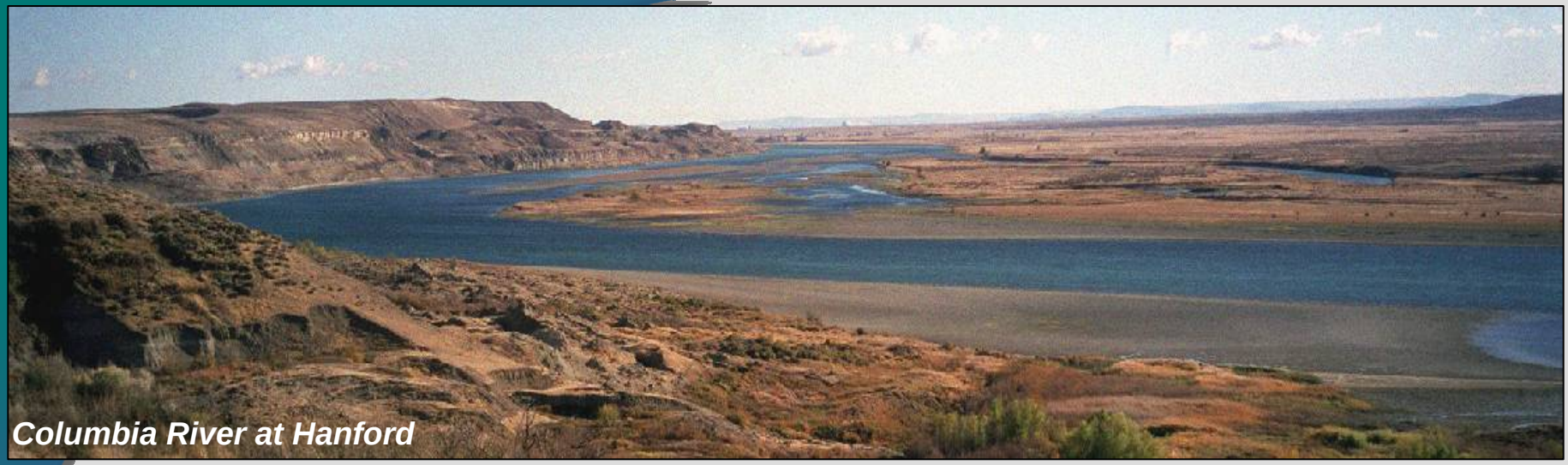

Fundamental Science in Support of Corrective and Remedial Action Decisions at the Hanford Site

John Zachara

Pacific Northwest National Laboratory, Richland, WA

ERSP Workshop ~ June 2006

Primary Collaborators

Jim Davis, USGS

Mark Freshley, PNNL

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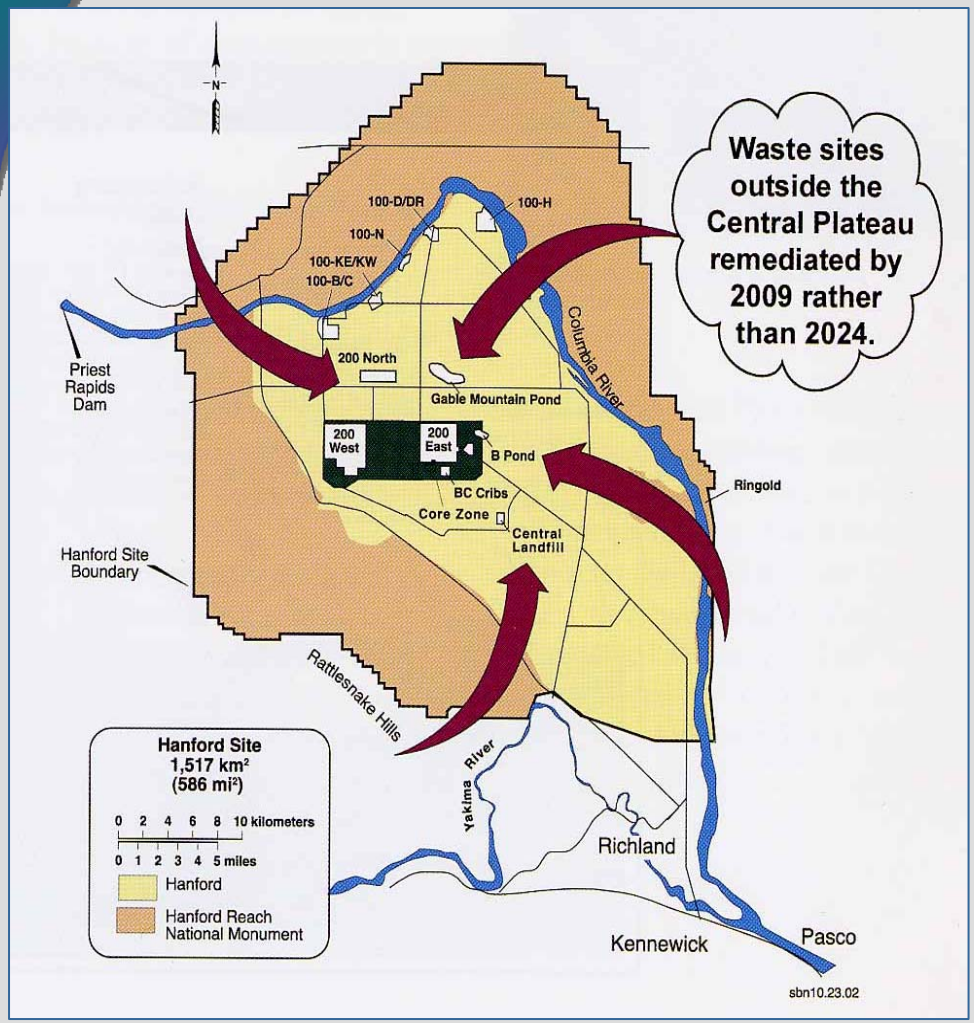
Hanford Site – DOE's Largest Legacy Waste Site

Hanford Site



- > 1000 contaminated "soil sites"

  [cribs, retention basins, disposal trenches, solid waste burial grounds]

  Pu, ^{137}Cs, ^{90}Sr, U, ^{99}Tc

- 177 massive storage tanks with 53 million gallons of HLW and LLW. 67 suspected leakers

  ^{137}Cs, ^{90}Sr, U, ^{99}Tc, Cr

- Over 15 well developed groundwater plumes

  U, Cr, ^{99}Tc, ^{129}I, ^{90}Sr, NO_3, CT

  - 200 Area plateau
  - Columbia River Corridor

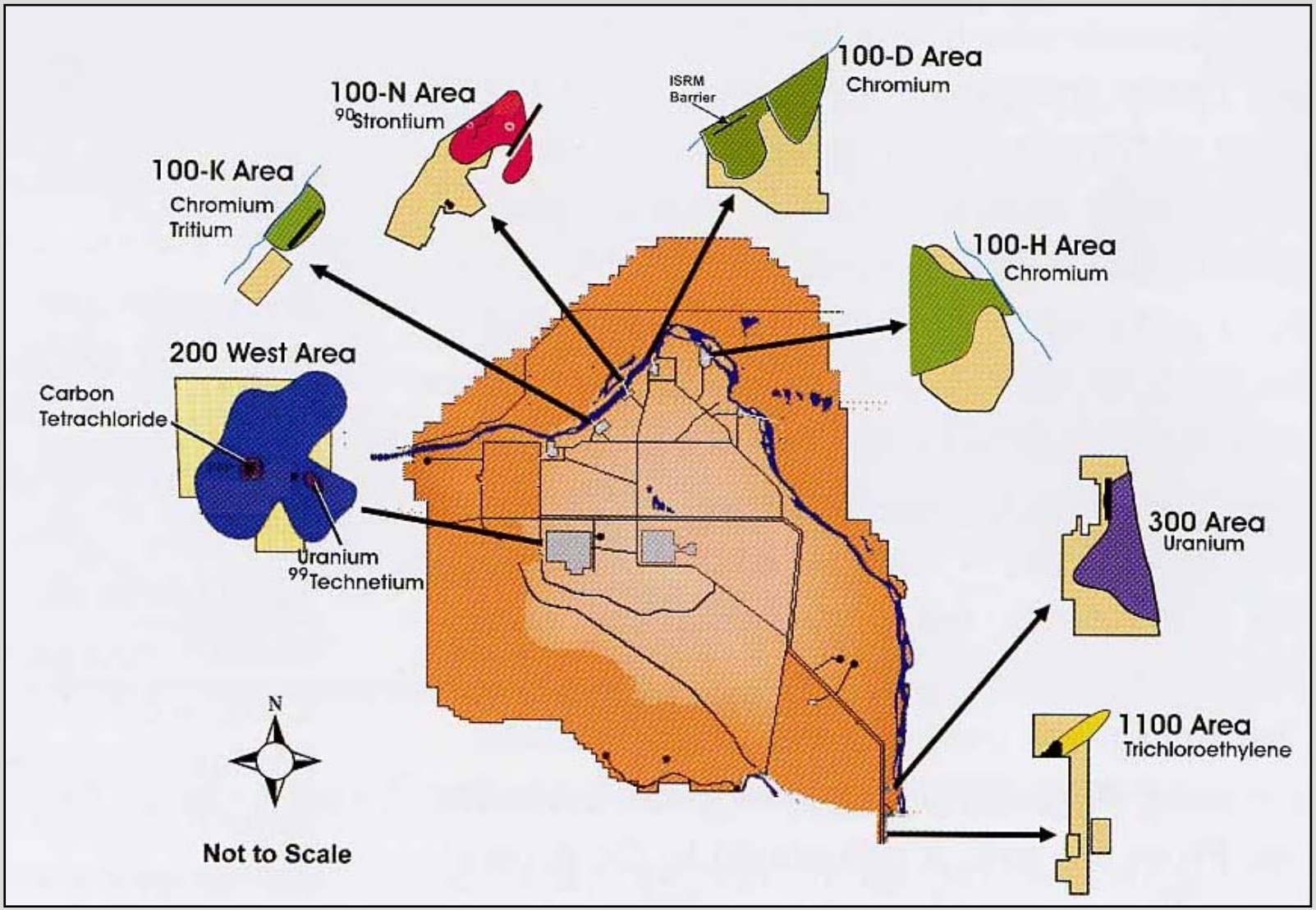
- 4 major canyon complexes
  - U plant, B plant, REDOX, PUREX

Hanford – One of the World's Largest Environmental Remediation Projects

- Definitive chemical inventories for waste sites, site-wide assessment model
- Massive excavations of contaminated soil from the river corridor to ERDF
- Remediation of select sites
  - In-situ redox barrier for Cr(VI) at 100-D
  - Pump and treat at 100 N (^{90}Sr) and 244-U (^{99}Tc, U)
- Characterization of leaked SST's and "high risk" soil sites to determine contaminant distribution and inventory
  - Conceptual model development
  - Modeling to project future migration and impact of corrective actions
- Remedial action evaluations for select river corridor sites
  - 100 N (^{90}Sr), 300-FF-5 (U)
  - Conceptual model development
  - Projections of long term plume evolution

In the future – tank farm closure, site closure, many contaminants left in-ground

Hanford Site Groundwater Contaminants



Construction of Underground HLW Storage Tanks at Hanford

Single shell tanks

- 149 tanks
- 35M gallons of wastes
- 190K tons of chemicals
- 132M curies of radioactivity
- 24% Cs-137, 75% Sr-90
- 67 “leakers”

Double shell tanks

- 28 tanks
- 20M gallons of wastes
- 55K tons of wastes
- 82M curies of radioactivity
- 72% Cs-137, 27% Sr-90

Subsurface Science Coordination/Linkage

- Initiated in 1999 with EM via TTP
- Objective was to link researchers with problem holders at Hanford
  - Expedite the impact of science on issues resolution and decision making
- Part of an overall S&T model for Hanford that was first in kind
  - Reviewed by NRC in 2001
    "Science and Technology for Environmental Cleanup at Hanford"
- OBER/ERSD initiates EMSP Linkage Project ~2002
- Sponsored workshops, technical exchanges, and targeted analyses/ calculations on Hanford materials
- Hanford Remediation and Closure Science Project (RACS) initiated in 2004
- Widely acknowledged as a success by DOE/RL, WADOE, stakeholders, and DOE contractors

The Linkage Concept

1. Align select EMSP P.I.'s (internal and external) with problem holders focusing on major, visible site campaigns leading to decisions
   - S-SX Tank Farm (^{137}Cs, Cr, Tc, °C) - CAA/FIR
   - B-BX-BY Tank Farm (high U, ^{90}Sr) - CAA/FIR
   - T-TX-TY Tank Farm (deep U) - CAA/FIR
   - 300-FF5 (groundwater U) - IROD/5y review
   - 100 N (groundwater ^{90}Sr) - IROD/5y review

2. or, high impact, generic science issues
   - Vadose zone water movement
   - U geochemistry
   - Tc remediation

3. Perform and provide "on target science" in time for impact
   - Facilitated by roadmap
   - RACS to fill major gaps

4. Feedback to ERSD and EM on key science needs
   - Linkage/input to EM/ERSD calls

Example Accomplishments (EMSP/ERSP, RACS)

1. Cause for expedited Cs migration in SX tank farm (CAA, FIR)
   - High Na and °C
2. Reason for anomalous Cr retardation beneath SX-108 (CAA, FIR)
   - Basic hydrolysis of ferrous silicates
3. Fate of 7 tons of U in the BX tank farm (CAA, FIR)
   - Precipitation of uranyl silicates
4. U(VI) source in the B tank farm groundwater plume (CAA/FIR; DQO)
   - Distinct isotopic signature from BX-102
5. Anomalous absence of ^{99}Tc in groundwater near BC cribs (CAA, ERD)
   - Capillary retention and lateral spreading in silt lens
6. Explanation for 300 A U(VI) plume stability (EPA IRoD Review; FFI)
   - Slow desorption kinetics/intraparticle reaction

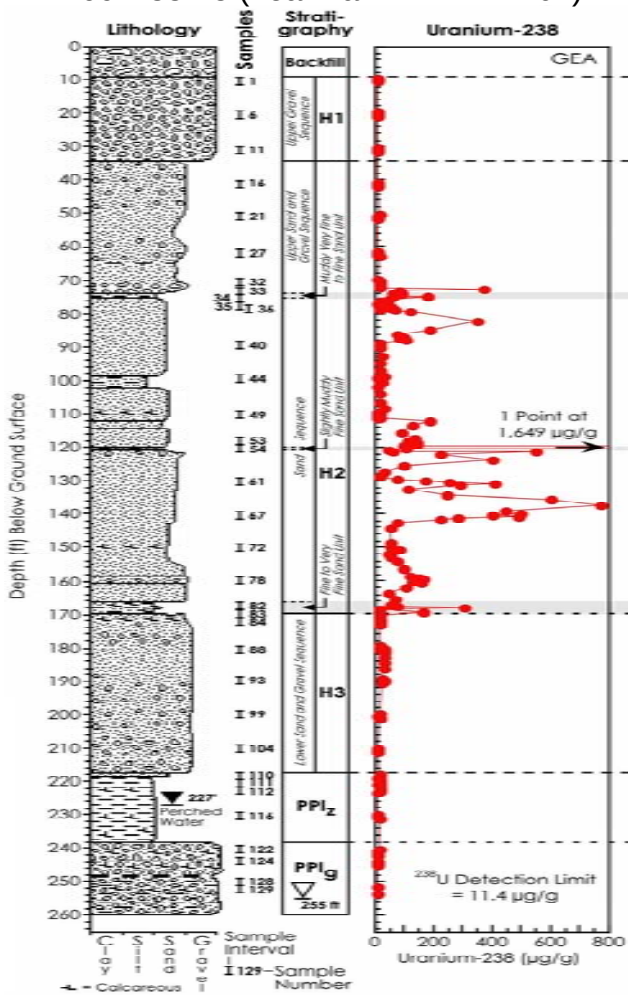
Metal Waste Overfill Releases 7-8 Tons of U(VI) to the Vadose Zone Near BX-102

B-BX-BY Tank Farm

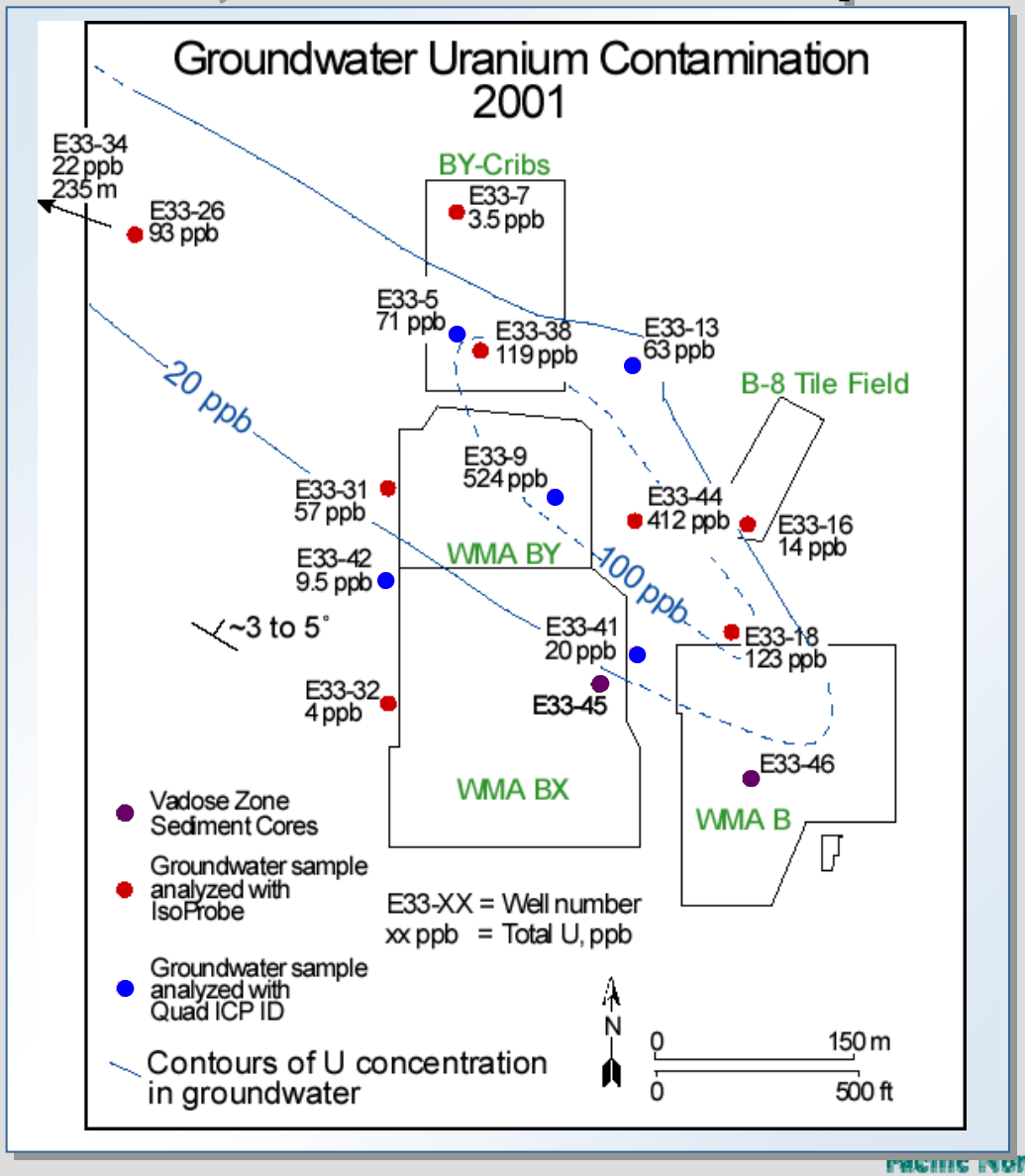
- Environmental S&T issues for U
  - Valence and chemical state
  - Physical distribution/mineralogic residence
  - Future migration potential (leachability, kinetics)

U Distribution

299-E33-45 (near Tank 241-BX-102)

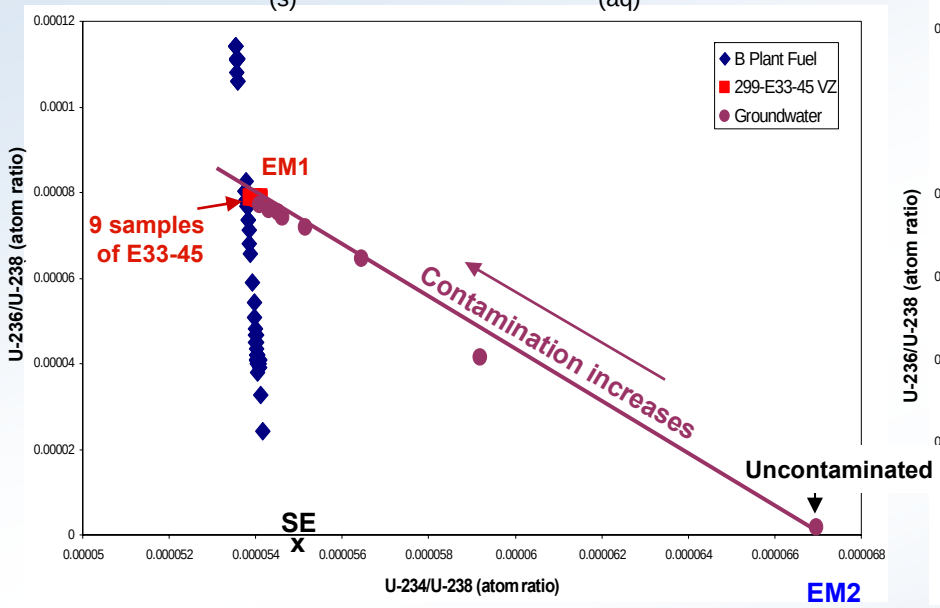


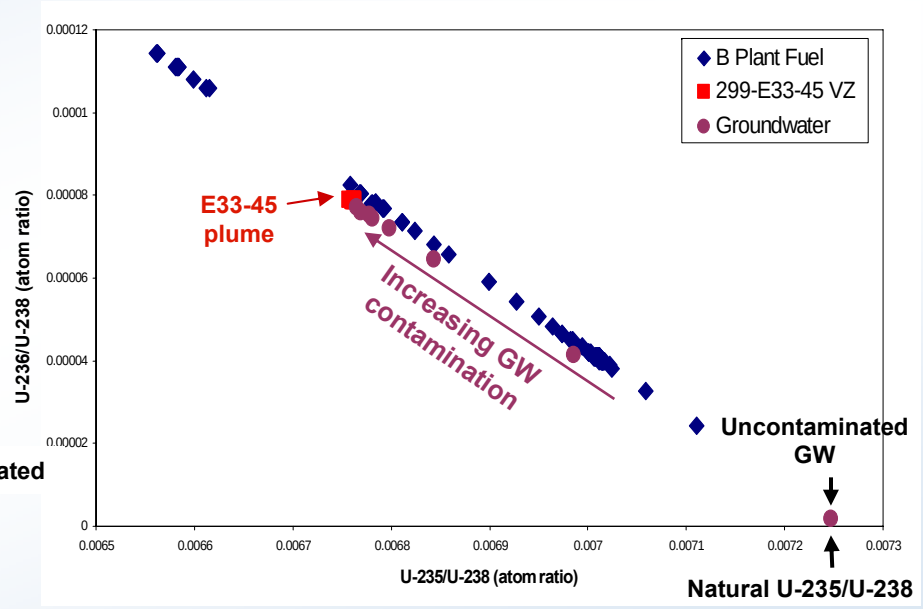
Groundwater U Plume in B-Tank Farm, Crib, and Trench Complex



High Resolution Isotopic Analyses Allow Identification of Potential Plume Sources

$\alpha \longleftarrow {}^{238}U_{(s)} \longrightarrow {}^{234}Th \Rightarrow {}^{234}U_{(aq)}$



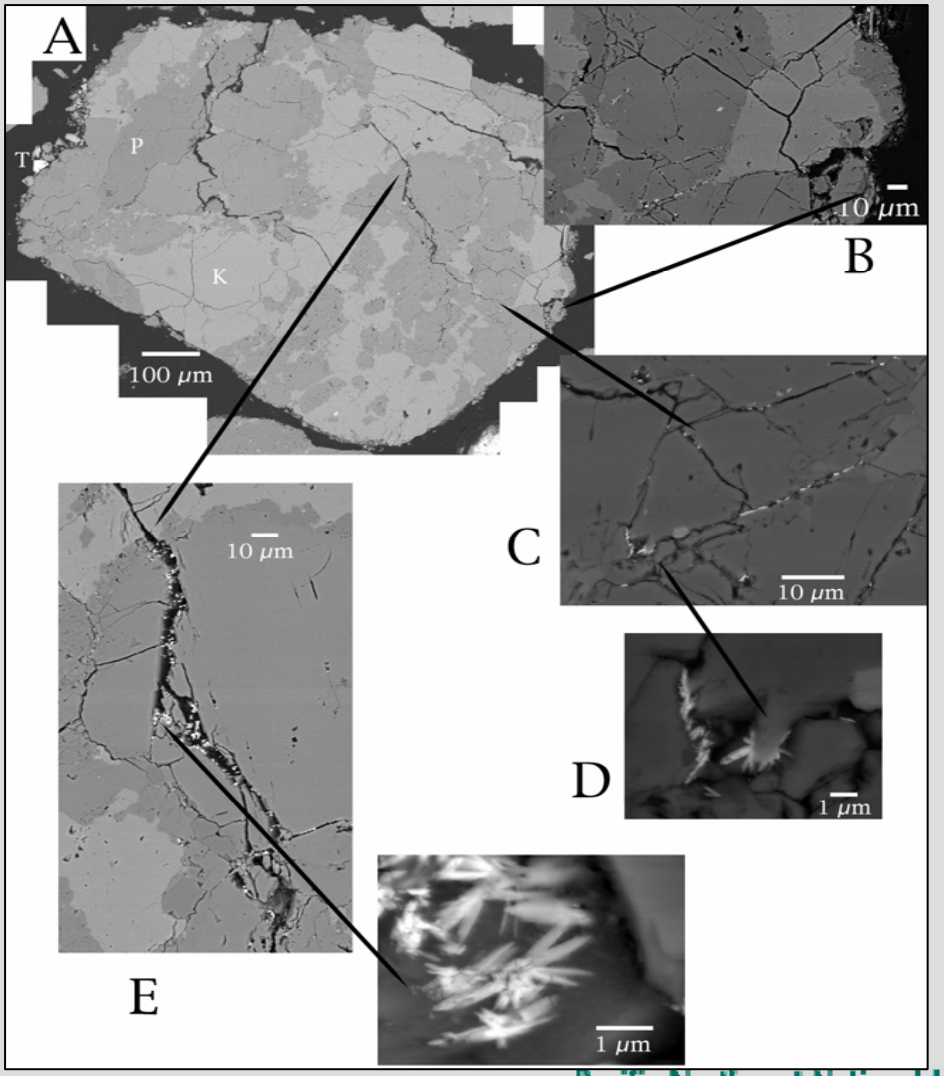


RW ^{234}U?

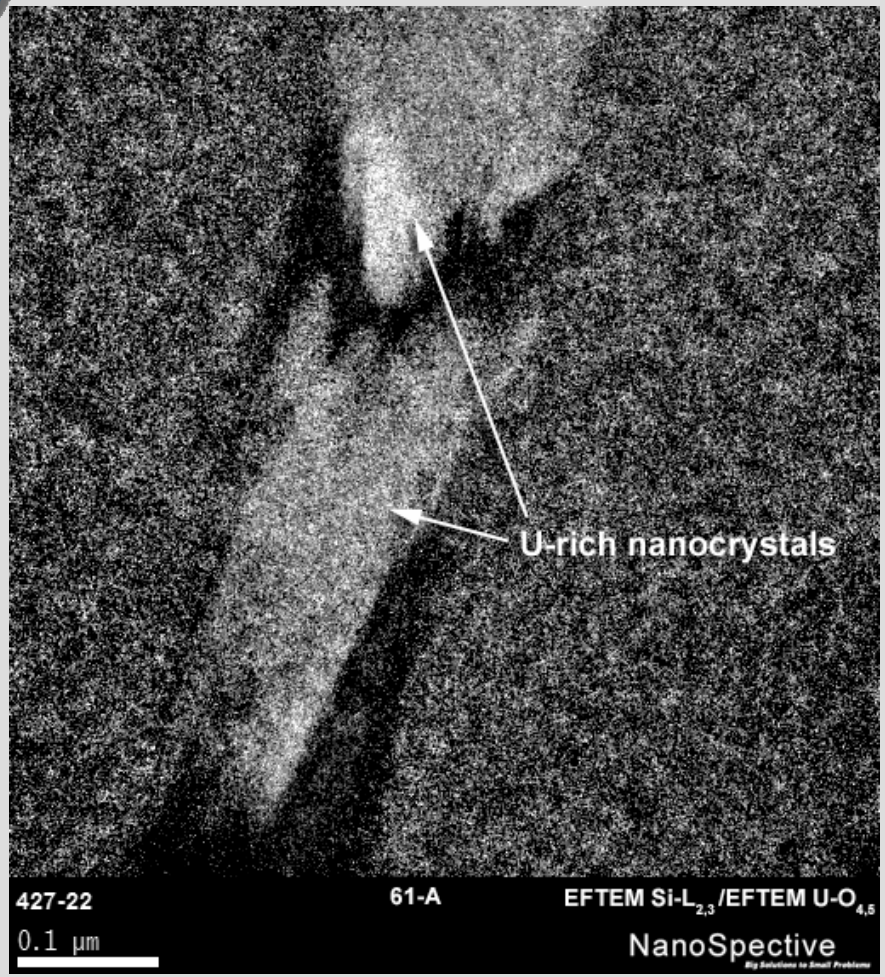
Metal Waste U(VI) has Precipitated within Fractures of Granitic Lithic Fragments in the Vadose Zone

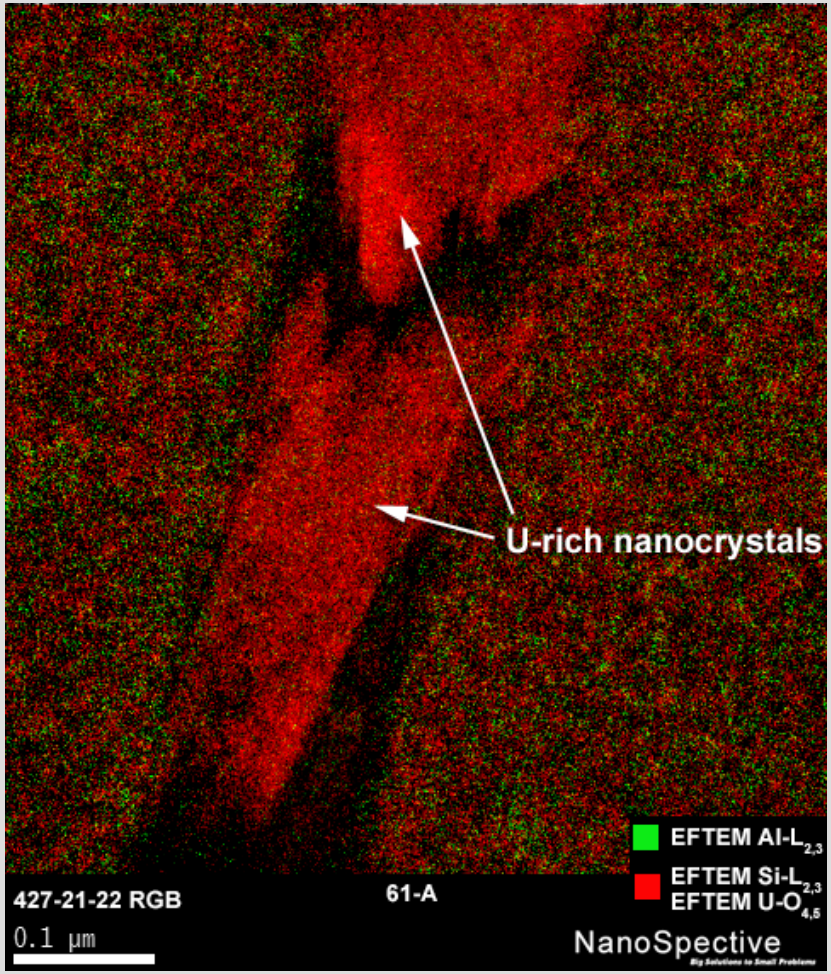
Precipitated U(VI):

- Appears as white crystallites in BSE images
- Is primarily localized to intragrain fractures of granitic lithic fragments that represent <15% of the sediment mass
- Preferentially form in Ca-rich feldspar domains (P)

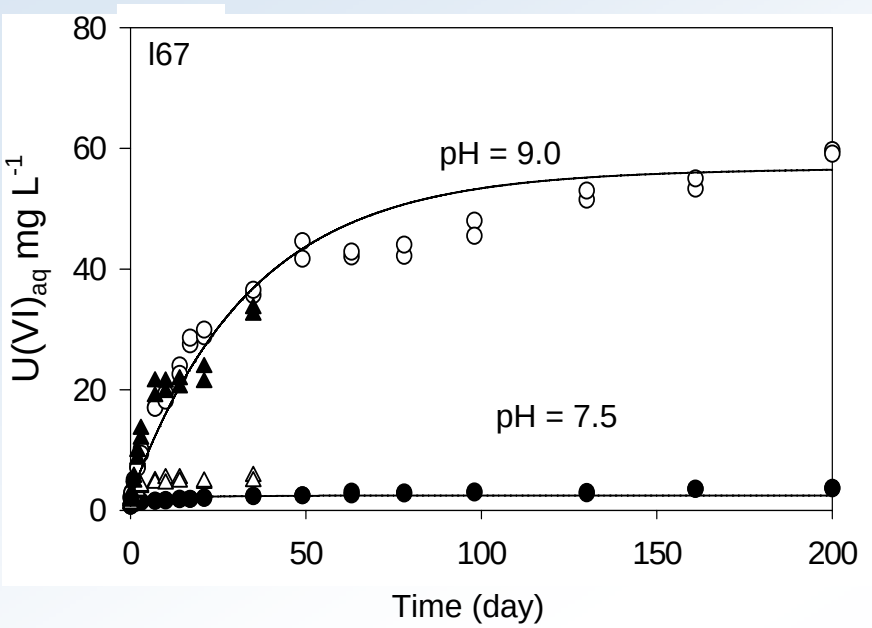


GIF Energy Analysis of Uranyl Precipitates U-Si and U-Si-Al Composites





Dissolution Behavior of U(VI) from Contaminated Hanford Sediment



Dissolution Model

Surface complexation

$$\equiv U(VI) + HCO_3^- \underset{k_{-1}}{\overset{k_1}{\Leftrightarrow}} \equiv U(VI) - HCO_3^-$$

Detachment

$$\equiv U(VI) - HCO_3^- \overset{k_2}{\Rightarrow} U(VI) - HCO_{3\,(aq)}^-$$

Kinetic relationships

$$\frac{dU(VI)aq}{dt} = k_2 K_1 \{\equiv U(VI)\}\{HCO_3^-\}$$

$$\frac{dU(VI)aq}{dt} = k\{\equiv U(VI)\}\{HCO_3^-\}\left(1 - IAP/K_{sp}\right)$$

$$\frac{dU(VI)_{aq}}{dt} = k[U(VI)_{solid}][CO_{2(tot)}]\left(1 - IAP/K_{sp}\right)$$

Microscopic Transport Model

"Big fractures" (f)

$$\frac{\partial C_f}{\partial t} + f_2 \frac{\partial C_m}{\partial t} = \left(\frac{D_f}{L_f^2}\right)\frac{\partial^2 C_f}{\partial l^2} + r_f$$

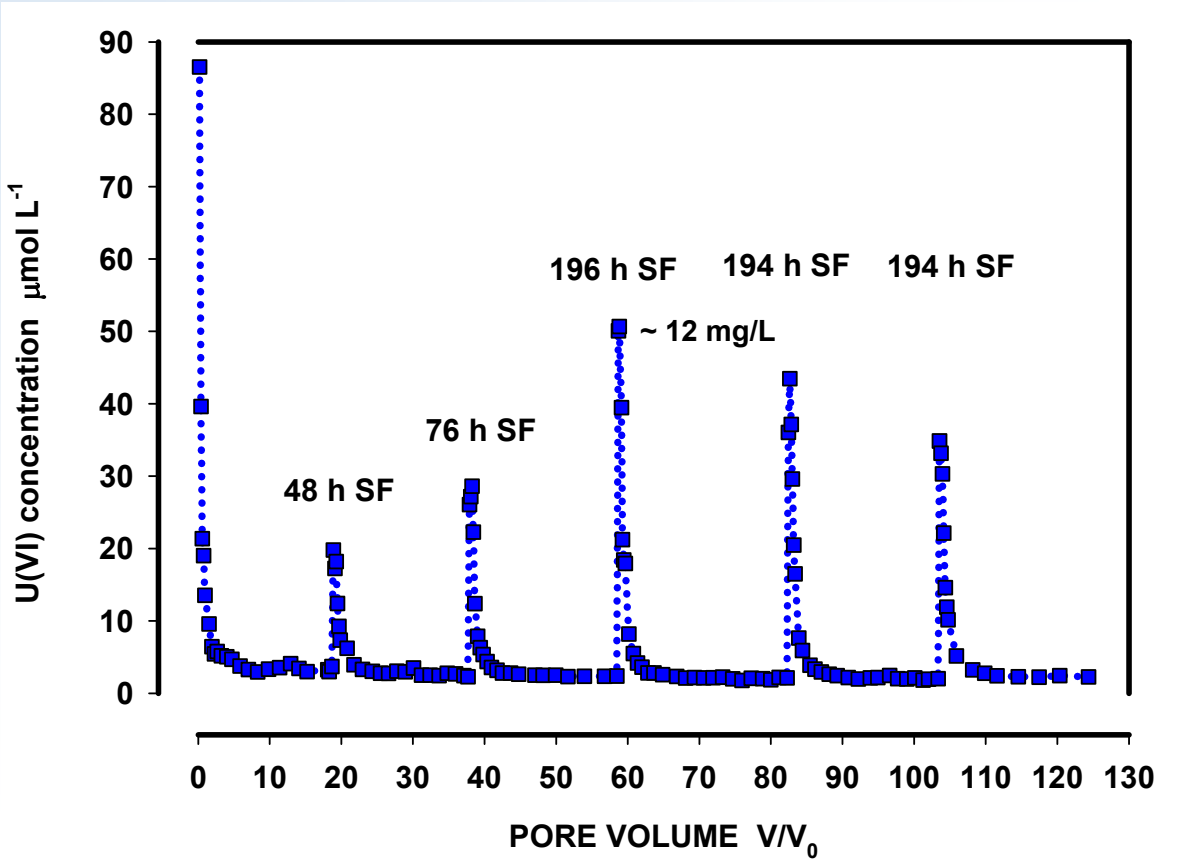
$$\frac{\partial m_f}{\partial t} = -r_f$$

"Small fractures" (m)

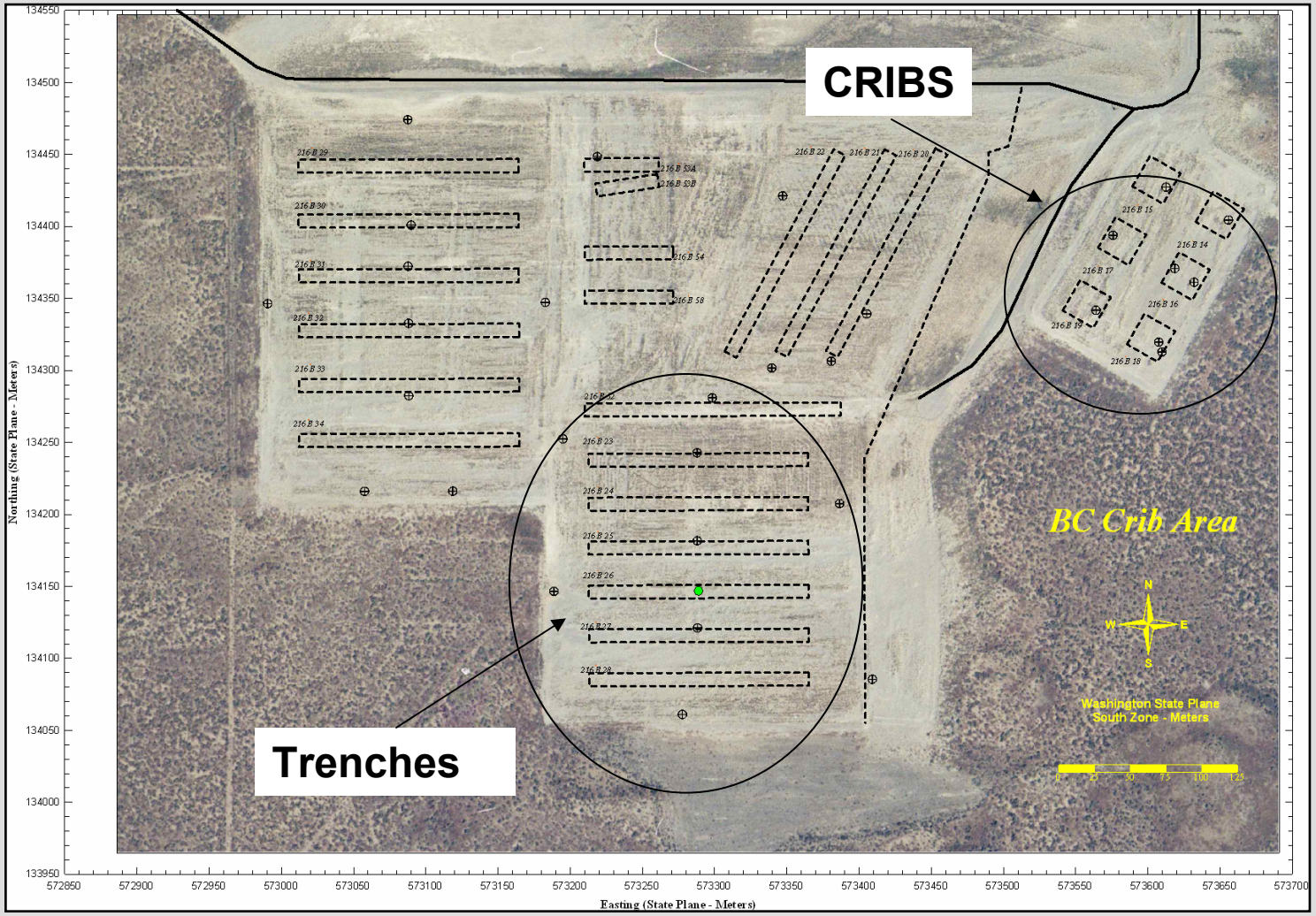
$$\frac{\partial C_m}{\partial t} = k_m (C_f - C_m) + r_m$$

$$\frac{\partial m_m}{\partial t} = -r_m$$

Column Study of U(VI) Release from BX-102 Sediments with Uranyl-Silicate Precipitates (RT = 1h, pH ~ 8.1)



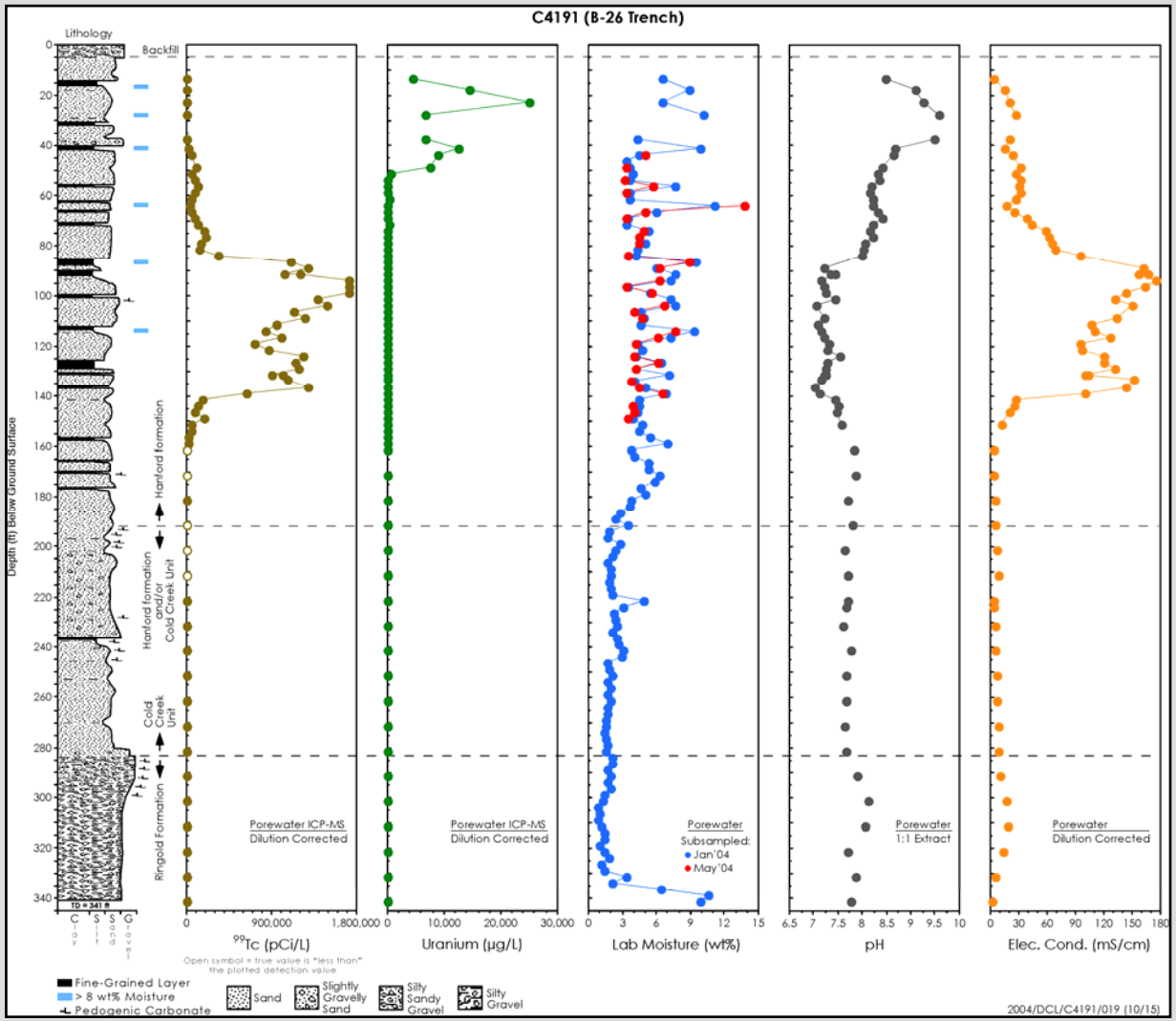
400 Ci of ^{99}Tc was Released to the BC-Crib Area: Where is it?



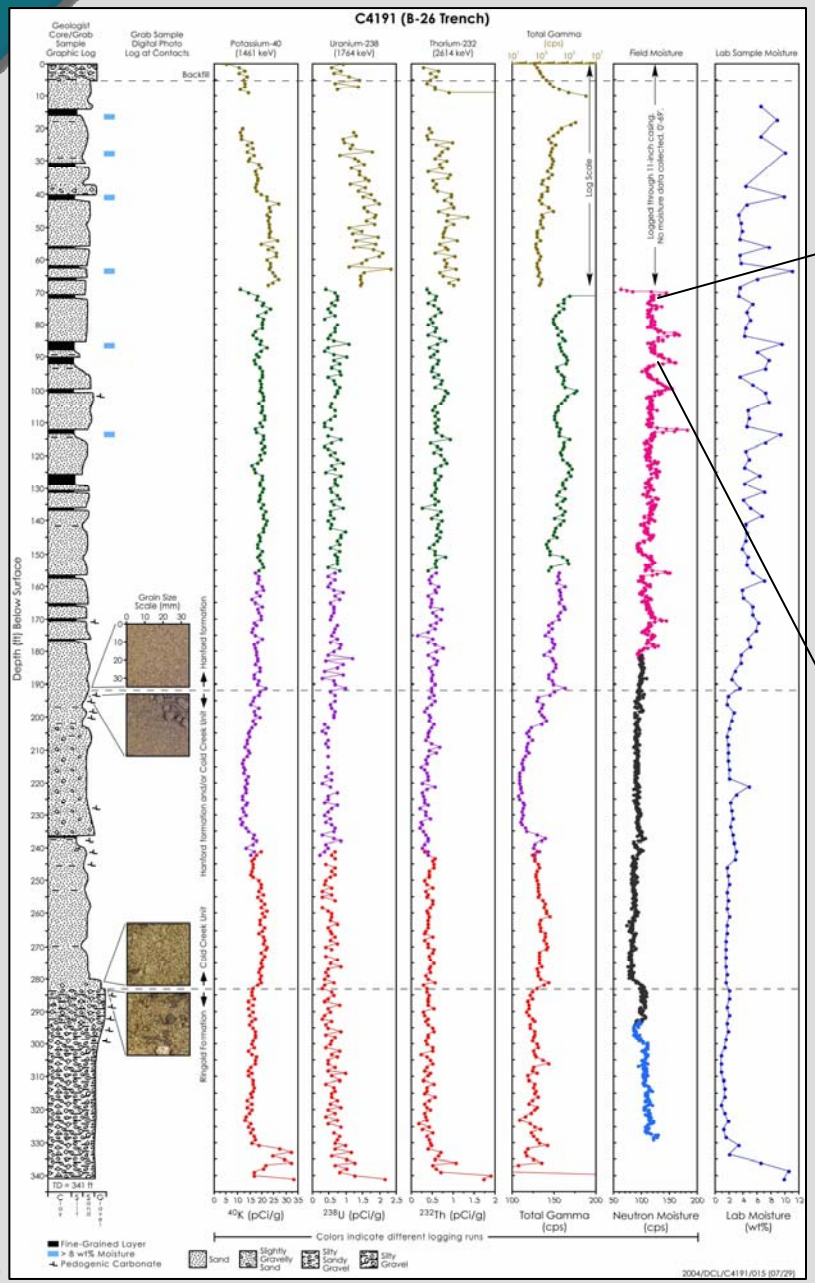
- The SAC model forecasts that a growing plume of ^{99}Tc should exist beneath the BC-cribs

State of Knowledge (C4191 Borehole)

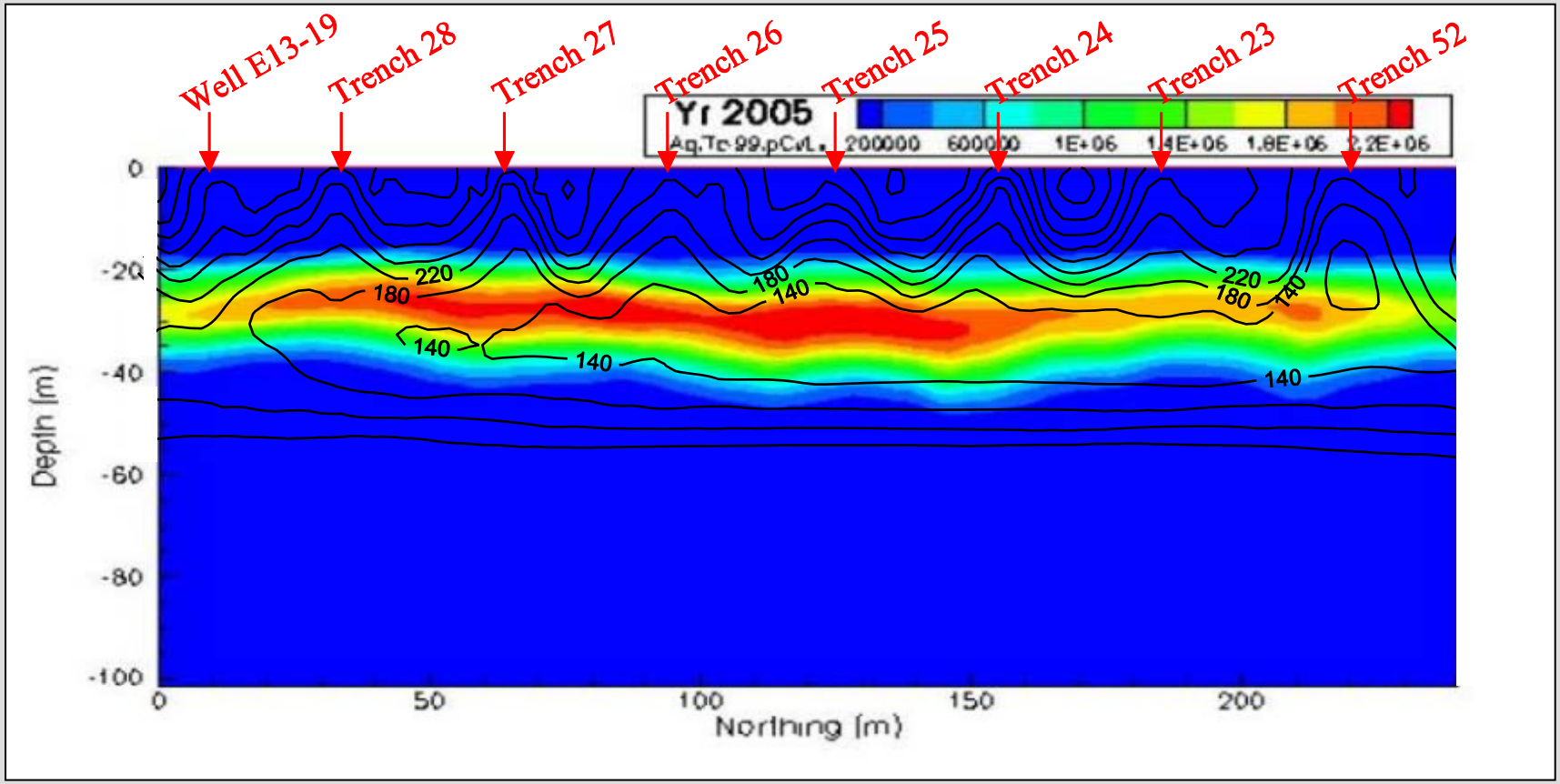
Lithology ^{99}Tc ^{238}U θ_{lab} pH EC



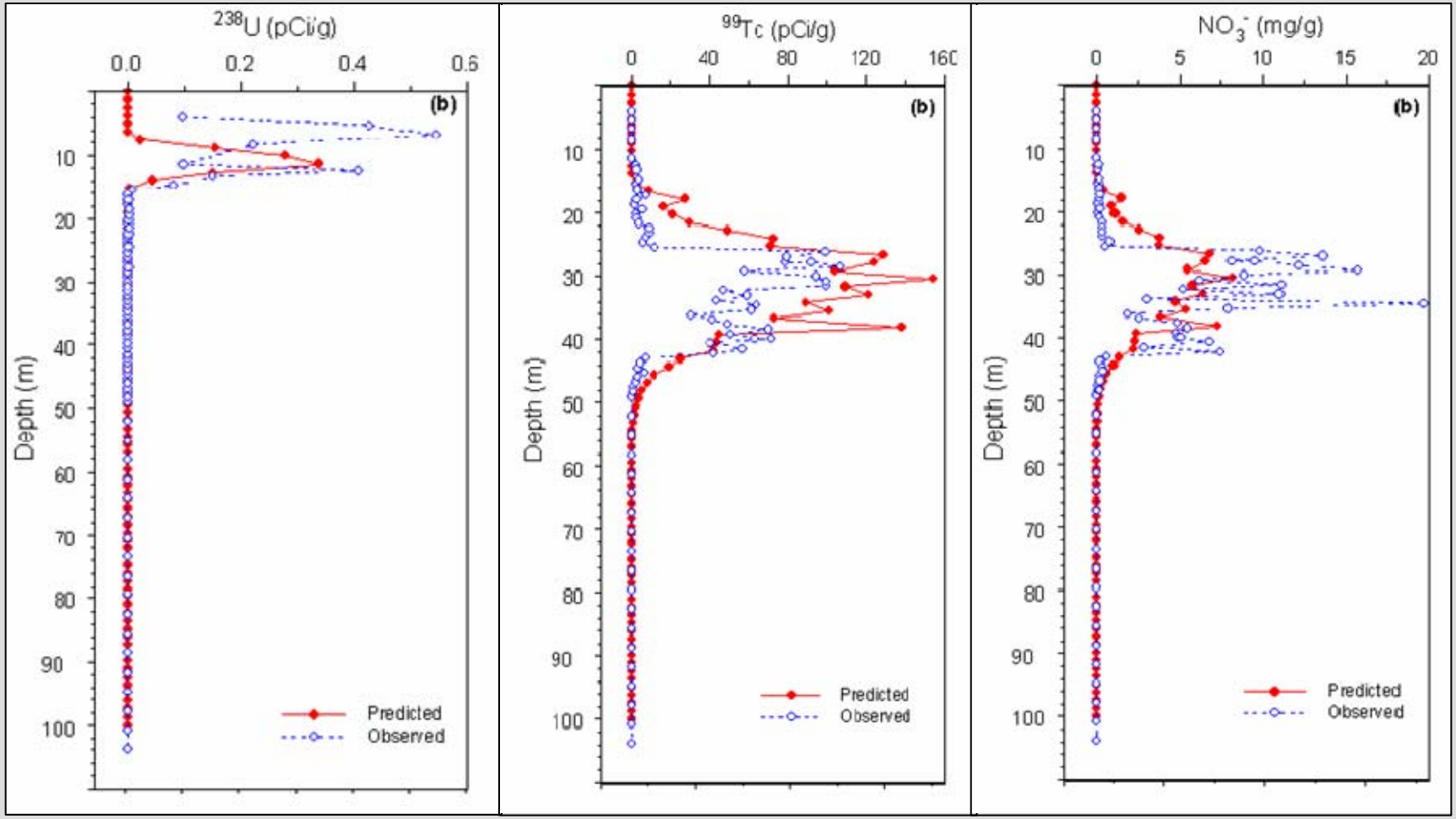
Evidence of Layered Heterogeneity



Predicted ^{99}Tc Distribution vs. Measured Resistivity



Predicted Solute Profiles for B-26 Using Capillary Spreading Model

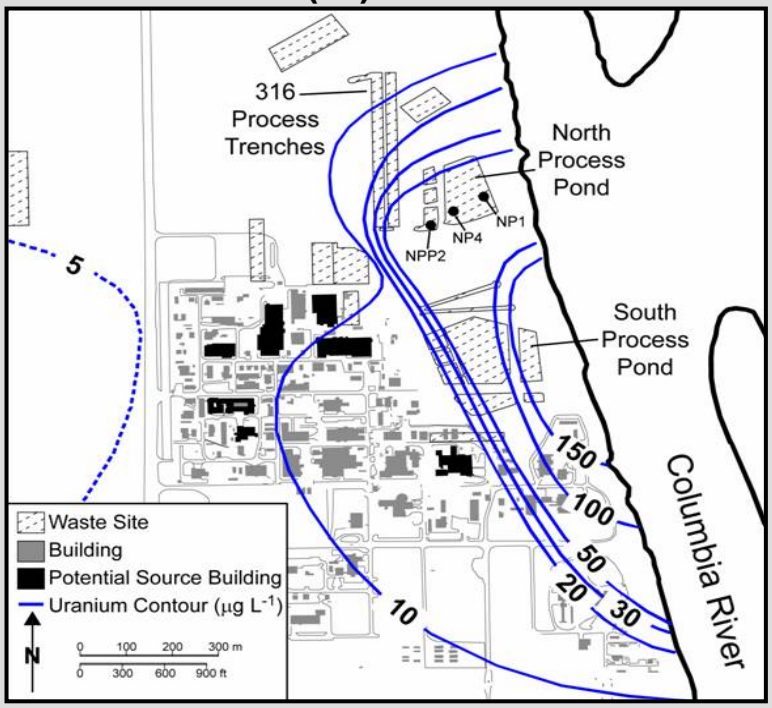


300 A Uranium Plume – A Decision Gone Bad

The North Process Ponds

- IRoD issued for MNA in 1995
- Basis was K_d-transport analysis that predicted plume dispersion to < DWS in 10 y

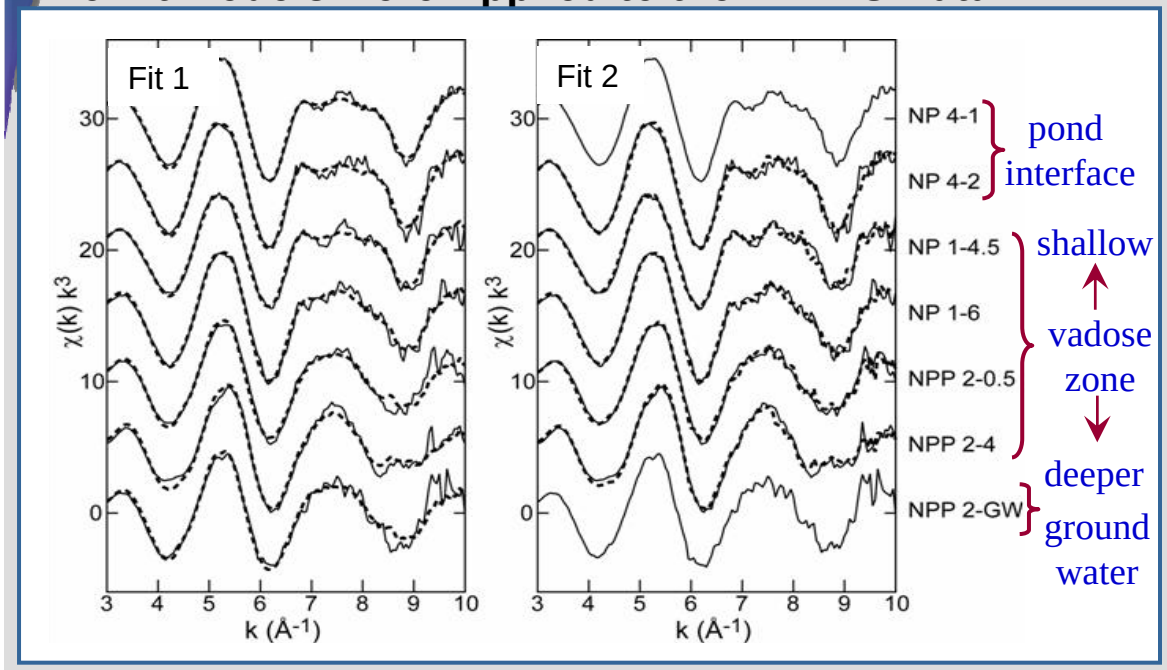
Extent of the U(VI) Groundwater Plume



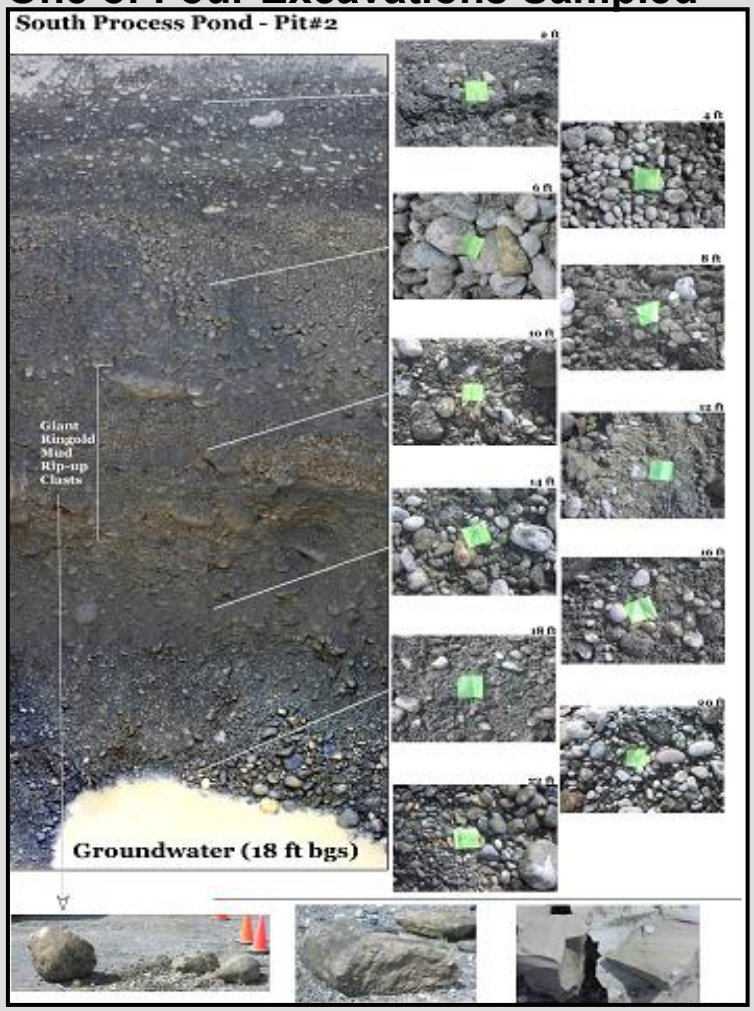
- Actual plume behavior quite different over past 10 y
- Resulting skepticism in simple models

Depth Transects of U Speciation Allow Formulation of Reaction Path Models

Two Fit Models were Applied to the EXAFS Data



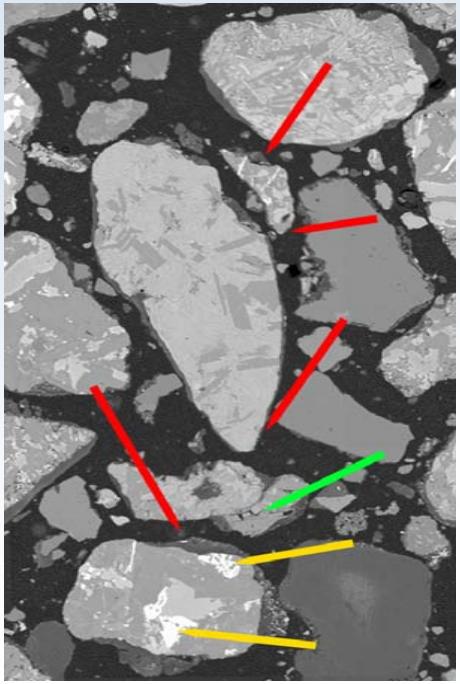
One of Four Excavations Sampled



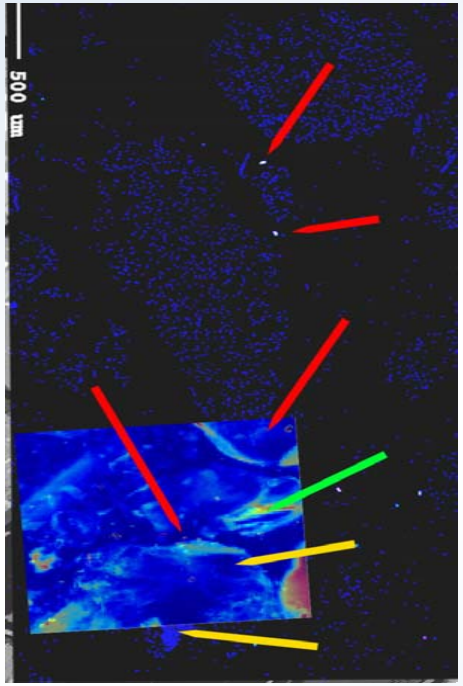
X-ray and Electron Microprobe Images of 300 A Sediment Thin Sections

BSE-XRF Overlay

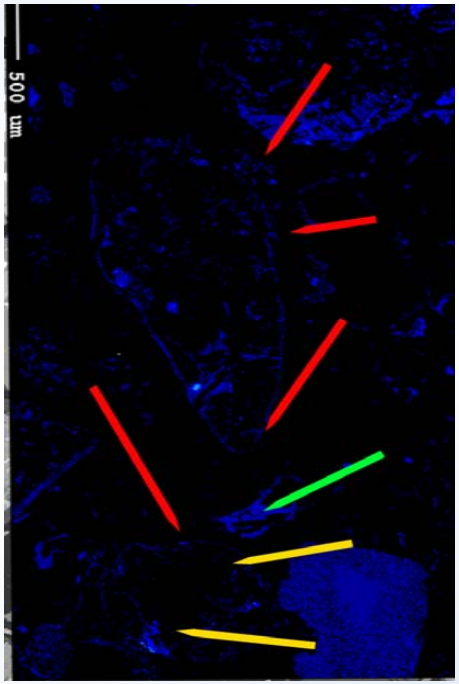
NPP2 - 4



BSE

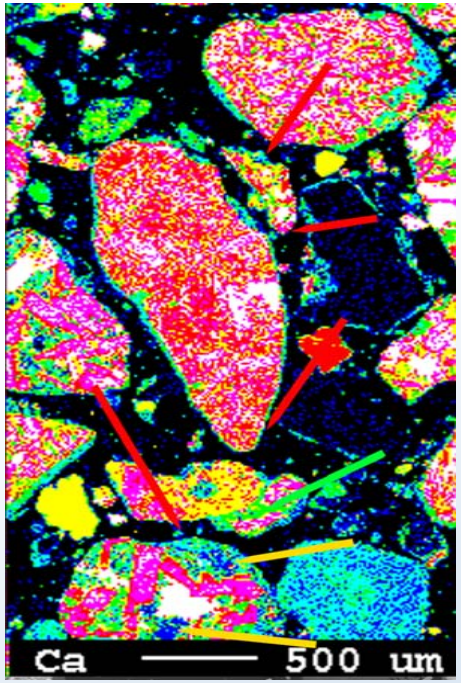


Copper



Uranium

--- 139 mg/kg ---



Calcium

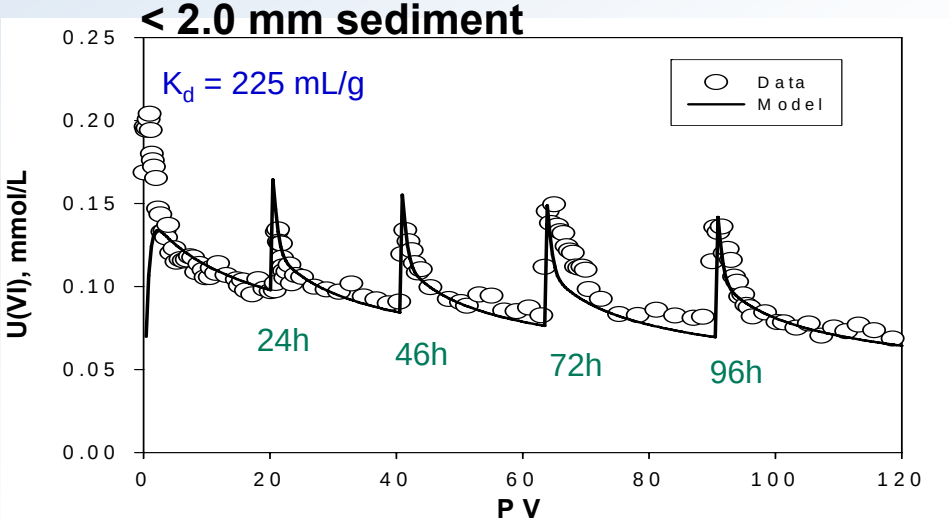
Large Column Experiment with NPP1-14 to Investigate Scaling of Reaction and Mass Transfer Parameters

Unseived Sediment with River Cobble and Mud

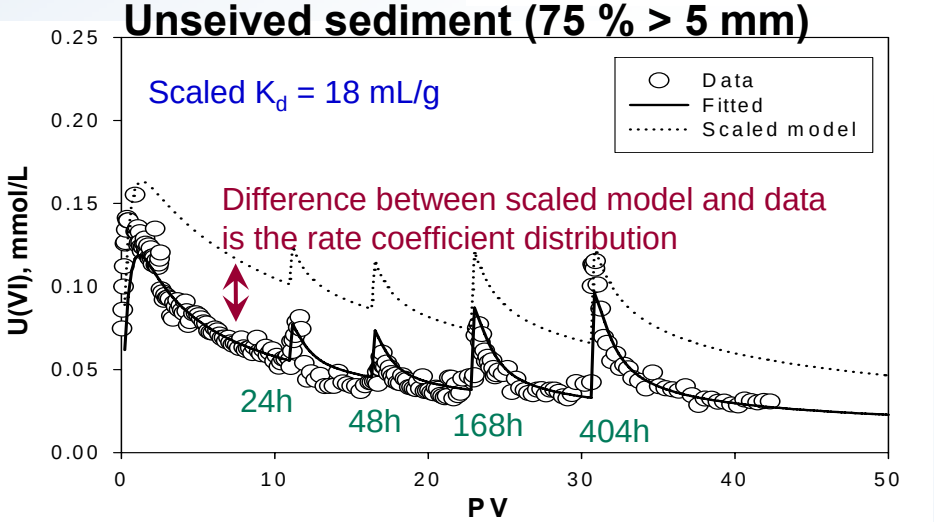
The 80 kg Column

Small and Large Column Results and Rate Constant Distribution from the Distributed Rate Model (DRM)

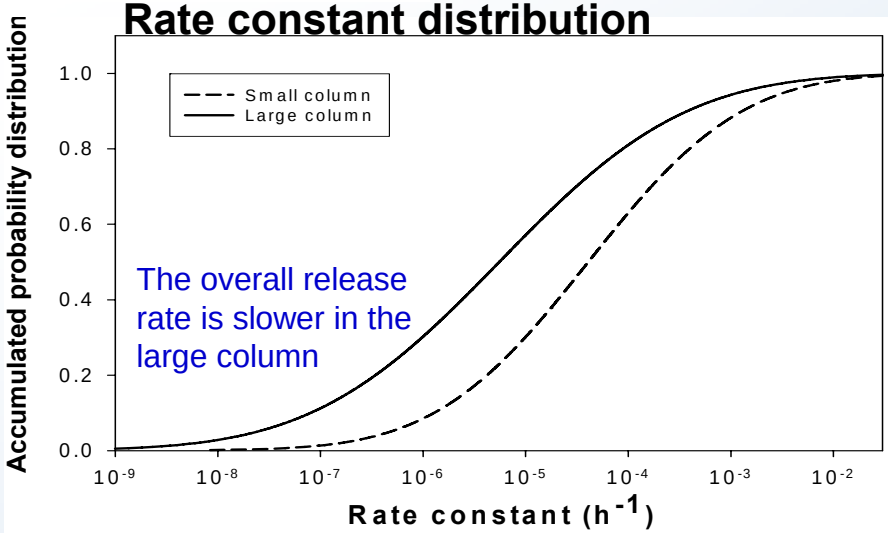
< 2.0 mm sediment



Unseived sediment (75 % > 5 mm)



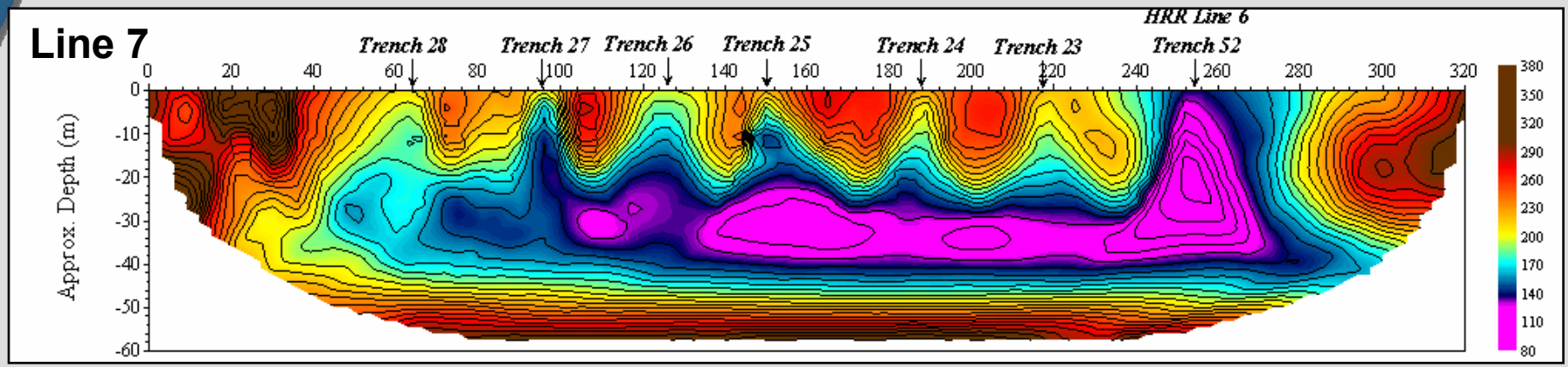
Rate constant distribution

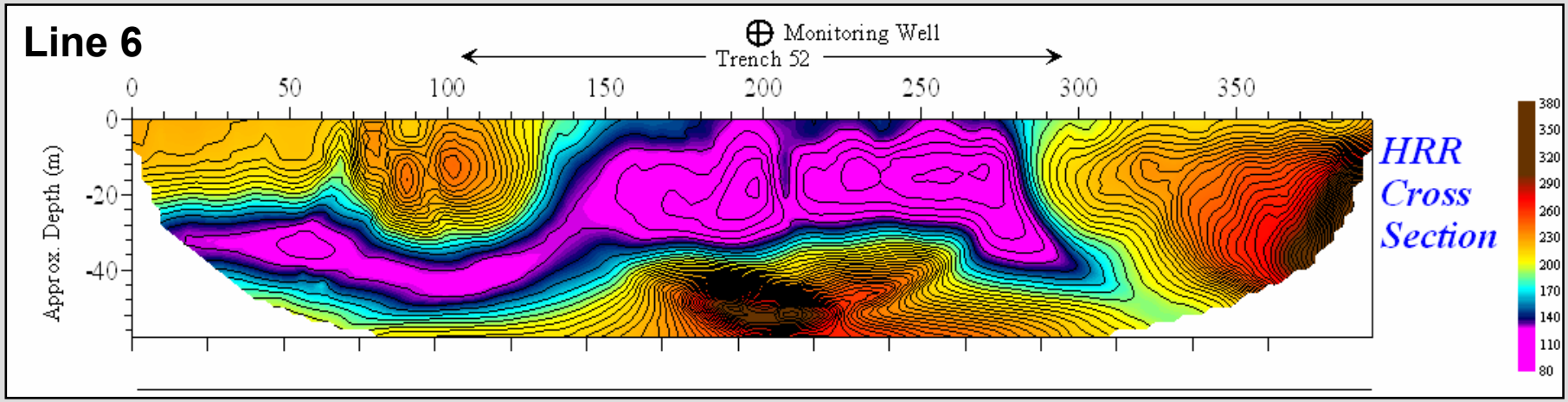


Concluding Remarks

- Science can enrich, provide technical basis for, and assure the long-term validity of decisions on complex issues and sites.
- For success, scientists must take responsibility for problem resolution
  - Research must be on-target in resolving issues or providing needed information, data, or parameters. Relevance is not good enough.
  - Research products must be useable without need for digestion, recalculation, etc.
  - Conceptual models must be transferable to workable numeric models
- Engineers, in turn, must realize when information is not sufficient to allow for a defensible long-term prediction or proposed remedy.
  - 300 A U-groundwater plume or 216-U-12 crib.
  - Sometimes simplified water and geochemical models are not good enough.
- All sites do not require science solutions, but a pervading scientific basis is essential.
- Cooperation and understanding is needed between parties when long-term protection of human health and the environment is the goal.

High Resolution Resistivity Surveys
(Rucker et al, 2004)



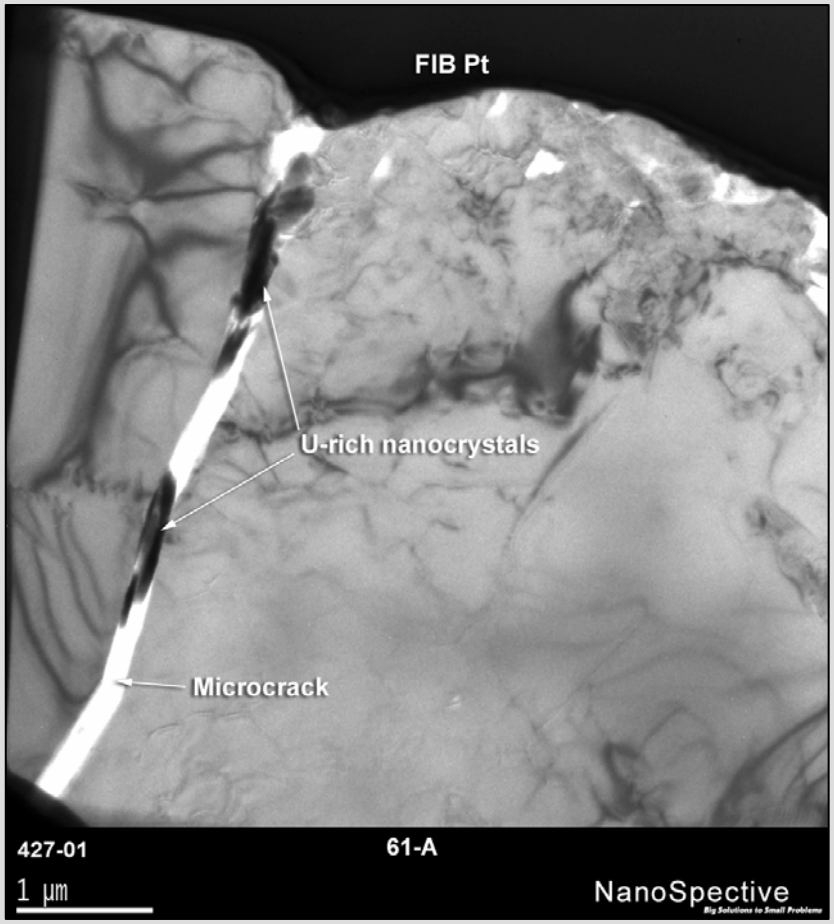


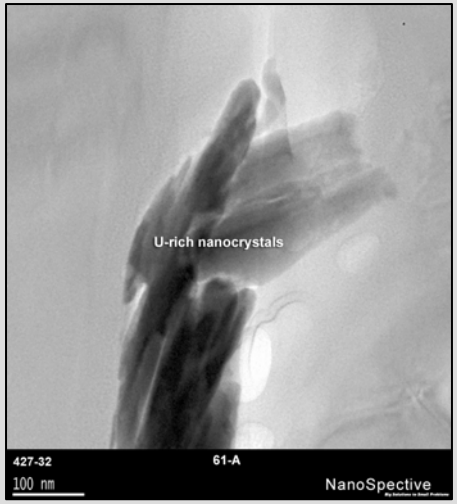
Estimated Composition of Bismuth Phosphate – Metal Waste Released from BX Tank 102

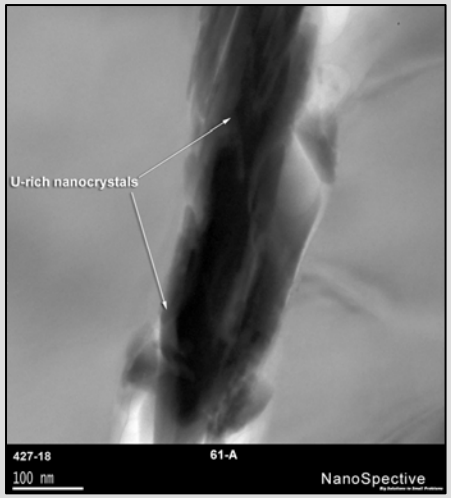
Temperature	80° C
H_2O mole fraction	0.926
H_2O weight fraction	0.816
Solution density	1.24 (g/cm^3)
Ionic strength	4.52
pH = 10.1	pe = 3.08

Primary Chemical Species (mol/L)	
$Al(OH)_4^-$	5.86×10^{-4}
K^+	2.73×10^{-3}
Na^+	2.92
Ca^{2+}	1.33×10^{-2}
Ni^{2+}	1.62×10^{-3}
OH^-	0.1
NO_3^-	0.53
NO_2^-	0.046
HCO_3^-	0.643
HPO_4^{2-}	0.36
CrO_4^{2-}	1.6×10^{-3}
Cs^+	3.44×10^{-6}
UO_2^{2+}	0.114
TcO_4^-	5.81×10^{-6}

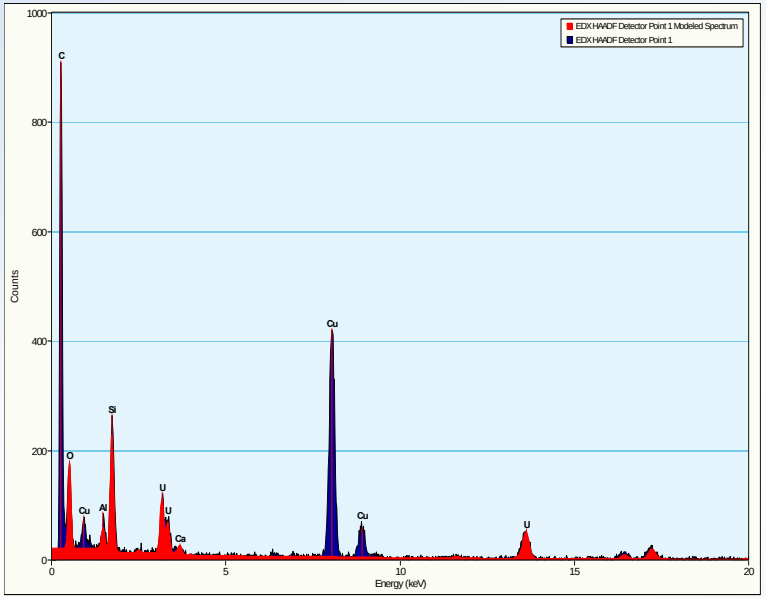
Isolated Fracture 2
Section Thickness ≈ 150 nm



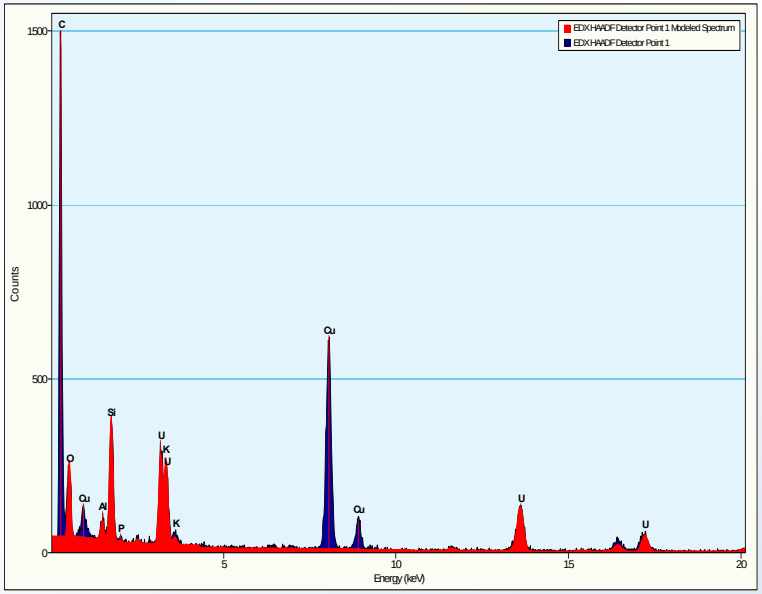




Energy Dispersive Spectroscopy of Crystallites 1 and 2



Elements present U, Si, O, Al, and Ca



Elements present U, Si, O, Al, K, and P

Uranophane	$Ca(H_3O)_2(UO_2)_2(SiO_4)_2(H_2O)_3$
Na-Boltwoodite	$(Na,K)(UO_2)(SiO_3OH)(H_2O)_{1.5}$
Weeksite	$K_{1-x}Na_x(UO_2)_2(Si_5O_{13})(H_2O)_4$

Target of Isotopic Analysis

^{238}U – most abundant natural isotope (99.28%)

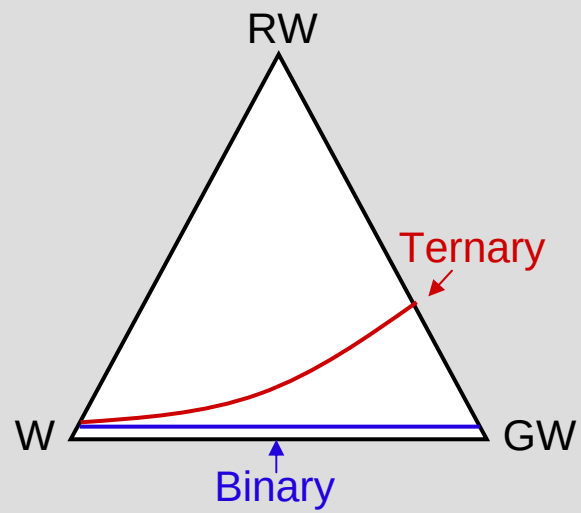
^{235}U – fissile natural isotope (.072%)

^{234}U – ^{238}U daughter (.0057%)

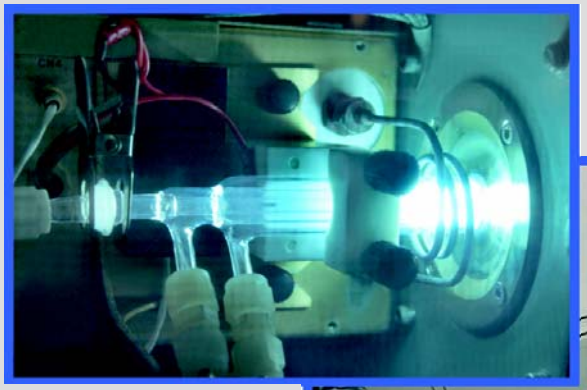
^{236}U – fission product

<u>End Member Mixing</u> (Based on U, not water volume)

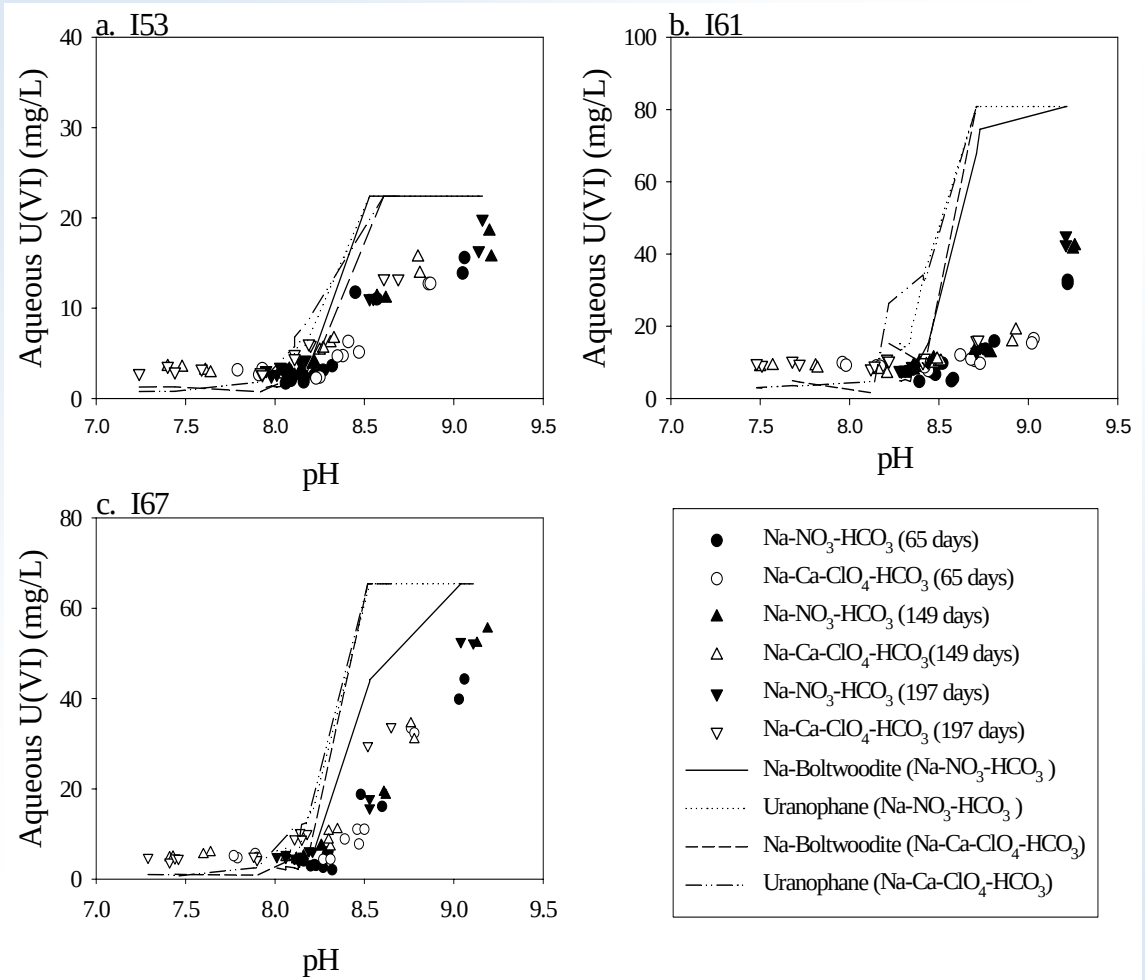
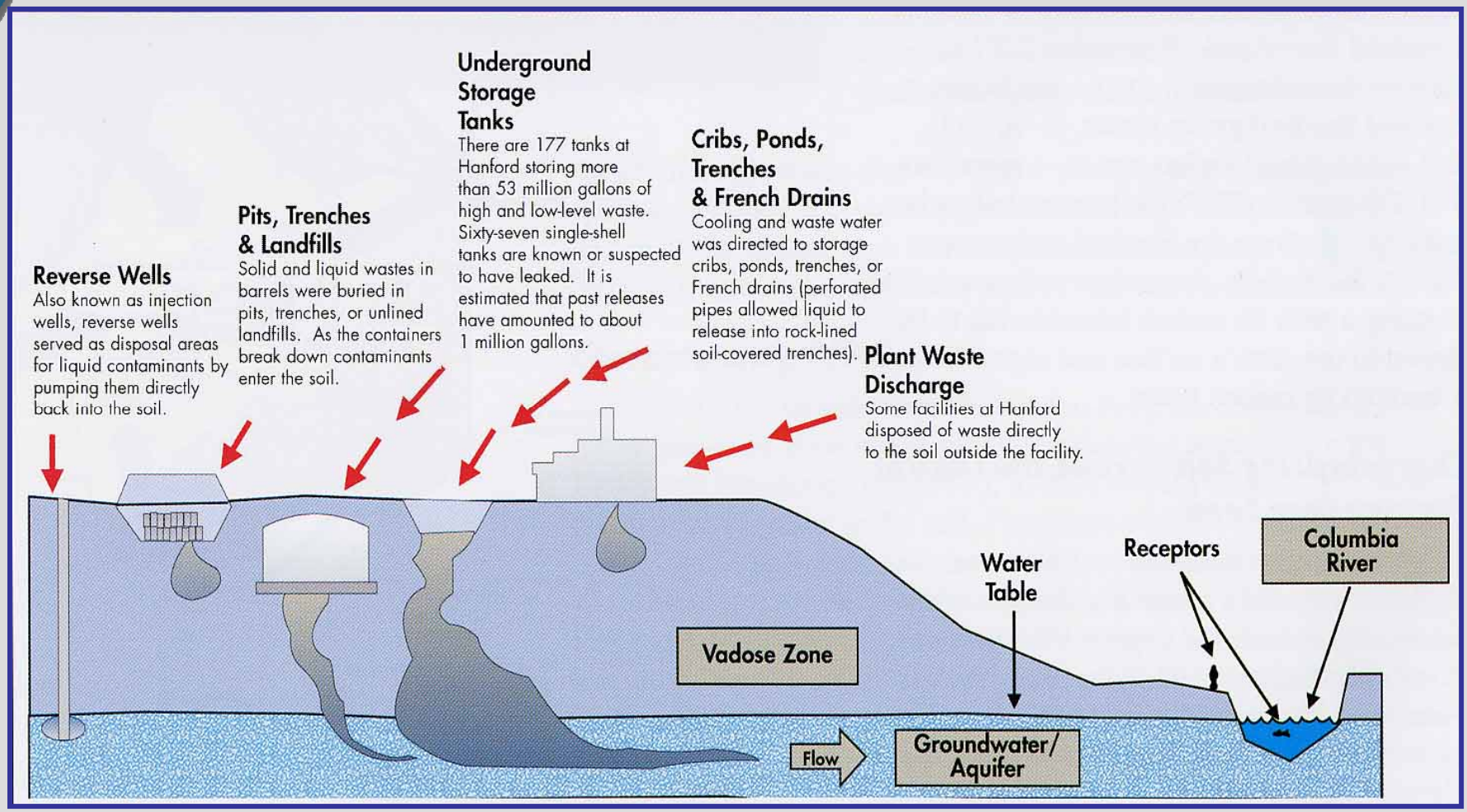
$$AA_s = \frac{[U_{EM1}]}{[U_{EM1} + U_{EM2}]} \bullet AA_{EM1} + \frac{[U_{EM2}]}{[U_{EM1} + U_{EM2}]} \bullet AA_{EM2}$$



Multi-Collector ICP Magnetic Sector Mass Spectrometry (MC-ICPMS) at LBNL/UCB



Solubility Behavior of Intragrain U(VI) Microprecipitates



Sources of Hanford Groundwater Contamination