U.S. Department of Energy

Office of Science

Integrated Field-Scale Subsurface Research Challenge

Environmental Remediation Sciences

Oak Ridge Field Research Center

Multiscale Investigations on the Rates and Mechanisms of Targeted Immobilization and Natural Attenuation of Metal, Radionuclide and Co-Contaminants in the Subsurface (project briefing)

Environmental Remediation Science Program

Oak Ridge National Laboratory
Argonne National Laboratory
Florida State University
Georgia Tech
Lawrence Berkeley National Laboratory
Stanford University
University of Oklahoma
University of Tennessee

Field Research Executive Committee (FREC)
Conference Call
November 15, 2007

OAK RIDGE National Laboratory

Team Members

- **Scientific Coordination:** Phil Jardine (PI), Dave Watson (Field Research Manager, ORNL) in consultation with project scientific disciplines.
- **Geophysics**: Susan Hubbard*, Ken Williams, J. Chen (LBNL), Greg Baker and David Gaines (UT), Les Beard (Battelle)
- **Geochemistry:** Scott Brooks*, Brian Spalding, Phil Jardine (ORNL), Ken Kemner (ANL)
- **Microbiology:** Joel Kostka* (FSU), Tony Palumbo and Chris Schadt (ORNL), Joe Zhou (OSU).
- **Biogeochemistry:** Craig Criddle* and Weimin Wu (Stanford), Baohua Gu (ORNL)
- **Hydrology:** Dave Watson* (ORNL), Jack Parker (ORNL/UT), Peter Kitanidis (Stanford)
- **Numerical Modeling:** Jack Parker* (UT), Craig Brandt and Fan Zhang (ORNL), Peter Kitanidis (Stanford), Jian Luo (Georgia Tech)
- **Data Management:** Craig Brandt* (ORNL)

*** Disciplinary lead**

Presentation Outline

- ORIFC Objectives / Goals / Site Description
- ORIFC Approach (Tasks A – D)
- Results and Future Research

  Task A: Define flowpaths and heterogeneities that control the fate and transport of contaminant plumes

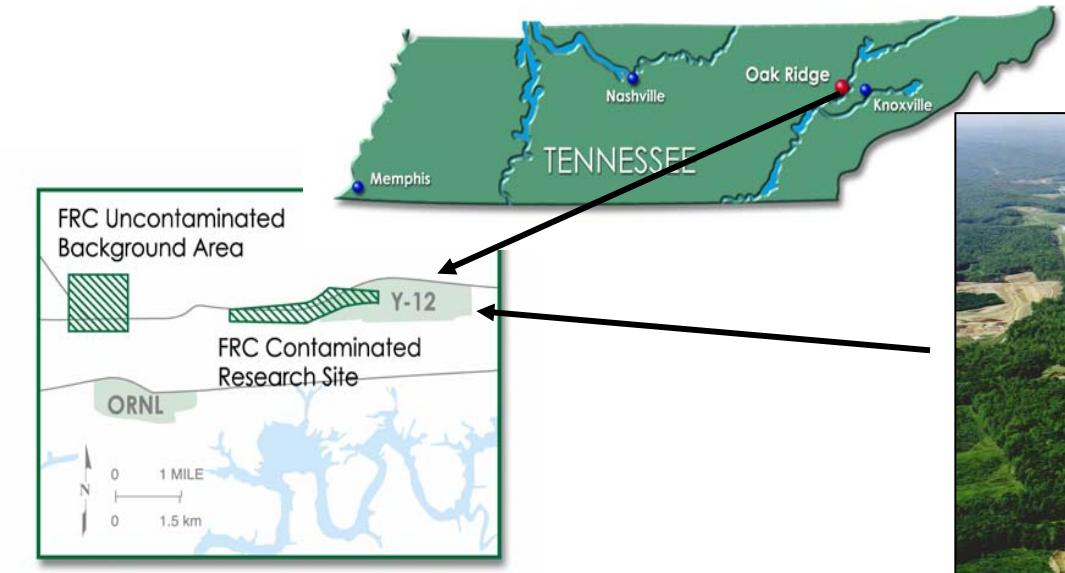
  Task B: Define and quantify natural attenuation rates & mechanisms across the Bear Creek watershed

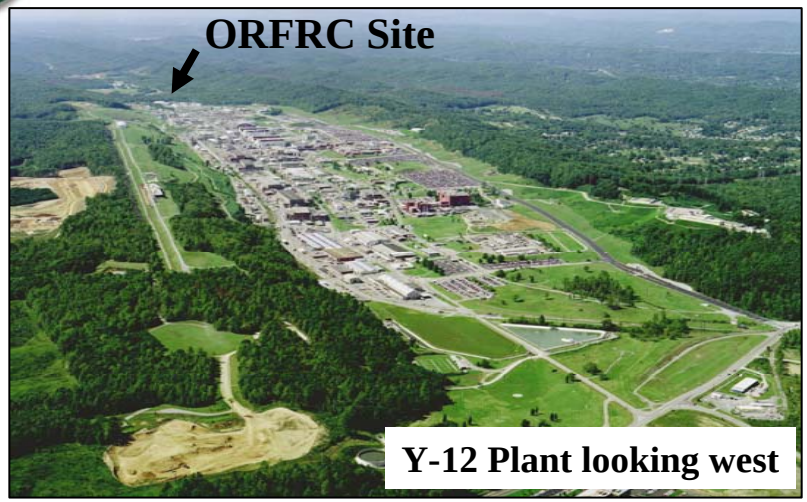
  Task C: Quantitative *in situ* immobilization strategies within secondary sources of the saprolite and carbonate units (U, Tc, nitrate)

  Task D: Multiprocess and multiscale numerical modeling and data analysis
- Data Management
- Information Sources / Management Documents / Technology Transfer

Location

Oak Ridge Integrated Field-Scale Research Challenge





Site Description

The Oak Ridge IFC is located in eastern Tennessee and contains contaminated and uncontaminated field facilities as well as on-site and off-site laboratory facilities.

At the contaminated site, unlined surface impoundments received acidic nitrate- and U-bearing waste from 1951 to 1983 at a rate of 2.5 million gallons/year. Attempts were made to neutralize the waste and the waste trenches were capped as a parking lot in 1988.

The region receives ~1400 mm rainfall / y with 10% contributing to groundwater recharge and 40% contributing to surface water recharge.

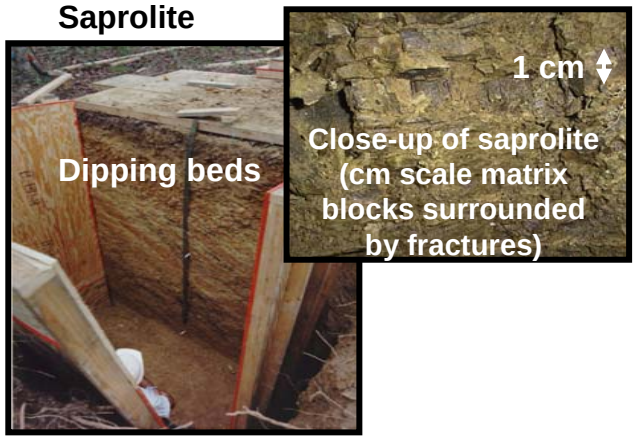
The subsurface media consist of fractured saprolite weathered from interbedded shale and limestone and is conducive to rapid preferential flow of water and solutes. The matrix porosity serves as a "secondary contaminant source" whose aerial extent is massive (tens of kilometers).

Both aqueous and solid phase geochemistry and microbiology are spatially and temporally diverse

Conceptual models have been developed for secondary sources, shallow and deep plumes, low and high pH saprolite plumes, and high pH gravel plumes.

ORNL media consisting of interbedded fractured weathered shales and limestone

Saprolite

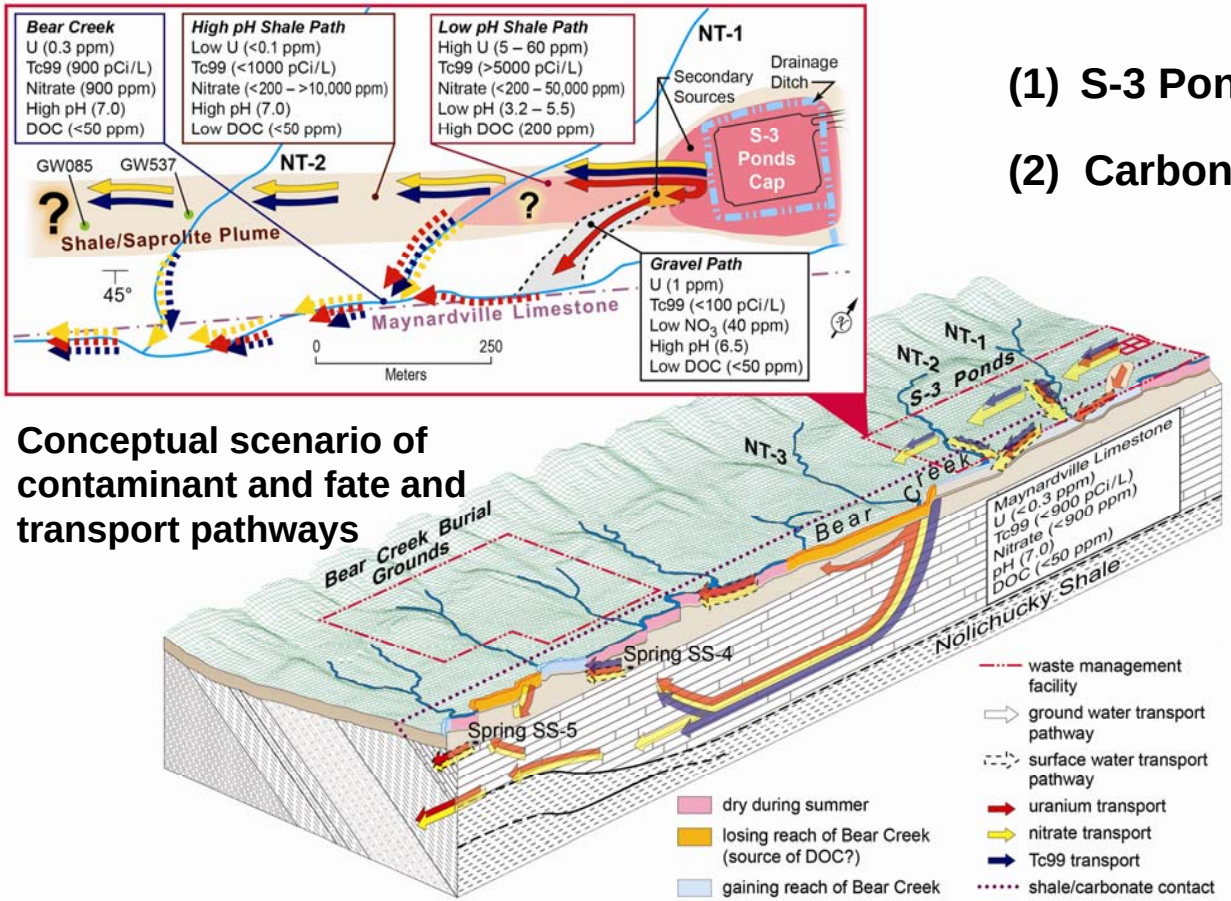


Underlying Bedrock

Site Description

Focus on several secondary source zones and flow pathways in the ORFRC that represent a range of scales. These source zones and pathways contain numerous transition zones characterized by pronounced shifts in hydrology, geochemistry, and/or microbiology.

Multi-scale targeted for *in situ* research



Conceptual scenario of contaminant and fate and transport pathways

(1) S-3 Ponds secondary source

(2) Carbonate gravel secondary source

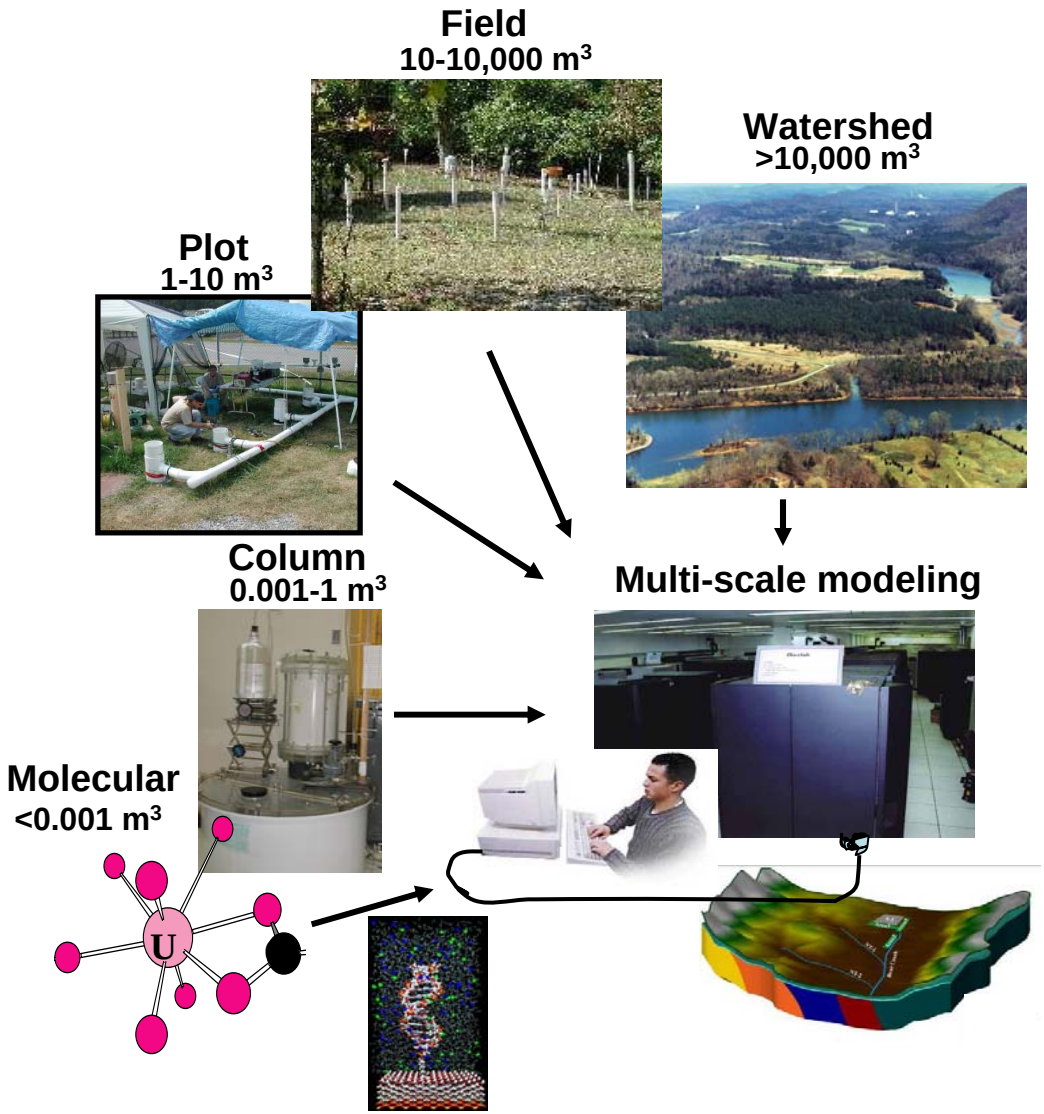
(3) Low pH shale/saprolite pathway

(4) Neutral pH carbonate gravel pathway

(4) Neutral pH Maynardville Limestone pathway

(6) Recharge pathway

Goals



To advance the understanding and predictive capability of coupled hydrological, geochemical, and microbiological processes that control in situ transport, remediation and natural attenuation of metals, radionuclides, and co-contaminants (i.e. U, Tc, NO_3) across multiple scales ranging from molecular to watershed levels.

Provide multi-process, multi-scale predictive monitoring and modeling tools that can be used at sites throughout the DOE complex to:

(1) inform and improve the technical basis for decision making, and

(2) assess which sites are amenable to natural attenuation and which would benefit from source zone remedial intervention.

Objectives

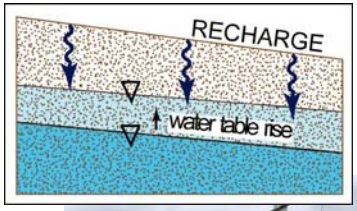
(1) quantify recharge and other hydraulic drivers for groundwater flow and dilution of contaminants along flow pathways and determine how they change temporally and spatially during episodic events, seasonally, and long term.

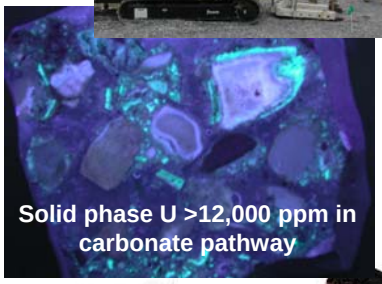
(2) determine the rates and mechanisms of coupled hydrological, geochemical, and microbiological processes that control the natural attenuation of contaminants in highly diverse subsurface environments over scales ranging from molecular to watersheds.

(3) explore novel strategies for enhancing the subsurface stability of immobilized metals and radionuclides.

(4) understand the long-term impacts of geochemical and hydrologic heterogeneity on the remobilization of immobilized radionuclides.

(5) improve our ability to predict the long-term effectiveness of remedial activities and natural attenuation processes that control subsurface contaminant behavior across a variety of scales.





Approach

Task A: Define flowpaths and heterogeneities that control the fate and transport of contaminant plumes

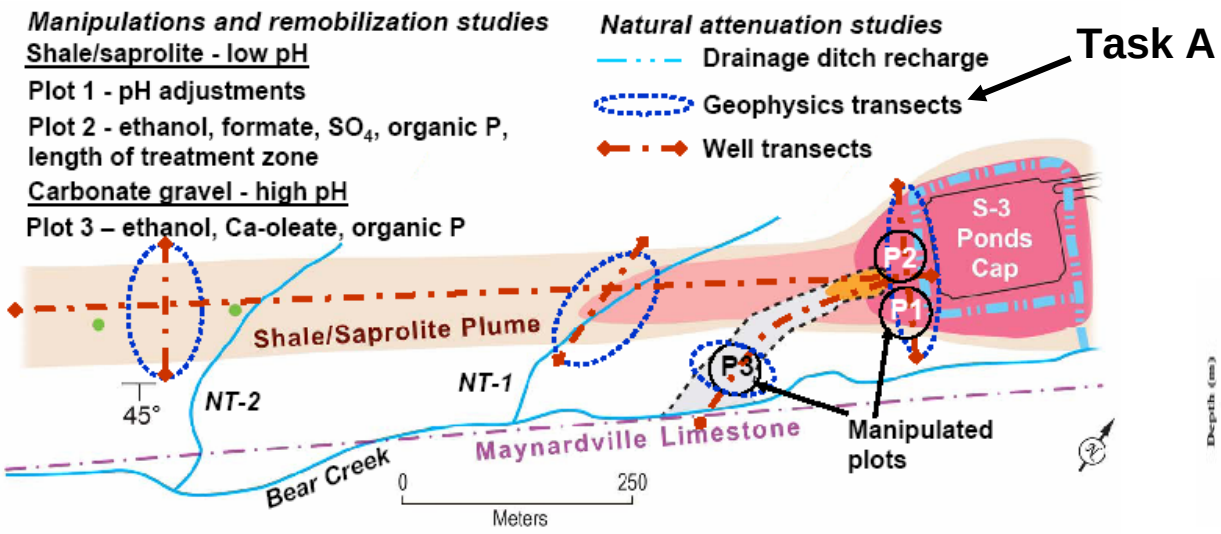
Link Geophysical Responses to Media

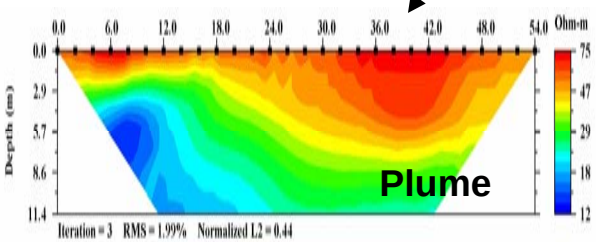
- Developing experimental apparatus that will permit development of geophysical-hydrogeochemical petrophysical relationships

Delineate Heterogeneity and Pathways

- Subsurface characterization using surface geophysics
- Start development of joint inversion framework for watershed characterization (using CPT and refraction datasets)

Location of research tasks at ORFRC





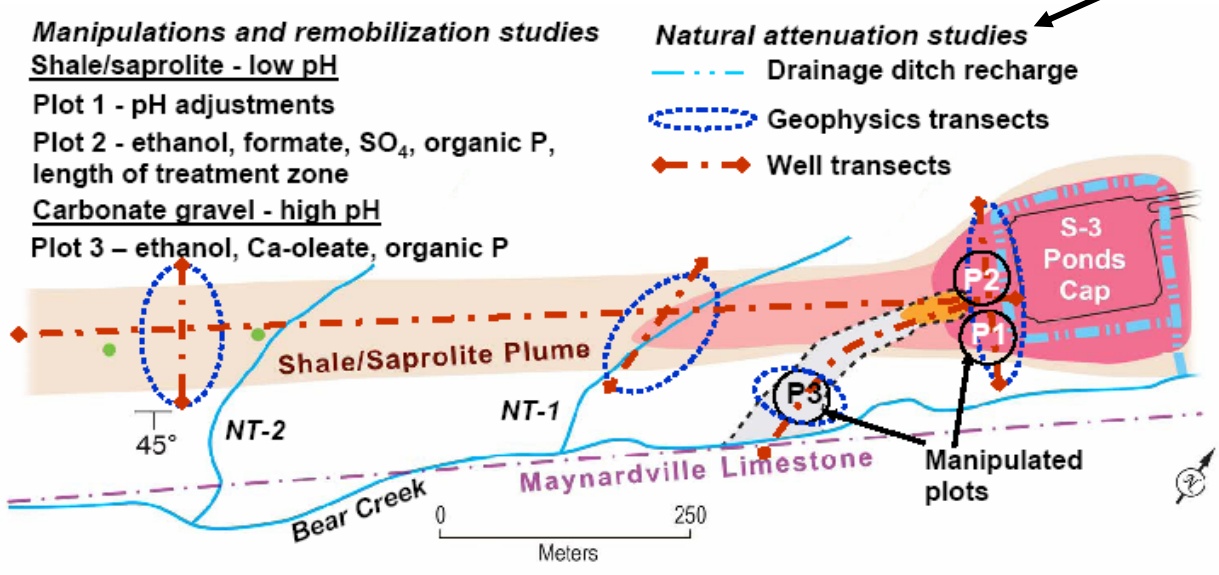
Approach

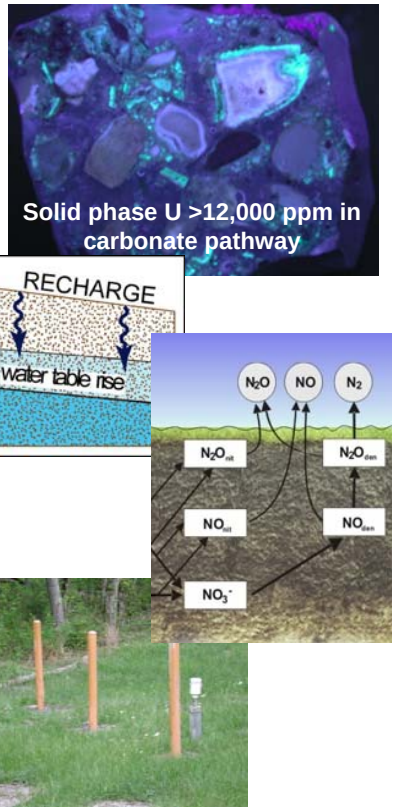
Task B: Define and quantify natural attenuation rates & mechanisms across the Bear Creek watershed

- **Impacts of coupled pH, redox conditions, microbial activity, reactivity, etc. on U, Tc, and nitrate natural attenuation (isotopes, spatial and temporal variability along pathways and transition zones).**
- **Impacts of recharge on geochemistry, contaminant dilution, O_2, carbon source, microbial activity, etc. on spatial and temporal plume dynamics.**

Location of research tasks at ORFRC

Task B



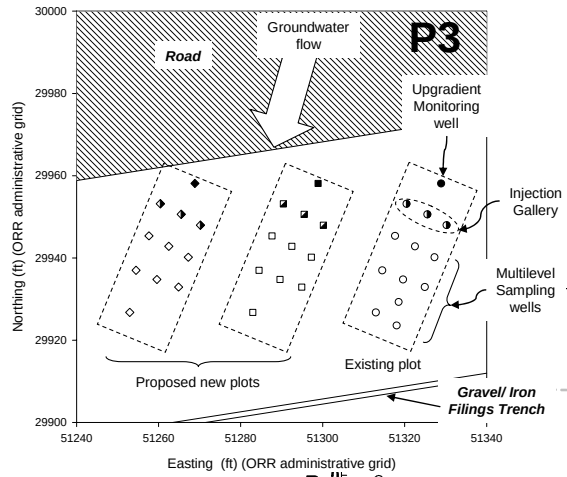


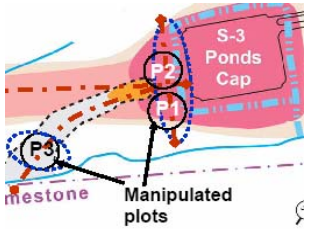
Approach

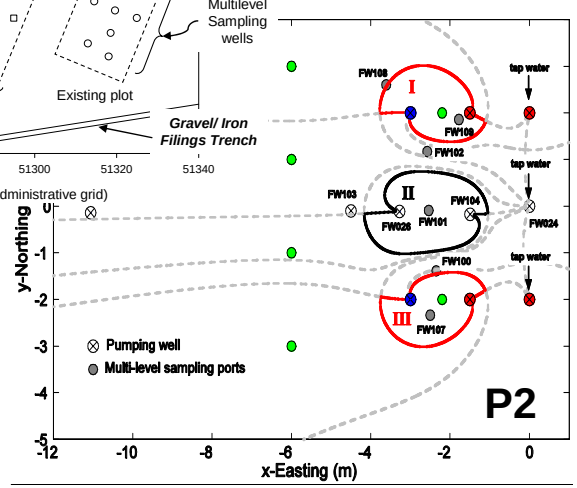
Task C: Quantitative *in situ* immobilization strategies within secondary sources of the saprolite and carbonate units (U, Tc, nitrate)

Targeted manipulation experiments: (1) sustained bioreduction, (2) pH adjustment, (3) organo-phosphate amendments, (4) slow release oleate amendments.

Monitor multi-scale hydrobiogeochemical and geophysical changes and propensity for contaminant remobilization.



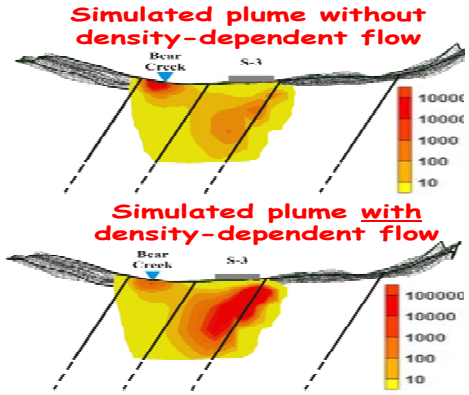




Task D: Multiprocess and multiscale numerical modeling and data analysis

Local plot scale modeling (Task C results) and Advanced Pattern Recognition techniques (Task B results).

Site wide modeling (HydroBioGeoChem) / upscaling and model accuracy (Tasks A-C results).



Task A - Results

Delineate Heterogeneity and Pathways

- Significant progress has been made on all four key geophysical and monitoring tasks which include (1) planning; (2) equipment fabrication and laboratory development; (3) geophysical characterization and error assessment at the field scale, and (4) the development of numerical approaches that are needed to integrate various datasets for quantitative characterization and monitoring purposes.
- Watershed scale datasets are being established which cross-correlate surface geophysical electrical resistivity and seismic refraction velocity measurements with observed groundwater geochemistry and depth to refusal at the ORIFC.
- Research is allowing us to track large scale spatial and temporal changes in contaminant plume dynamic as a function of long-term seasonal patterns and short-term storm events.

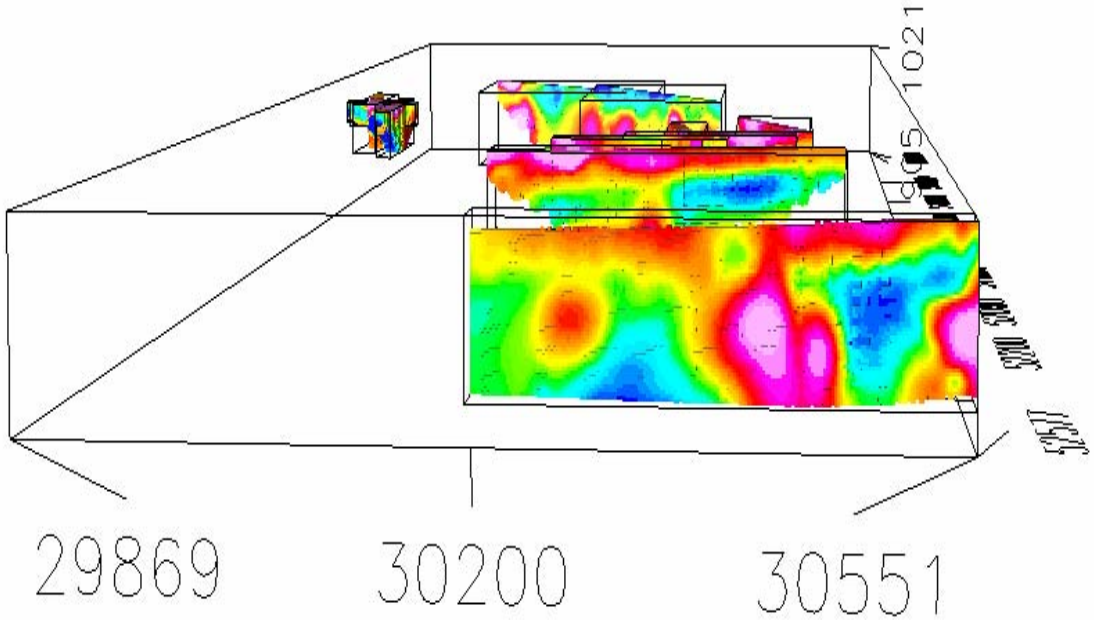
Results – Task A

DATA ACQUISITION

- Surface geophysical data to augment existing datasets:
  - Numerous coupled surface seismic refraction and electrical resistivity lines were performed at various source areas, along plume transects, and the distal ends of plumes
  - Significant data has been processed
- Geoprobe conductivity profiles, refusal, and water quality data cross-correlated with ERT and seismic lines.

DATABASE DEVELOPMENTS

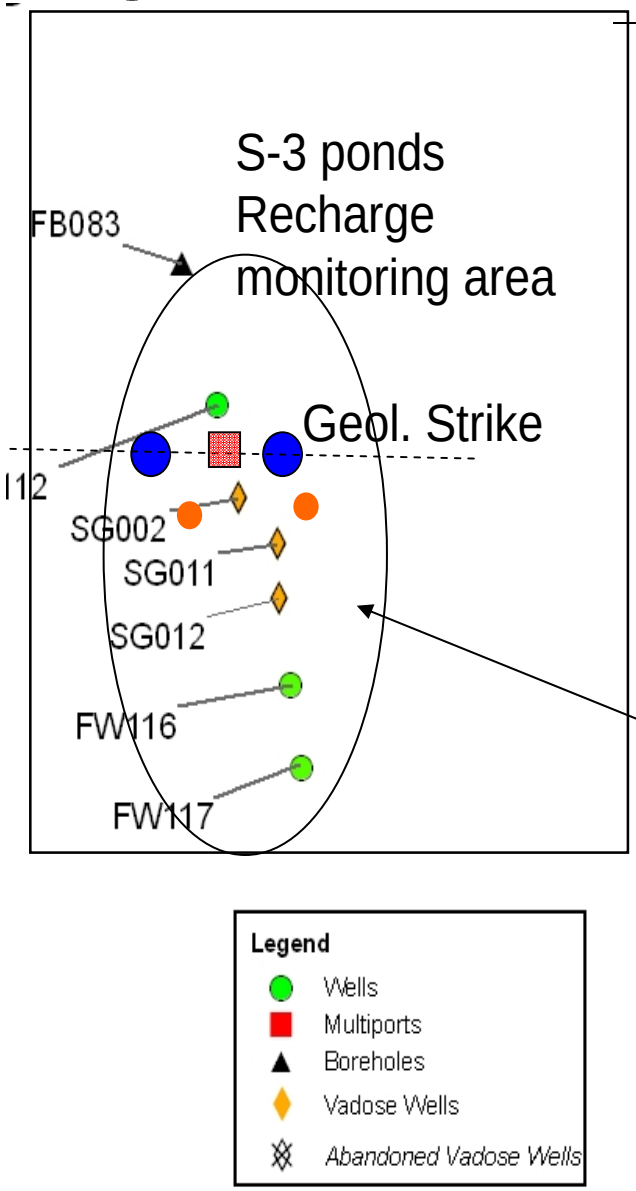
- Developed nomenclature guidelines for geophysical datasets;
- Visualization system developed for geophysical data using Oasis Montaj



OTHER

- Structural interpretation of Bethel Valley Quadrangle (thesis by P. Lemiszki) based on integration and visualization using large-scale structural maps

Results – Task A



Linking Geophysical Response to Media and Time-Lapse Geophysical Error Analysis

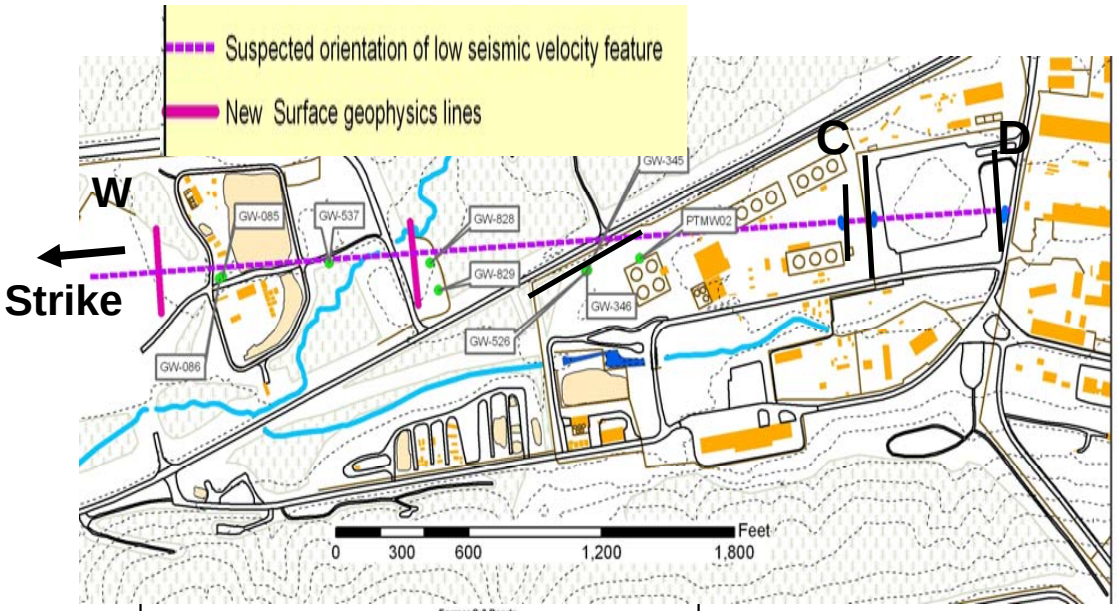
- **Define and constrain standard operating procedures through redundant time-lapse near-surface seismic surveys (error analysis)**
- **Collection of hydrogeochemical-geophysical-microbiological datasets, which will in turn be used to develop site-specific, field-scale petrophysical relationships.**
- **Coupled hydrological-geophysical modeling framework for integrating disparate datasets and for exploring the impact of recharge on TDS at the local scale**

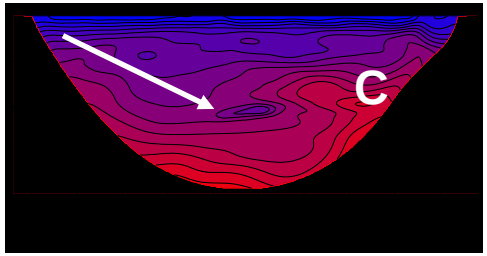
NUMERICAL APPROACH BEING DEVELOPED TO:

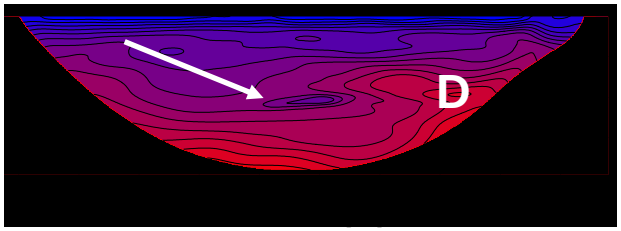
1. **Systematically incorporate hydrological, geophysical, geochemical datasets at S-3 local scale site using the TOUGH2 family of codes.**
2. **Synthetically explore the sensitivities of the ERT signatures to variations in lithology versus TDS;**
3. ***Investigate the temporal lag between high recharge events and subsurface TDS responses at S-3*;**
4. **Using dense datasets, gain insight at the local scale which can then be transferred to the site-wide modeling effort using sparser but more spatially extensive datasets (such as surface ERT data).**

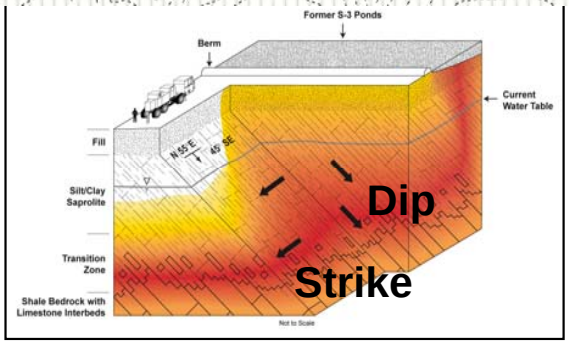
Results – Task A

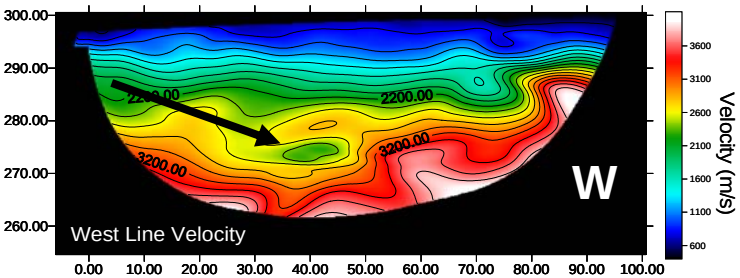
Origin of Low Velocity Anomaly: Seismic refraction profiles indicate an anomalous and laterally continuous north-dipping feature down the watershed providing confirmation of the utility of the geophysical technique to define lithologic features involved in contaminant transport.







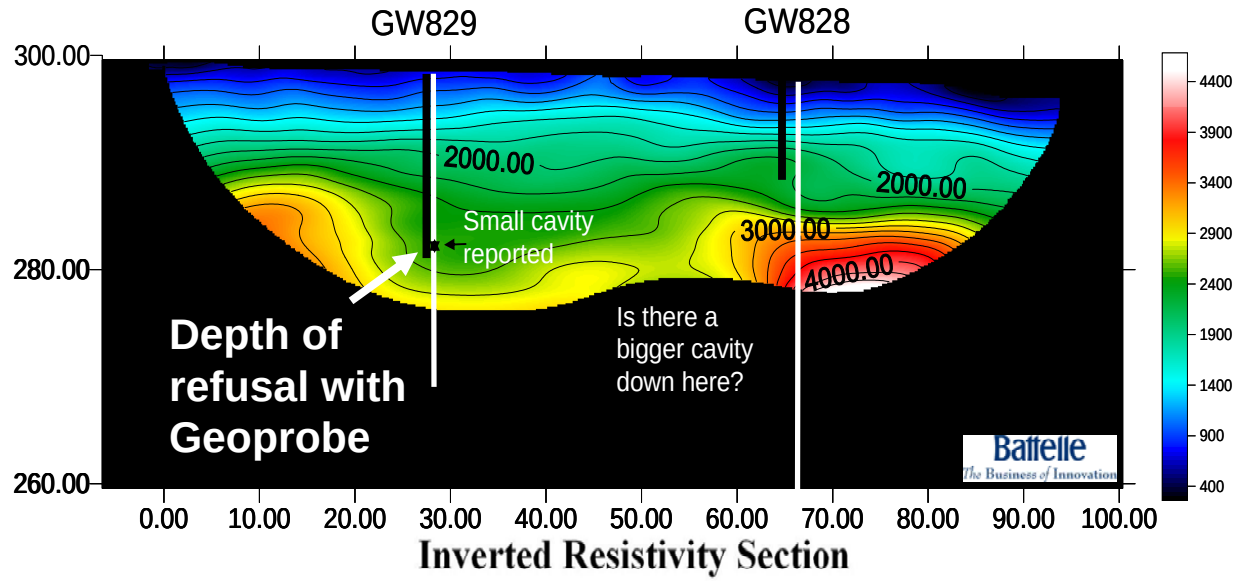


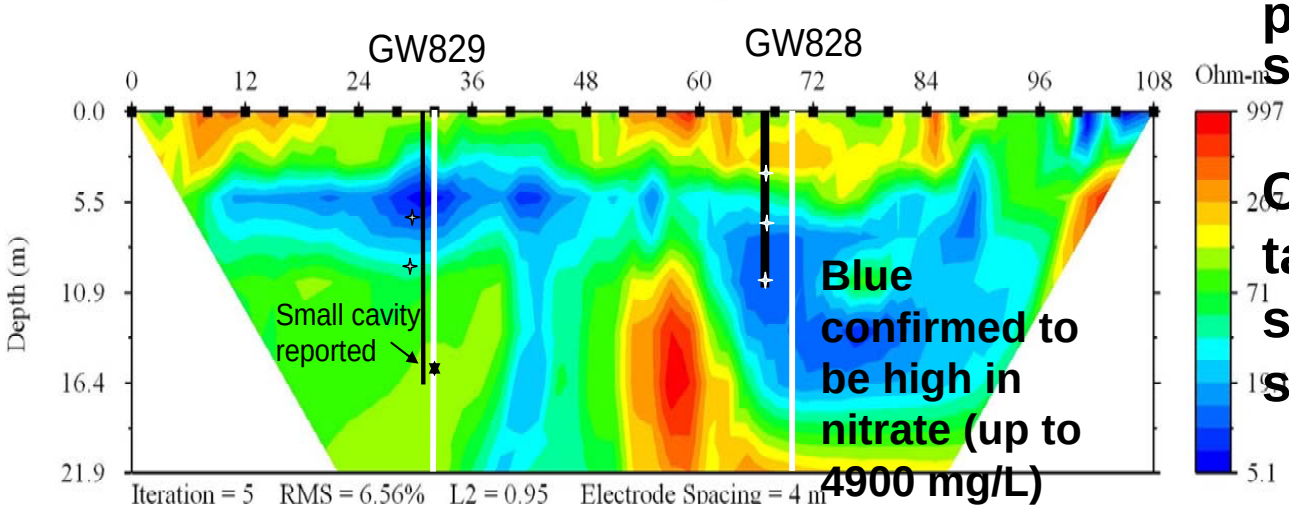


Surface seismic refraction data indicate the location of subsurface anomaly many Km down the valley – drilling is underway to further explore properties of anomaly

Results – Task A

Seismic and resistivity sections at NT-2 (far-field)





As was noted near the source (Watson et al., 2004), groundwater quality consistent with surface ERT geophysics findings.

Suggests wide range utility of ERT for quantifying contaminant plumes at the watershed scale

Confirmed to be good targets for geophysics studies that collect time series data of recharge

Future Research – Task A

- Continue to delineate watershed-scale subsurface heterogeneities and contaminant pathways

- Continue investigations on coupled hydrological-geophysical modeling for integrating disparate datasets and for exploring the impact of recharge on TDS at the local scale

- Investigate the temporal lag between recharge events and subsurface TDS responses with particular emphasis on periods immediately preceding and following both major and minor climate events that indicate both the rate and effect of climate-driven subsurface recharge.

Task B - Results

Define and quantify natural attenuation rates & mechanisms across the Bear Creek watershed

- Watershed scale databases that couple contaminant concentration, pH, redox conditions, microbial activity, reactivity, etc. on U, Tc, and nitrate natural attenuation (geophysics, isotopes, spatial and temporal variability along pathways and transition zones).

- Impacts of recharge on geochemistry, contaminant dilution, O_2, carbon source, microbial activity, etc. on spatial and temporal plume dynamics.

- Coupled hydrobiogeochemical measurements with real-time geophysics for quantifying large scale spatial and temporal changes in contaminant plume dynamics as a function of long-term seasonal patterns and short-term storm events.

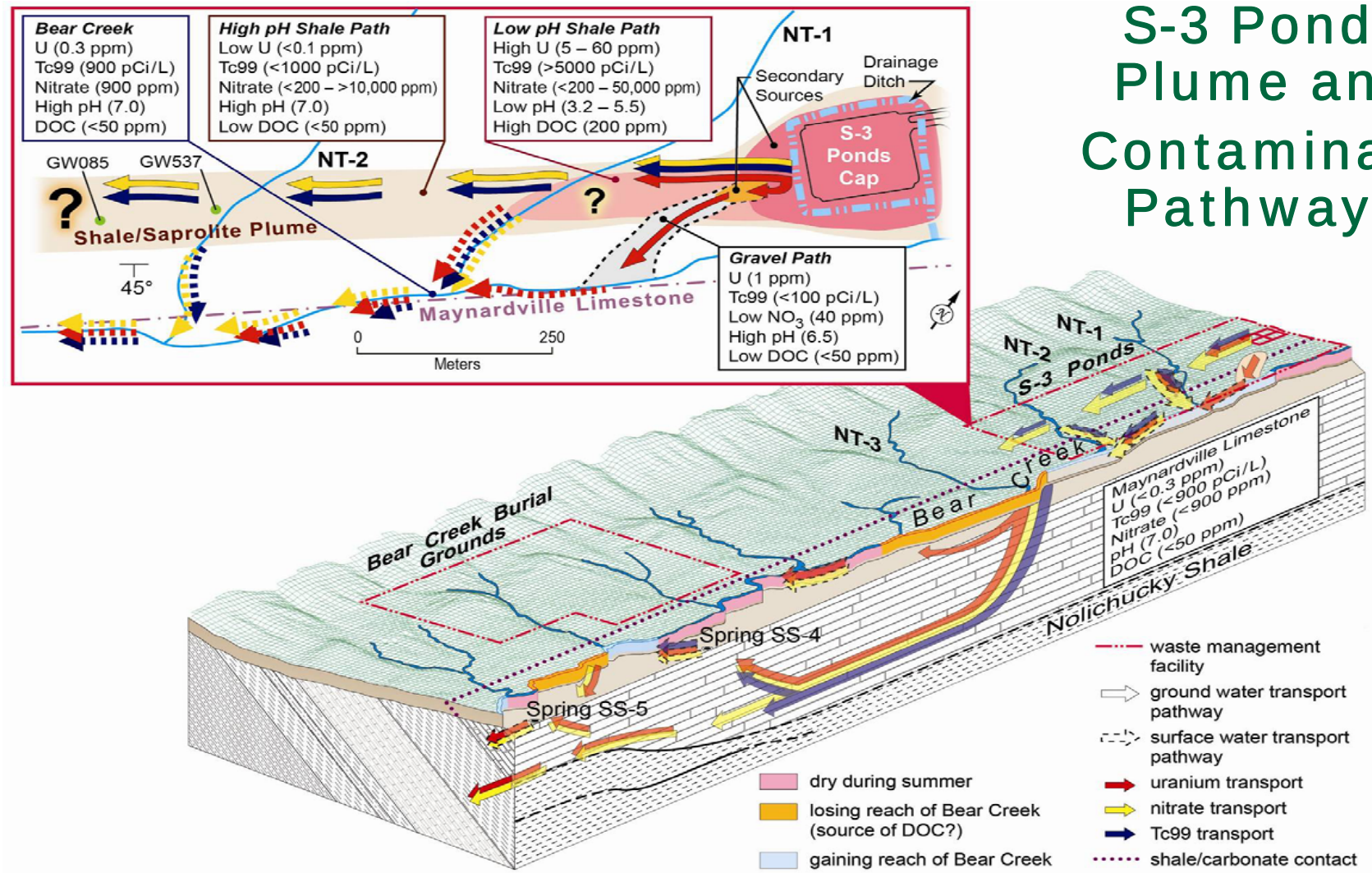
- Development and implementation of novel measurement strategies to quantify contaminant natural attenuation rates and mechanisms.

Results – Task B

Watershed contaminant, geochemical, microbial profiles

Define and quantify natural attenuation rates & mechanisms across the Bear Creek watershed

S-3 Ponds Plume and Contaminant Pathways

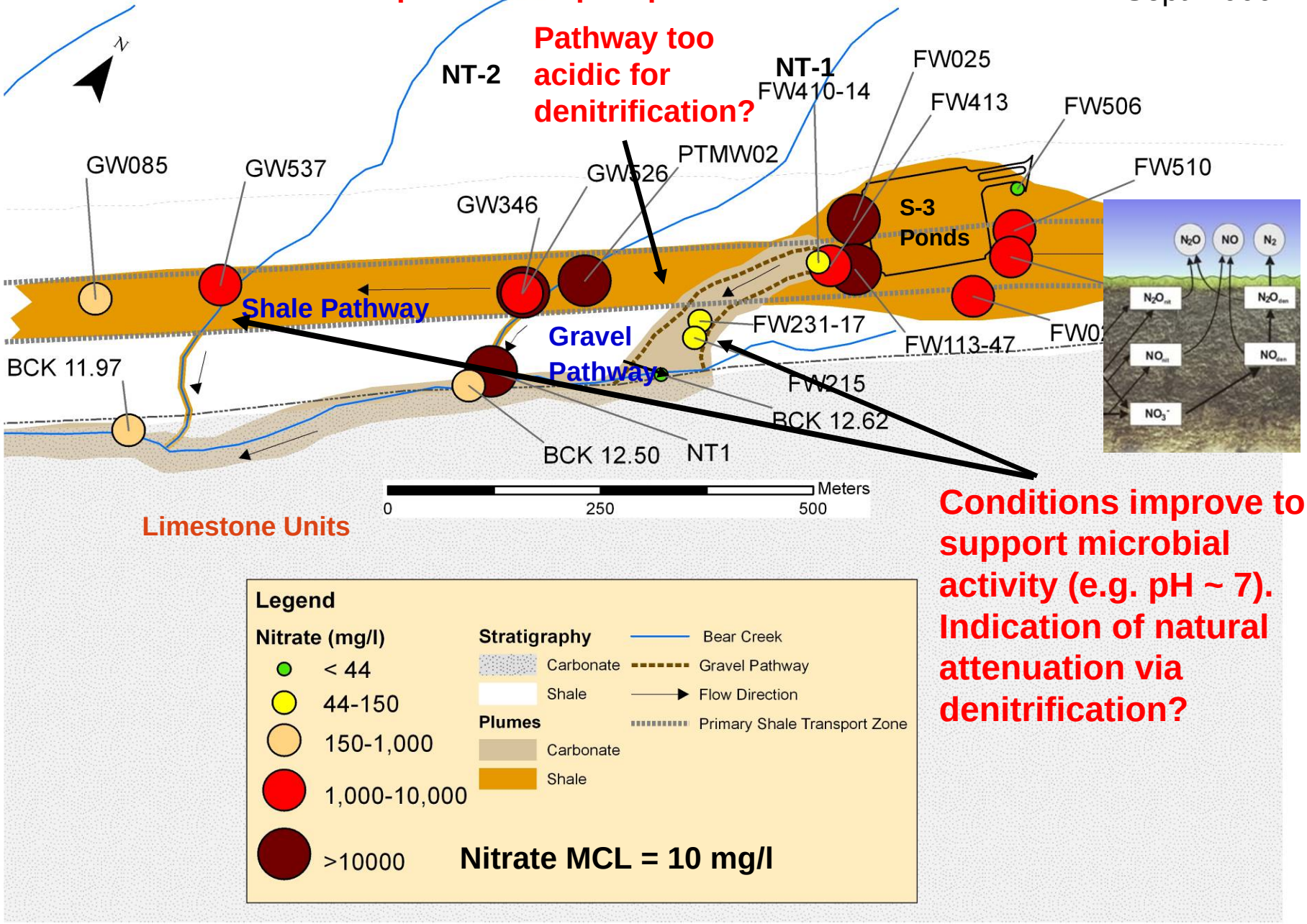


Task B

Nitrate Concentration Down the Valley

Isotopes and coupled processes to the rescue

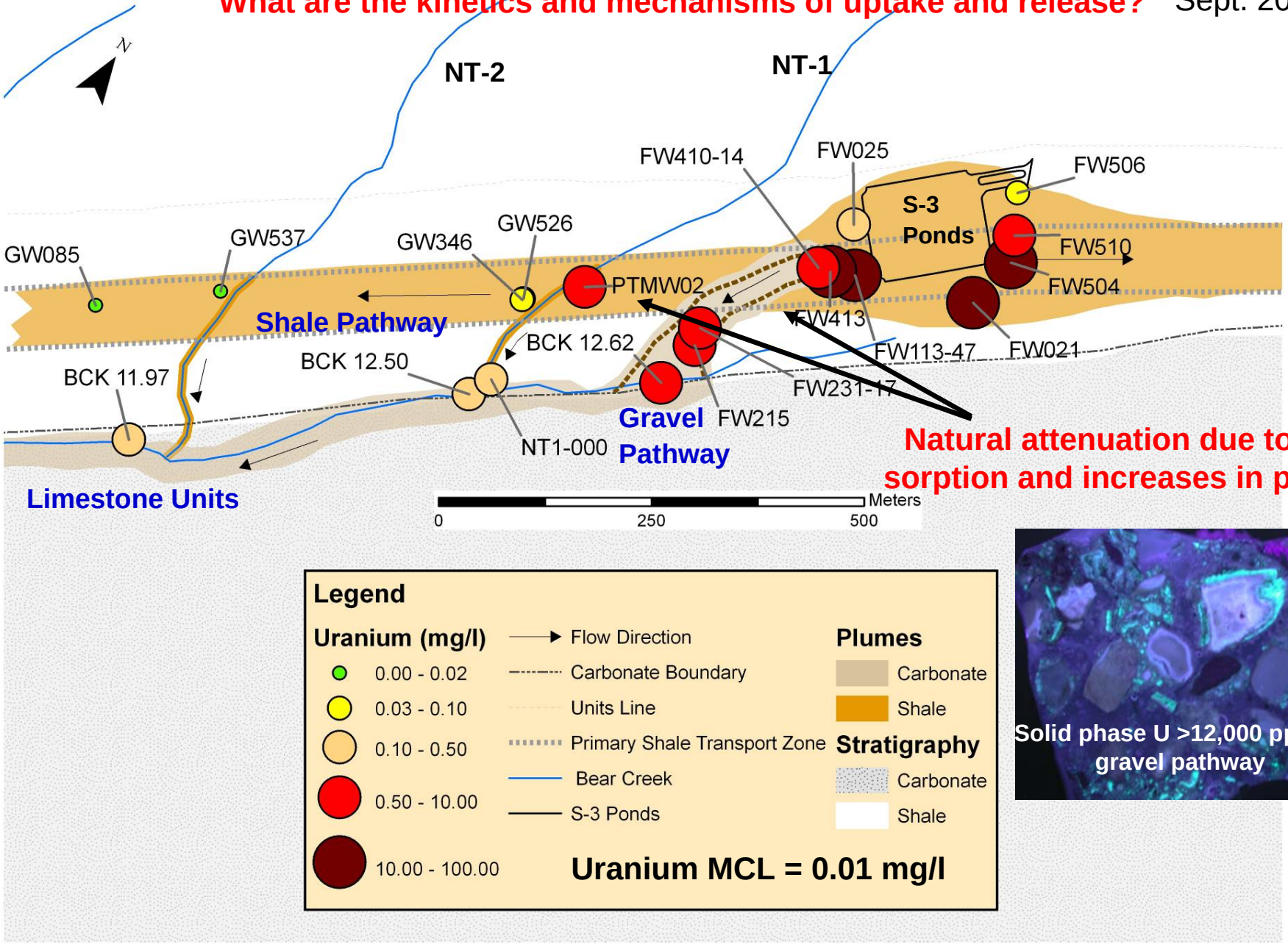
Sept. 2006

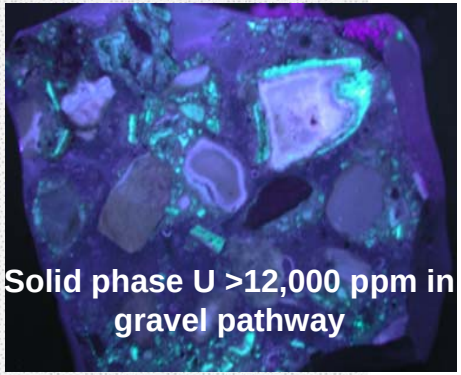


Conditions improve to support microbial activity (e.g. pH ~ 7). Indication of natural attenuation via denitrification?

Task B Uranium Concentration Down the Valley

What are the kinetics and mechanisms of uptake and release? Sept. 2006



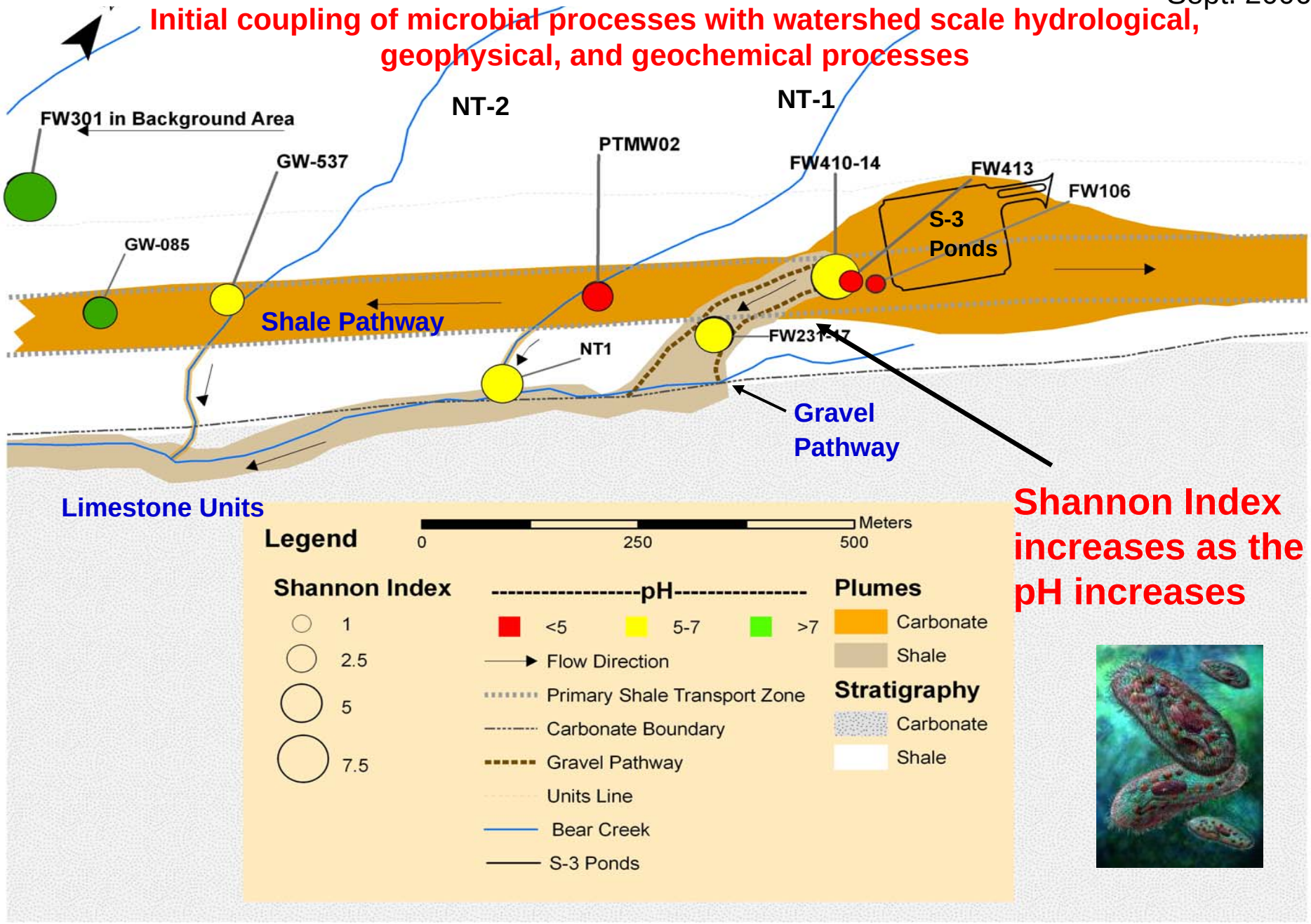


Task B

Shannon Index vs pH Down the Valley

Sept. 2006

Initial coupling of microbial processes with watershed scale hydrological, geophysical, and geochemical processes



Shannon Index increases as the pH increases

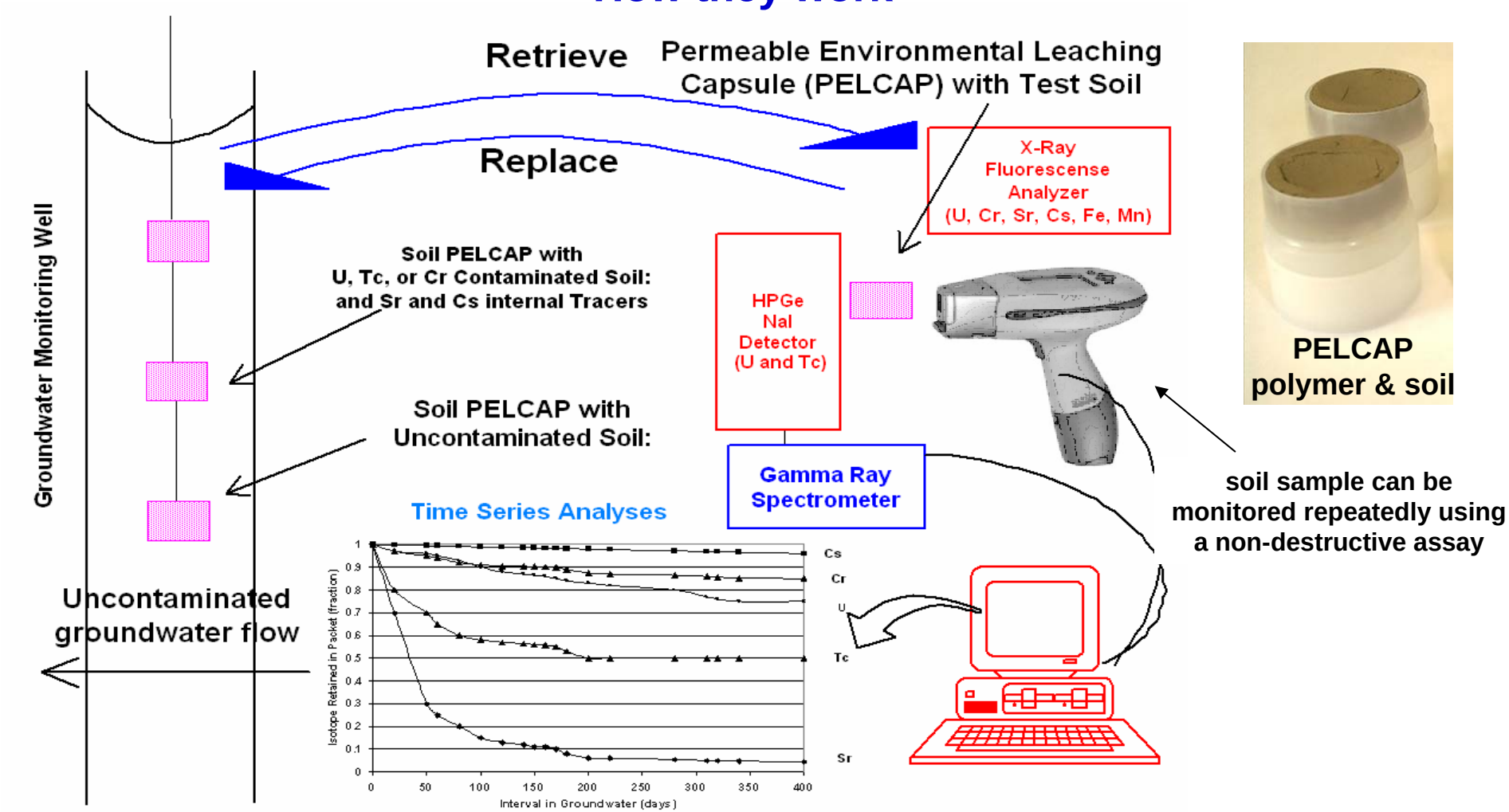
Results – Task B

Implementing novel measurement strategies

Quantifying *In situ* Reactive Contaminant Behavior Across the Watershed

Permeable Environmental Leaching Capsules (PELCAPs)

How they work



Results – Task B

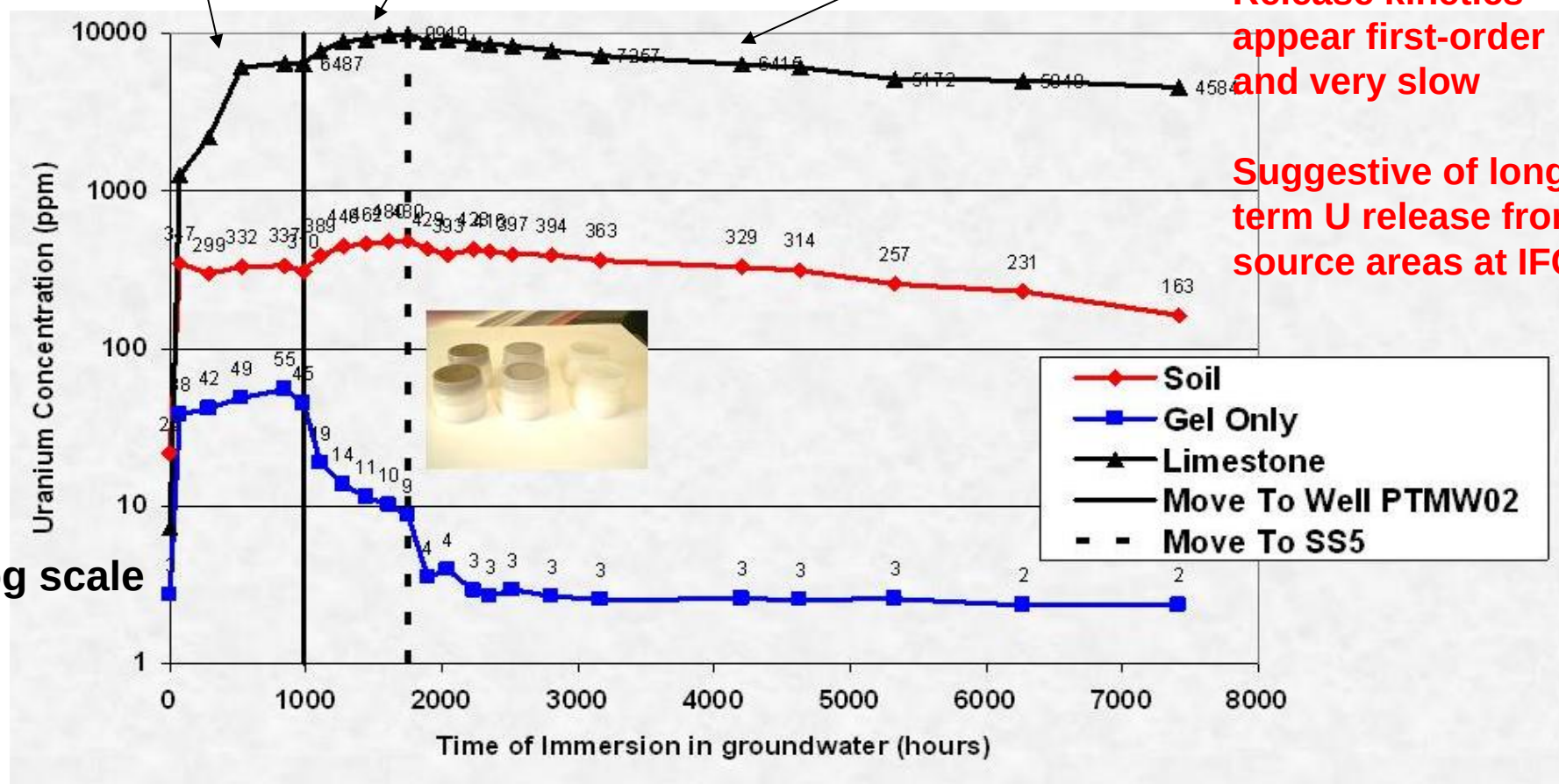
Implementing novel measurement strategies

In situ **uptake and release of U in IFC groundwater using the PELCAP methodology. Polymer-encapsulated soils behave very similarly to un-encapsulated soils with respect to U other inorganic ion interactions.**

Rapid uptake in highly contaminated GW

Slow uptake/release in slightly contaminated GW

Release in uncontaminated GW



Release kinetics appear first-order and very slow

Suggestive of long-term U release from source areas at IFC

Log scale

Results – Task B

Implementing novel measurement strategies

Quantifying Isotopic Signatures of Aqueous and Dissolved Gas Species to Assess Contaminant Behavior Across the Watershed

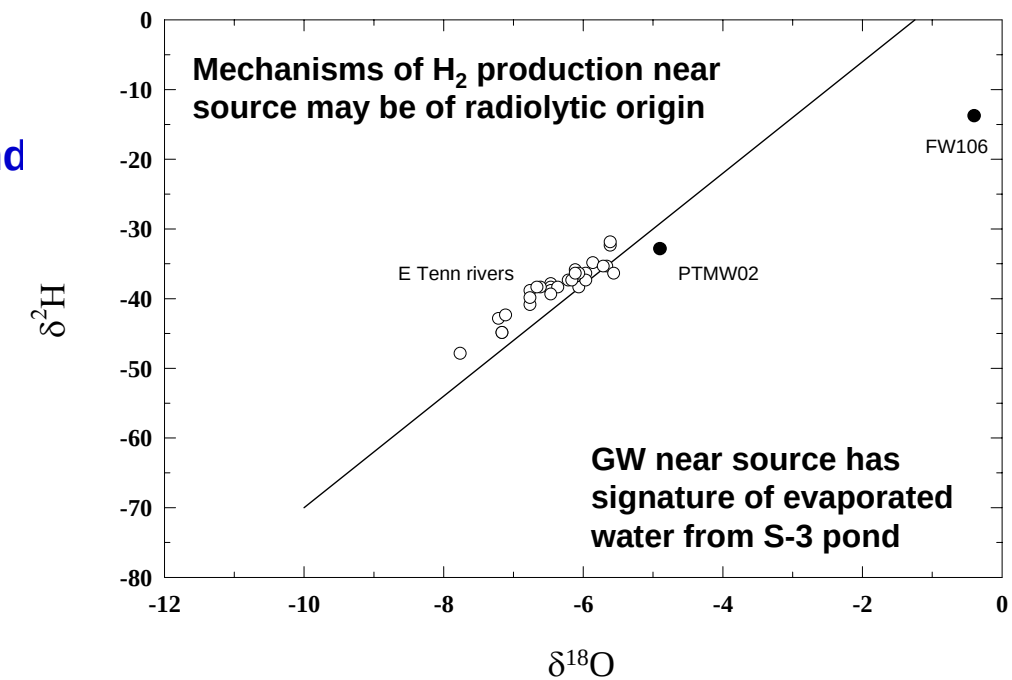
Quantify suite of stable isotope ratios in different solute and gaseous species (e.g., $^{15}N/^{14}N$ in nitrate, N_2O, and N_2; $^{18}O/^{16}O$ in nitrate; $^{2}H/^{1}H$ in dissolved H_2 gas; and $^{13}C/^{12}C$ in acetate, citrate, natural DOC, CO_2, and CH_4) within contaminant plumes of multiple scale.

Target drastically different groundwater geochemistry to provide quantitative information on the *in situ* rates and mechanisms of nitrate natural attenuation and source identification in heterogeneous field-scale environments.

Last weeks watershed-wide field sampling campaign on >20 GW wells and numerous surface waters

- **Geochemistry**
- **Isotopes N,O,C,H**
- **N_2/Ar as bioindicator of denitrification**
- **Microbial characterization PCR**
- **Hg (related to new SFA)**

(results forthcoming)



Results – Task B

Implementing novel measurement strategies

Quantifying Dissolved Gas Species to Assess Contaminant Behavior Across the Watershed

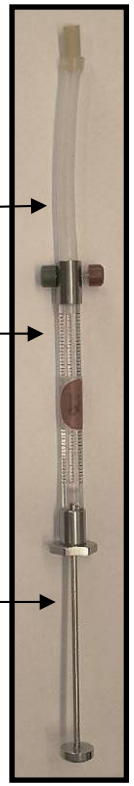
Technique involves passive gas diffusion into gas tight syringe sampler

This integrated fixed gas sampling and analysis protocol is unique and should greatly facilitate monitoring of fixed gases as indicators of microbial and chemical processes

Gases diffusion into permeable silica from GW (4 d equil.)

Gas tight syringe upon retrieval

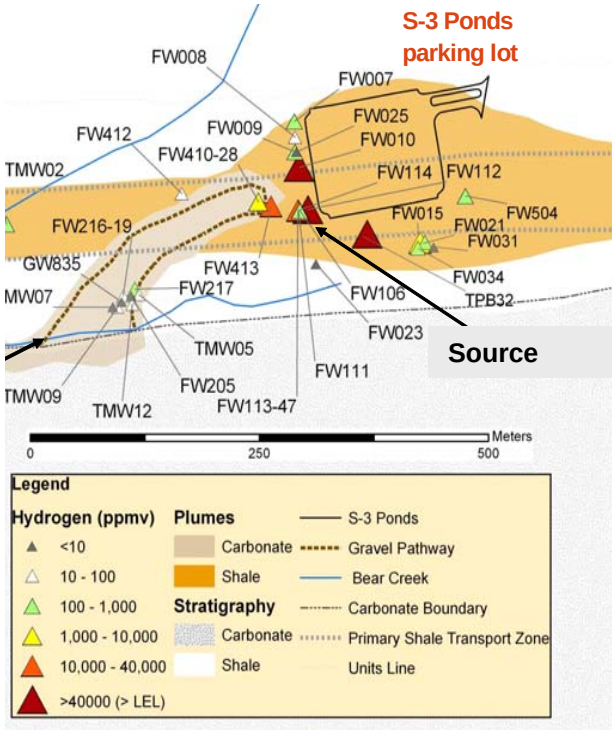
Direct injection into GC



Over a thousand passively-collected samples at the ORIFC indicate an unusual average composition: 56% CO_2, 32.4% N_2, 2.6% O_2, 2.6% N_2O, 0.21% CH_4, 0.093% H_2, and 0.025% CO.

ORNL continues to assist PNNL at the Rifle IFC site with dissolved gas analysis before and during *in situ* biostimulation tests.

Distribution of H_2 at the ORIFC



Results – Task B

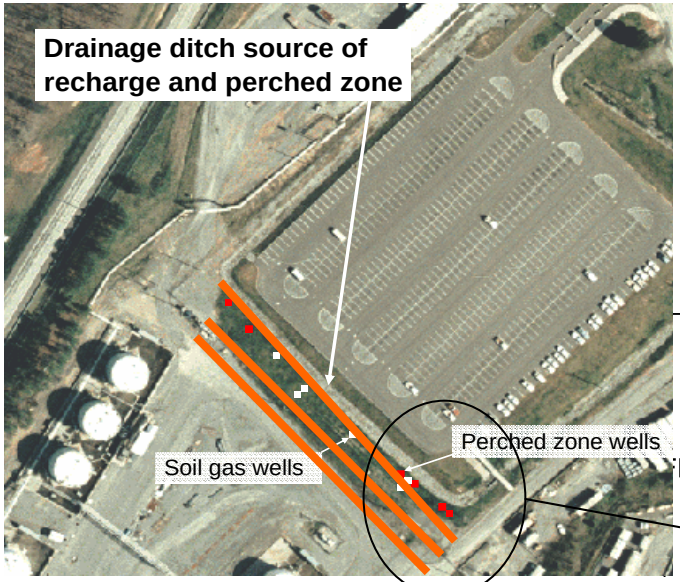
Implementing novel measurement strategies

Microbial Processes at the Watershed Scale

- **Optimized and standardized common methods for groundwater and sediment sample collection, processing and nucleic acids extraction across labs on the team.**
- **Development and standardization of common methods for QPCR across the team that allow for quantitative estimates of population numbers for important metal reducing FRC taxa (*Geobacter, Anaeromyxobacter* & others) and functional genes involved in processes of interest (dsrA, gltA and nirK/S).**
- **Development and testing of tRFLP methods for rapid screening of overall community diversity and activity.**
- **Experimental design and sampling of material for comparison of groundwater vs. sediment (planktonic vs. attached) populations.**

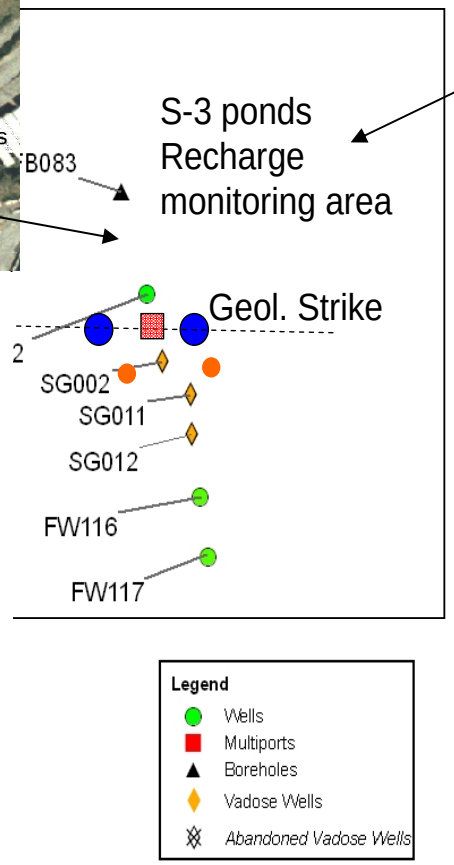
Results – Task B

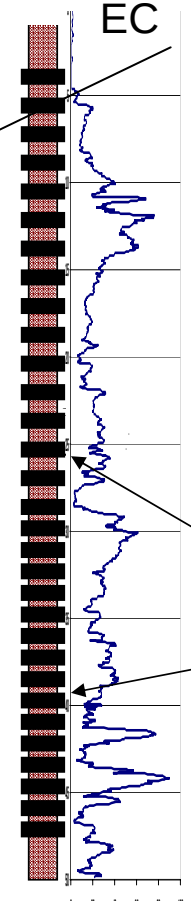
Quantifying temporal and spatial recharge impact



Monitoring Natural Recharge

Coupling of traditional hydro-geo-micro measurements with novel real-time geophysics





TD ~52' BGS

1.1-10.1m (3.6-33.13'):15 Electrodes @0.6m spacing

10.4-14.9m (34,12-48.88') 15 Electrodes @0.3m spacing

Monitoring perched water table dynamics and interaction with GW as a function of storm events (next page) coupled with real time geophysics

Use of temperature profiles to quantify recharge

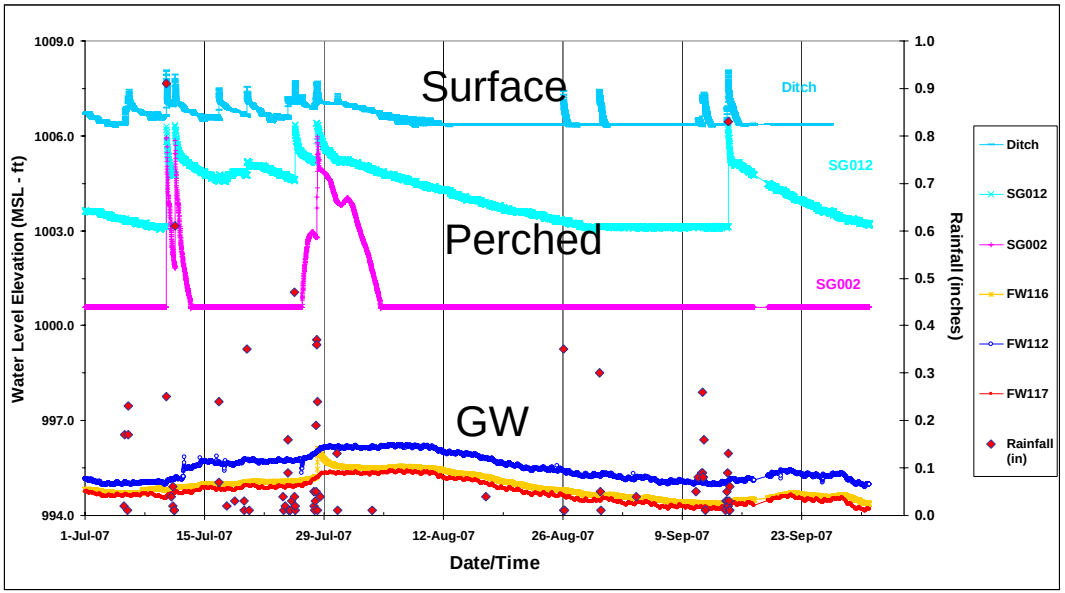
Long-term temporal / spatial resolution of recharge impact on contaminant plumes

Future Research – Task B

- Continue to collect watershed scale databases that couple contaminant concentration, pH, redox conditions, microbial activity, reactivity, etc. on U, Tc, and nitrate natural attenuation (geophysics, isotopes, spatial and temporal variability along pathways and transition zones). Link with smaller scale observations and couple with site-wide multiprocess, multicomponent numerical model.

- Continue to quantify the impact of recharge on geochemistry, contaminant dilution, O_2, carbon source, microbial activity, etc. on spatial and temporal plume dynamics.

- Coupled hydrobiogeochemical measurements with real-time geophysics for quantifying large scale spatial and temporal changes in contaminant plume dynamics as a function of long-term seasonal patterns and short-term storm events.



Task C - Results

Quantitative *in situ* immobilization strategies within secondary sources of the saprolite and carbonate units (U, Tc, nitrate)

- **Two highly successful sets of field scale experiments were conducted in Area 3 that investigated the stability of a subsurface bioreduced zone and impact of nitrate intrusion on U solution and solid phase reoxidation and mobilization. These experiments involved well coordinated efforts between hydrology, geochemistry, and microbiology.**

- **Batch and column scale pH manipulation experiments have been completed that involve a well coordinated effort between geochemists, microbiologists, geophysicists, and numerical modelers. The column flow experiments are currently being scaled-up in order to determine optimal parameters (e.g. pore water velocities, reactant concentrations, and mass transfer rates) for field scale manipulation experiments. Extensive coordination between geochemistry, geophysics, microbiology, and numerical modeling has become routine during the design and implementation of the experiments.**

- **Research has been initiated on the use of Ca-oleate as a slow release electron donor source for subsurface microbial stimulation and bioreduction of U(VI).**

Results – Task C

Stability of Bioreduced U

Stability of bioreduced U in the presence of intruding groundwater oxidants

Demonstration of long-term stability of U in reduced zone

Test time: January to May, 2007

Approaches: Investigations on the ability to maintain low concentrations of U in GW

Test 1: Tracer test of the reduced zone and invasion of outside nitrate laden contaminated ground water

Test time: March 12, 2007 (day 1297)

Approaches: Injection of Br into outerloop injection well FW024, followed by removal of hydraulic protection of the treatment zone and monitoring invasion of nitrate from GW

Test 2: Reoxidation of reduced zone by injection of nitrate*.

Test time: June 21, 2007 (day 1398)

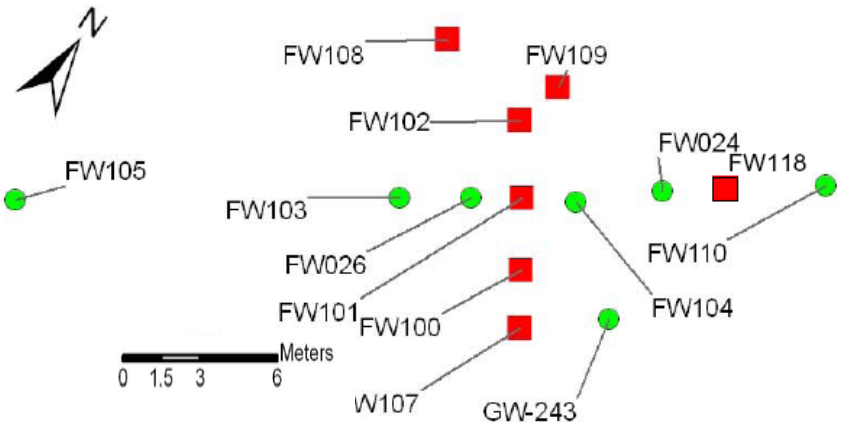
Approaches: Injection of nitrate and Br into innerloop injection well FW104, monitoring the Br and nitrate in MLS, followed by injection of ethanol into FW104 to investigate bioreactions by denitrifiers, sulfate reducers and Fe(III) reducers

***Dissolved oxygen injection previously conducted in 2006 (Wu et al., 2007).**

Results – Task C

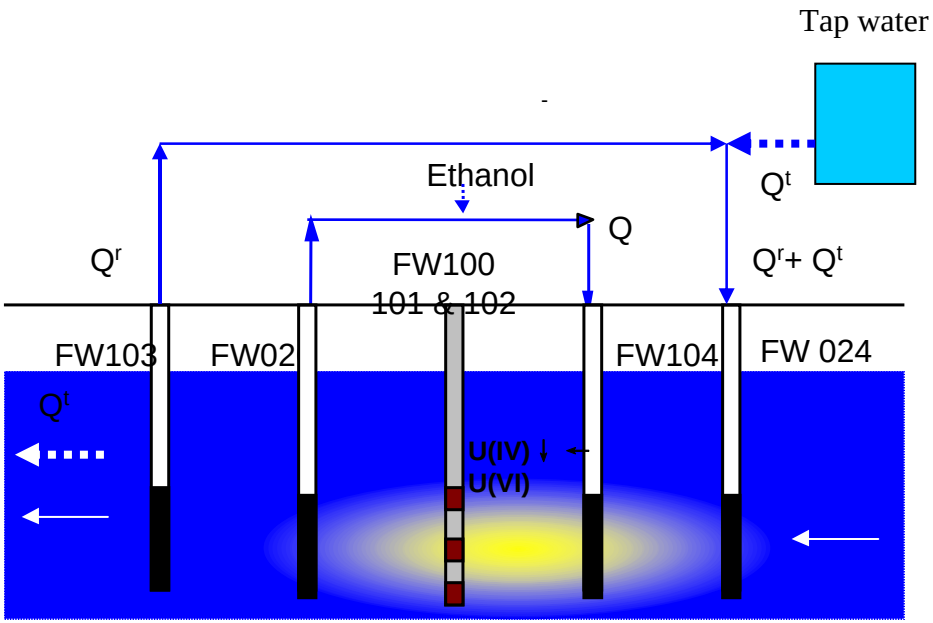
Stability of Bioreduced U

Field Experimental Set-up



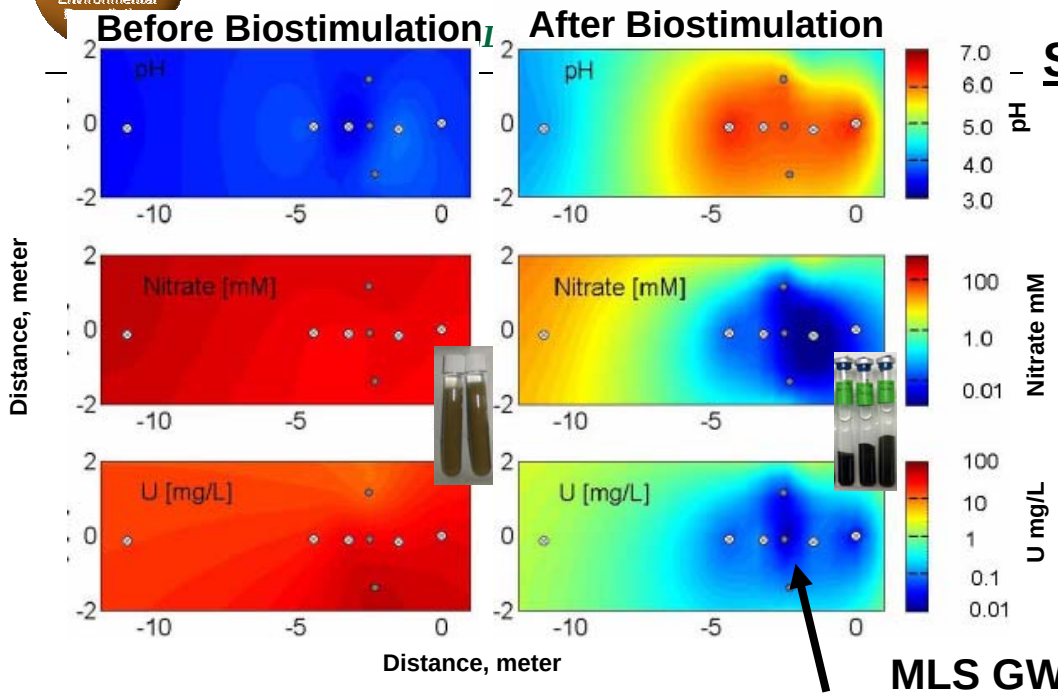
Well system map of Area 3 treatment zone

FW024: outerloop injection
FW104: innerloop injection
FW026: innerloop extraction
FW103: outerloop extraction



During biostimulation, clean water is injected to outer loop injection well FW024 to protect inner loop from invasion of outside contaminated groundwater that has high concentrations of nitrate, U, etc.

Results – Task C



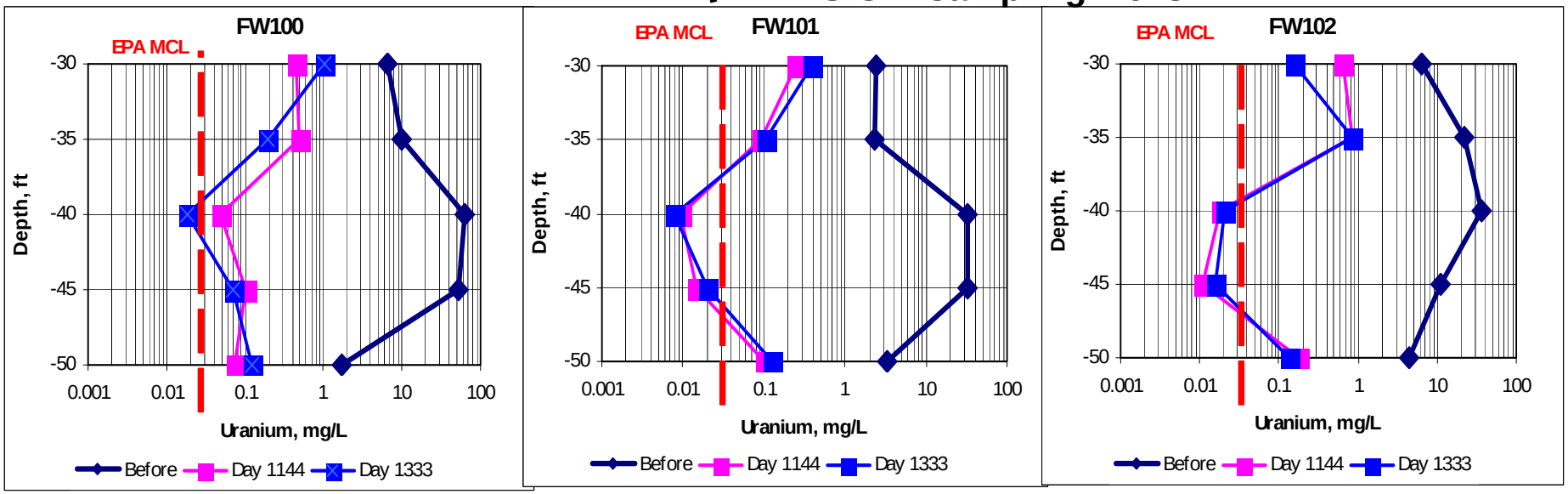
Sustained bioreduction of U *in situ*

Uranium concentrations in MLS wells FW100, FW101 and FW102 have been changed significantly during more than three year biotreatment

In fast flow zone, uranium concentrations below US EPA MCL (30 µg/L) were achieved

Many lines of evidence indicate U(IV) formation on the solid phase

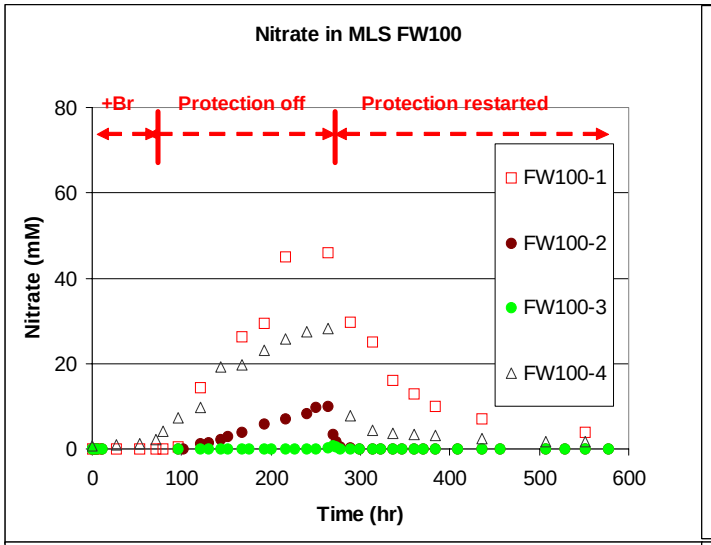
MLS GW sampling wells

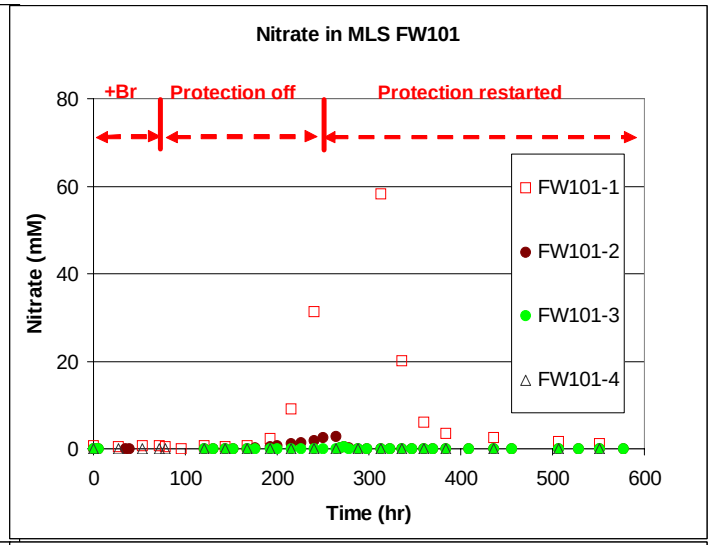


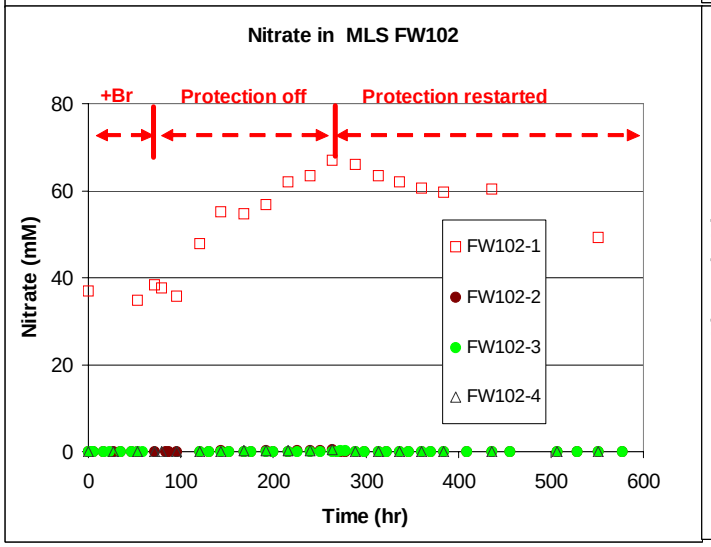
Results – Task C

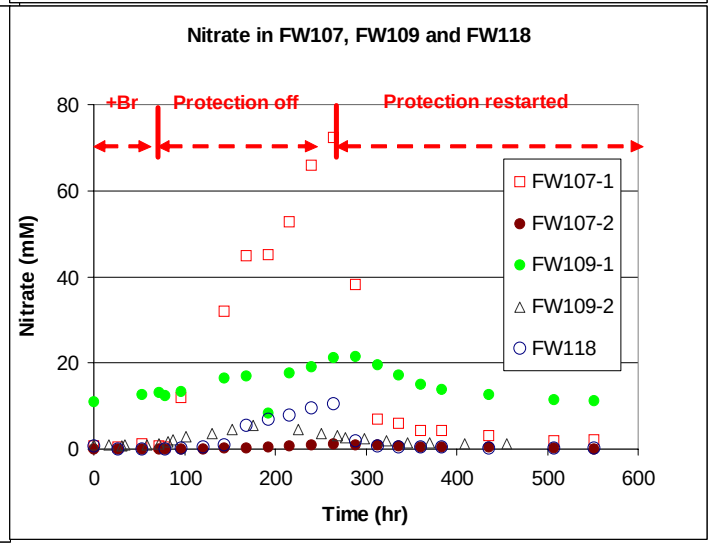
Stability of Bioreduced U

Test 1 : Passive Nitrate Intrusion into Bioreduced Zone









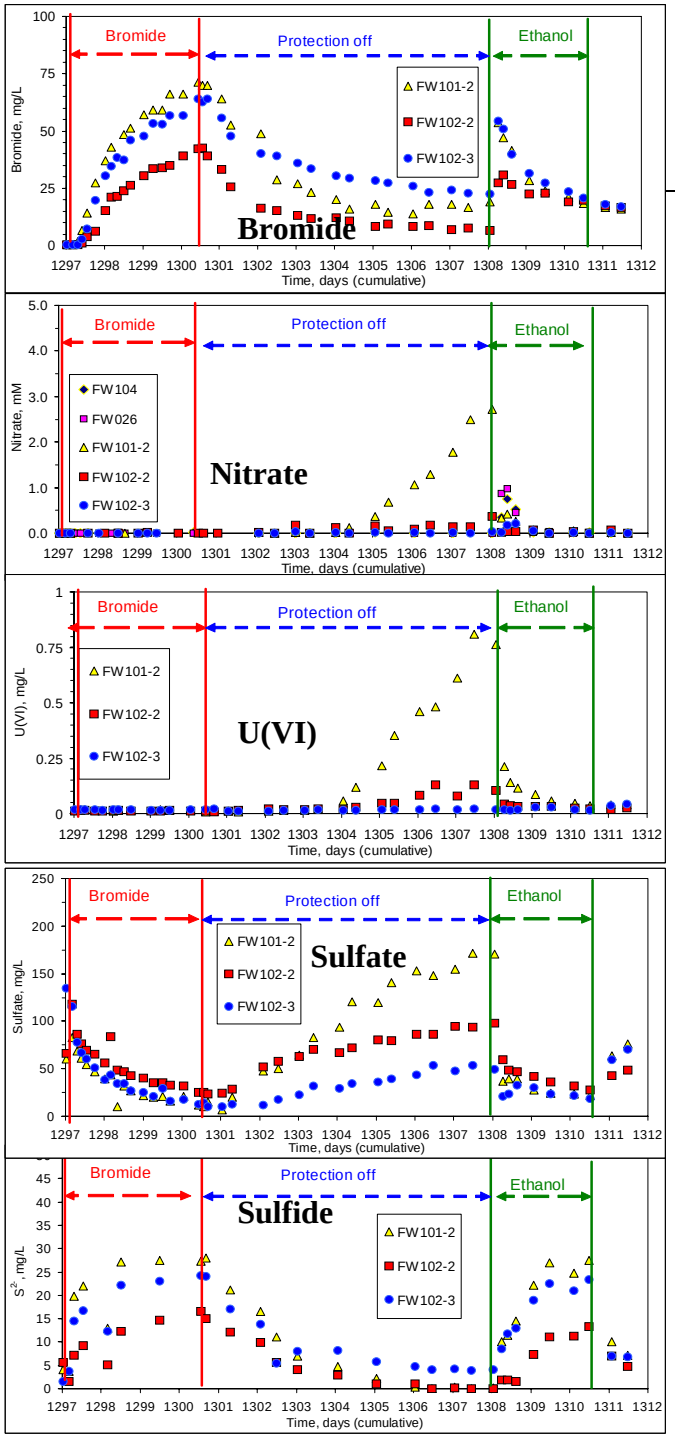
When outer loop recirculation is terminated and thus protection of inner loop (experimental area) nitrate contaminated groundwater invaded the treatment zone

The results suggested that 1) most nitrate come from the bottom well (50 ft); 2) nitrate invaded from all surrounding area; 3) more nitrate invaded from south side (FW100 and FW107); and 4) FW102 at north side was less impacted by invasion of nitrate.

These results indicated that hydraulic control of flow field may be essential during small scale tests near the source.

Results – Task C

Stability of Bioreduced U



Geochemical Response of Inner-loop Experimental Area During Passive Nitrate Intrusion

Bromide initially injected to outerloop and ethanol injected into inner experimental loop. Nitrate was not detected and U concentrations remain low. Sulfate concentration decrease and sulfide concentrations increase indicating reduced conditions.

Outerloop hydraulic protection (containing Br) is than terminated. Br and nitrate concentrations decreased and increase, respectively, due to invasion of natural groundwater. U concentrations increase most likely due to oxidation of U(IV) to U(VI) by nitrate. Sulfate concentration increase and sulfide concentration decrease as zone becomes less reducing.

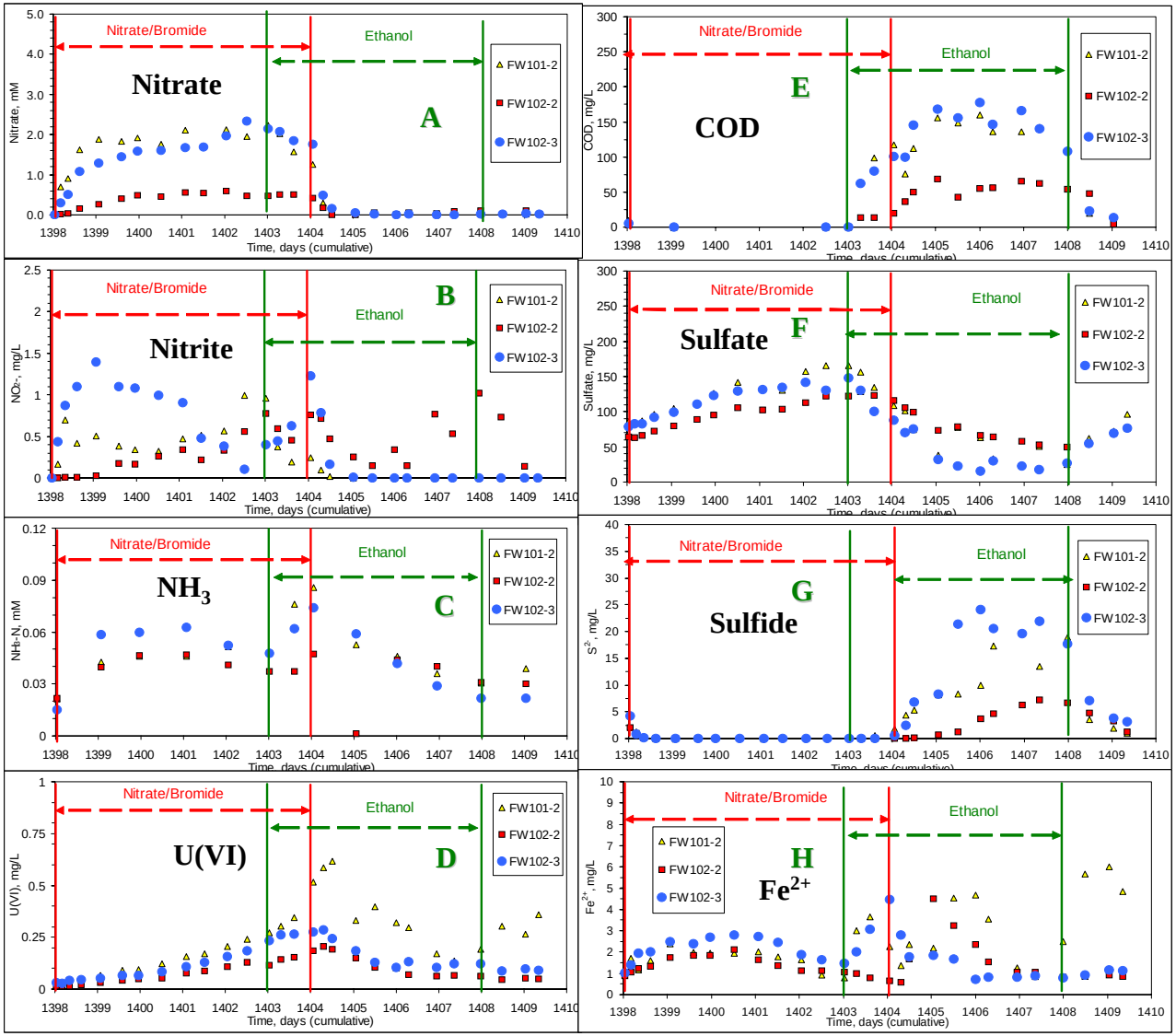
Outer loop protection than resumed and inner loop experimental ethanol re-injected to stimulate microbial activity. Nitrate reduction begins and U(VI) is reduced. As well, sulfate is reduced and sulfide accumulates.

Ethanol is than terminated and U concentrations remain low, sulfate concentrations rebound, and sulfide concentrations decrease.

Results – Task C

Stability of Bioreduced U

Test 2: Geochemical Response of Bioreduced Zone to Nitrate Injection



Nitrate oxidizes and remobilizes Bioreduced U

During nitrate injection, the metabolic products nitrite and NH_3-N increased (B and C). U(VI) concentrations increased during and after nitrate was injected (D)

When ethanol injection was resumed with continued added nitrate, COD increased (E) and nitrate decreased (A). Nitrite decreased and NH_3-N increased during this period. Sulfate concentrations also decreased (F) and sulfide concentrations remained low (G); however, Fe(II) increased (H) and U(VI) concentrations continued to increased (D)

When nitrate injection was terminated and ethanol continued, nitrate disappeared (A) and nitrite and NH_3-N decreased (B). U(VI) eventually decreased when nitrate was consumed (D). Sulfate reduction became significant (F,G) and Fe(II) decreased in MLS (H).

Microbial / XAS pending

Results – Task C

Immobilization of U through pH manipulation

Subsurface pH Manipulations for Long-Term U Immobilization

Goal: Provide long-term immobilization and stabilization of contaminant U and Tc through subsurface pH manipulation

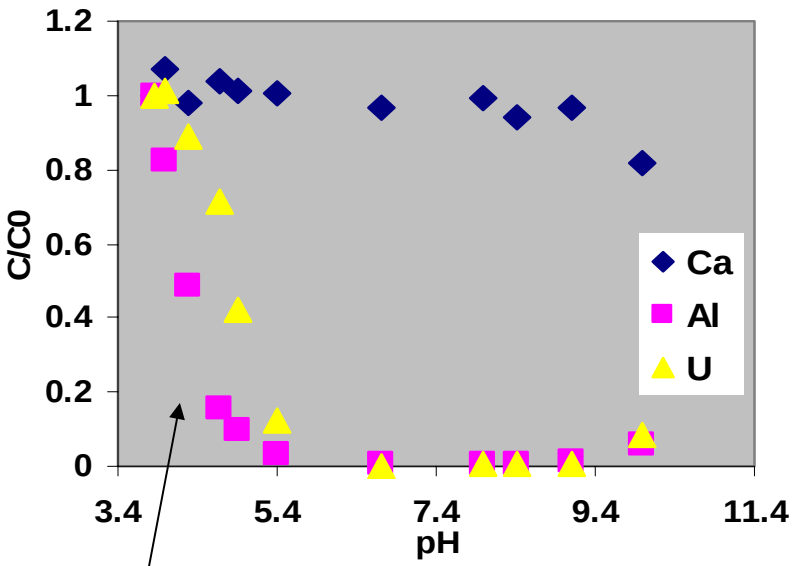
- **Investigate strategies for adjusting groundwater pH to effectively immobilize U(VI) and Tc(VII) through sorption and/or co-precipitation with Al-oxyhydroxides.**
- **Investigate controlled additions of silicate [as $Si(OH)_4$] and hydroxide to induce the formation of sparingly soluble aluminosilicates and thus an increased stability of immobilized U(VI) and Tc(VII).**
- **Investigate the influence of increased pH towards enhancing subsurface microbial activity, community diversity and rates of denitrification downgradient of a field-scale pH-manipulation zone**

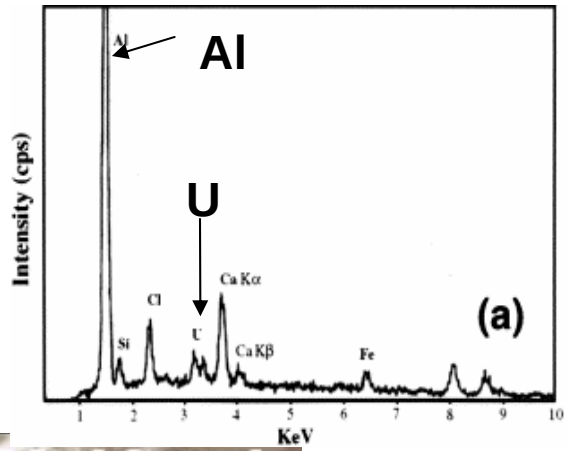
Results – Task C

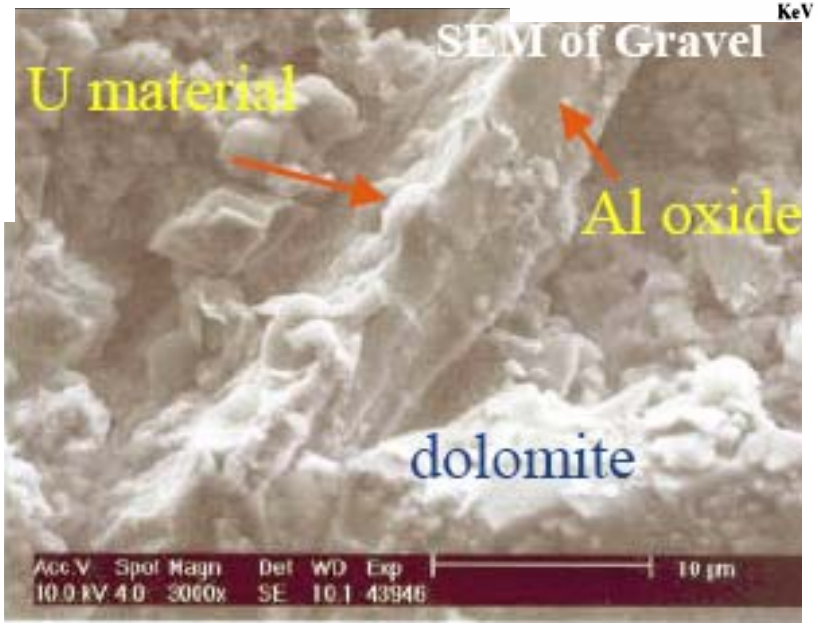
Immobilization of U through pH manipulation

Strong correlation between Uranium and Aluminum at the IFC

IFC Groundwater near source





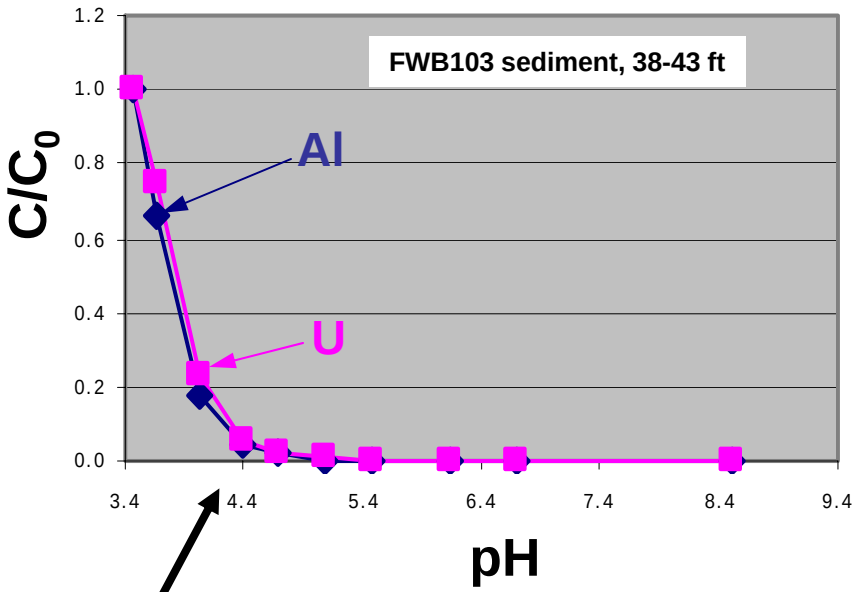


Aluminum precipitates from solution with increase in pH with U loss to follow

Results – Task C

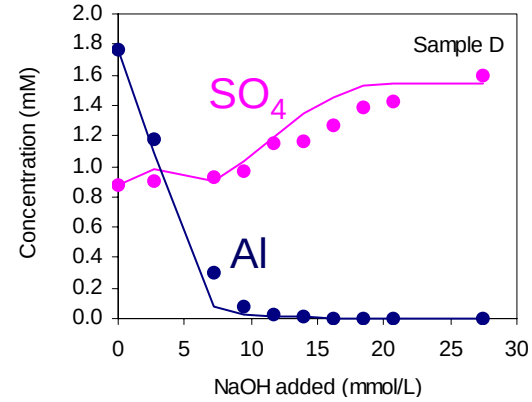
Immobilization of U through pH manipulation

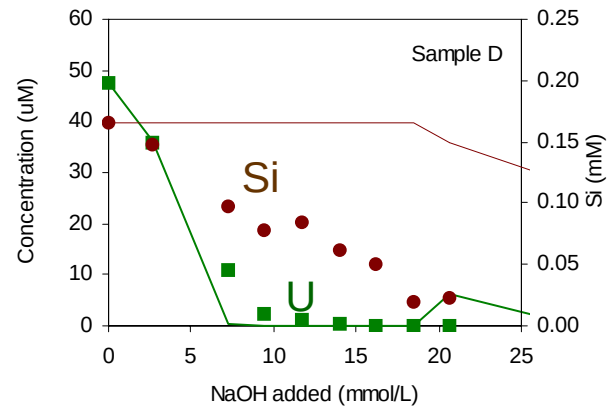
Titration of Sediments

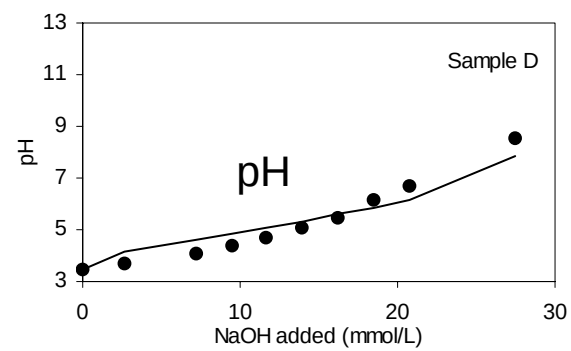


Greater than 90% precipitation or coprecipitation of U with Al at pH >4.4. Anions influence precipitation reactions

Modeling





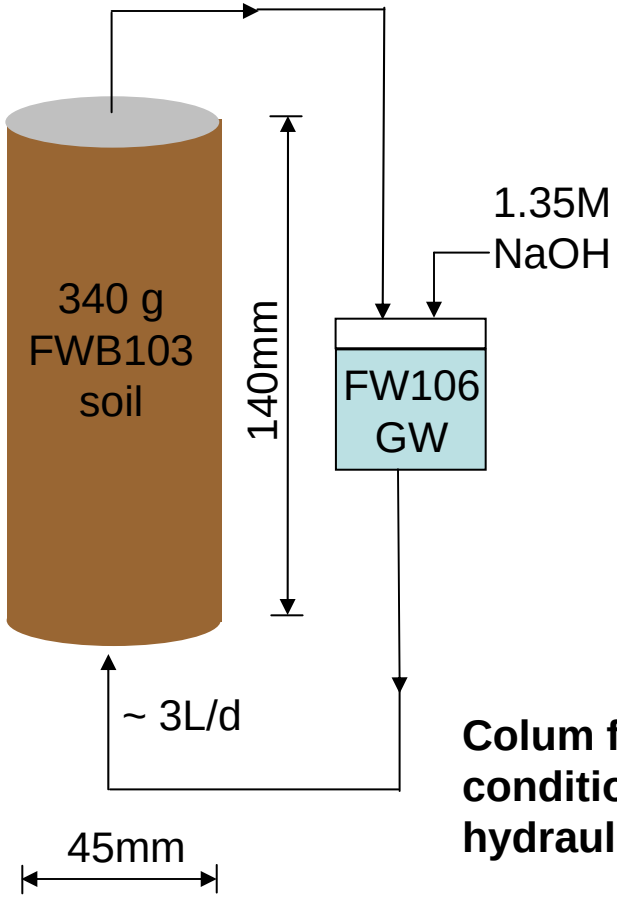


Using our calibrated soil buffer model, the whole reaction path did an adequate job describing the aqueous phase concentration changes

Results – Task C

Immobilization of U through pH manipulation

Column Flow pH Adjust Experiments



Colum flow experiments determine optimal parameters for in situ conditions (e.g. concentrations, flow rates and interruptions, hydraulics, mass balances)

$KOH/Ca(OH)_2/Si(OH)_4$ ratios and the formation of precipitates
Precipitation / deposition rates and mechanisms with profile depth

Core material from IFC pH adjustment site (distributed to LBNL, FSU, ANL)

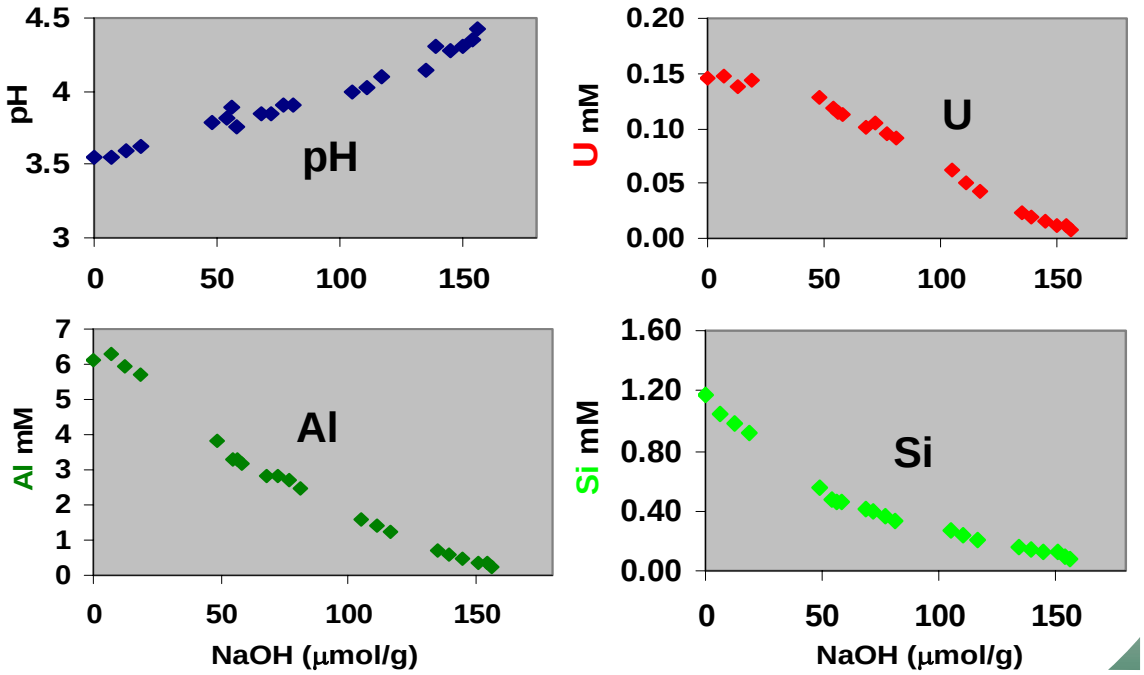
Results – Task C

Immobilization of U through pH manipulation

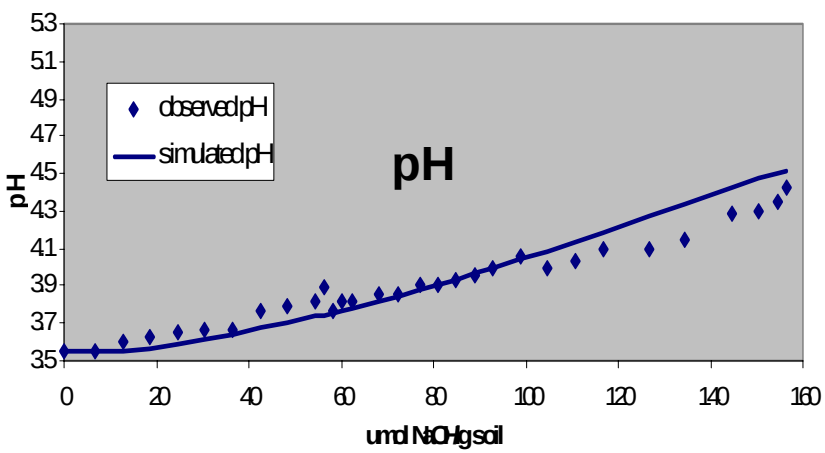
Effluent pH, U, Al and Si from column recirculation investigations

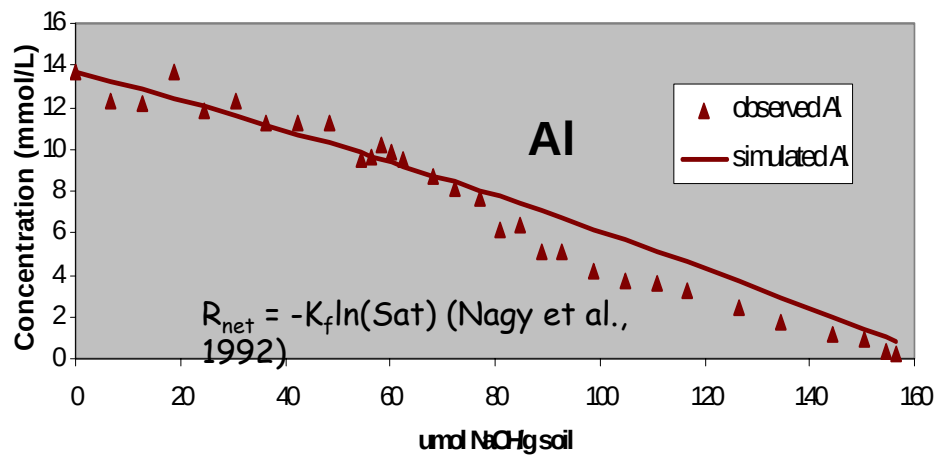
Slow increase in soil pH results in precipitation or co-precipitation of Al-Si oxides with possible inclusion or surface sorption of U

Coupled flow and transport model with rigorous geochemical reaction path describes data well



Modeled column effluent data

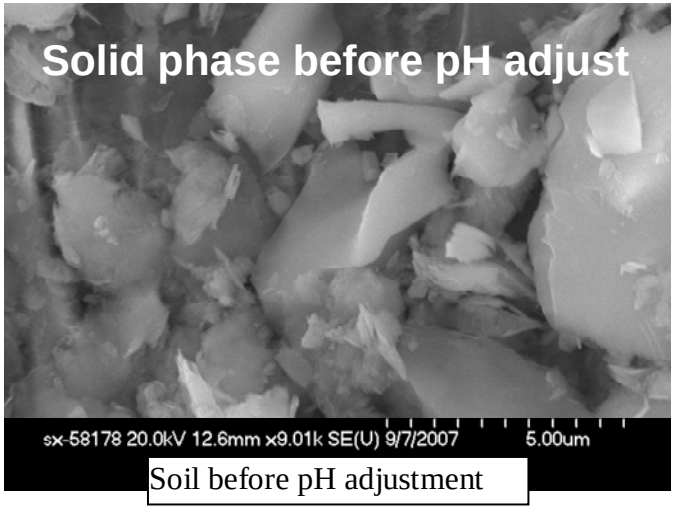




Results – Task C

Immobilization of U through pH manipulation

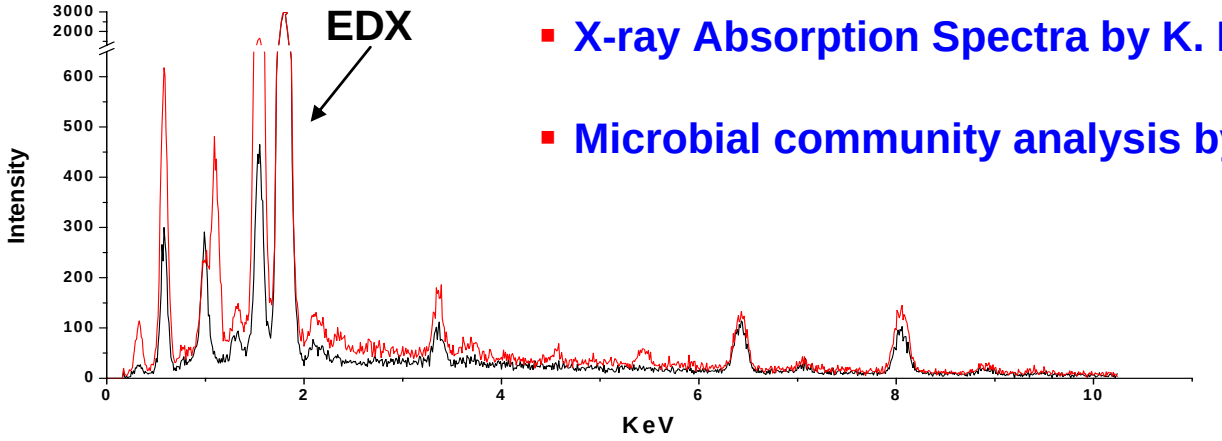
Detailed Chemical and Microbiological Analyses



Soil before pH adjustment

Soil after pH adjustment

Other Analyses:



- **X-ray Absorption Spectra by K. Kemner at ANL**
- **Microbial community analysis by J. Kostka at FSU**

Results – Task C

Immobilization of U through pH manipulation

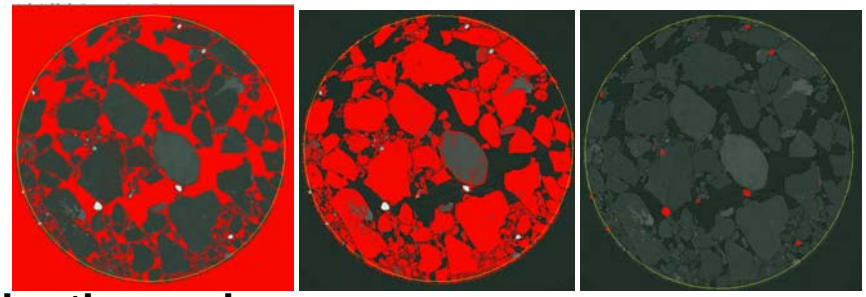
Intermediate Flow Experiments

Large column

Test tube for scale

In progress

Realistic environmental conditions, especially in the presence of carbonate (pressurized)



Needed for geophysical calibration and modeling during scale-up to field

Geochemical, mineralogical, and microbiological characterization before and after manipulation

Microtomographic imaging being performed at LBNL Advanced Light Source to explore changes in matrix structure and geophysical attributes associated with evolved precipitates at ~the scale of the process

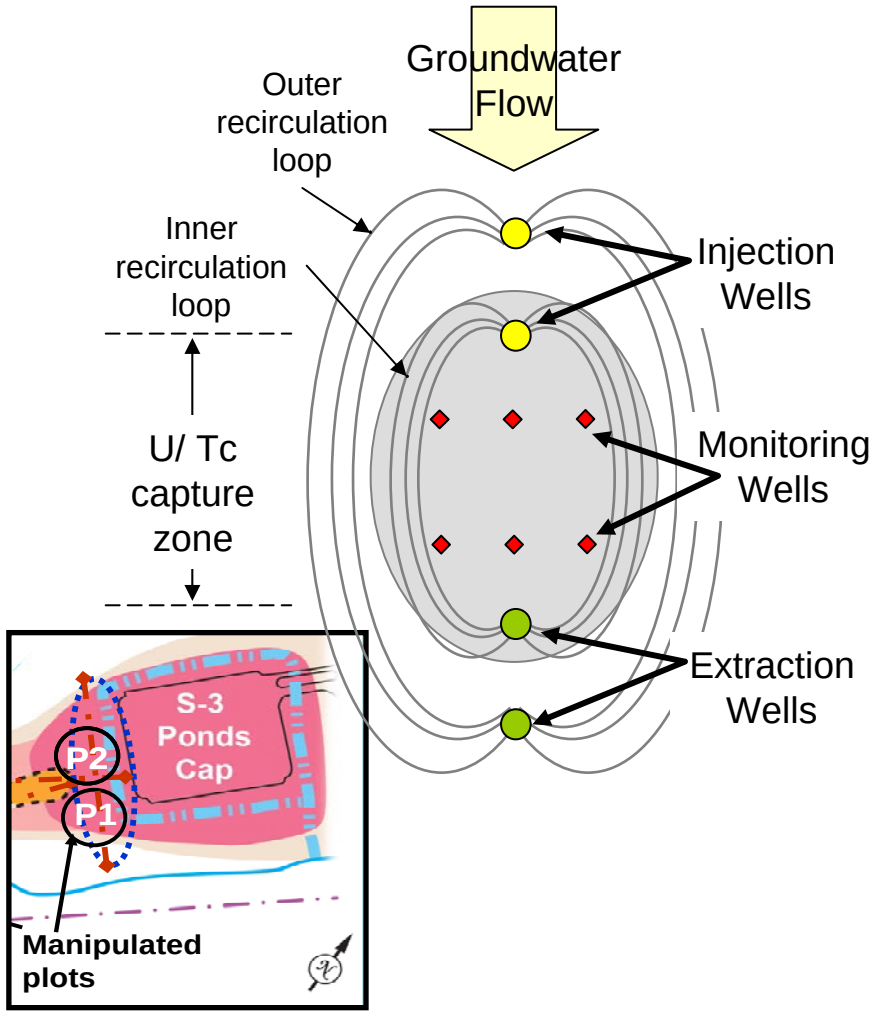
Lab equipment set up to enable development of biogeochemical-geophysical petrophysical relationships (with particular attention to development of precipitates and seismic imaging). Core and groundwater from IFC pH manipulation site sent to LBNL

Future Research – Task C

Immobilization of U through pH manipulation

U and Tc Source Control and Immobilization through Subsurface pH Adjustment

Near-term Field Exp.



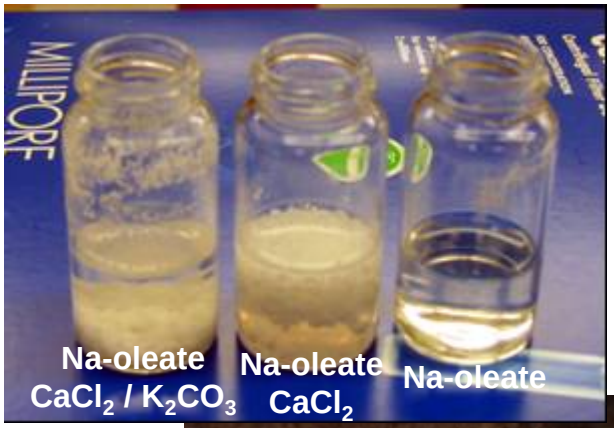
- **Field plot set up and characterization (e.g., multi-tracers studies, geophysical, mineralogical, and microbiological analysis - baseline).**
- **Controlled pH adjustment - first field injection experiment.**
- **Monitoring the precipitation or coprecipitation of U/Tc and the formation and transport of Al-oxyhydroxides for creating a subsurface capture zone for U(VI)/Tc(VII) immobilization.**
- **Post tracer studies, geophysical, microbiological, mineralogical, and speciation studies.**

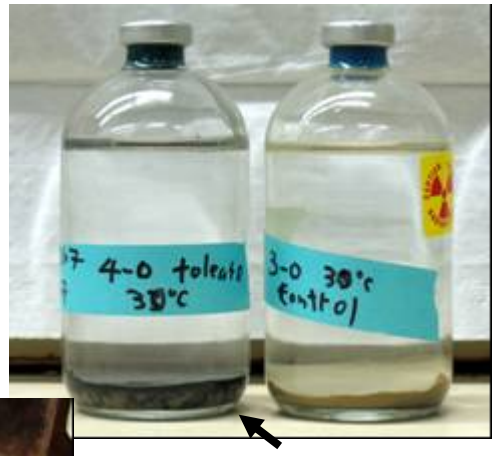
Results – Task C

Immobilization of U via slow release electron donor

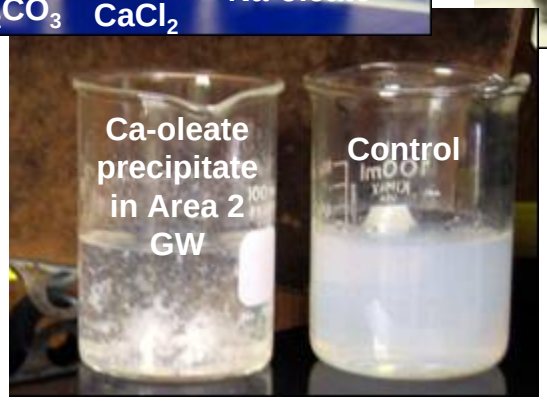
Targeted U Immobilization with Ca-oleate

Research has been initiated on the use of Ca-oleate as a slow release electron donor source for subsurface microbial stimulation and bioreduction of U(VI). Research will investigate the rates and mechanisms of the oleate precipitation reaction, the mode of subsurface delivery, and the specific microorganisms that are stimulated and knowledge of what their specific activity is with regard to U(VI) reduction.





The microcosm test is a feasibility screen test to verify the presence of oleate degraders in Area 2.



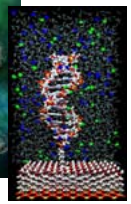
Sulfate-reducers are likely syntrophic partners during this incubation period. Notice heterogeneity of the black sports in the microcosms.

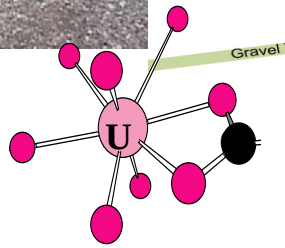
In addition, oleate degradation is also observed in sediments from MLS wells of Area 3.

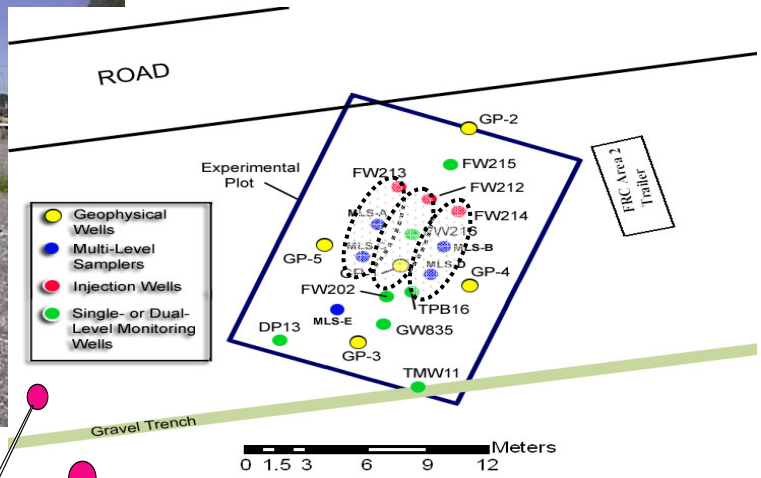
Future Research – Task C

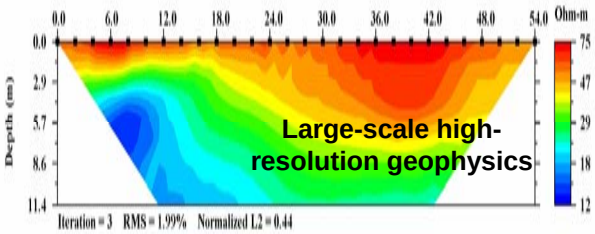
- Targeted U and Tc immobilization through up-scaled oleate and organo-phosphorous experiments via intermediate and field investigations

- Intensive coupling of hydrology, geochemistry, geophysics, microbiology, and interfacial surface spectroscopy.









Task D - Results

Multiprocess and Multiscale Numerical Modeling and Data Analysis

- Model Implementations as a function of scale: HydroGeoChem used to analyze lab data and field experiments on the Oak Ridge IFC site. Calibrated model used to simulate large scale nitrate transport.

- Modeling of U and Tc Immobilization through pH Adjustment

  - GW titration modeling
  - Soil pH buffer modeling
  - Soil titration modeling
  - pH manipulation column modeling

- Investigations of various numerical methods to solve transport problems

- GW heat transfer model for estimating GW recharge and surface water discharge associated with precipitation events

Results – Task D

Modeling Approach

HydroGeoChem (HGC) v.5 serves as the primary modeling tool (multi-process multi-component flow and transport code)

Capabilities:

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

Results – Task D

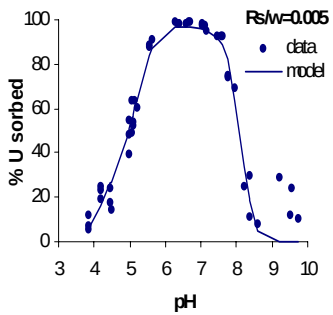
Investigating various numerical methods to solve transport problems

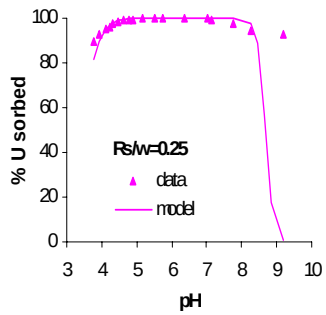
- ELLAM for highly nonlinear transport equations for multiphase flow and reactive chemical transport
- LEZOOMPC for nonlinear transport problems with moving sharp-front
- Five numerical schemes to solve advective-dispersive transport equations
- Three coupling strategies to deal with reactive chemistry involving kinetic and/or equilibrium reactions
- GMS: pre- and post-processor of groundwater simulation for finite element or finite difference grid develop, material property and boundary condition assignment, and simulation results visualization

Results – Task D

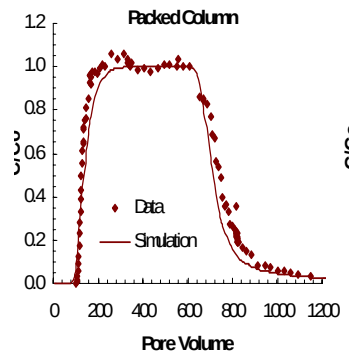
Model Implementations: HydroGeoChem has been used to analyze lab data and field experiments on the Oak Ridge IFC site

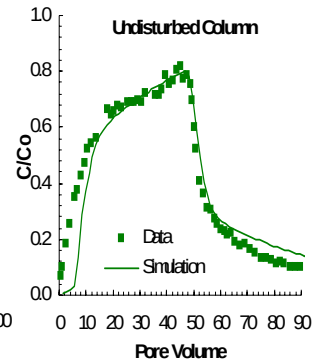
Batch U-Sorption Experiments



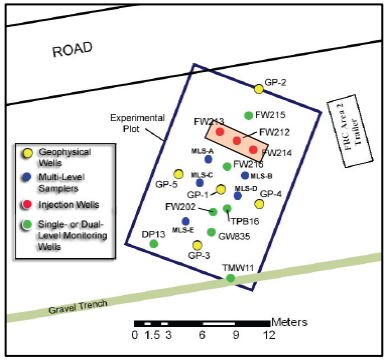


Lab U-Column Experiments

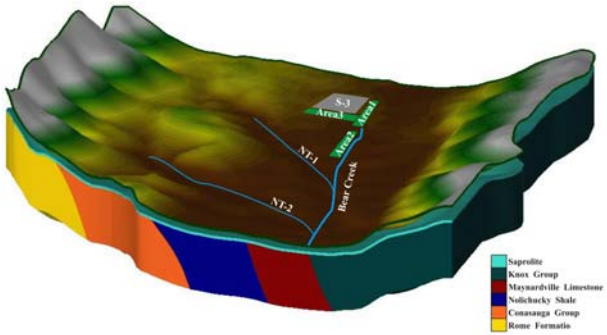




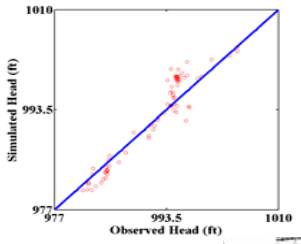
Areas 2 and 3 Field Scale Manipulations

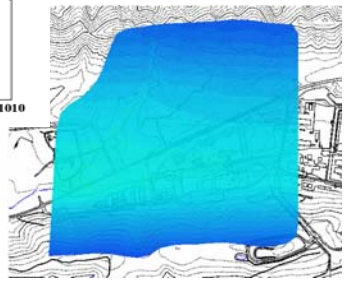


Model domain ~160 acres

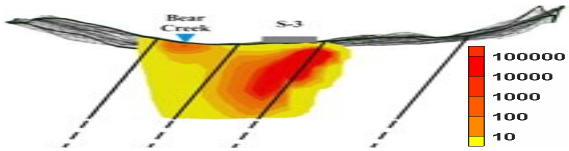


Groundwater calibration

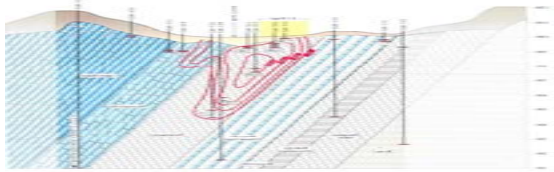




Simulated NO_3^- plume with density-dependent flow



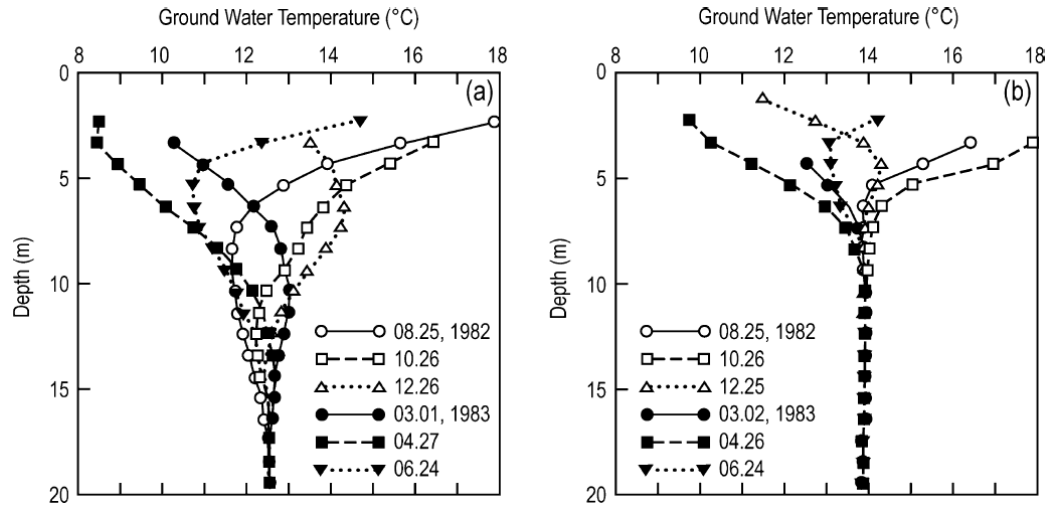
Observed plume



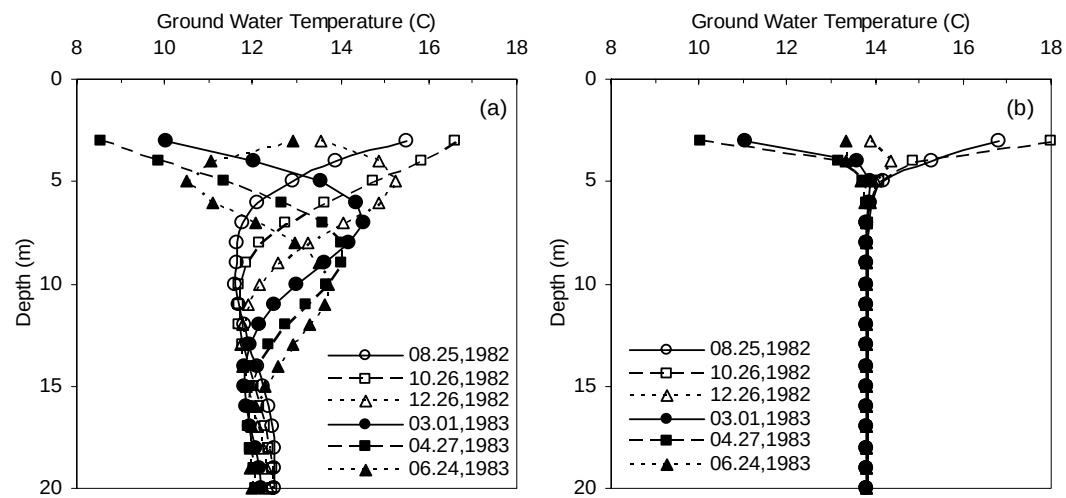
Results – Task D

GW heat transfer model

- Temperature profiles in the surficial zone potentially provide information about seasonal precipitation events and interchange with surface water
- Temperature data can be used in inverse problems to estimate GW recharge and surface water discharge associated with precipitation events



Seasonal temperature variation (Taniguchi, 1993)



Preliminary Hypothetical simulation

Future Research – Task D

Planned Modeling Efforts:

- Calibrate and test soil titration model for different materials at the site (i.e., gravel fill zone)
- Set up local-scale model to perform simulations for planning and analysis of field-scale pH manipulation experiments
- Implement microbial kinetics and perform initial sensitivity analyses
- Advance multi-scale research on coupled hydrological and biogeochemical processes with computational studies that improve the understanding of controlling mechanisms at the molecular scale and lead to the success of the confluence of molecular-scale processes with field-scale behavior.
- Continued modeling of subsurface heat transfer processes using heat as a tracer to investigate groundwater recharge and discharge.
- Watershed level coupled processes fate and transport modeling.

Data Management

Characterization and other data of wide appeal are being loaded into a central database

- Data is searchable and accessible via a Web interface.
- Both list and map-based queries are becoming available.

Data resulting from investigator experiments will be documented using a Web-based metadata entry tool

- Controlled vocabulary and indexing terms will ensure consistency in the data descriptions.
- The metadata will contain hyperlinks to the associated data.
  - Initially the metadata and associated data will have access limited to project personnel.
  - However, all data and documentation will eventually be searchable and accessible by anyone from the ORFRC website.
- Each investigator will create their own data sets in consultation with IFRC-ORFRC data manager.
- All data will be stored on ORNL file server.

Management and Operational Milestones

The OR Field Research Center Management Plan tiers from the Office of Science Strategic Plan (DOE 2004b), ERSP Strategic Plan (DOE 2006) and ERSD Management Plan for the Integrated Field Challenge (IFC) Projects (DOE 2007) and is one of a set of high-level planning documents (available at http://public.ornl.gov/nabirfrc/) that govern the operation of the ORFRC and implementation of the IFC and other projects. These include the following plans:

- **Environmental Assessment and FONSI (DOE 2000 a,b)**
- **Quality Assurance Plan (Brandt et al., 2001; revised 2004; revised 2007)**
- **Site Characterization Plan and Addendum (Watson et al., 2001; Watson and Roh 2004)**
- **Health and Safety Plan (Watson and Quarles, 2001; revised 2007) (tiered from the ORNL HAZWOPER Program Manual, 1993)**
- **Research Safety Summary (ORNL, 2007)**
- **ORIFC Management Plan**
- **ORIFC Researcher's Guide (ORNL, 2005 revised)**
- **ORFRC Closure Plan (Bogle and Watson, 2006)**
- **Implementation Plan for the Integrated Field-Scale Challenge Project (ORNL, 2007)**

Each Plan is a living document and are constantly revised, reviewed, and reimplemented as new research are initiated at the ORFRC.

Information Sources and Technology Transfer

A publicly accessible ORFRC website and listserver (http://www.esd.ornl.gov/nabirfrc/) has been revised to reflect the reflect the new ORIFC project and remains available for the distribution of information and data to the broader scientific community, EM, regulators and the public. Project characterization data and research findings are periodically transferred to the Oak Ridge Environmental Information System for use by environmental decision makers.

Over 30 new and 70 previous peer-reviewed publications (100 total) have resulted from the new IFC project and past ORFRC site characterization and research, respectively. Site-wide conceptual and numerical models have been developed and continue to be improved. ORIFC groundwater and sediment samples have been sent to 12 independent ERSD researchers this past year.

The project PI and Field Research Manager have been active participants in the DOE Oak Ridge Reservation Closure Project Team in order to ensure remediation planning needs are addressed and technical insights are transferred into DOE remediation efforts

Backup Slides

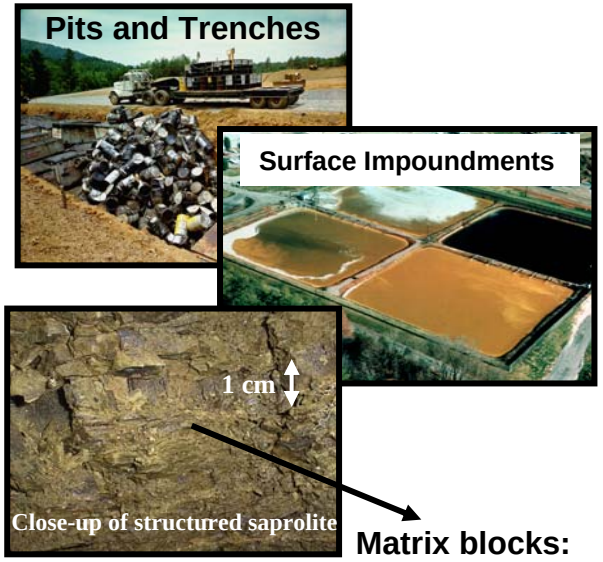
Purpose / Rationale

Historical disposal of wastes from the operation of three industrial plant sites on the Oak Ridge Reservation (ORR) has created extensive areas of subsurface inorganic, organic, and radioactive contamination (thousands of unlined trenches, pits, ponds).

These wastes have resulted in approximately 1,500 acres of contaminated groundwater on the ORR.

Much of the original contamination is now present as <u>secondary sources</u> within the soil-rock matrix outside of the original disposal sites.

The secondary source areas are extensive and encompass regions on the watershed scale (tens of km).



Matrix blocks: source / sink for contaminants

A significant limitation in assessing remediation needs of the secondary contaminant sources is the lack of information on the rates and mechanisms of coupled hydrological, geochemical, and microbial processes that control contaminant migration.

Contaminant fluxes emanating from the secondary sources are often so high as to prevent complete attenuation of the groundwater plumes.

Interventions such as source actions (reduction of the soluble contaminant concentration at the source or controlling the flux from the source to groundwater by decreasing recharge) may be a prerequisite for effective and rapid natural attenuation.

Relevance

This project is intimately connected with the ORR Groundwater Strategy Document (DOE 2004) which emphasizes the need for timely and focused research investigations on natural hydrogeologic systems at the ORR to help evaluate the technical feasibility and cost-effectiveness of various remediation strategies including natural attenuation.

The results of our proposed research will have maximum impact on ORR groundwater remediation decisions since groundwater decisions are slated for 2012 – 2015, which is the same time period that our project ends.

- **We will provide an enhanced scientific understanding of subsurface processes through improved multi-scale characterization and numerical modeling tools that are needed to predict contaminant fate and transport under a variety of remediation scenarios.**

David Watson is an invited member of the ORR Groundwater Core Team that seeks to "facilitate the identification, funding, and implementation of high-priority science and technology investigations" as related to ORR site groundwater issues.

- **This team works with state regulators, remediation contractors, and the DOE ORR Closure Project Core Teams to focus efforts on *the goal of site closure*.**

Characterization data and research findings from the ORFRC will continue to be input into the Oak Ridge Environmental Information System (OREIS), which is the long-term repository for data generated by the ORR EM and compliance programs for use in decision making.

Hypotheses Driven Approach

H1. *Geochemical Controls on Contaminant Attenuation*:

Microbial denitrification is the only geochemical mechanism for permanently decreasing NO_3^- flux (rate governed by pH and electron donor).

The master variable for U, and possibly Tc, attenuation is pH (i.e. aluminum hydrolysis and the presence of carbonates).

H2. *Recharge Controls on Hydraulics, Geochemistry, and Microbiology*:

Recharge immediately adjacent to the contaminant source is the main hydraulic driver for groundwater flow and dilution of contaminants

It is this recharge that dictates temporal and spatial variability of geochemical and microbiological processes in the saturated zone.

H3. *Secondary Source*:

The secondary source strength is of a magnitude that attenuation of contaminant plumes will not occur rapidly unless an action is taken (reducing concentration and/or by controlling recharge).

H4. *Transition Zone*:

Important from a remedial perspective since (1) characterized by steep gradients in subsurface properties, (2) transient in space and time, (3) most active zones with respect to geochemical and microbially mediated metal and radionuclide transformations.

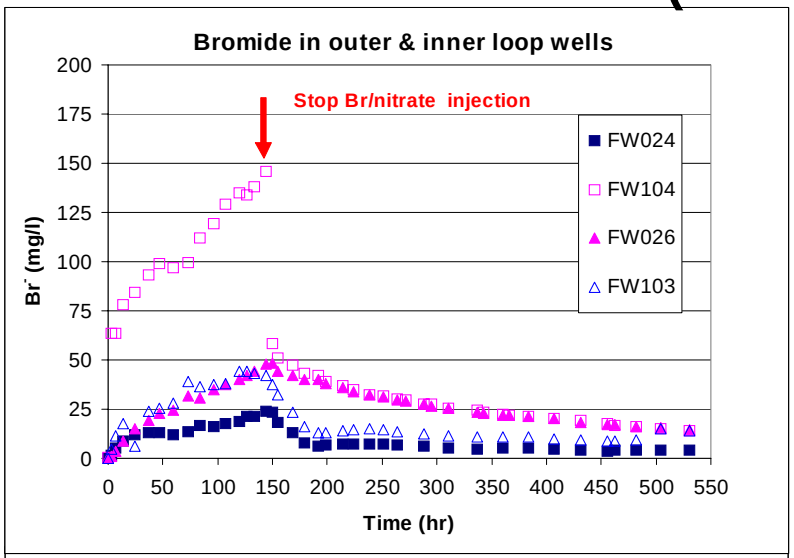
H5. *Enhanced Stability*:

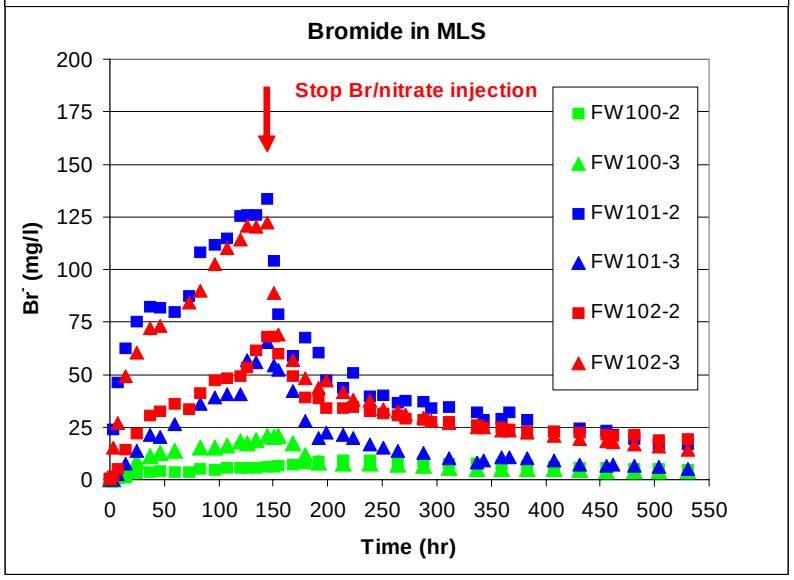
Enhanced subsurface stability of U and Tc can be achieved through remedial strategies that (1) maintain a favorable geochemistry and microbial ecology, (2) minimize biogeochemical heterogeneity, and (3) counteract or inhibit mechanisms of reoxidation and remobilization.

Results – Task C

Stability of Bioreduced U

Test 2: Reoxidation of reduced zone by injection of nitrate (Br as nonreactive tracer)





The Injection

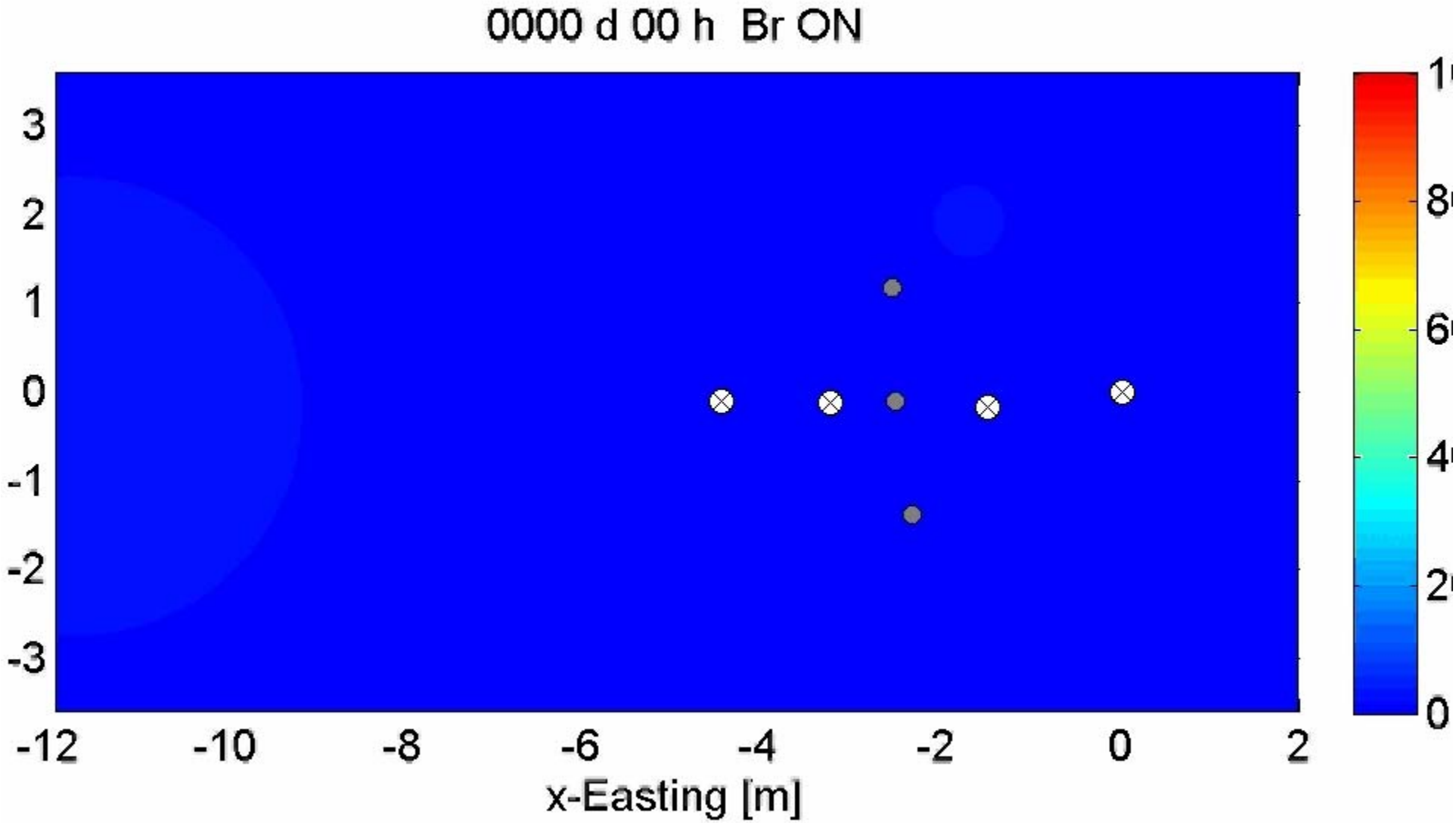
Nitrate and Br injected into bioreduced inner loop for 6 days.

Results of the tracer test confirmed that 1) innerloop extraction well FW026 and outer loop extraction well FW103 received about 30% of water injected; 2) inner loop MLS FW101(blue color) and FW102 (red color) were connected to innerloop injection FW104; and 3) FW100 were poorly connected to FW104.

Nitrate was delivered to both inner and outer loop during the tracer test.

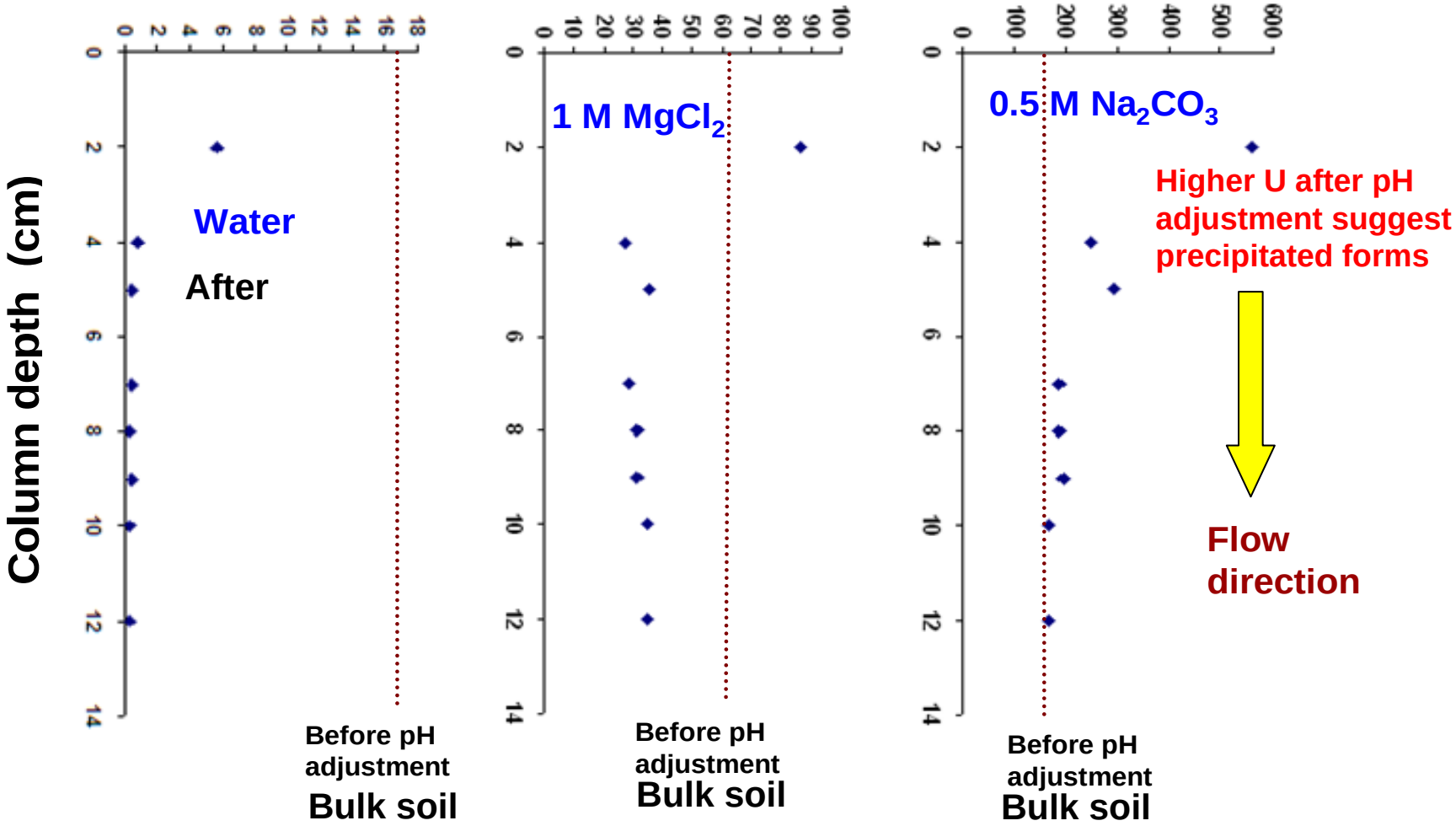
The study of geochemical changes during reoxidation by nitrate was focused on inner loop MLS FW101-2, 102-2 and 102-3 (next page).

Test 2: Movement of Br into reduced zone coupled with the injection of nitra



Results – Task C

Immobilization of U through pH manipulation

U distribution profile in soil column after sequential extraction with water, 1 M $MgCl_2$, and 0.5 M Na_2CO_3

U Distribution Profile (mg/g)