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Use of an Alternative Paradigm to Support Optimization of In Situ Remedies at Metal and Radionuclide Contaminated Sites

'The Virtual Test Bed'

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The EM Challenge

107 major sites (1995) → 16 sites (2016)

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The EM Challenge

- Remediation of large complex groundwater plumes of metals and long-lived radionuclides (e.g., Tc, I)
- Transition from active remediation systems (P&T) to passive methods (Monitored Natural Attenuation)
- DOE sites (RL, SRS, Paducah, LANL, LM)

How do we do that?

- Enhanced attenuation – In situ remedy that reduces mobility of contaminants to achieve goals that are sustainable for long time periods

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Enhanced Attenuation Remedies

Monitored Natural Attenuation (MNA):
Let natural processes do the work and monitor progress

Enhanced Attenuation (EA):
Engineered remedy that increases attenuation capacity of aquifer

Attenuation-based remedies leave contaminants in subsurface

- Require a high burden of proof that contaminants will not re-mobilize and become a threat again
- Strategic design helps meet the burden of proof

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The Problem: SRS F-area Basins

Groundwater plume resulted from 30 years of discharge of low activity wastewater from an industrial nuclear facility. Major contaminants of concern are metals, uranium, tritium, and radioactive iodine.

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F-area Basins Remedial Timeline

1955 Waste Discharged to Basins

1988 Basins Closed/Capped

1991 Pump-Treat

1997 Funnel-and-Gate/ Base Injection

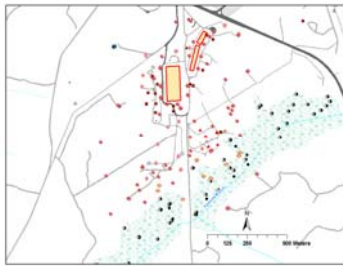
2003 Present

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F-Area Basins Monitoring Network

Large number of well/sampling locations where groundwater is sampled and analyzed

Only a small number of locations are required by regulatory agreement



Monitoring by Function

Baseline approach

- Quarterly monitoring of contaminant concentration
- Yield limited insight into the conditions and processes that control plume stability and contaminant migration

Monitoring by Function

Add inexpensive measurements of controlling processes such as boundary conditions and geochemical master variables to provide functional assessment to supplement analysis of a reduced number of groundwater samples

- Hydrologic Boundary Conditions
- Master Variables

Boundary Conditions

Overall physical and hydrological driving forces

Data types include meteorology, hydrology, geology, land use, operation/remediation history, e.g.

- changes in production of water from wells (process/potable/municipal/agricultural)
- changes in discharge of water to basins/streams, dams, etc.
- new infrastructure and construction
- discontinuation of active industrial processes

Generally easy to measure and often overlooked

Data Sources

- Precipitation – Precipitation gauges and telemetry, satellite data, groundwater level monitoring
- Evapotranspiration – Landsat satellite data
- Stream/River Flow – USGS databases, stream flow gauges, satellite data
- Precipitation chemistry (Acid rain, Hg deposition) – NADP maps, point monitoring
- Surface water (lakes, ponds, drainages, etc.) – Army Corps of Engineers, local authorities, etc.
- Pumping Wells (New and existing wells) – Local municipalities
- Discharges (Industry outfalls etc.) – Local and government agencies
- Infrastructure/Construction – Local and government agencies

Master Variables

Master Variables are the key variables that control the chemistry of the groundwater system

- Redox variables (ORP, DO, chemicals)
- pH
- Specific Conductivity
- Biological Community (Breakdown/decay products)
- Temperature

Existing sensors and tools to measure these variables inexpensively are commercially available

Field Demonstration of Approach

Technical Problem

- How do you test a new paradigm for long-term monitoring without doing years of long-term monitoring?

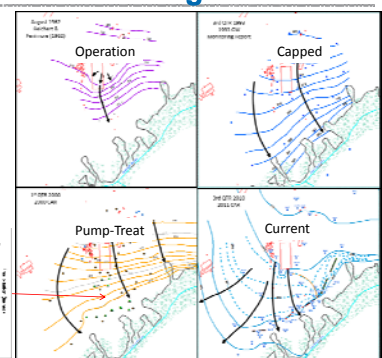
Approach

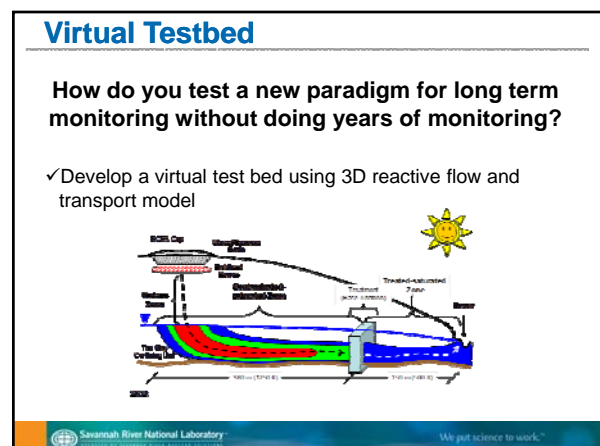
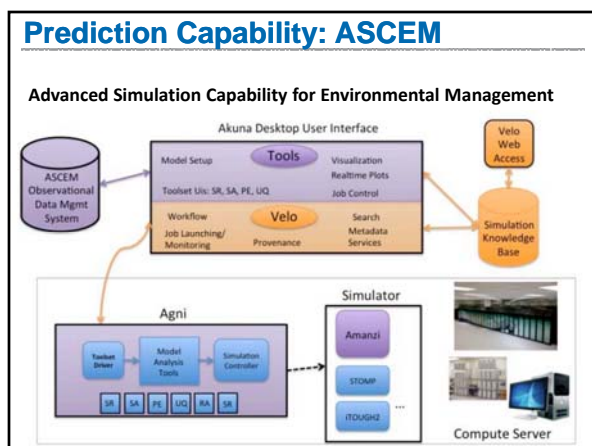
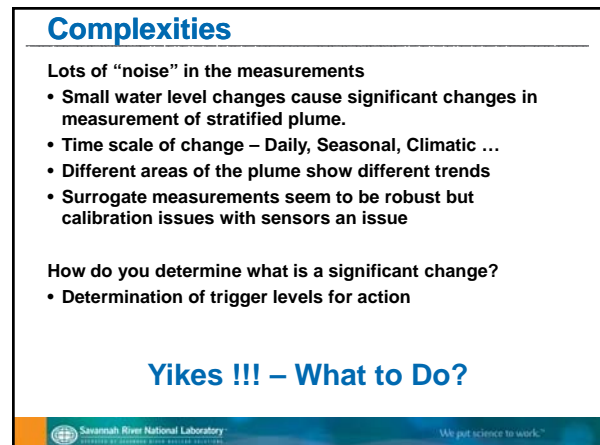
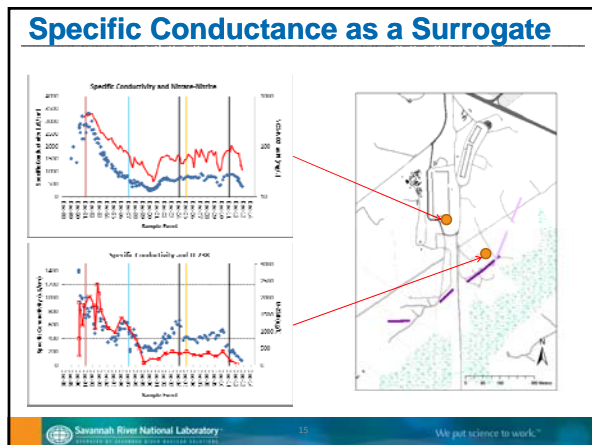
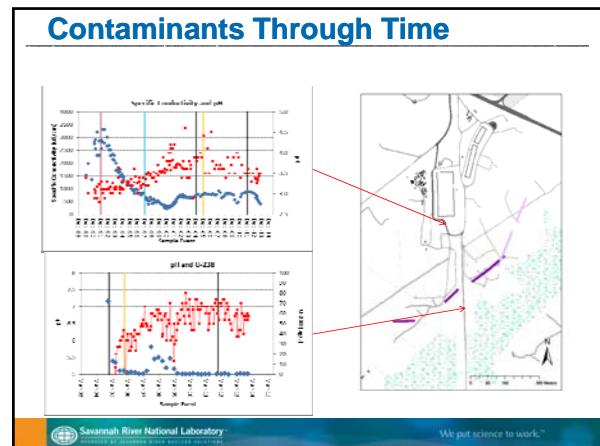
- Use monitoring data from a waste site with a long history of data and well characterized changes to boundary conditions and master variables
- Identify key controlling variables and implement strategy at a well characterized test bed

Groundwater Flow Through Time

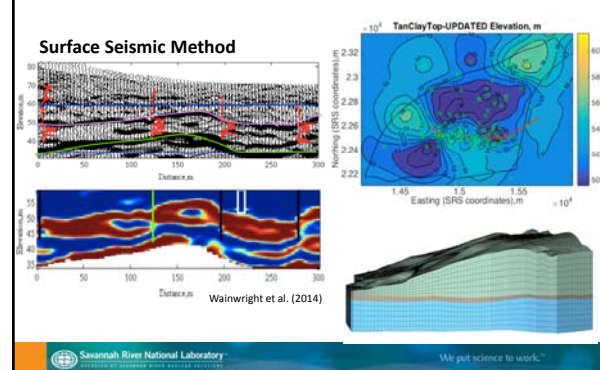
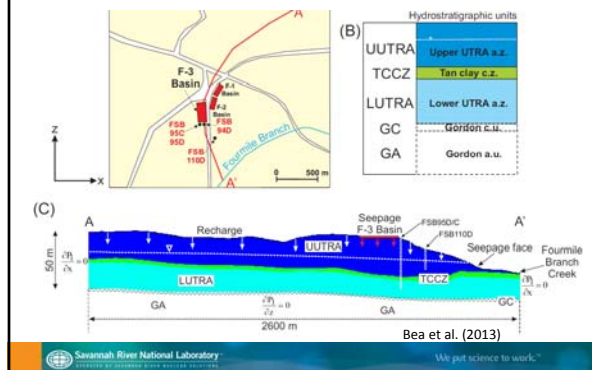
Water level measurements indicate distinct changes in flow pattern

Precipitation predictive of water level in some wells

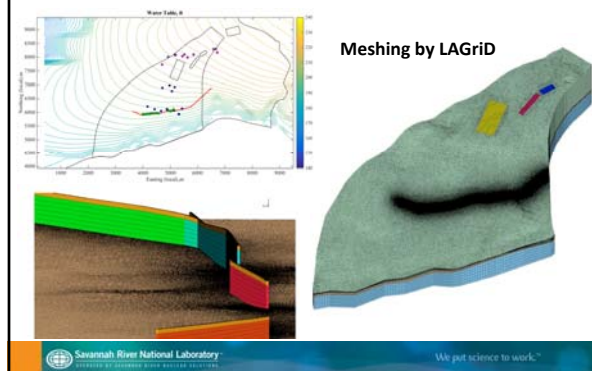




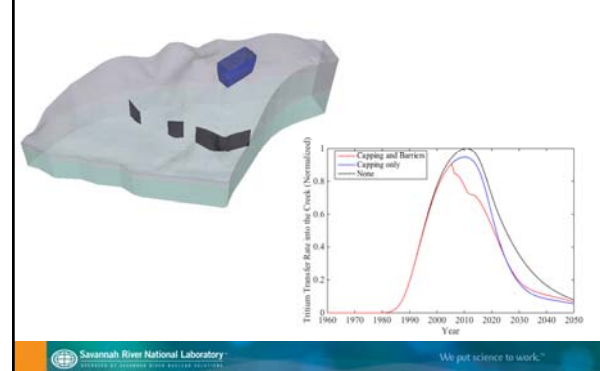
3D Mesh Development



3D Mesh for Artificial Barriers



Effect of Barriers on Tritium Plume



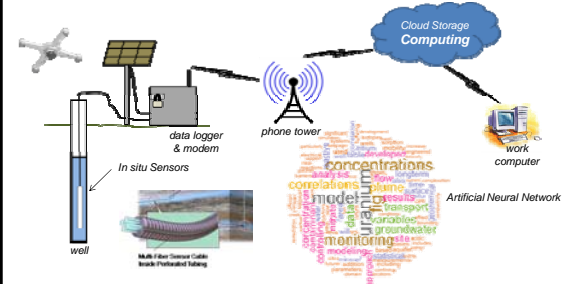
Geochemistry Development

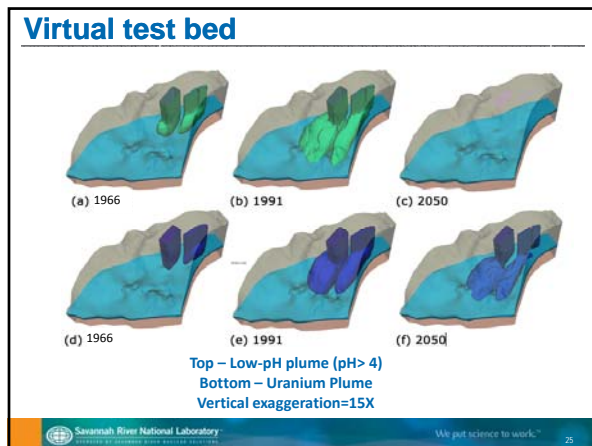
- **Complex geochemistry**
 - pH Dependent
 - Aqueous complexation
 - Surface complexation
 - Mineral dissolution/precipitation
 - Cation exchange
 - Decay

Surface complexation, cation exchange		log ₁₀ K (25°C)
Surface complexation/Complexation		
$(\text{SO}_4/\text{UO}_2)^+ + \text{HCO}_3^- + \text{H}^+ + \text{UO}_2^{2+}$		-0.84
Cation Exchange		
$\text{Na}^+ - \text{Na}^+ \cdot \text{X}^-$		0
$\text{CaX}_2 - \text{Ca}^{2+} \cdot \text{X}^-$		1.0
$\text{AlX}_3 - \text{Al}^{3+} \cdot \text{X}^-$		0.116
$3\text{H}^+ - \text{H}^+ \cdot \text{X}^-$		0.021
Mineral dissolution/precipitation		
	log ₁₀ K (25°C)	Ref.
Kaolinite $\rightarrow \text{2Al}^{3+} + \text{2SiO}_2(\text{aq}) + \text{5H}_2\text{O} - \text{6H}^+$	-7.57	(3)
Gordite $\rightarrow \text{Fe}^{3+} + \text{2H}_2\text{O} - \text{3H}^+$	0.1718	(8)
Silicophen $\rightarrow \text{4UO}_2^{2+} + \text{H}_2\text{O} - \text{2H}^+$	-0.0463	(9)
Gibbsite $\rightarrow \text{Al}^{3+} + \text{3H}_2\text{O} - \text{3H}^+$	7.318	(9)
Jarosite $\rightarrow \text{Al}^{3+} + \text{SO}_4^{2-} + \text{6H}_2\text{O} - \text{H}^+$	-3.8	(9)
Barytocalcite $\rightarrow \text{4Al}^{3+} + \text{SO}_4^{2-} + \text{13H}_2\text{O} - \text{10H}^+$	22.251	(9)
Quartz $\rightarrow \text{SiO}_2(\text{aq})$	-3.005	(9)
Aqueous complexation		
	log ₁₀ K (25°C)	
$\text{OH}^- \rightleftharpoons \text{H}_2\text{O} - \text{H}^+$	13.99	
$\text{AlOH}^{2+} \rightleftharpoons \text{Al}^{3+} + \text{H}_2\text{O} - \text{H}^+$	4.96	
$\text{AlOH}_2^+ \rightleftharpoons \text{Al}^{3+} + \text{2H}_2\text{O} - \text{2H}^+$	10.19	
$\text{AlOH}(\text{OH})_2 \rightleftharpoons \text{Al}^{3+} + \text{3H}_2\text{O} - \text{3H}^+$	16.16	
$\text{AlOH}_2\text{OH} \rightleftharpoons \text{Al}^{3+} + \text{4H}_2\text{O} - \text{4H}^+$	22.88	

New Paradigm

- **Big Data methods** for real-time data analysis and early warning systems
- **Virtual Test Bed: ASCEM modeling tool** for predicting long-term performance
- **New sensing technologies** for automated remote continuous monitoring
 - In situ sensors, geophysics, fiber optics, UAVs



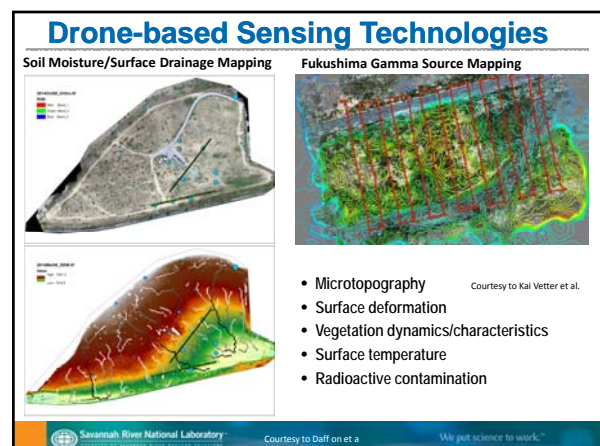
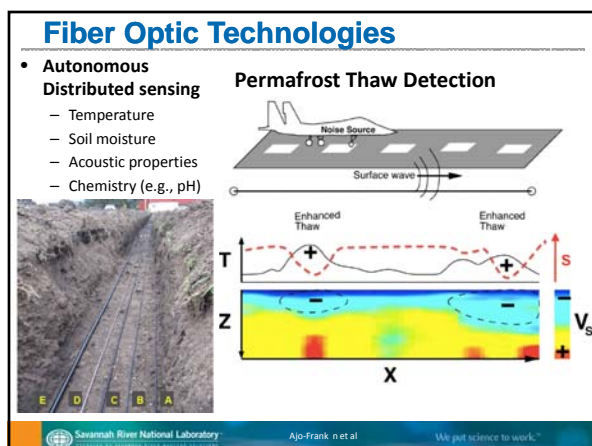
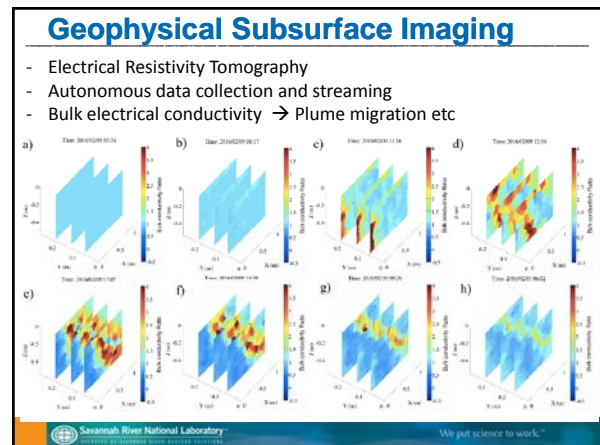
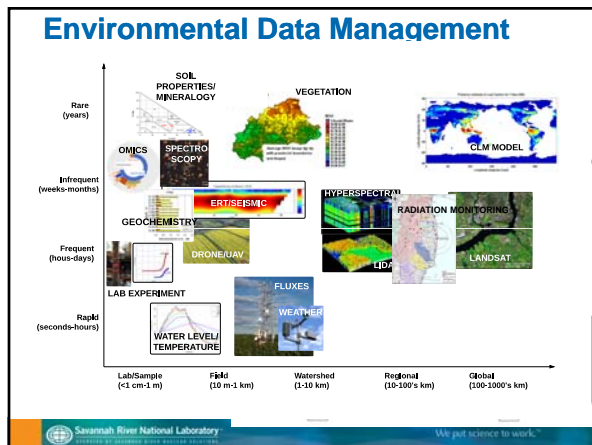


What Now?

Developing specific strategy for F-area

- Master variables and sensor/well locations through time for different contaminants
- Change in absorption/mobility for contaminants in system as pH evolves
- Establish trigger levels for boundary conditions
- Test hypotheses using virtual test bed
- Develop recommendations for key geochemical events for complex plumes of metal and radionuclides
- Investigate new methods for monitoring that are multidimensional to focus on measurement of changes.

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Summary

Real/Virtual Test Bed at SRS F-Area

- Data analysis confirmed the feasibility of in situ monitoring
- ASCEM 3D flow and transport simulations quantified the correlations (spatially and temporally variable) but also the future trajectory
- UQ/sensitivity analysis: the long-term feasibility of monitoring

Cost-effective strategies for long-term monitoring of contaminants (incl. Tritium)

- **In situ sensors, data streaming and data analytics** for automated continuous monitoring
- **Advanced technologies:** geophysics, fiber optics, UAVs
- **Data Analytics: QA/QC, correlations** between master variables and contaminant concentrations
- **Integrated approach** (data + modeling) for system understanding/estimation