Integrated Field-Scale Research Challenge

Enhanced Contaminant Stability Strategies for Source Control (Task C)

ERSP Annual PI Meeting
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Objectives

Overall: manipulate biogeochemical conditions to ensure a long-term and sustainable decrease in subsurface contaminant flux. Explore novel strategies for enhanced subsurface immobilization and stability of metals and radionuclides.

Specific:

1) Evaluate pH adjustment as a simple immobilization strategy.

2) Expand the existing bioreduction zone to test in situ contaminant stability strategies at a significantly larger-scale.

3) Evaluate dual substrate addition for more effective delivery of electrons to SRB and FeRB and improved reduction and immobilization of U(VI).

4) Evaluate use of a slow release electron donor for maintenance of microbial activity and enhanced long-term stability of immobilized U & Tc.

5) Test in situ immobilization of U and Tc by microbial production of phosphate upon delivery of slow release organo-phosphate.

6) Characterize ecology/geochemistry of efficient and stable immobilization.
Field Evaluation of Different Processes

**Manipulations and remobilization**
- Shale/saprolite - low pH
  - Plot 1 - pH adjustments
  - Plot 2 - ethanol, formate, SO$_4$, organic P
  - Length scale of reduction zone
- Carbonate gravel - high pH
  - Plot 3 - ethanol, Ca-oleate, organic P

**Natural attenuation**
- Drainage ditch recharge
- Geophysics transects
- Well transects

Manipulated plots: P1, P2, P3
Shale/saprolite plume
NT-1, NT-2
Bear Creek
Maynardville Limestone
S-3 Ponds Cap
Manipulated plots

Length scale of reduction zone
U and Tc source control and immobilization can be achieved by subsurface pH adjustment

**Opportunity:**

U and Tc form precipitates or co-precipitates with Al-oxyhydroxides.

The stability of U and Tc is increased by the formation of lower-solubility aluminosilicates.

Increased downgradient denitrification due to increased pH.
pH adjustment for U and Tc source control and immobilization

Laboratory and field column tests are coupled with numerical modeling to determine operational parameters.

Slow, steady-state injection of dilute KOH and/or Si(OH)$_4$ in a hydraulically controlled well system is used to raise pH and prevent immediate formation of Al precipitates.

Formation and transport of meta-stable Al-oxyhydroxides is monitored within a zone where U(VI)/Tc(VII) are immobilized.

Enhanced microbial activity and denitrification result from increased pH.
Hydrogeochemical control plus intermittent additions of ethanol decreased aqueous U concentrations to very low levels, stable in the absence of O$_2$ and NO$_3^-$.

U concentration changes in monitoring wells before and after three years of biostimulation. U in fast flow region (40-45 ft depth) dropped below EPA MCL of 30 ppb.
Dual electron donor addition i.e ethanol and formate is expected to enhance reduction rate and subsurface penetration

1. Formate is an intermediate of ethanol degradation and formate at elevated levels inhibits ethanol degradation

\[
\text{CH}_3\text{CH}_2\text{OH} + 2 \text{HCO}_3^- \rightarrow \text{CH}_3\text{COO}^- + \text{H}^+ + 2 \text{CHOO}^-
\]

2. Both formate and ethanol support U(VI) reduction in groundwater from FRC to below US EPA MCL (< 0.126 µM or 0.03 mg/L).

FeRB, SRBs, and denitrifiers known to reduce U(VI) are found in the reduced zone.

X-ray Absorption Spectroscopy confirm in situ bioreduction of U(VI) to nanoparticulate U(IV) (uraninite)
Biomanipulation and contaminant sequestration by organo-P

U-phosphates have low solubility and high stability.

Organo-phosphates can be degraded by microorganisms, releases phosphate that precipitates U:

\[
\text{Glycerol- or tributyl-phosphate} \rightarrow \text{phosphate}
\]

\[
\text{Phosphate + U} \rightarrow \text{U-PO}_4^{2-} \text{ complex}
\]
Two new subplots

Subplot I with high nitrate will be subject to biomanipulation, with multiple electron donor.

Subplot II is the original reduced zone, and will be used to test stability and remobilization.

Subplot III will be treated with organo-P
Plot 3: Concepts to be tested

1. Biomanipulation with calcium oleate as a **slow release electron donor**

Inject aqueous K-oleate, mix with groundwater. This will be followed by rapid formation of Ca-oleate precipitates:

$$2\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOK} + \text{Ca}^{2+} \rightarrow (\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COO})_2\text{Ca} \downarrow + 2\text{K}^+$$

Ca-oleate precipitates serve as a slow release e-donor providing long-term source of hydrogen and acetate (Yang and McCarty, 2000).

Tracer Br will be injected with K-oleate to quantify Ca-oleate retardation.

2. Biomanipulation with organic-P
**Plot 3: Two new subplots**

Proposed work:

Subplot I - current ethanol-fed subplot (control).

Subplot II - organo-P immobilization

Subplot III - calcium oleate immobilization
Measurement and Monitoring

- **Hydrological and geochemical monitoring**: monitor changes in major analyte concentrations in groundwater and sediment.

- **Microbial community analysis**: Monitor changes in major populations in groundwater and sediment.

- **Geophysical methods**: monitor changes in response to manipulations.

- **Spectroscopy**: High-resolution interfacial spectroscopy techniques such as XANES and EXAFS analysis to monitor changes in the speciation of U in relation to process manipulation and stability.
Recent accomplishments

- Laboratory pH titration of subsurface coupled with mechanistic numerical modeling.

- Bioreduction and immobilization of U are continuing in Plot 2. U concentrations in the groundwater have remained below the US EPA MCL (<0.03 mg/L) for more than three months.

- Two new geoprobe wells were installed in Plot 2 to guide well field expansion.

- One tracer test was completed in Plot 2 to determine the flow patterns and entry of groundwater into the treatment zone for future expansion design and stability studies.

- MicroXAFS measurements completed showing the U-rich rind surrounding subsurface gravel material in Plot 3.

- U XAFS measurements identified monomeric U(IV) & uraninite in sediments from samples in Plot 2.
Outcomes

- Field evaluation of U/Tc immobilization and stabilization through controlled pH adjustment.

- U and Tc reduction by stimulation of microbial activities by delivery of electron donors and phosphate-producing reagents.

- Determination of the changes in U flux and speciation before and after manipulation.

- Microbial community dynamics associated with manipulation and optimal population structure related to remediation rate and stability.

- Information needed for optimization of remediation strategies.

- Reactive transport models of nitrate and U reduction, reoxidation by nitrate and oxygen, and solute flux under various conditions.

- Analysis of natural attenuation of nitrate, U and Tc

- Trained students and post-graduates and peer-reviewed publications in high impact journals.