PNNL/Alabama/ORNL
Project Activities and Results

Principal Investigators:

Timothy D. Scheibe, PNNL
Eric E. Roden, University of Alabama
Scott C. Brooks, ORNL
John M. Zachara, PNNL

Other Contributors

- NABIR FRC Staff (well construction and sediment collection, groundwater analyses)
- ORNL:
  - Wiwat Kamolpornwijit (groundwater sampling and analysis)
  - Melanie Mayes (intact core excavation and operation)
  - Young-Jin Kim (uranium sorption and transport studies)
- University of Alabama
  - Ken Overstreet (sediment collection and core logging)
  - Santosh Mohanty (laboratory slurry experiments)
- PNNL:
  - Yilin Fang (reactive transport modeling)
  - Frank Spane (hydraulic test design and analysis)

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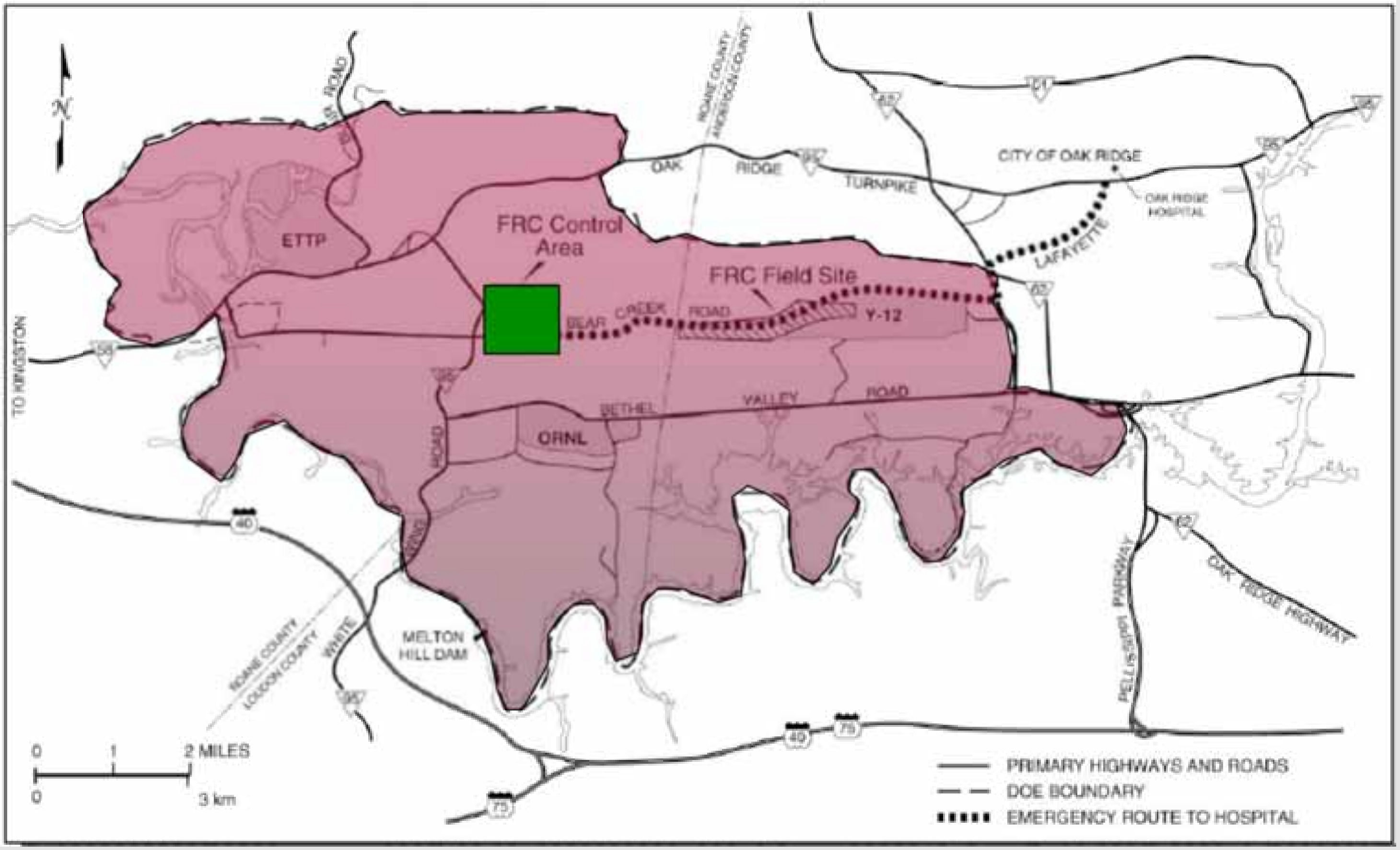


FRC Control Area
FRC Field Site
ETTP
ORNL
Y-12
CITY OF OAK RIDGE
OAK RIDGE HOSPITAL
OAK RIDGE TURNPIKE
LAFAYETTE
BEAR CREEK ROAD
BETHEL VALLEY ROAD
MELTON HILL DAM
TO KINGSTON
OAK RIDGE HIGHWAY
PELLISSIPPI PARKWAY
ROANE COUNTY
LOUDON COUNTY
ANDERSON COUNTY
0 1 2 MILES
0 3 km
PRIMARY HIGHWAYS AND ROADS
DOE BOUNDARY
EMERGENCY ROUTE TO HOSPITAL

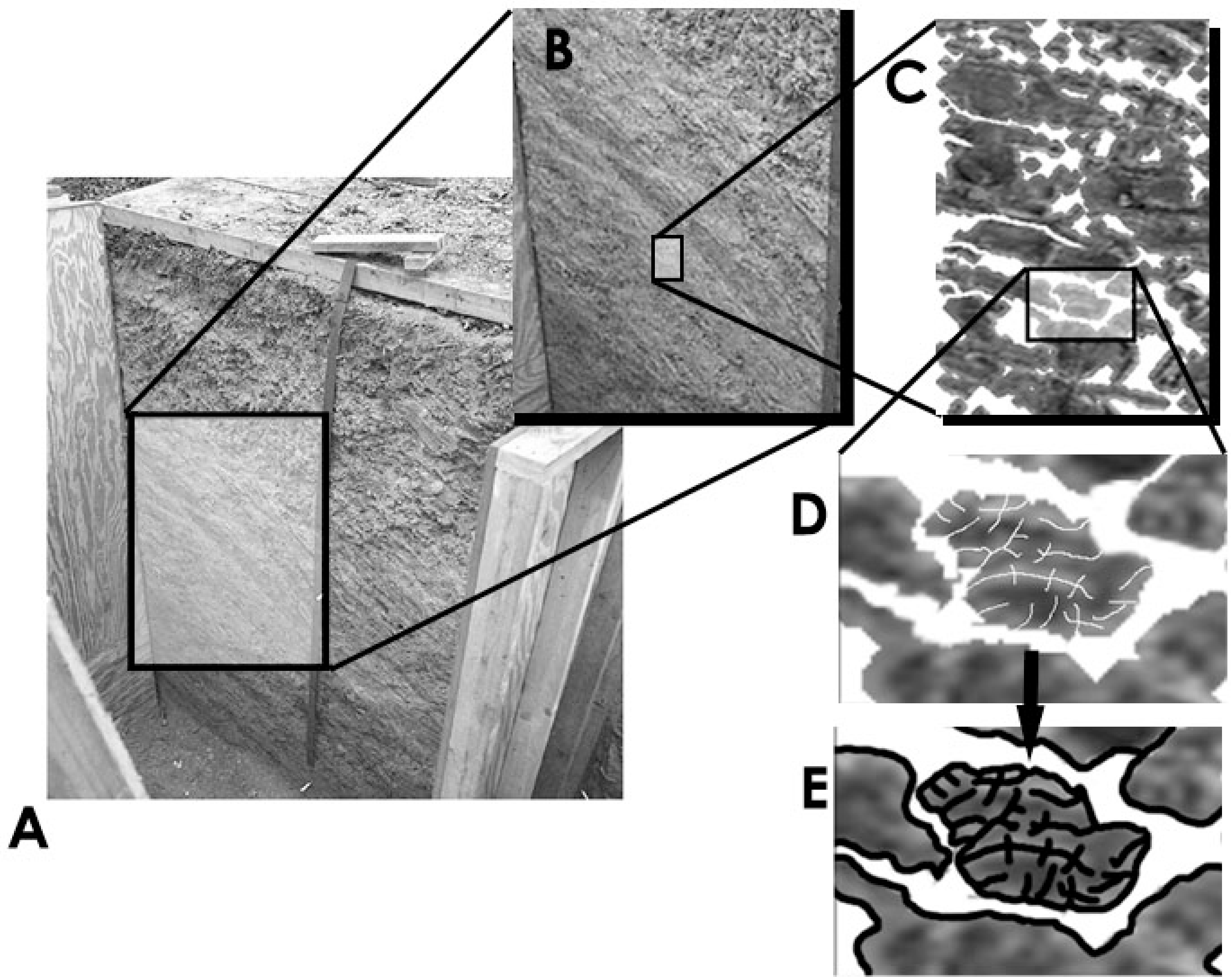
Fractured Saprolite

Problem

- 10-20% of porosity is accessible by active pumping
- 10-20% of porosity will respond to pumping on intermediate time scales
- 60-80% of porosity (and associated contamination) is hydraulically inaccessible (controlled by slow diffusive mass transfer)

Hypothesis

- Mobile radionuclides in low-permeability porous matrix regions of fractured saprolite can be effectively isolated and immobilized by stimulating localized in-situ biological activity in highly-permeable fractured and microfractured zones within the saprolite.

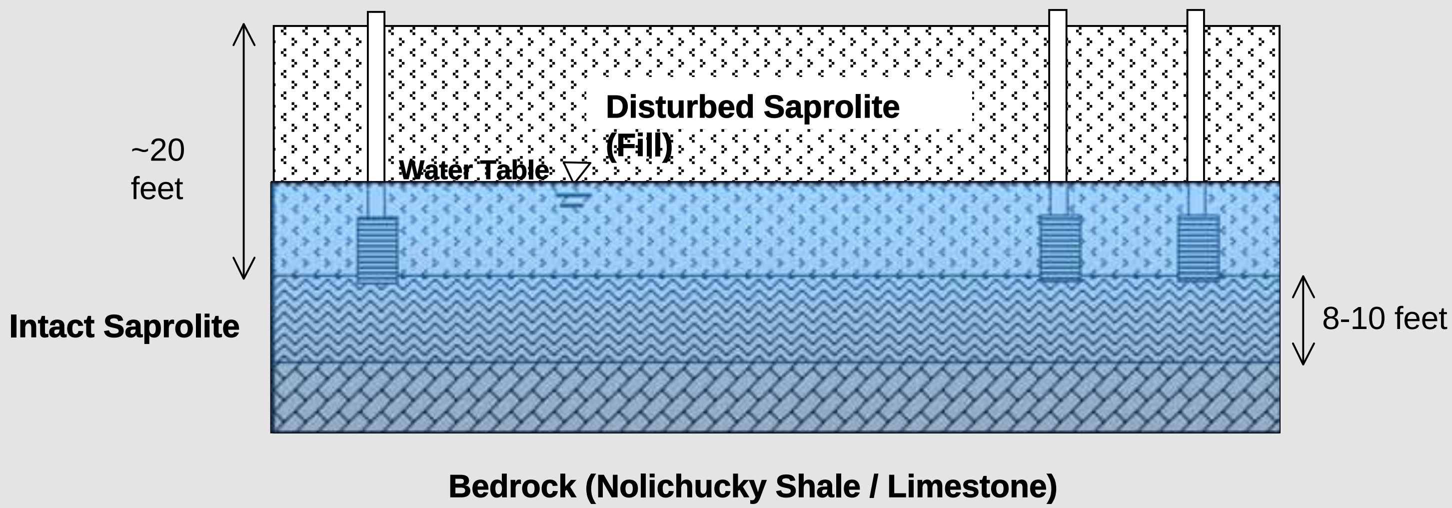

B
C
D
E
A

Progress Areas

- Field Site Development and Characterization
- Laboratory Fe/U Reduction Potential Analyses
- Bench-Scale Proof-of-Principle
- Numerical Model Application

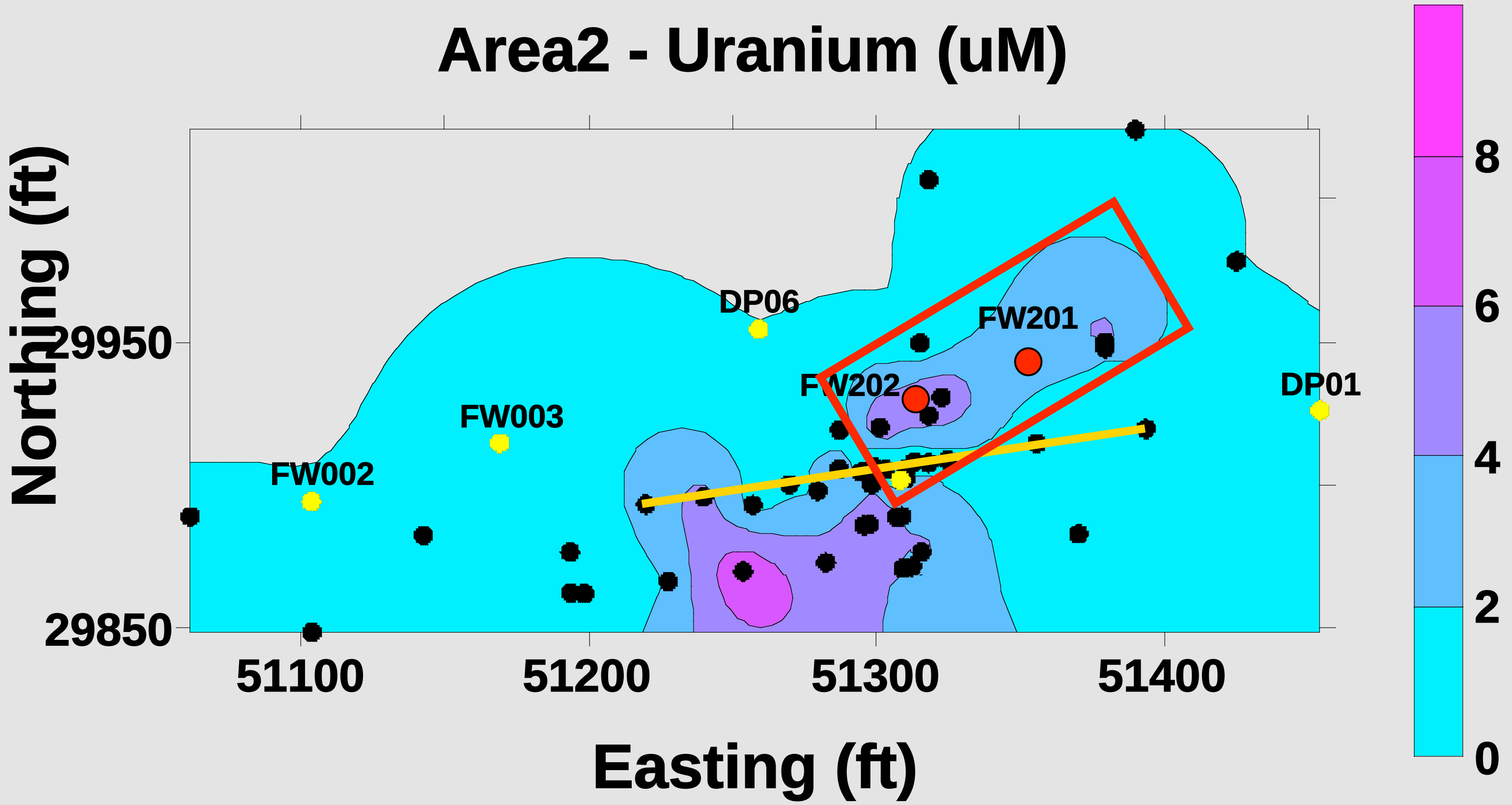
Field Site Development

Area 2 Stratigraphy



Exploratory Wells FW201, FW202

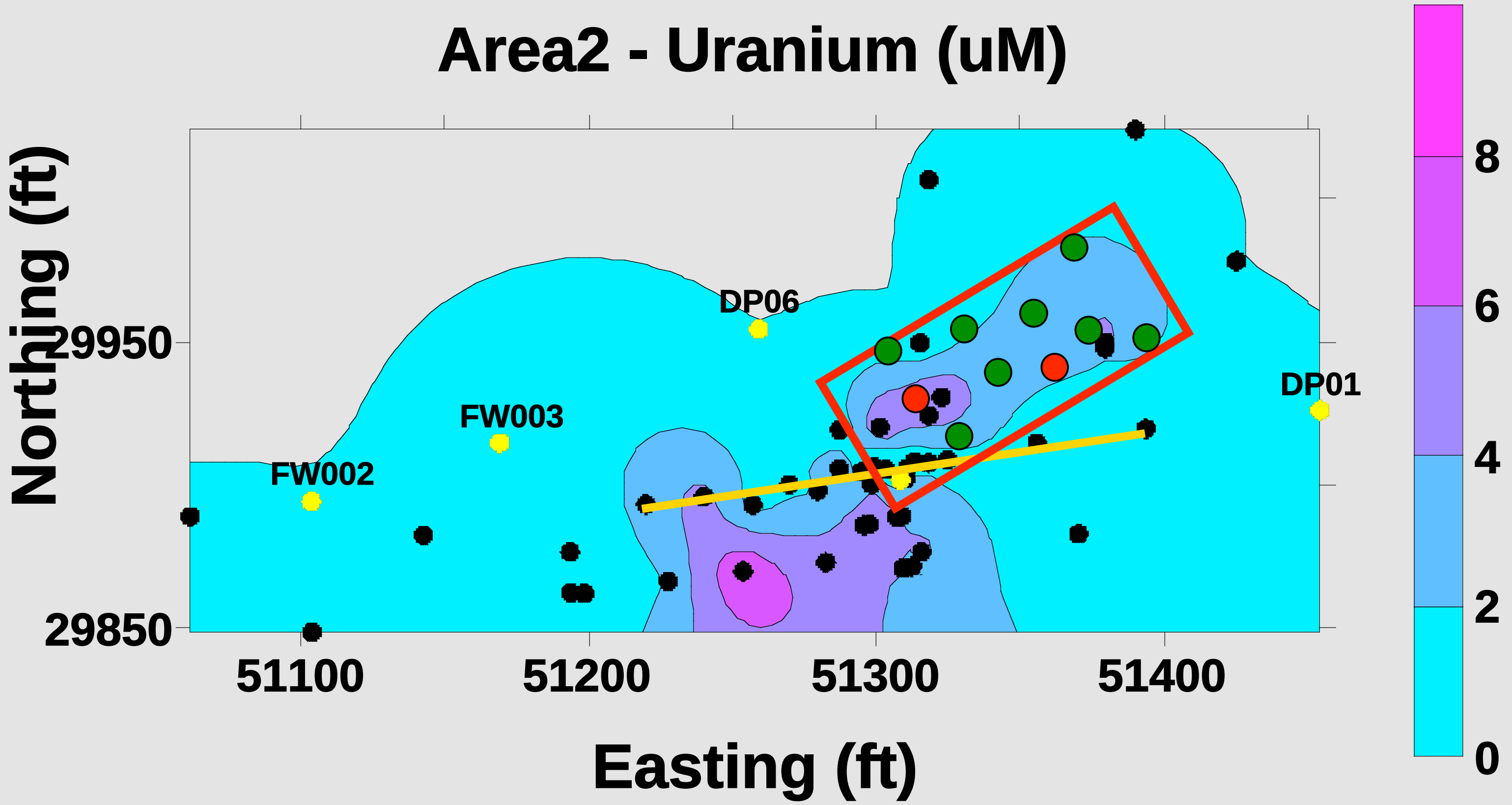
- May 2003



Well Installation – Round 1

Round 2 Well Installation
Detailed Characterization Wells

- August 2003



Groundwater Constituents

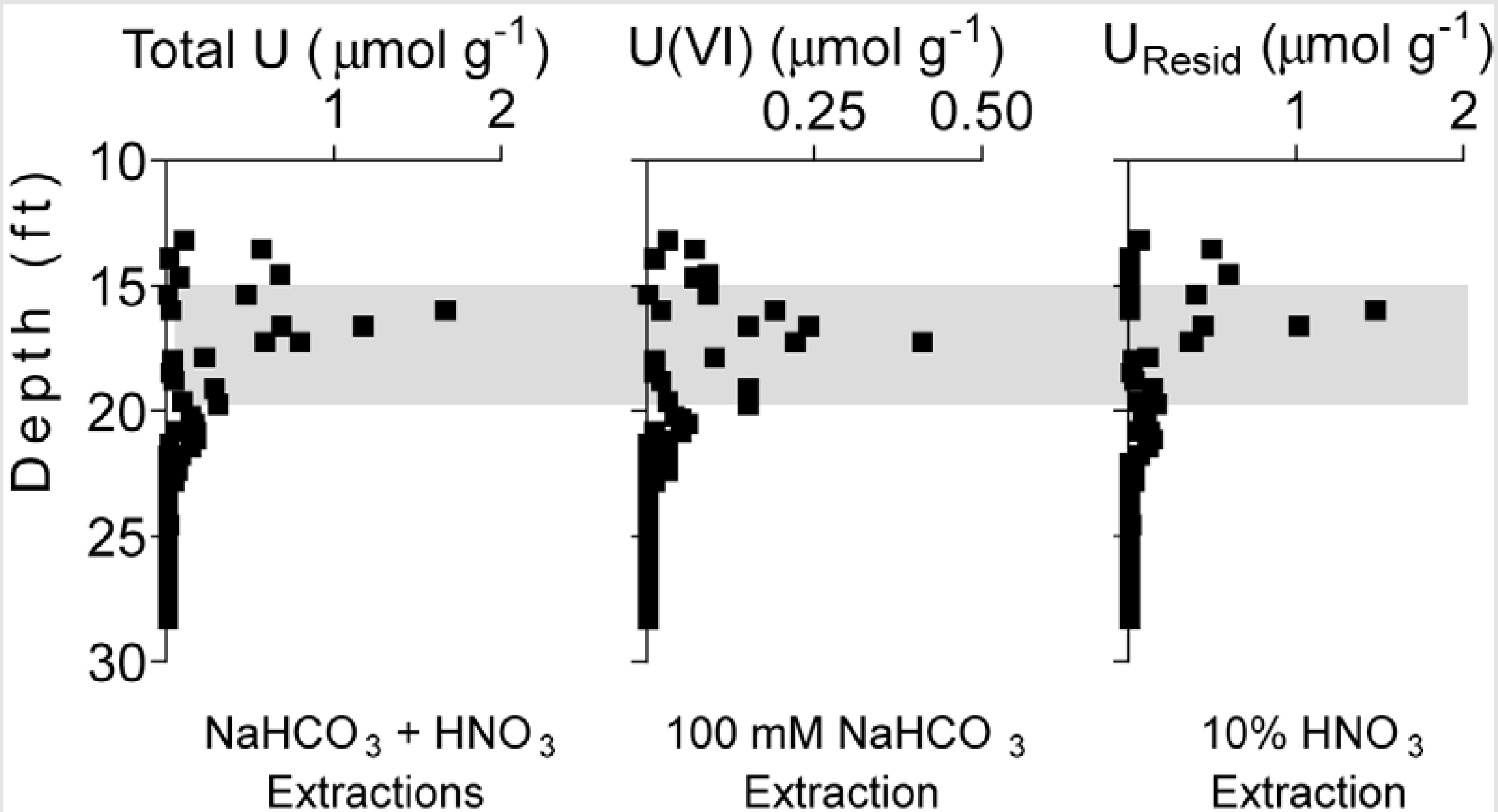
- U in μM range
- pH circumneutral
- Nitrates as high as ~125 mM !

- Sediment-associated U low (<< 1 μmol/g)

Date	Well	pH	NO3- (ppm)	SO4= (ppm)	U (ppb)
08/26/03	FW204	7.30	237.4	118.6	547.4 441.1
	FW205	6.87	495.0	65.8	77.4 74.1
	FW206	6.59	684.2	34.4	15.7 15.6
	FW207	6.83	368.2	48.9	180.5 150.6
	FW208	5.48	3077.7	11.3	69.3 67.4
	FW209	6.26	1078.2	13.4	239.7 238.8
	FW210	6.36	7719.5	12.0	185.7 117.6
	FW211	6.33	1584.3	62.1	421.8 428.8

Note: Top number for U is unfiltered; bottom is filtered.

Sediment Extractions FWB201 and FWB202



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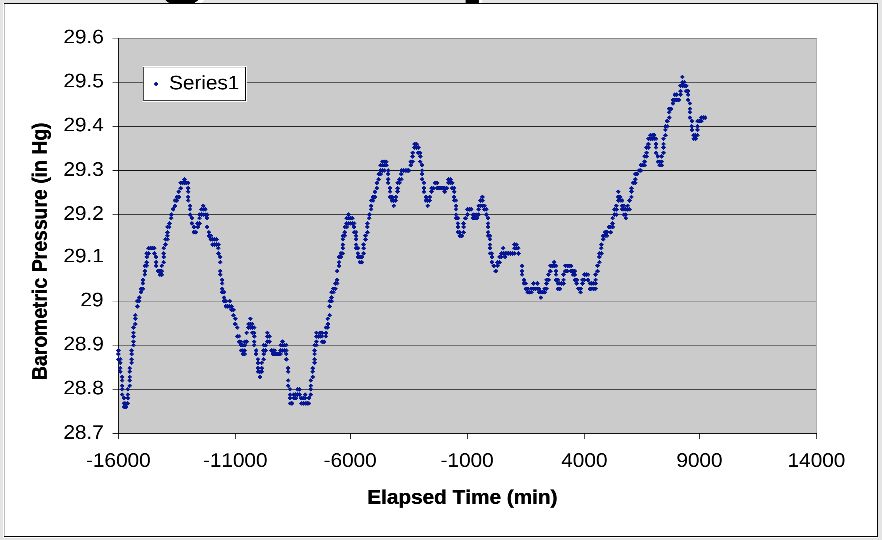
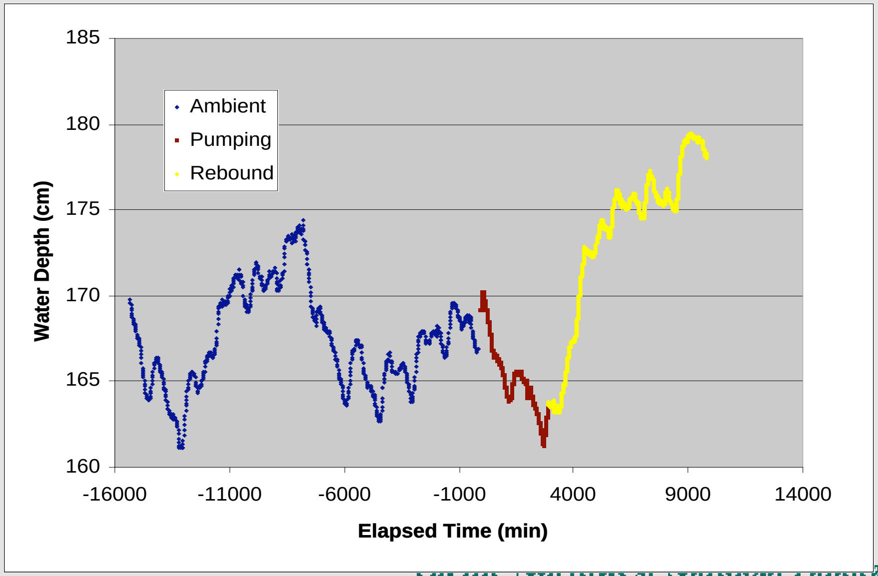
Hydraulic Testing – Deep Zone

- Installed in-well pressure transducers with dataloggers in several wells
- Tracked ambient water level fluctuations in response to rainfall, barometric pressure, seasonal variations
- Tracked water level response to pumping in FW207.





Hydraulic Testing – Deep Zone

- Conclusions:
  - Barometric response in lower zone strong, can be accounted for. Nature of barometric response is consistent with double-porosity conceptual model.
  - Estimated K = 4×10^{-7} m/s
  - Primary connectedness in E-W direction (parallel to geologic strike)
  - Low sustainable pumping rates (tens of ml/min)
  - Estimated direction of maximum head gradient ~ 30 degrees west of south.

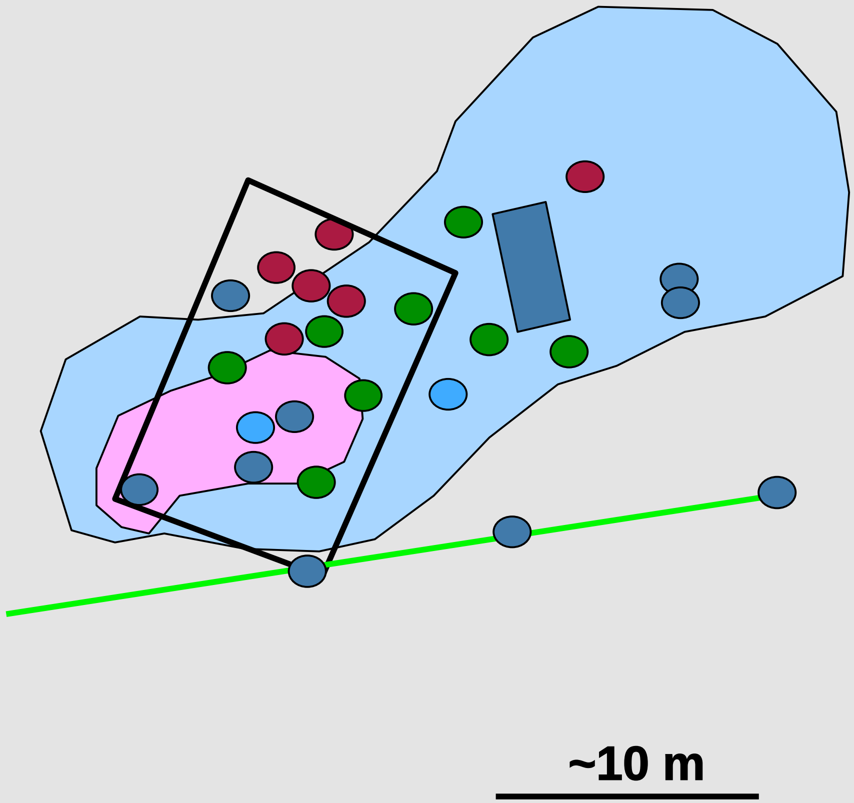
Disturbed or Undisturbed Saprolite?

- Factors:
  - Lower levels of uranium contamination
  - Much higher levels of nitrate
  - Low water movement rates
- Conclusion: Shift focus to upper zone (disturbed saprolite or "fill" zone).
  - Structure less well-defined, but still prevalent
  - Higher levels of U(VI)
  - Low levels of nitrate
  - Significant sustainable pumping rates

Round 3 Well Installation – Feb. 2004

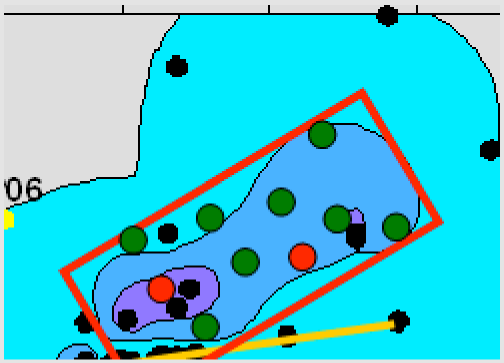
Purposes:

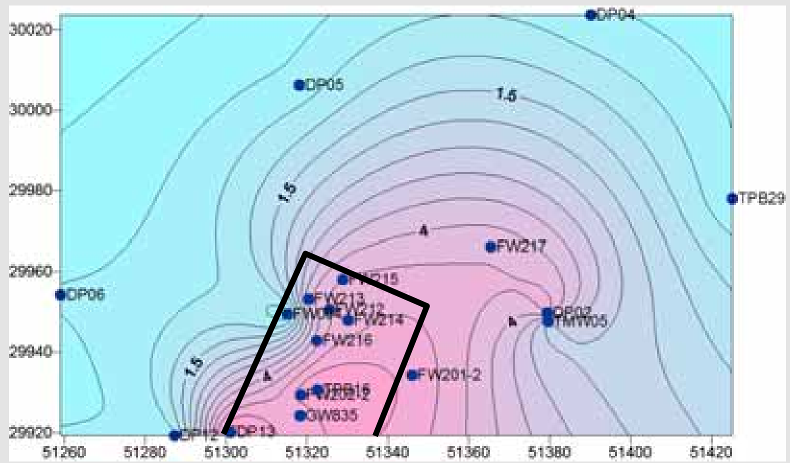
- Confirm head gradient direction
- Prepare for tracer injection to establish flow direction
- Construct wells to be used as part of biostimulation flow cell
- Refine understanding of contaminant distribution



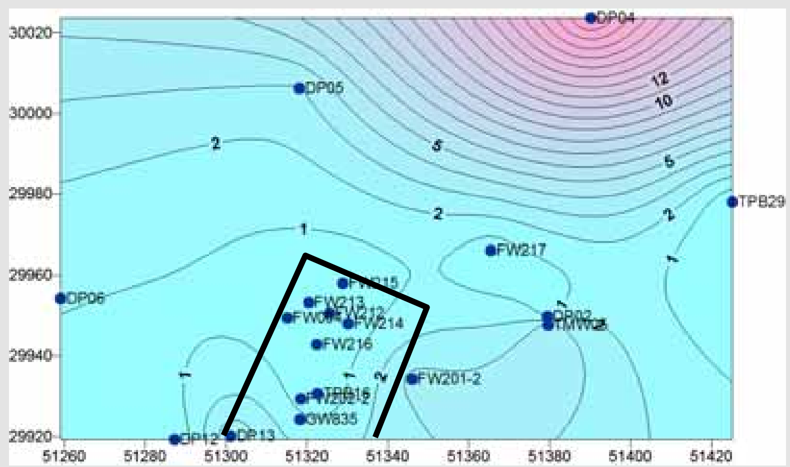
Aqueous Chemistry

- $U(VI)_{aq}$ ~ 4-5 μM



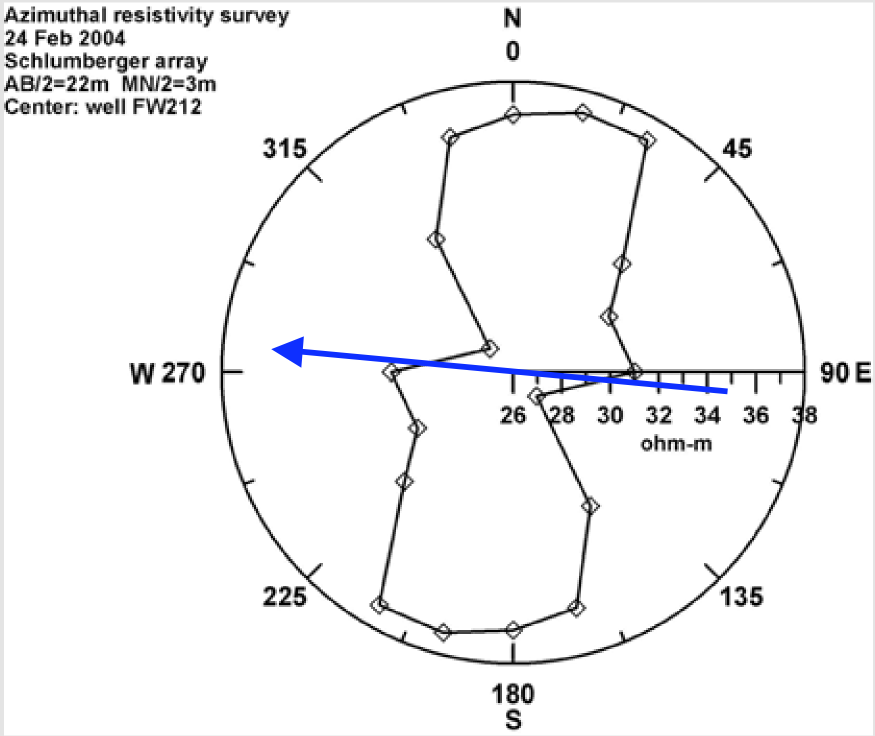


- NO3 ~ 0.5 mM

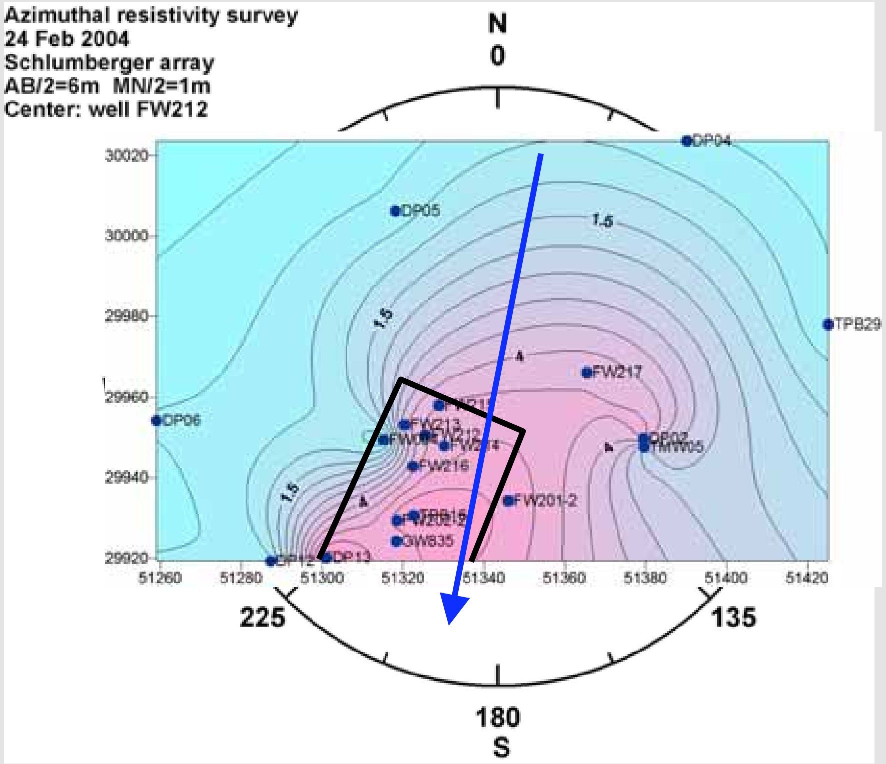


Azimuthal Resistivity Survey

Deep zone



Shallow zone



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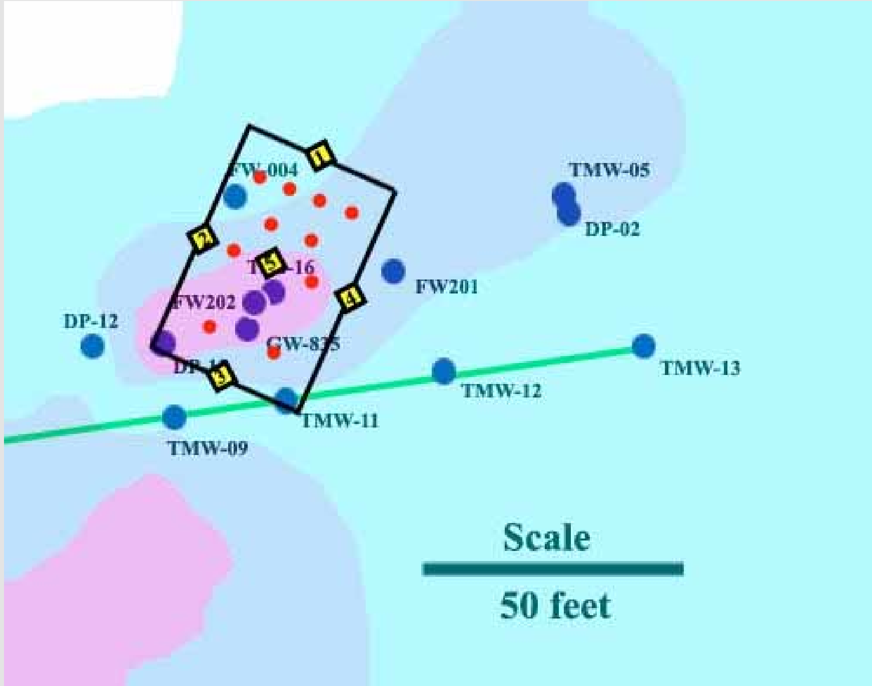
Next Steps

- Hydraulic characterization of undisturbed zone
  - Slug interference testing
  - Tracer test
- Completion of flow cell infrastructure
  - Additional injection/monitoring wells
  - Geophysical tomography wells on perimeter

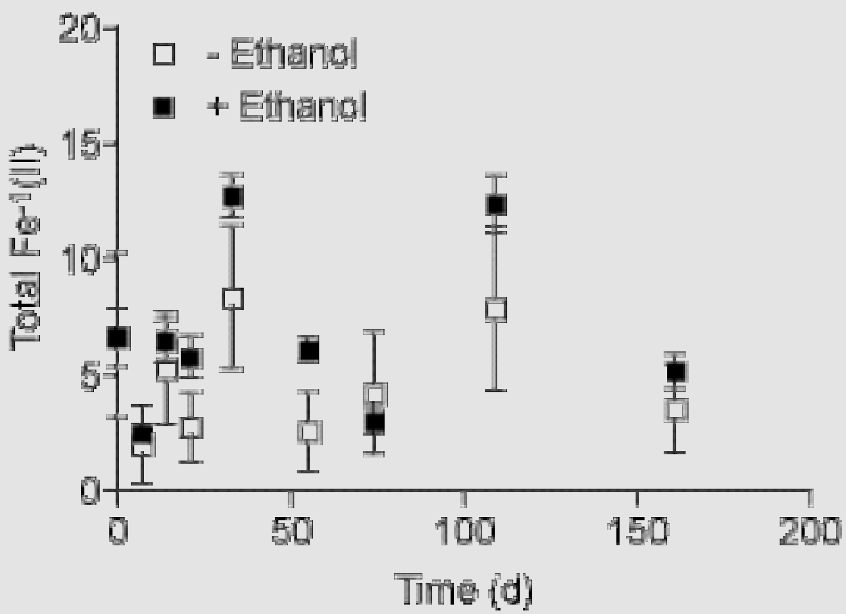


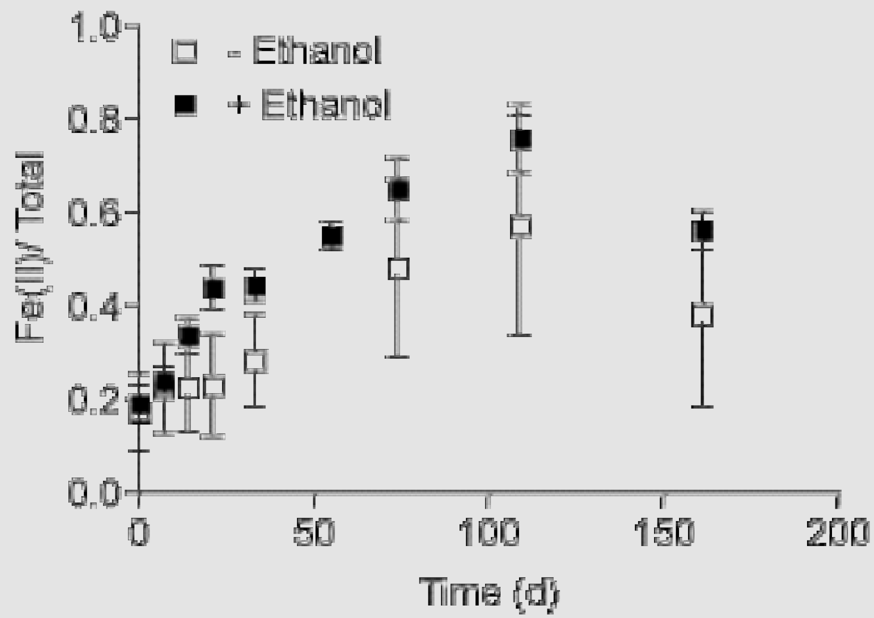
Laboratory Fe/U Reduction Potential Experiments

- Sediment laboratory wet-chemical analysis and molecular analysis of sediment and groundwater samples

Results from Intact Saprolite

- Area 2 Sediment (23-26 ft) slurry incubations (twelve samples each with and without 10 mM ethanol)





Variability associated with non-uniform solid:solution ratio in samples

Normalizing to total Fe shows trend of increased reduction in +Ethanol flasks

Reduction of 100 μM U(VI) Spike*

* Uranyl acetate added at day 96; U(VI) and U_{Resid} measured at day 161

Next Steps

- Sediment from disturbed saprolite zone (most recent well installation) has been obtained
- New slurry experiments will be initiated shortly.

Element 3: Bench-scale testing of hypothesized process

► Undisturbed column studies

- **Perform proof-of-principle experiment at bench scale.**
- **Derive rate constants for use in upscaling studies.**
- **Identify reaction network and examine solid phase reaction products.**

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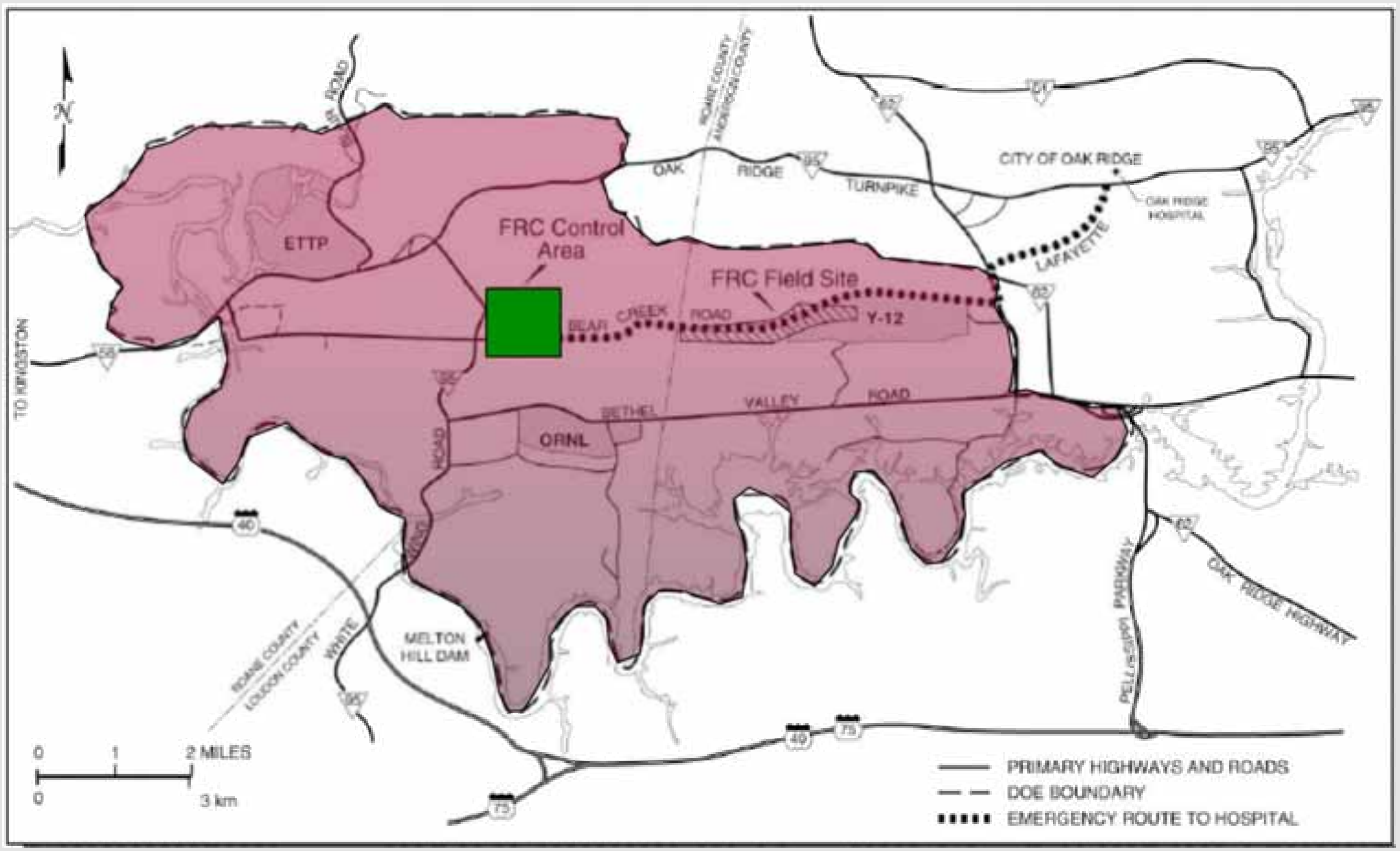

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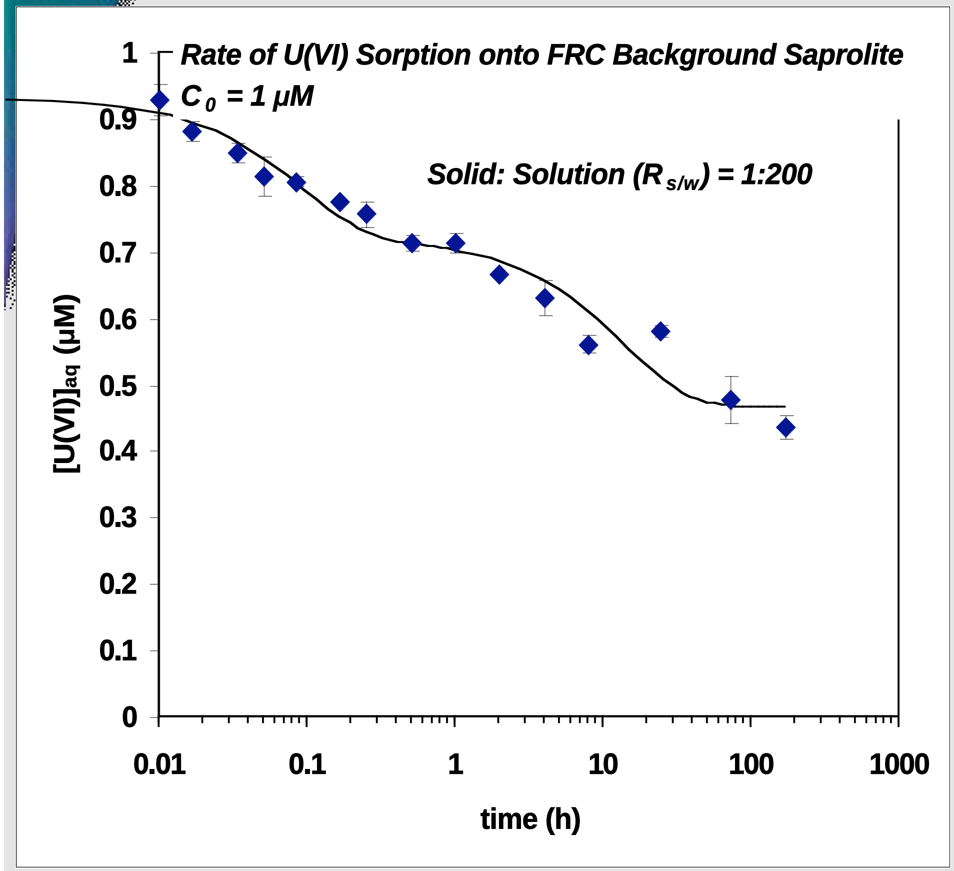
Intact Column Studies

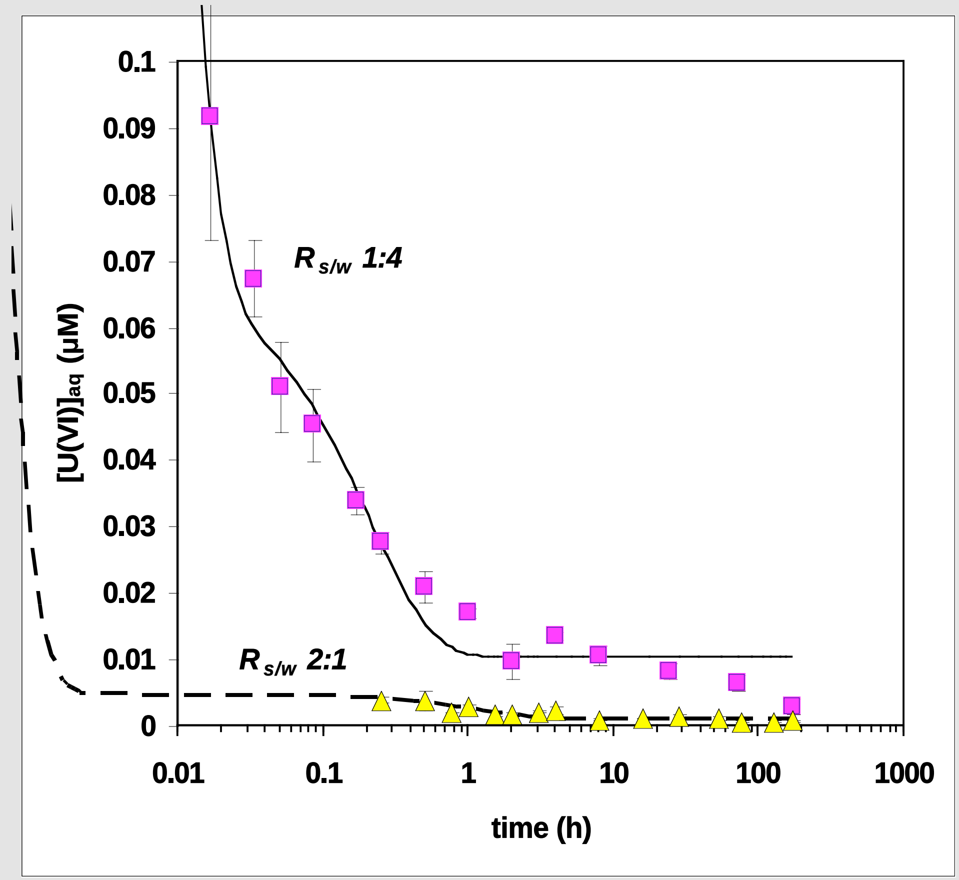
Amorphous Fe (ammonium oxalate extraction) 11.0 ± 0.2 mmole/kg
Total Fe (citrate-dithionate-bicarbonate) 320 ± 10 mmole/kg
Total Mn (acidic hydroxylamine hydrochloride) 3.1 ± 0.1 mmole/kg

Status and Next Steps

- Three cores have been collected and set up in the laboratory
- The columns have been fully water saturated and are being partially desaturated under controlled vacuum
- Loading of micropores with uranium under vacuum will be started shortly
- Three different treatments will be applied
  - Control (tracer only)
  - Tracer plus electron donor
  - Tracer, electron donor, and electron shuttle

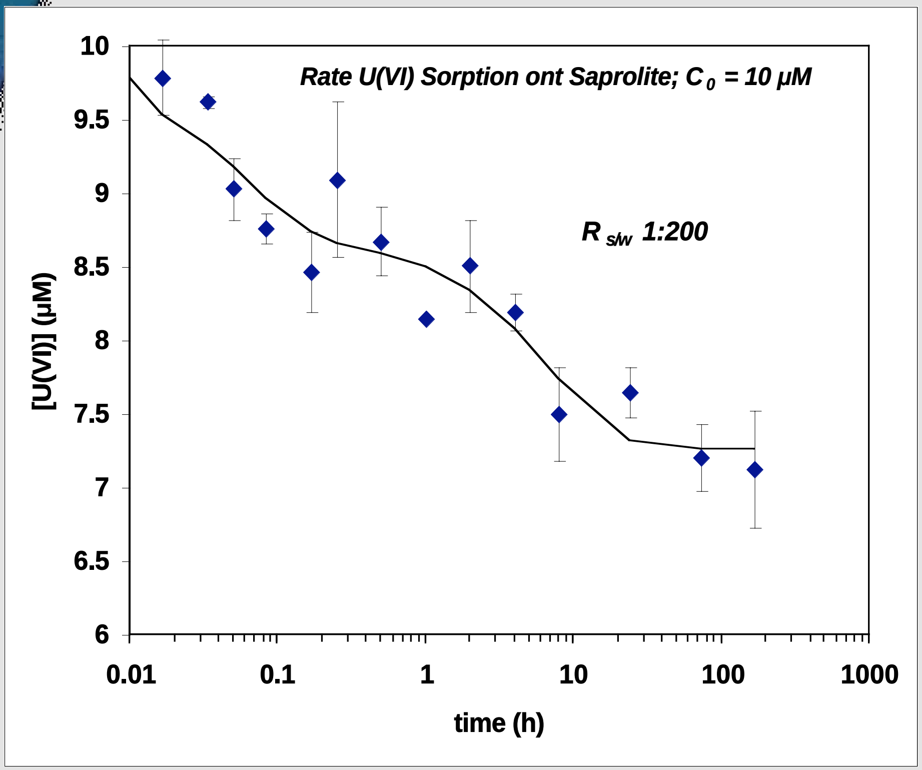
Batch U(VI) Sorption Studies
FRC Background Sediments

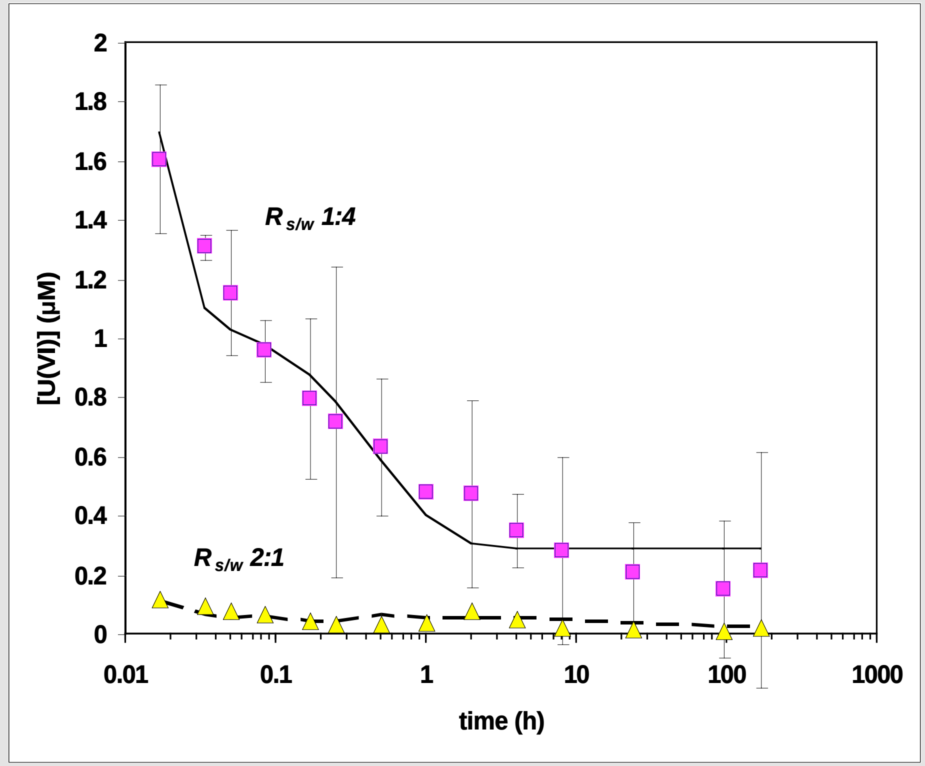




C_0 = 1 µM

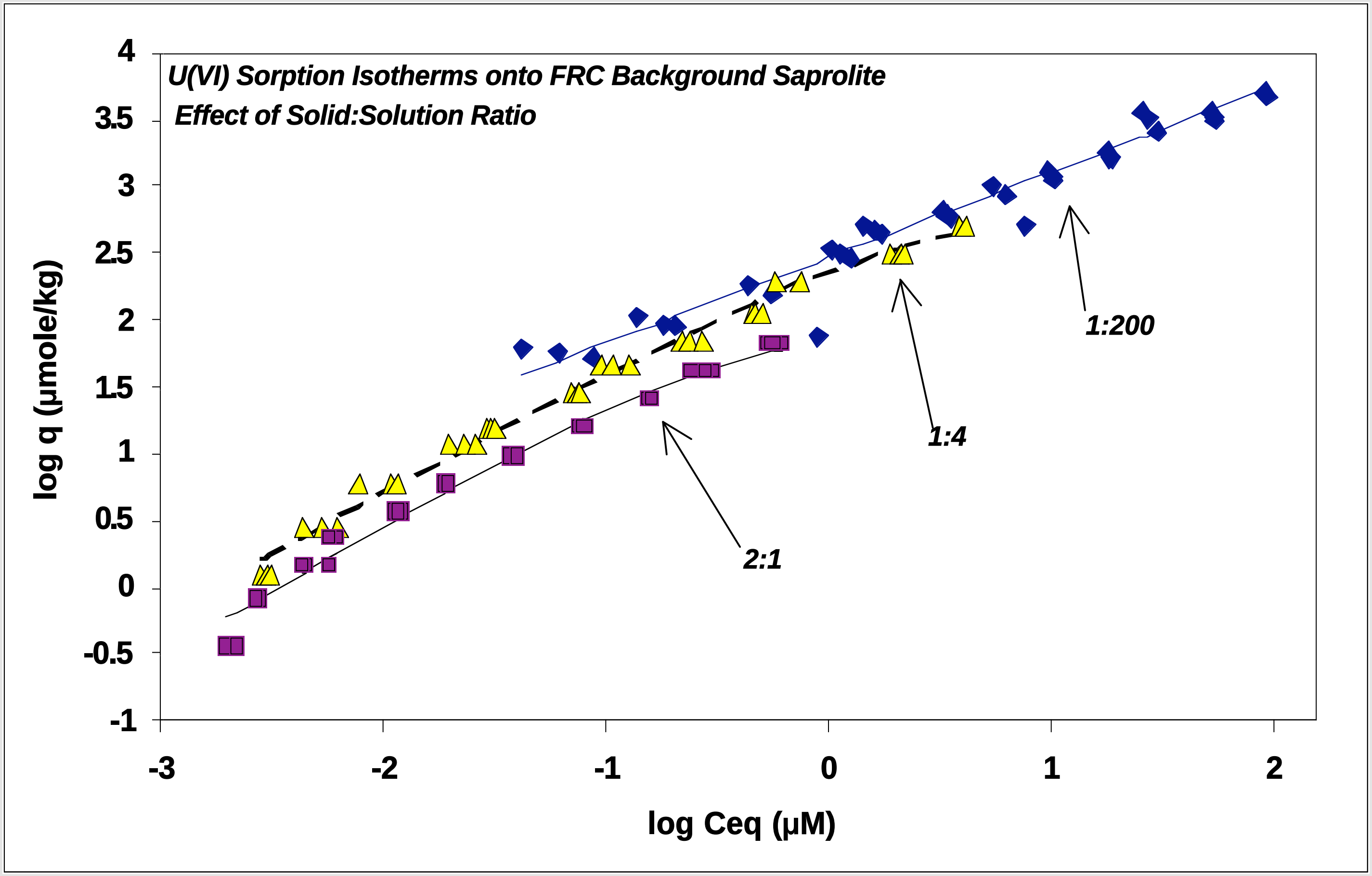
Batch U(VI) Sorption Studies
FRC Background Sediments



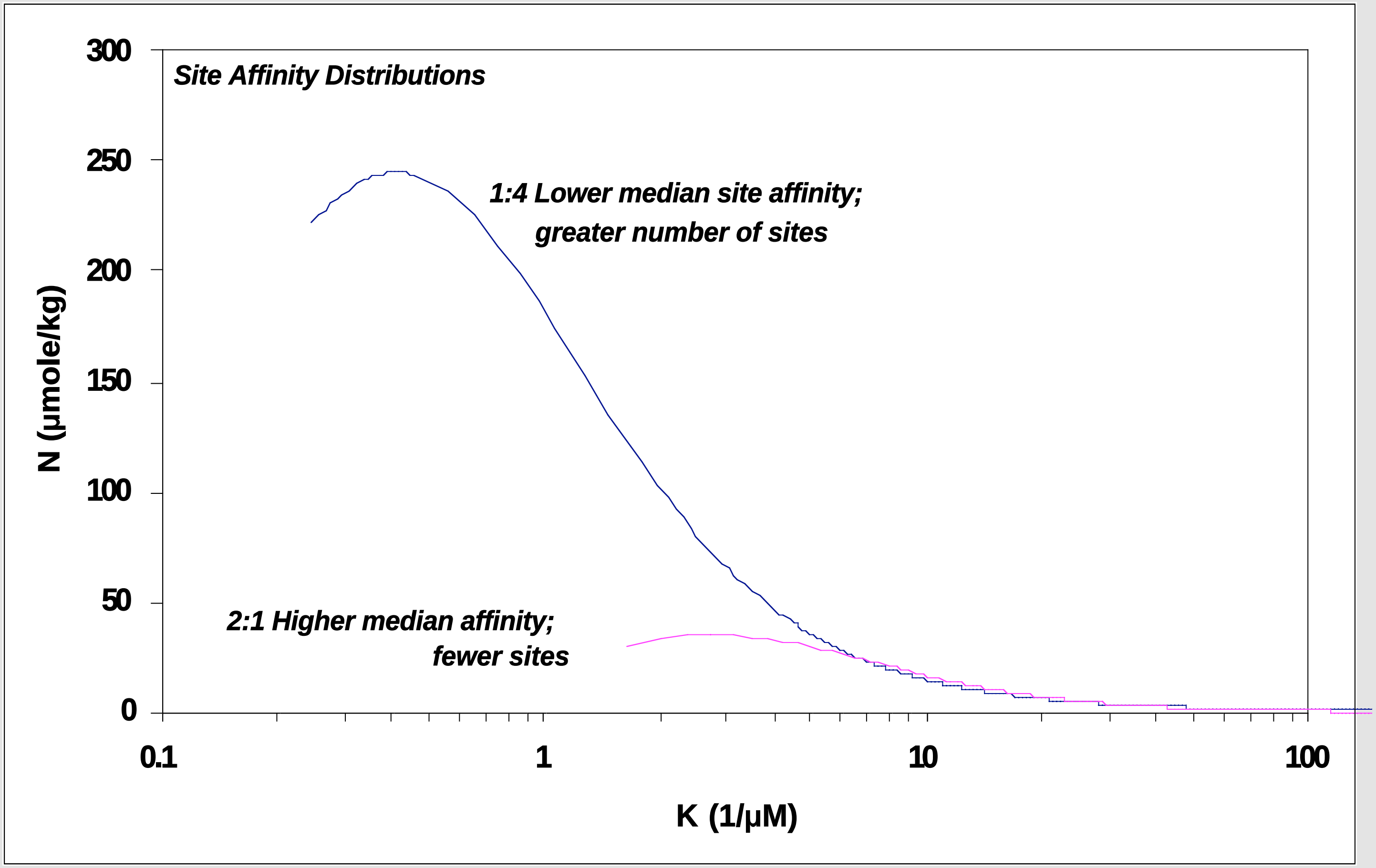


C_0 = 10 µM

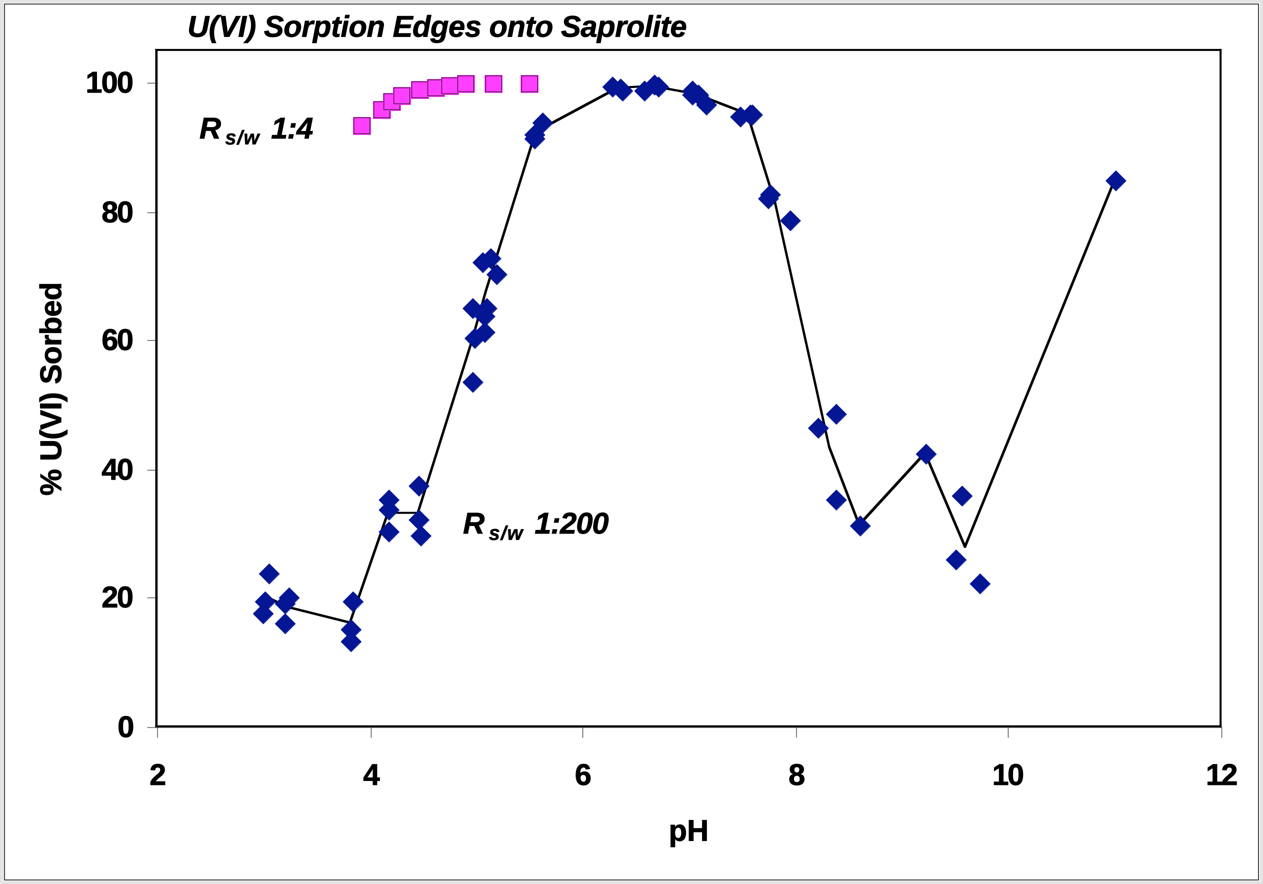
Effect of Solid:Solution Ratio
FRC Background Sediments



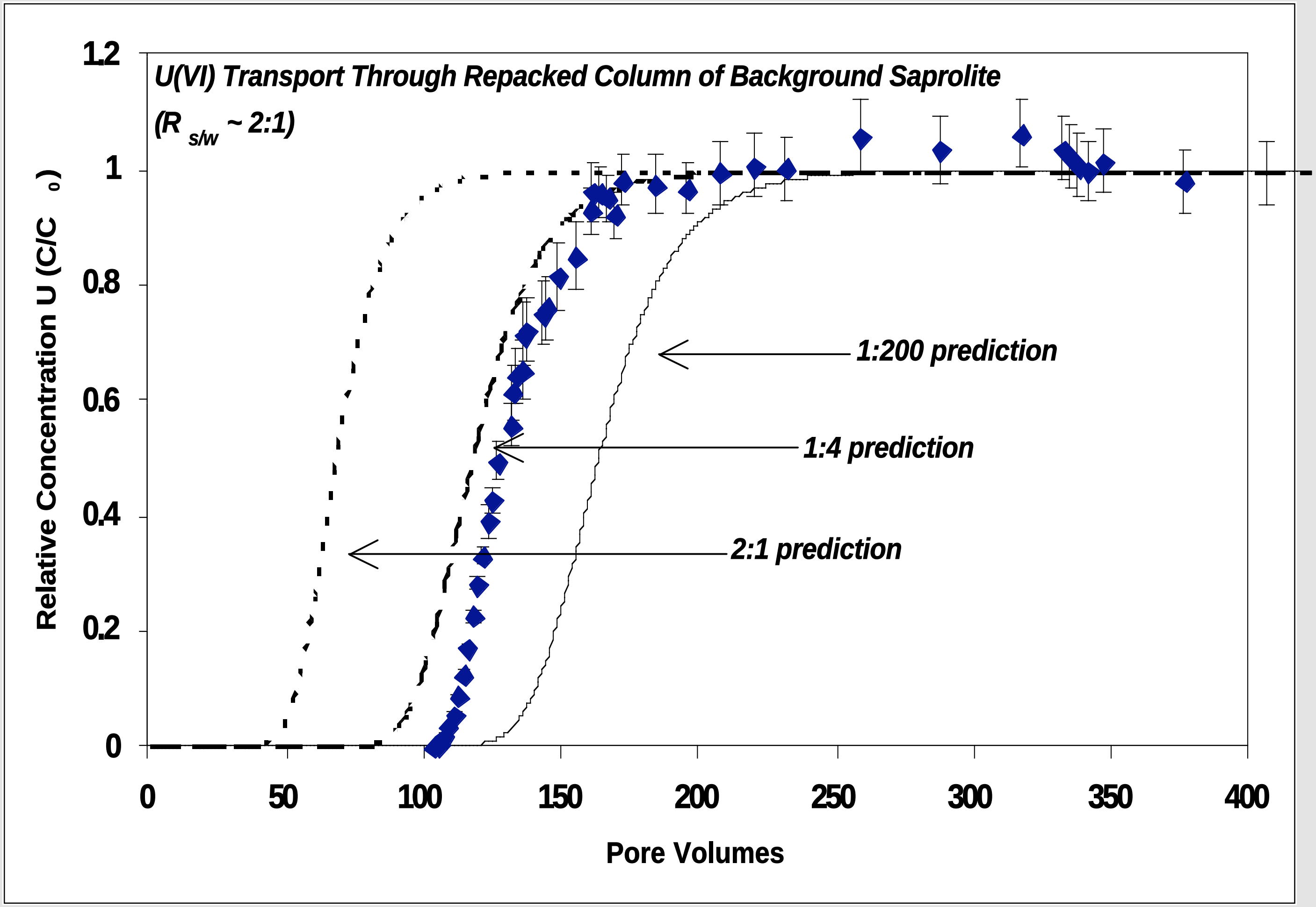
Site Affinity Distributions
Background Area Sediments



U(VI) Sorption Edges
Background Area Sediments

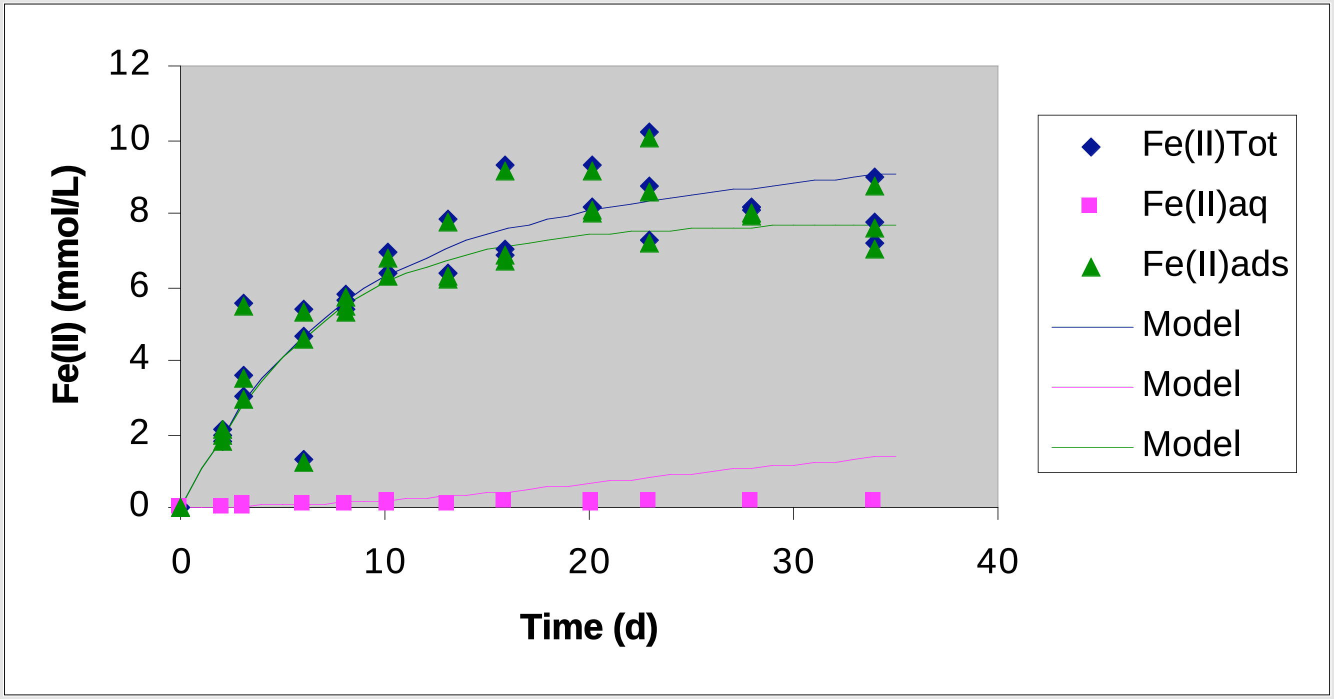


U(VI) Transport through Repacked Column
Background Area Sediments



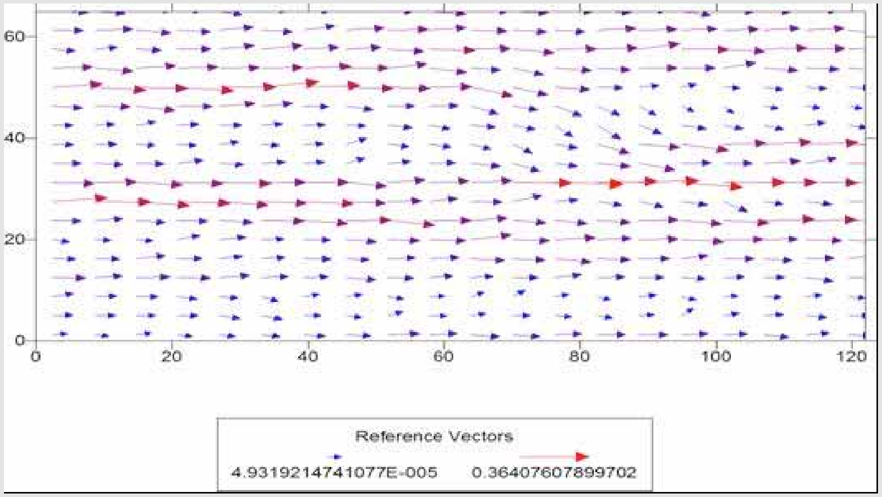
Numerical model application

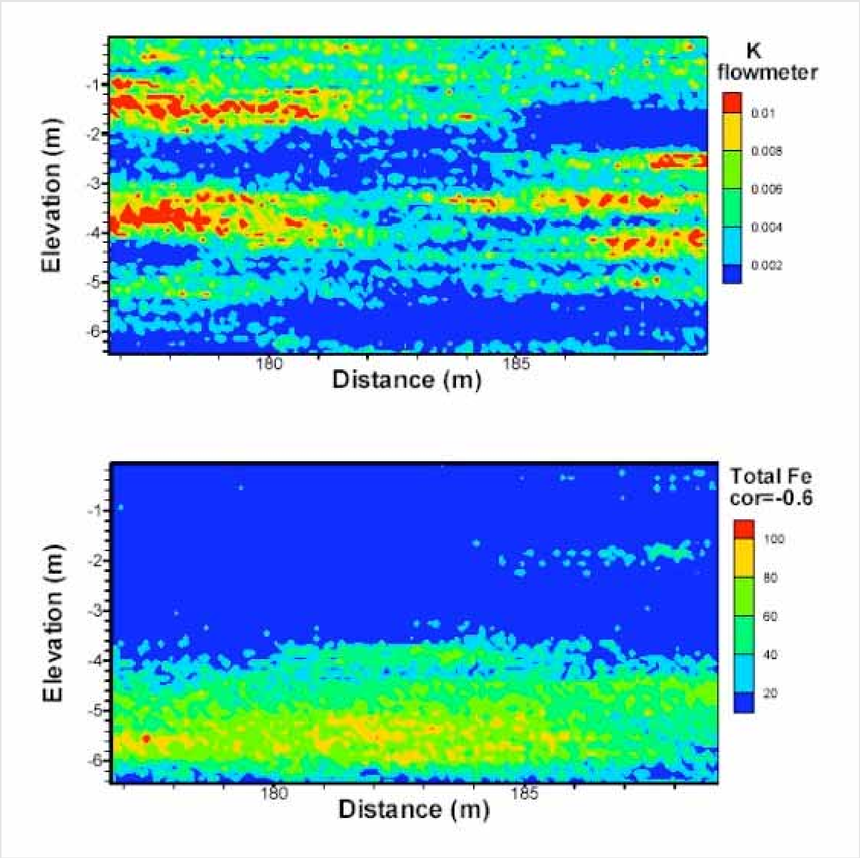
• Related NABIR research (Roden/Burgos) has developed reaction-based models of coupled iron(iii) oxide and U(VI) reduction kinetics including sorption of Fe(II) and U(VI) and site blocking.



Numerical Model Application

- We have developed a 2D simulation framework with heterogeneous aquifer properties.





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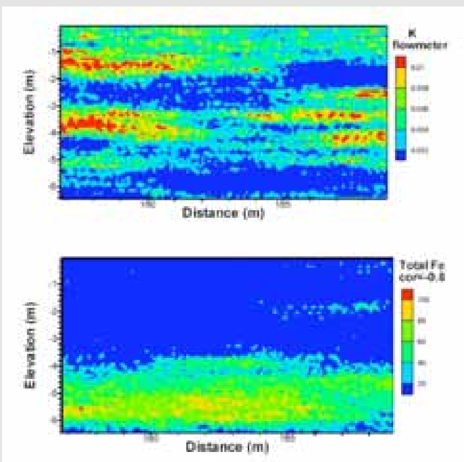
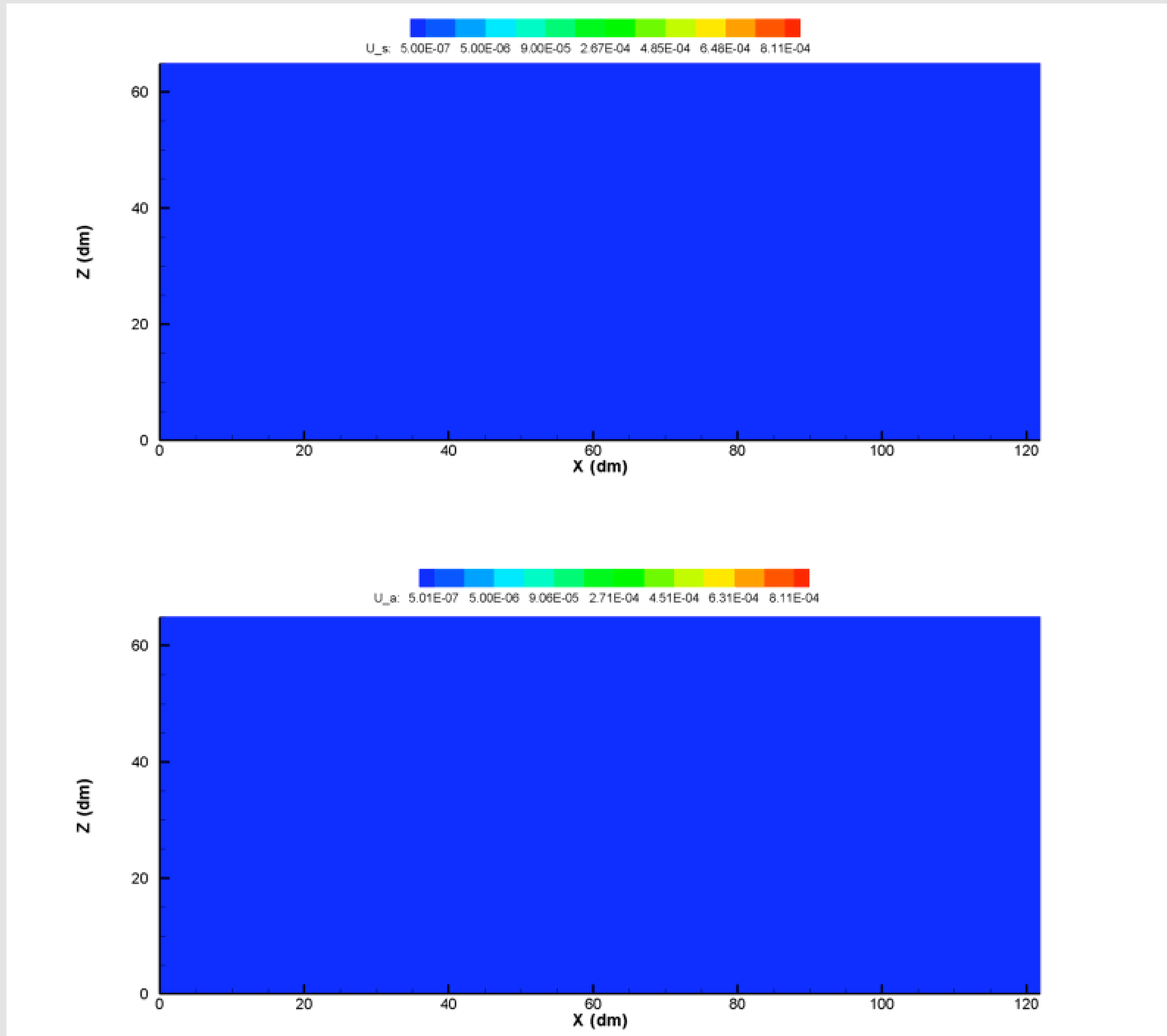
U(VI) Sorption – 1000 days

Sorbed U(VI)

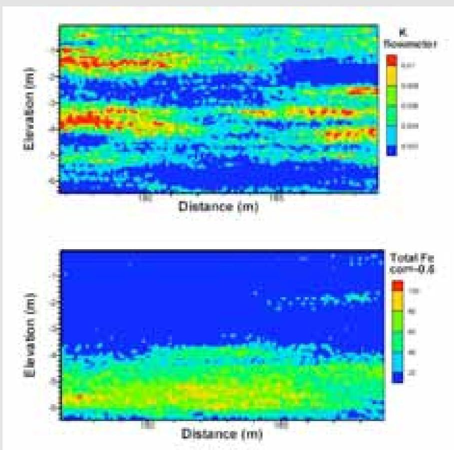


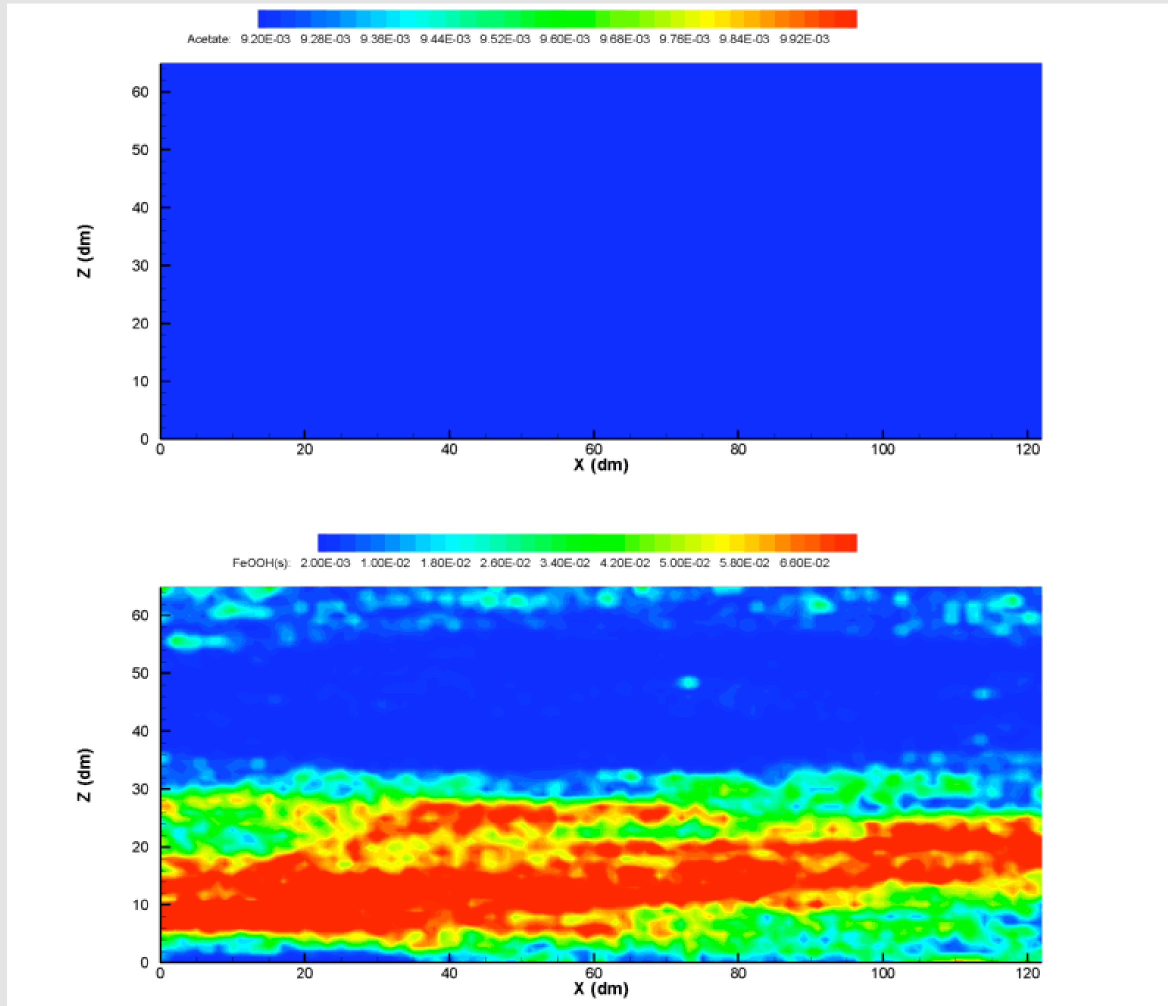


Aqueous U(VI)

Uranium and Iron Reduction

Acetate





$FeOOH_s$

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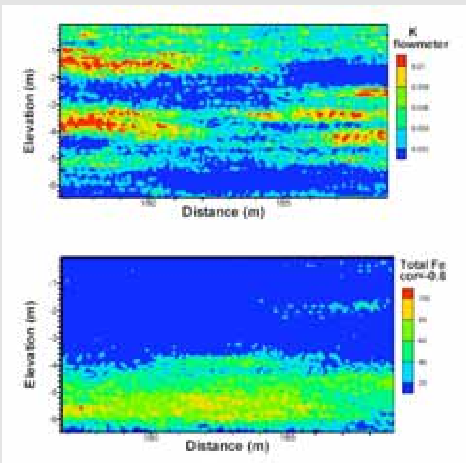
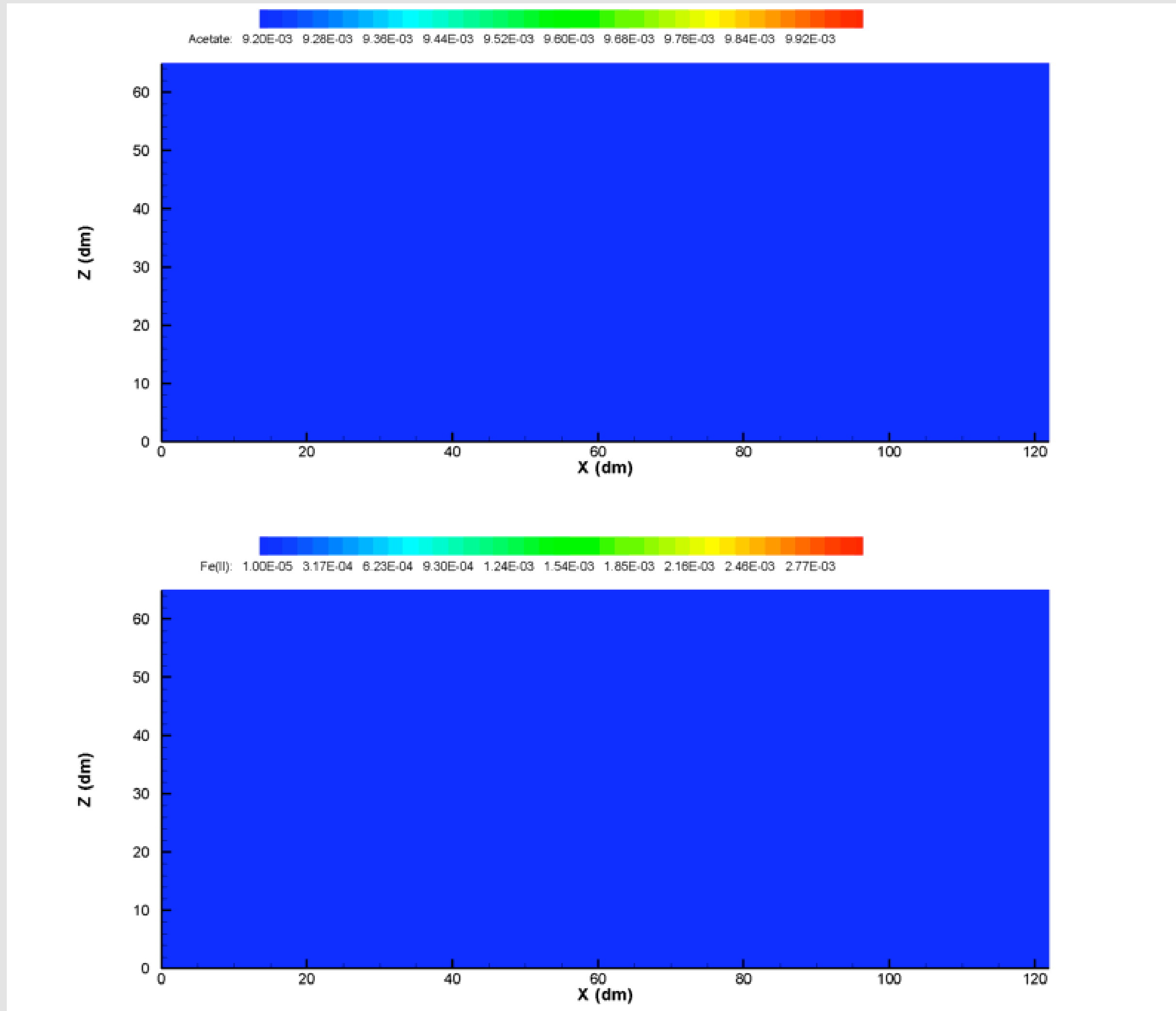
Uranium and Iron Reduction

Acetate

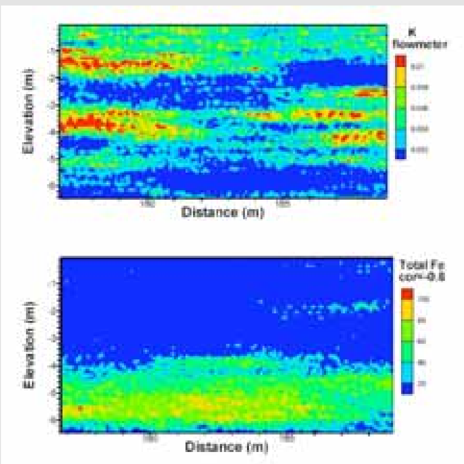


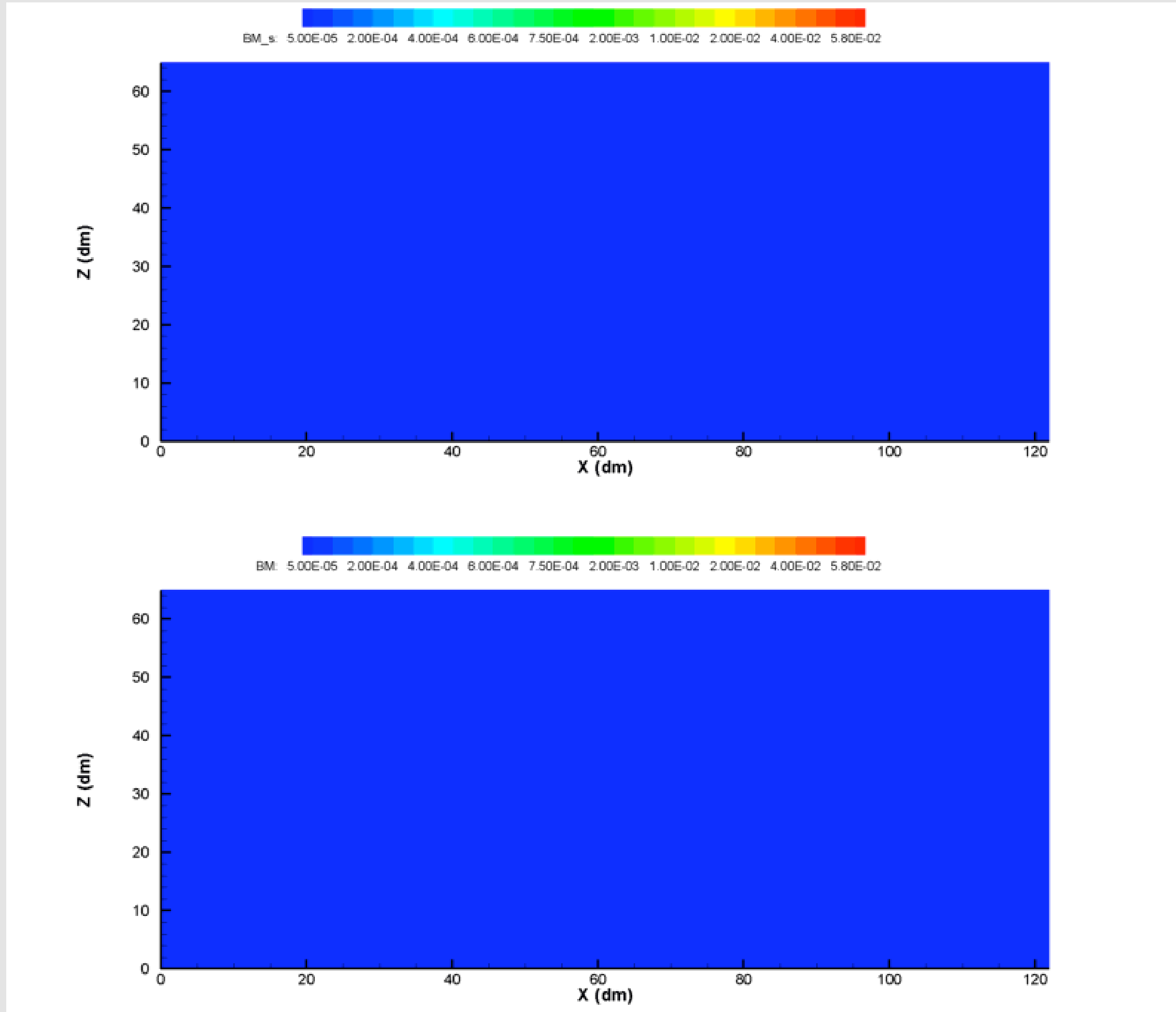


$Fe(II)_{aq}$

Uranium and Iron Reduction

Biomass$_s$



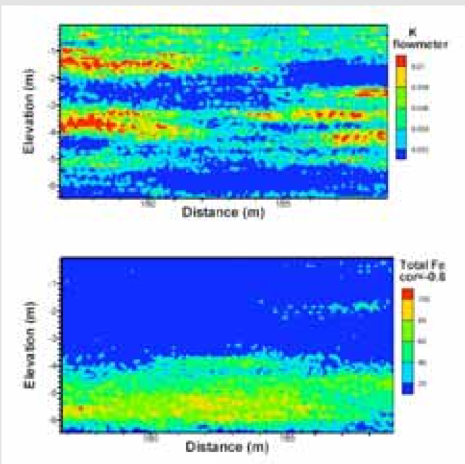


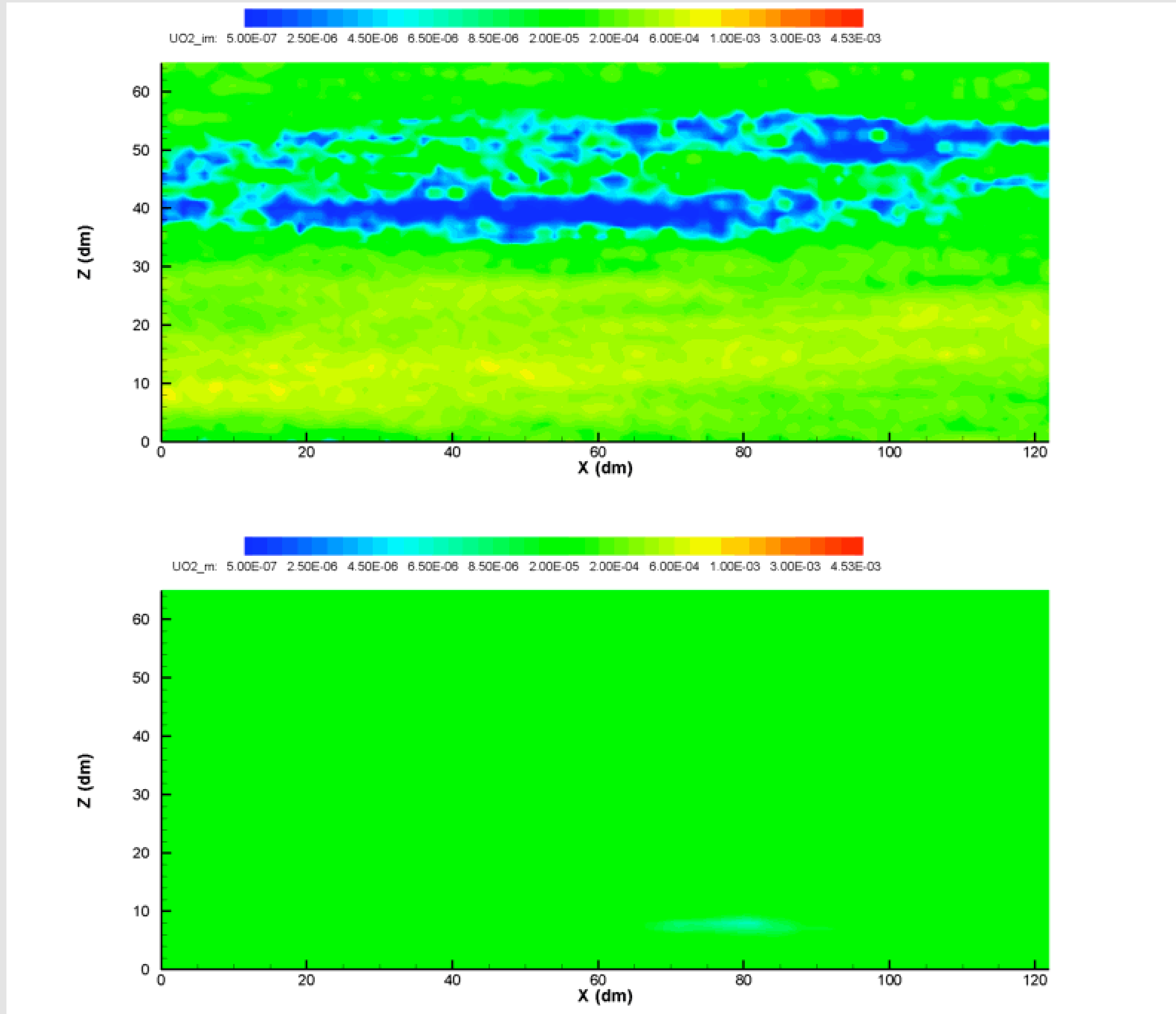
Biomass$_{aq}$

Uranium and Iron Reduction

$U_{immobile}$

(U(VI)sorbed + U(IV)solid)





$U(VI)_{aq}$

Next Steps

- Link fracture flow and reactive transport models
- Apply model to FRC site (Area 2)
- Incorporate site-specific heterogeneity information as it becomes available
- Use for field-scale experimental design

For More Information…

- **Project website (contact tim.scheibe@pnl.gov for access information)**
- **NABIR FRC website**
  (http://www.esd.ornl.gov/nabirfrc/)