Working Together: Getting the Best Results Through Partnerships:

Why Superfund sites can be attractive research sites for academics: Vineland Superfund Site

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Lamont-Doherty Earth Observatory
COLUMBIA UNIVERSITY | EARTH INSTITUTE

Issues for Academic-EPA Partnerships

Academic needs/issues

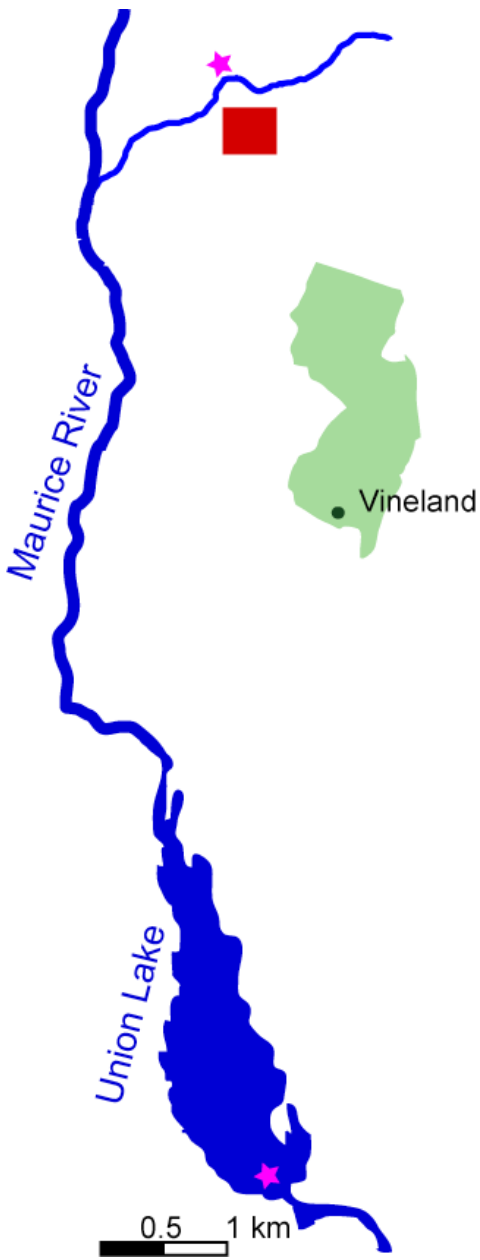
- Science
  - Data & infrastructure
  - Basic Science: take advantage of high concentrations or mixtures to study processes
  - Applied Science: Novel approaches to remediation
- Access
  - Continued access to the site is key
  - Who manages the site? Responsible party or EPA.
- Education
- Timelines & Grad Students
  - Time line to start govt grants - over 1 yr
  - graduate studentships (5+ yrs for PhD; 2-3 yrs for MS). SRP funding cycles are in 2 - 5 year blocks.
  - Mega sites with long timelines (Hudson River, Vineland)

Benefits to EPA

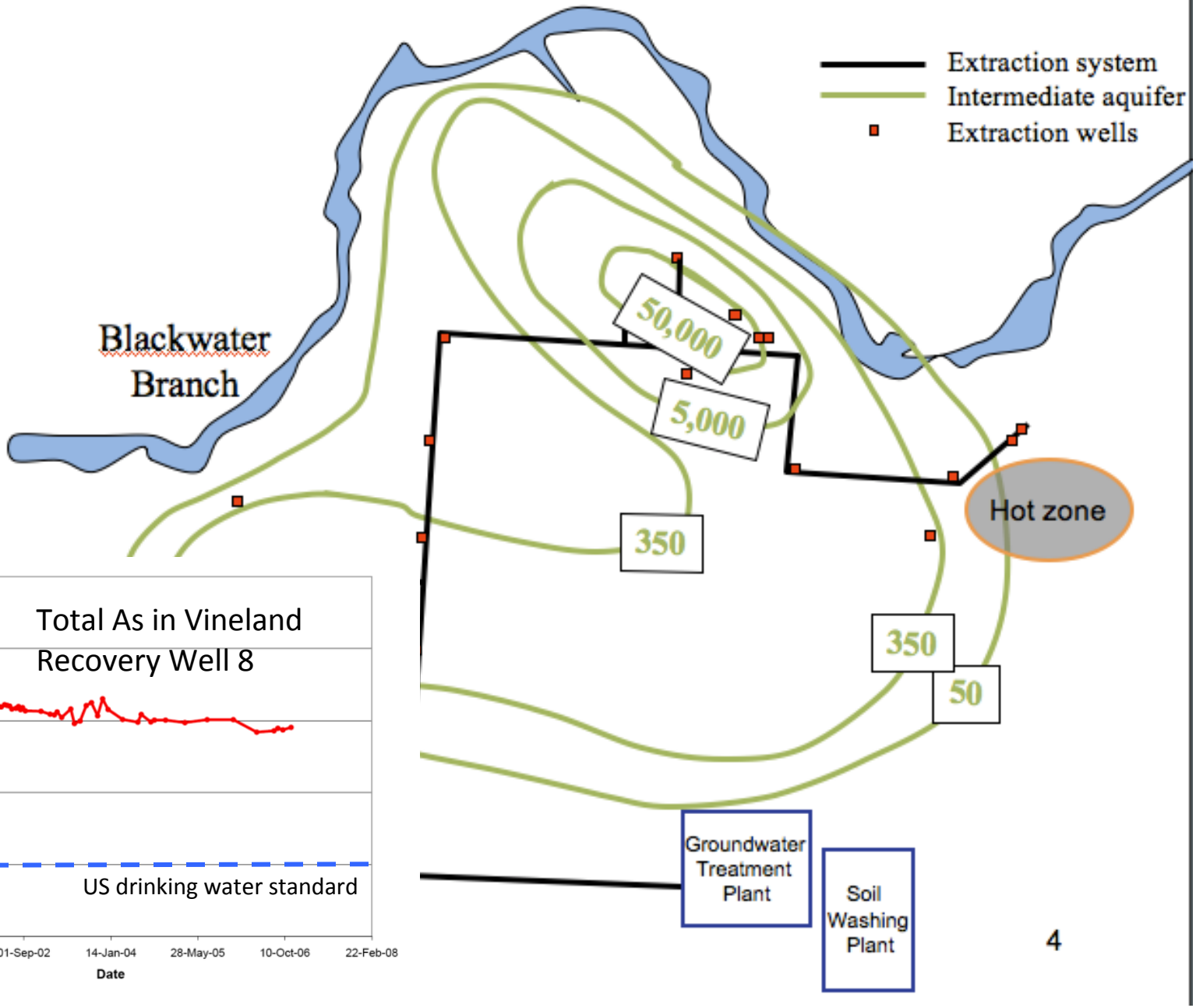
- Additional resources focused on site
- Transfer of novel approaches
  - Access to newest scientific information
  - Technology transfer
  - Site assessment
  - Site remediation
- Flexibility in scale of effort
  - Little investment from EPA's side
  - Build trust/relationship over time
- Community trust
- Education of future EPA personnel

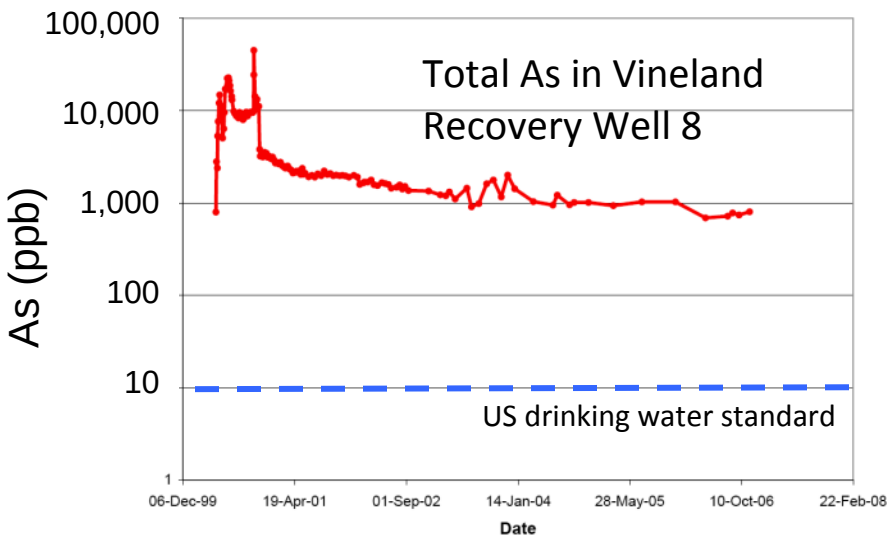
Vineland Superfund Site

- Biocide factory (1950-1994)
- Historical gw conc total As ≈ 50,000 ppb (organic and inorganic)
- Multiple environments and issues:
- On Site
  - Vadose zone soils (soil washing plant)
  - Aquifer solids - Pump and treat efficiency
- Off Site
  - Downstream transport of As and flood plain soils and sediments
  - Union Lake - bottom sediments and remobilization



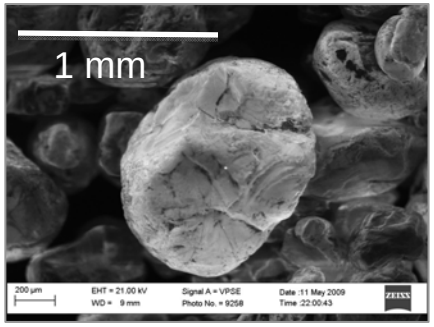
Vineland Chemical Co. Superfund site

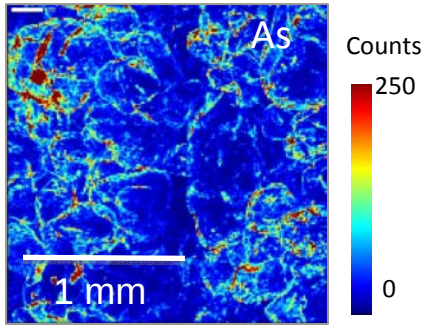




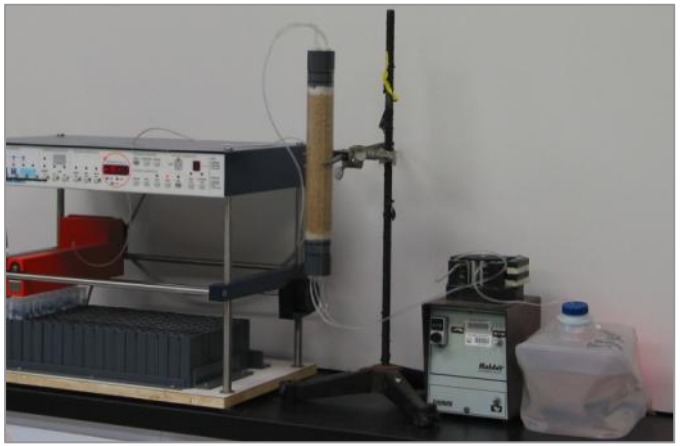
Multi-Scale Approach

Small Scale and Mechanistic Studies



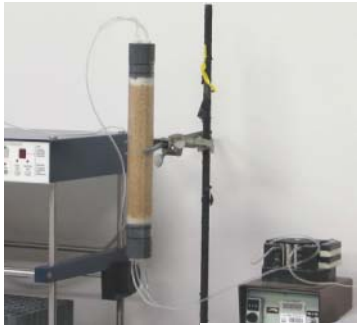


Bench Scale Lab Studies



Pilot Scale Field Study

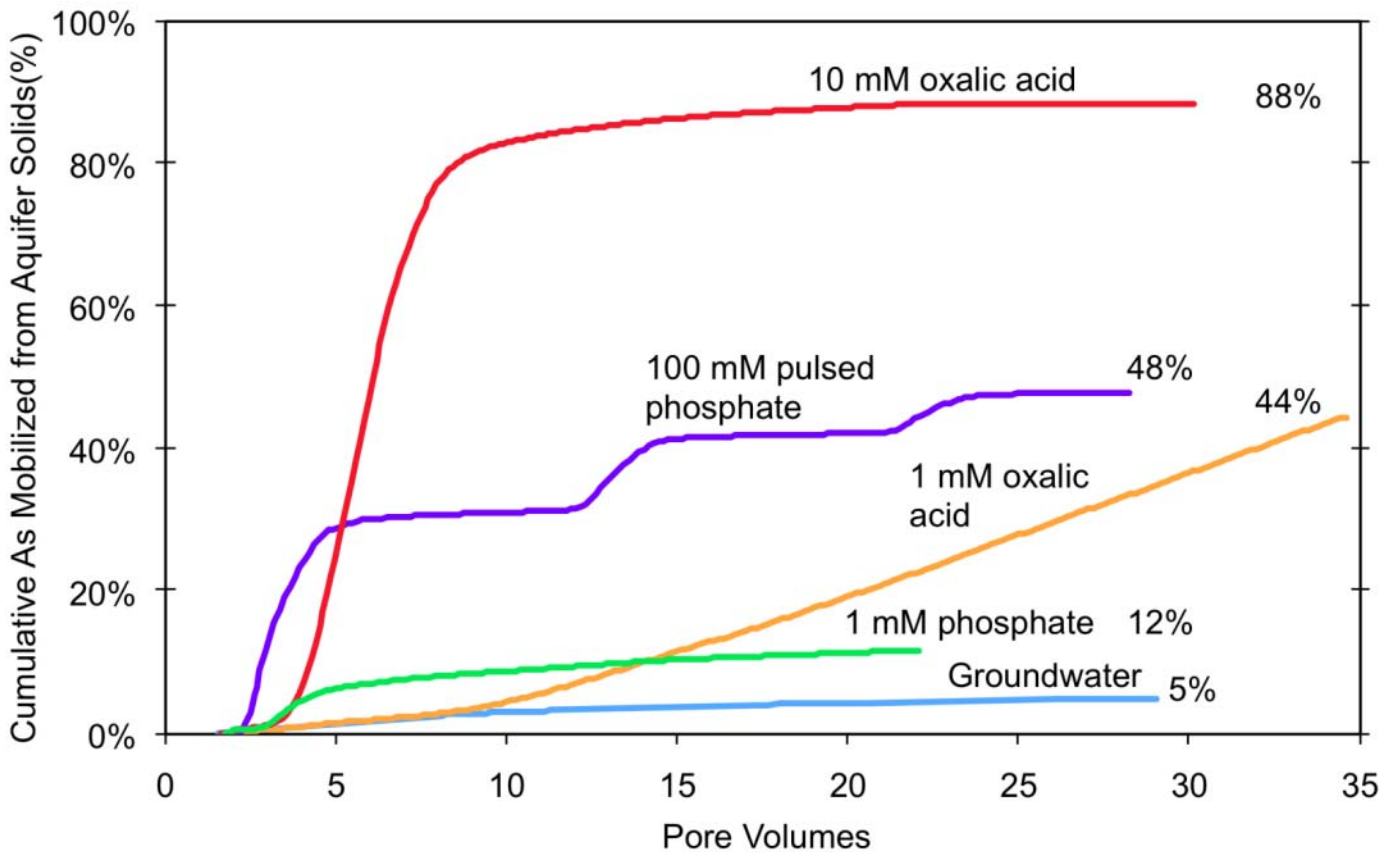
Laboratory Column Experiments



Solids:
Contaminated aquifer solids (81 mg/kg As)

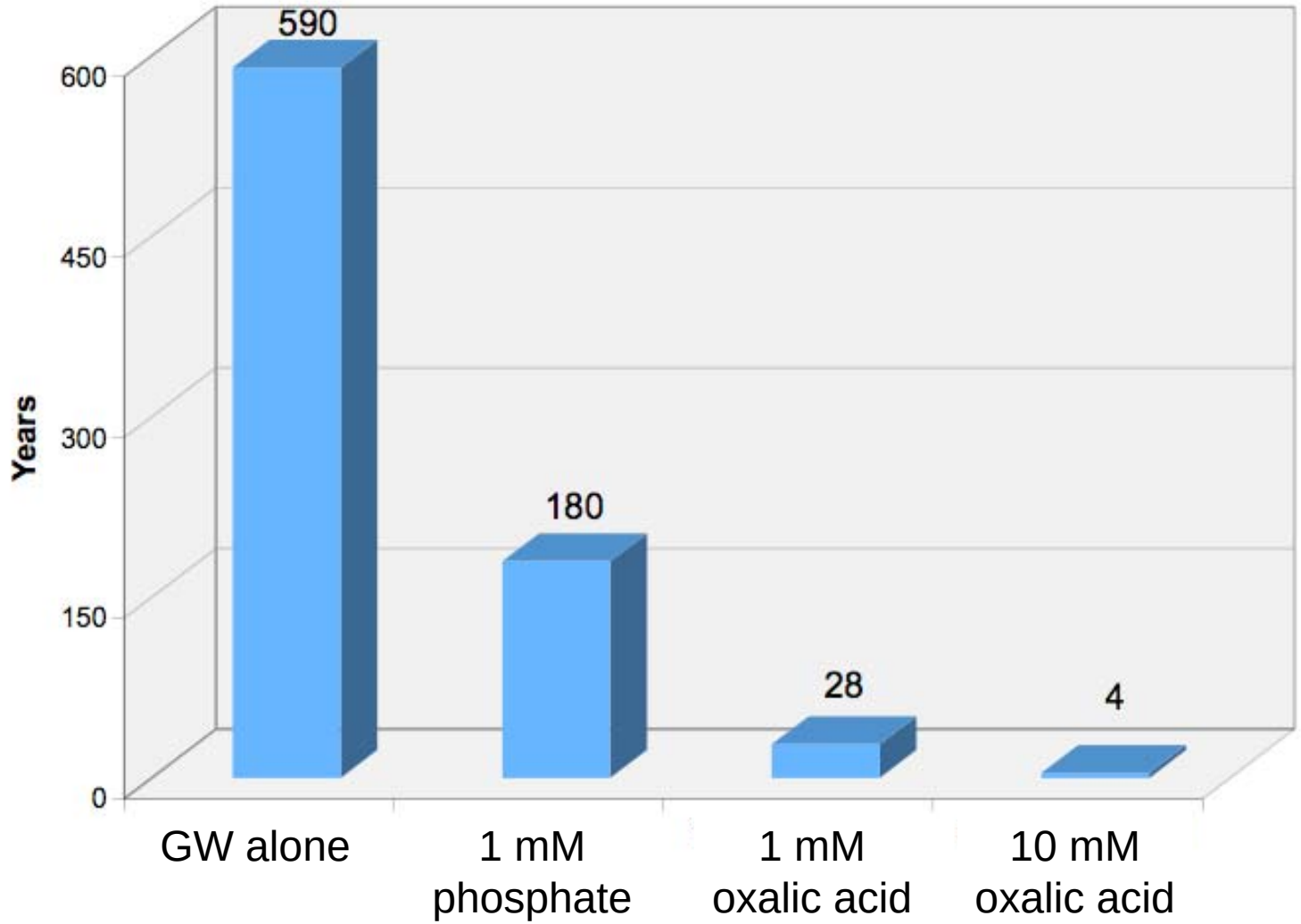
Influent:
1) Vineland GW
2) GW + 1 mM oxalic acid
3) GW + 1 mM phosphate
4) GW + 10 mM oxalic acid
5) GW +100 mM phosphate (pulses)

Flow rate: 2-3 m/d
Analysis by ICP MS

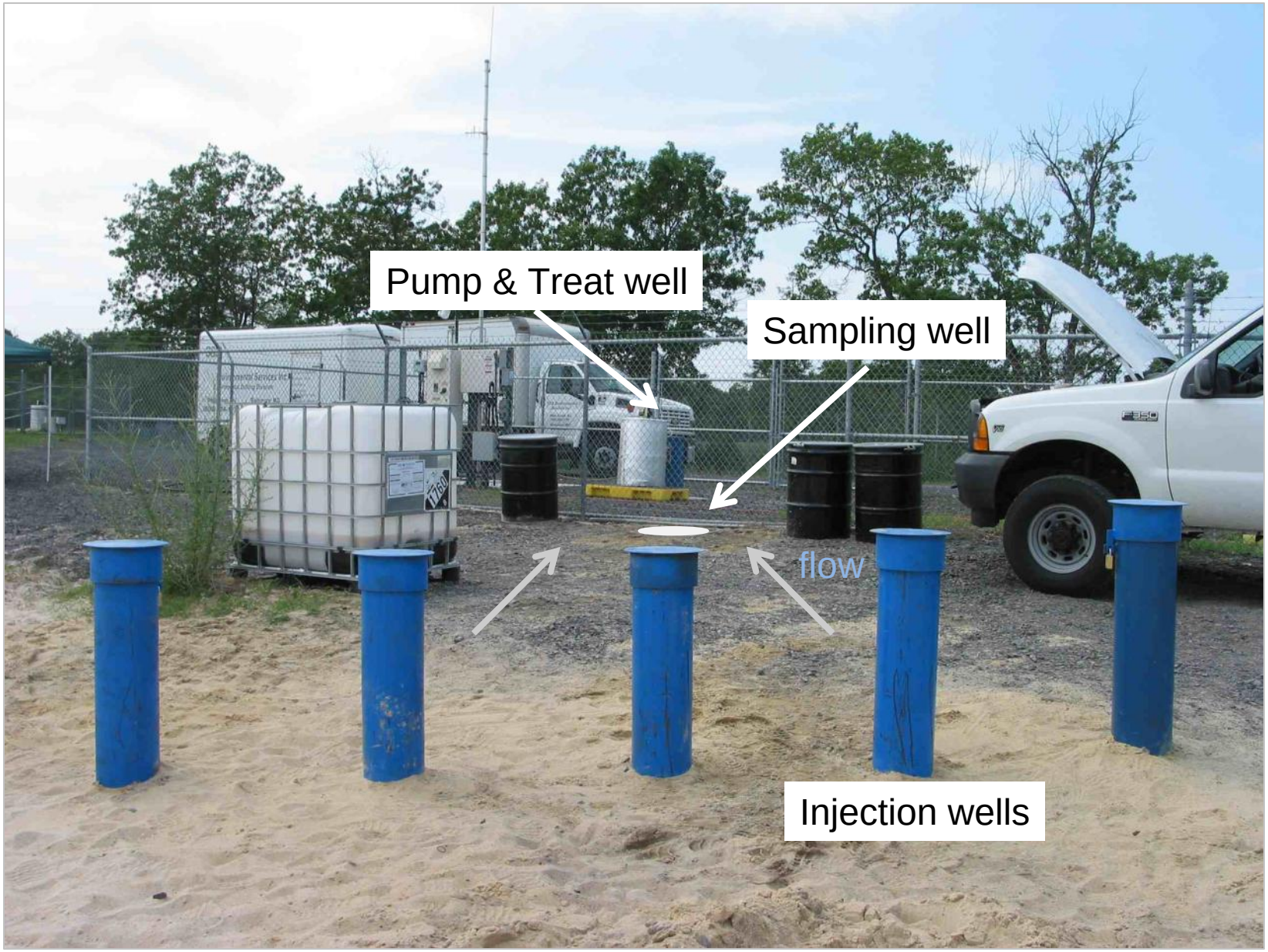


Extrapolations to the Study Site

Estimated Number of Years to Clean Aquifer Solids to 20 mg/kg



Field Study Set Up



Field Study Set Up

Injection Manifold System

- 1 chemical metering pump
- 15 injection points
- flow rate per port <±4%

Phase I:

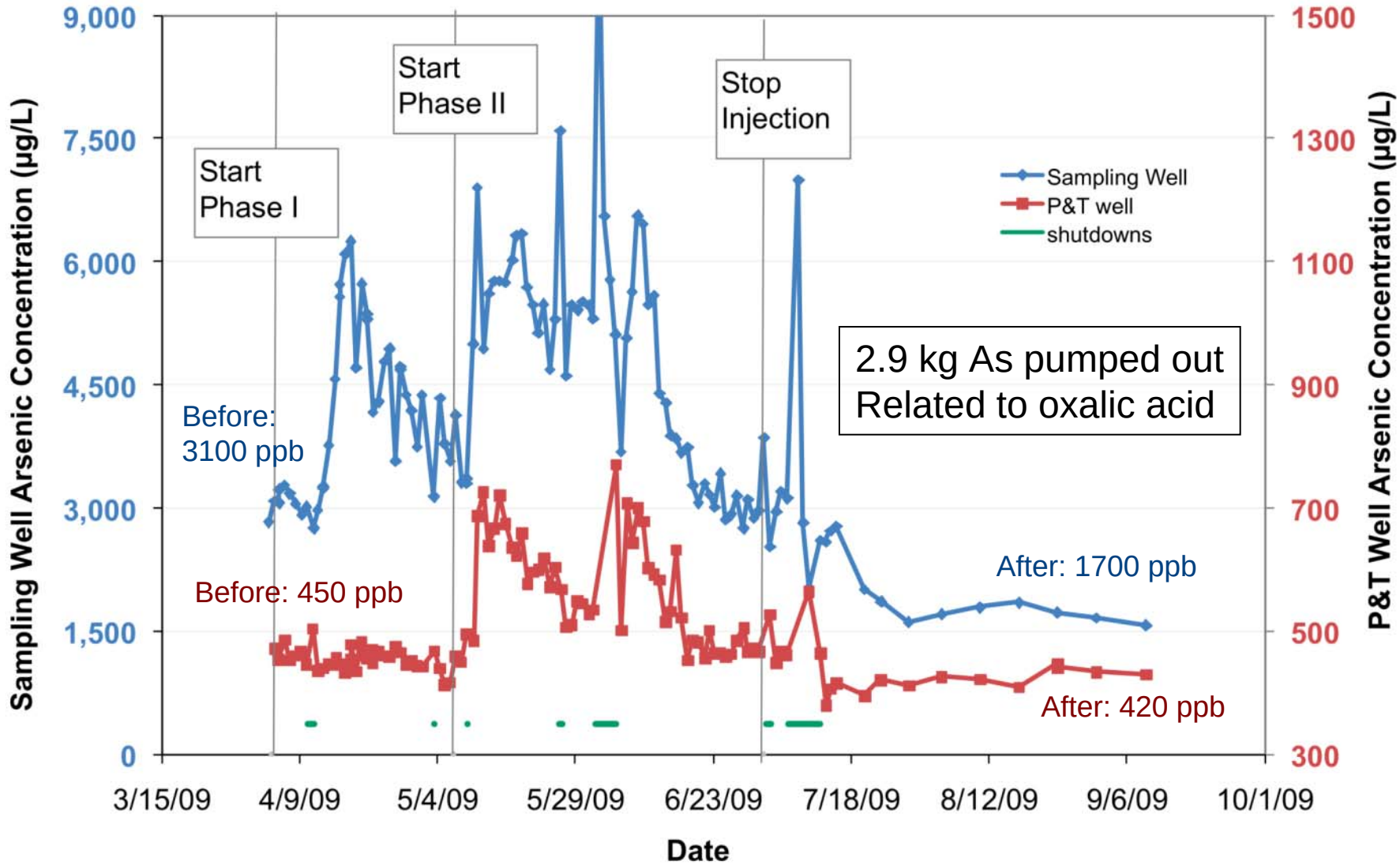
- April 4 - May 7
- 100 mM oxalic & Br
- 0.27 L/min total injection rate

Phase II:

- May 7 - July 2
- 400 mM oxalic & Br
- 0.56 L/min total injection rate

Total oxalic acid injected: ~2000 kg

Field Results: Arsenic Concentrations



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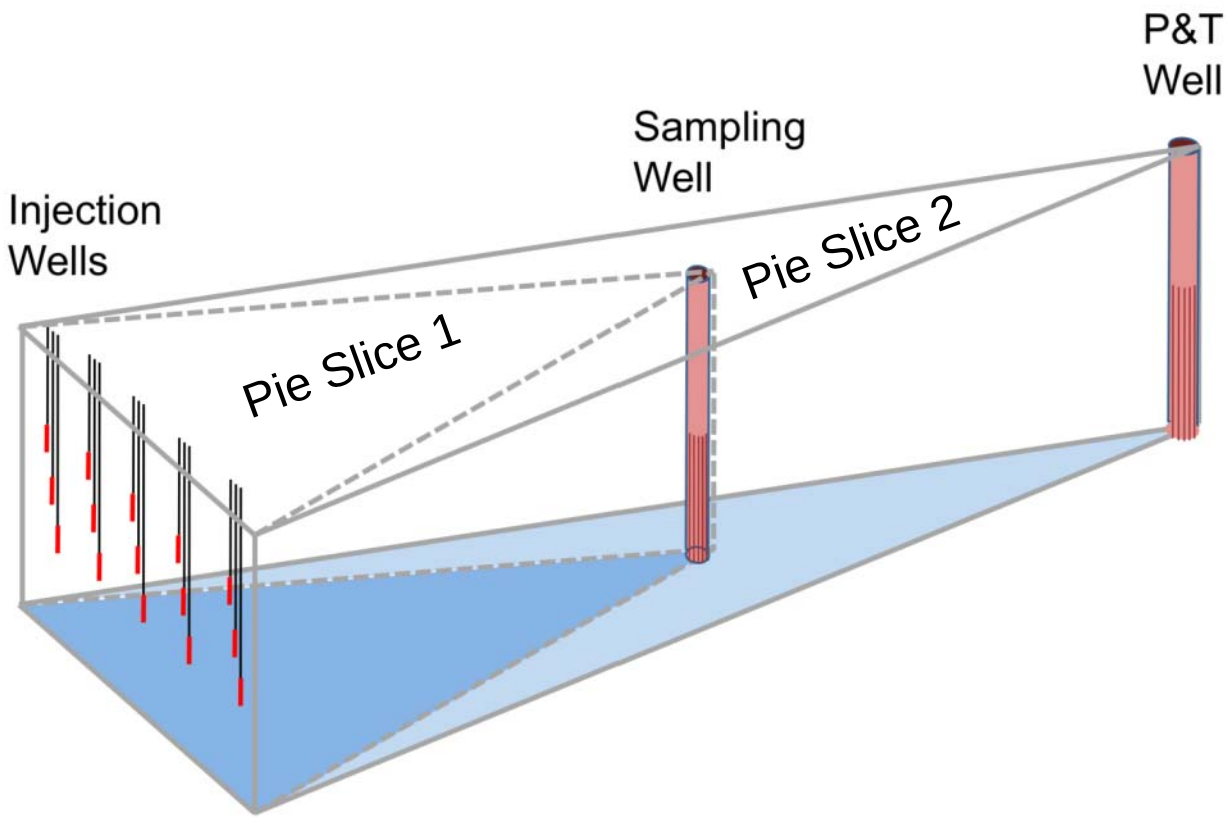
Results: Arsenic Mobilization

Assumptions for estimating As in impacted area:

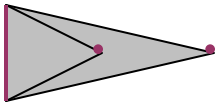
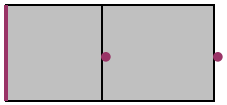
1) Thickness affected = 8 ft (based on groundwater modeling)
2) Uniform distribution of oxalic acid (no preferential flow paths)
3) [As] of solids before treatment = 31 mg/kg (avg XRF data)*Dry Density*Volume



Inventory Mass of As (before treatment):

Pie Slice 2 = 3.4 kg

Results: Arsenic Mobilization Scenarios

		Captured at sampling well	Captured at P&T well	Total captured
	Total mass removed	0.5 kg	2.4 kg	2.9 kg
Geometry	Pre-treat inventory	% removed at sampling	% removed at P&T	% Total captured
	3.4 kg	15%	70%	85%
	6.8 kg	7%	35%	43%

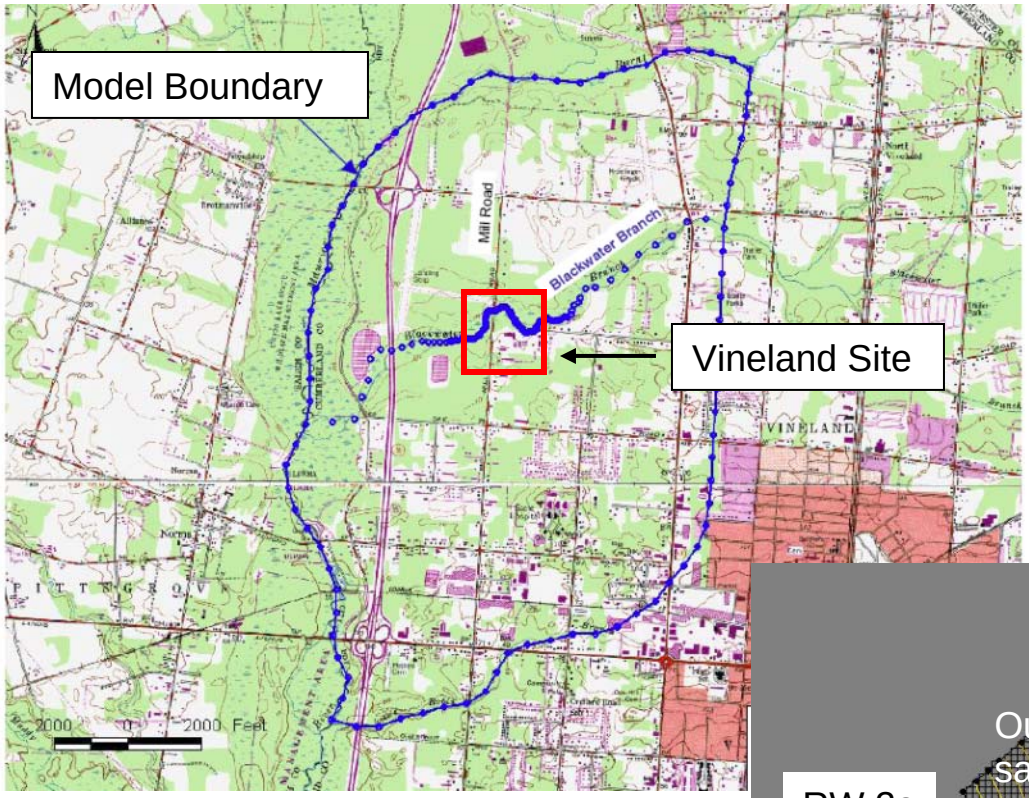
(48% As removal based on three before (2008) and after (2009) matched core sections)

Assistance with Sample Collection

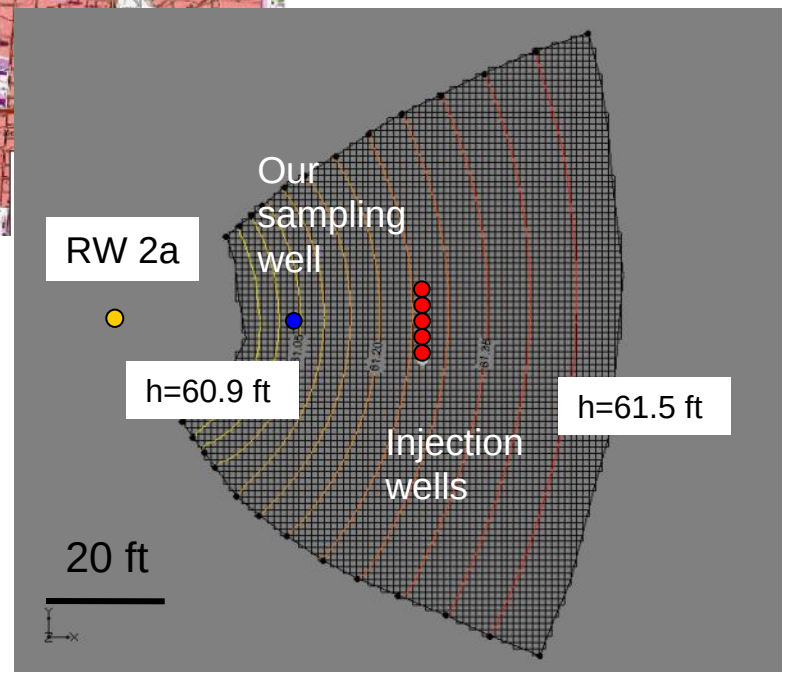
Collection of aquifer solids for column experiments

Site access during split spoon sampling to obtain aliquots for Columbia

Assistance with Hydrological Modeling (USACE)



USACE groundwater flow model boundary - includes area much larger than site



Provided parameters for local transport model run by Columbia

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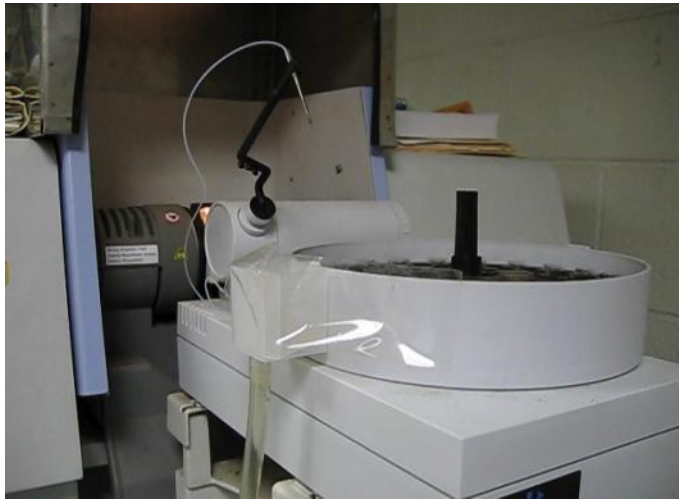
Assistance During Pilot Study

Storage and oxalic acid prep space

Set up of wastewater tanks and removal of water via tanker truck



Daily access to Sevenson GFAA and laboratory space during pilot study

Future Directions

- Scaling up/additional testing of idea
  - Will require more active partnership with EPA/USACE
    - Plan & conduct next experiment together
    - Modeling exercises for how to do injection in sustainable way for larger portion of site
      - Trench system, layer of solid oxalic acid?
      - Active manipulation of pumping wells?
      - Additional extraction wells?
  - More careful characterization of aquifer heterogeneities
      - Geophysical measurements
      - Determination of dispersivities (degree of mixing)
      - Additional coring work?

Acknowledgements

Vineland site managers and staff

R. Naman (USEPA)
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B. O'Shea
K. Doobay

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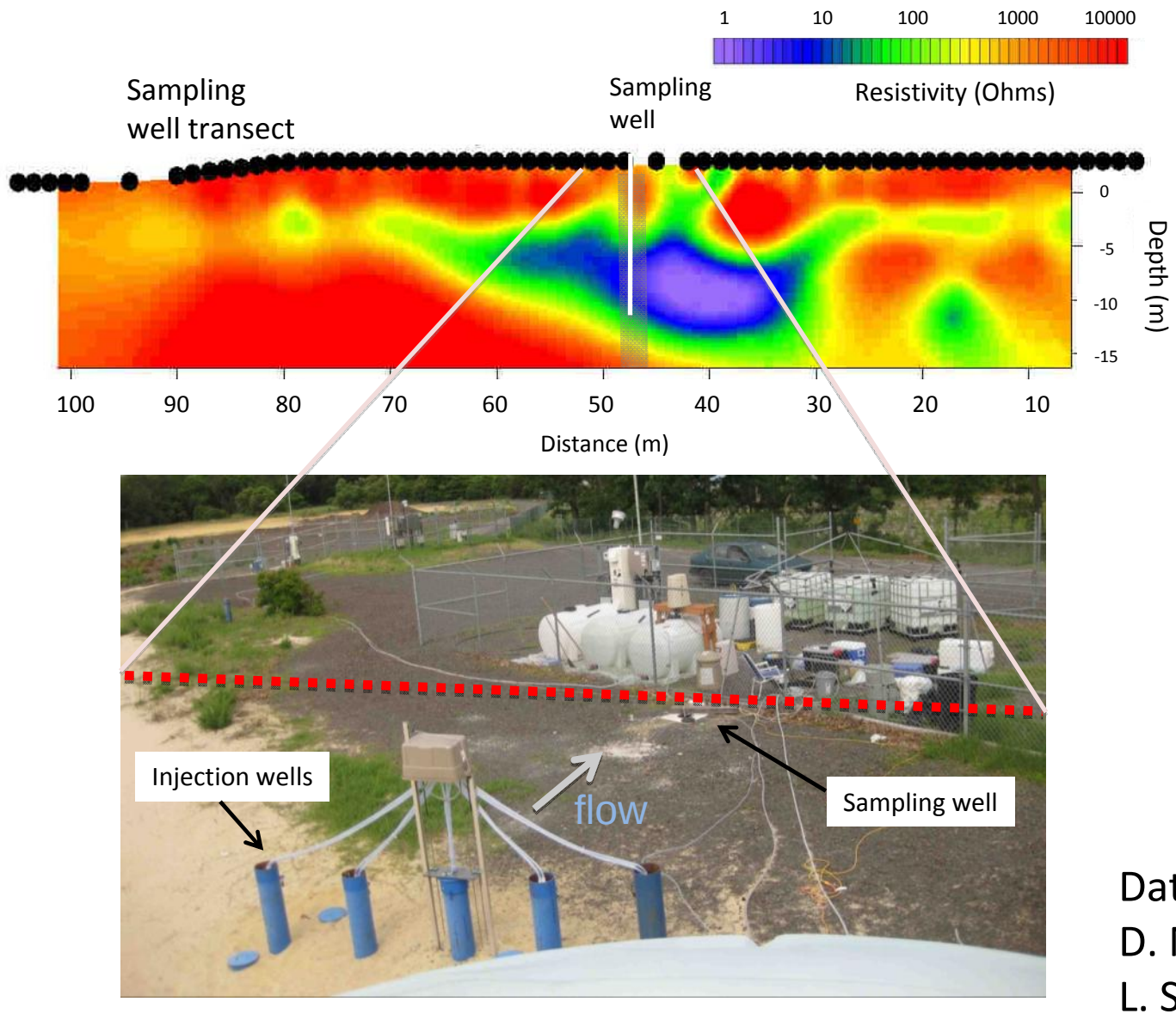
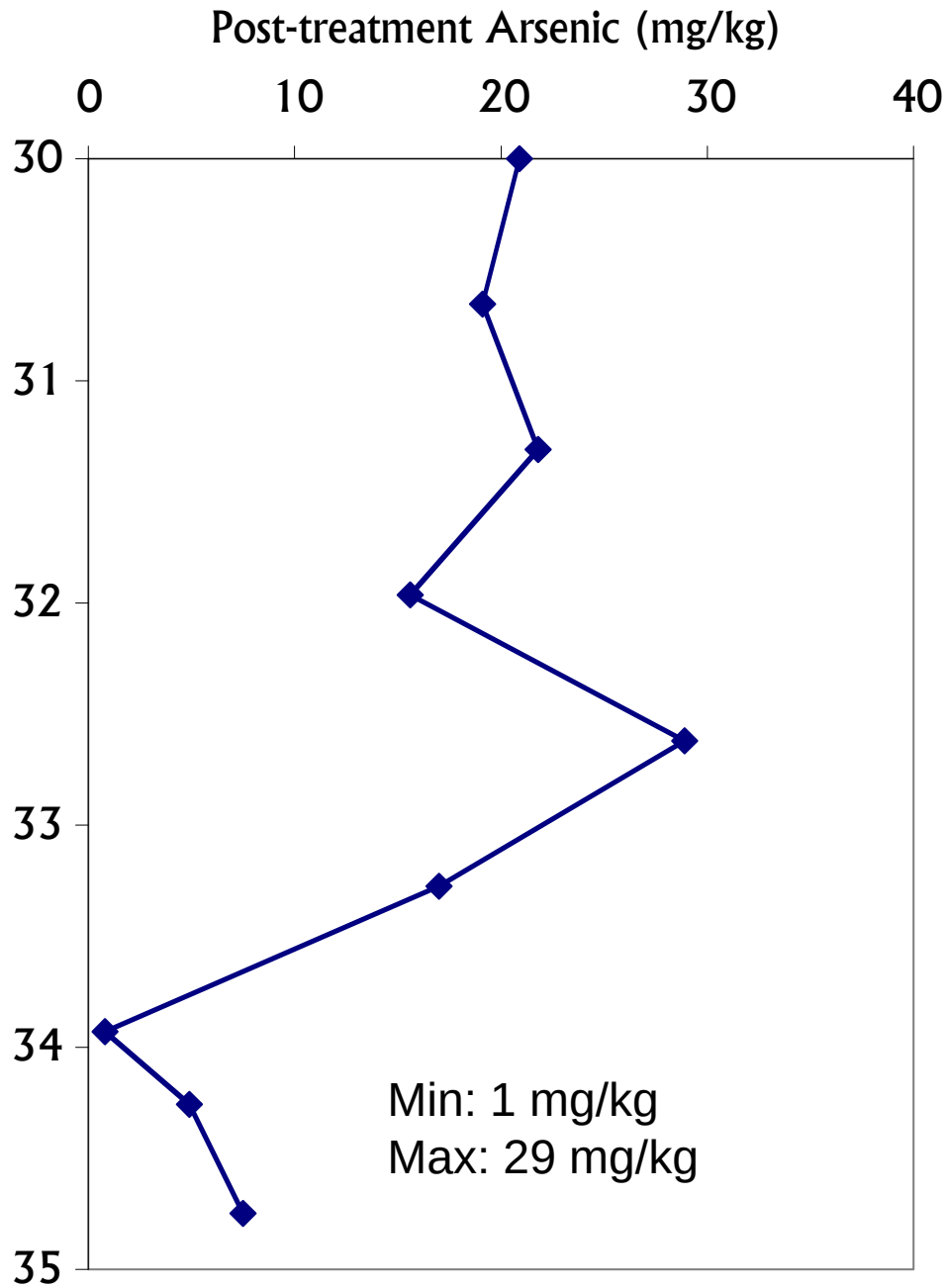
Back up Slides

Field Results: Geophysical Survey



Data from
D. Ntarlagiannis
L. Slater

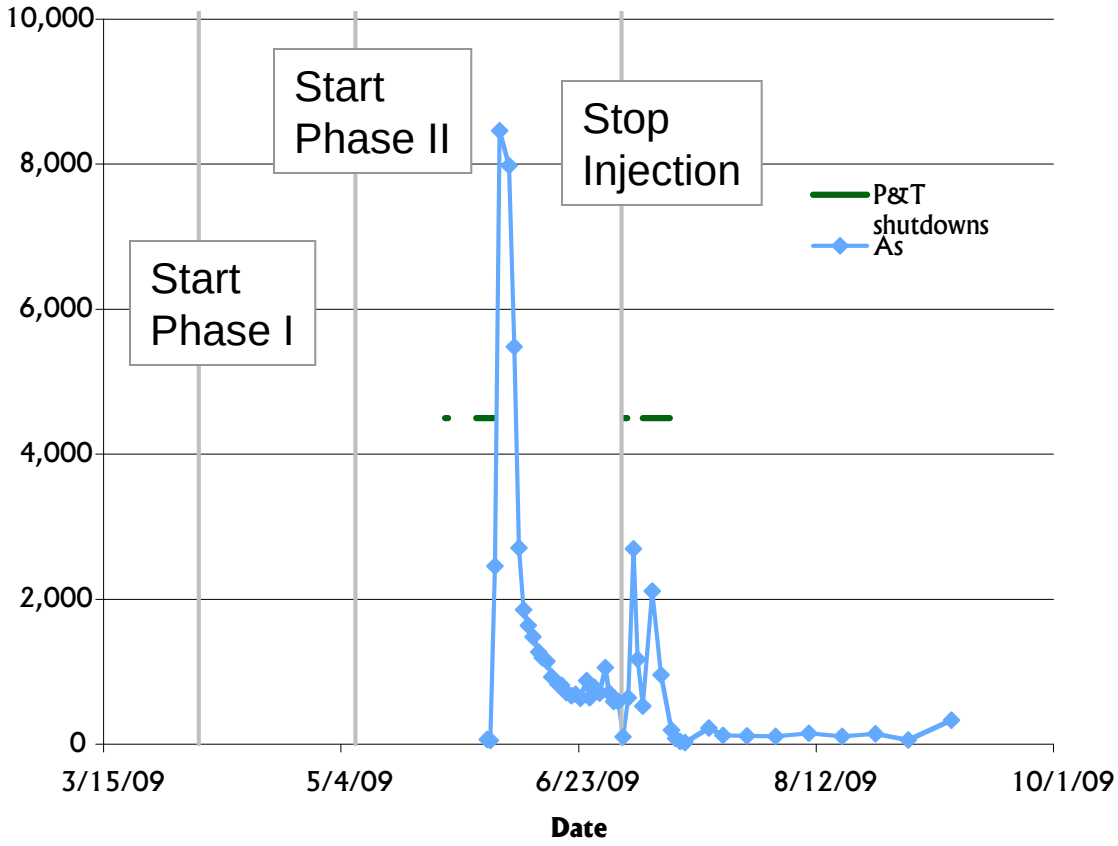
Results: Evidence for Unanticipated Flow Paths

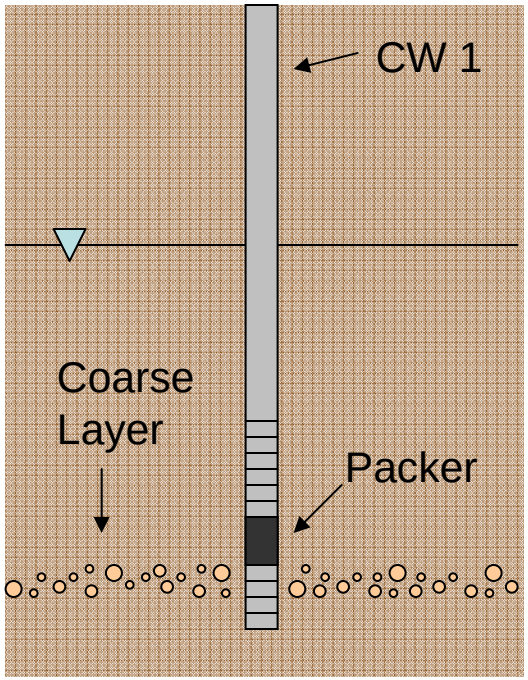


KW11
30-35 ft
(middle,
CW2 side)

Results: Evidence for Unanticipated Flow Paths

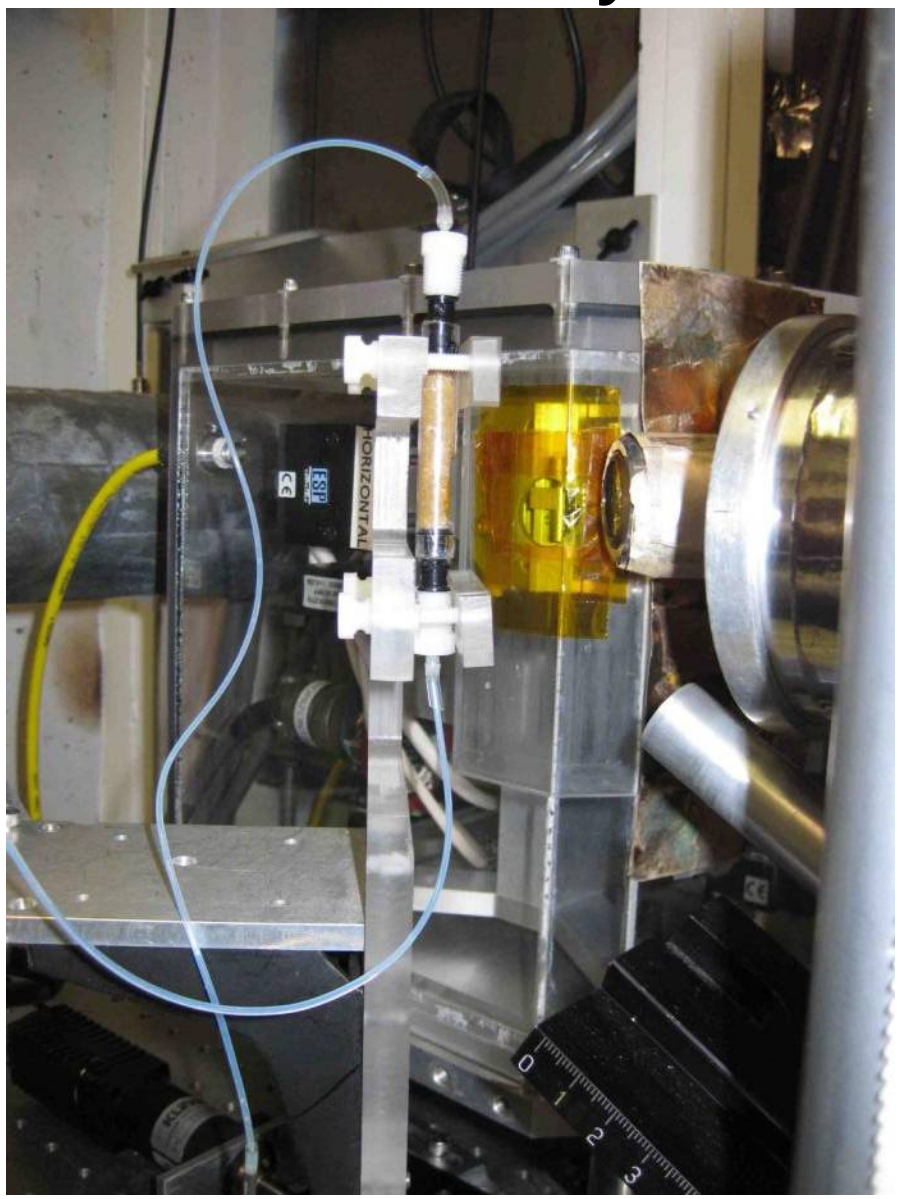
Arsenic Concentrations in the Coarse Layer at CW 1





Additionally, Br concentrations in the coarse layer averaged 4 mg/L and oxalic acid concentrations averaged 11 mM during this time. These concentrations are similar to those seen excluding the coarse layer.

Mini columns with 10 mM oxalic acid in the synchrotron beamline



Purpose:

1) Show that it is possible to run a column in the beamline and gather information about a particular part of the column at multiple points during the experiment
2) Investigate the mechanism of action of oxalic acid for mobilizing arsenic
3) Use the µXRF data to evaluate As removal rate information. Can this information be used to predict ideal flow rates for larger scale systems (field scale)?

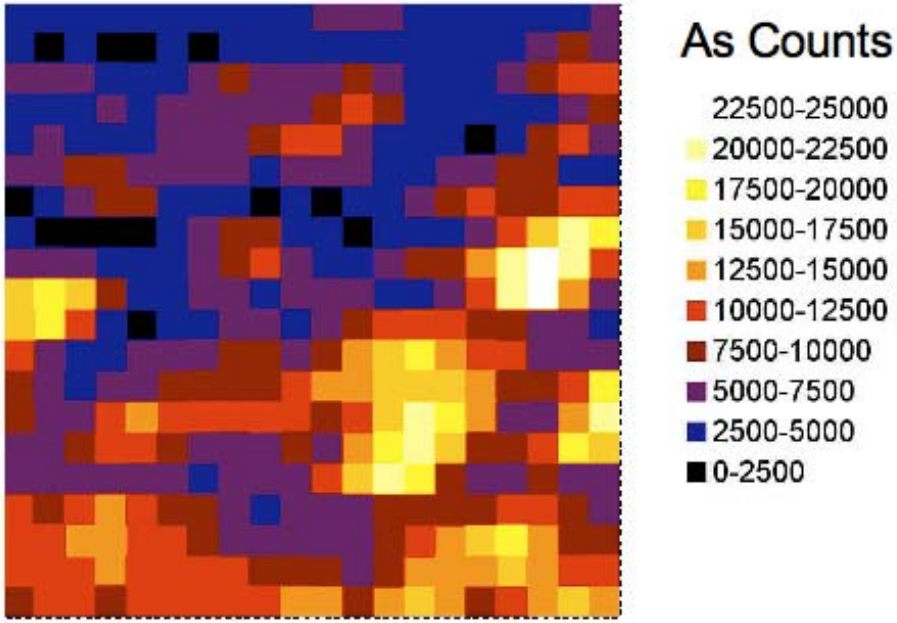
Information gathered in the beamline:

-As and Fe µXRF counts on a 0.16 x 0.16 mm portion of a column several times throughout oxalic acid treatment

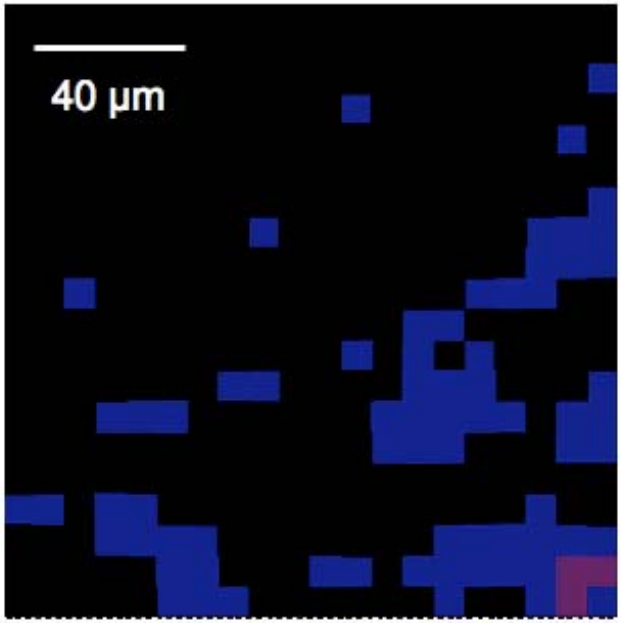
-Fe XANES before and after oxalic acid treatment

Arsenic and Iron Removal

As Map Before Oxalic Acid Treatment



As Map After Oxalic Acid Treatment



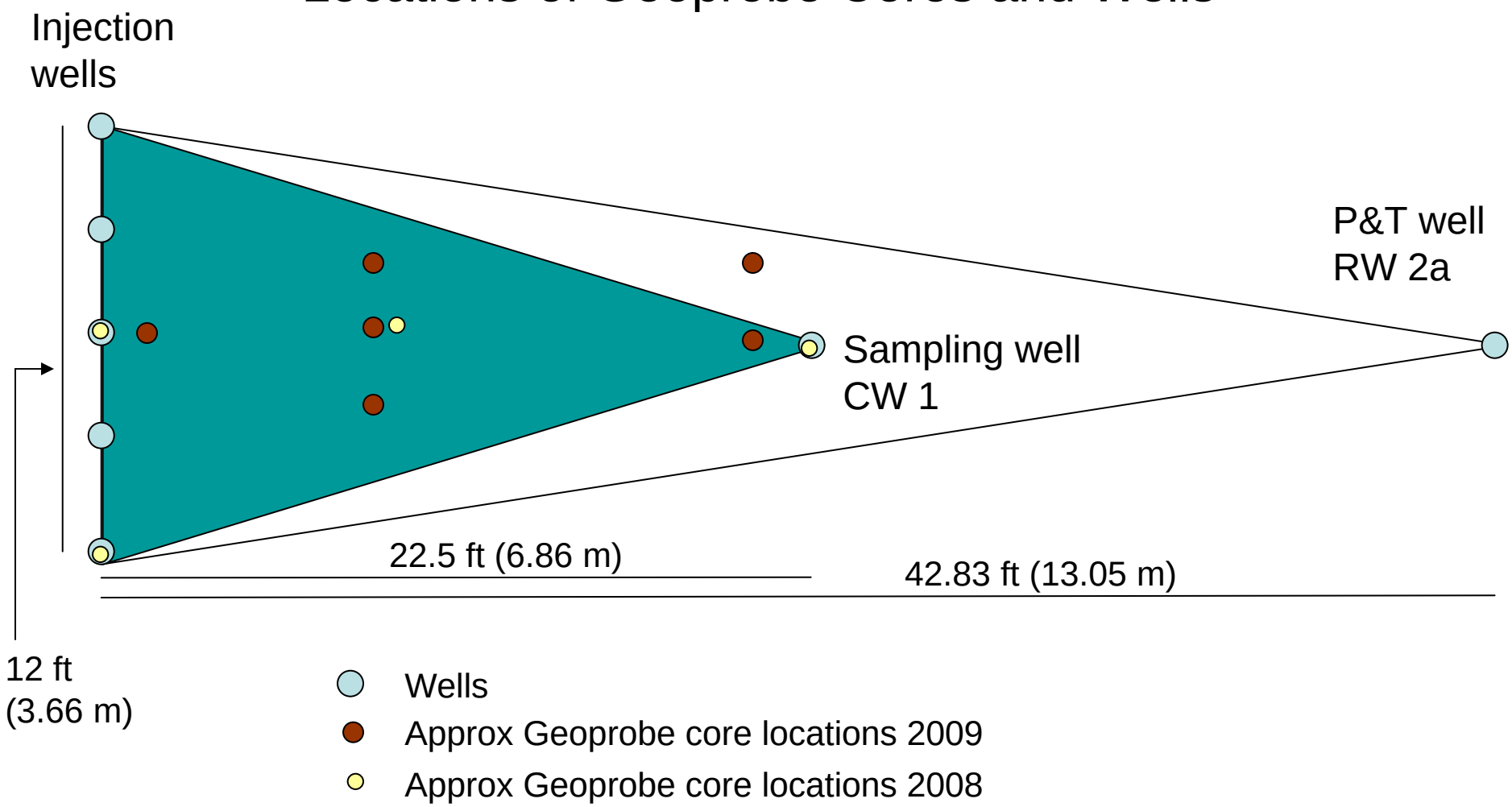
	Percent Removed			
	Maximum	**Minimum**	**Average**	**Most common***
Arsenic	102%	44%	79%	80-85%
Iron	81%	-112%	25%	neg%

*All negative #s were lumped into one bin.

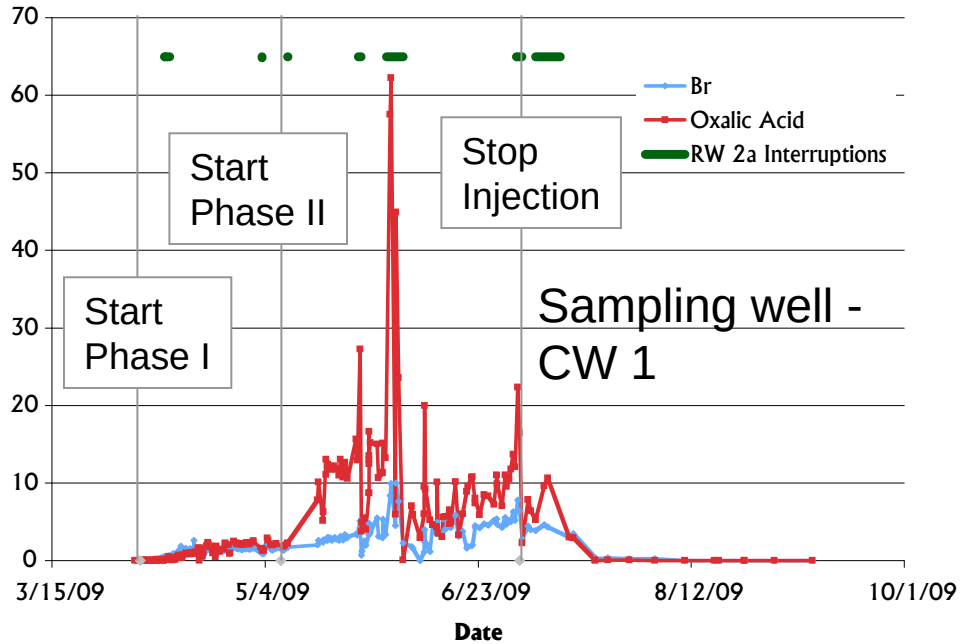
Field Study Conclusions

- 3-month oxalic acid treatment resulted in removal of a significant amount of arsenic (~3 kg of As)
  - Where it came from and % of total is difficult to quantify
    - based on pretreatment inventories: 43% to 85%
    - 47% based on comparison of 2008 and 2009 mean solids data
  - Evidence for unanticipated flow paths
- Water affected by treatment was captured completely (based on Bromide tracer)
- ~60% of the injected oxalic acid was captured
  - Degradation and/or adsorption
  - Longterm fate of oxalic acid is degradation based on fate of natural soil acid

Locations of Geoprobe Cores and Wells



Field Results: Br and Oxalic Acid



	Br Recovery (%)	Oxalic Acid Recovery (%)
Sampling well	20%	15%
P&T well	100%	45%
Total	120%	60%

*Subset of Br samples to be re-run.