Pacific Northwest
NATIONAL LABORATORY

Comparison of In Situ Phosphate Amendments for Sequestration of Uranium and Technetium 23241

November 13, 2023

Hilary P. Emerson

A Lawter, MMV Snyder, JE Szecsody, N Huerta, and RD Mackley

U.S. DEPARTMENT OF ENERGY BATTELLE

PNNL is operated by Battelle for the U.S. Department of Energy

Talk Preview

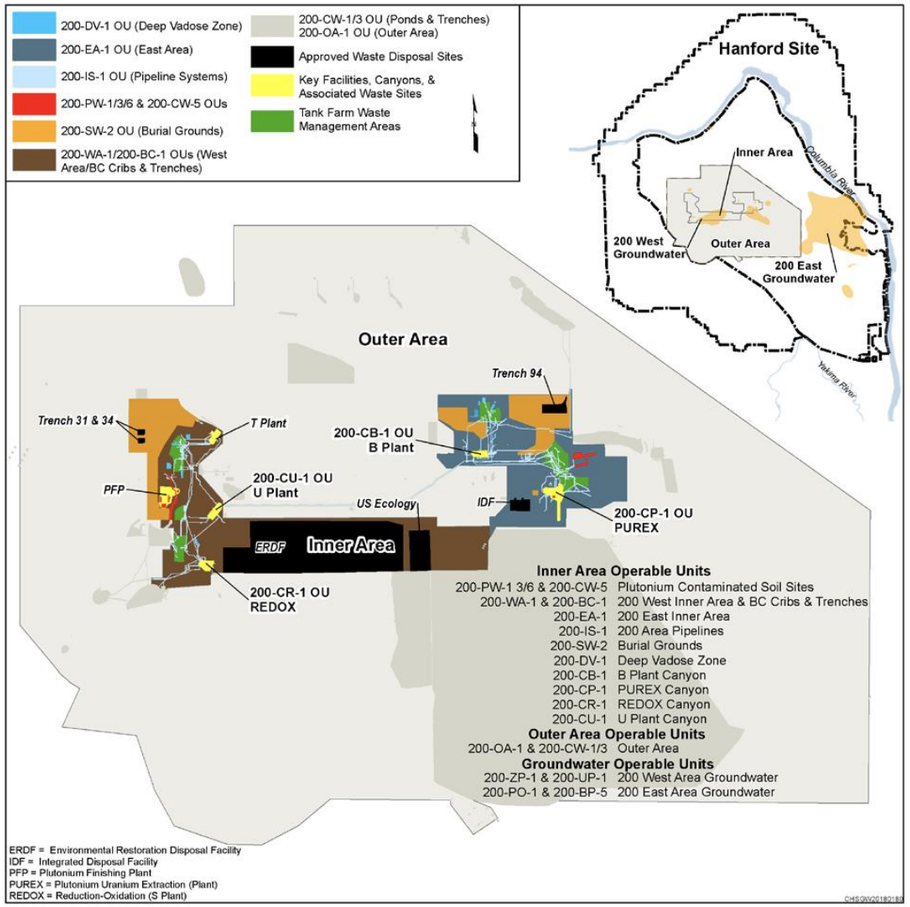
Presenting select technologies being tested as part of a treatability study for remediation of the Central Plateau at the Hanford Site

- What is the remediation challenge?
- Where are the targeted site areas?
- What is the approach for assessing the technologies?
- Which technologies are being tested?
- Are these technologies moving forward with additional testing?

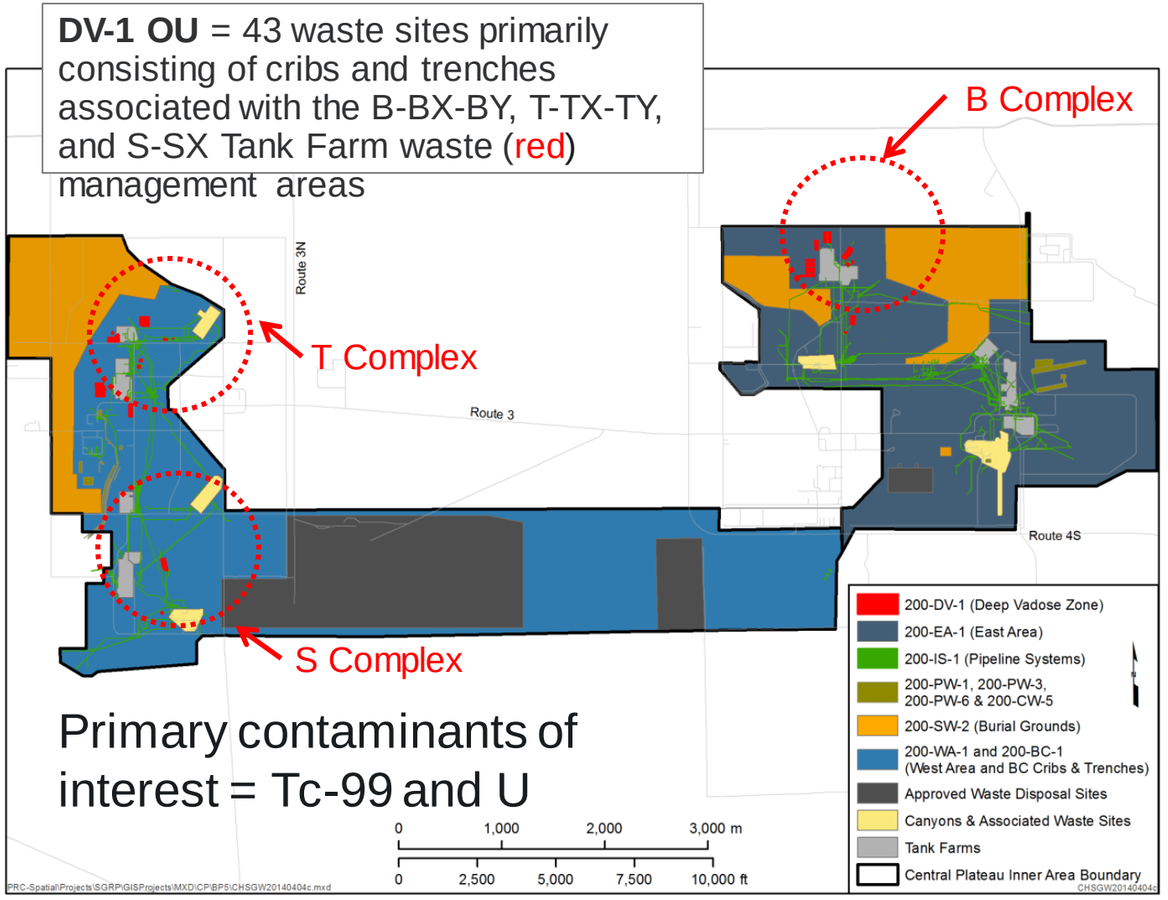
REMPLEX
CENTER FOR THE REMEDIATION OF COMPLEX SITES
@PNNL

200-DV-1 Operable Unit (OU) Background

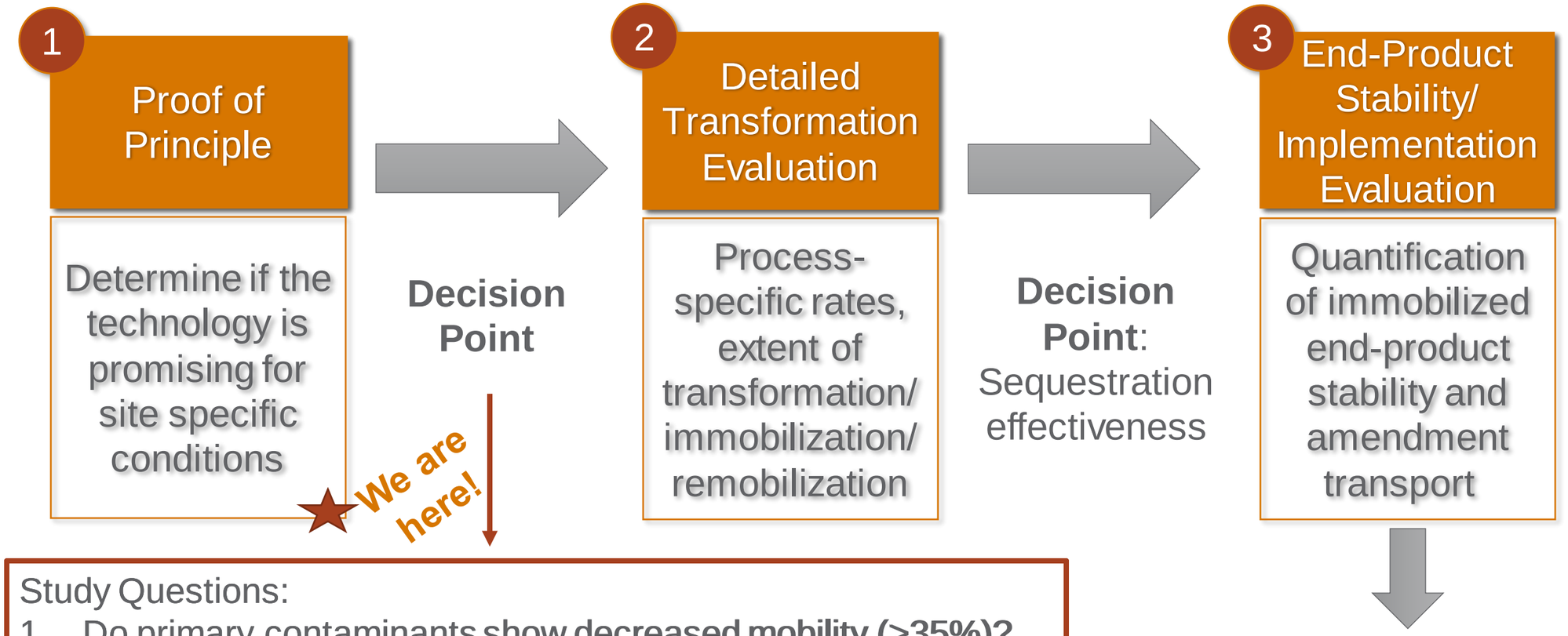
Established in 2010 by the Department of Energy, Environmental Protection Agency, and Washington State Department of Ecology, the OU is composed of selected challenging liquid-disposal waste sites across the Hanford Central Plateau with vadose-zone contamination. Other liquid-disposal waste sites are distributed to the 200-EA-1, 200-WA-1, and 200-BC-1 OUs.



DV-1 OU = 43 waste sites primarily consisting of cribs and trenches associated with the B-BX-BY, T-TX-TY, and S-SX Tank Farm waste (red) management areas



Laboratory Approach for Treatability Testing



Study Questions:

1. Do primary contaminants **show decreased mobility (>35%)?**
2. Do co-contaminants affect primary contaminant mobility?
3. Do co-contaminants become less mobile?

Final Determination for Field-Scale Treatability Study
e.g., is a minimum of 50% sequestration achieved?

REMPLEX
CENTER FOR THE REMEDIATION OF COMPLEX SITES
@PNNL

Approach generalized from detailed guidance in DOE/RL-2019-28, Rev. 0

What Technologies Were Tested?

Liquid amendments

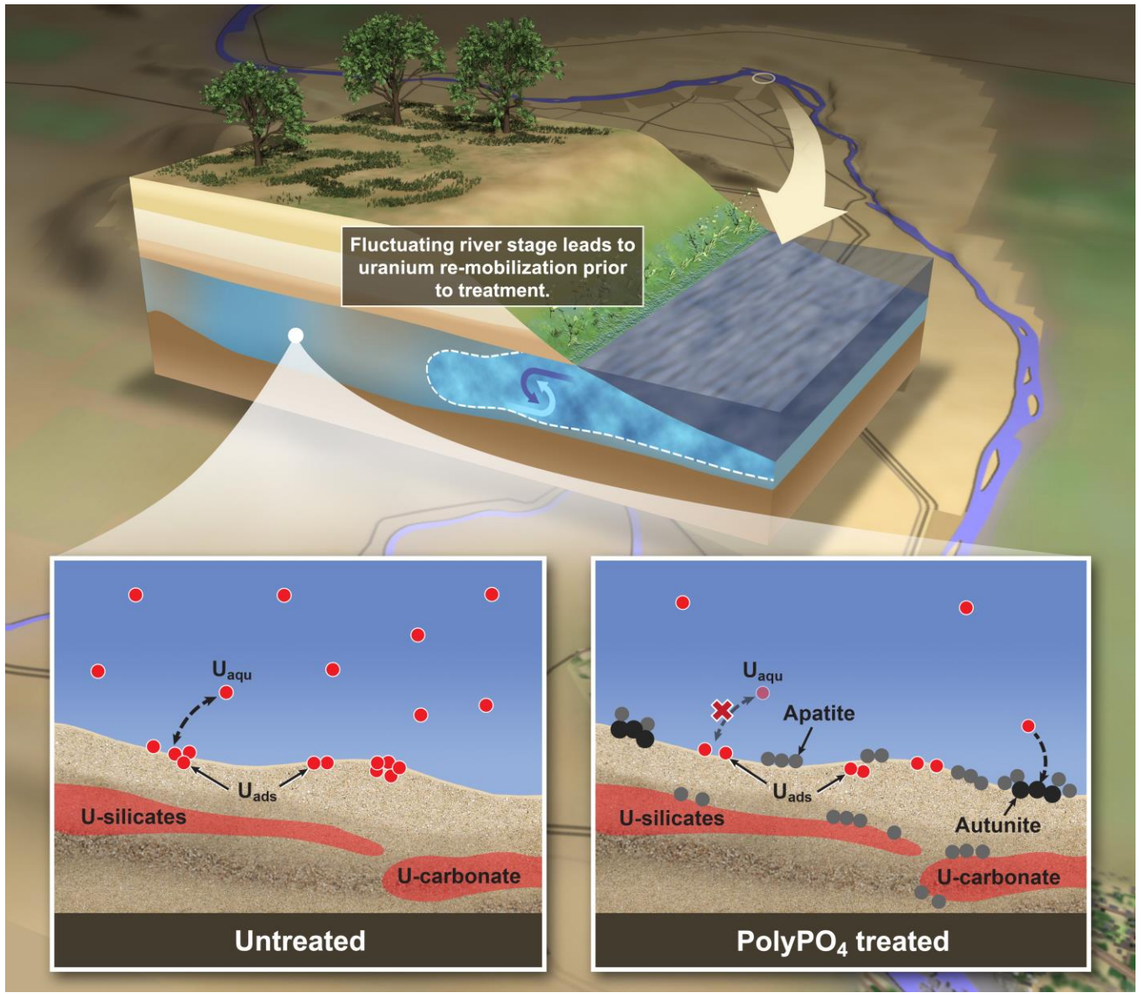
- Polyphosphate – poly-PO_4
  - Chains of phosphate slowly break apart and precipitate with calcium
- Calcium-citrate-phosphate – Ca-Cit-PO_4
  - Citrate slowly degraded by microbes to release calcium for precipitation with phosphate

Particulate amendments

- Tin apatite – Sn-apatite
  - Delivery fluid required (e.g., xanthan gum)

Immobilization mechanisms

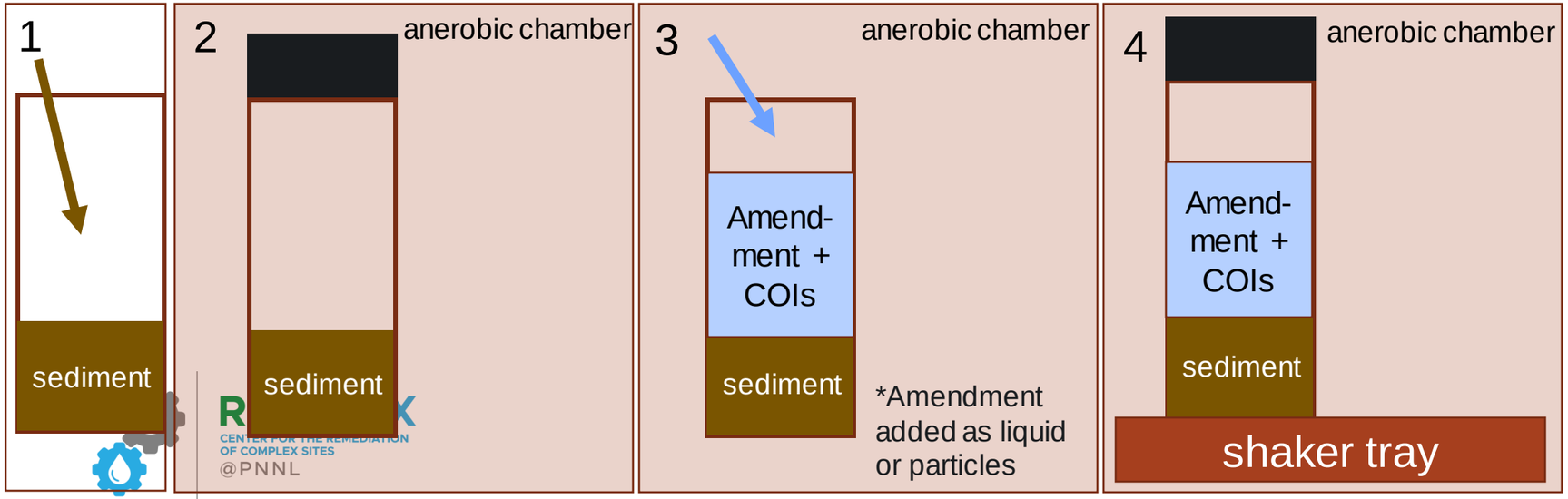
- Adsorption
- (Co)precipitation
- Coating
- Reduction (not for poly-PO_4)



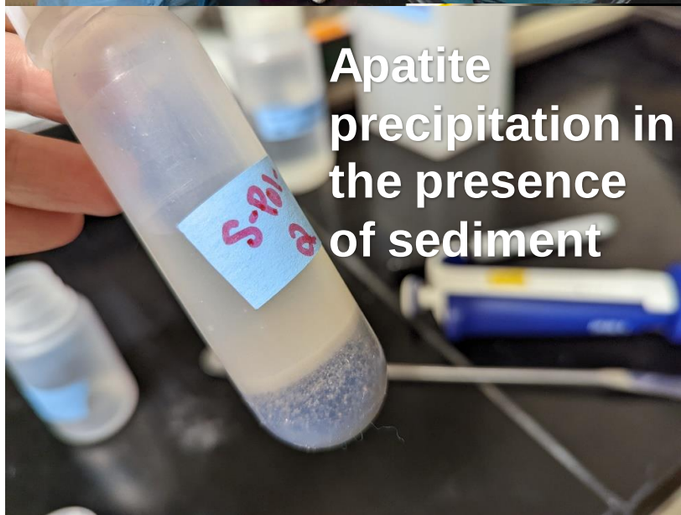
Previous Implementation: Immobilization mechanisms for poly-PO_4 treatment in Hanford 300 Area along Columbia River Corridor

Methods

- Amendments:
  - Two methods of forming apatite from liquids: Poly-PO_4 and Ca-Cit-PO_4 with the same total concentrations of phosphate and calcium
  - Particulate Sn-apatite
- Site conditions = BY Cribs water table or perched water = Hanford formation sediments + groundwater simulant + amendment
- Measure U & Tc-99 immobilization with and without Co-contaminants of interest (Co-COIs): CrO_4^{2-}, IO_3^-, Sr^{2+}, NO_3^-
  - Added in aqueous phase to represent most mobile phases (most conservative case)



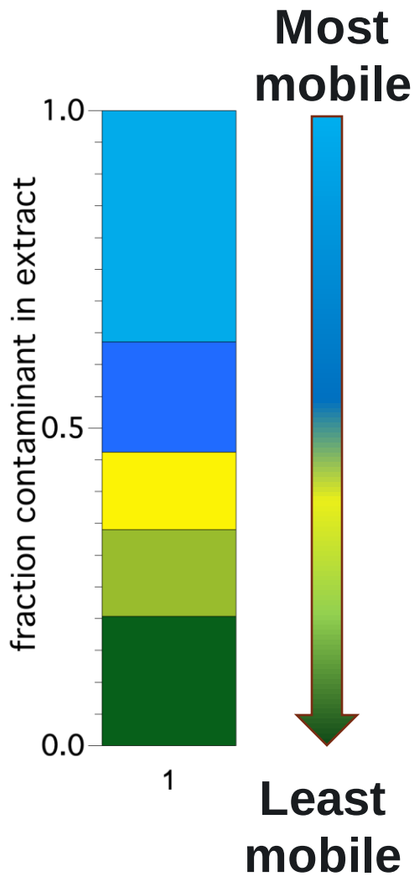
COI = contaminant of interest



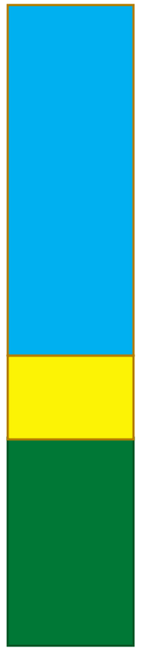
Contaminant Mobility: Approach and Definitions

- Sequential extractions of increasing acidity to characterize contaminants in different solid phases
- Useful to define change in contaminant mobility from remedial technology application
- “Immobile” fraction is used for the >35% decreased mobility criterion in Decision Point 1

Aqueous	Aqueous + Extract 1: Anaerobic Groundwater or Pore Water
Adsorbed	Extract 2: Anaerobic 0.5M $Mg(NO_3)_2$
Reduced, Easily Oxidized	Extract 3: Aerobic 0.5M $Mg(NO_3)_2$
Precipitates: Carbonates	Extract 4: pH 2.3 acetic acid
Precipitates: Silicates + oxides + (?)	Extract 5: 8M HNO_3, 95°C



Definitions in this study:



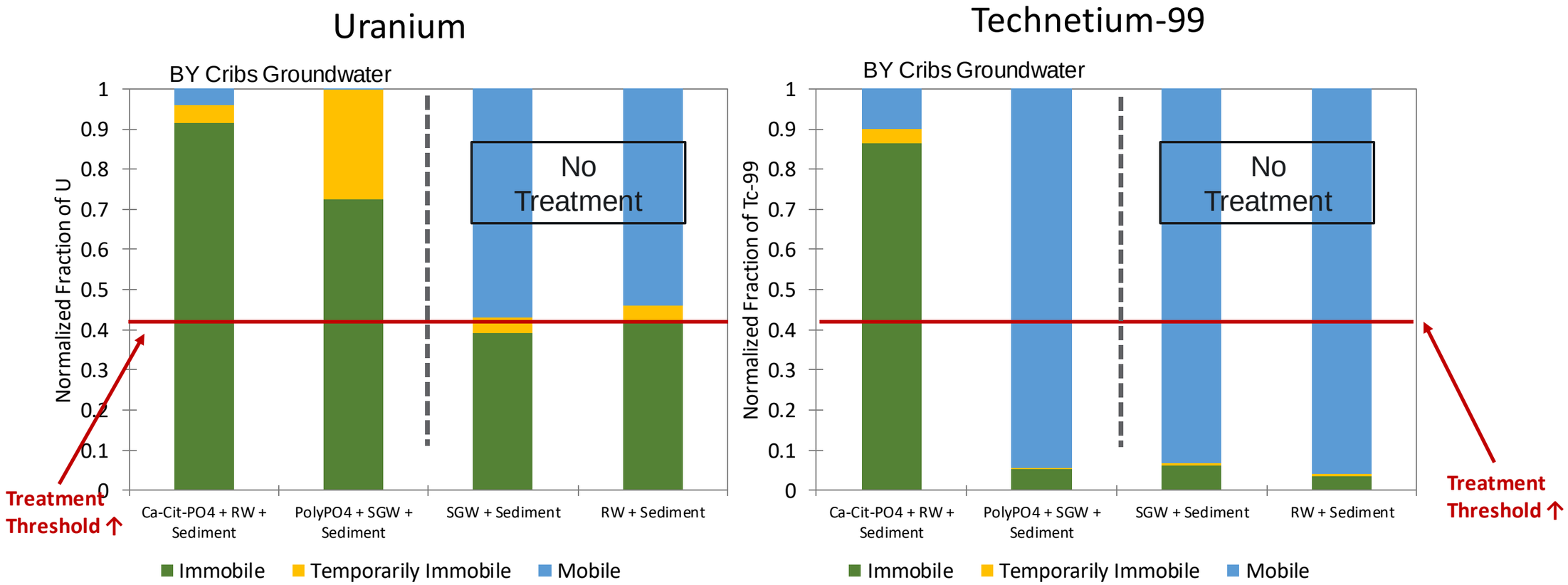
Mobile
Aqueous + Extract 1 + Extract 2

Temporarily immobile
Extract 3

Immobile
Extract 4 + Extract 5

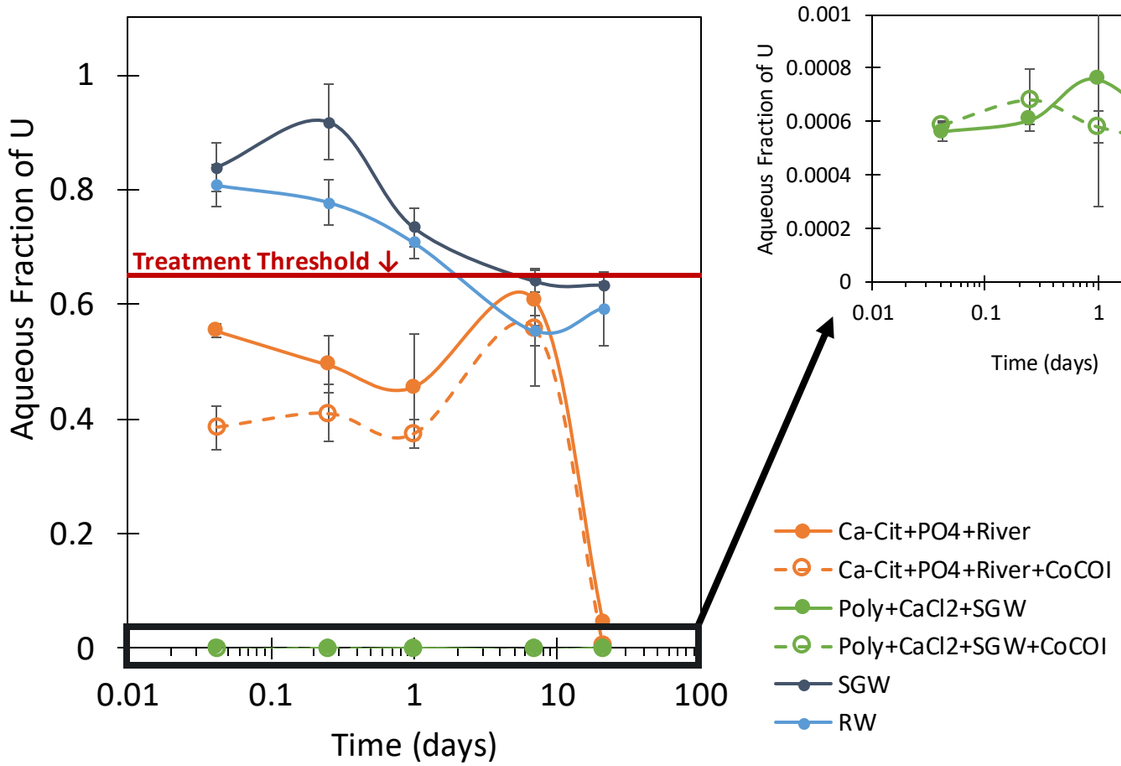
REMPLEX
CENTER FOR THE REMEDIATION OF COMPLEX SITES
@PNNL

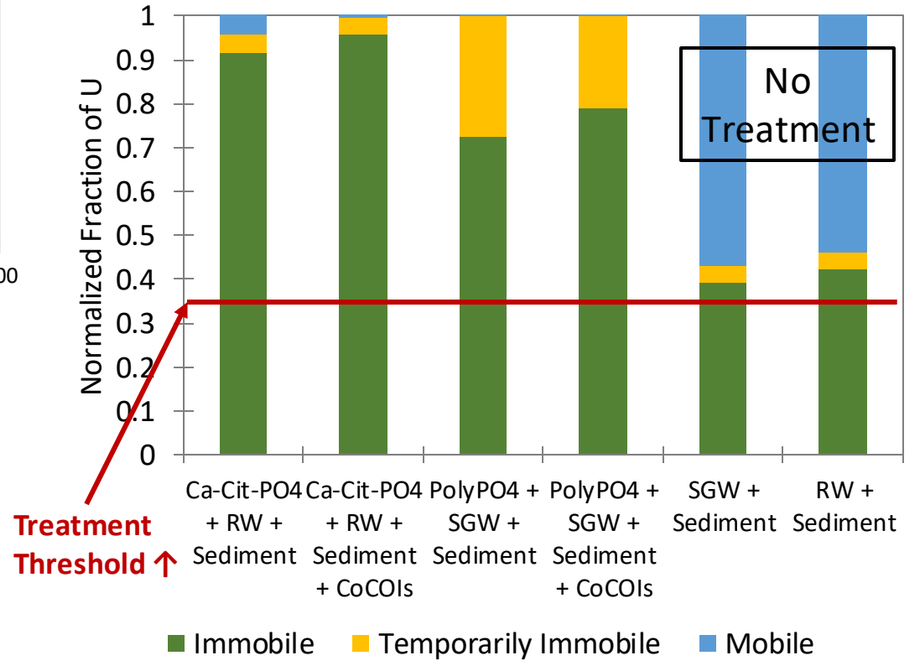
Liquid Amendments: Summary



- $Ca\text{-}Cit\text{-}PO_4$ is effective for both U and Tc-99 under both BY Cribs and perched water conditions; some decrease in Tc-99 immobilization in perched water conditions (high NO_3)
- $Poly\text{-}PO_4$ is only effective for U and is less effective under perched water conditions (high NO_3)

Liquid Amendments: U Immobilization in BY Cribs Groundwater

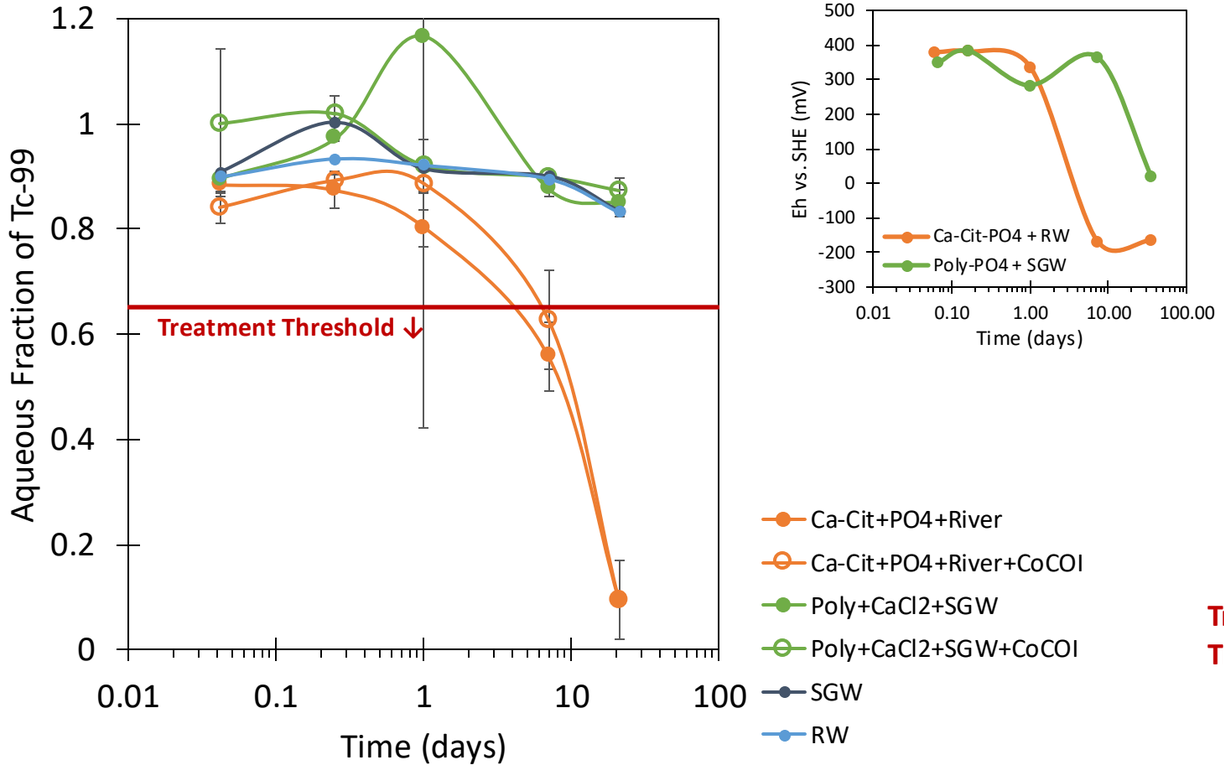


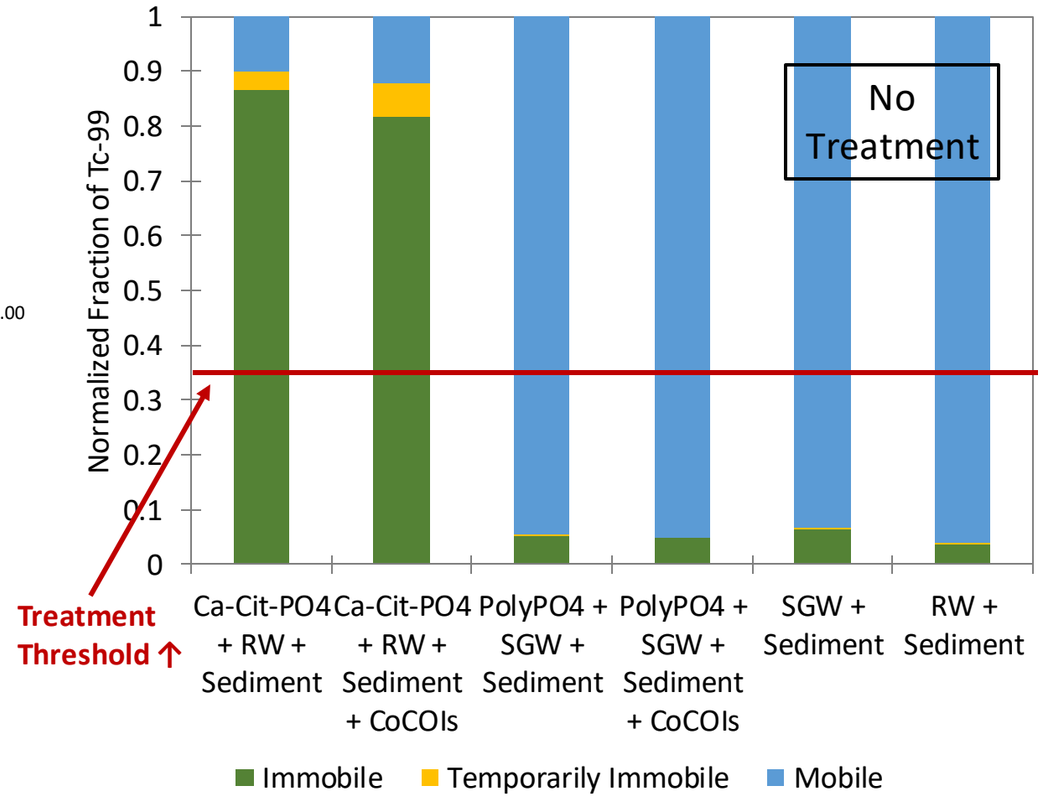


- Treatment threshold for U met with both technologies
  - Within hours for poly-PO_4
  - Within weeks for Ca-Cit-PO_4
- Sequential extractions confirm significant fraction is immobilized by amendments
- No impact of Co-COIs on amendment efficacy
- Significant impact of sterilizing sediments and solutions on Ca-Cit-PO_4 amendment efficacy

REMPLEX CENTER FOR THE REMEDIATION OF COMPLEX SITES @PNNL

Liquid Amendments: Tc-99 Immobilization in BY Cribs Groundwater

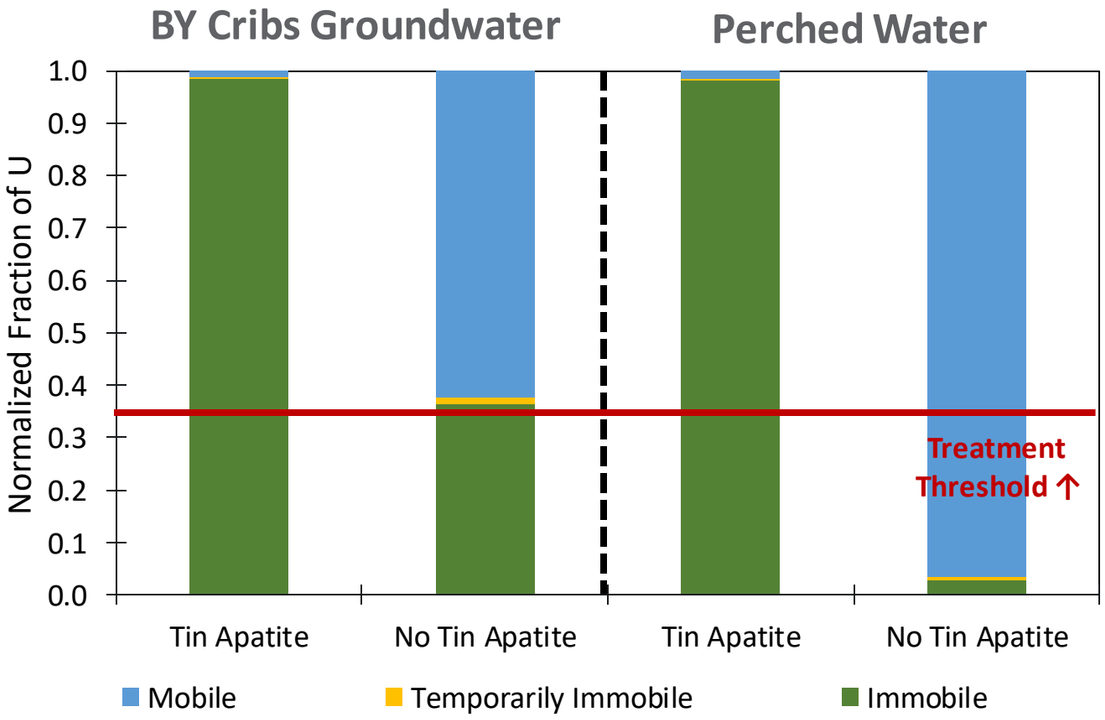




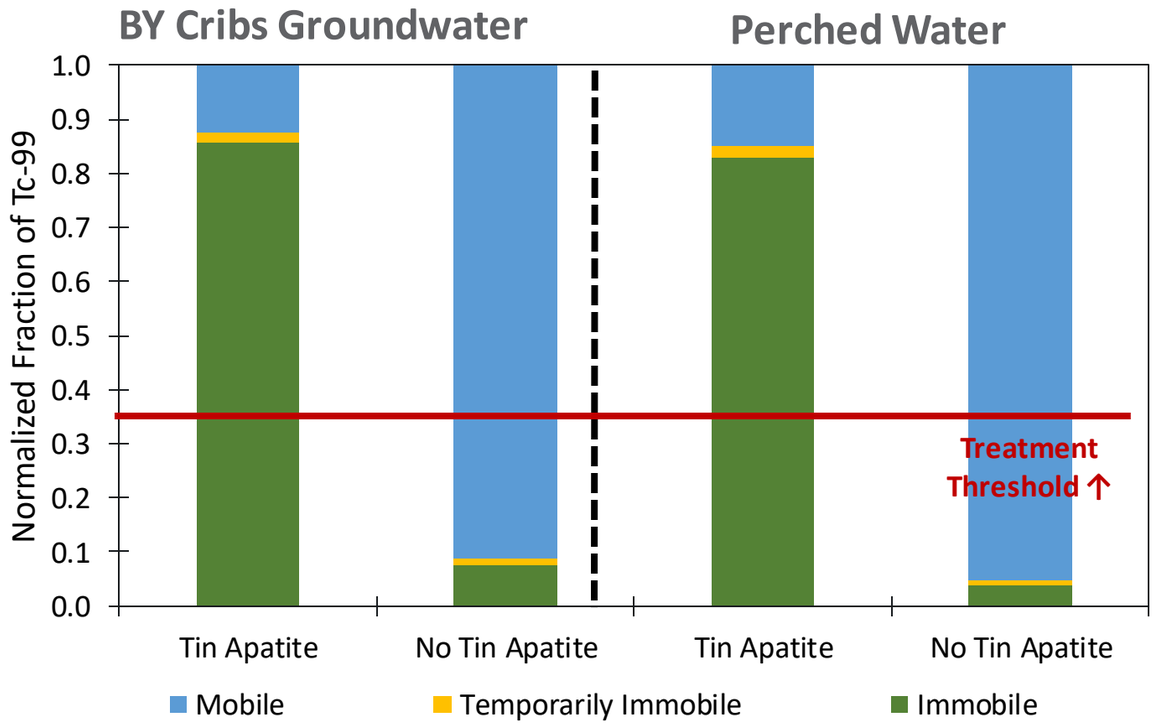
- Treatment threshold met only for Ca-Cit-PO_4 after weeks of reaction
- Sequential extractions confirm a significant fraction is immobilized by amendments
- No impact of Co-COIs on amendment efficacy
- Significant impact of sterilizing sediments and solutions on Ca-Cit-PO_4 amendment efficacy

Particulate Amendments: Summary

Uranium



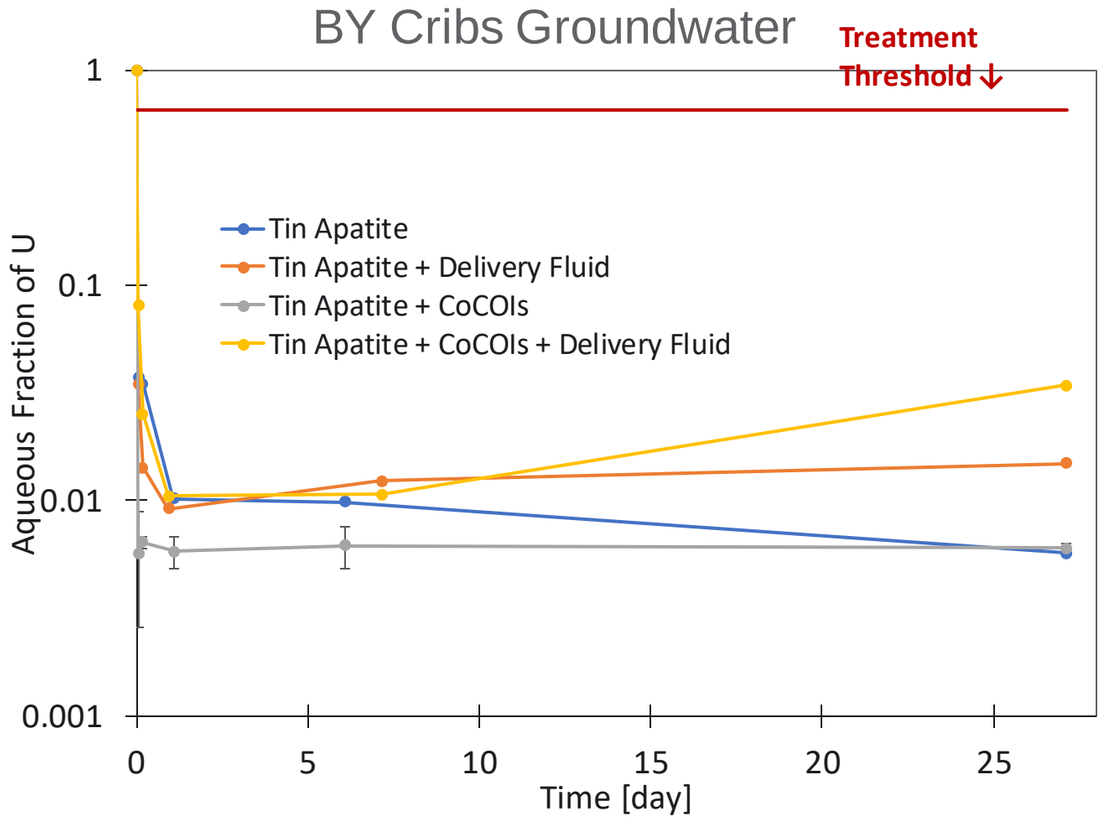
Technetium-99

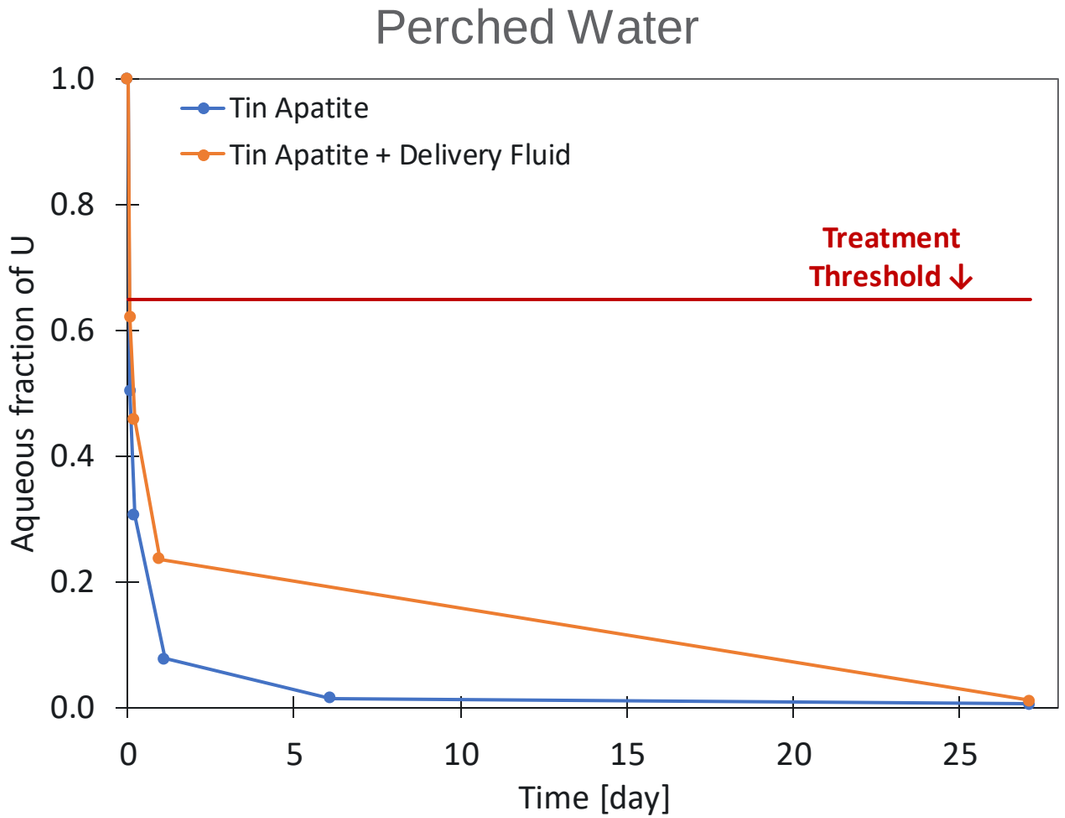


REMPLEX
CENTER FOR THE REMEDIATION OF COMPLEX SITES
@PNNL

- U and Tc-99 were successfully removed from aqueous phase by tin apatite
- Extractions indicate amendment immobilized most of the primary COIs (U: 98%; Tc-99: 84%)
- Immobilization kinetics were very rapid (i.e., occurred within first hour of treatment)

Particulate Amendments: Uranium Removal





Note the log scale

- Immobilization kinetics were faster in groundwater (hours) as compared to perched water (days to weeks)
- Presence of Co-COIs impacted U removal in perched water but not groundwater; no impact for Tc-99 (not shown)

Conclusions

- Ca-Cit-PO_4 is *effective* for both U and Tc-99 under site specific conditions
- Poly-PO_4 is *effective* for U under site specific conditions
- Immobilization (per extractions) $\Rightarrow$ **Sn-apatite > Ca-Cit-PO_4 > poly-PO_4**
  - Ineffective for Tc-99 for poly-PO_4
  - Less Tc-99 immobilized in perched water for Ca-Cit-PO_4
- Removal speed $\Rightarrow$ **Sn-apatite > poly-PO_4 > Ca-Cit-PO_4**
  - Removal was slower in perched water for U for Sn-apatite and poly-PO_4
- Path forward
  - Proof-of-principle testing for poly-PO_4 with additional reductants
  - Additional testing under site-specific conditions for Ca-Cit-PO_4 and Sn-apatite

Pacific Northwest
NATIONAL LABORATORY

Funding for this work was provided by the U.S. Department of Energy Richland Operations Office under the Deep Vadose Zone – Applied Field Research Initiative.

Pacific Northwest National Laboratory is operated by Battelle Memorial Institute for the Department of Energy under Contract DE-AC05-76RL01830.

Thank you

Hilary Emerson
hilary.emerson@pnnl.gov