U.S. Department of Energy

Office of Science

Oak Ridge Field Research Center

Environmental Remediation Sciences

Environmental Remediation and Stewardship Research

Oak Ridge Integrated Field-Scale Research Challenge

Task D - Multi-Process and Multi-Scale Modeling and Data Analysis

Task Leader: Jack Parker

ERSD Annual PI Meeting
Lansdowne, Virginia
April 16-19, 2007

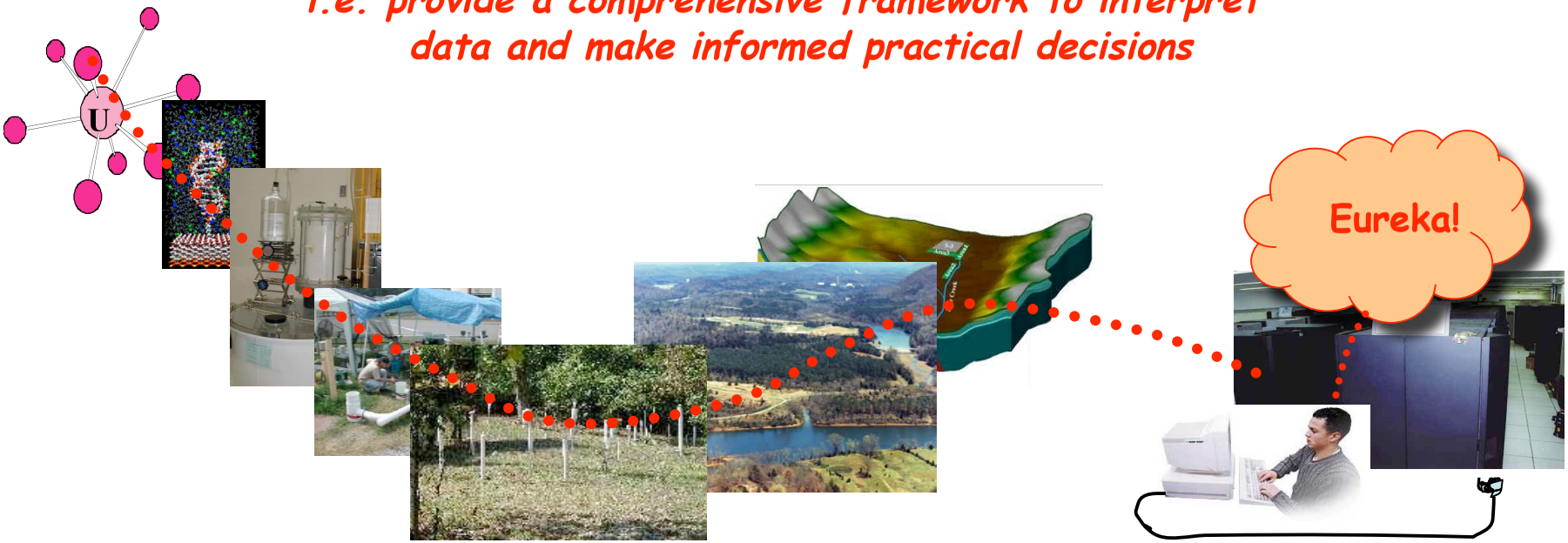
OAK RIDGE National Laboratory

Task Objectives

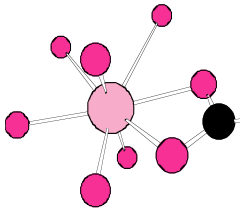
Gain an improved understanding of hydrologic, geochemical and biological processes and their interactions at relevant time and space scales

Develop practical, site-independent tools for evaluating effects of natural and engineered processes on long-term performance

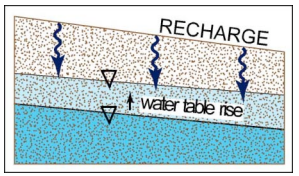
i.e. provide a comprehensive framework to interpret data and make informed practical decisions



Important Model Processes



- Flow in fractured, dipping, heterogeneous rock/saprolite
- Fluid flow due to density gradients
- Advective-dispersive dissolved phase transport
- Diffusive fracture-matrix mass transfer
- Microbial population/biomass models
- Colloid transport
- Permeability changes associated with biogeochemical processes
- Atmospheric coupling (recharge, oxygen exchange, plant uptake)
- Equilibrium and kinetic geochemical reactions:
  - Aqueous speciation, complexation, polymerization reactions
  - Oxidation-reduction reactions
  - Precipitation-dissolution reactions
  - Hydrolysis reactions
  - Adsorption-desorption reactions
  - Acid-base reactions
  - Cation-anion exchange reactions (pH dependent charge)
  - Microbially-mediated reactions and biomass growth



Modeling Tasks at Multiple Scales

- **Lab-Scale Modeling Studies (ORNL, UT)**
  - Batch experiment analysis
  - Packed and undisturbed column analysis
  - Develop and calibrate geochemical/microbial reaction models

- **Local Field-Scale Experiments (ORNL, UT, Stanford, Ga Tech)**
  - Recharge manipulation experiments
  - pH manipulation experiments
  - Org-P and Ca-oleate injection experiments
  - Validate models and calibrate parameters under field conditions
  - Test upscaling of lab model results

- **Site-Wide Modeling (ORNL, UT)**
  - Plume-scale analysis of groundwater monitoring, soil sampling and geophysical data in conjunction
  - Upscale parameters from lab and local field-scale studies
  - Assess plume-scale impacts of natural and engineered factors on long-term performance

Modeling Approach

HydroGeoChem (HGC) v.5 will serve as the primary modeling tool

Capabilities:

- Three-dimensional domain with any spatial structure
- Transient sat/unsat flow in heterogeneous, fully anisotropic media
- Multispecies aqueous phase transport and coupled flow and transport including density-dependent flow
- Adaptable to model reaction-flow coupling (e.g., pore clogging)
- Generic biogeochemical reaction network capability (equilibrium and kinetic)
- Diffusion-limited mass transfer kinetics
- Coupled with nonlinear inversion code PEST to perform parameter estimation
- Readily applicable to any DOE site

A geochemical reaction network for aqueous and surface U reactions has been implemented in HGC and experimentally validated

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Model Implementation

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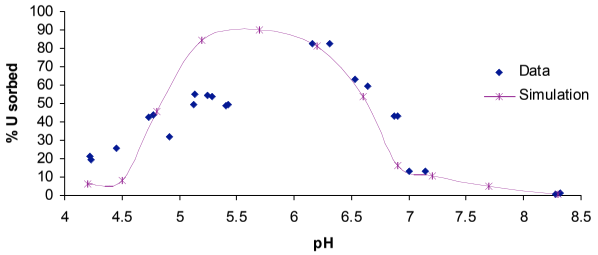
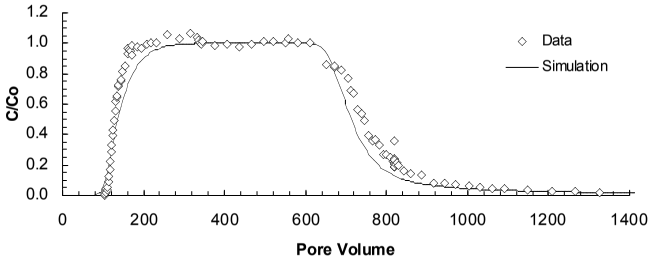
HydroGeoChem has been used to analyze lab data and field experiments from the Oak Ridge site

Batch U-Sorption Experiment

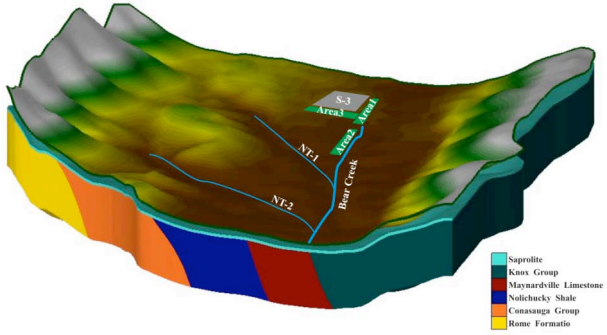


Lab Column Experiment

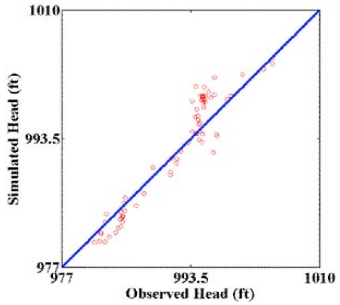


and to implement a site-wide model for the FRC site

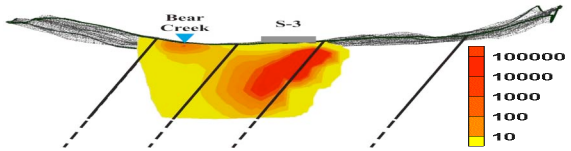
Model domain ~160 acres



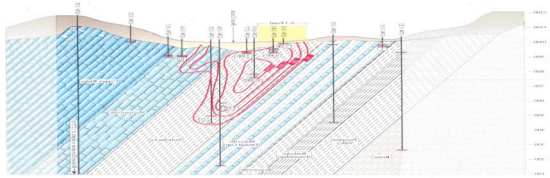
Groundwater calibration



Simulated plume with density-dependent flow



Observed plume



Microbial Reaction Model Integration

Microbial reactions are generally formulated using Monod kinetic models that involve a number of growth, utilization and inhibition coefficients

Will incorporate a microbial reaction model developed by Stanford into HGC

Statistical models will be developed to predict microbial community structure and functional parameters from geochemical and other data using

- Discriminant function analysis
- Multiple linear regression
- Feedforward neural networks

Modeling pH Effects

Implement Soil Buffer / pH Dependent Surface Charge Model

Employ Spalding's (2001) soil polyprotic acid model

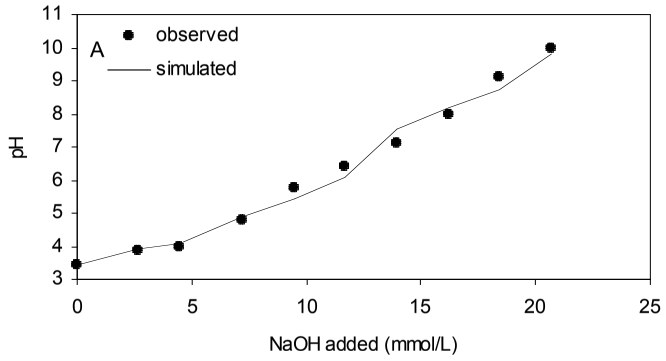
$$H_4X \rightleftharpoons H_3X^- + H^+ \rightleftharpoons H_2X^{2-} + 2H^+ \rightleftharpoons HX^{3-} + 3H^+ \rightleftharpoons X^{4-} + 4H^+$$

plus Al/Fe hydrolysis, Ca/Mg/Mn carbonate/hydroxide rx, ion exchange rx, etc.

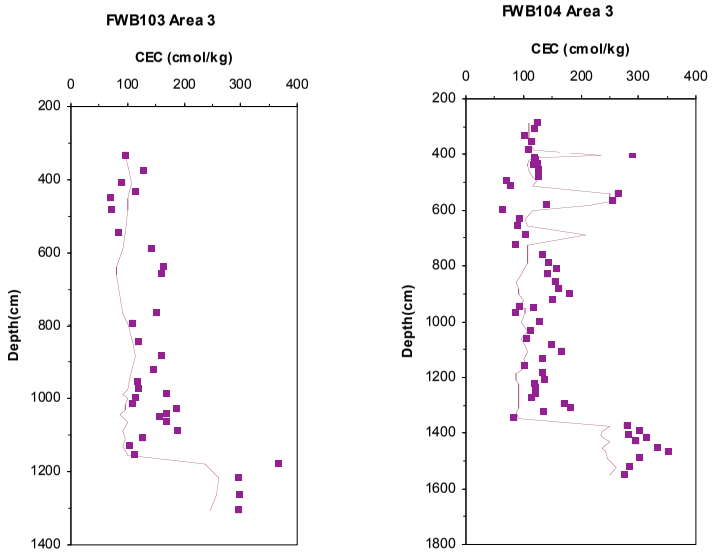
Calibrate pKa values and exchange selectivity coefficients to pH vs CEC characterization data and batch soil titration experiments (c/o: Baohua Gu, Dave Watson)

Preliminary Results: Model versus Data

Soil titration curve

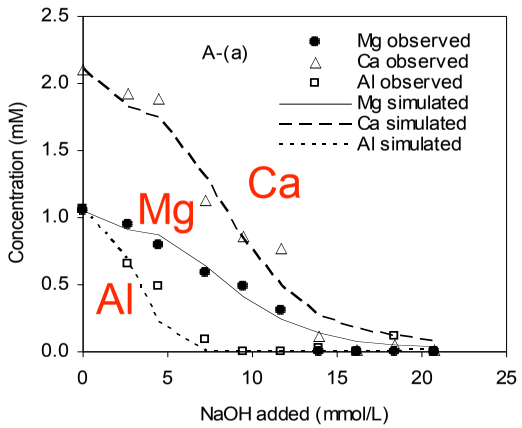


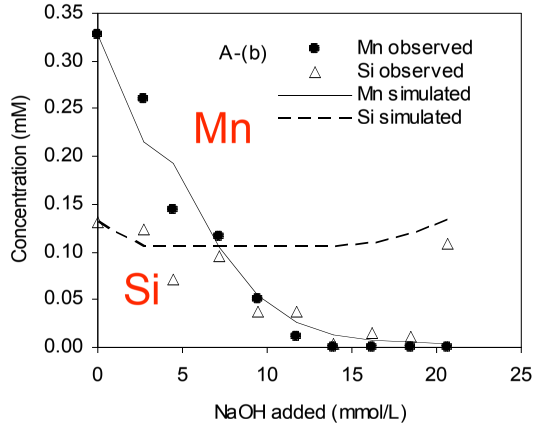
Cation exchange capacity versus depth due to pH variations

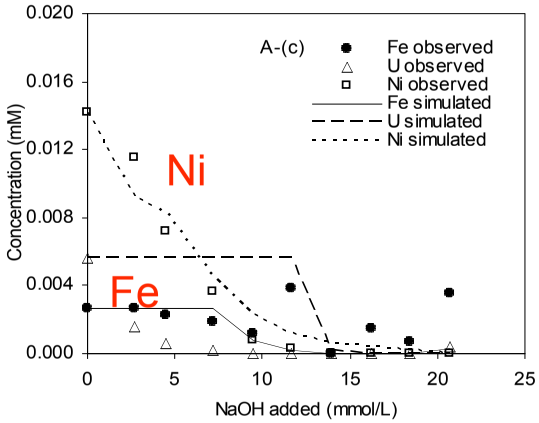


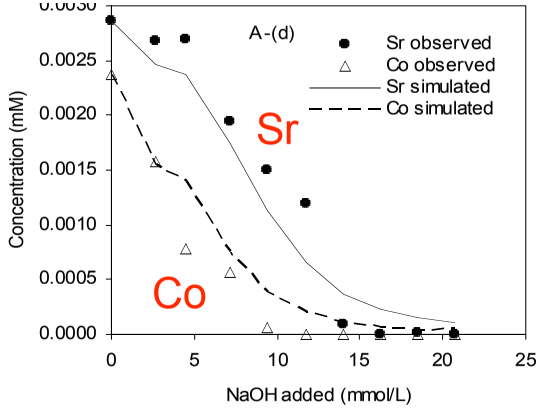
Modeling pH Effects…

Observed and model-predicted aqueous phase metal concentrations versus base added









Results clearly demonstrate the critical importance of pH to geochemistry. Favorable initial modeling results validate the proposed modeling framework, which will be comprehensively tested by planned field pH manipulation experiments

Integration of modeling and multi-scale experiments maximizes research benefits and utility

Bench scale

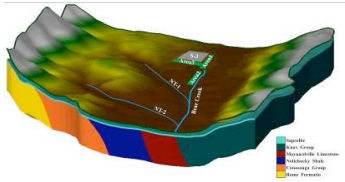
Field Plots

Development
Calibration
Verification

Experimental design

Development
Calibration
Verification

Experimental design



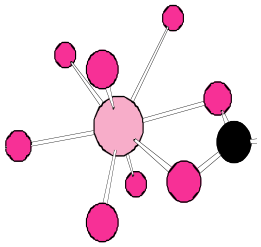
Multi-scale modeling

Development
Verification

Experimental design

Model validation

Molecular



Ultimate goal:
Remediation
Stewardship
Management

Watershed

FY07-FY08 Plan

Planned Modeling Efforts:

- Calibrate and test soil titration model for different materials at the site (i.e., gravel fill zone)
- Incorporate in site-wide model and evaluate U transport predictions from historical S-3 Pond disposal ops
- Extend reaction network to incorporate Al polymer species and determine relevant equilibrium and kinetic parameters
- Perform simulations for planning and analysis of field pH manipulation experiments (local-scale models)
- Implement refinements in site-wide model based on initial geophysical testing results
- Implement microbial kinetics in model and perform initial sensitivity analyses