

# Optimization of a Combined Active and Passive In Situ Stabilization Approach for High Concentration Metals in Groundwater

**Lucas Hellerich PhD, PE, LEP**

**Woodard & Curran**

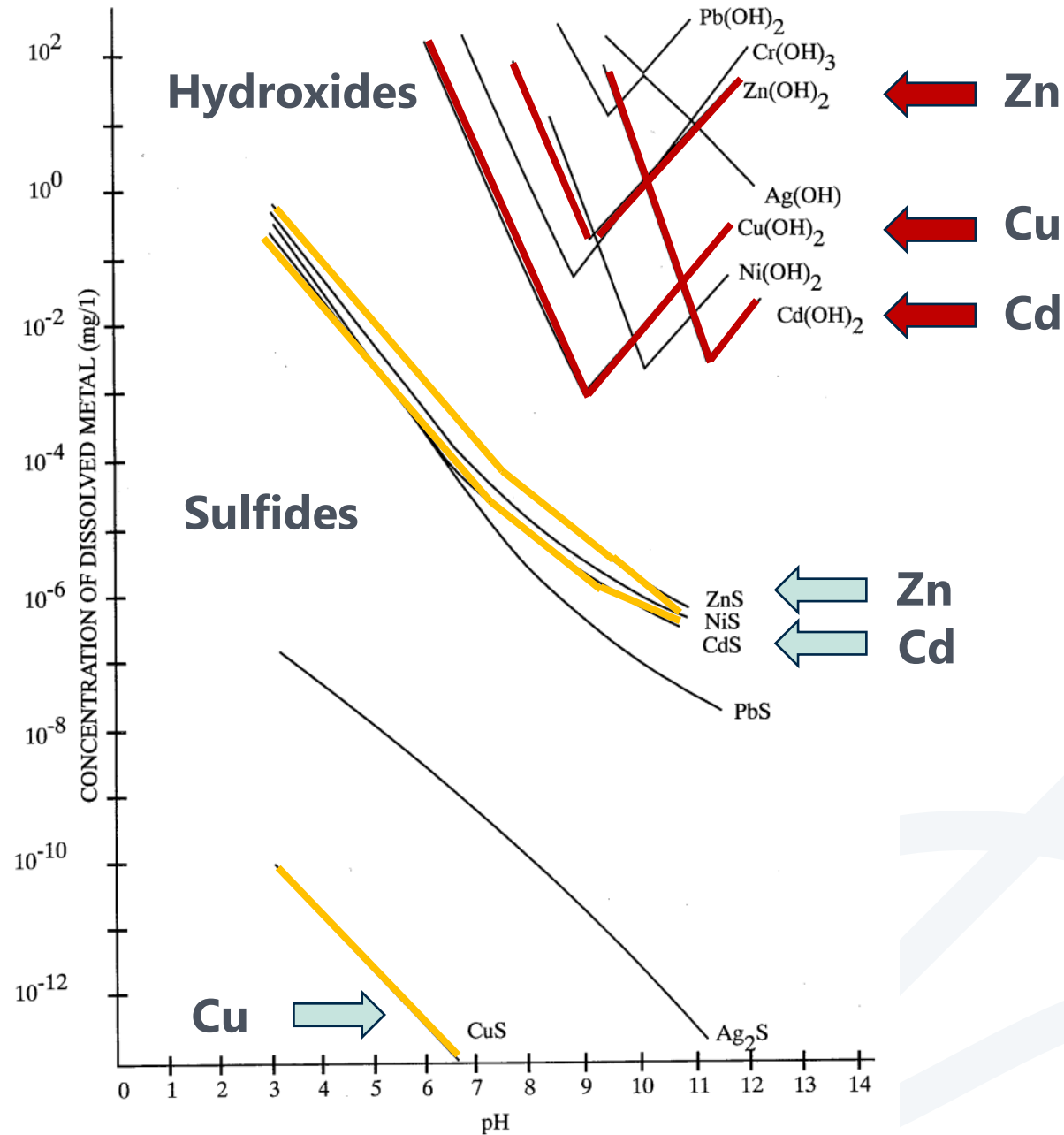
**June 6, 2024**

**2024 Battelle Chlorinated Conference**



Forming low solubility metal precipitates can be an effective remediation strategy

Decreasing solubility



Source: EPA/600/2-82-011C, 1981

# Agenda



Conceptual site model

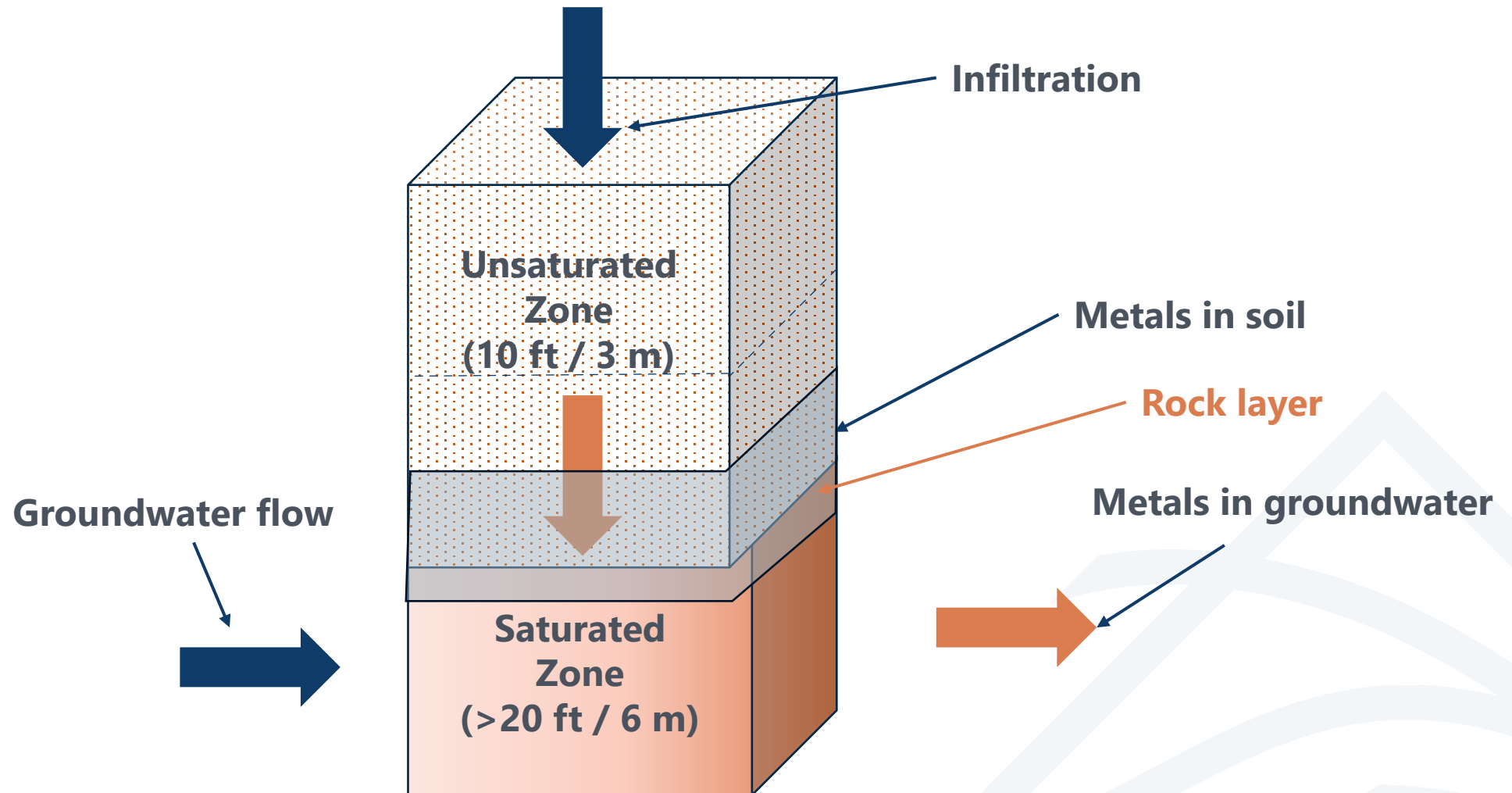


Technology evaluation and selection

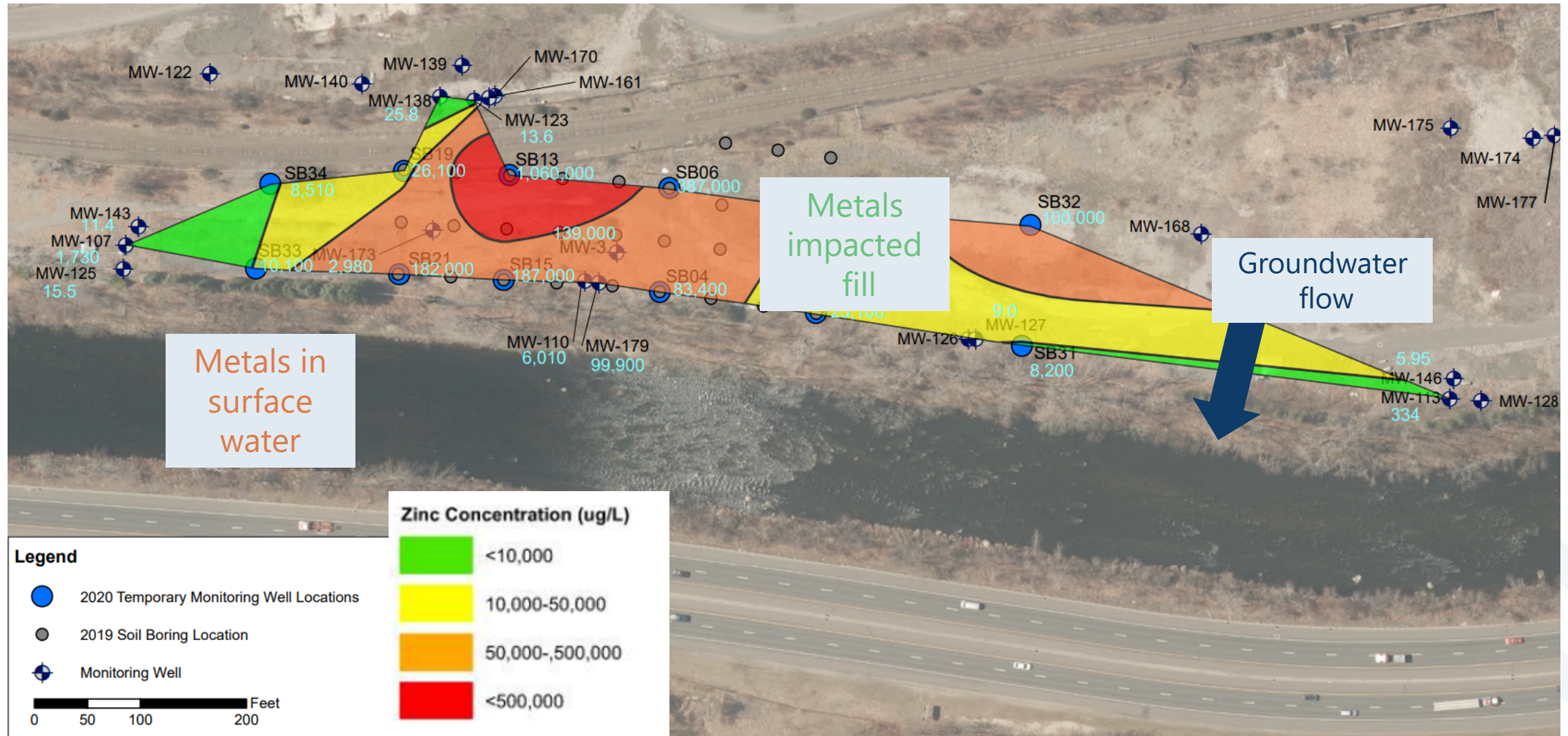


Pilot test implementation and results

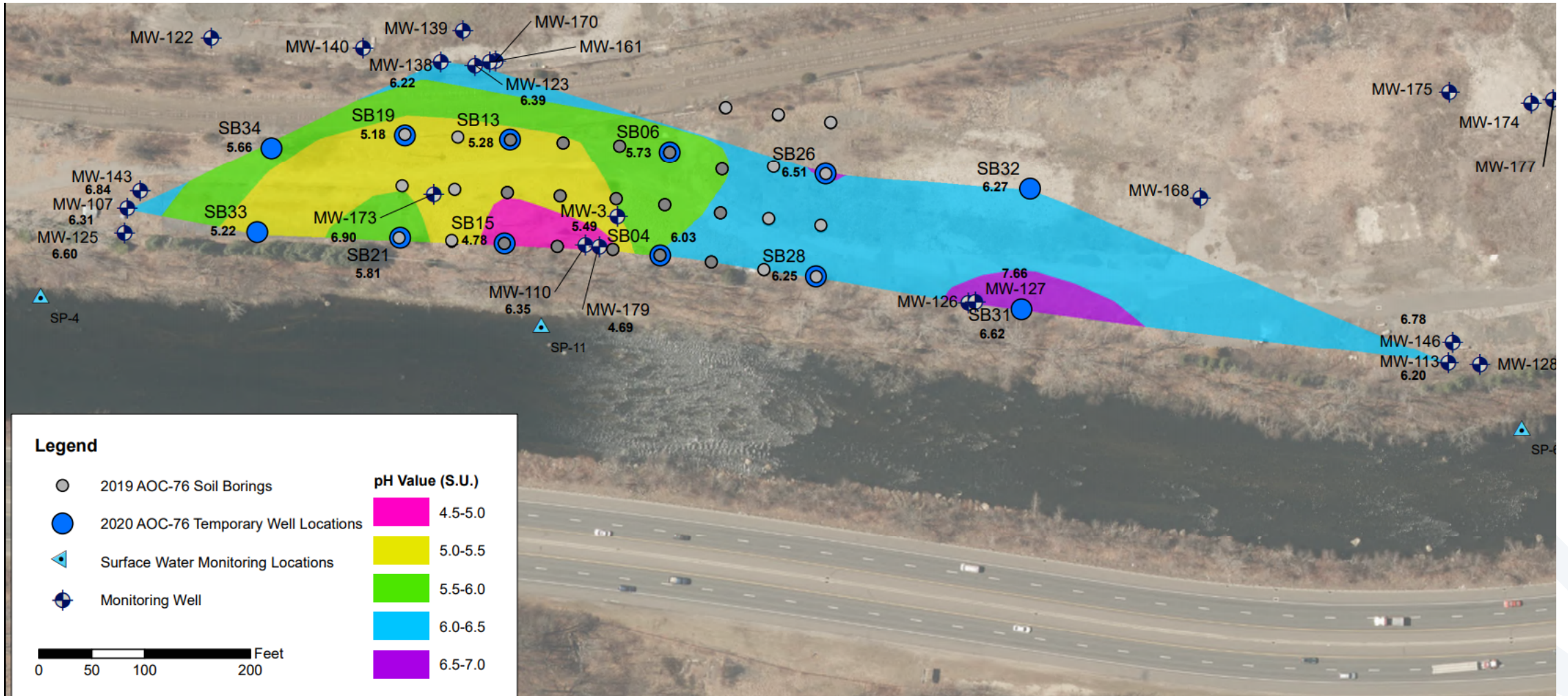
# CSM for metals leaching and migration



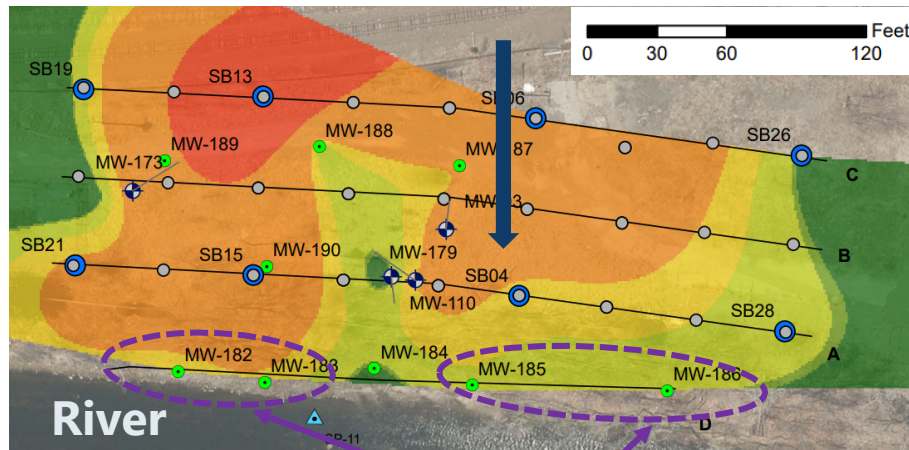
# Metals solubilize in groundwater and discharge into surface water



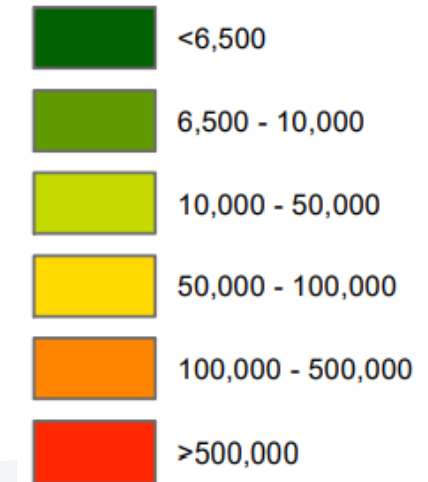
# Acidic pH increases solubility of metals



# Metals concentrations exceed criteria at the river by approximately 10X - 15X



## Zinc Concentration (ug/L)



**Surface Water Protection  
Criteria (SWPC) exceedances**

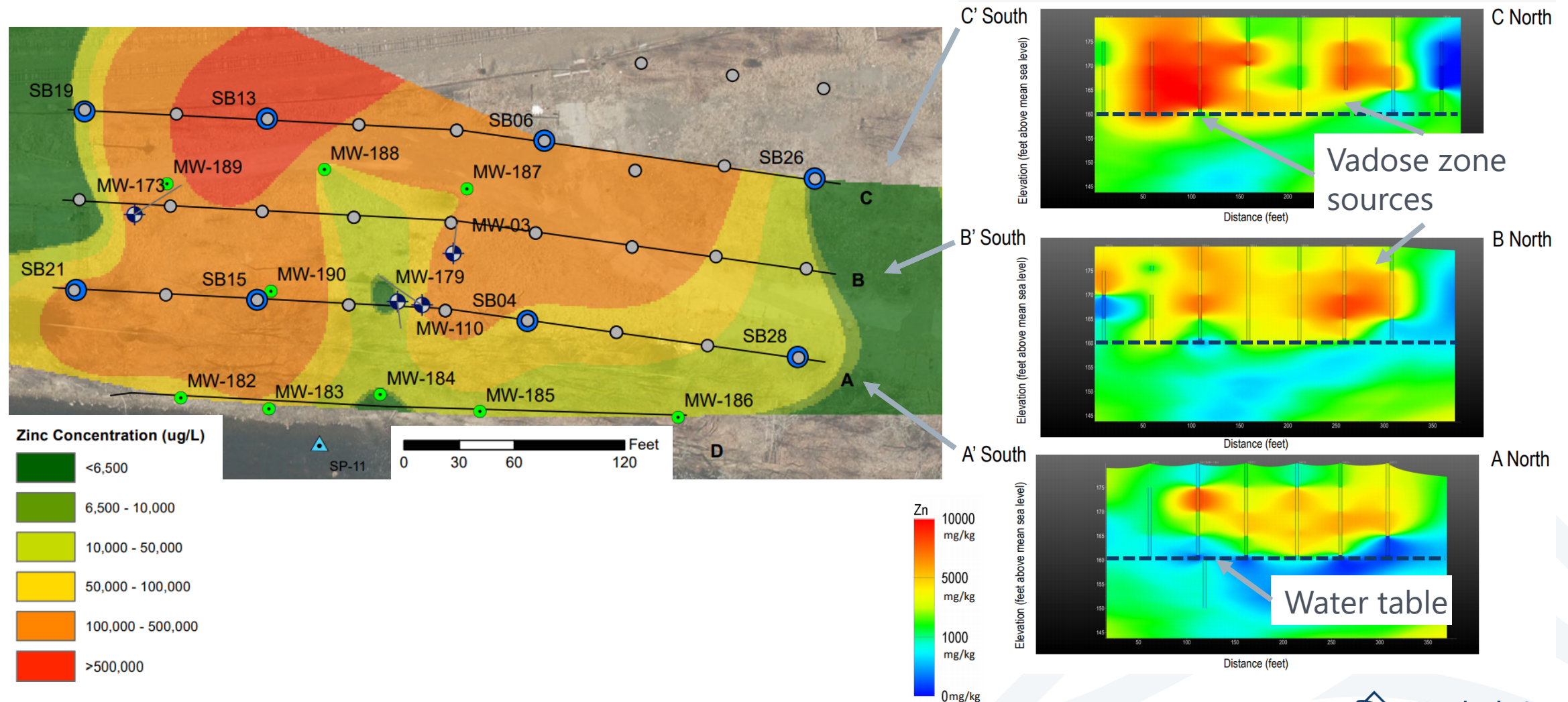
## SWPC

**Cd = 12.5 ug/L**

**Cu = 480 ug/L**

**Zn = 6,500 ug/L**

# HRSC, 3-D modeling and data visualization used to identify vadose and saturated zone source areas



# Site conditions constrain remediation options



**Near river**



**Plume area**



**Source area**

# Agenda



Conceptual site model



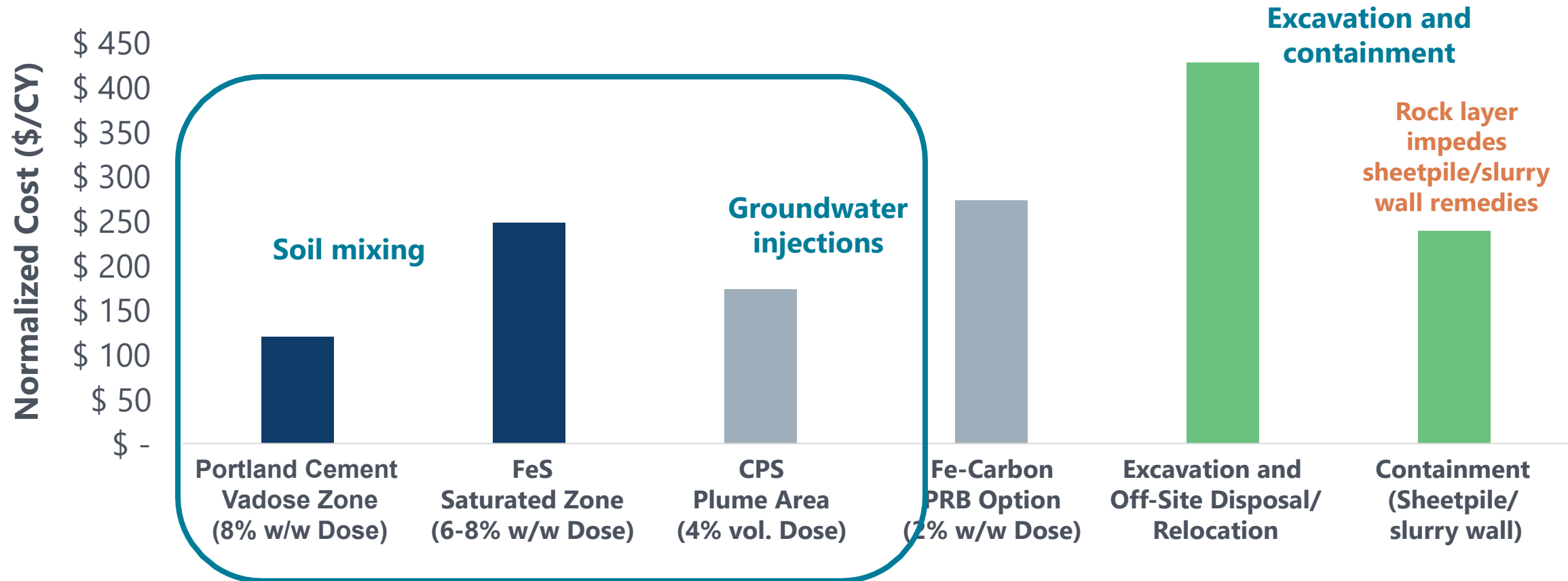
Technology evaluation and selection



Pilot test implementation and results

# Site-specific in situ remediation costs are significantly less than excavation and off-site disposal

## Normalized Costs for Remediation Technologies



# Treatability testing for the saturated and unsaturated zones showed that calcium polysulfide (CPS), iron sulfide, and Portland Cement performed best

## Saturated zone

| Saturated 1 (SB-13)                   | Dose (% Weight) | Cd | Cu | Zn |
|---------------------------------------|-----------------|----|----|----|
| Portland Cement                       | 5               |    |    |    |
| Portland Cement (3%) + Metafix 1 (2%) | 5               |    |    |    |
| Metafix 1                             | 3               |    |    |    |
| MetaFix 1 (3%) + FerroBlack-H (1%)    | 4               |    |    |    |
| Metafix 1                             | 7               |    |    |    |
| Metafix 1 Modified                    | 5               |    |    |    |
| FerroBlack-H                          | 3               |    |    |    |
| FerroBlack-H                          | 8               |    |    |    |
| Provect-IRM (3%) + FerroBlack-H (1%)  | 4               |    |    |    |
| Calcium polysulfide                   | 8               |    |    |    |
| Calcium polysulfide                   | 12              |    |    |    |

## Unsaturated (vadose) zone

| Vadose 2 (SB-15)                      | Dose (% Weight) | Cd | Cu | Zn | SPLP Cd | SPLP Cu | SPLP Zn |
|---------------------------------------|-----------------|----|----|----|---------|---------|---------|
| Portland Cement                       | 5               |    |    |    |         |         |         |
| Portland Cement (5%) + Metafix 1 (2%) | 7               |    |    |    |         |         |         |
| Metafix 1                             | 1               |    |    |    |         |         |         |
| Metafix 1                             | 3               |    |    |    |         |         |         |
| Metafix 1 Modified                    | 3               |    |    |    |         |         |         |
| Metafix 1 (3%) + FerroBlack-H (1%)    | 4               |    |    |    |         |         |         |
| FerroBlack-H                          | 3               |    |    |    |         |         |         |
| FerroBlack-H                          | 8               |    |    |    |         |         |         |
| Provect-IRM (3%) + FerroBlack-H (1%)  | 4               |    |    |    |         |         |         |

> 99 %  
concentration  
reduction

< 99% and > 80%  
concentration  
reduction

< 80%  
concentration  
reduction

# Agenda



Conceptual site model



Technology evaluation and selection



Pilot test implementation and results

# Remedy Steps & Metrics

**Complete the pilot study construction**



**Collect performance monitoring data**



**Design and construct the full-scale remediation**

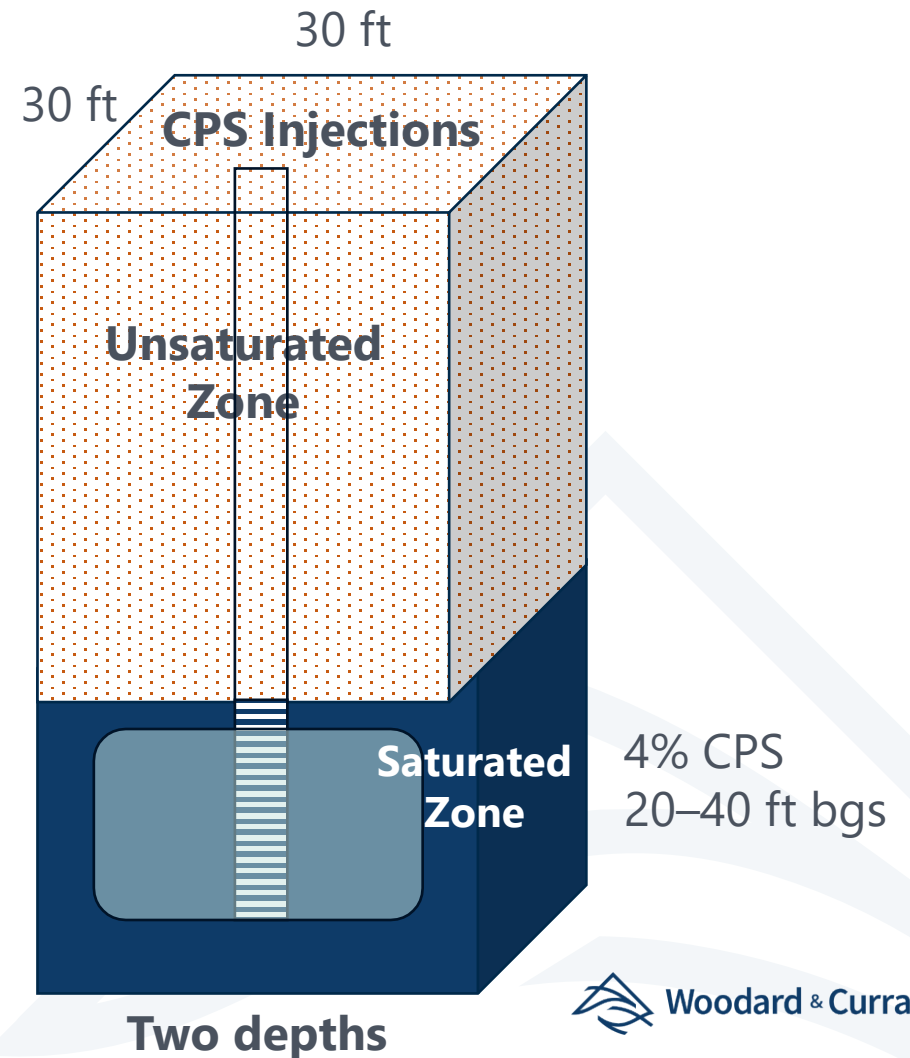
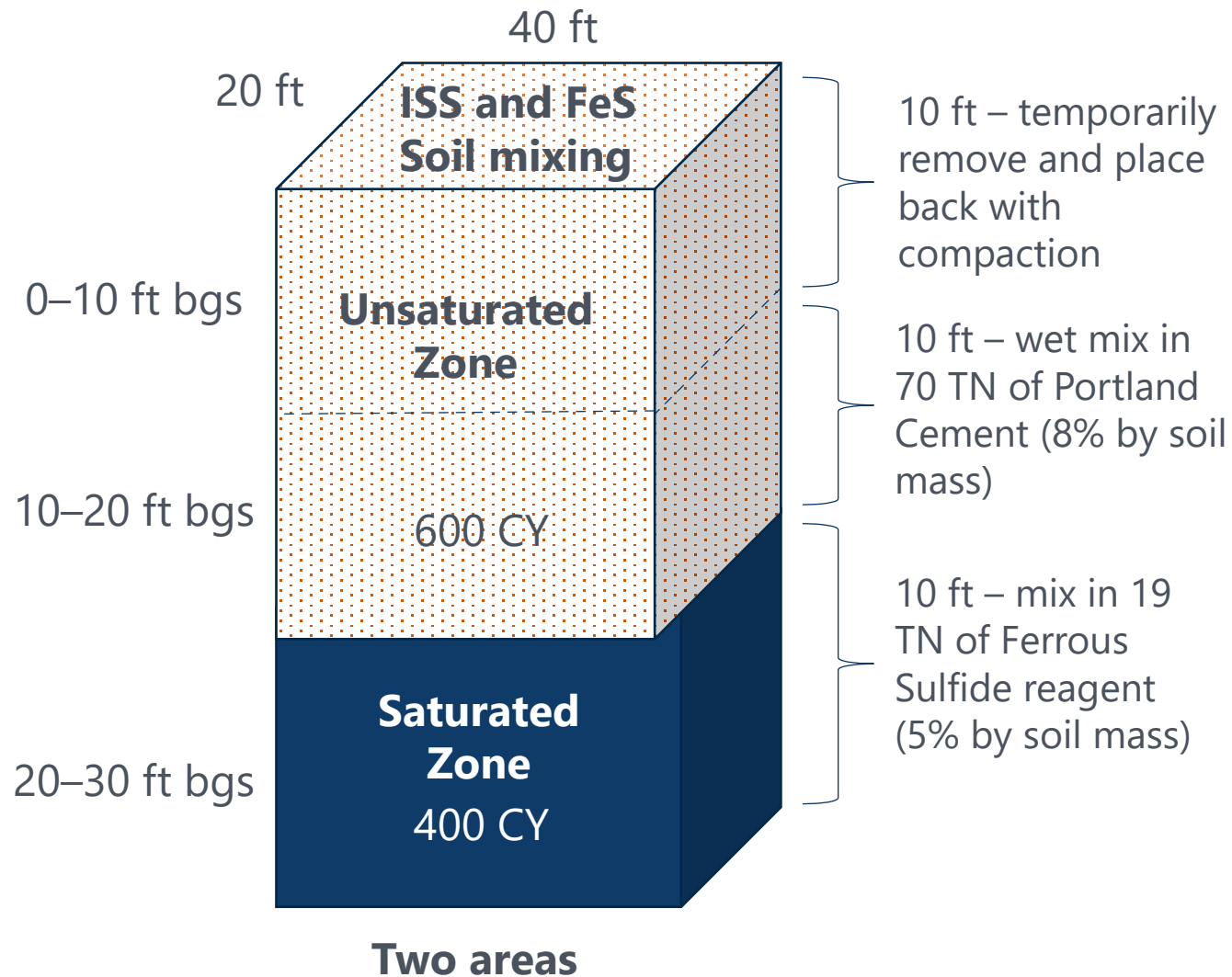


**Geotechnical metrics**  
UCS = 50 - 100 psi  
 $K < 10^{-6}$  cm/s

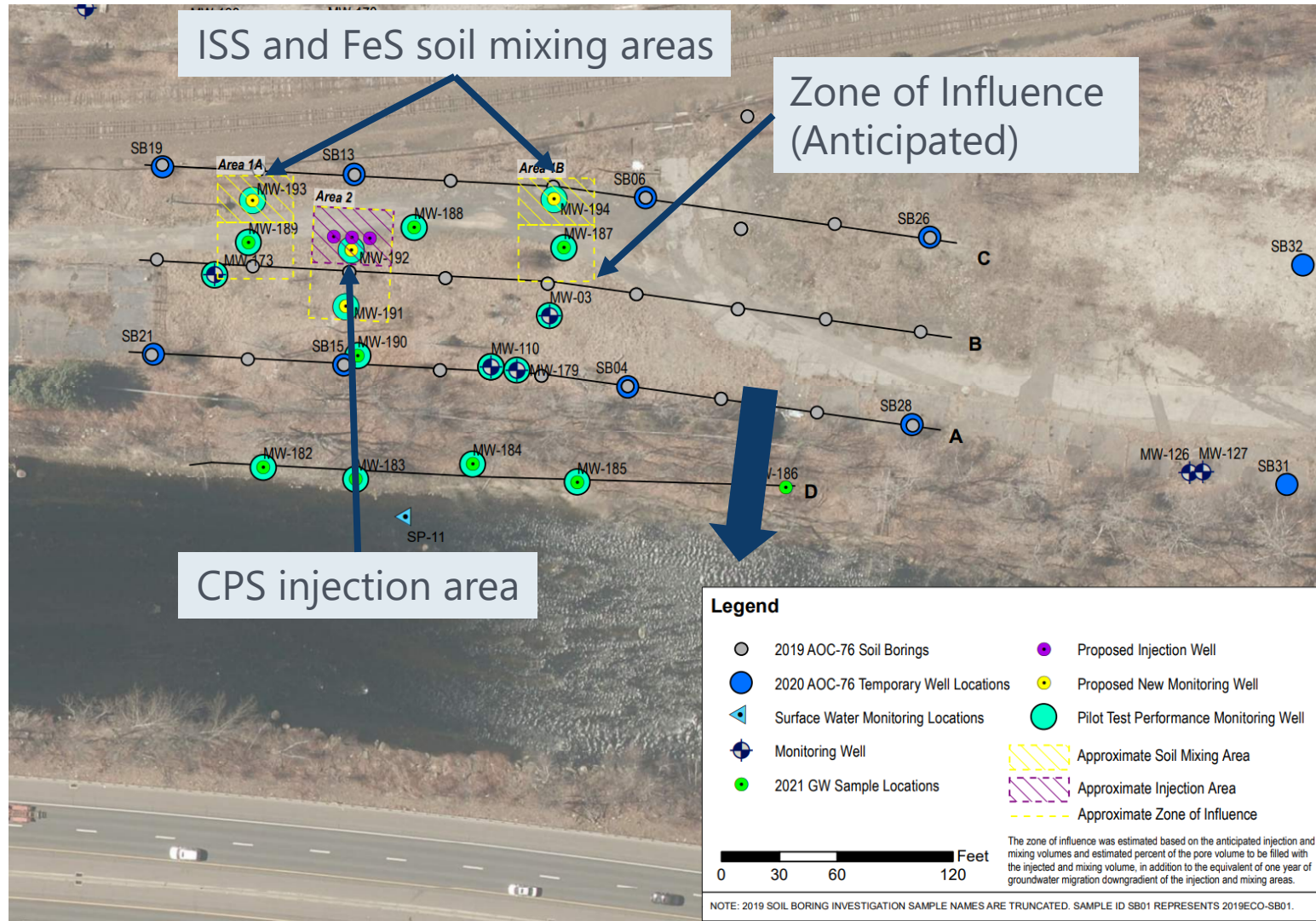


**Groundwater metals concentrations decrease by 90% and pH increases to 6 – 8.5**

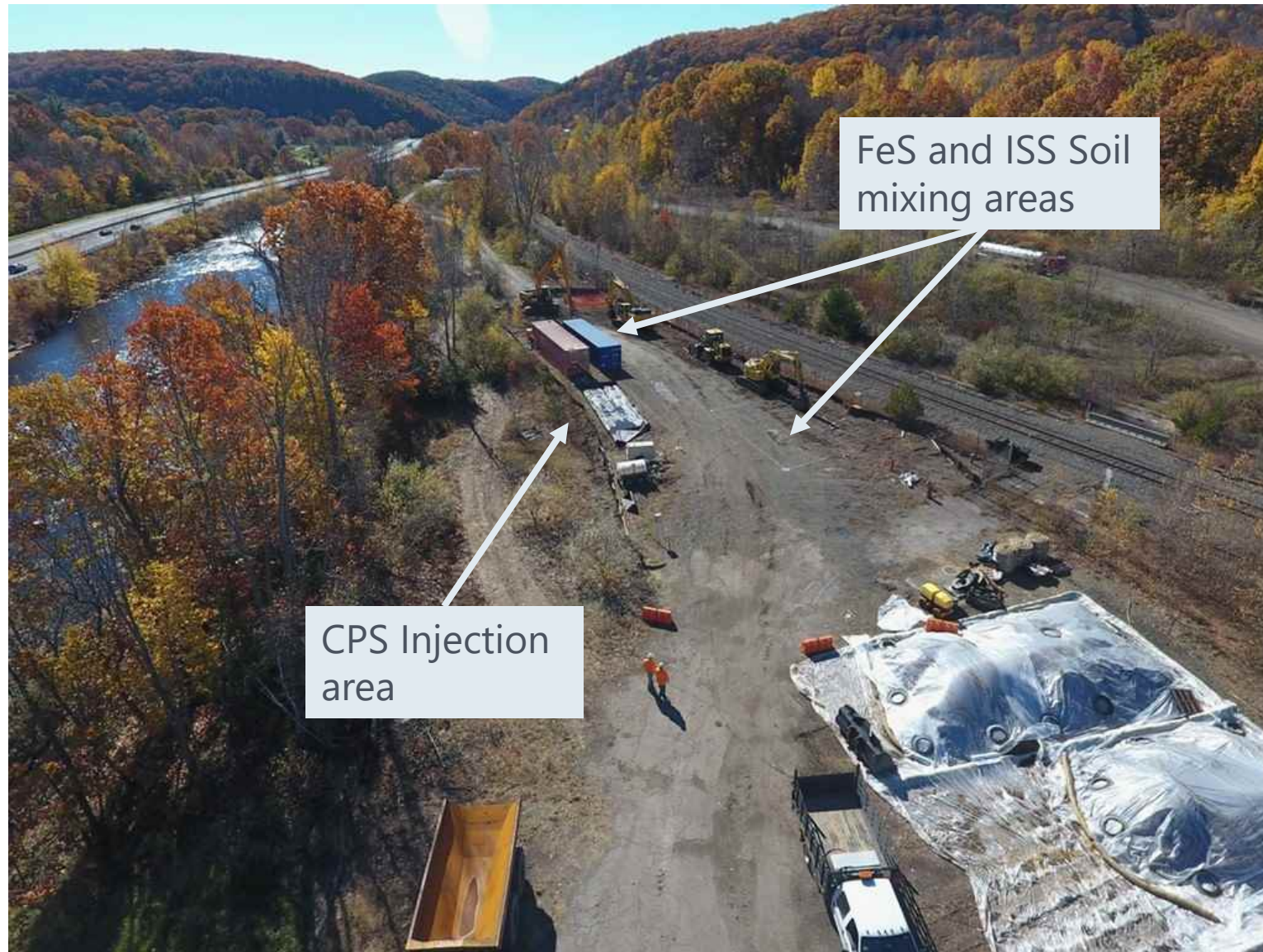
# Field Pilot Test: In-Situ Solidification & Stabilization (ISS) of Soil and Geochemical Precipitation in Groundwater



# Pilot Testing Layout

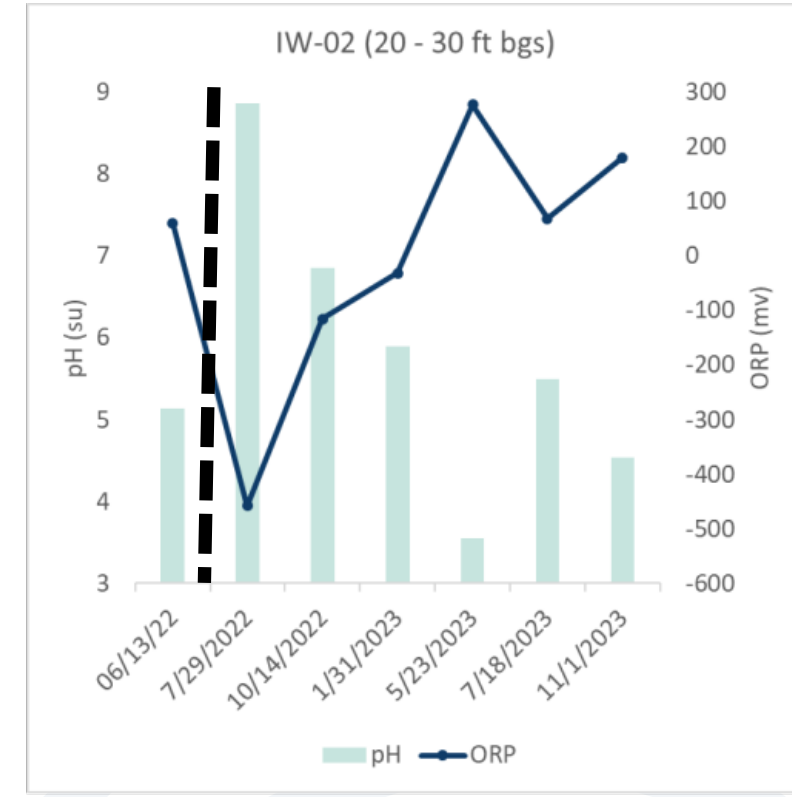
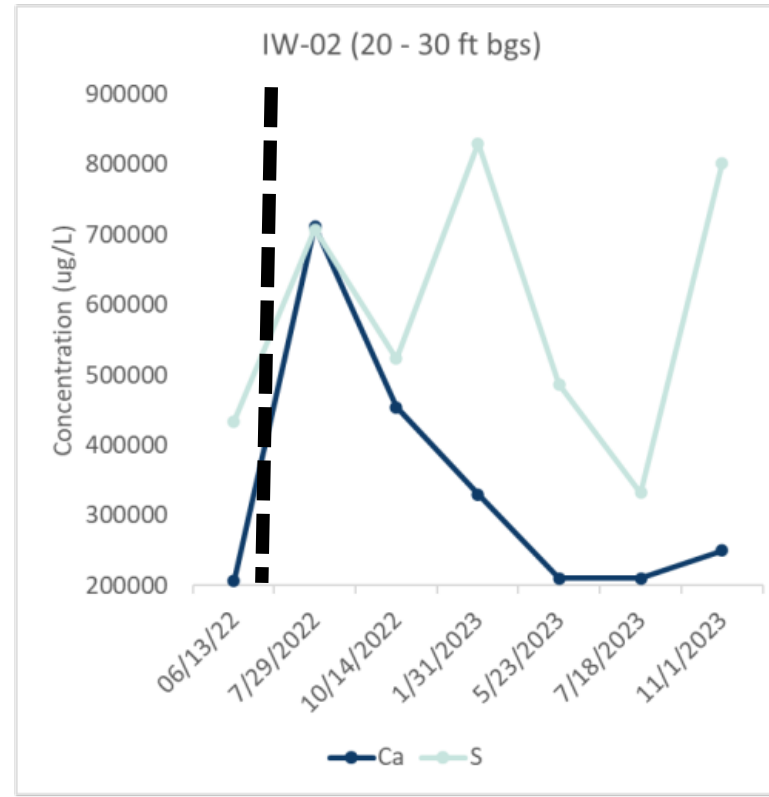
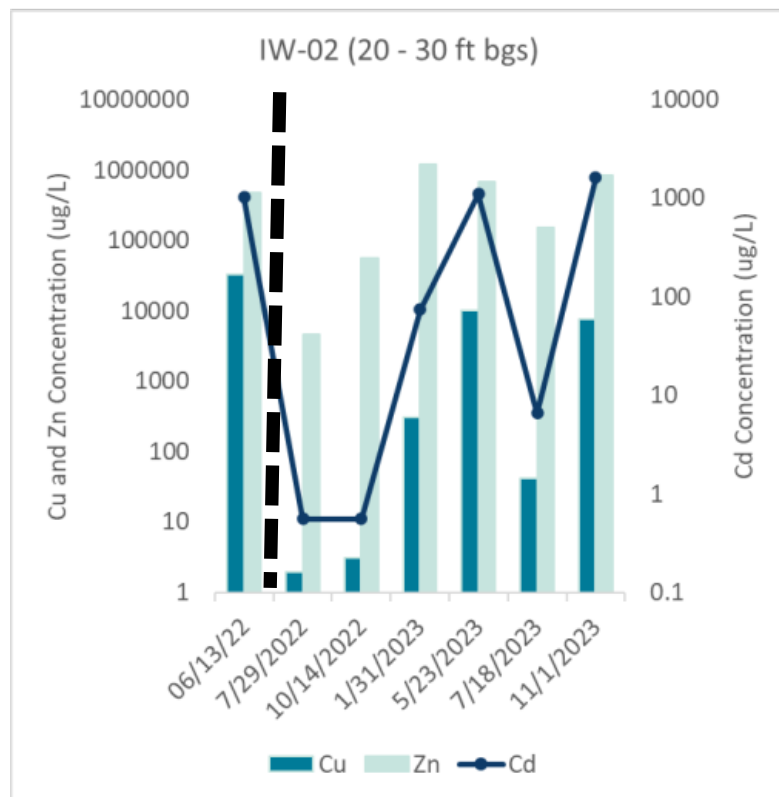
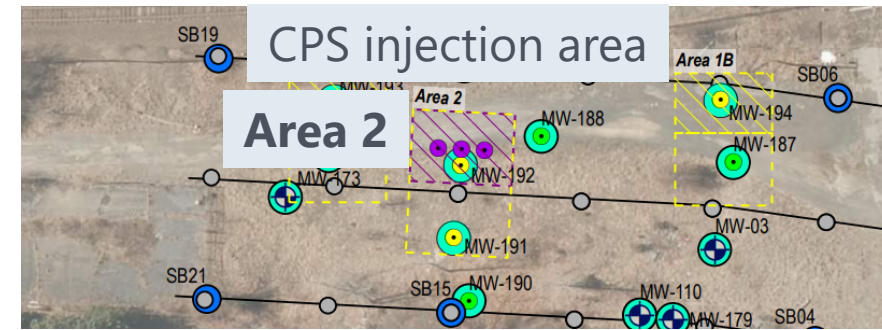


# Pilot Test Remediation Area



# Calcium polysulfide results (20–30 ft bgs)

## Area 2

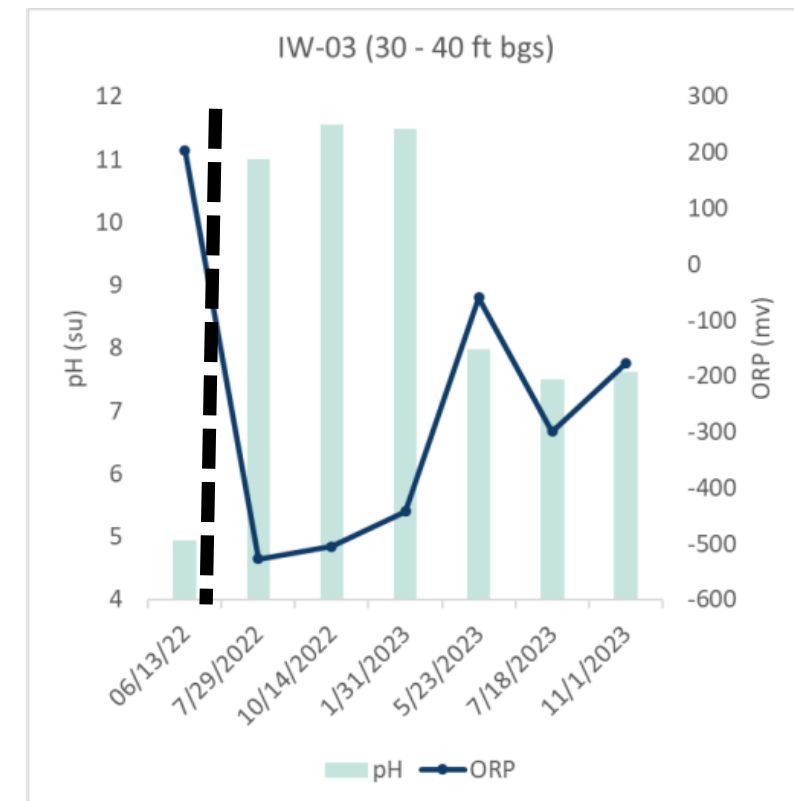
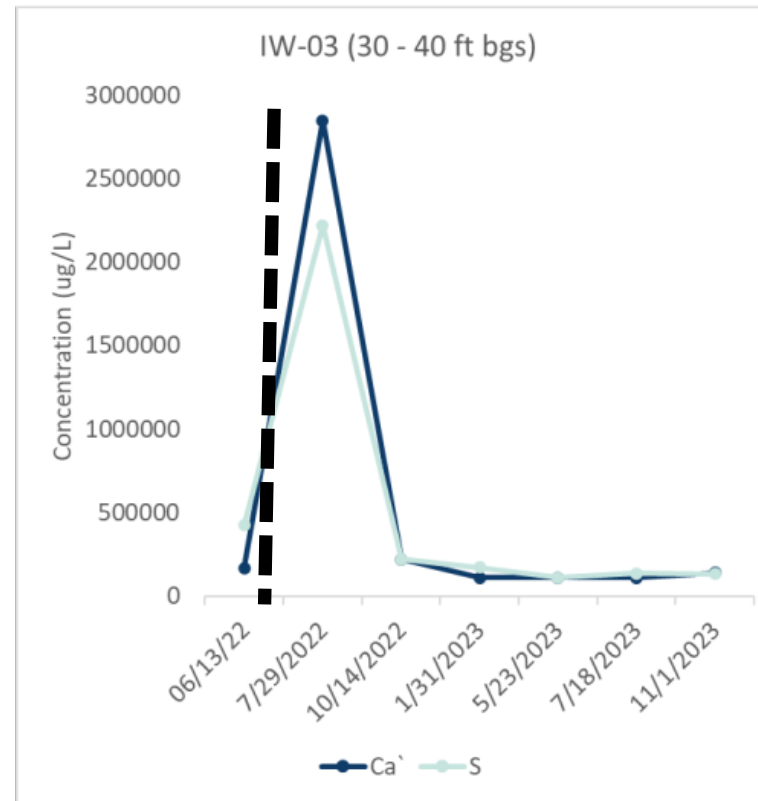
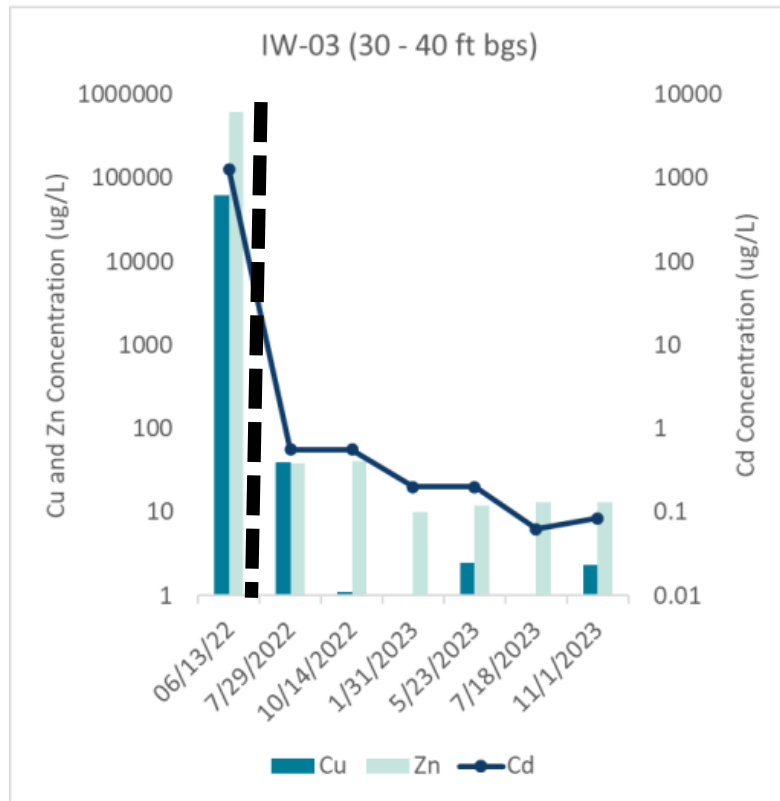
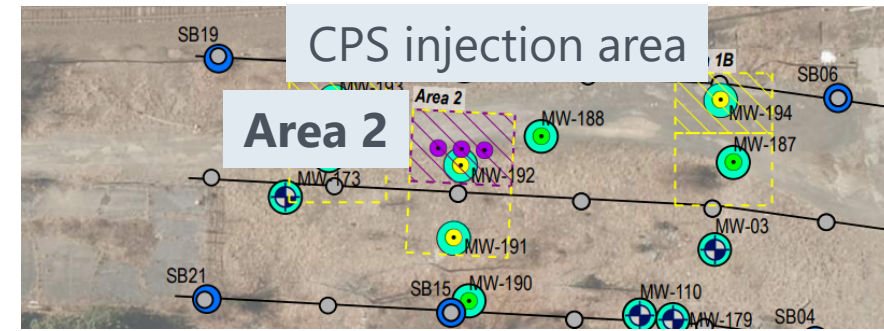


Injection event

CPS provided about six months of treatment in shallow groundwater

# Calcium polysulfide results (30–40 ft bgs)

## Area 2

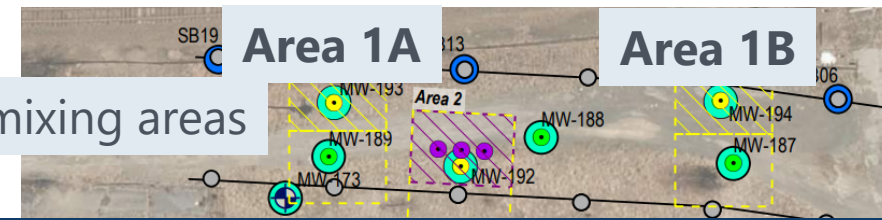


Injection event

CPS provided at least one year of  
treatment in shallow groundwater

# FeS and ISS soil mixing results (18–28 ft bgs)

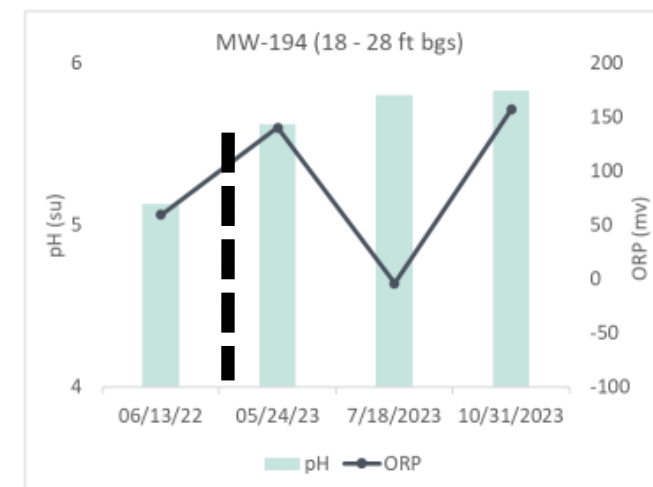
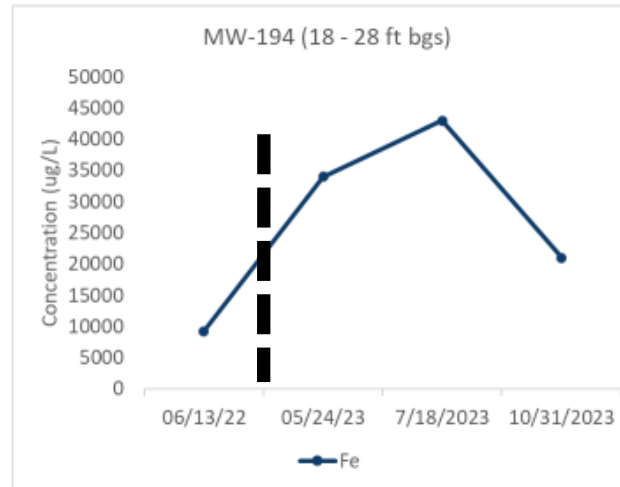
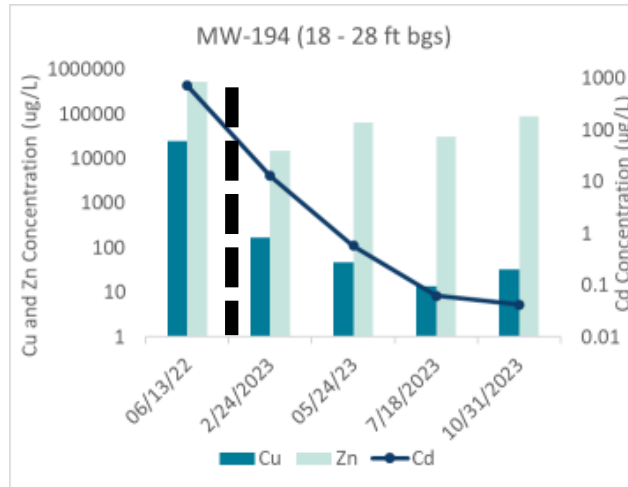
ISS soil mixing areas



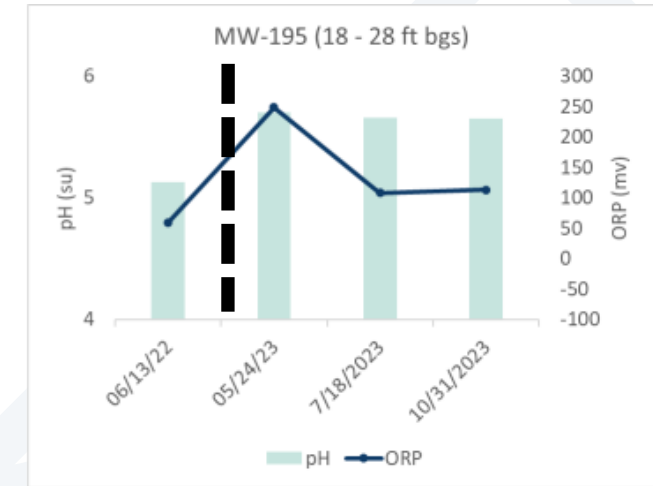
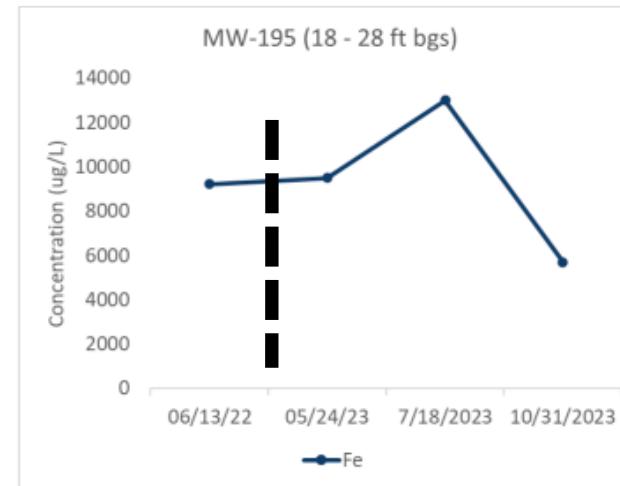
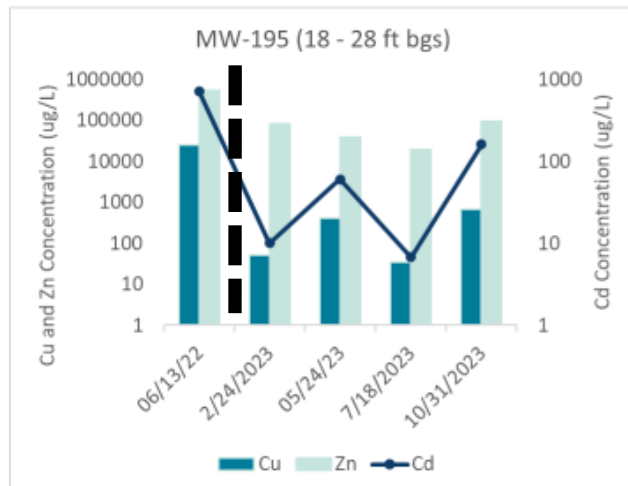
Fe-S and ISS provided at least 1.5 years (and counting) of OOM treatment within the source area

Area 1A

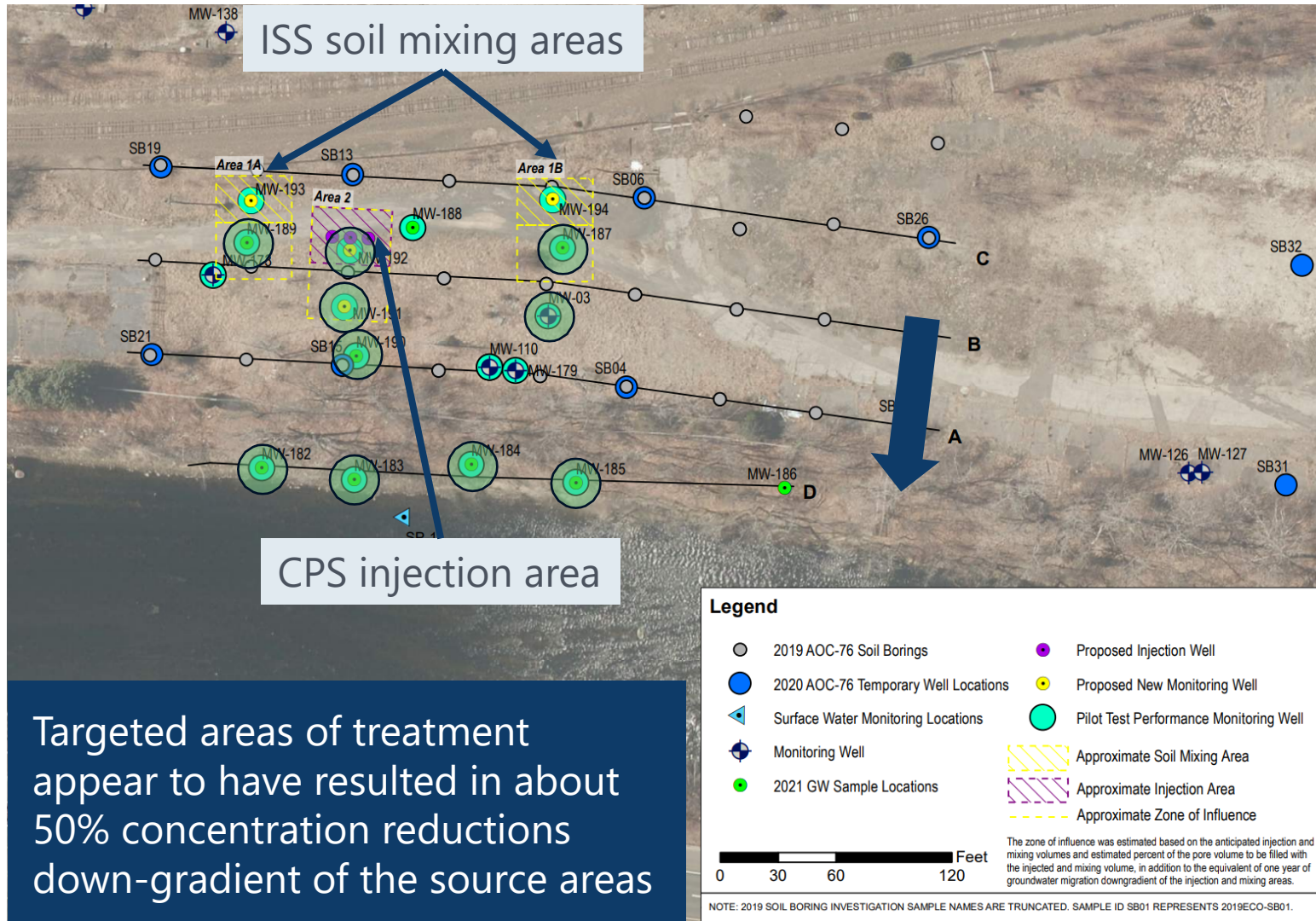
Soil mixing



Area 1B



# Zone of Influence of Treatment Areas



Targeted areas of treatment appear to have resulted in about 50% concentration reductions down-gradient of the source areas



Reduced concentrations of Cd, Cu, and Zn

Moderation of pH and/or reduction of ORP not observed outside of treatment areas

# Lessons Learned: Full-Scale Design Considerations

- ▶ ISS formulation (8% w/w cement; 8% w/w FeS) in Area 1A achieved treatment goals
  - Groundwater Cd, Cu, and Zn concentrations substantially reduced
  - UCS > 50 psi
  - $K < 10^{-6}$  cm/s
- ▶ Extensive rock layer impeded soil mixing—larger excavation cells will improve ability to mix within rock layer
- ▶ Further focusing of soil mixing at water table interface and performing in larger cells
  - Highest flux zones
  - Where highest concentrations intersect water table
- ▶ Incorporate permeability reduction via grouting within the rock layer

# Full-scale considerations for the combined full-scale remedy

- ▶ CPS injection rates of 2–4 gpm per well (10 gpm for three wells) achieved
- ▶ Current CPS dose (4% w/w) is adequate for 30–40 ft bgs
- ▶ Higher CPS dose is required for 20–30 ft bgs (higher metals concentrations)
- ▶ Adaptively injecting CPS outside of source areas
  - Flexible application
  - Cost effective delivery of reductant
- ▶ Incorporation of a low permeability liner to further reduce costs
  - Can cost-effectively address pollutant mobility criteria exceedances and leachable metals in vadose zone
  - Can readily be integrated into development

# Q&A

Thank you!

**Lucas Hellerich**

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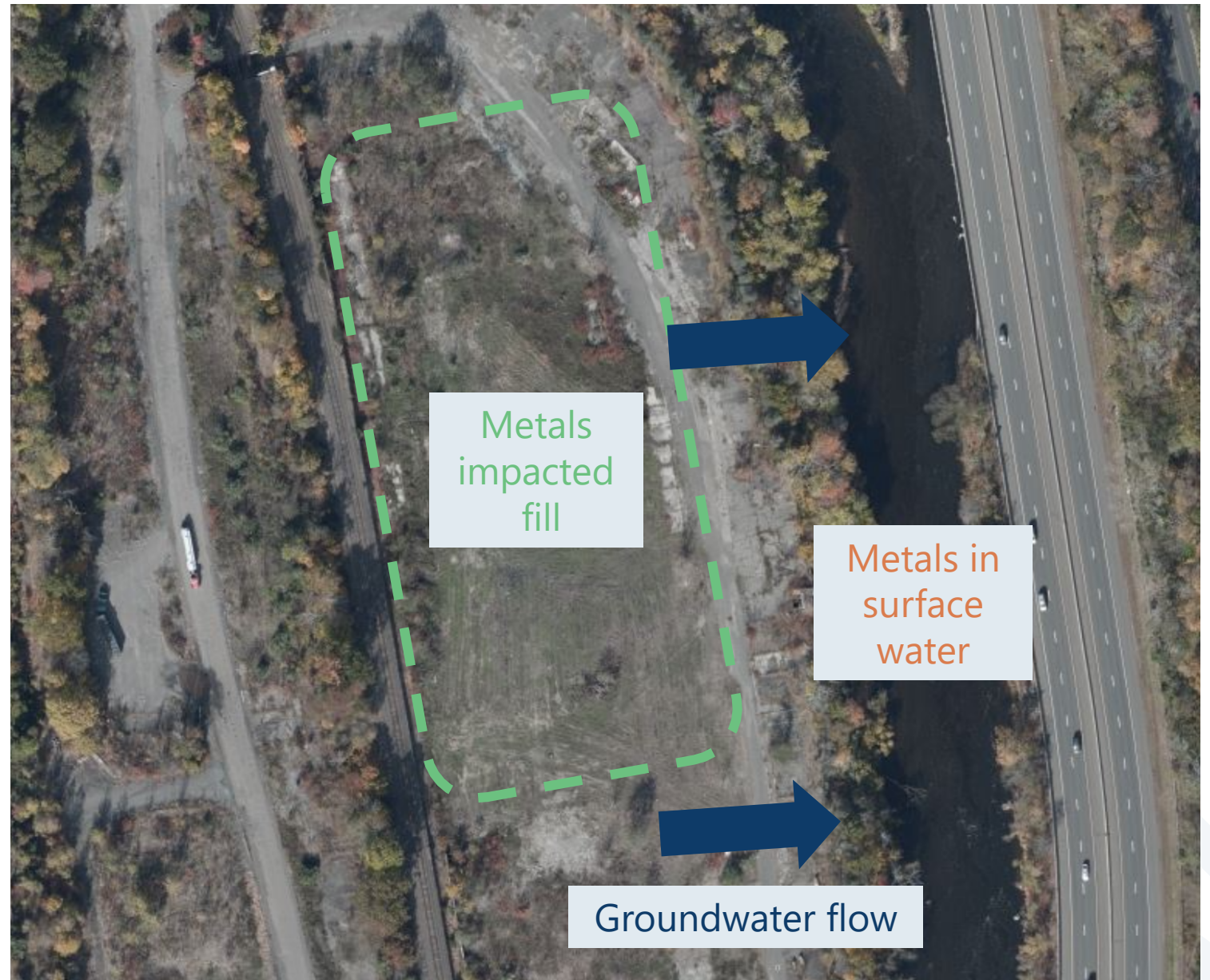
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# Co-Authors

- ▶ Ramin Ansari, Lanxess, USA
- ▶ Nick Hastings, PG, LEP, Woodard & Curran
- ▶ Samantha Olney, PG, Woodard & Curran
- ▶ Trevor King, PE, Woodard & Curran
- ▶ Dan Brockmeyer, LEP, Woodard & Curran



- ▶ Cadmium, copper, and zinc in groundwater are discharging to surface water above criteria

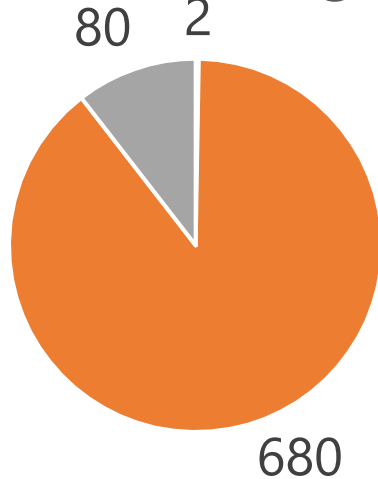


Extensive sub-grade rock layer is present at the base of the vadose zone source materials

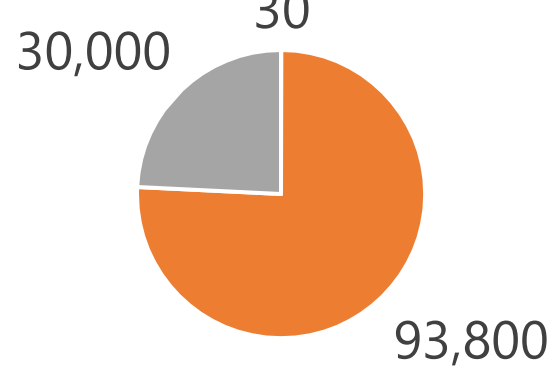


# Majority of the metals mass is in the vadose zone and at the groundwater "smear" zone

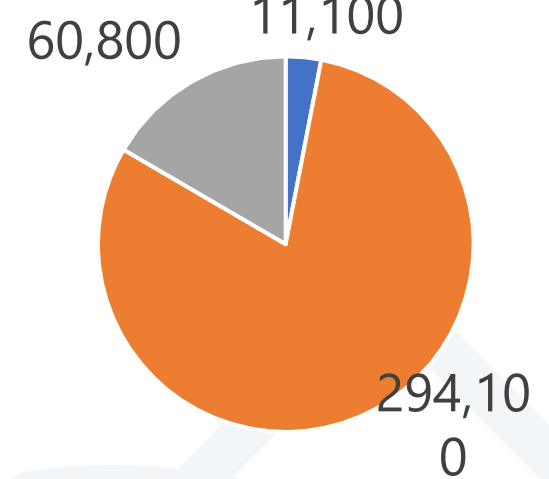
**Cadmium (kg)**



**Copper (kg)**



**Zinc (kg)**



- Groundwater
- Vadose Zone Soil
- Saturated Zone Soil

# Multi-phase treatability study was conducted

## Site Media

- Groundwater
- Unsaturated (vadose) zone soil
- Saturated zone soil

## Unsaturated Zone

- Soil + "rainwater"
- Reduction of concentrations and leachability from soil
- Reagents (different doses)
- Portland cement
- Ferrous iron

## Saturated Zone

- Soil + groundwater
- Concentration reduction
- Reagents (different doses)
  - Portland cement
  - Ferrous iron
  - Calcium polysulfide



# Pilot Test Remediation Area



# Pilot Test Remediation Soil Mixing



Rocks ranging  
in size from  
approximately  
0.5 ft to 5 ft

# Soil Mixing – Reductant Mixing and ISS



FeS from 18–25 ft bgs (mostly shallower due to rock layer)



Portland Cement from 8–18 ft bgs