Field-Scale Estimation and Simulation of Biogeochemical Heterogeneity

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ABSTRACT

Many bioremediation experiments have been conducted at the DOE Rifle (CO) IFRC site to facilitate the reduction of U(VI) to U(IV) and to explore the role of the associated coupled physical and biogeochemical processes. At the Rifle IFRC and elsewhere, it is common to use time-lapse wellbore-based aqueous geochemical data with mechanistic models to assess the progress of the remediation-induced system transformations. In this work, we strive to identify the diagnostic signatures of biostimulation by using hydrological, geochemical, and geophysical data through two different yet complementary approaches:

- *Data-driven statistical (or 'top-down') approach. We consider the multivariate geochemical concentrations as hidden random processes (observed at borehole locations but unknown at other locations) and the time-lapse geophysical data as observations at each location along the 2D profiles. We use a Bayesian approach and Hidden Markov models to estimate the unknown parameters. The developed statistical approach can provide information on the probability of being in each redox stage over time and space following biostimulation and on the diagnostic parameters as functions of aqueous geochemical concentrations and geophysical attributes.*
- *Mechanistic reactive transport modeling (or 'bottom-up') approach. We use flowmeter and slug test data to set up the initial distribution of permeability. The initial distribution of porosity was obtained by assuming a correlation between porosity and IP data at the initial time and by matching bromide breakthrough data. We use inverse reactive transport modeling of time-lapse geochemical data to determine key parameters that control the reactive transport processes. After obtaining a good match with the geochemical data, we compare the predicted aqueous and solid phase geochemistry from the reactive transport model with the IP data to understand key controls on the IP data and whether the IP data are useful for monitoring and diagnosing changes in the biogeochemical processes during the biostimulation experiments.*

The data-driven statistical and mechanistic approaches are complementary to each other. The top-down approach is expected to be especially useful for rapid identification of critical system transitions based on streaming monitoring data and for constraining mechanistic transport models where various reaction pathways are possible. The established methods can be used to link geochemical and geophysical signatures and eventually to help understand and predict subsurface biogeochemical processes using constraints from different types of measurements.

1. Estimation of Field-scale Bioremediation Status Using Geochemical and Geophysical Data

Background

- Bioremediation time frame for the field bioremediation experiments:
  - Winchester (2007): starting on 08-Aug-2007, lasting 31 days.
  - Big Rusty (2008): starting on 20-July-2008, lasting 110 days
  - Buckskin (2009): starting on 20-July-2009, lasting 30 days.
- Geochemical and geophysical data:
  - Time-series of aqueous geochemical data includes Fe(II), uranium, sulfate, sulfide, acetate, bromide concentrations.
  - Time-lapse spectral IP data along the profile near boreholes D01-D02-D03-D04 (red line segment): (1) 2007 and 2008 IP data have 6 frequencies between 0.125Hz and 4Hz at 19 time-steps; (2) 2009 IP data have 13 frequencies between 0.0625Hz and 256Hz at three time-steps.

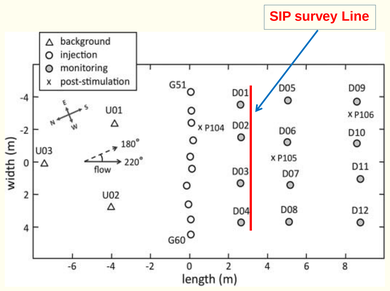


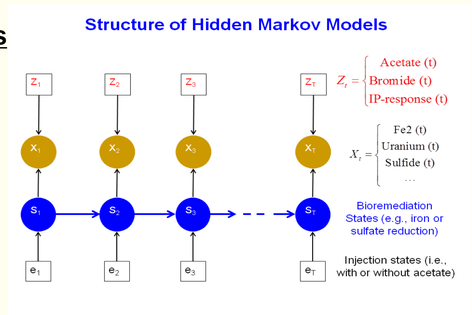
Figure 1: Spectral induced polarization (SIP) survey profile (Array A) and geochemical sampling boreholes (D1, D2, D3, and D4).

Hypothesis

- Geophysical methods can be used to quantify the evolution of biogeochemical end-products (precipitates, electro-active ions) in a minimally invasive manner.
- Field-scale time-lapse geophysical data can be used to identify the spatio-temporal distribution of biogeochemical parameters and redox status at the field-scale.
- The quantified biogeochemical parameters and redox status can be used to guide and monitor remedial methods and to constrain/validate RTM.

Hidden Markov Models

Figure 2: Structure of hidden Markov models. The underlying redox states at each time are unknown but they depend on the concurrent geochemical and geophysical data.



Parameter Estimation and Model Selection

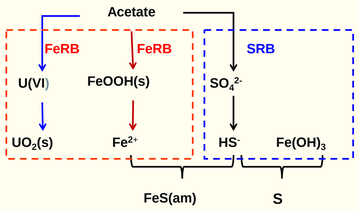


Figure 3: Identified main reaction networks at the Rifle site, from which the state-dependent models are developed.

We follow the main steps below to estimate parameters and identify unknown states.

- Specify state-dependent models based on main reaction networks given in Figure 3 to link the underlying states to the concurrent geophysical and geochemical data.
- Estimate unknown model parameters using expectation-maximization (EM) methods and select the best model using Bayesian information criterion.
- Obtain transition matrix between each state and transition sequences at each location.

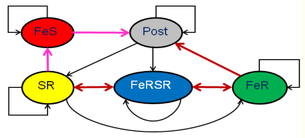
Figure 4: Transition matrix among five identified states based on the current models and available data sets, where FeS--a state dominated by iron precipitation, Post--a state close to background, FeRSR--a state where both iron and sulfate reduction occur, SR—a state dominated by sulfate reduction, FeR– a state dominated by iron reduction.

Transition matrix and state-transition sequences

	FeS	Post	FeRSR	SR	FeR
FeS	0.889	0.111	0.000	0.000	0.000
Post	0.000	0.965	0.022	0.013	0.000
FeRSR	0.000	0.000	0.459	0.177	0.364
SR	0.054	0.000	0.018	0.910	0.018
FeR	0.000	0.053	0.183	0.000	0.764

- Relatively strong transition among iron reduction, sulfate reduction, and concurrent reduction (see blue values), compared to other pairs.

- **Two transition paths:**
  - Sulfate reduction to iron sulfide precipitation to post-injection (pink path).
  - Sulfate reduction, or concurrent reduction to iron reduction to post-injection (brown path).



Borehole D1

- Long sulfate reduction (SR) characterized by persistent, elevated sulfide concentrations.
- Iron reducers remove Fe(III)-oxides and produce Fe(II). They also remove uranium over the entire period of concurrent metabolism (i.e., growth of iron reducers is concurrent with sulfate reducers and our current conceptual model is that these iron reducers continue to remove uranium while sulfate reducers are also active, although the sulfate reducers are not reducing/removing the uranium).

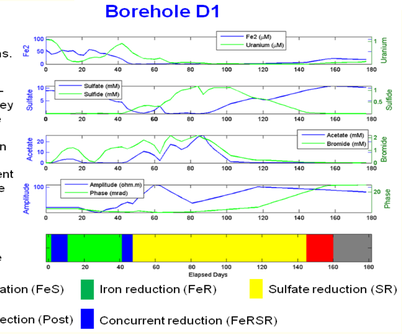


Figure 5: State transition sequences as a function of time at borehole D1.

2. Understanding Biogeochemical Processes Using Coupled RTM and Geophysical Monitoring

Background

Understanding subsurface biogeochemical processes is challenging due to the heterogeneity of porous media and the complexity of reaction network. Geophysical methods are often used as non-invasive tools for monitoring subsurface biogeochemical processes. However, geophysical data in general provide "bulk" indication of processes instead of mechanistic understanding. In this work, we use a biostimulation experiment at Rifle, Colorado, as an example to couple reactive transport modeling with hydrologic, geochemical, and geophysical data. Our objective is to

- mechanistically understand subsurface biogeochemical processes during biostimulation experiments,
- identify key controls that determine geophysical signature,
- examine if and under what conditions geophysical signature provide a powerful monitoring tool for subsurface biogeochemistry.

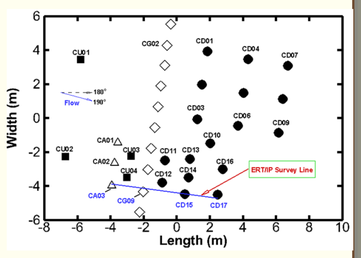
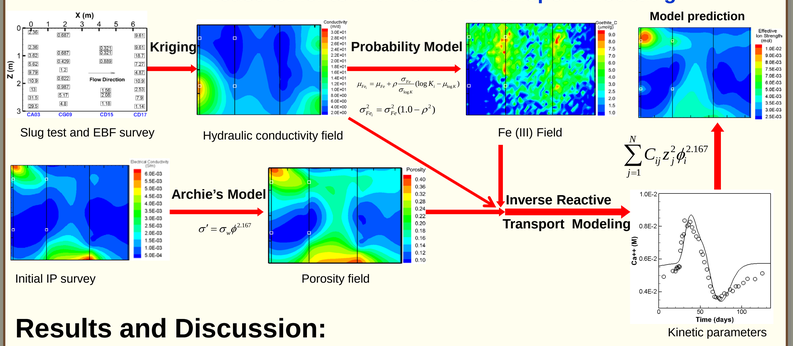


Figure 6: Well layout at 2010 Rifle field experiment. Also shown includes background wells (squares), bicarbonate injection wells (triangles), acetate injection wells (diamonds), and monitoring wells(circles). We focus on the CA03-CG09-CD15-CD17 transect that has IP survey data.

Hypothesis

- Subsurface biogeochemical dynamics can be captured through coupled biogeochemical reactive transport modeling and geophysical monitoring.
- Geophysical signatures can monitor and diagnose changes in the biogeochemical processes.
- Reactive transport modeling, constrained by physical and geochemical measurement data, can provide mechanistic understanding on key biogeochemical processes that determine geophysical signature.

Methodology: Integration of hydrological, geophysical, and geochemical measurements with reactive transport modeling



Results and Discussion:

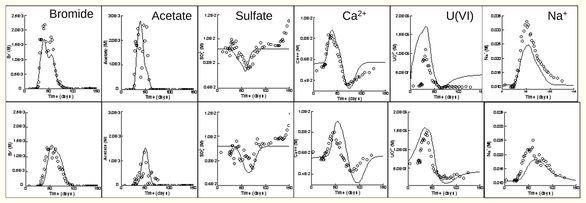


Figure 8: Comparison of modeling outputs (solid lines) with breakthrough data (circles) of bromide, acetate, sulfate, Ca^{2+}, U(VI), and Na^+ from two monitoring wells of CD15 (first row) and CD17 (second row).

- **Agreement between the modeling and the geochemical field data indicates the model has captured the dynamics of the system.**
- **U(VI) mobility is controlled by surface complexation due to bicarbonate amendment and U(VI) bioreduction is limited to iron-reduced bacteria(FeRB), which is stimulated due to acetate amendment.**

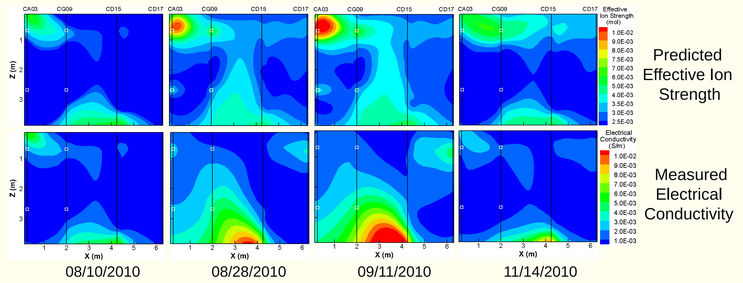


Figure 9: Comparison between spatiotemporal profiles of predicted effective ionic strength (first row) and measured electrical conductivity (second row). Effective ionic strength is defined as $\sum_{j=1}^{N} C_{ij} z_j^2 \phi_i^{2.167}$ for each grid block *i*. Here c_{ij} *is* the concentration of species j predicted by the mode after fitting the geochemical data, and z_j is the charge of species *j* in grid block *i*. Φ_i is the porosity in grid block *i*. *N* is the number of the species.

- **Similarity in spatiotemporal patterns between effective ion strength and bulk electrical conductivity (derived from ERT/IP surveys) indicates geophysical methods can provide signatures to monitor biogeochemical processes during coupled bicarbonate/acetate amendment bioremediation experiments.**
- **Fluid ion strength and porosity play a vital role in linking geochemical and geophysical signatures for better understanding induced biogeochemical transformation.**

Summary

- We developed a hidden Markov model (HMM) based on main reaction networks to identify statistically important states and transitions associated with field-scale bioremediation using multiple borehole aqueous geochemical data.
- The identified five states (i.e., iron reduction, sulfate reduction, concurrent reduction, iron sulfide precipitation, and post injection) have different geochemical features and correspond well to the spectral IP data.
- Hydrologic and geophysical data-based biogeochemical reactive transport modeling successfully captures the dynamics of coupled biogeochemical processes at the field-scale.
- Similarity between spatiotemporal patterns of effective ion strength and bulk electrical conductivity indicates the potential of using geophysical measurements for monitoring of subsurface biogeochemical processes.
- Results indicate that the spatial distribution of porosity and aqueous ionic strength are both critical in determining the geophysical signature.

References

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Funding for this study was provided by the U.S. Department of Energy, BER Program Contract DE-AC020SCH11231 to the LBNL Sustainable Systems Scientific Focus Area