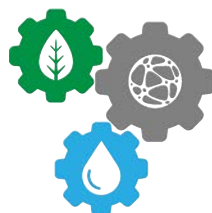




Integrating Key Capabilities for the Remediation of Complex Sites

October 27, 2020

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Vicky Freedman



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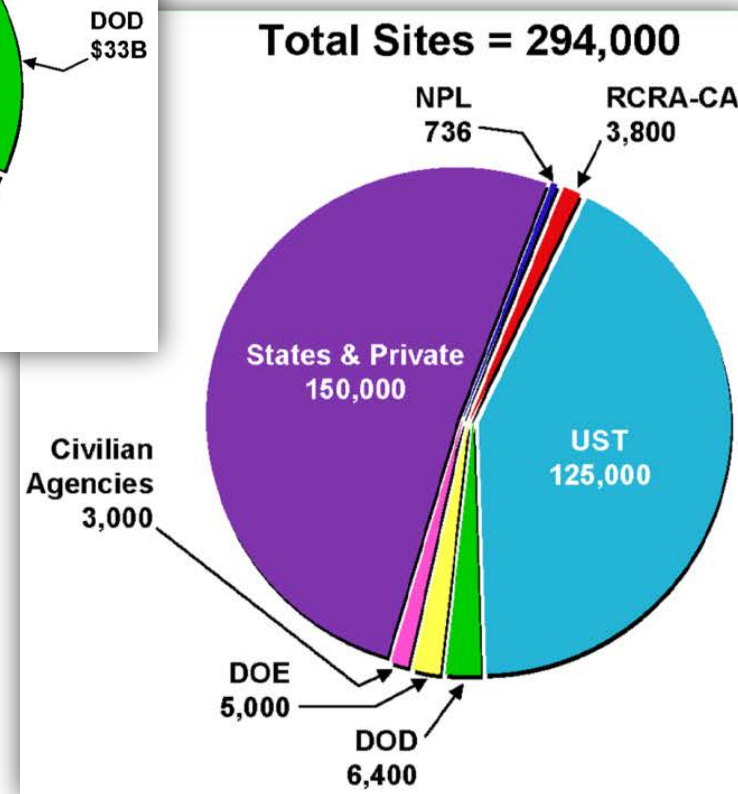
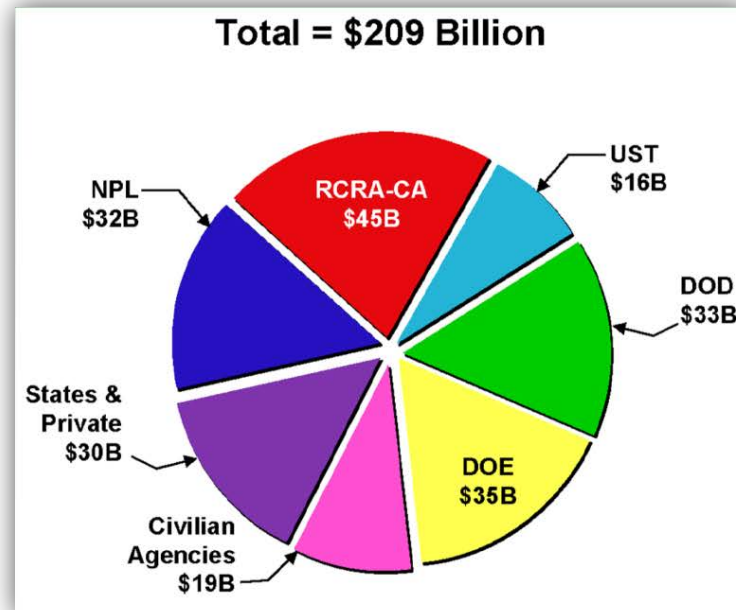
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Agenda

- Complex Sites
 - Challenge
 - Distinguishing features
- Key Capabilities
 - QCSM development
- Iodine-129 Remedy Selection Support

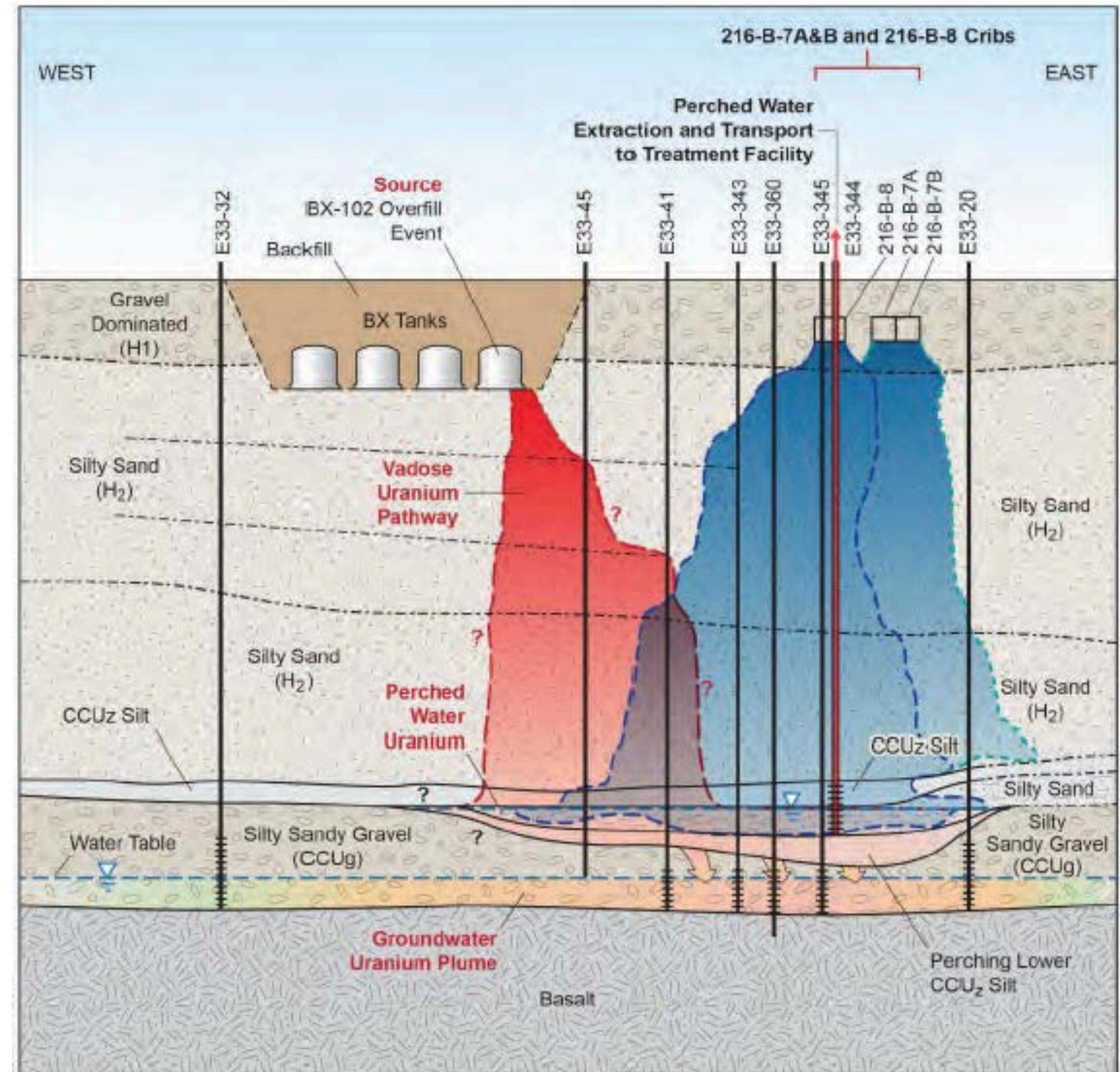
The Challenge of Complex Sites



- EPA, 2004
 - Technical complexities limiting remediation and closure of ~300,000 sites and ~\$200B
- National Research Council, 2013
 - Technical complexities preventing closure of ~13,000 sites 50-100 years
 - “...extensive groundwater contamination, heterogeneous geology, large releases and/or source zones, multiple and/or recalcitrant contaminants, heterogeneous contaminant distribution in the subsurface, and long time frames since releases occurred.”
- Interstate Technology & Regulatory Council, 2017
 - “Sites where remediation progress is uncertain, and remediation is not anticipated to achieve closure or even long-term management within a reasonable timeframe.”

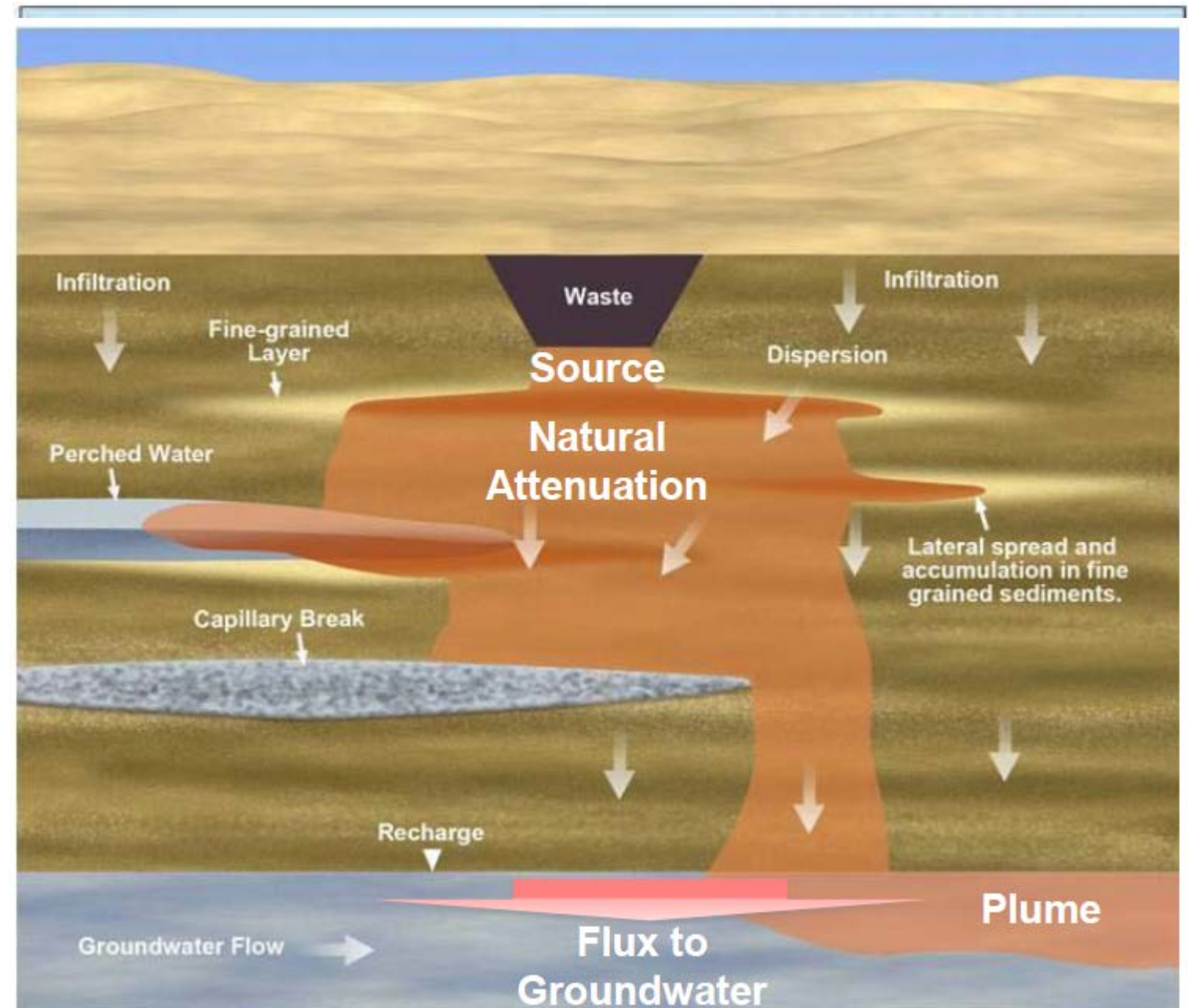
What Makes a Site Complex?

- Multiple sources & contaminants
- Comingled plumes



What Makes a Site Complex?

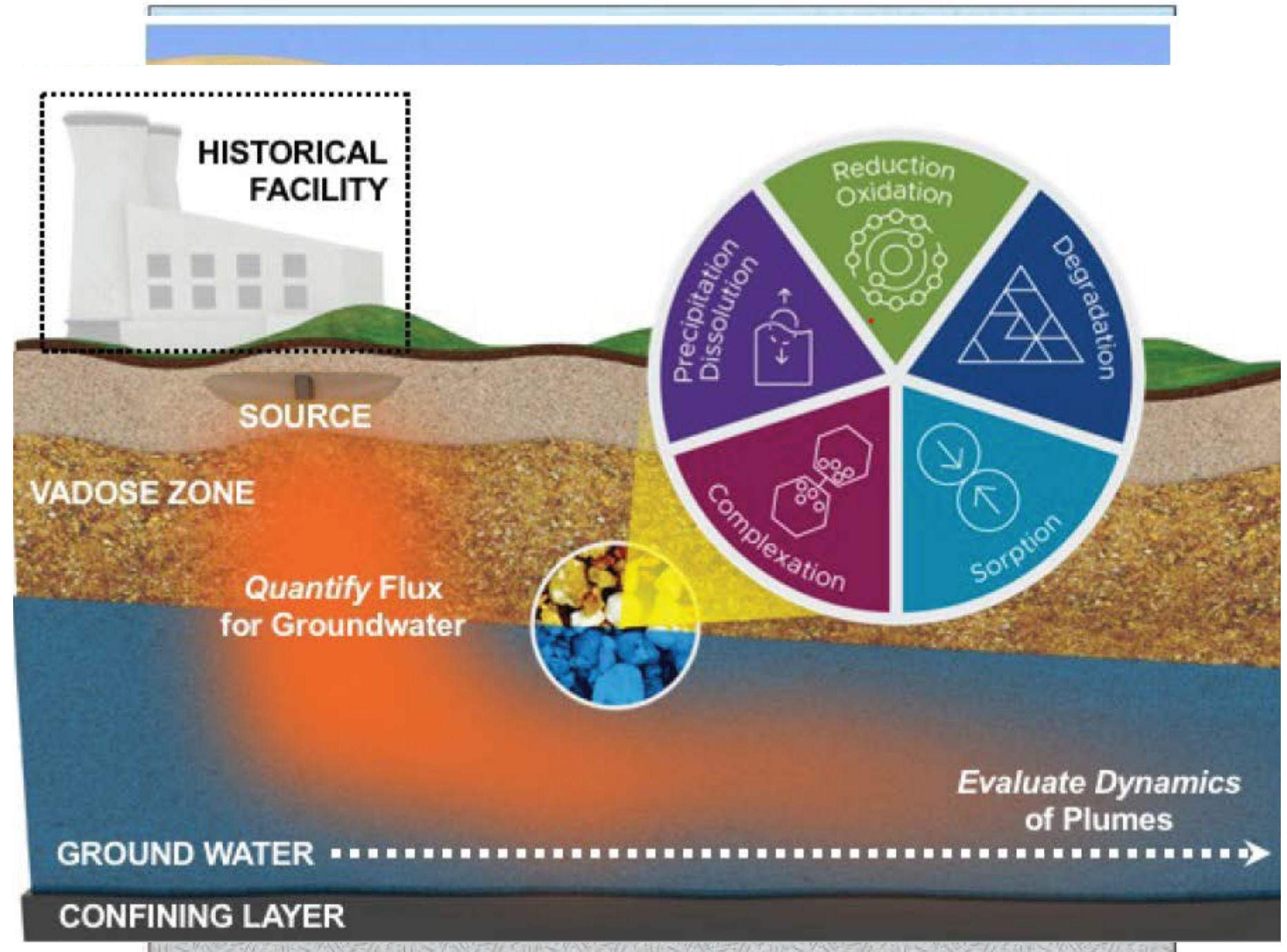
- Multiple sources & contaminants
- Comingled plumes
- Complex geology



Adapted from Dresel *et al.* 2011

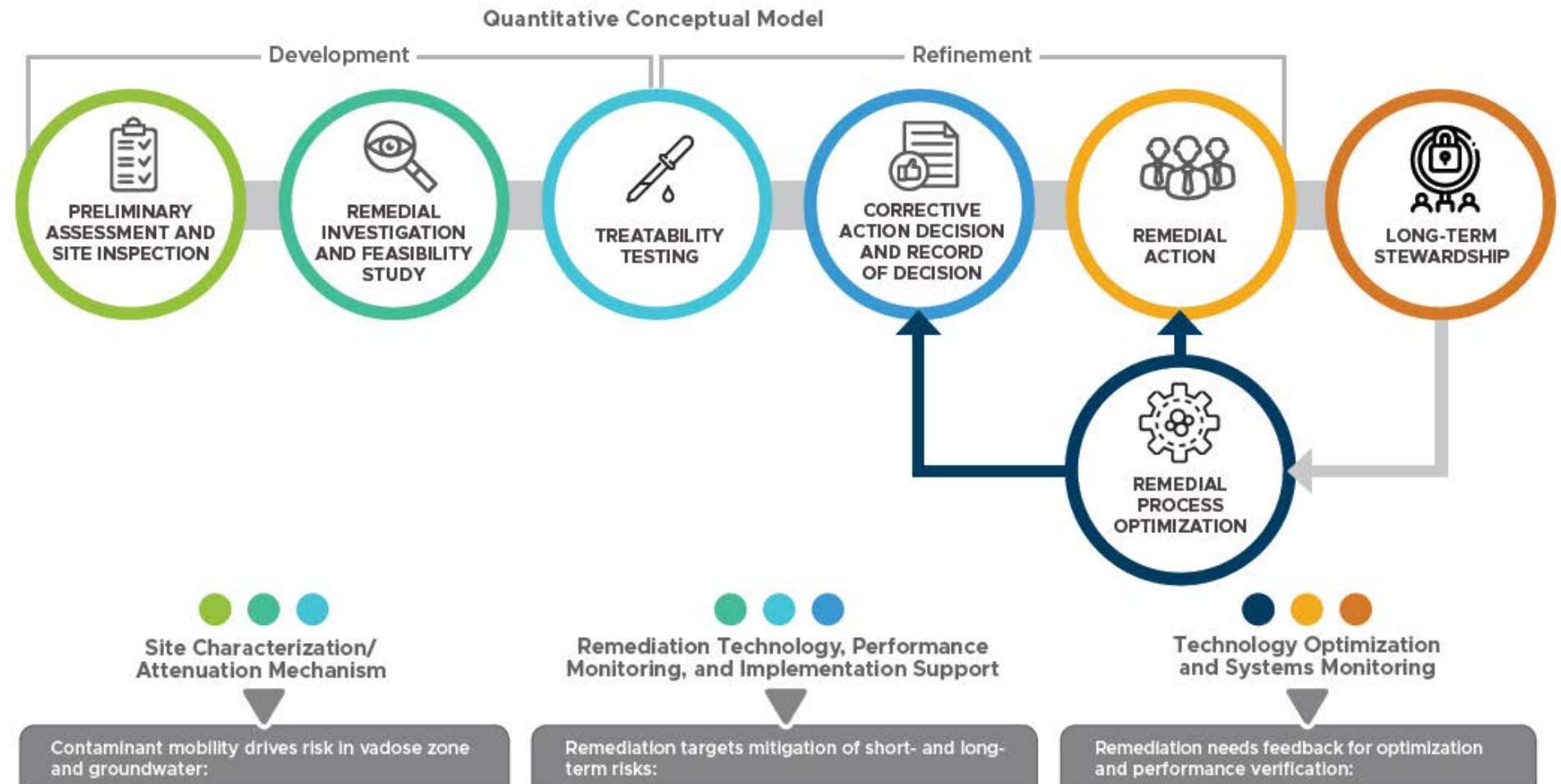
What Makes a Site Complex?

- Multiple sources & contaminants
- Comingled plumes
- Complex geology
- Impact of biogeochemical processes on fate & transport



Complexity: Integrating Across the Lifecycle of Remediation

- Evolving data and analysis needs throughout RCRA/CERCLA process
- Adaptive management critical to achieving end states



Core Capabilities Critical to Complex Site Remediation

				
Core Competency	Nature & Extent	Remedial Design	Remedial Action	End States
Domain Expertise	<ul style="list-style-type: none"> Subsurface heterogeneity & contaminant behavior Characterization of controlling processes Metal & radionuclide speciation Computational & numerical modeling 	<ul style="list-style-type: none"> Quantification of contaminant flux & attenuation mechanisms Fate of inorganic & radionuclide contaminants Moisture & contaminant flux control Materials development 	<ul style="list-style-type: none"> Remediation systems engineering Multi-phase flow & transport Monitored natural attenuation Surface barriers 	<ul style="list-style-type: none"> Remediation & D&D decision science Advanced imaging & systems-based monitoring Systems assessment Data analysis & tool development NEPA/environmental assessment
Distinguishing Capability	✓ Quantitative conceptual site models	✓ Technical basis for adaptive management	✓ Synergistic remedial approaches	✓ Risk-indicator & adaptive predictive monitoring
Metrics	<ul style="list-style-type: none"> 114 staff, 1300+ publications DOE-EM, DOE-SC, DOE-FE, NRC, EPA 	<ul style="list-style-type: none"> 34 staff, 400+ publications DOE-EM, EPA, DOD 	<ul style="list-style-type: none"> 74 staff, 900+ publications DOE-EM, EPA, DOD 	<ul style="list-style-type: none"> 96 staff, 600+ publications DOE-EM, EPA, NRC



Internationally and Nationally Recognized Expertise to Provide Continuity in Remediation and Stewardship



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Solution Development – Leverage existing capabilities spanning all TRLs, to provide solutions in adaptive remediation and long-term stewardship that enable risk-based remediation

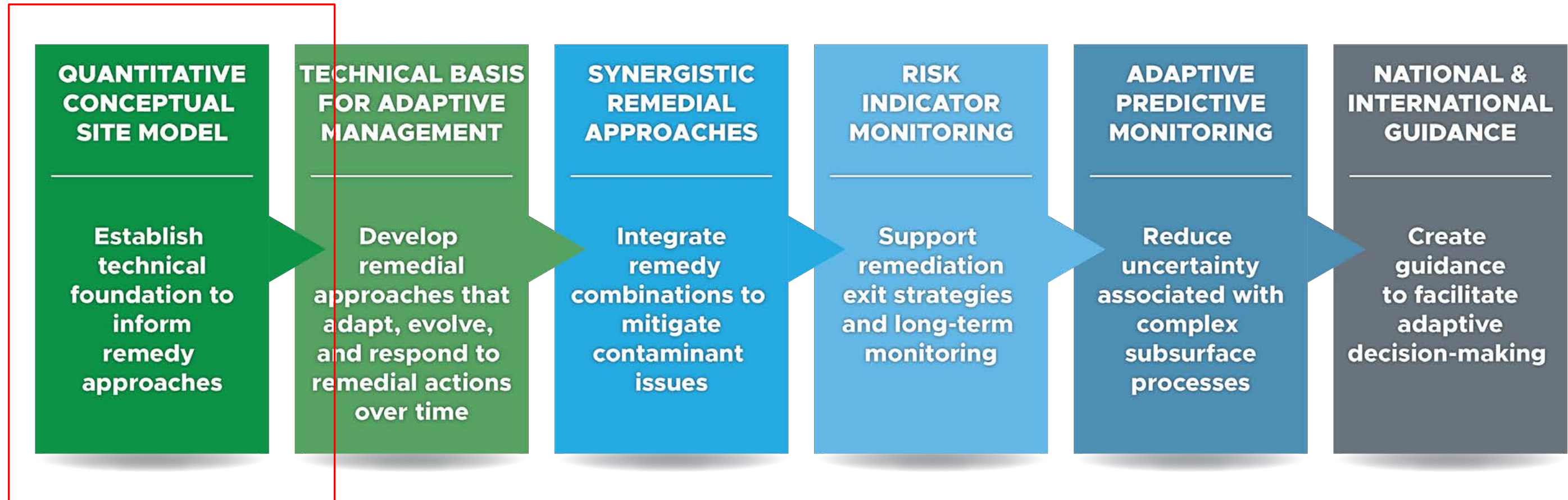


Multi-institutional Collaborations – Integration and leveraging across federal and private partnerships to facilitate solution development



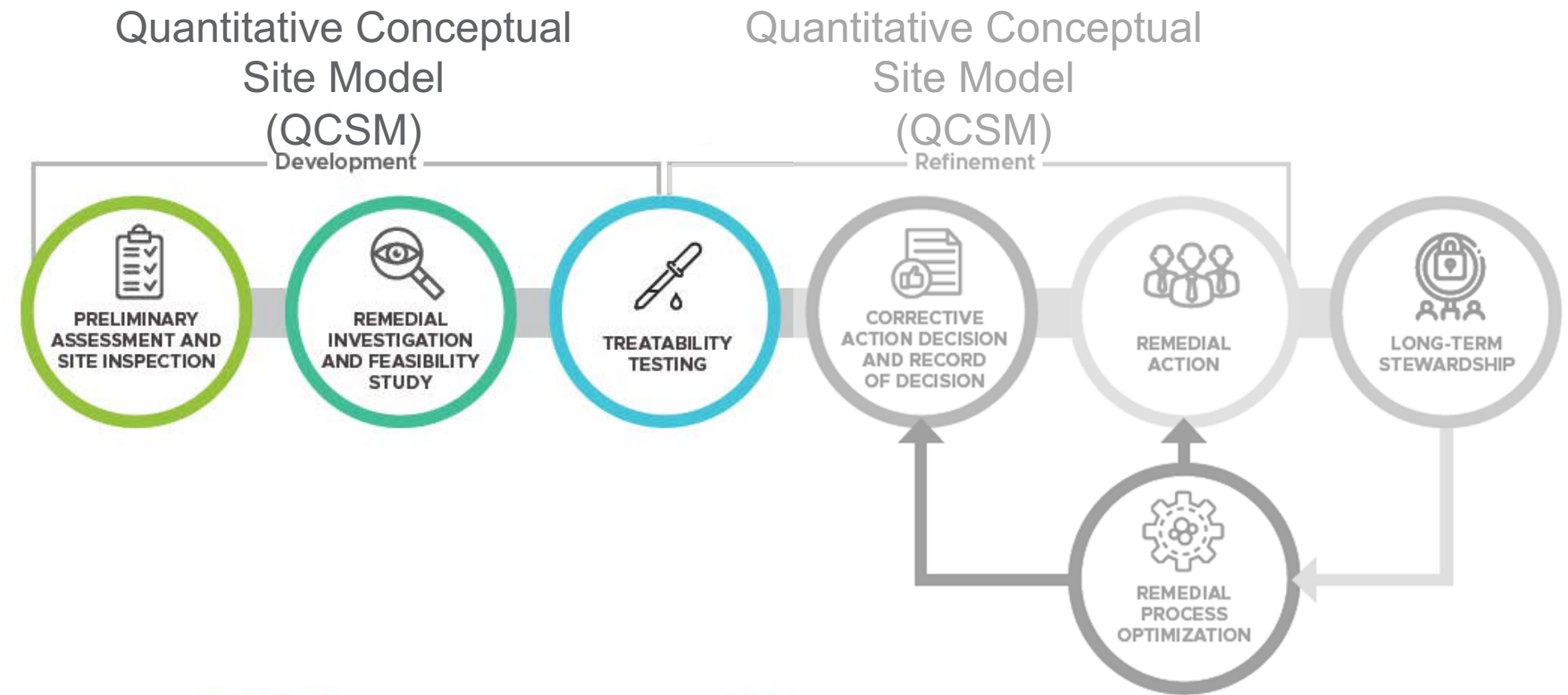
Technical Leadership – Independent technical resource with proven track record of supporting deployment of advanced technologies and alternative strategies

RemPlex Framework



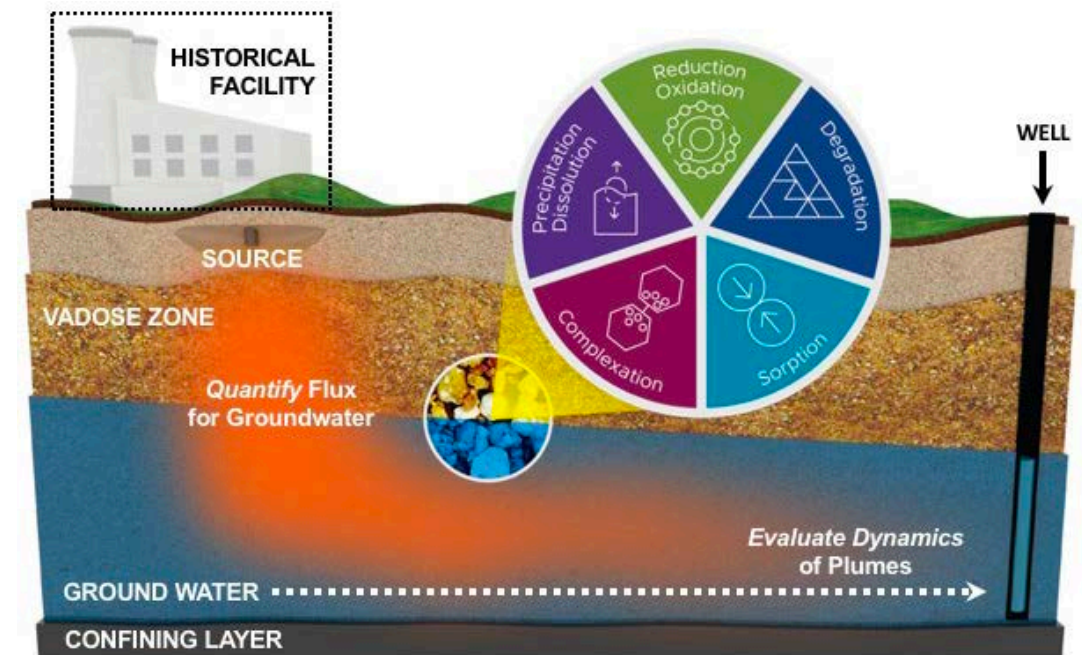
Quantitative Conceptual Site Model (QCSM)

- Technical foundation to inform remedy approaches and timeframe
- Target developing actionable information on contaminant distribution and interaction with the subsurface environment
- Integrated with analysis and modeling to develop the “quantitative” aspects



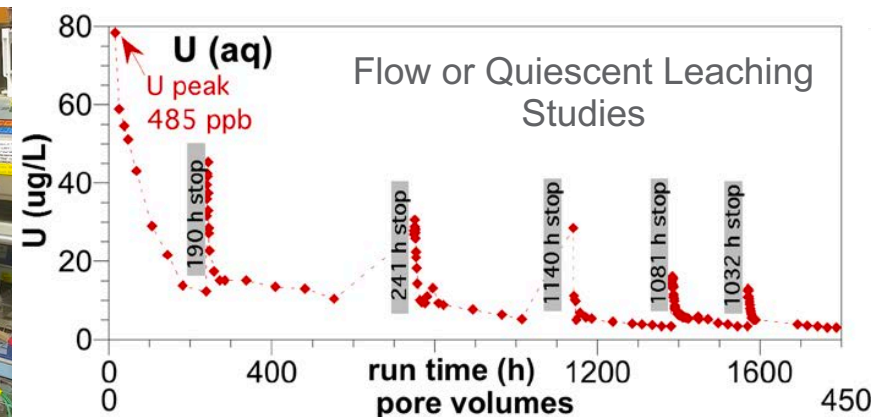
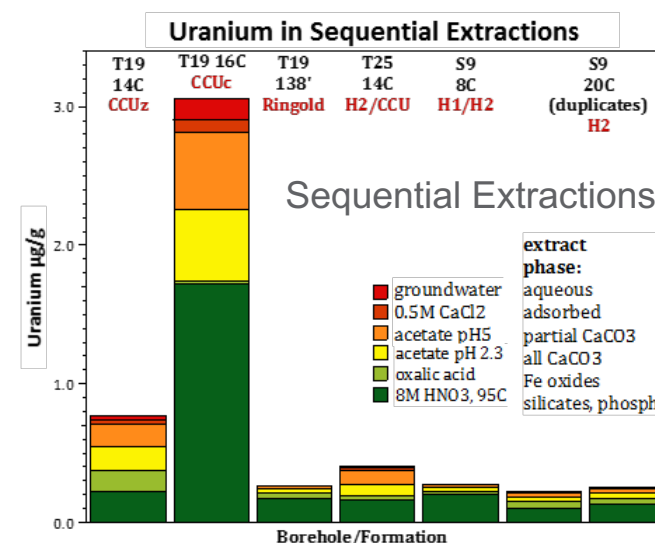
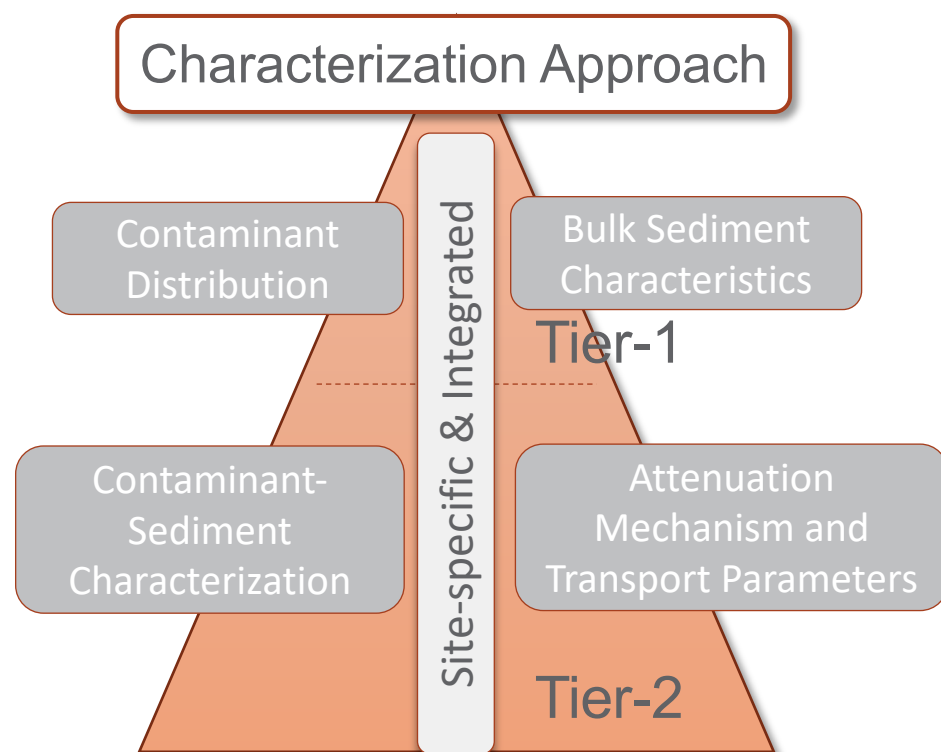
Characterization of Contaminant Mobility/Behavior

- Contaminant mobility drives risk in vadose zone and groundwater
 - Understand contaminant distribution and attenuation
 - Quantify flux into groundwater
- Evaluate risk and role of natural attenuation
- Technical basis for mitigation design and implementation
- Technical approach for remedy performance assessment

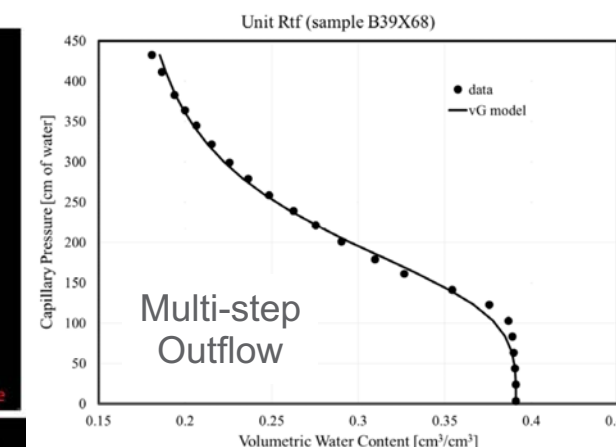
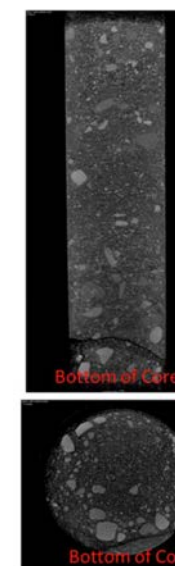


Integrated Characterization

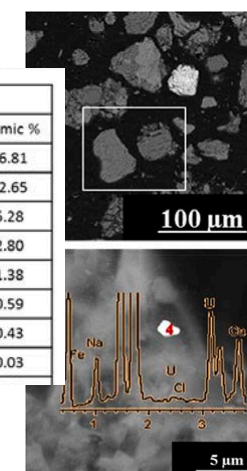
- Site-specific, integrated approach of analytical capabilities focusing on:
 - Waste chemistry and speciation in the subsurface
 - Attenuation mechanisms
 - Controlling features and processes



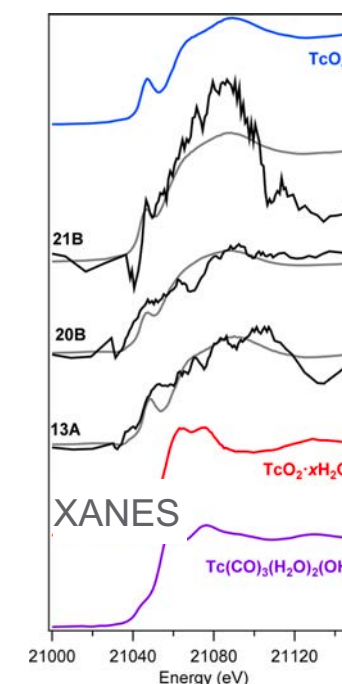
XMT



SEM-EDS



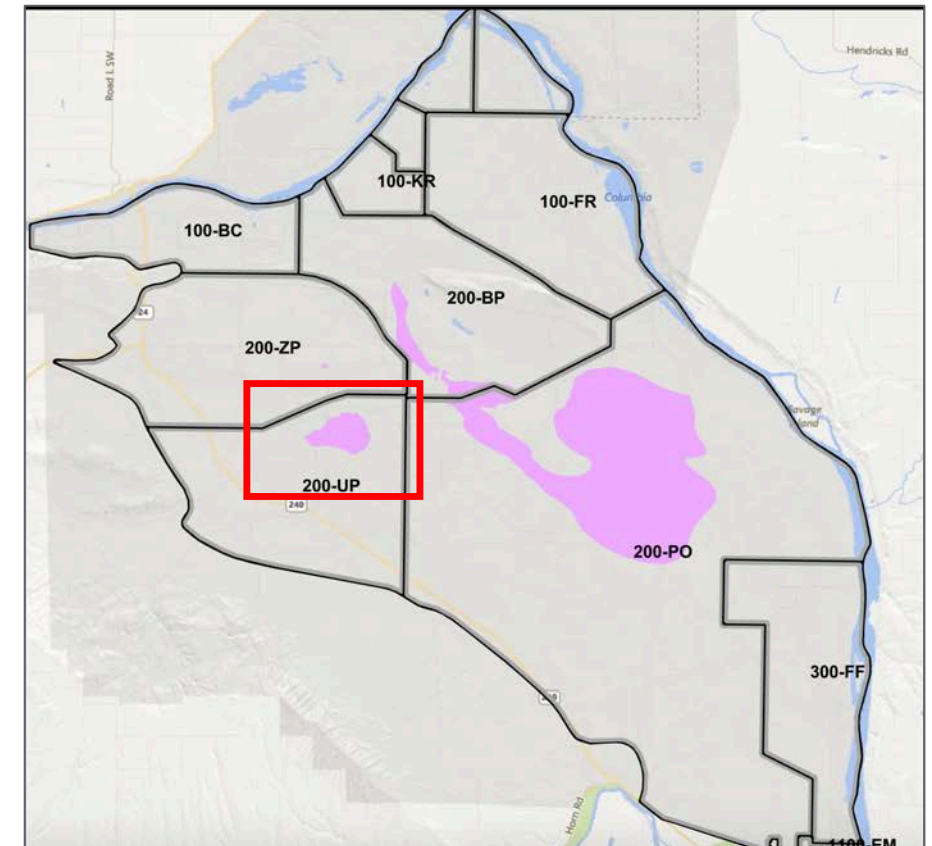
Grain 4	
Element	Atomic %
C	56.81
O	32.65
Si	5.28
Al	2.80
Na	1.38
Ca	0.59
U	0.43
Fe	0.03



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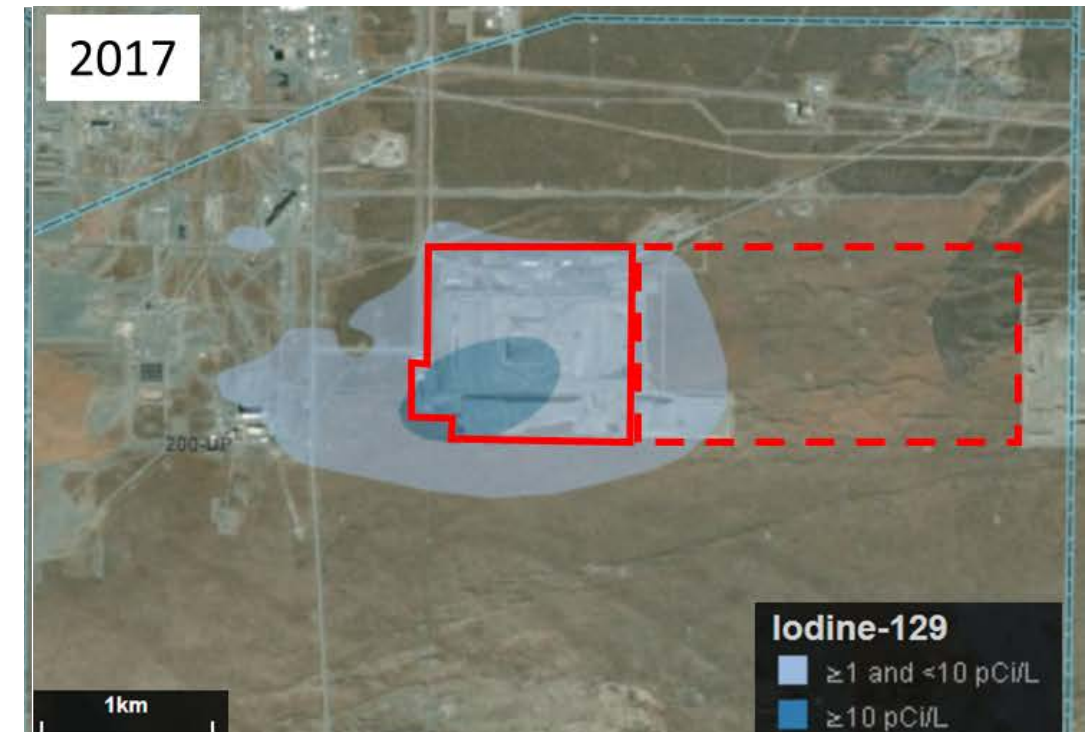
Integrated Assessment of I-129 in Groundwater

- Feasibility study for ^{129}I determined no existing treatment technologies to achieve the federal drinking water standard of < 1 pCi/L in the 200-UP-1 Operable Unit at the Hanford Site
- Current remedy is hydraulic control
- Interim Record of Decision (ROD) dictated three elements be investigated
 - Close conceptual model data gaps for ^{129}I
 - Investigate potential remedies for iodine (in situ and ex situ)
 - Consider whether an Applicable or Relevant and Appropriate Requirements (ARAR) Technical Impracticability (TI) waiver for ^{129}I is appropriate



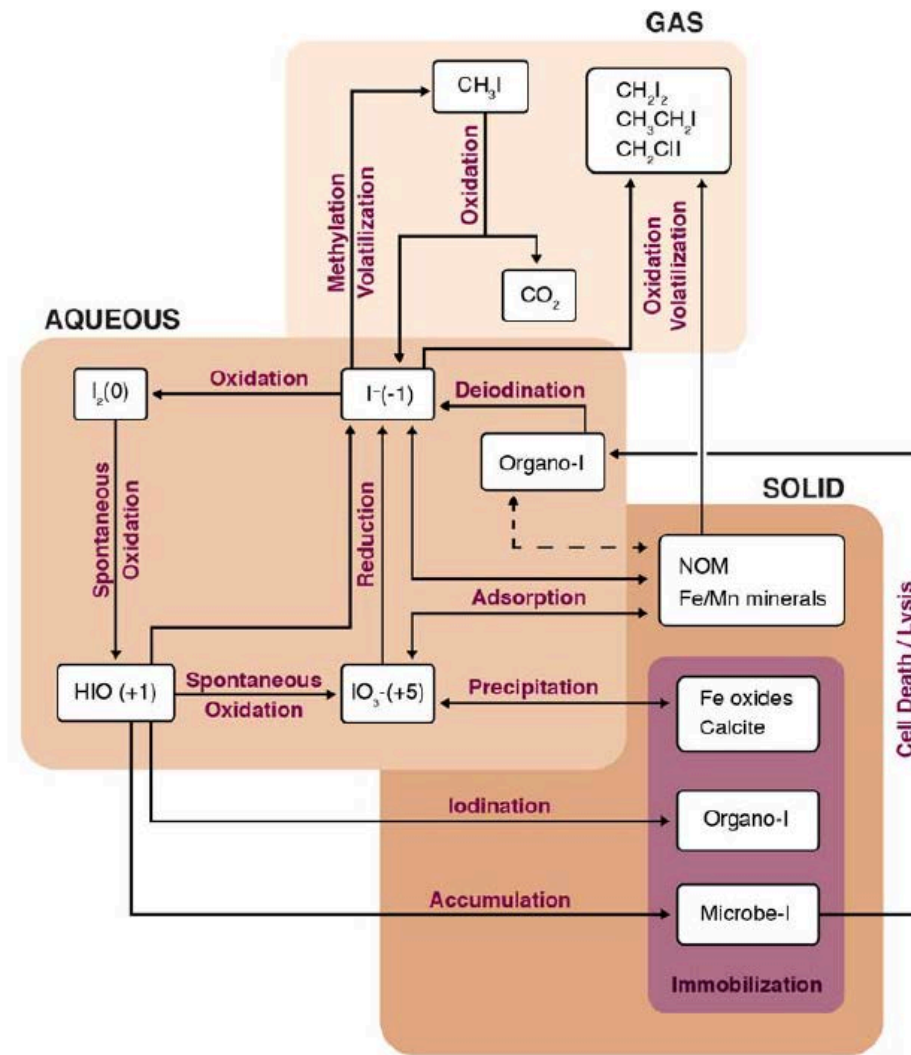
Iodine at 200-UP-1

- Current ^{129}I conditions in groundwater are relatively dilute
 - 1 pCi/L to up to 23 pCi/L
 - Entire plume: 3-km² area, 1.2-km wide, 45-m thick
 - High-concentration zone: 0.2-km² area, 300-m wide, 30-m thick
- Detached plume; no continuing source
- Natural stable iodine (^{127}I) is also present in the aquifer at much greater concentrations than ^{129}I



Plume core is located beneath Environmental Restoration Disposal Facility (ERDF). ERDF footprint is shown in solid red line; expansion zone is shown with dashed line.

¹²⁹I Quantitative Conceptual Site Model



- Iodide, iodate, and organo-I are the prevalent aqueous species; iodate predominates
- Solid-phase interactions immobilize iodine from the aqueous phase
- Iodate associates with calcite and iron oxides
- Nominal capacity for sediments to volatilize iodine
- Manuscript comparing/contrasting iodine conceptual models between Savannah River and Hanford sites (Neeway et al. 2019)

Technology Identification

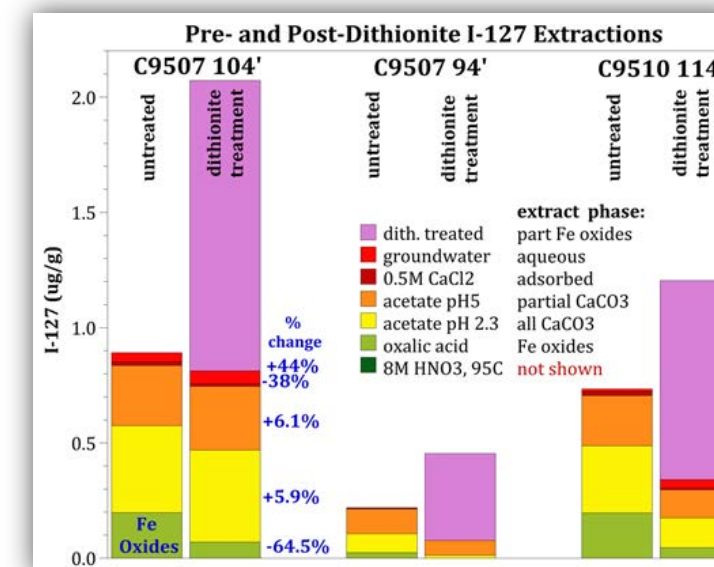
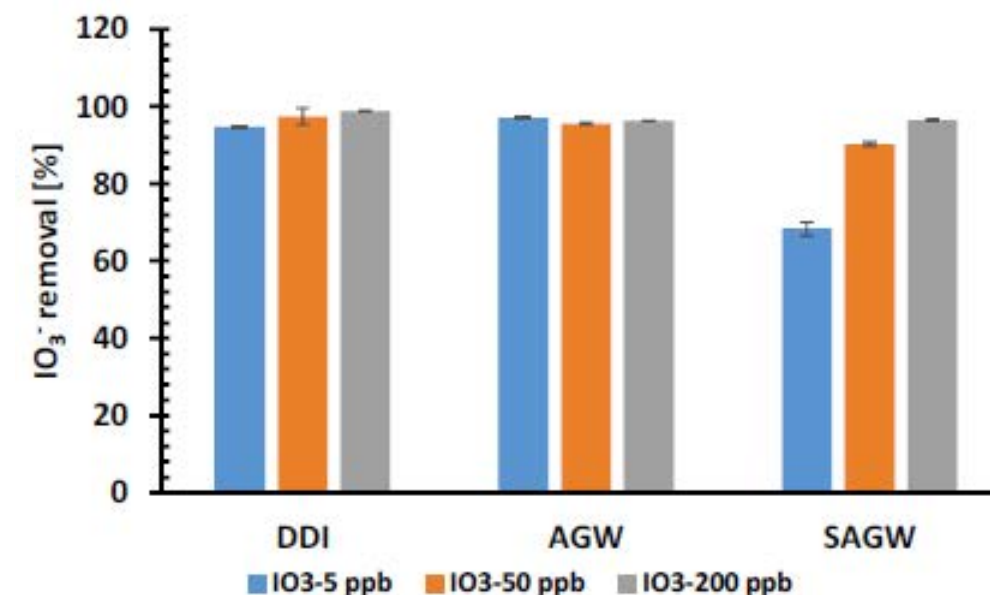
- Literature review to identify promising technologies
- Laboratory scoping tests where further evaluation was needed
- Extended evaluation/scale-up to evaluate whether treatability testing was needed
- Evaluation based on ability to meet the maximum contaminant level of 1 pCi/L in groundwater

Technology Identification

- Literature review to identify promising technologies
- Laboratory scoping tests where further evaluation was needed
- Extended evaluation/scale-up to evaluate whether treatability testing was needed
- Evaluation based on ability to meet the maximum contaminant level of 1 pCi/L in groundwater
 - **In situ sequestration**
 - **In situ mobilization to enhance P&T extraction efficiency**
 - **Ex situ extraction within P&T system**
- No microbial-based technologies selected for evaluation
 - Demonstrated to be insignificant process in the conceptual model evaluation
 - Operational difficulties associated with ex situ treatment (P&T)

In Situ Sequestration Technology Screening

- Calcite co-precipitation
 - 70% removal of iodate only
- Iron oxide sorption/co-precipitation
 - ~98% removal of iodate
 - ~70% removal of iodide
 - Iodate adsorbs
 - Iodate and iodide can be incorporated during ferrihydrite precipitation
- Dithionite
 - Up to 4X more and 3X faster leaching of iodine
- Commercial resins

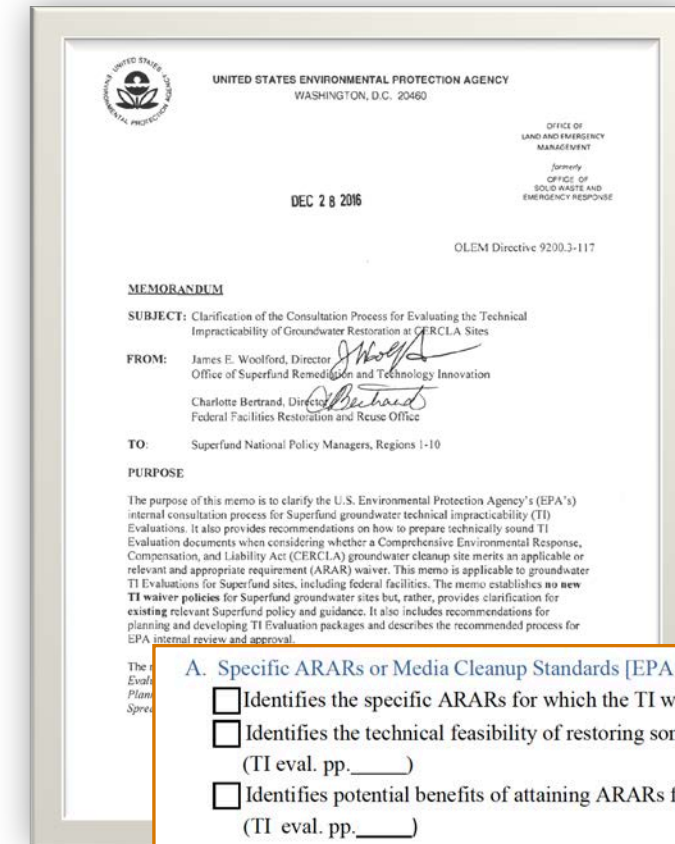


Technology Evaluation Conclusions

- Practicability of all candidate technologies was low, driven by site and contaminant properties that hinder effectiveness and/or implementability of the technologies
- Effectiveness-Implementability-Cost evaluation included technology maturity
 - CERCLA process requires treatability testing for existing technologies that can be adapted for site-specific needs
- Technology evaluation results can be used to support consideration of a TI waiver

TI Waiver Support

- Created checklist based on EPA memo (2016)
 - Conceptual site model
 - Background information
 - Geologic and hydrologic information
 - Contaminant source and release information
 - Contaminant distribution, transport and fate parameters
 - Remedial action performance analysis
 - Restoration timeframe analysis
 - Other applicable technologies



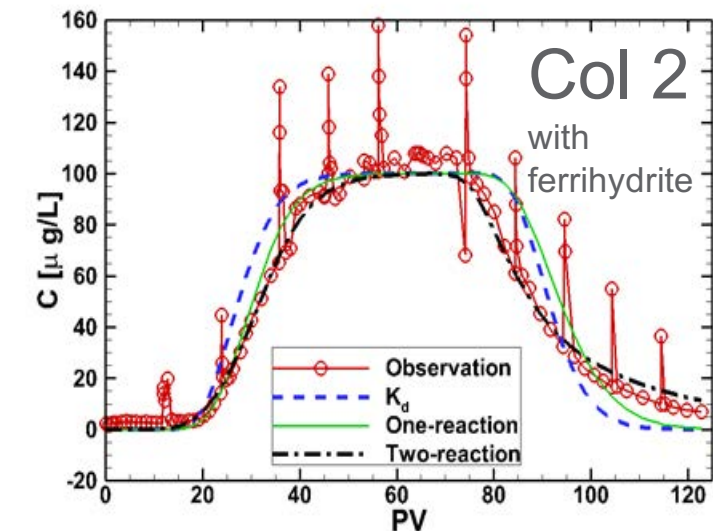
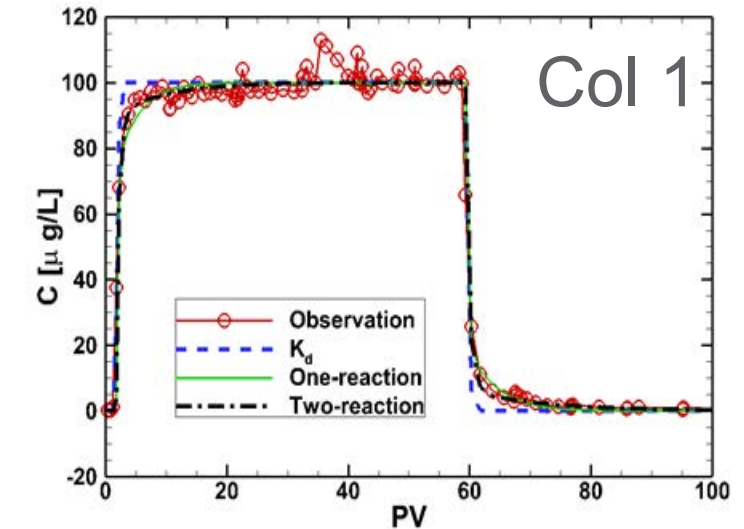
EPA Memo 2016

- The Eval. Plan. Spec.
- A. Specific ARARs or Media Cleanup Standards [EPA 1993, 4.4.1]**
- ☐ Identifies the specific ARARs for which the TI waiver is sought (TI eval. pp.____)
 - ☐ Identifies the technical feasibility of restoring some of the groundwater contaminants (TI eval. pp.____)
 - ☐ Identifies potential benefits of attaining ARARs for some of the specific COCs (TI eval. pp.____)
- B. Spatial Extent of TI Decisions [EPA 1993, 4.4.2]**
- ☐ Specifies the spatial distribution (vertical and horizontal) of subsurface contaminants in the unsaturated and saturated zones where the TI is sought (TI eval. pp.____)
 - ☐ Identifies the spatial extent of the TI zone as small as possible (TI eval. pp.____)
 - ☐ Identifies the vertical limit of the TI zone in either absolute (e.g., mean sea level) or relative (e.g., aquifer system) terms (TI eval. pp.____)
- C. Development and Purpose of the Site Conceptual Model [EPA 1993, 4.4.3, Figure 4]**
- 1. Background Information [EPA 1993, 4.4.3]**
- ☐ Groundwater classification (TI eval. pp.____)
 - ☐ Location of potential environmental receptors (TI eval. pp.____)
 - ☐ Nearby wellhead protection areas or sole-source aquifers (TI eval. pp.____)
 - ☐ Location of water supply wells (TI eval. pp.____)



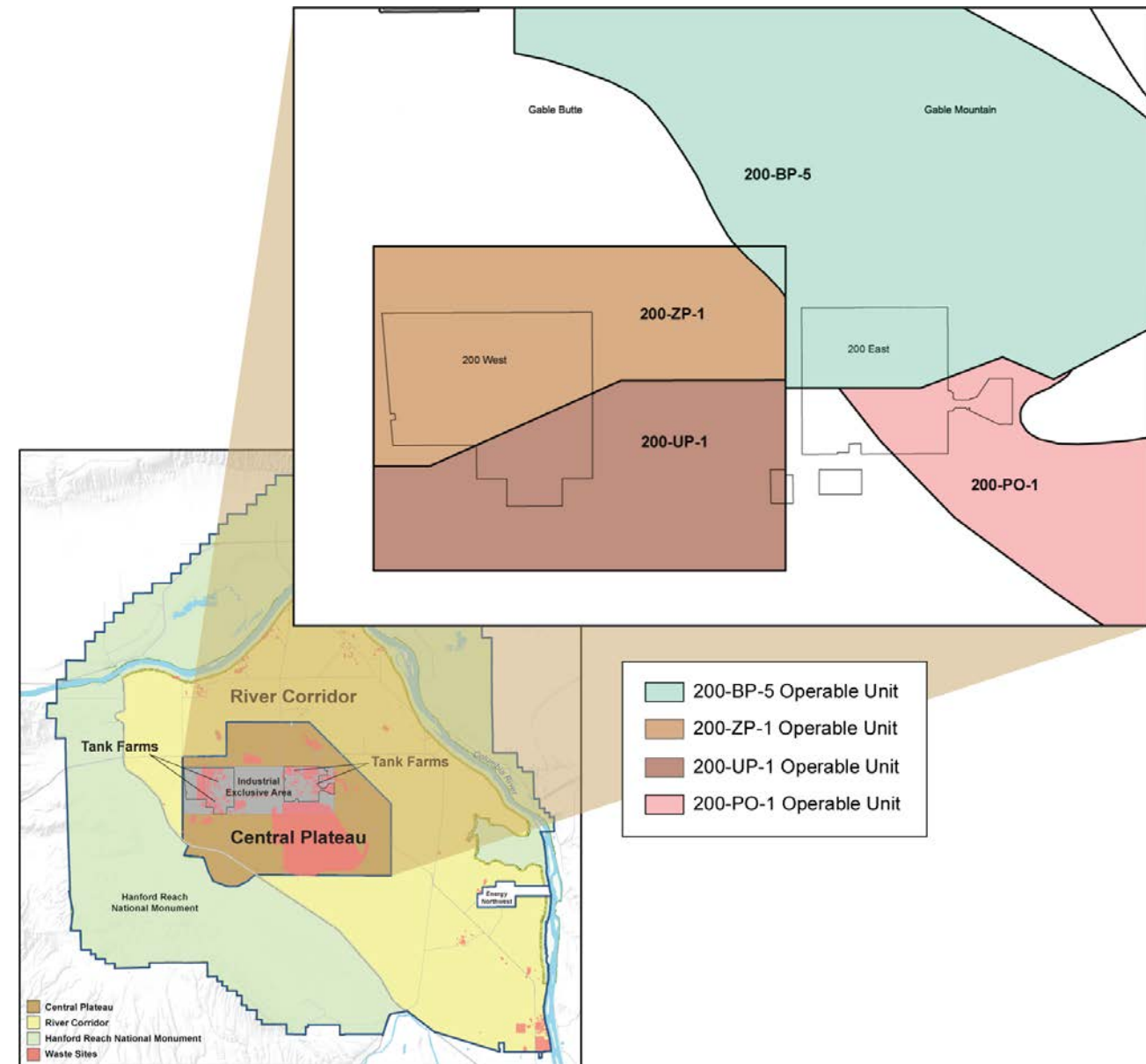
Bench-Scale Simulation

- Most of the simulated iodine remains sorbed to sediment above the water table, with a lesser amount held in solution above the water table
- Iron oxide sorption impact on plume behavior
 - Iodine sorption slows plume at first contact with 'fresh' sediment
 - When sorption sites are filled, the plume moves rapidly, but stalls again as fresh sediment is encountered
 - With a combination of high sorption and limited capacity, the plume behaves differently than for equilibrium sorption
- Langmuir isotherm includes finite capacity
- Knowledge transferred to site contractor responsible for modeling



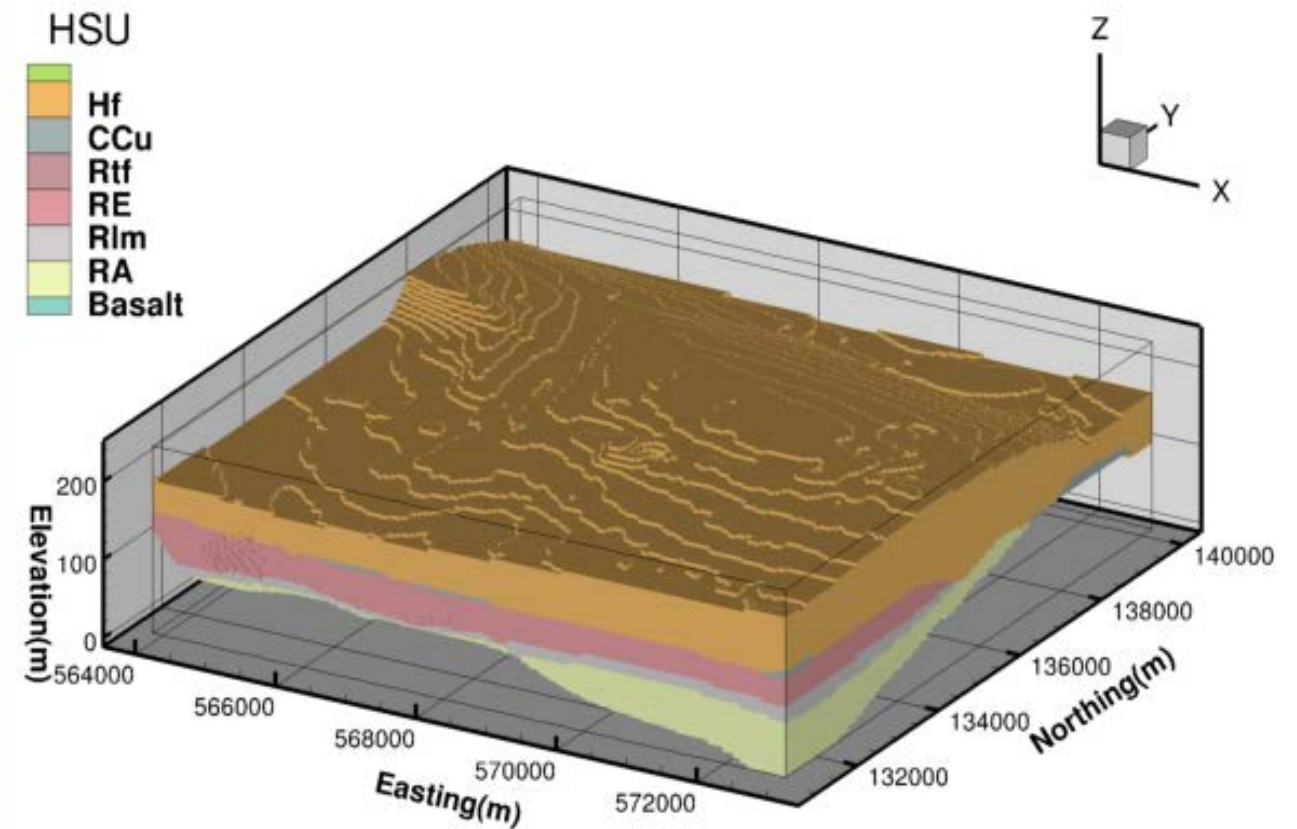
Field-Scale Simulation

- Consider coupled vadose zone and groundwater system to evaluate context for potential remediation approaches
- Use of high-performance computing (eSTOMP) makes it possible to simulate both the vadose zone and groundwater within a single model



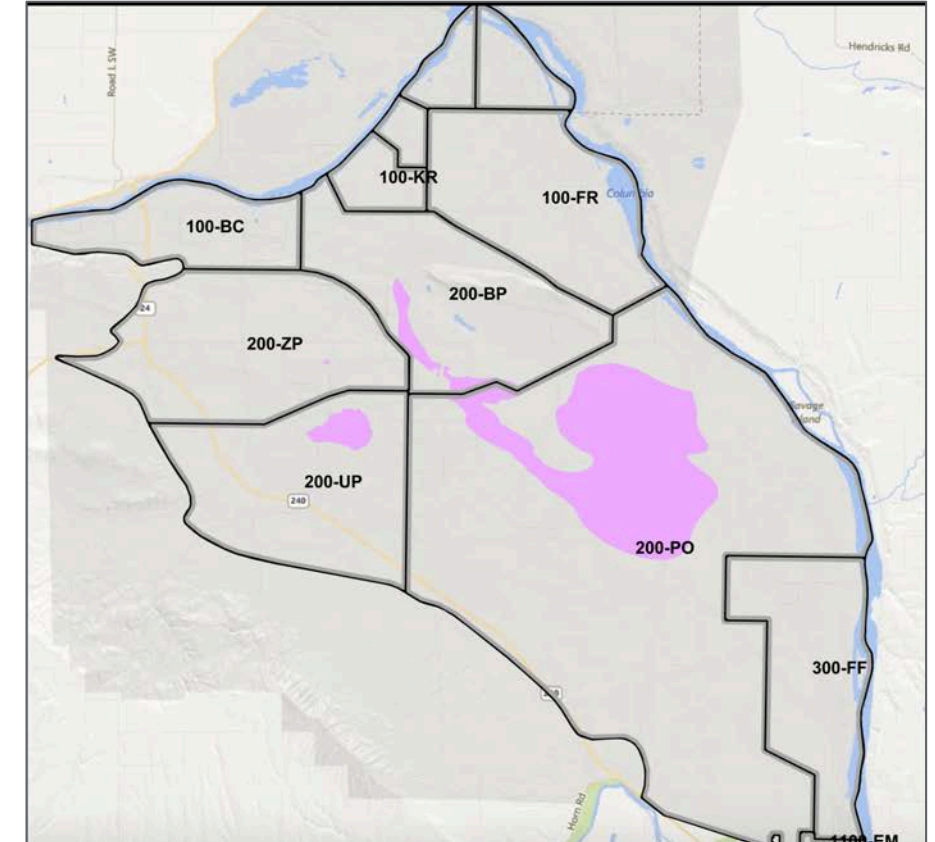
Modeling Approach

- Address the Restoration Timeframe Analysis described by the ARAR TI guidance documents (EPA 1993,EPA 2016)
 - Source term evaluation
 - Historical releases of iodine (1944 – 2016). K_d values of 0.0 and 0.1 cm^3/g bracket observed field transport behavior
 - Field and laboratory data Integration
 - Aqueous speciation of both ^{129}I and ^{127}I and transport behavior

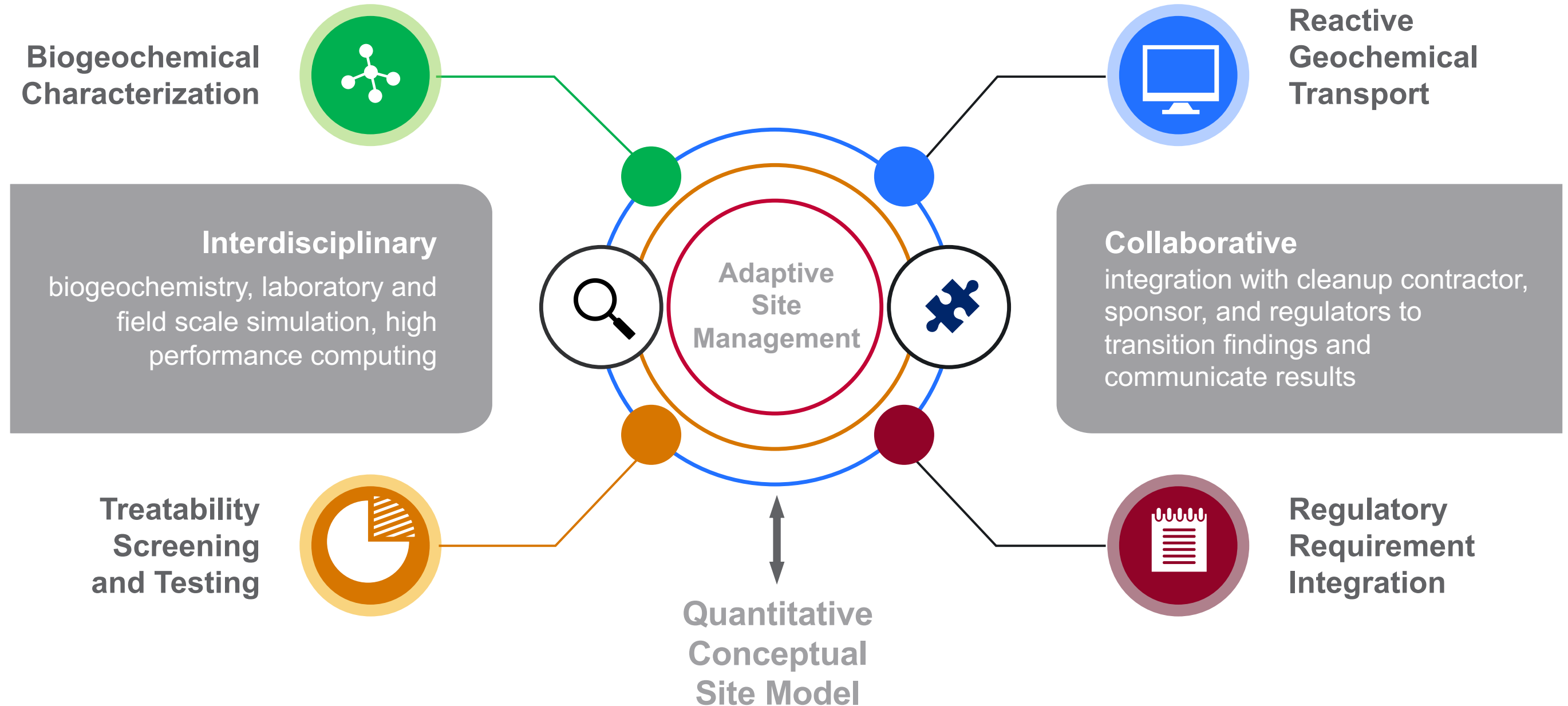


Continuing Support for Fate and Transport Assessments

- Novel, rapid technique for simultaneous iodine speciation (iodide/iodate) measurements using ion chromatography (IC) joined with collision/reaction cell inductively coupled plasma mass spectrometry (ICP-MS), collectively referred to as IC-ICP-MS
- Measures iodine species in the vadose zone and groundwater at levels below the federal DWS 1 pCi/L (~ 5.6 ng/L)
 - Relative to standard methods, new technique has 2 to 5 times lower detection limits
 - Detection limits for ^{129}I were ~1.81 ng/L for iodate and ~2.62 ng/L for iodide



Capability Integration and Remedy Management



RemPlex Resources

- Today's seminar recording and the presentation slides will be posted on:
<https://www.pnnl.gov/remplex-seminars>
- Next seminar: December 1
- Calcium carbonate minerals as scavengers of metals and radionuclides for natural attenuation and remediation



The poster features a landscape background with a large glass sphere in the foreground reflecting the scene. The PNNL logo is in the top left, and the RemPlex logo is in the top right. The main title 'REMPLEX SEMINAR' is in large white letters on a green background. Below it, the topic 'Calcium carbonate minerals as scavengers of metals and radionuclides for natural attenuation and remediation' is written. A circular date badge shows 'DEC 01' and '12:30 P.M. PT'. A paragraph of text describes the seminar's focus on calcium carbonates. Two headshots of speakers, Amanda Lawter and Nik Qafoku, are shown with their names below. At the bottom, a Zoom icon and link are provided, along with contact information for more details.

REMPLEX SEMINAR

Calcium carbonate minerals as scavengers of metals and radionuclides for natural attenuation and remediation

DEC 01
12:30 P.M. PT

Calcium carbonates (CaCO_3) are ubiquitous, naturally occurring minerals in subsurface sediments. In addition, calcium carbonate coatings are common in many terrestrial environments and are known to cover a variety of reactive mineral surfaces in soils and sediments, altering their reactivity and chemical behavior. For these reasons, contaminant interactions with CaCO_3 minerals are relevant to contaminant fate and transport. The objective of this presentation is to provide examples of significant advancements that have been made recently toward identifying related contaminant (e.g., U, I, and Cr) attenuation mechanisms, and provide the necessary technical basis for developing in-situ remediation techniques and natural attenuation strategies.

Amanda Lawter Nik Qafoku

Join Zoom for Government meeting (click icon to join now)
pnnl.zoomgov.com/j/1619206961 | Meeting ID 161 920 6961

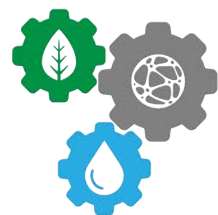
Learn more about the Center for the Remediation of Complex Sites, our capabilities, and partnership opportunities by contacting us at (509) 375-2017, remplex@pnnl.gov, or pnnl.gov/projects/remplex



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