Halting Migration through Coprecipitation: A Nontraditional Approach to Treatment of Dissolved Arsenic in Groundwater

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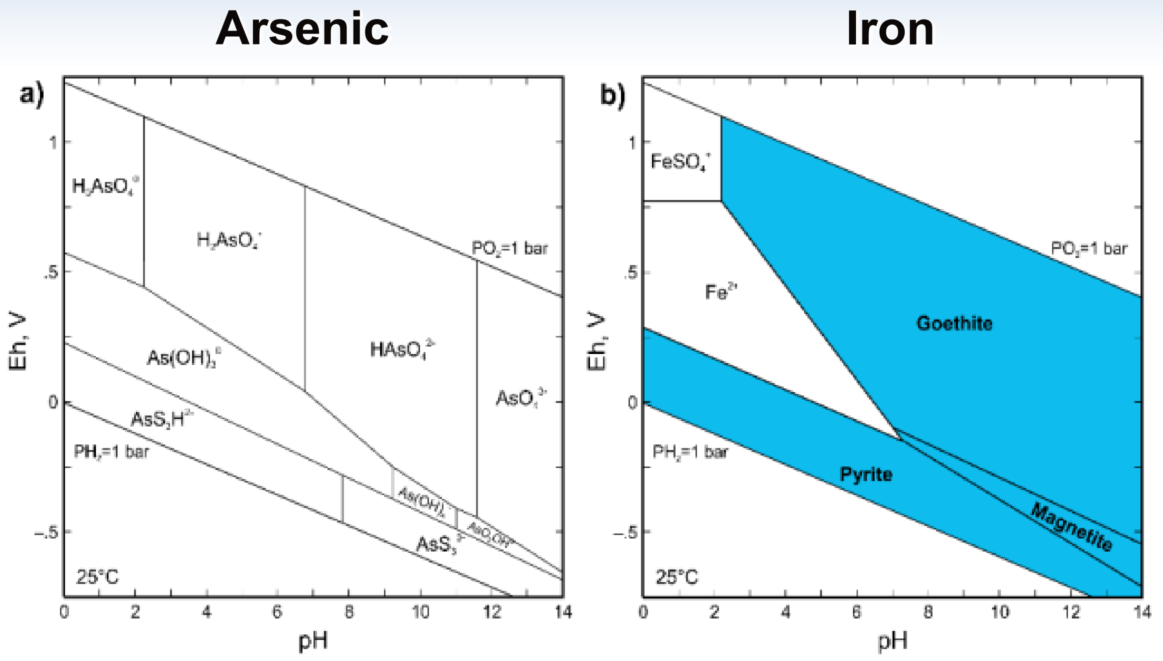
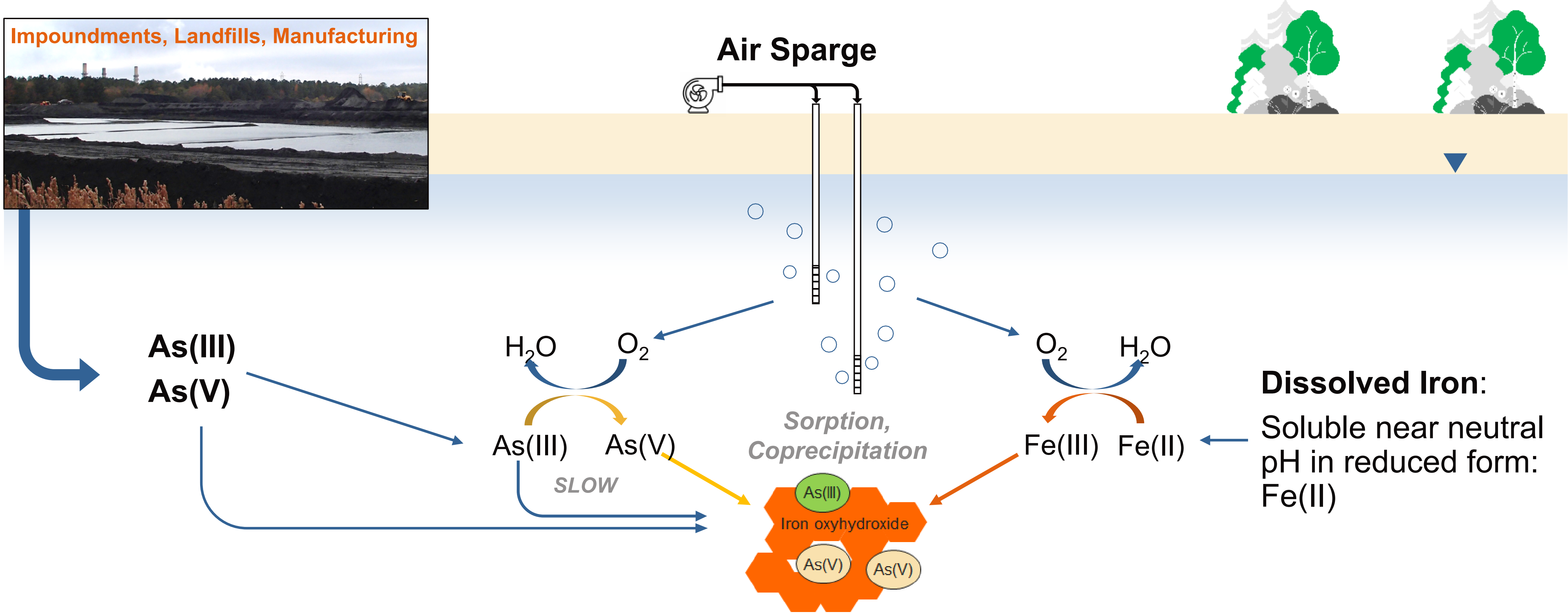
Concept Overview

- Arsenic and iron can be released in manufacturing waste, but can also be naturally occurring:
  - Released under reducing conditions
  - Exacerbated by capping
- Iron may be injected for in-situ metals treatment, and is widely used for chemical treatment in-situ



Ford et al., U.S. EPA, 2007

Concept Overview

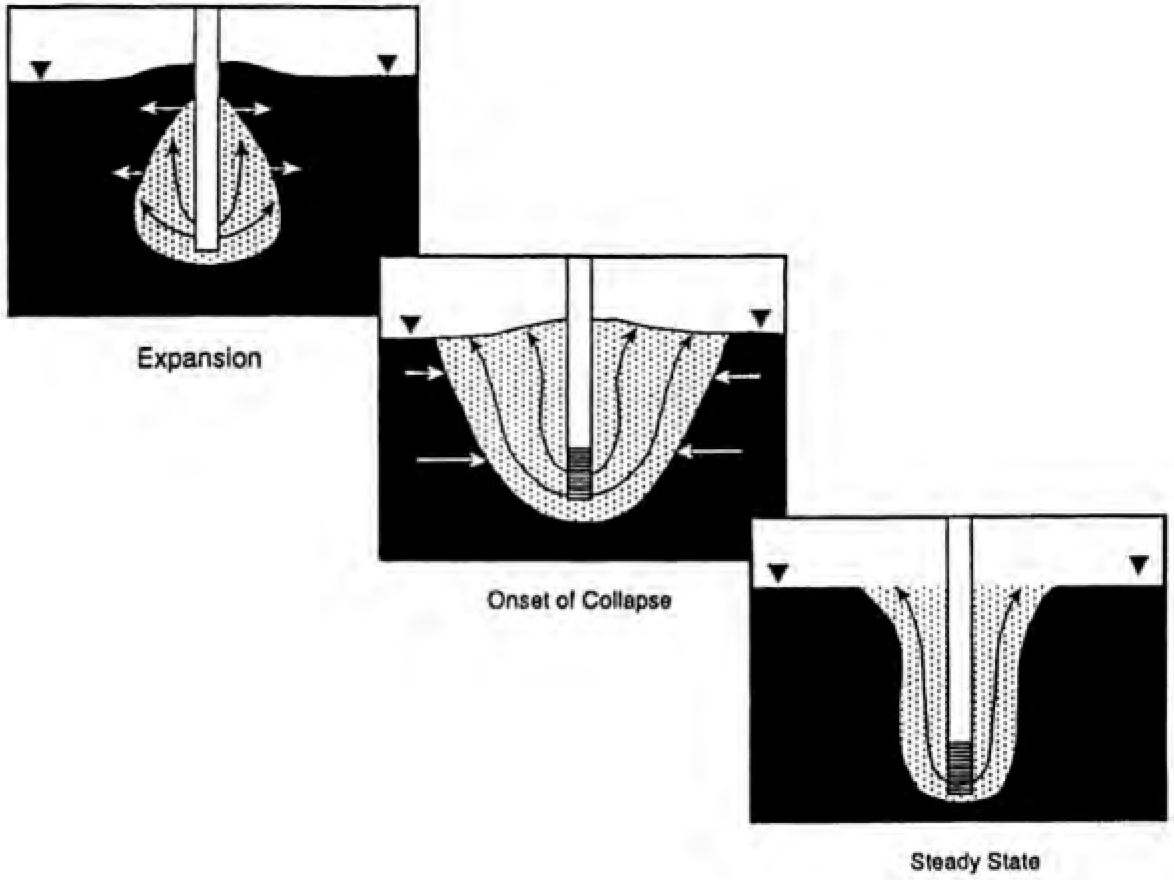


***In-Situ* Arsenic Treatment with Iron**

Implementation

Hydrogeologic / Engineering Considerations

- Air injection pressures and aquifer capacity
  - Aquifer texture/lithology: Sandy units ideal
  - Presence of confining layers
- Air distribution potential
- Arsenic and iron depth, spatial distribution



USACE, 2013

Implementation

Geochemical Considerations

- **Redox status of the aquifer**
- Iron oxidation kinetics: pH dependent
- Iron to arsenic ratio: How high is high enough?
- Acid generation: Consumption of alkalinity

- Must overcome overall reducing capacity.
- Ferric iron must be stable post sparge

Dissolved Fe(II) $\xrightarrow{\text{Fast; Abiotic and Microbial}}$ $Fe(OH)_3$

Dissolved Mn(II) $\xrightarrow{\text{Slow; Microbial}}$ Mn(III/IV)O/OH

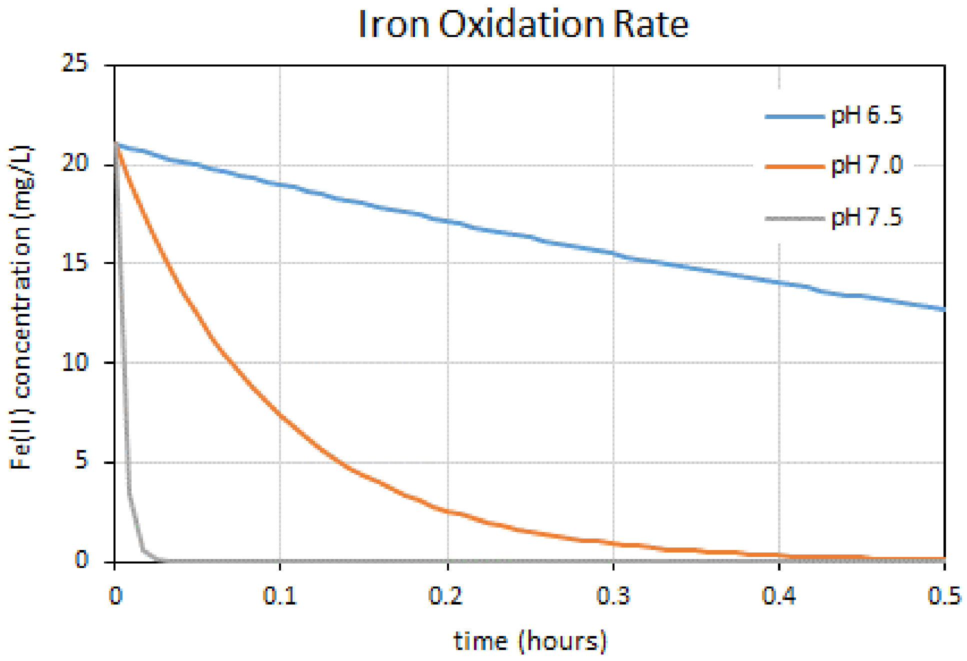
Diss/Tot Organic Matter $\xrightarrow{\text{Microbial}}$ CO_2, HCO_3^-

Implementation

Geochemical Considerations

- Redox status of the aquifer
- **Iron oxidation kinetics: pH dependent**
- Iron to arsenic ratio: How high is high enough?
- Acid generation: Consumption of alkalinity

- Solution pH: Controls thickness of O_2:Fe(II) reaction front



Estimated using relationship from Singer & Stumm (1970):

$$\frac{dm_{Fe^{+2}}}{dt} = -\left(2.91e\text{-}9 + 1.33e12\ a_{OH}^{2} P_{O_2}\right) m_{Fe^{+2}}$$

Implementation

Geochemical Considerations

- Redox status of the aquifer
- Iron oxidation kinetics: pH dependent
- **Iron to arsenic ratio: How high is high enough?**
- Acid generation: Consumption of alkalinity

Adsorption

TABLE 1. Material Properties and Experimental Conditions[a]

	HFO	goethite	magnetite
sorption density[d]			
As (V)			
mol As per mol Fe	0.24	0.016	
sites per nm^2	2.6	2.0	
As (III)			
mol As per mol Fe	0.31	0.016	0.025
sites per nm^2	3.5	2.0	2.2

[a] All experiments conducted at room temperature (23 ± 0.4 °C) with 0.01 M $NaClO_4$ background electrolyte medium. [b] Measured by N_2 BET. [c] Assumed value (*36*). [d] Obtained from sorption isotherm.

Dixit & Hering (ES&T 2003)

- Equivalent to:
  - Ferrihydrite: 3:1 Fe to As (g/g)
  - Goethite: 50:1 Fe to As (g/g)

- Rule of thumb: **10:1 is good, 100:1 is better**

Implementation

Geochemical Considerations

- Redox status of the aquifer
- Iron oxidation kinetics: pH dependent
- Iron to arsenic ratio: How high is high enough?
- **Acid generation: Consumption of alkalinity**

Fe(II) oxidation by oxygen generates acidity:

$$4\,Fe^{2+} + O_2 + 10H_2O = 4Fe(OH)_3 + 8\,H^+$$

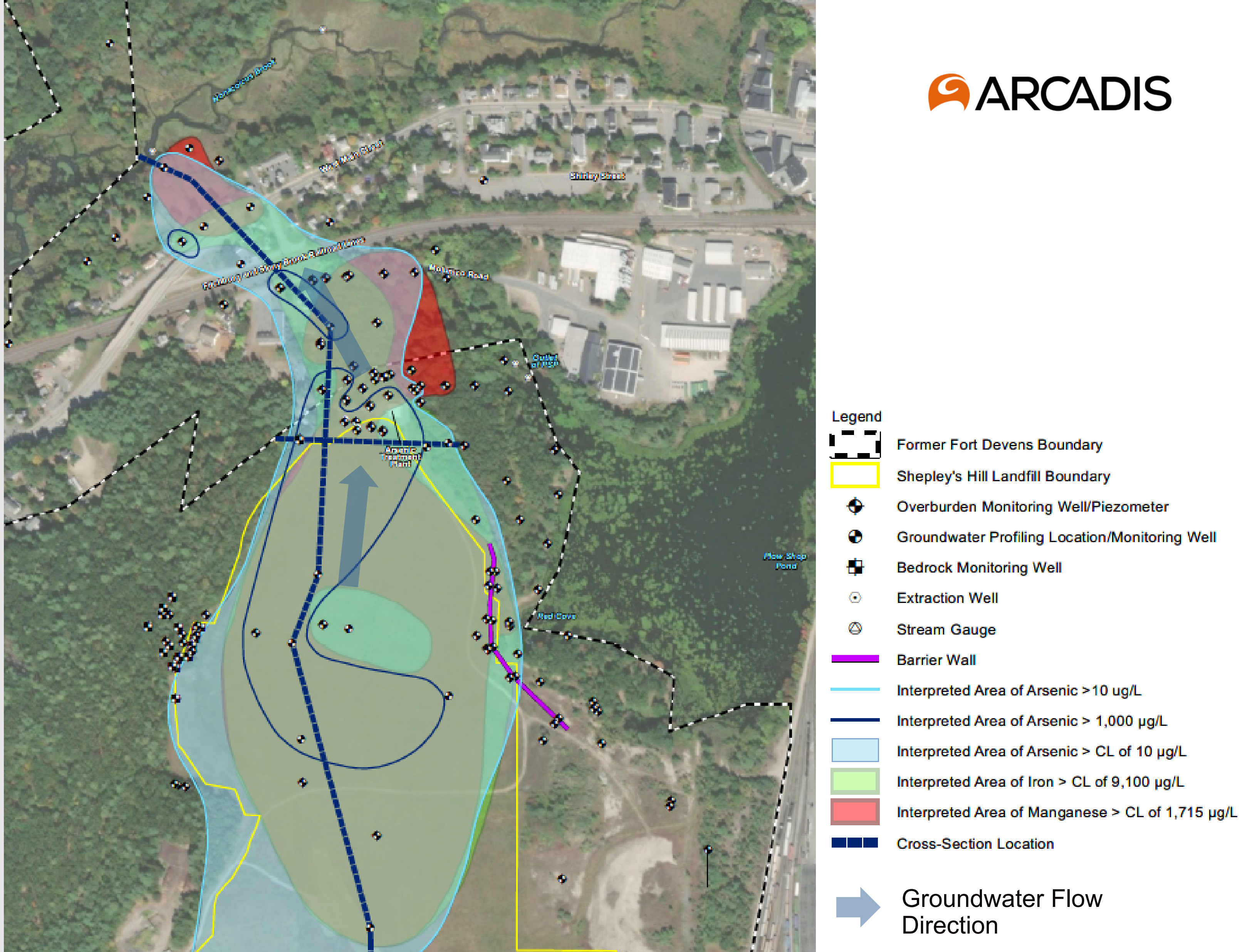
Solution and solid-phase alkalinity sufficient to buffer?

Shepley's Hill Landfill

- Groundwater extracted and treated to remove As

Sources include:

- Upper unconsolidated sediments - Released due to Fe/Mn oxyhydroxide reduction
- Bedrock - Released due to sulfide oxidation; less correlation with Fe/Mn
- Landfill - Demolition debris, incinerator ash, etc. with some arsenic



ARCADIS

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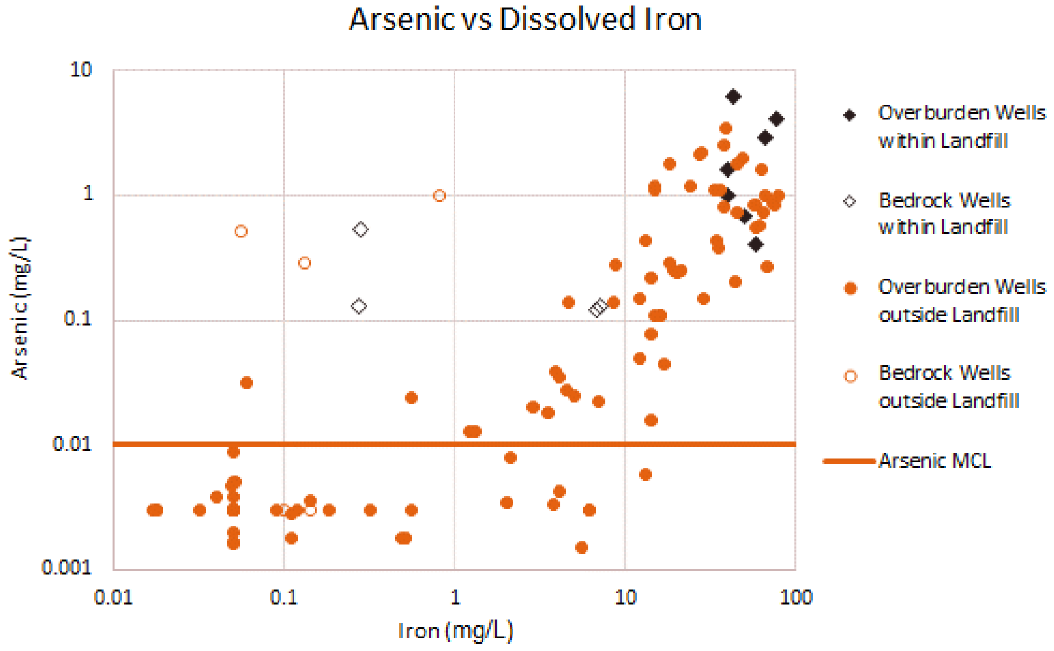
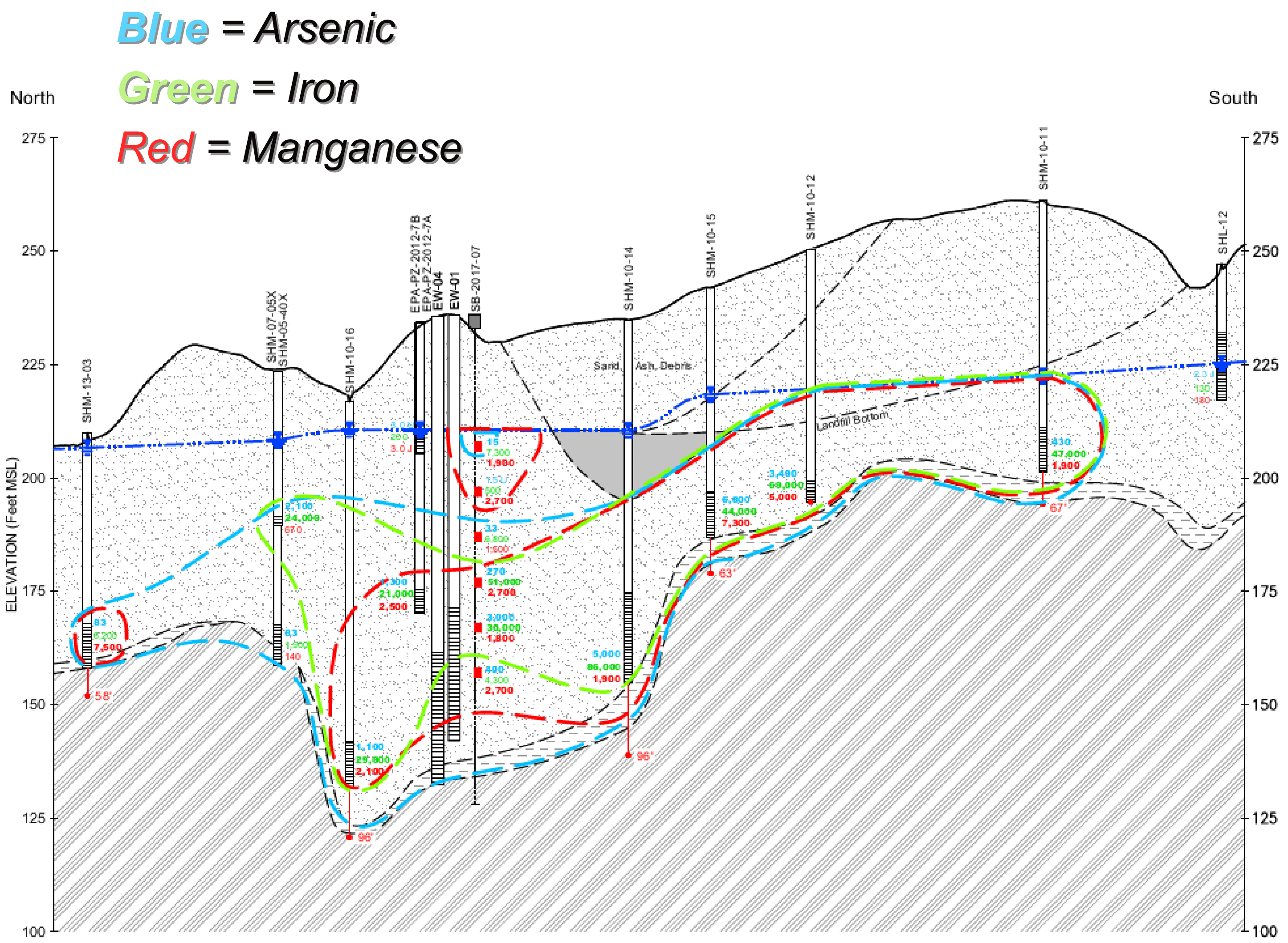
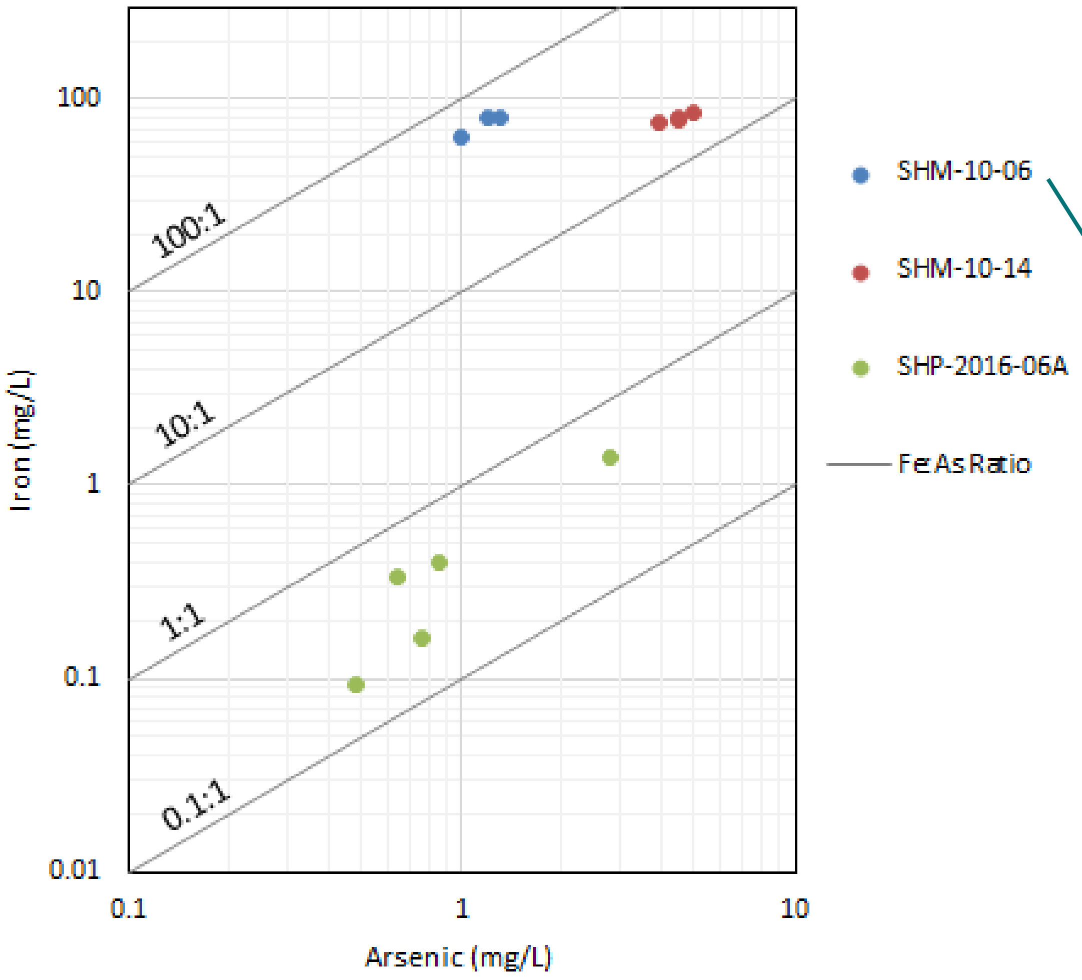
Shepley's Hill Landfill

- As, Fe, Mn concentrations increase with depth, present close to the bedrock interface.
- There are areas where As is/is not co-associated with Fe.





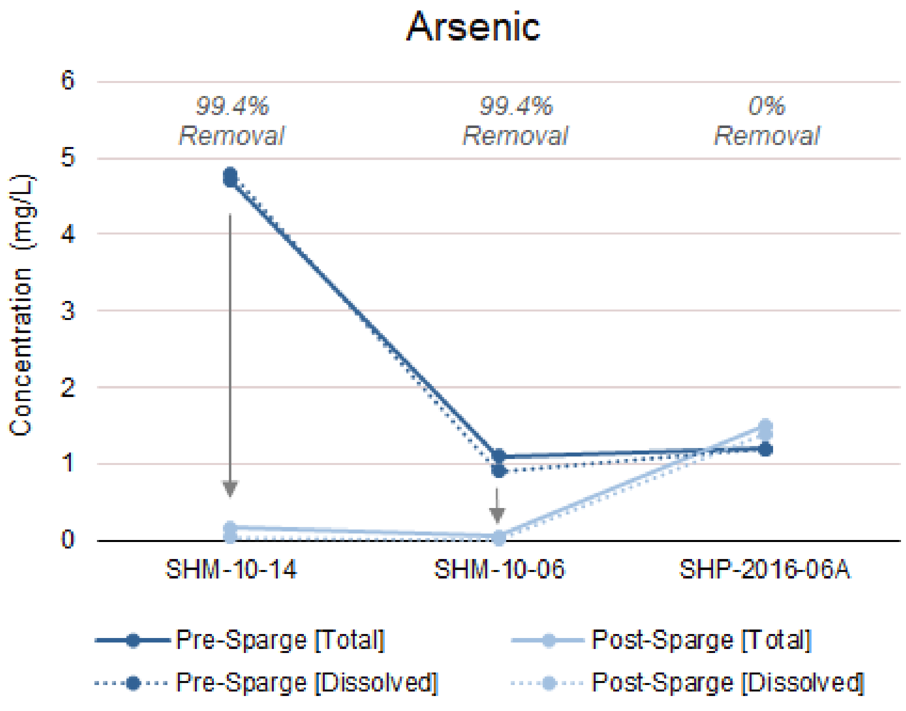
Arsenic Treatability Evaluation: Bucket Tests



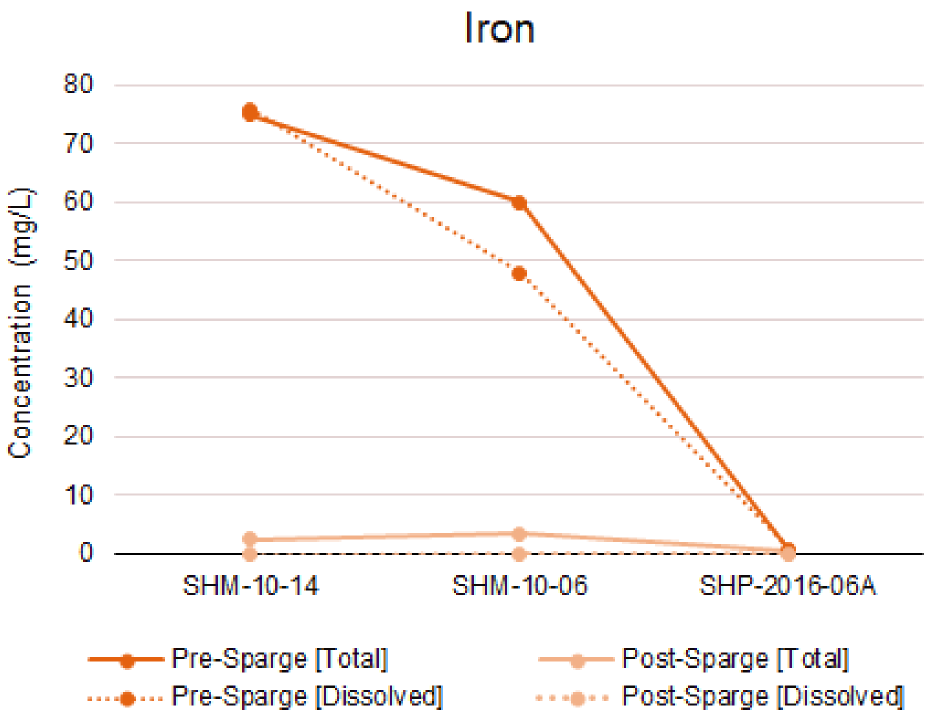
- Simple setup: 5-gallon buckets, fish tank aerator and air stones
- Field parameters monitored continually
- Samples for lab analysis collected before & after

Arsenic Treatability Evaluation: Bucket Tests

- Greater As removal with higher starting dissolved Fe and higher Fe:As ratios
  - No treatment at SHP-2016-06A
  - Dissolved As below MCL at SHM-10-14 and SHM-10-06



- Iron didn't readily settle out to < 1 mg/L
  - High Fe locations: Residual total arsenic associated with suspended particulates
  - SHP-2016-06A: Iron particulates present, but arsenic remained dissolved!



Air Sparge Pilot Test

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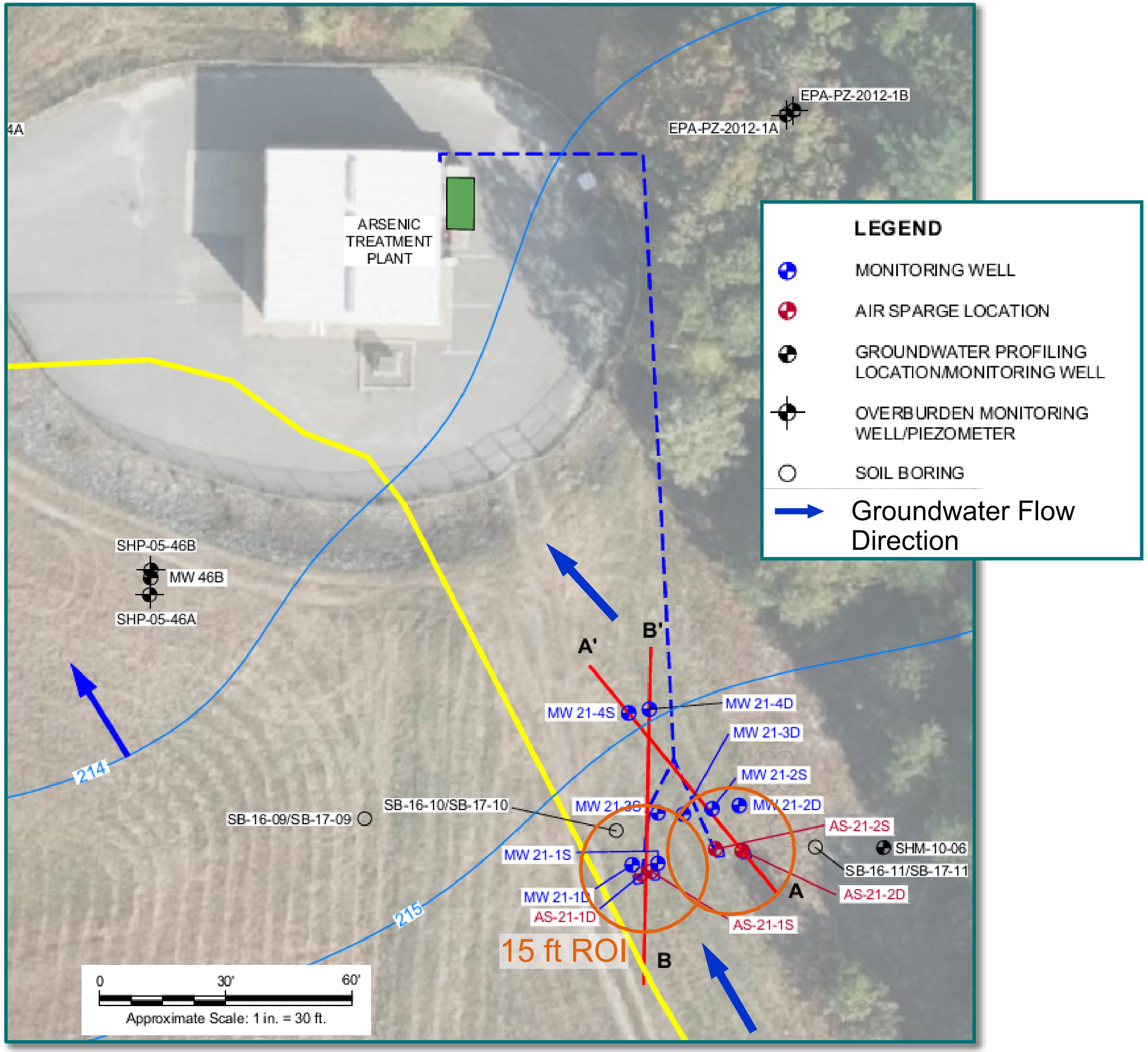
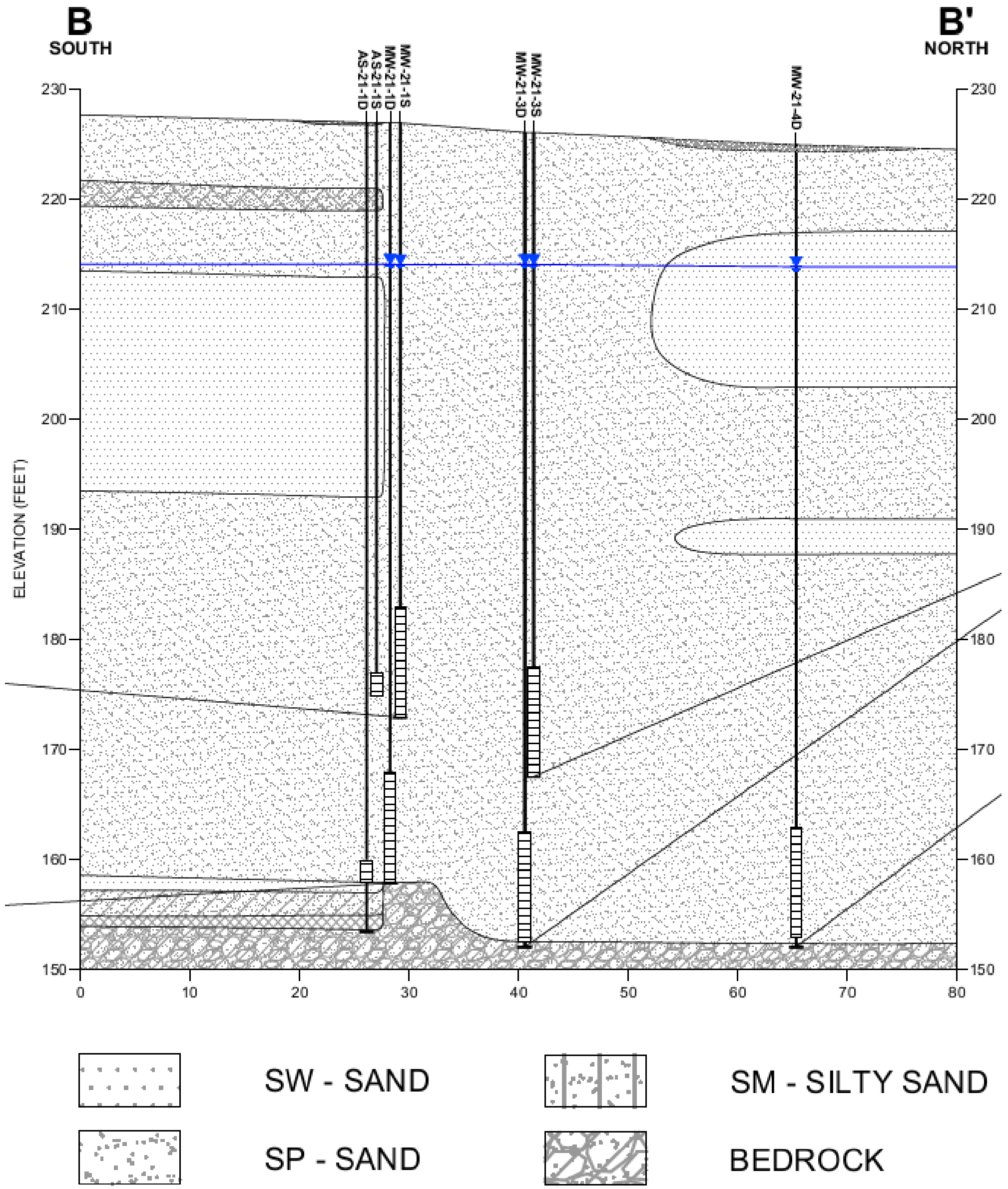
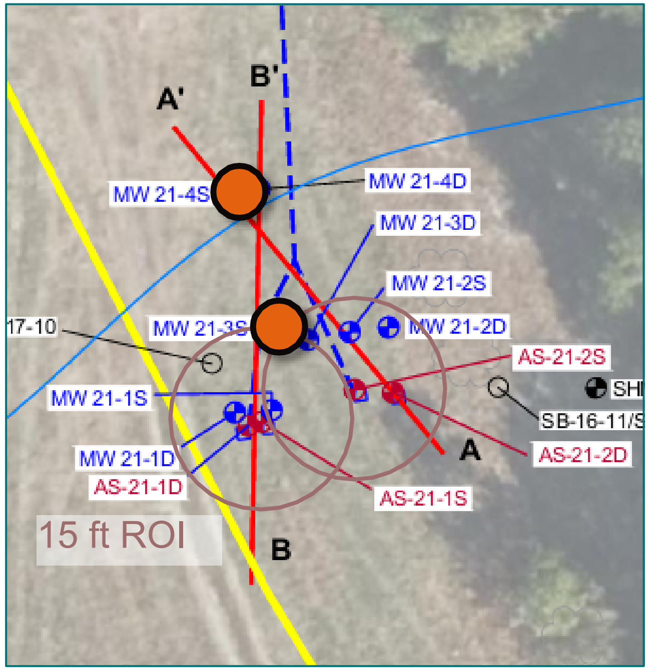


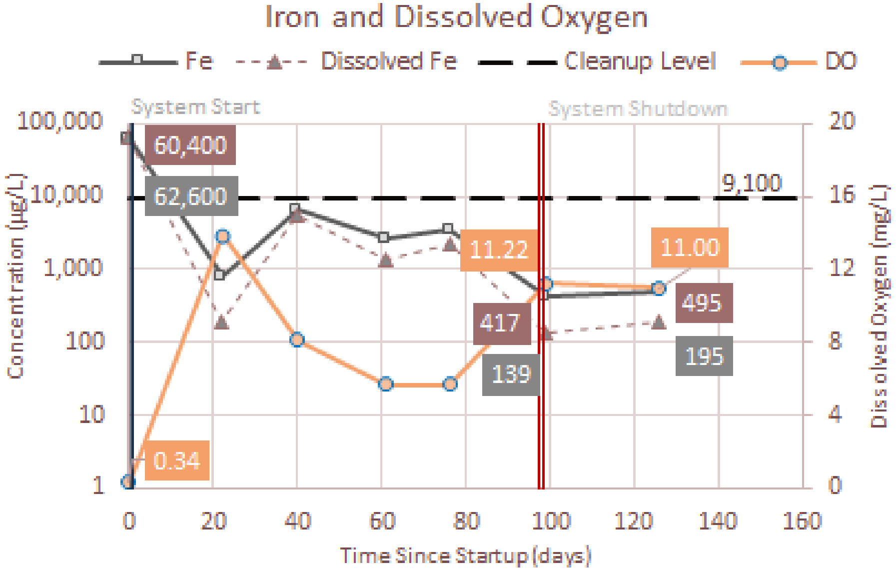


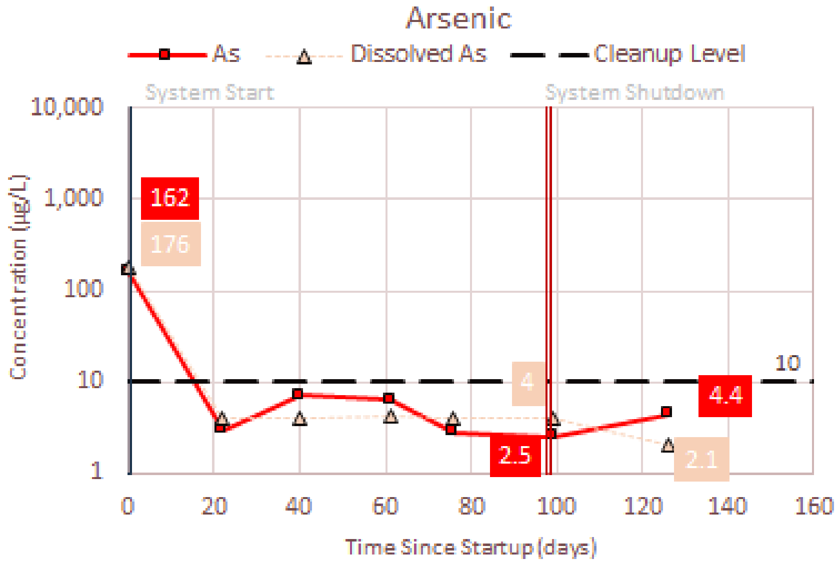
SHL Test Results – Shallow



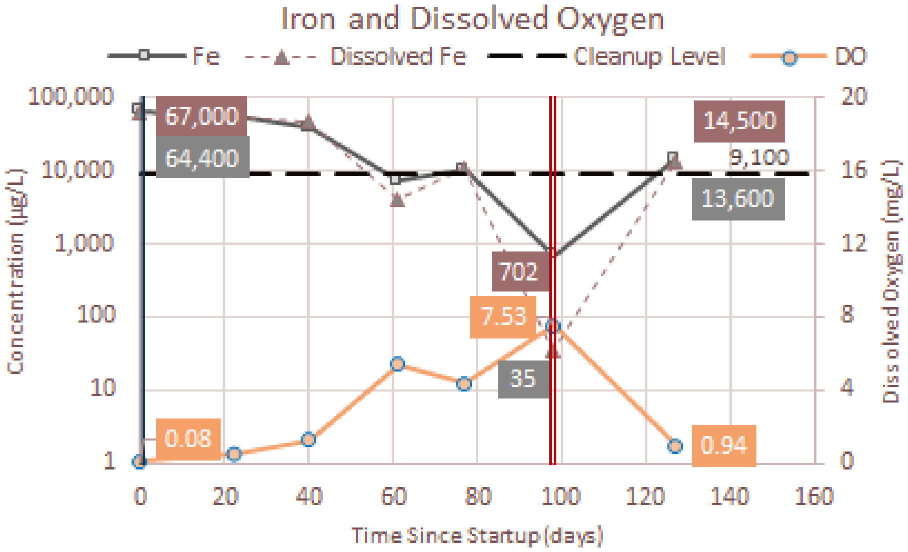
Very positive results in shallow performance monitoring wells

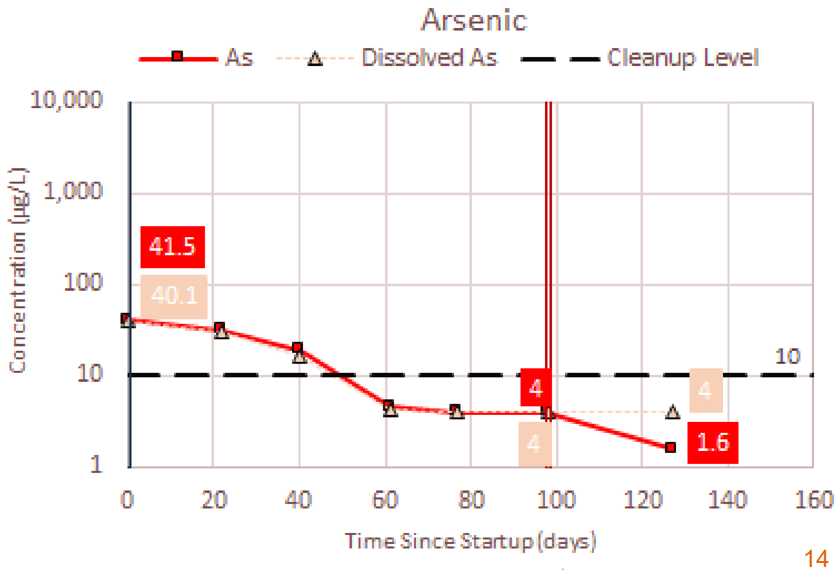
~15 ft from Sparge





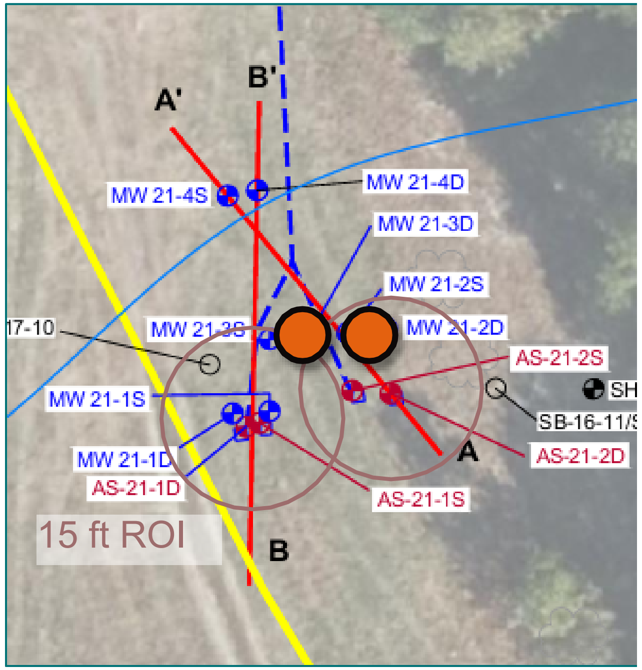
~40 ft from Sparge



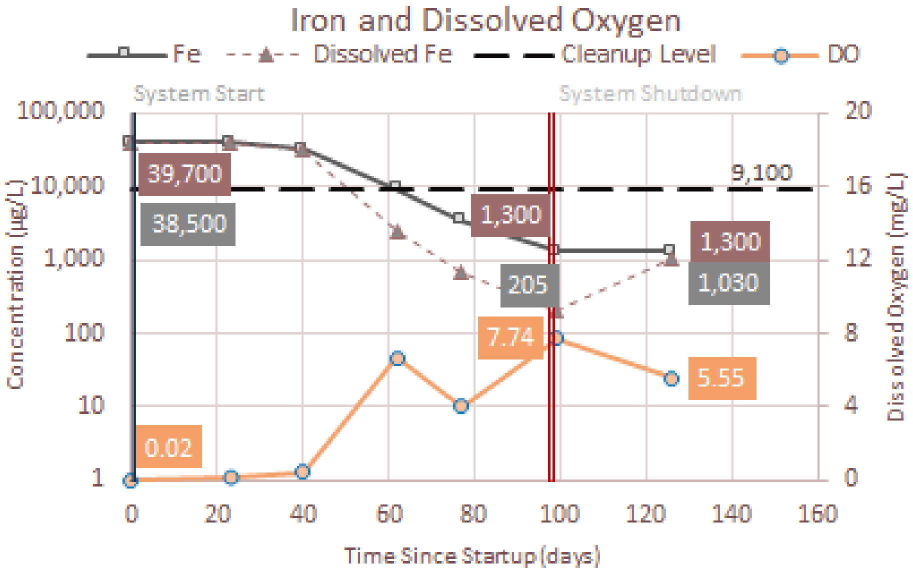


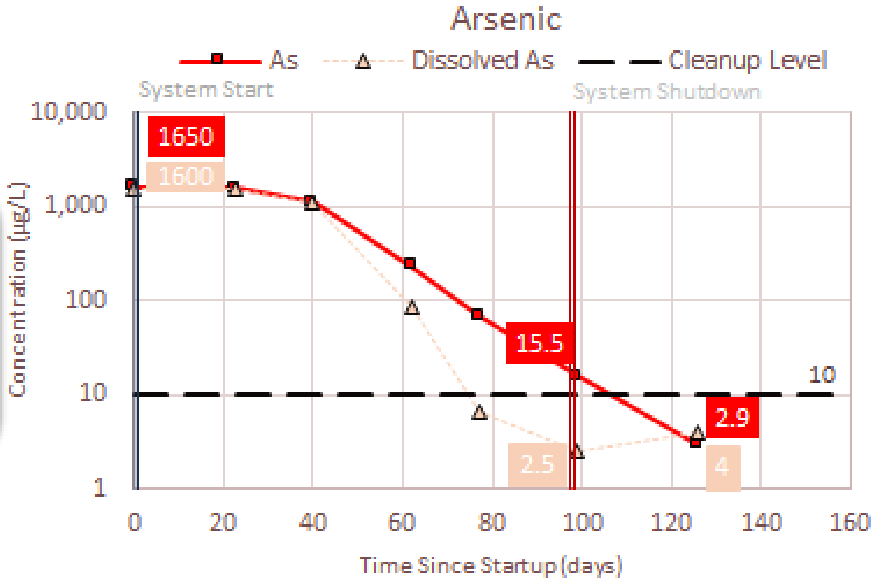
SHL Test Results – Deep

ARCADIS

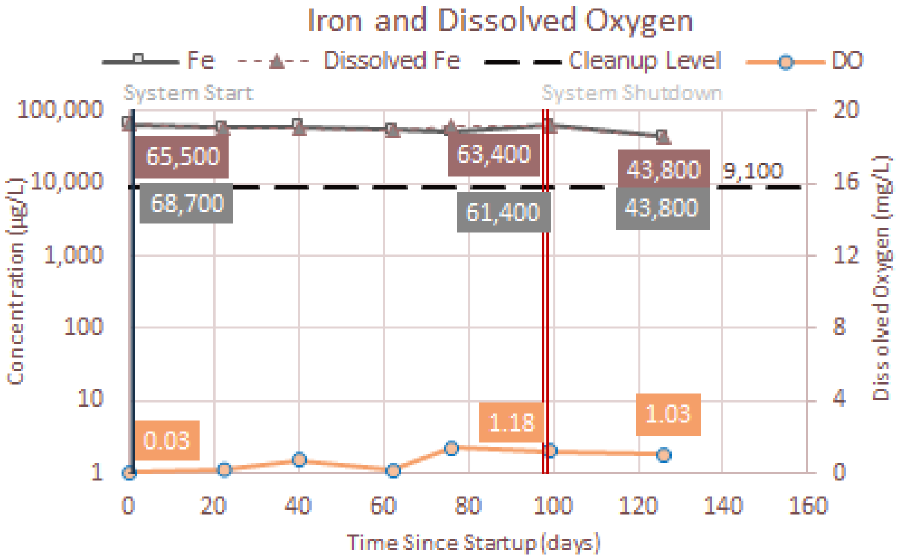


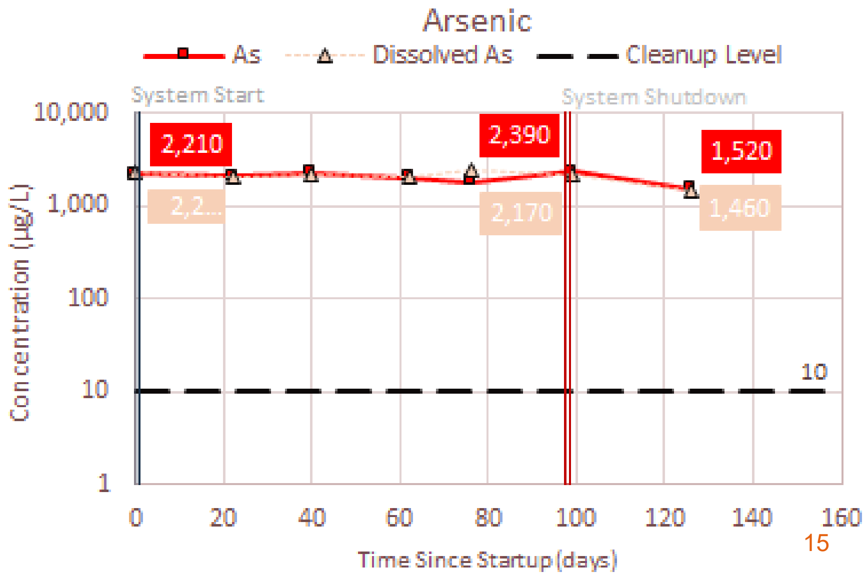
~10 ft from Sparge





~15 ft from Sparge



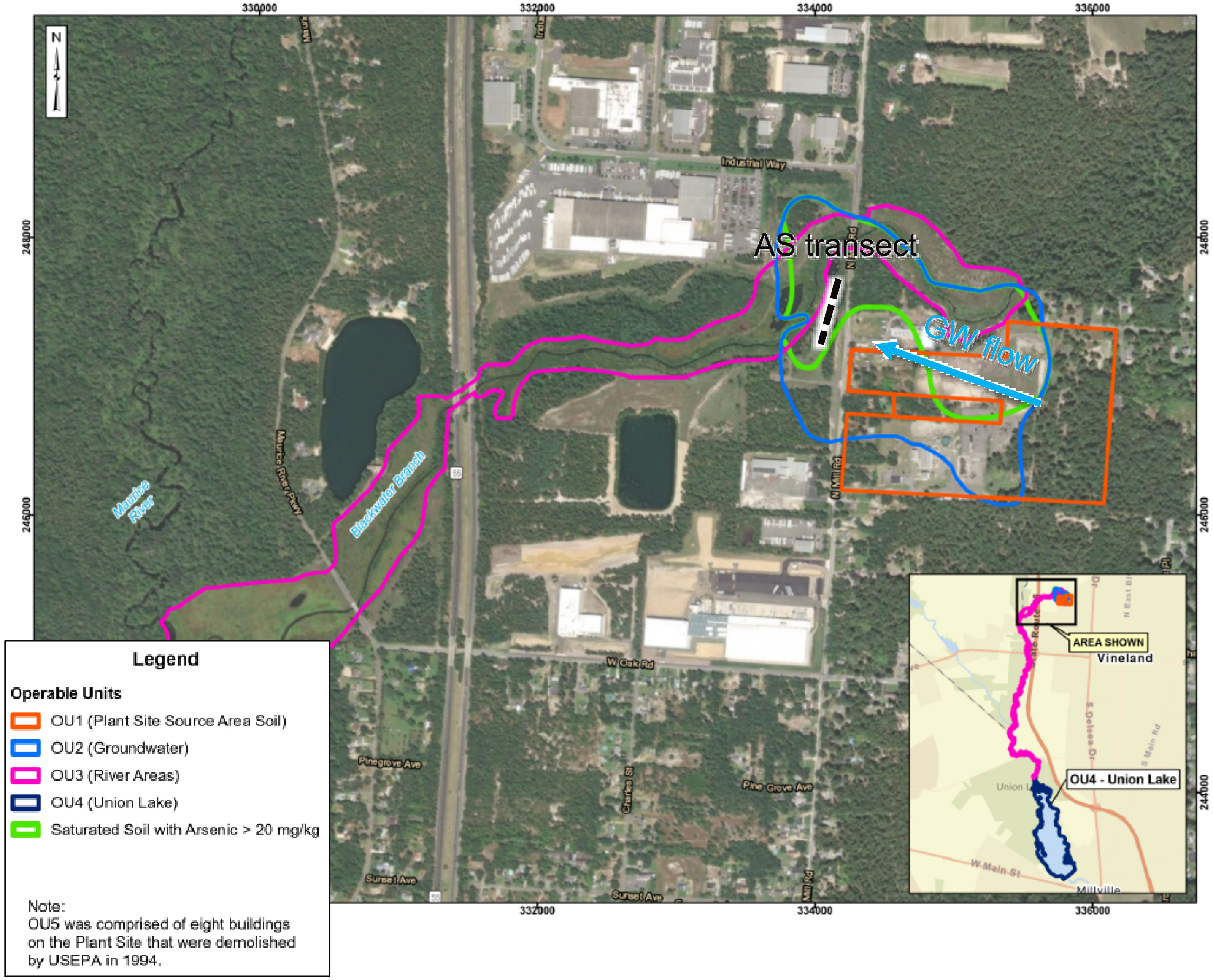


Mixed results in deep performance monitoring wells

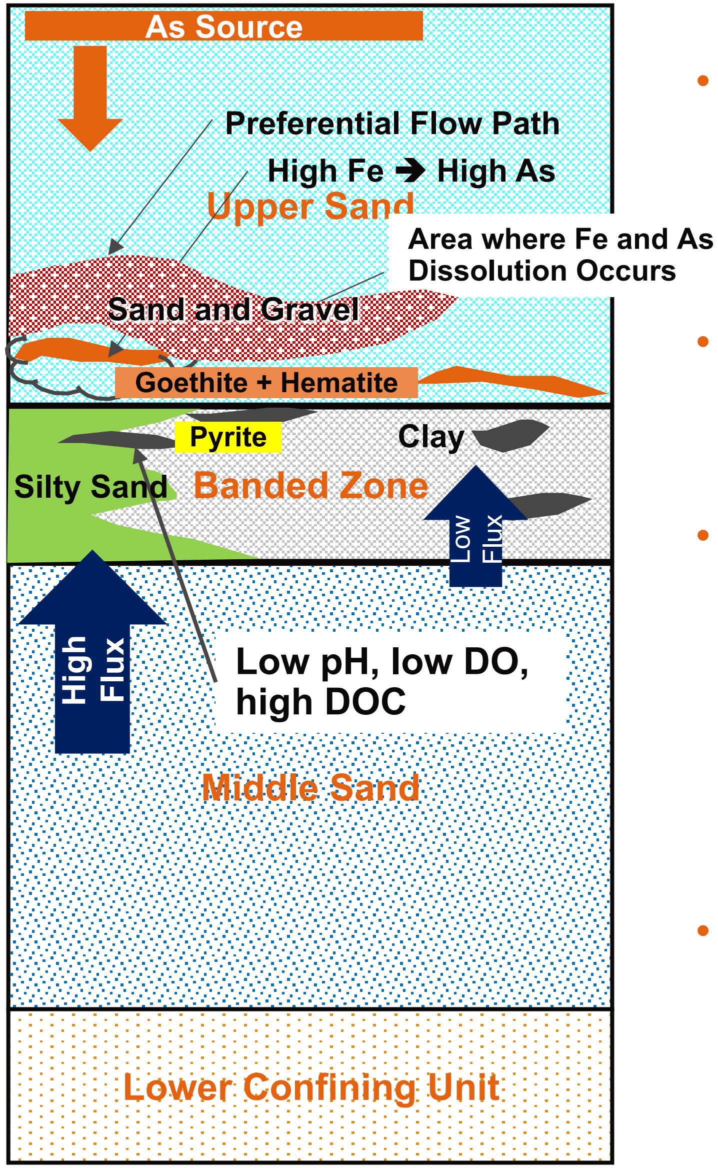
Vineland Chemical Company (VCC) Superfund Site

Vineland, Cumberland County, NJ

- Manufactured arsenic-based herbicides and fungicides (MSMA): 1950 - 1994
- Arsenic waste salts generated as byproduct: 1,100 tons waste per year.
- Multiple “Operable Units”:
  - Active water pump & treat system
  - Soil excavation.
- Air Sparge Pilot Test
  - Arsenic co-associated with iron
  - Pilot tested for residual arsenic source mass to Blackwater Branch



Vineland: Hydro/Geochemical Conceptual Model

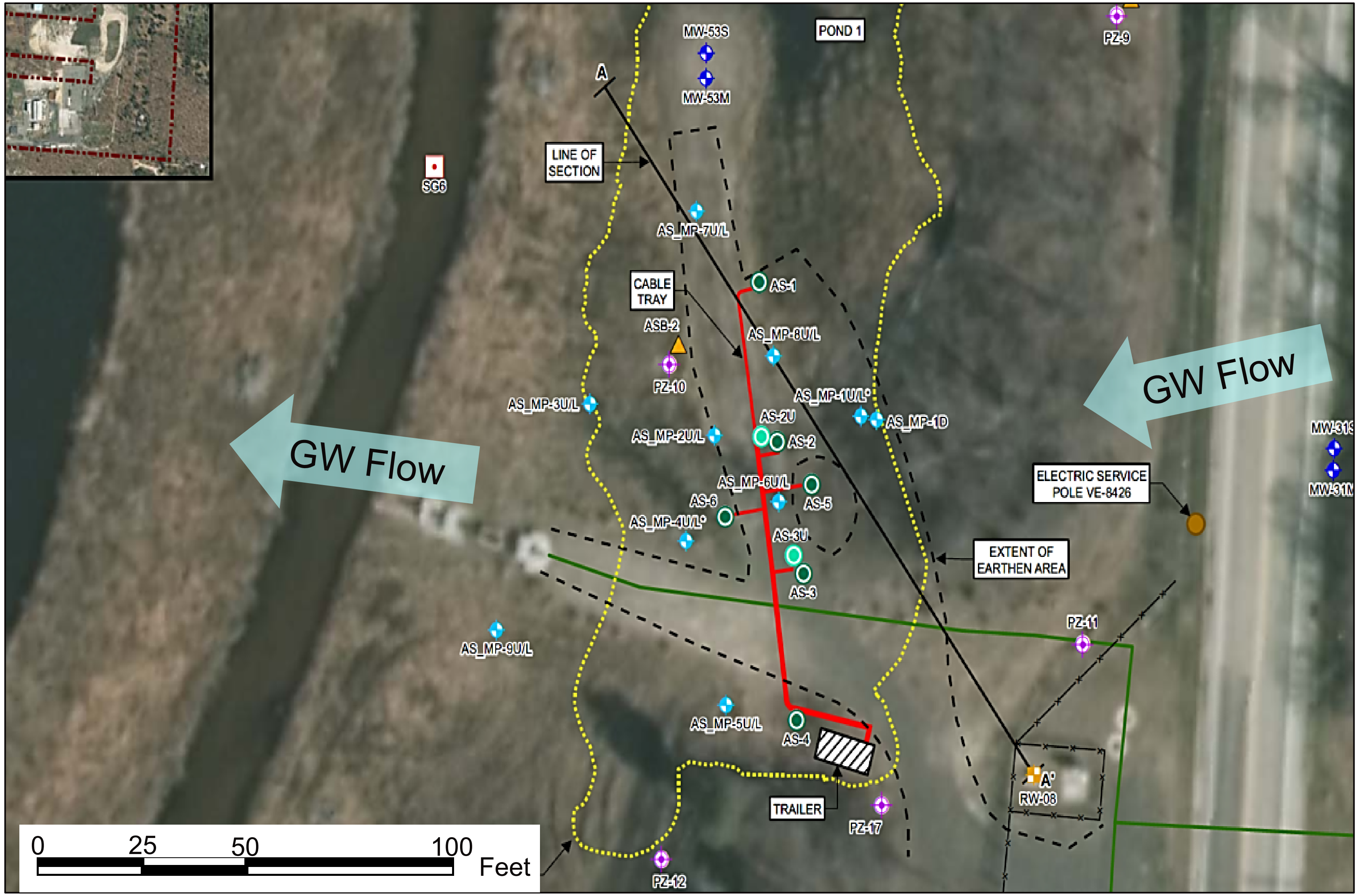


- **Upper Sand**
  - Variably high pH (> 9); sodium hydroxide in MSMA production
  - Sodium arsenite brine in vadose zone; density flow to Sand/BZ interface
  - Generally oxidizing
- **Banded Zone**
  - Tidal marsh sediment
  - Low pH, organic matter, pyrite present
- **Initial deposition of arsenic at upper sand/banded zone interface**
  - Upward hydraulic gradient through Banded Zone
  - Low DO/ORP, low pH, high DOC soils in BZ
  - Reduction, dissolution of ferric iron in BZ soils
  - Dissolved Fe and As transported to Upper Sand
  - Oxidation and precipitation of Fe co-precipitation of As
- **Active pump-and-treat**
  - Stronger upward hydraulic gradient, increased groundwater flux
  - High pH in soils expected to decrease over time through flushing

Vineland: Pilot Test System Construction

ARCADIS

- Installed in 2015, expanded in 2016, operated until March 2023.
- Upper and Lower AS intervals:
  - 2 Upper: 22-24 ft bgs
  - 6 Lower: 31-33 ft bgs, BZ interface
- 18 nested monitoring points
  - "U" (upper) wells: ~16-21 ft bgs
  - "L" (lower) wells: ~ 27-32 ft bgs
- Deep monitoring point:
  - AS_MP-1D (40-45 ft bgs)



AIR SPARGE BORING

AIR SPARGE INJECTION WELL AND XRF SAMPLE

SHALLOW AIR SPARGE INJECTION WELL AND XRF SAMPLE

AIR SPARGE MONITORING POINT (* = WITH XRF SAMPLE)

Vineland: Pilot Test

ARCADIS

- Interim progress published in 2019
- EPA/600/R-19/102

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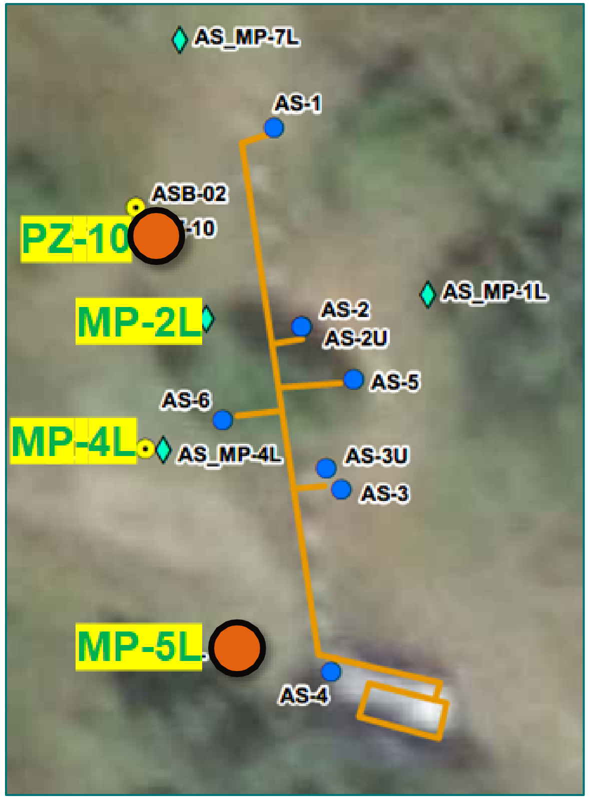
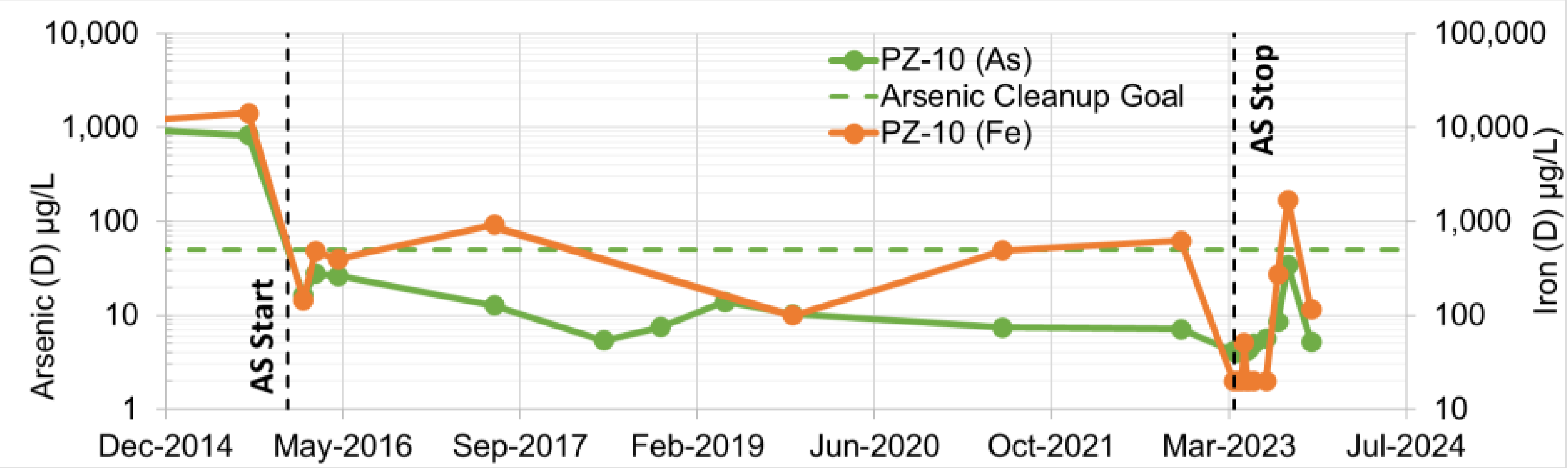
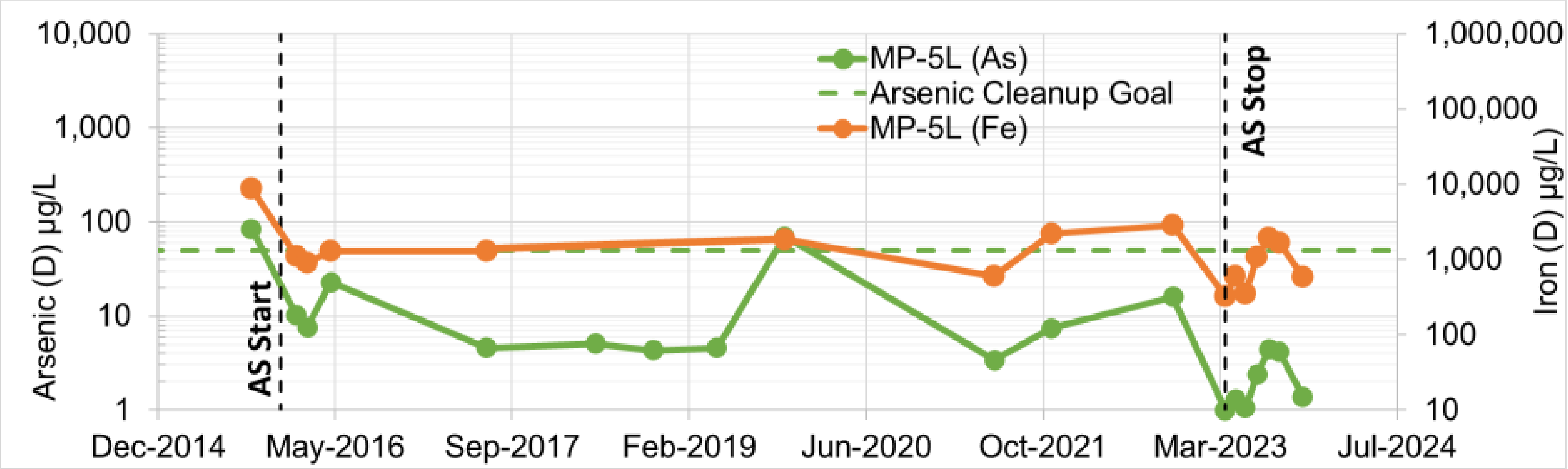
Vineland: Pilot Test Results



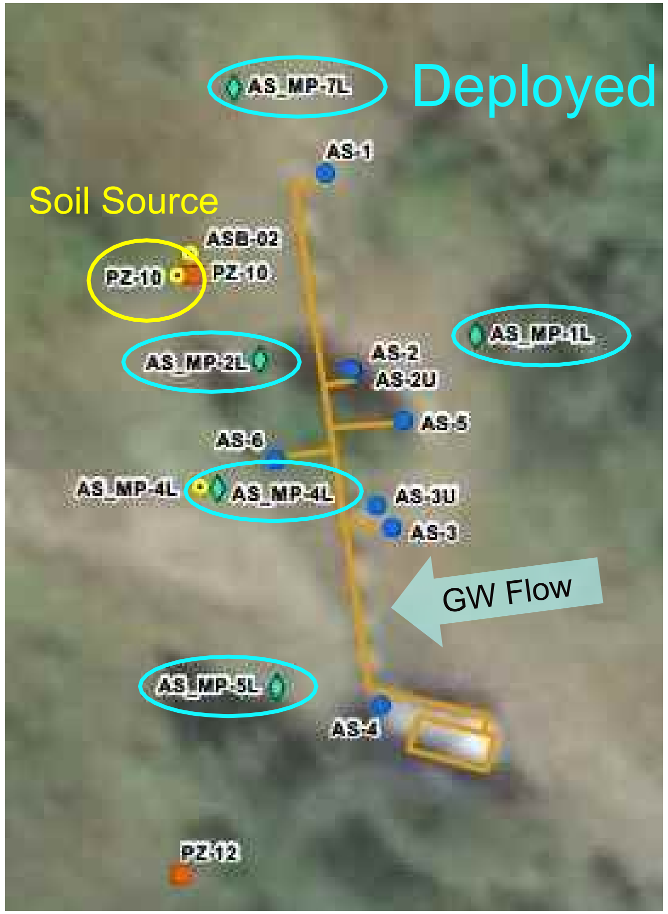




High effectiveness observed downgradient

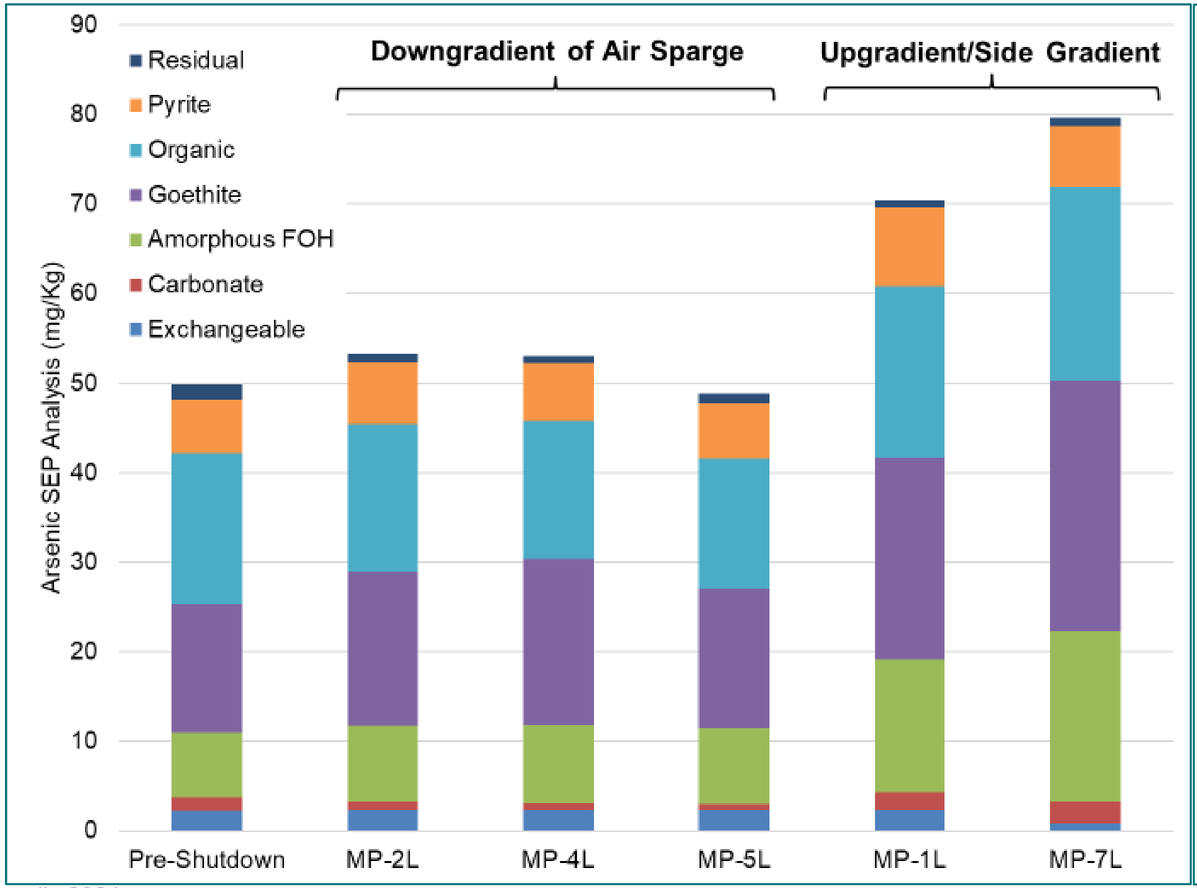
Vineland: Post-Pilot Soil Stability and Arsenic Uptake

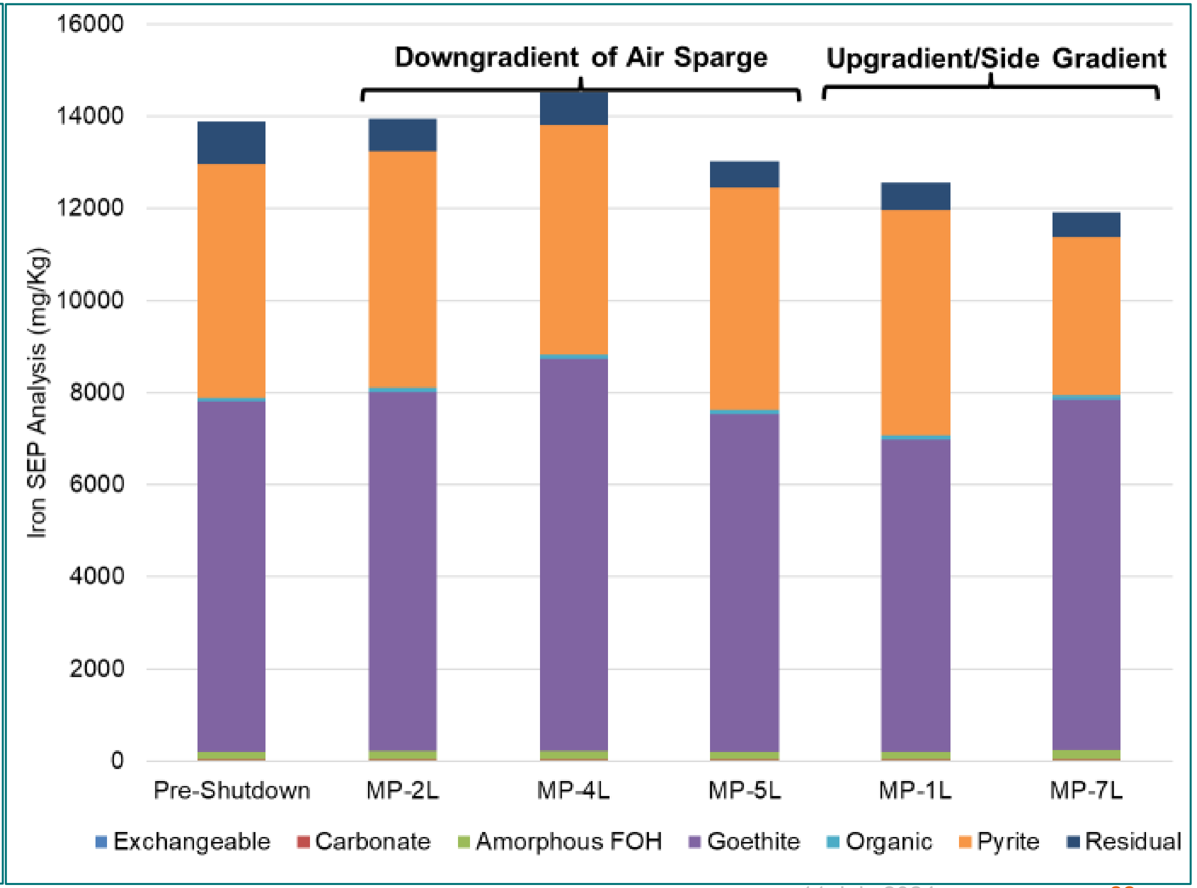
- Iron and arsenic in groundwater remained low despite decrease in DO and ORP following shutdown
- To evaluate iron/arsenic stability:
  - Soil from PZ-10 (successful MW, post-sparge) collected, placed in MinTrap™ cylinders with water-permeable mesh, and placed in upgradient and downgradient wells for 5 months
  - Removed and analyzed by Sequential Selective Extraction (SSE or SEP)



Vineland: Post-Pilot Soil Stability and Arsenic Uptake

- Little to no change in iron concentrations when placed upgradient (no Fe re-reduction)
- Continued uptake of arsenic, primarily in amorphous and crystalline iron oxides.





Summary

- Iron + Oxidant approach using air sparge: Effective means of precipitating Fe(II) in groundwater, sequestering arsenic
- Site-specific hydrogeological and geochemical factors must be considered
- Devens SHL:
  - Variable Fe : As ratio across the Site
  - Oxygen distribution at depth more difficult
- Vineland:
  - Good arsenic treatment downgradient
  - Long term stability looks promising

Thank You!

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