the precipitate-coated dispersed cells. The final stage leads to a volume fraction increase but a specific surface area decrease. This model was consistent with SEM and TEM imagery associated with the column experiments described by Williams et al. (2005) and with the distinct changes in geophysical signatures after biostimulation.

Figure 3 illustrates the estimation result, including the geophysically-obtained estimates of the evolution of: precipitate volume fraction (left), dispersed cells (left center), radius of the aggregated precipitate clusters (right center) and permeability (right) at a single column sampling point over the duration of the experiment. In all figures, the geophysically-obtained estimates compare favorably with measurements obtained using geochemical or hydrological datasets collected during the column experiment. This study is further described by Chen et al. (2009), and suggests that the developed state-space approach permits the use of geophysical datasets for providing quantitative estimates of end-product characteristics and hydrological feedbacks associated with biogeochemical transformations. Although tested here on laboratory column experiment datasets, the developed framework provides the foundation needed for quantitative field-scale estimation of biogeochemical parameters over space and time using direct, but often sparse wellbore data with indirect, but more spatially extensive geophysical datasets.

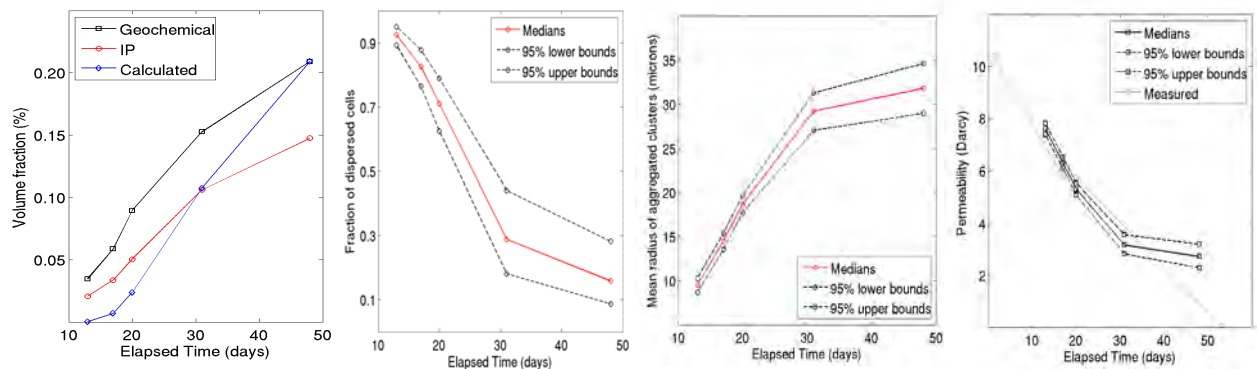


Figure 3. Comparison of geophysically-obtained estimates of the evolution of dispersed precipitates (left), their volume fraction (left center), aggregated bioclusters (right center) and permeability (right) over the duration of a biostimulation experiment poised for sulfate reduction and thus the production of sulfides. This study (further described by Chen et al., 2009) is the first to illustrate the use of time-lapse geophysical data for quantifying complex and coupled biogeochemical-hydrological properties associated with in-situ remediation treatments.

3. Summary and Existing Challenges

The DOE ERSP-sponsored research described above was performed along three different, important fronts for advancing biogeophysics: laboratory experiments to develop an understanding about geophysical sensitivities and to develop petrophysical relationships; field-studies to explore the resolution and sensitivities of geophysical attributes to transformation over field-relevant scales; and stochastic approaches to integrate the wide array of time-lapse datasets (both direct and indirect measurements) that are collected during remediation experiments as we strive to quantify the spatiotemporal distribution of associated end-products. The studies described above were conducted in conjunction with biostimulation experiments that have been and are being conducted at chromium, uranium and strontium-contaminated aquifers associated with the Hanford 100, Rifle IFRC, and INEL VZRP sites, respectively.

Although these case studies indicate the potential that geophysical methods hold for improving our understanding of subsurface biogeochemical response to in-situ treatments, many challenges remain. Many of the obstacles described in the 2009 Q1 and Q2 PART reports (for using geophysical data to characterize subsurface hydrogeological properties) are often exasperated when using geophysical methods to monitor biogeochemical processes, in part because biogeophysics is at a very early stage of development, and our understanding of geophysical responses to biogeochemical end-products is still developing. Scale matching issues can be even more significant with biogeophysics than with hydrogeophysics because many of the biogeochemical properties of interest occur at grain boundaries or in pore spaces that are much smaller than the support scale of the geophysical measurement. Non-uniqueness of the geophysical responses is problematic because geophysical signatures often respond to hydrogeological as well as biogeochemical heterogeneity. Because plume evolution or remediation treatments can lead to the occurrence of multiple geochemical processes that simultaneously contribute to the geophysical signature (i.e., the evolution of gasses, biofilms and precipitates), it can be challenging to deconvolve the influences of the individual contributions to the geophysical signature. Biogeochemical end-products products can also alter the initial hydrological properties (such as through clogging or dissolution), which can further impact the geophysical signature.

Some of these key challenges are being addressed through interrelated synchrotron science, environmental geophysics, and reactive transport modeling components of the LBNL SFA 'Evolution of Pore Structures and Flowpath' Research Challenge, which is described at http://esd.lbl.gov/research/projects/sustainable_systems/challenges/evolution.html.

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