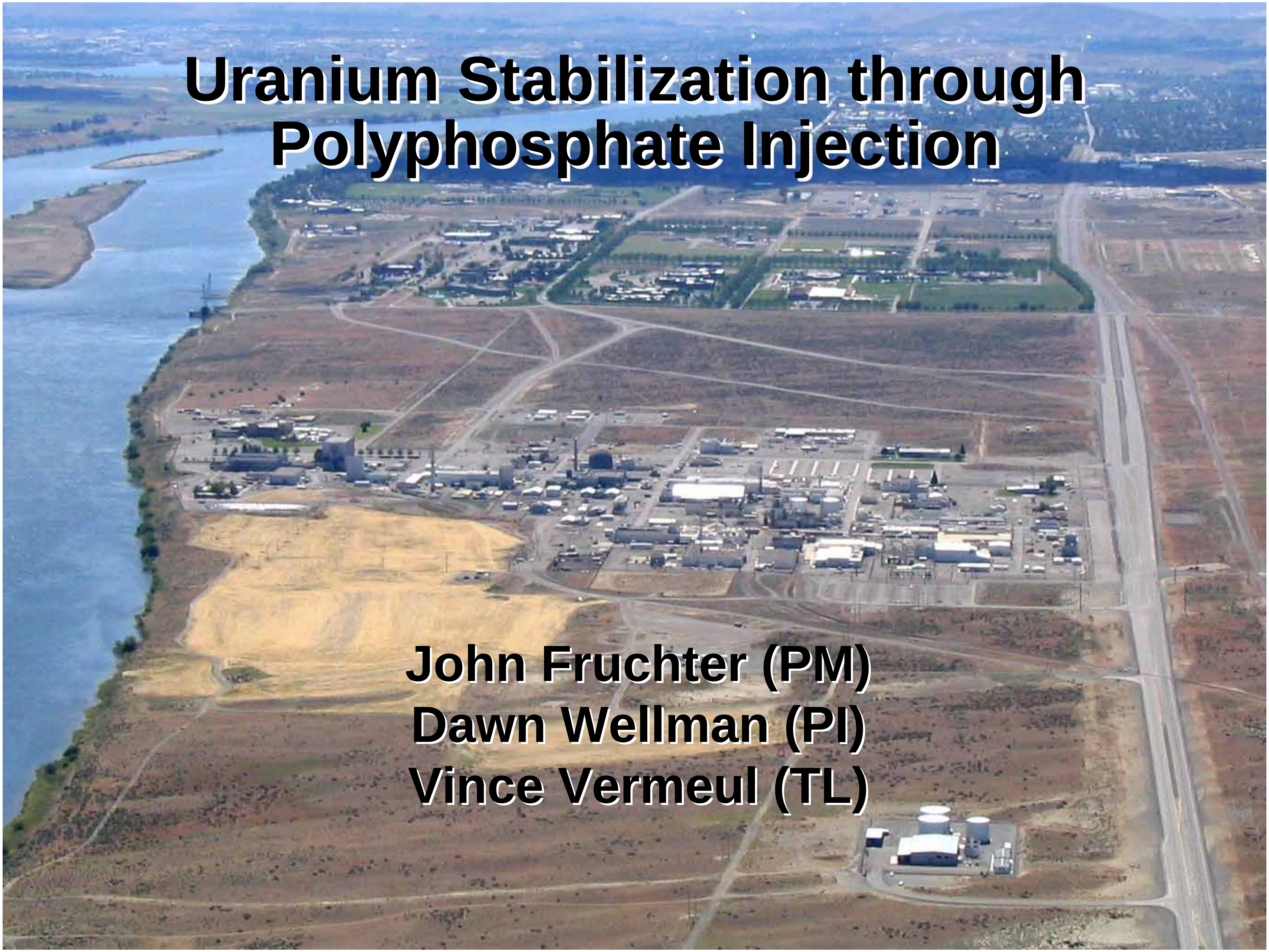
PNNL EM-22 Projects Status Report

John Fruchter

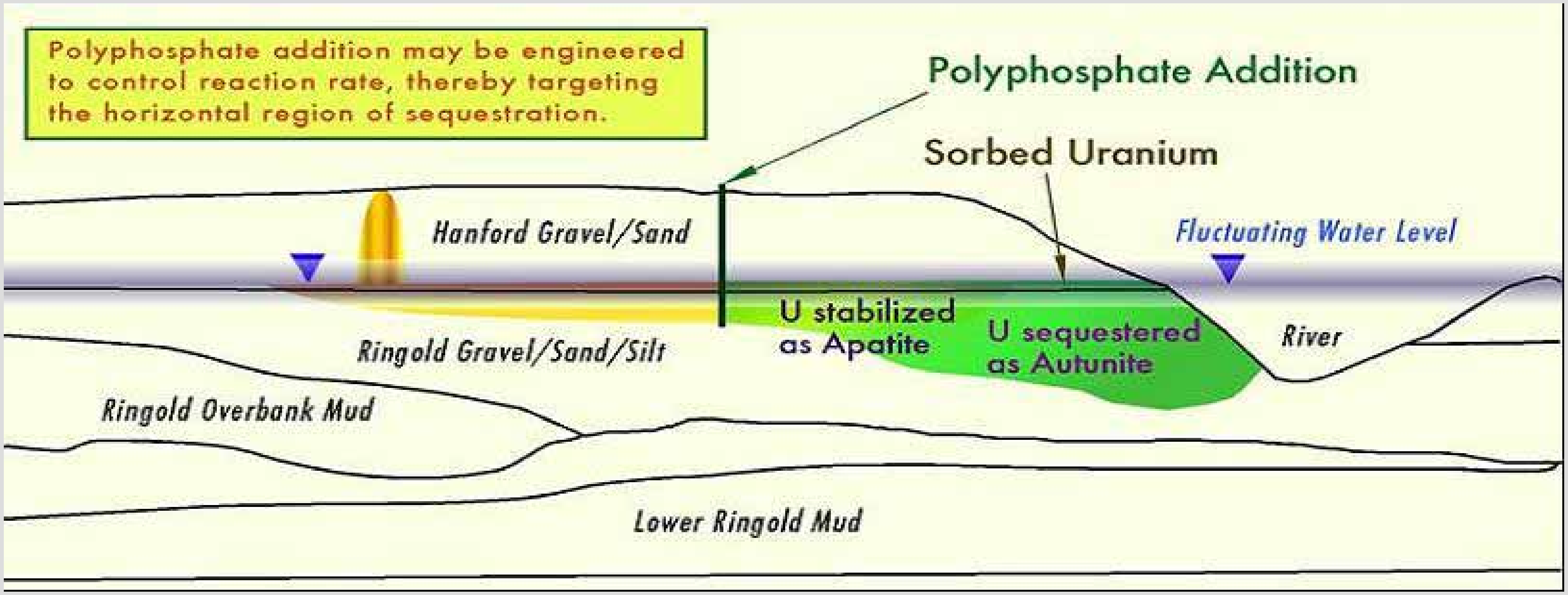
March 27, 2007



Uranium Stabilization through Polyphosphate Injection

John Fruchter (PM)
Dawn Wellman (PI)
Vince Vermeul (TL)

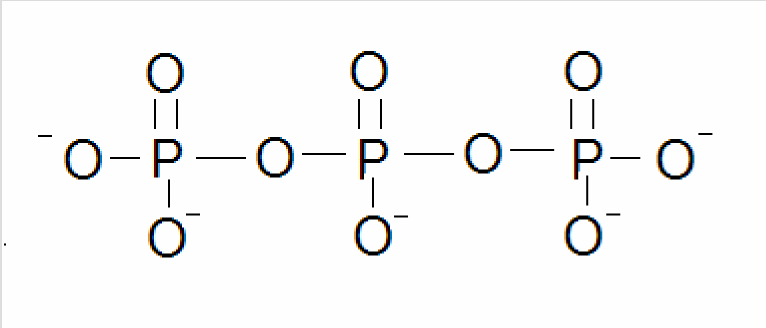
Deployment of Phosphate Amendment for In-Situ Immobilization of Uranium



- Injection of soluble polyphosphate
- Lateral plume treatment
- Uranyl phosphate mineral (autunite) formation
  - Immediate sequestration
- Apatite formation
  - Sorbent for uranium
  - Conversion to autunite
- Enhancement of MNA

Advantages of Polyphosphate Technology

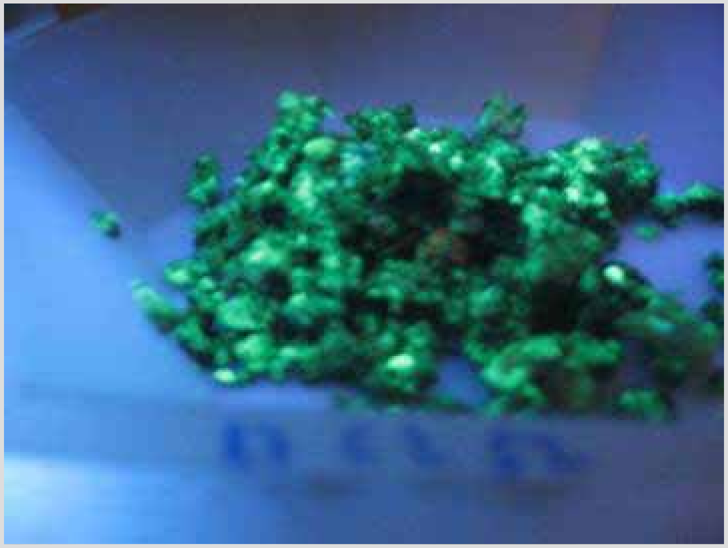
- Direct treatment of uranium
- Time release
  - Controllable kinetics based on to polymer length
- Provides immediate and long-term control of aqueous uranium

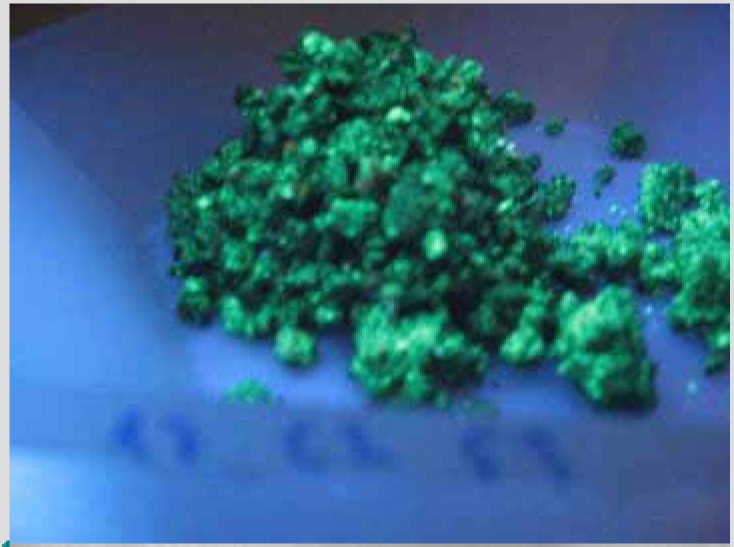


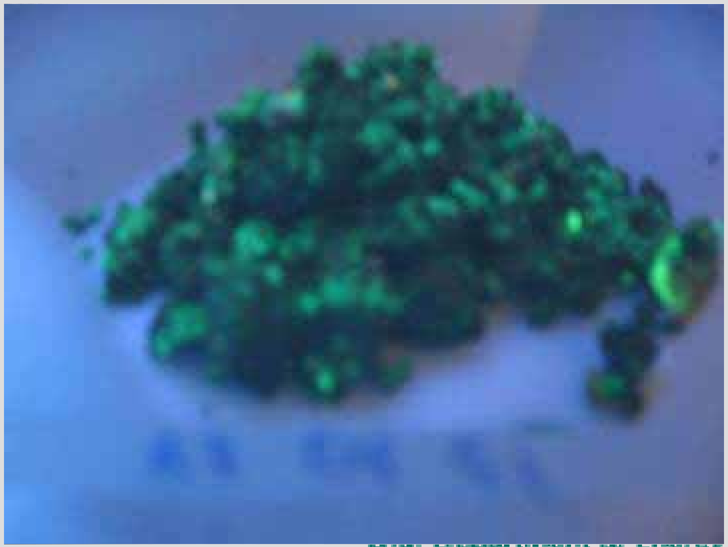
Amendment Formulation

- Phosphate
  - Tripolyphosphate
    - Sorbs to sedimentary material (calcite, Fe and Al oxide, clay)
    - Forms fine ppt. w/ Ca
  - Orthophosphate
    - Sorbs to sediment bound polyphosphate complexes increasing rate and degree of precipitation
  - Pyrophosphate
    - Forms heavy, fast settling ppt. w/ Ca
- Calcium

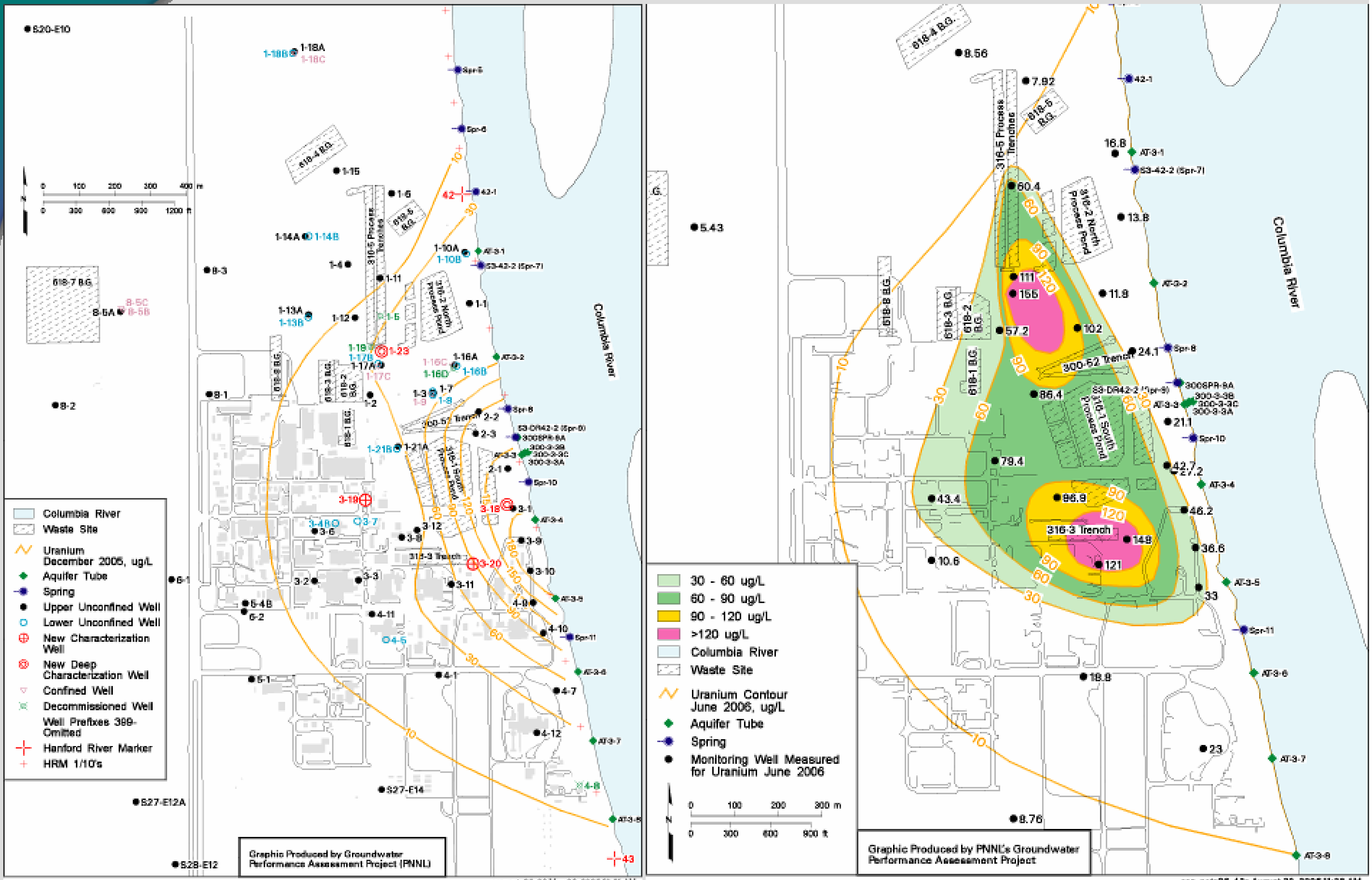
Post-Test Preliminary Analysis



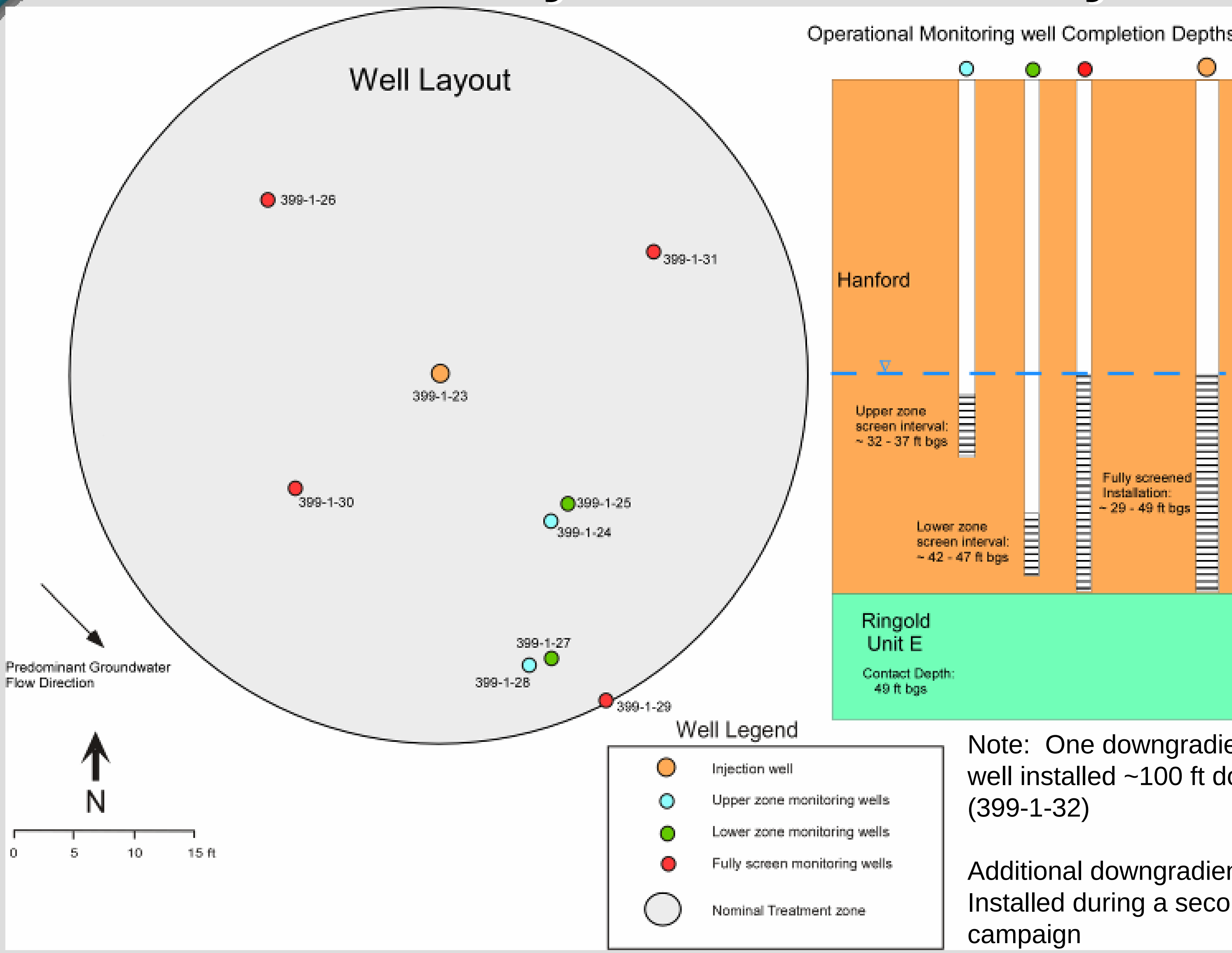




Treatability Test Site Location



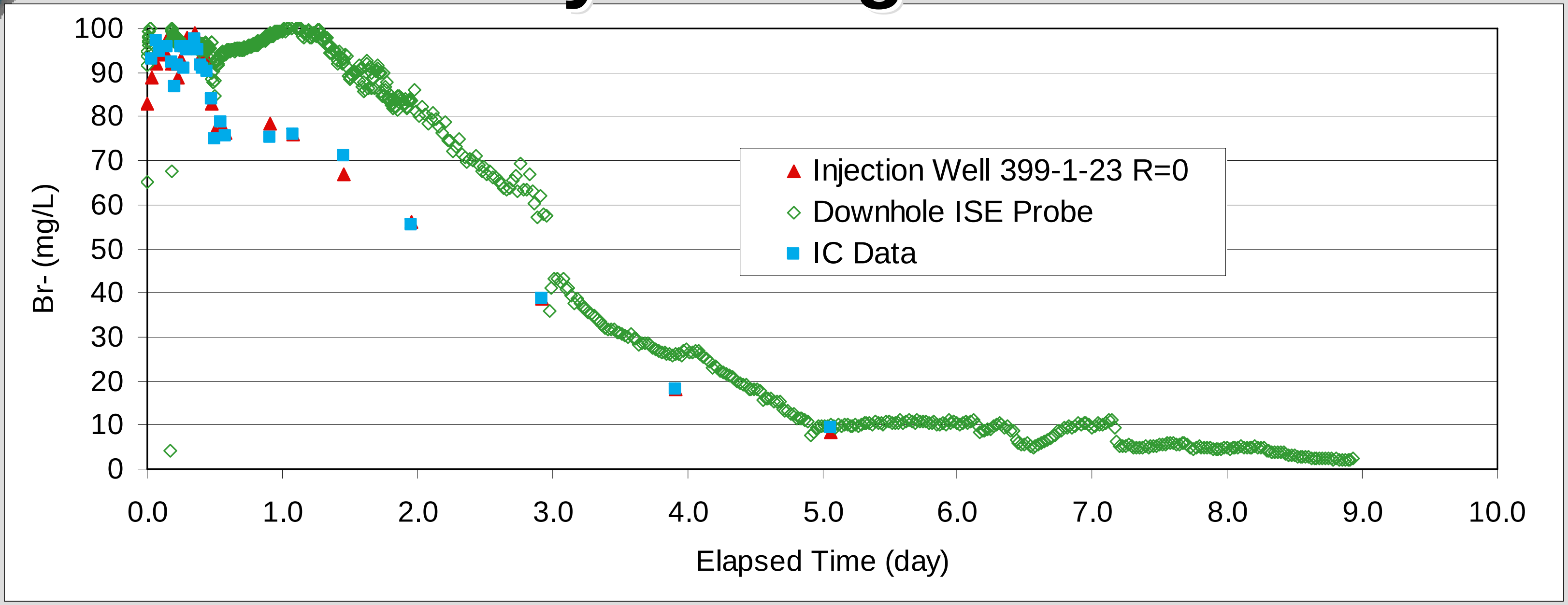
Treatability Test Site Well Layout

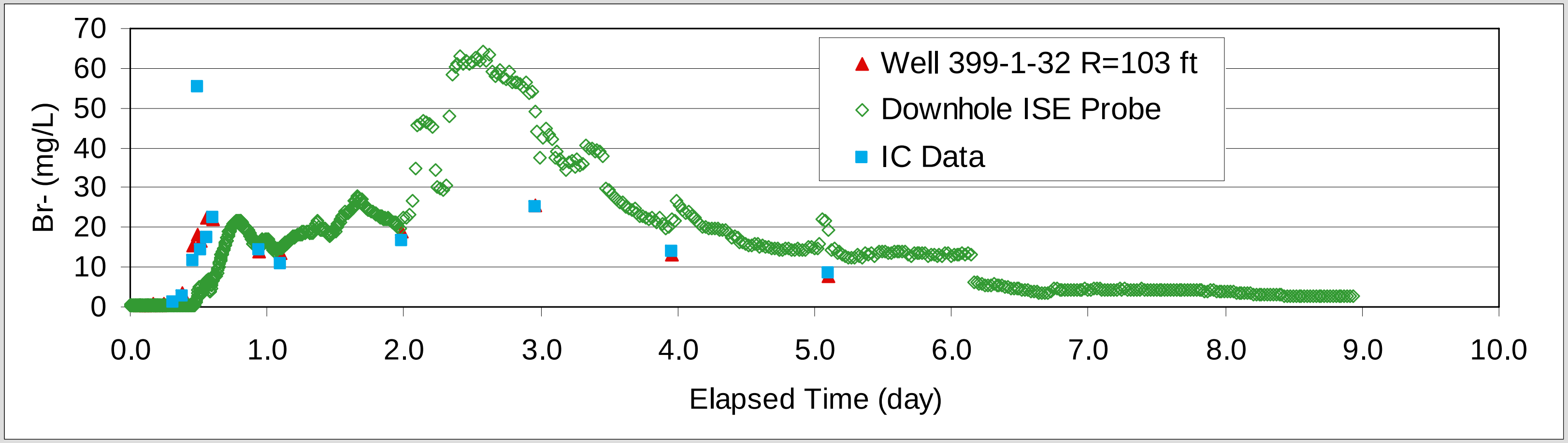


Note: One downgradient monitoring well installed ~100 ft downgradient (399-1-32)

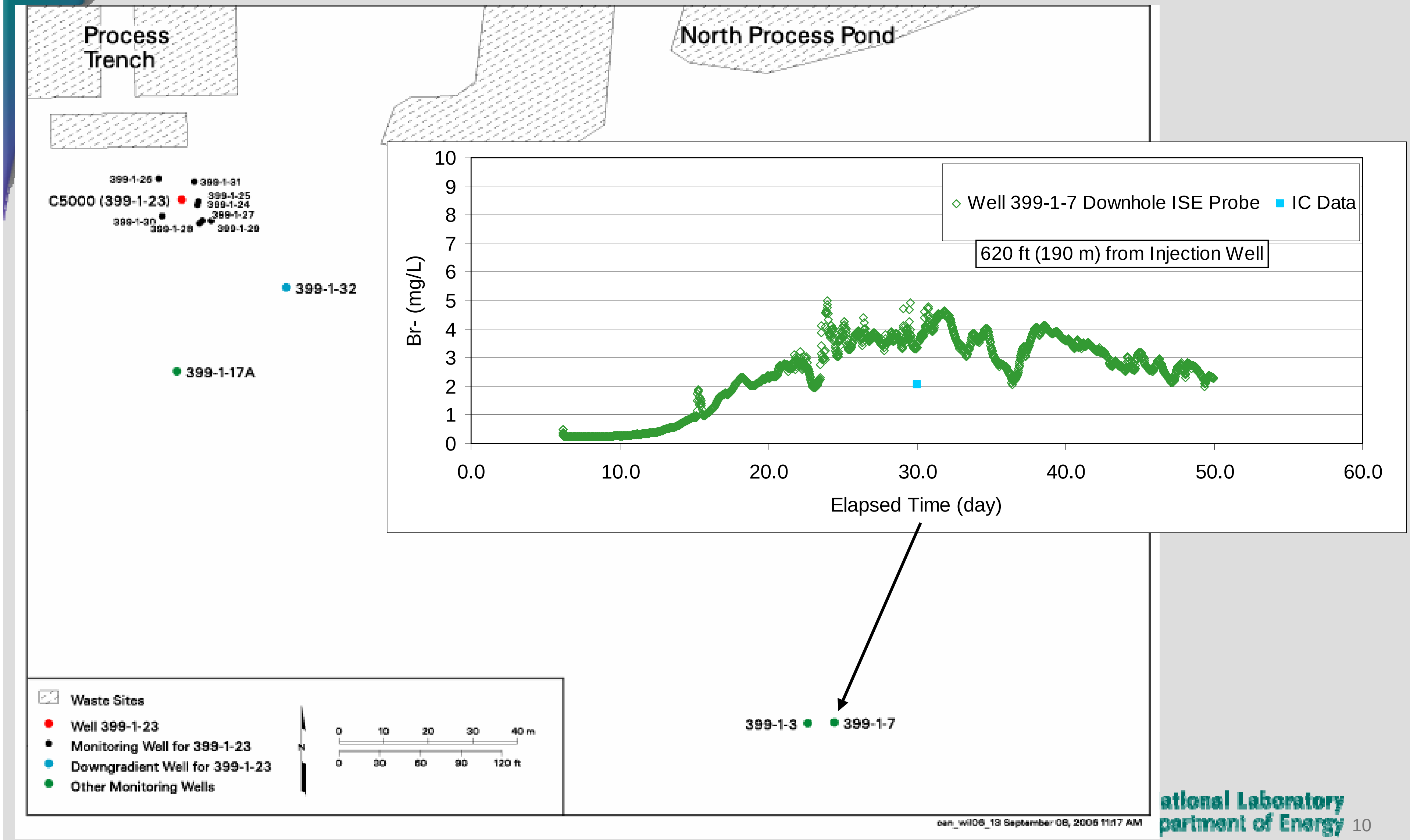
Additional downgradient wells will be Installed during a second drilling campaign

Tracer Test Results – Injection Well and Primary Downgradient Well





Tracer Results for Downgradient Well 399-1-7 (190 m SE from injection well)



Polyphosphate Injection to Treat Uranium at the 300 Area

- Field-scale tracer injection test conducted December 2006. Evaluation of site-specific characterization data and design analysis for the polyphosphate injection test are ongoing.
- Selection of amendment formulation is nearing completion. Larger-scale column studies to assess amendment transport are ongoing.
- Field-scale polyphosphate injection test scheduled for June, 2007 (during high water-table conditions)

300 Area Vadose and Smear Zone

- Evaluate polyphosphate remediation technology for both direct stabilization of uranium within the deep vadose and smear zones and long-term reduction in aqueous uranium flux to the underlying aquifer
  - Effects of unsaturated conditions on the precipitation kinetics of autunite and apatite
  - Stability of normally hydrated minerals, namely autunite, under unsaturated conditions
  - Effect of phosphate on uranium co-precipitated with calcite

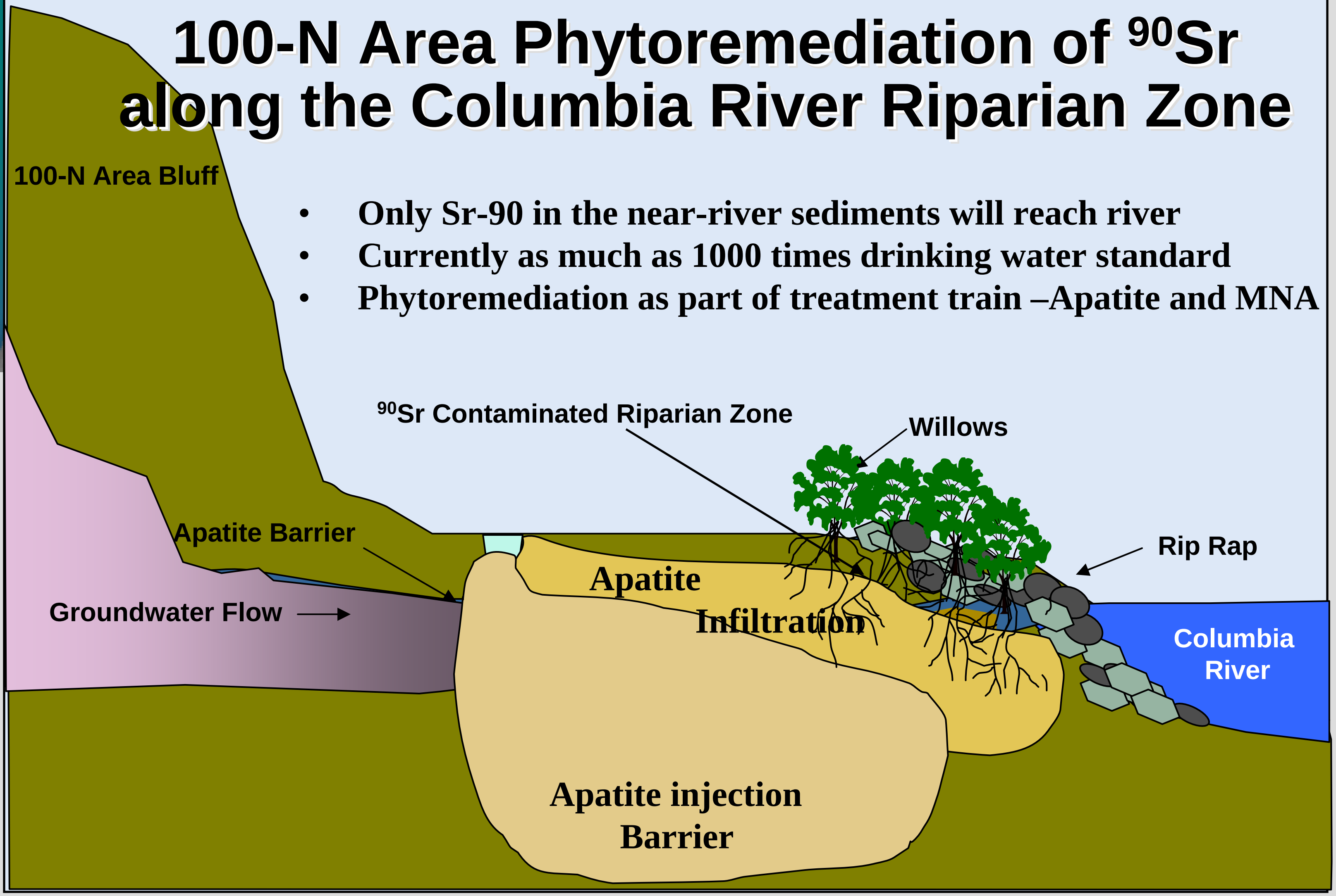
100-N Area Strontium-90 Treatability Demonstration Project: Phytoremediation Along the 100-N Columbia River Riparian Zone

C. C. Ainsworth - Geochemistry

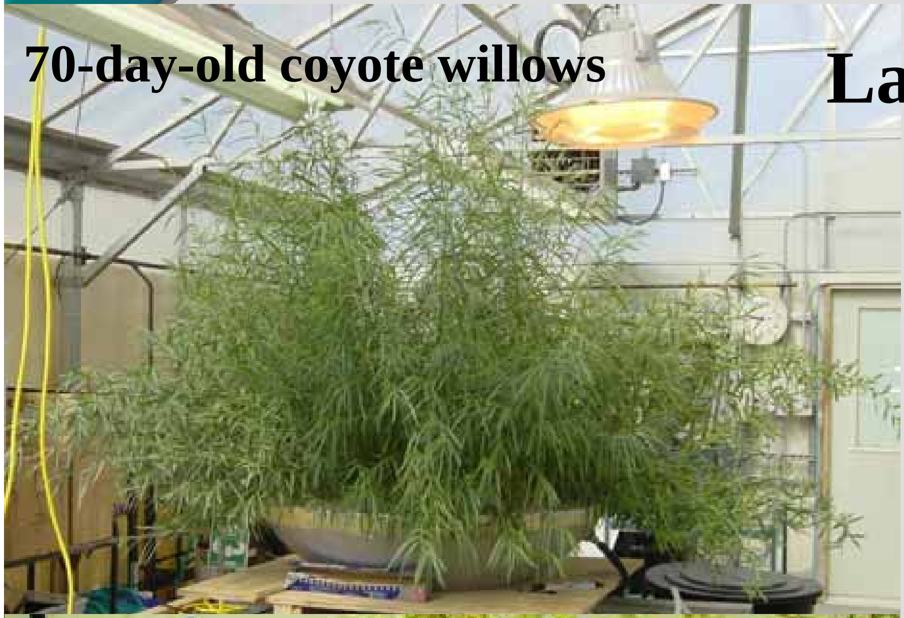
R. J. Fellows – Plant Physiology

100-N Area Phytoremediation of ^{90}Sr along the Columbia River Riparian Zone

- **Only Sr-90 in the near-river sediments will reach river**
- **Currently as much as 1000 times drinking water standard**
- **Phytoremediation as part of treatment train –Apatite and MNA**



100-N ^{90}Sr Remediation – Conclusions



Laboratory Studies – FY 04

- **Hydroponic studies**
  - ✓ No significant differentiation of Ca and Sr uptake by willows
  - ✓ No Sr – ^{90}Sr differentiation
- **Willow extraction of ^{90}Sr from contaminated 100-N soil**
  - ✓ Extraction - 0.065 nCi/g
  - ✓ Estimated to be 0.39 nCi/g
- **FY-04 studies indicate that:** Coyote willow phytoremediation is a viable option.

Demonstration of 100-N Area Phytoremediation of ^{90}Sr

❖ Effort (FY06-FY08)

- Management practices – optimize biomass production and ^{90}Sr removal (6 mo. FY06)
  - Fertility practices – greenhouse – Completed 11/01/07
- Control of off-site transport (FY06 – FY08)
  - Different harvesting strategies (biannual), Barriers
  - Demonstration plot – 100-N riparian zone
- Biomass production in natural environment (FY06 – FY08)
- Impact on pore water and ground water (FY06 – FY08)
  - Aquifer tube sampling through growing season
  - Soil sampling of root zone

100-K Area Phytoremediation Test Site

Placing Plants

Root Initials on Stake

Completed Planting

Phytoremediation to Treat Strontium-90 at 100-N Area

- Phytoremediation enclosure completed at the 100-K Area.
- Ground preparation completed.
- 60 Coyote Willow stakes planted and fertilized.

Proposed Project Enhancements

Suggested by Review Committee

Potential for Food-Chain Interactions

- Engineered barriers and management practices will prevent intrusion of large animal herbivores and off-site transfer of plant detritus but will have limited effect on mobile phytophagous insects. Pesticide application is not acceptable given the proximity of the Columbia.

- Three major means resident and transitory insects may accumulate ^{90}Sr:
  - consumption of pollen - obviated by harvesting prior to flowering
  - consumption of sap - aphids
  - consumption of the foliage and tender shoots - moths and grasshoppers

- The objective of this task is to evaluate the potential for contamination of insects that may consume plant material grown in soils contaminated with ^{90}Sr.

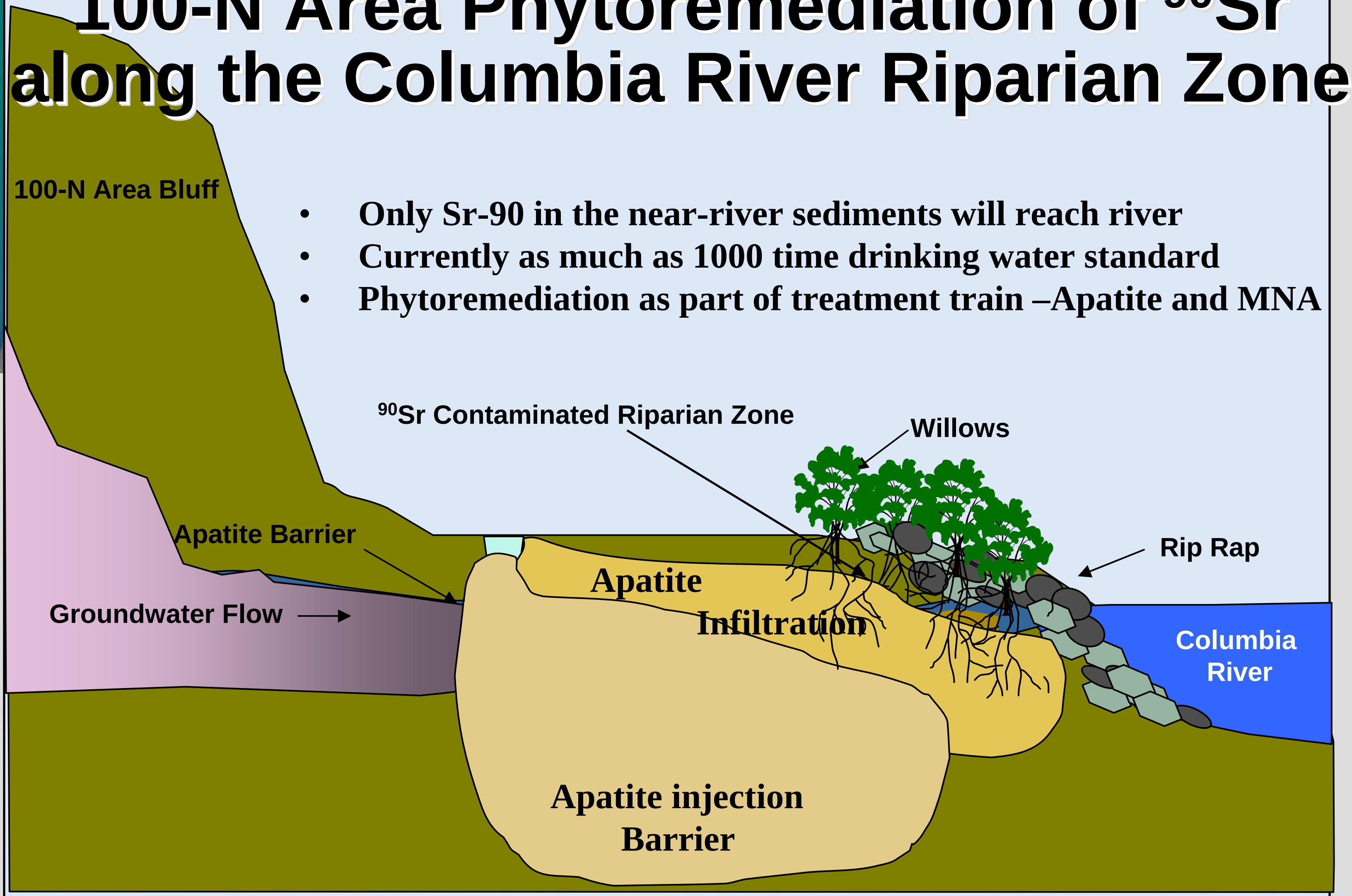
Strontium-90 Immobilization by Apatite: Emplaced by Infiltration

John Fruchter, Jim Szecsody, Carolyn Burns, Mark Rockhold, Mart Oostrom (PNNL)

Bob Moore (Sandia National Lab)

100-N Area Phytoremediation of ^{90}Sr along the Columbia River Riparian Zone

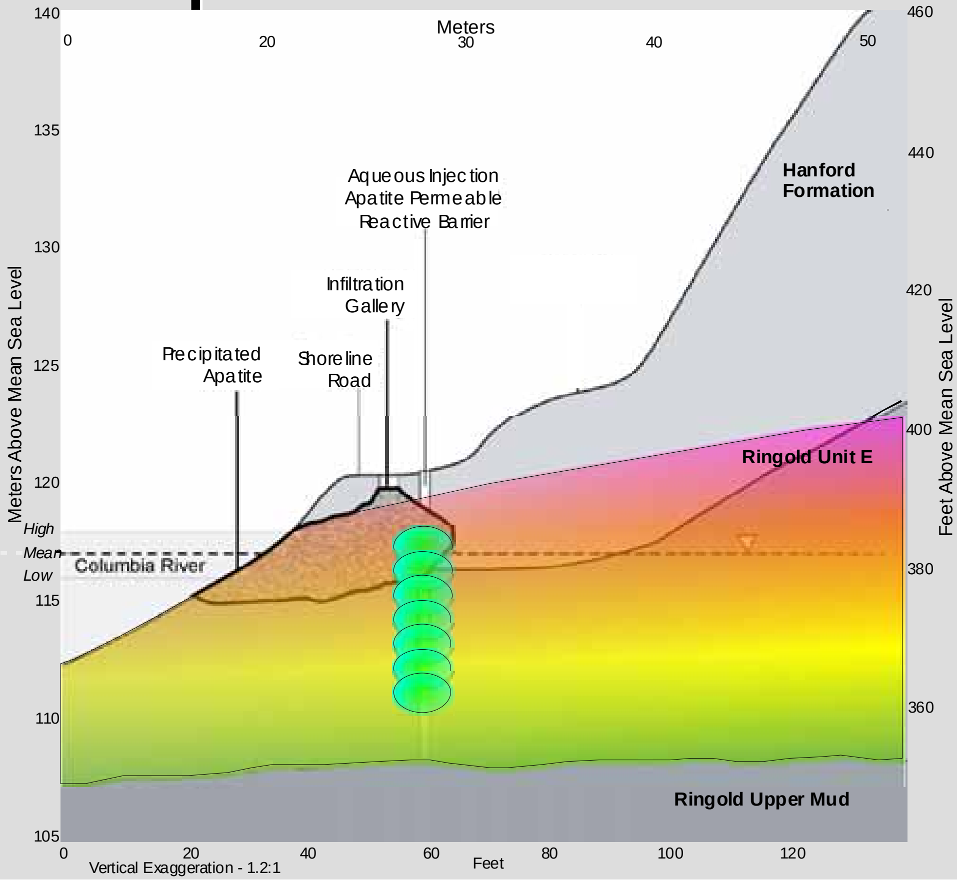
- Only Sr-90 in the near-river sediments will reach river
- Currently as much as 1000 time drinking water standard
- Phytoremediation as part of treatment train –Apatite and MNA

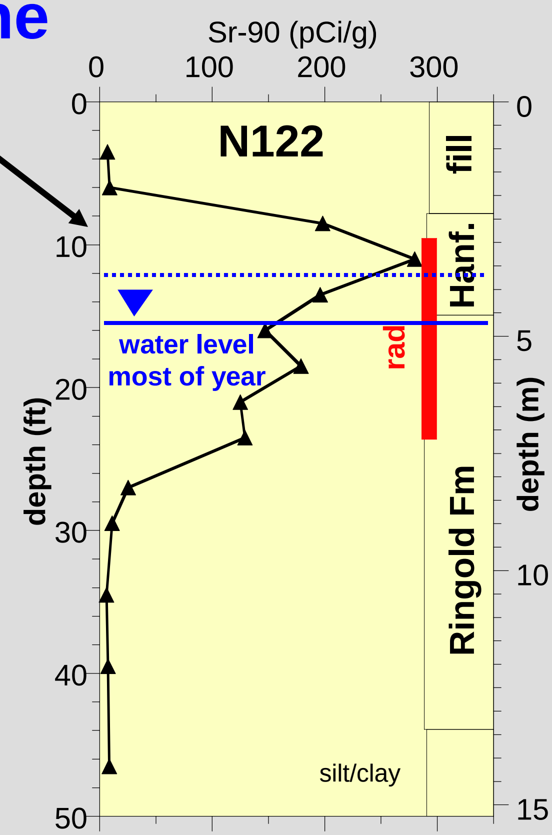


100-N Area Need for Sr-90 Immobilization

- **Need for apatite placement in vadose zone at low river stage (30-70% of Sr-90)**

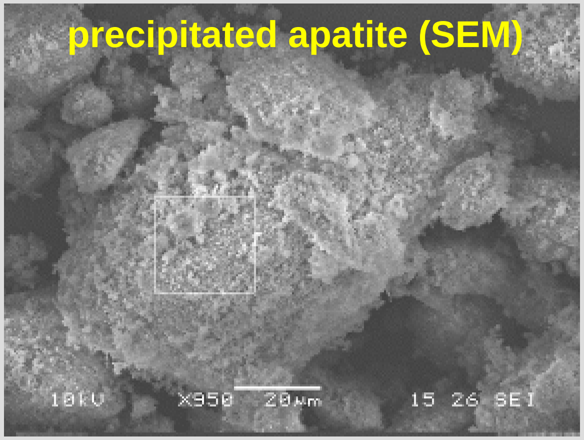
- **Develop infiltration strategy to achieve uniform apatite distribution**



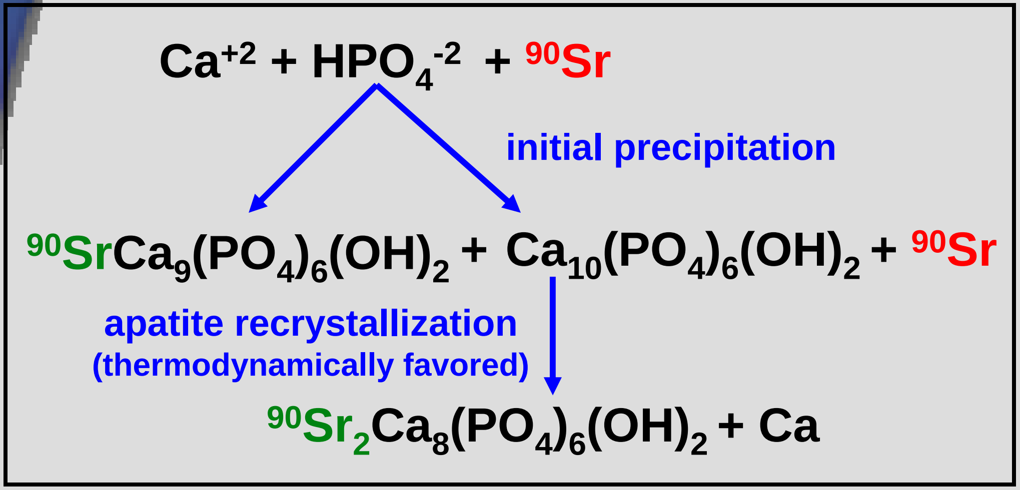


Summary: Sr-90 Immobilization by Apatite Emplaced by Solution Infiltration

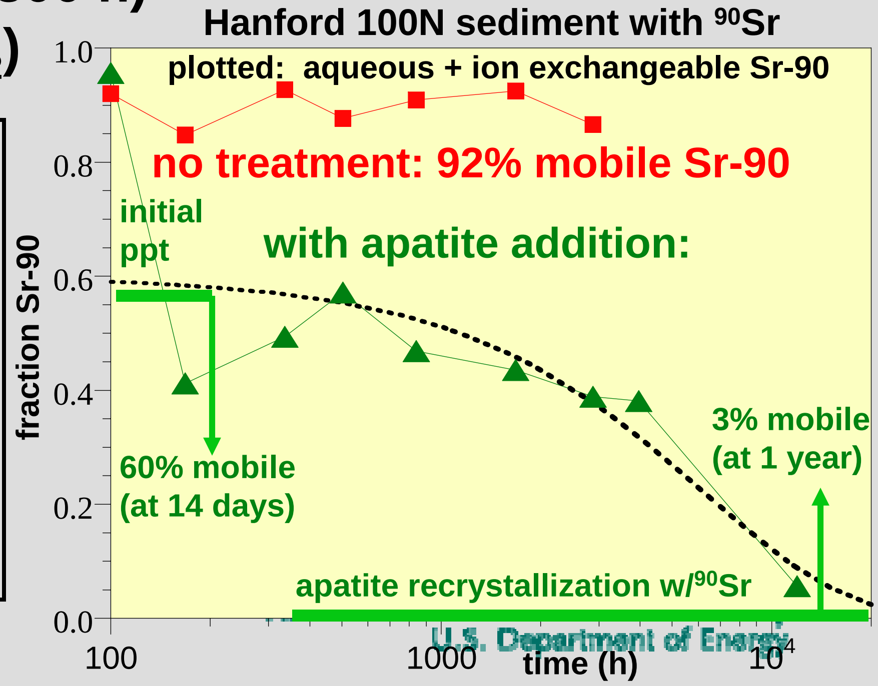
1. Infiltration of a Ca-citrate-PO_4 solution at low water saturation will biodegrade citrate, so apatite forms (previously only injected in aquifers)



2. Apatite removes Sr-90 by two processes:
   - during initial apatite precipitation (<300 h)
   - during recrystallization (72-180 d $t_{1/2}$)



Ca/Sr-apatite is extremely insoluble



Task 5: Scaleup to 2-D Infiltration of Solution

Objectives:

1. Measure apatite solution infiltration in (a) homogeneous, and (b) layered system and resulting apatite spatial distribution.
2. Modify solution composition and/or infiltration rate to achieve a more uniform apatite distribution (example: faster infiltration to infiltrate past low-K layer)

Plan: homogeneous 2-D exp. (late FY07)
layered 2-D exp. (FY08)

2-D experimental system at PNNL/EMSL:

- Automated dual gamma system for tracking of infiltrating plume nonintrusively
- Aqueous sampling during experiment to measure citrate biodegradation rate
- Sediment sampling and electron microprobe analysis to measure apatite precipitate

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Progress to Date

- **Basic concept works:**
  - **- Citrate biodegrades to CO_2 over a wide variety of biomass**
  - **- Sr-90 sorbs by ion exchange**
  - **- Sr-90 is incorporated into apatite (in initial ppt, slow incorp.) (at least 10% substitution for Ca)**

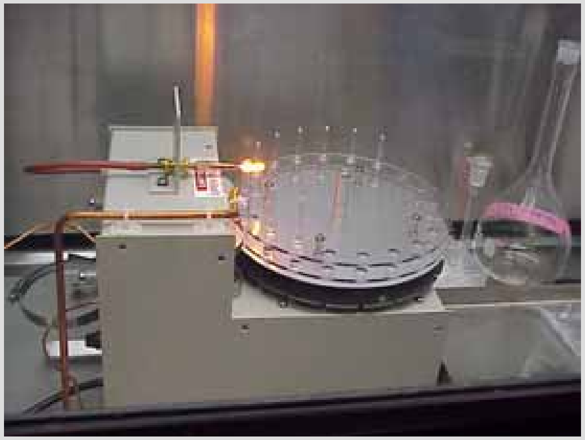
- **Sr-90 incorporation rate into apatite slower at high ionic strength (spent apatite solution will advect out of system in field):**
  - **- 72 day half life (in groundwater)**
  - **- 180 d half-life (in spent apatite solution)**

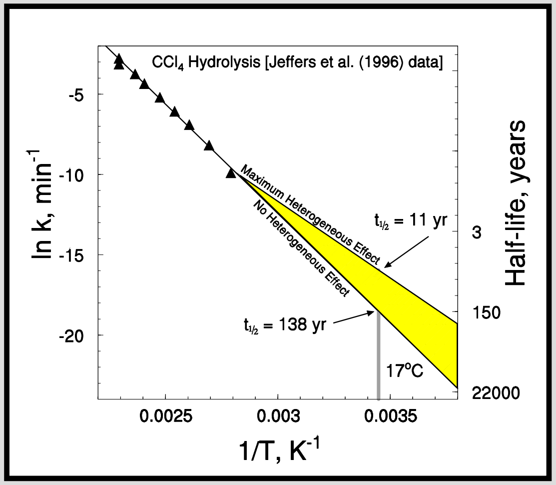
- **Modeling milestone reached:**
  - **- Simulations used to design newer/larger scale experiments**

Bontchew, R., and Moore, R. 2007, Mechanism of formation of Sr- and Sr/Ca hydroxyapatites, Radiochemica Acta, draft

Carbon Tetrachloride and Chloroform Attenuation Parameter Studies: Heterogeneous Hydrolytic Reactions

J. E. Amonette
M. J. Truex
J. S. Fruchter





CT and CF Attenuation Parameter Studies: Heterogeneous Hydrolytic Reactions

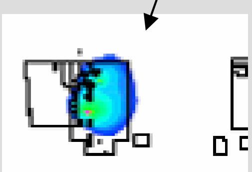
Large uncertainty in abiotic degradation rates (K_a) limits the ability to predict fate and transport and to develop cost-effective remediation plans for CT and CF plumes in 200 West Area

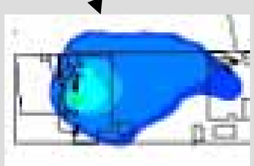
Project provides critical physical-chemical data for CT and CF hydrolysis reactions under groundwater conditions (T, surfaces)

- First determination of K_a(Het) for CT and CF
- Maximum increase for K_a from Het could be 8x for 1000 ppb CT
- Clarification of K_a(Hom) for CF
- Improved K_a's will strengthen technical basis for remediation decision

K_a

?





Type of Hydrolysis	CT		CF	
	Hom	Het	Hom	Het
Neutral	X*	?	X	?
Basic			X	?

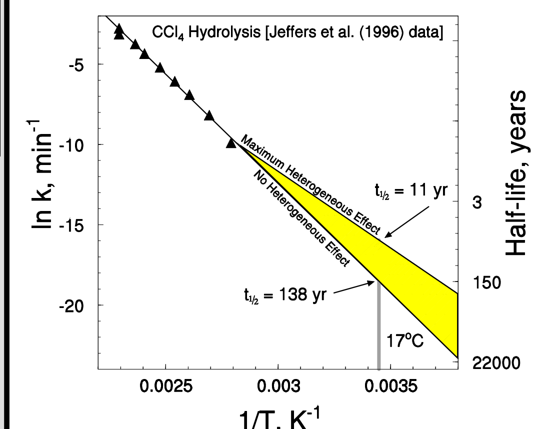
*Currently funded by Hanford Groundwater Project

Homogeneous (Hom)—Occurring in solution phase only

Heterogeneous (Het) —Involves interface between solution and solid phase

Neutral—Insensitive to pH (H_2O is active agent)

Base-catalyzed—Rate increases with pH (OH^- is active agent)

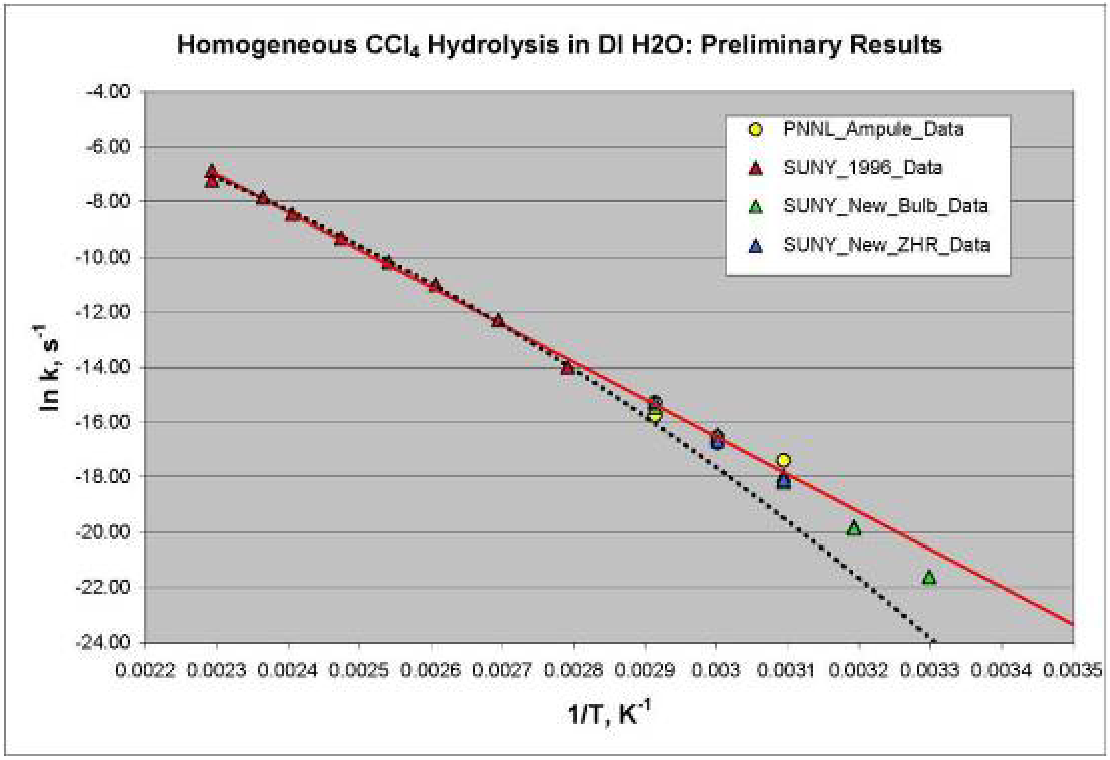


Problem → **Project Approach** → **Potential Impact**

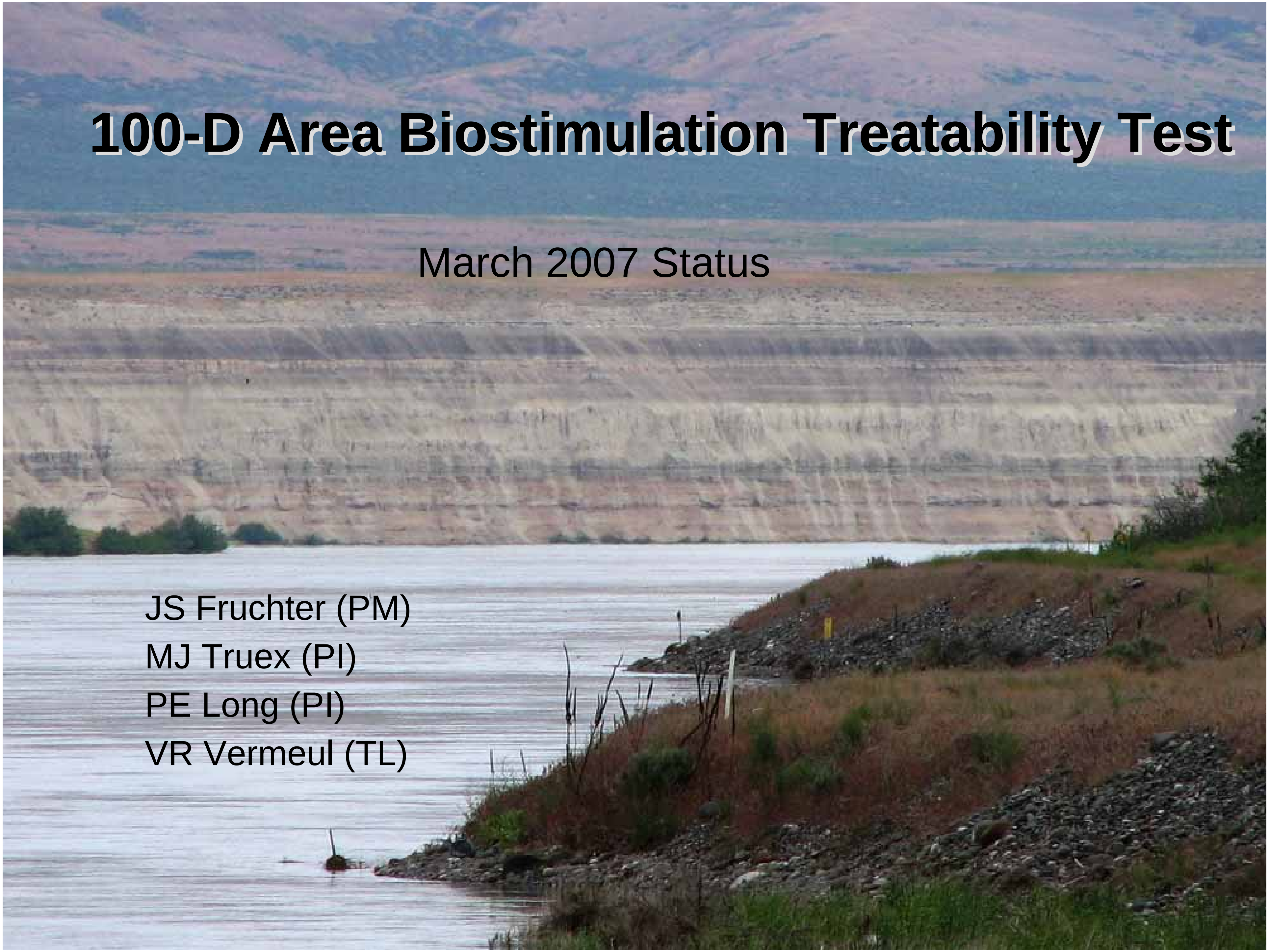
PNNL Experiments: Large Headspace Ampules

Results

- Started CF homogeneous studies at pH 3 in December; 1st sampling analyzed in February
- Completed CF homogeneous test run at high pH w/varying amounts of dissolved Si; samples being analyzed now
- Plan to start CF homogeneous experiments at high pH once Si issues resolved
- Methodology developed for heterogeneous experiments



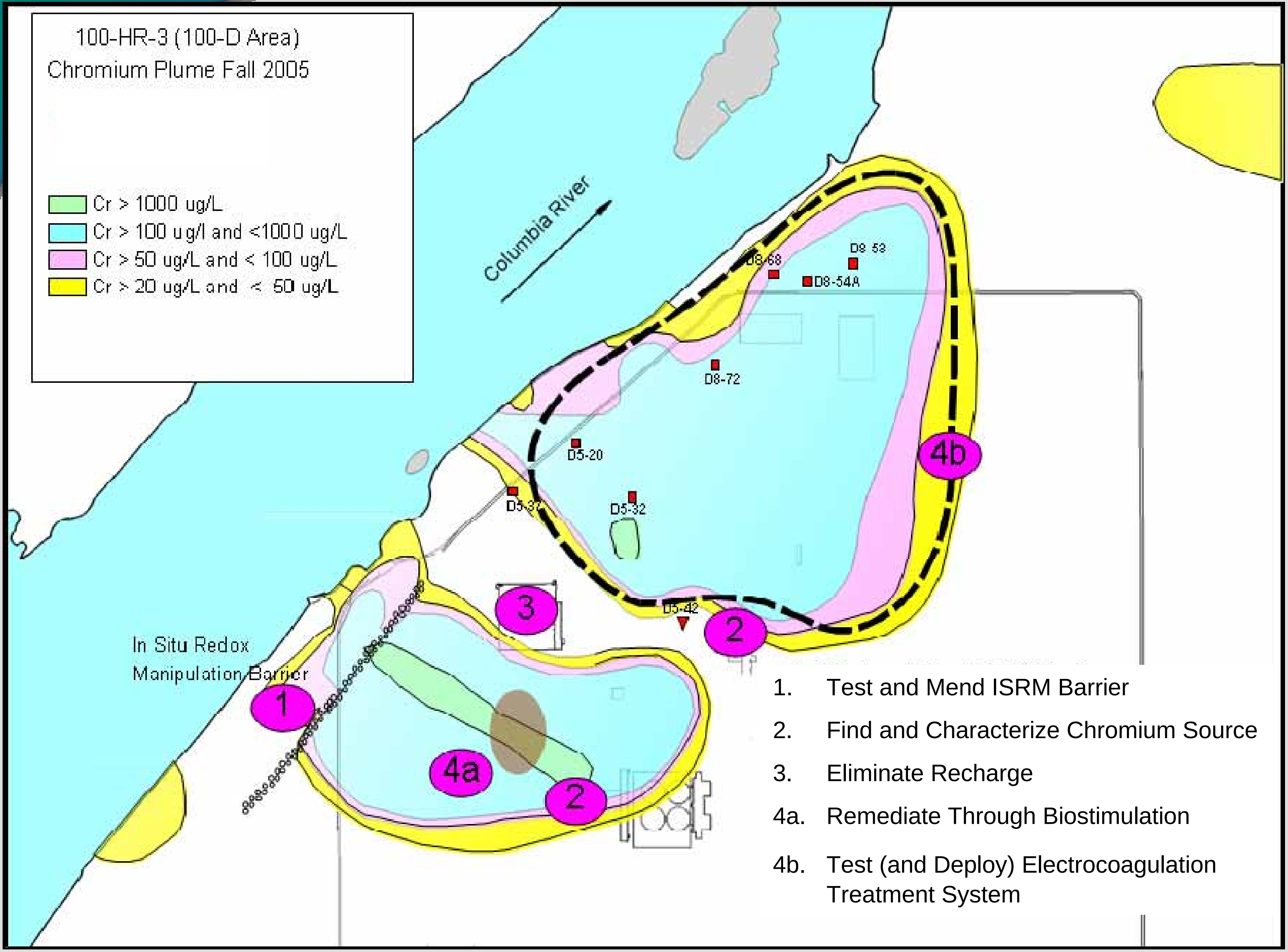
Example of results from sister project (CCl_4 homogeneous hydrolysis)



100-D Area Biostimulation Treatability Test

March 2007 Status

JS Fruchter (PM)
MJ Truex (PI)
PE Long (PI)
VR Vermeul (TL)



1. Test and Mend ISRM Barrier
2. Find and Characterize Chromium Source
3. Eliminate Recharge

4a. Remediate Through Biostimulation

4b. Test (and Deploy) Electrocoagulation Treatment System

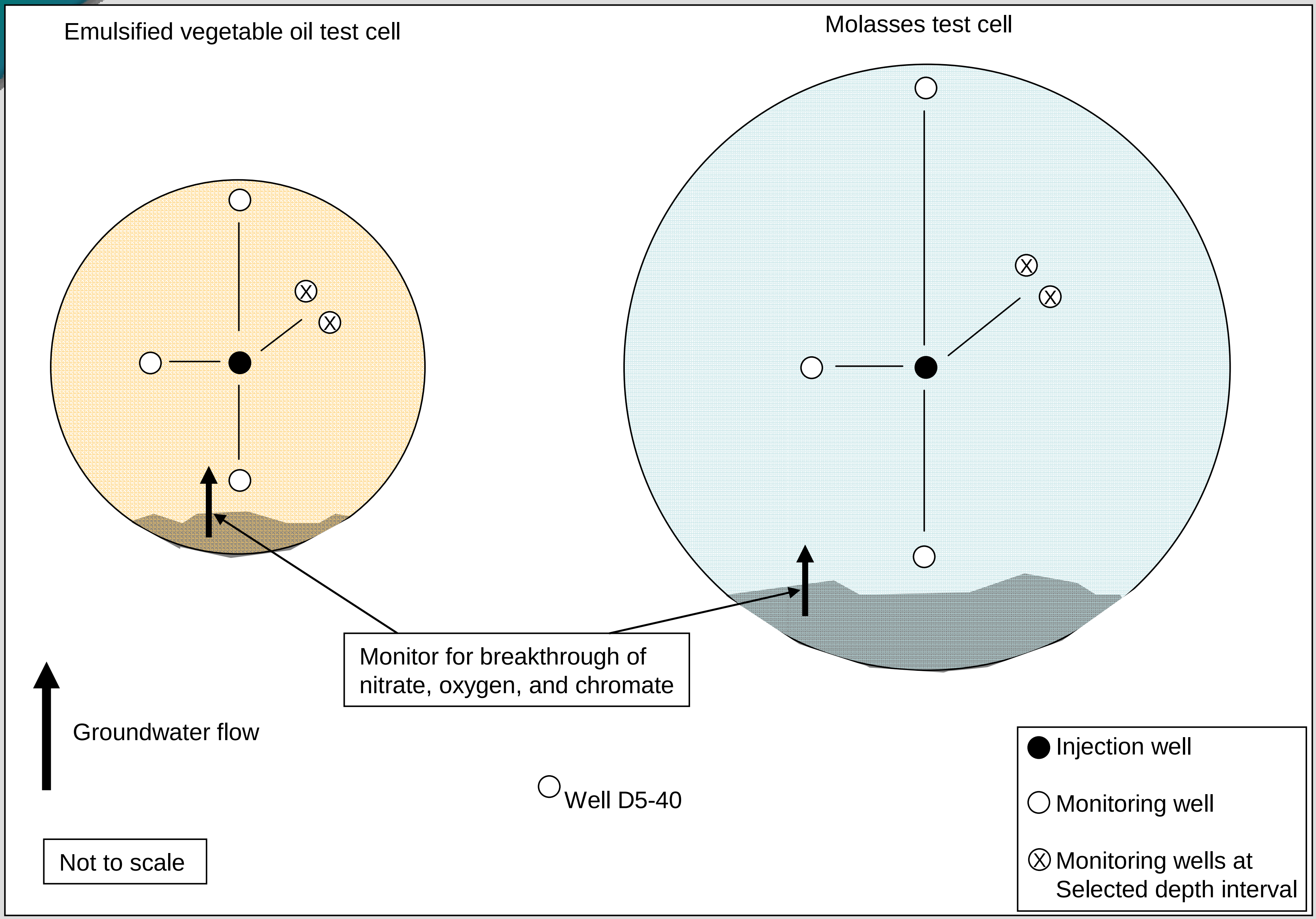
Overview

- Two approaches for a biobarrier
  - Soluble substrate (e.g., molasses)
    - Inject soluble substrate
    - Build biomass
    - Barrier reduces influx until biomass is decayed (~1 yr)
    - Re-inject substrate
  - Immiscible substrate (e.g., vegetable oil)
    - Inject immiscible substrate
    - Substrate slowly dissolves and reduces influx until substrate is gone (2-10 yr)
    - Re-inject substrate

Purpose of Test

- Determine design information that can be used for future implementation of a biostimulation barrier to reduce nitrate, oxygen, and chromate concentrations over a barrier length of 500-700 meters
  - Large-scale barrier, deep aquifer, and inability to use push technology for subsurface access are specific challenges to be addressed in developing the design information.

Treatability Test Concept



Laboratory Studies

- Microcosm Testing
  - Verification of stoichiometry and kinetics of biological reactions in Ringold Formation using selected substrates and substrate from 100-H Area test
- Emulsion Design Experiments
  - Determine emulsion properties and injection design to obtain large radial injection distance in the Ringold Formation
  - Industry consultant will provide input to tests
  - Key factors
    - Emulsion stability
    - Large scale of injection
    - Ringold Formation particle size
      - Wide distribution of particle sizes
      - Presence of fines filling interstitial space between larger sediment particles

Biostimulation to Protect the ISRM Barrier at 100-D Area

- The treatability test plan has been completed and submitted for DOE and regulatory review.
- Well locations have been staked. The latest estimate indicates a drilling start date in early April.
- Microcosm tests have been initiated.
- Planning and experimental design work has begun on the immiscible substrate studies (supplemental funded activity).
- Subcontracts are in place:
  - Bob Borden: Industry/university expert for biological barriers
  - Susan Hubbard: Geophysical method for monitoring substrate distribution (LBNL)

Chromium Vadose Zone Characterization and Geochemistry

Pacific Northwest National Laboratory

P. E. Dresel   J. S. Fruchter

C. C. Ainsworth   S. V. Mattigod

N. P. Qafoku   J. P. McKinley

Project Objectives

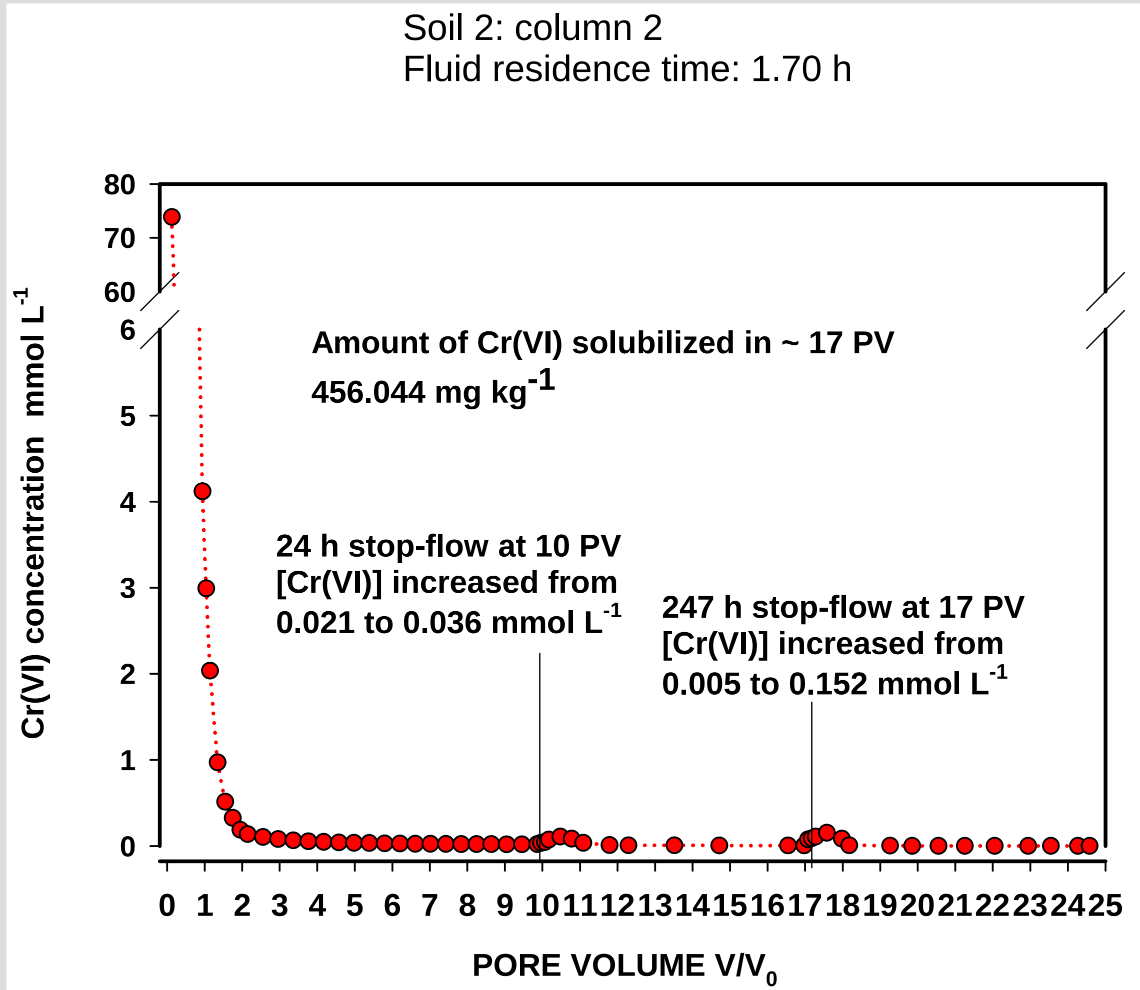
- Determine leaching characteristics of Cr(VI) from 100 Area contaminated sediments
- Elucidate possible Cr(VI) mineral and/or chemical associations that may be responsible for Cr(VI) retention in sediments
  - Macroscopic solubility studies
  - Micro-scale characterization
- Construct a conceptual model of Cr(VI) geochemistry in the Hanford 100 Area vadose zone to provide a basis for testing and selecting potential remedial measures

Column Leaching of Site B Sediment

H_2O extractable Cr(VI) at t = 0: 476 mg kg^{-1}

Old Spill Site

Cr(VI) Surface conc.
3,500 mg/kg

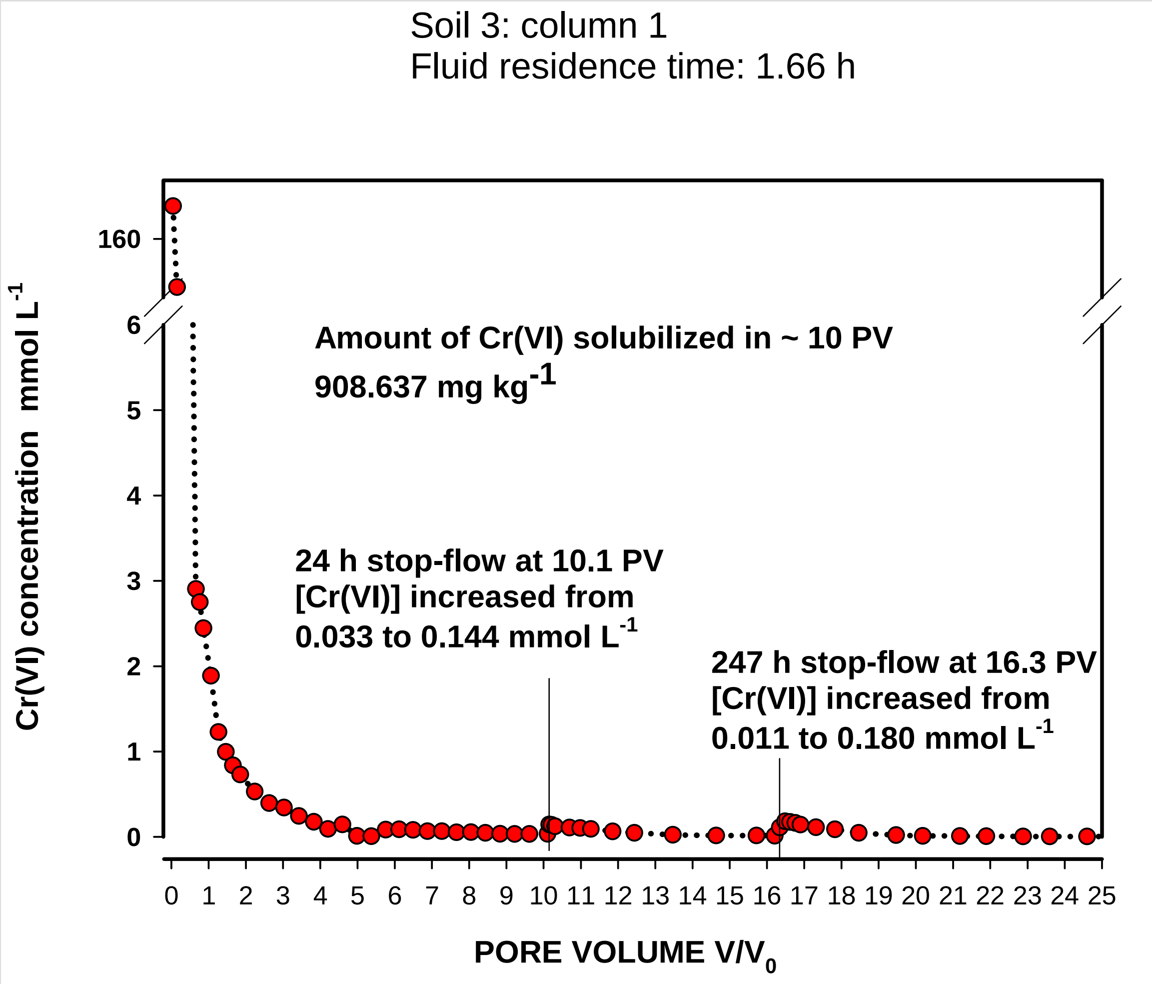


Column Leaching of Site D Sediment

H_2O extractable Cr(VI) at t = 0: 828 mg kg^{-1}

New Spill Site

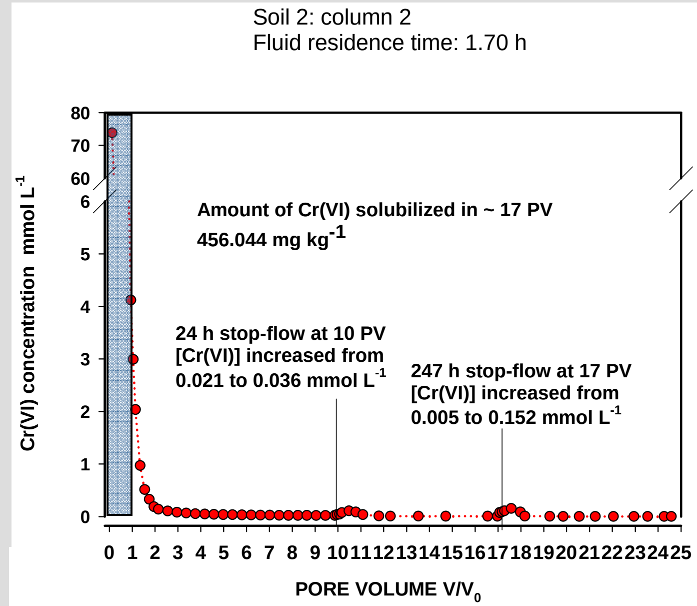
Site of recent pipeline discharge: est. volume 5 to 10 gal at 6 to 8% Cr(VI).

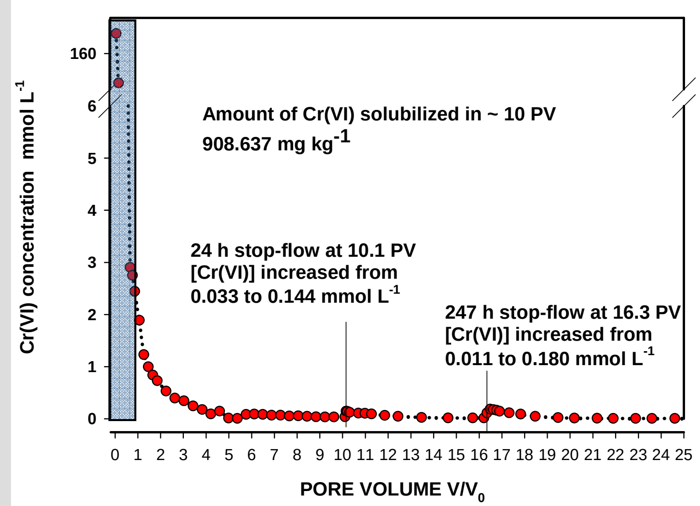


Early Release of Cr(VI)

- Majority of Cr(VI) is released in the first pore volume
  - Highly soluble or in solution
- Implications for remediation strategies
  - Majority of Cr(VI) is highly soluble promoting aqueous phase reactions
  - Possibility of pushing Cr(VI) ahead of reacting fluid

Pore Volumes	Site B		Site D	
	mmol/kg	mg/kg	mmol/kg	mg/kg
1	8.161	424.4	12.987	675.3





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Proposed Continuation Work: Vadose Zone Cr(VI) Remediation

- Test two vadose zone remediation strategies on existing, well characterized sediments from current work
  - Hydrogen sulfide gas
  - Calcium polysulfide
- Issues to be investigated
  - Current studies show three significant pools for Cr(VI) with different leaching behaviors
  - How do these behaviors impact alternative remediation methods?
    - Rate of reduction
    - Solid phase solubilites
    - Transport of unreacted Cr(VI) ahead of reduction front
  - Effectiveness of gaseous vs. aqueous reduction