# DPT Jet Injection for Enhanced Treatment of Chloropicrin in Low-Permeability Soils: A Five-Year Review

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Battelle – Thirteenth International Conference on Remediation of Chlorinated and Recalcitrant Compounds – Denver, CO – June 2-6, 2024

# Controlled Hydraulic Fracturing Methods

- Traditional DPT
- DPT Jet Injection
- Cased-Hole Jet Fracturing

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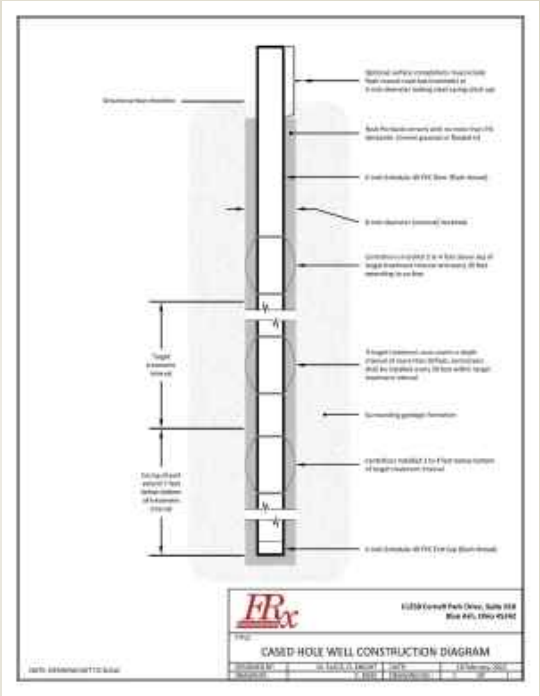
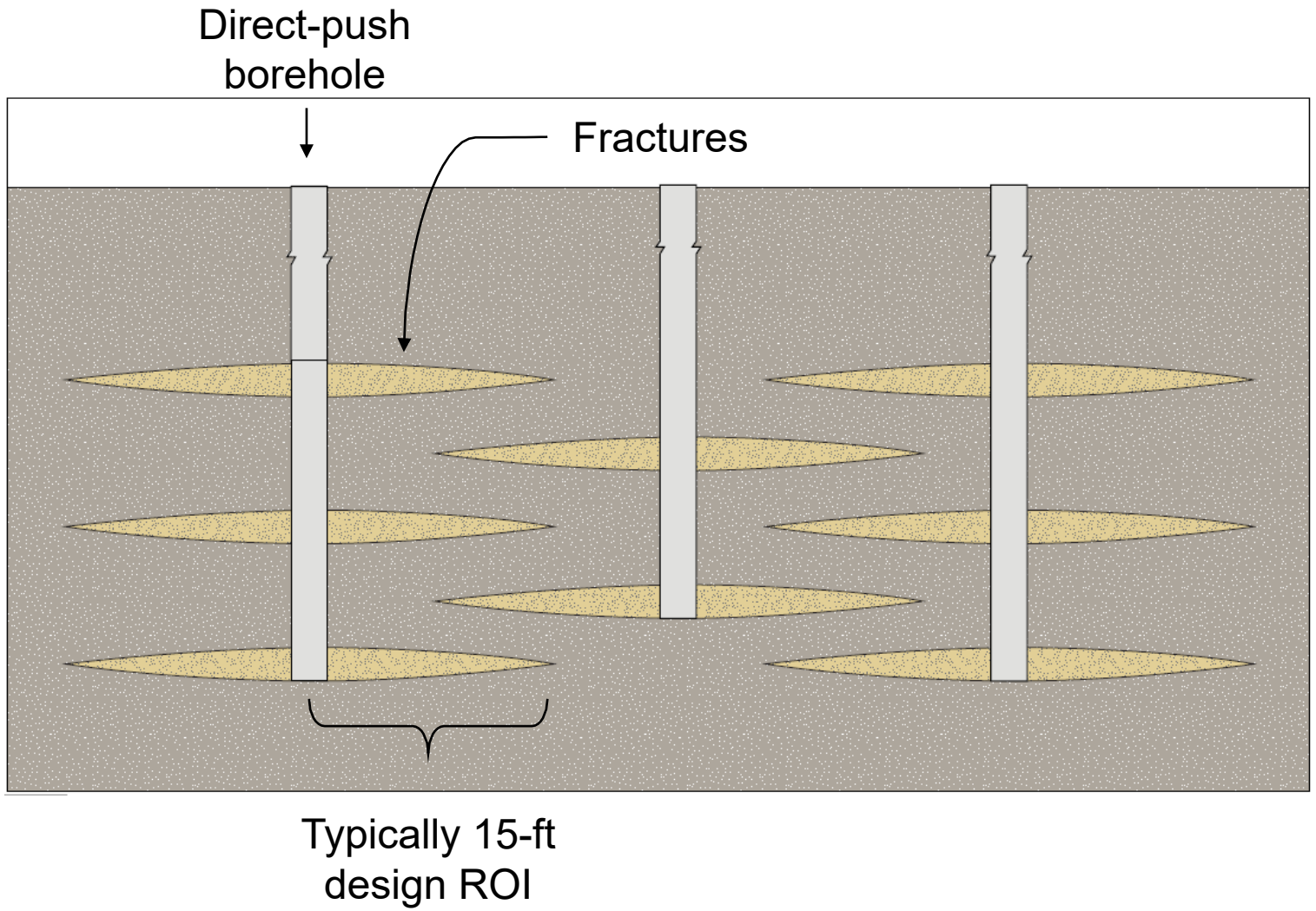
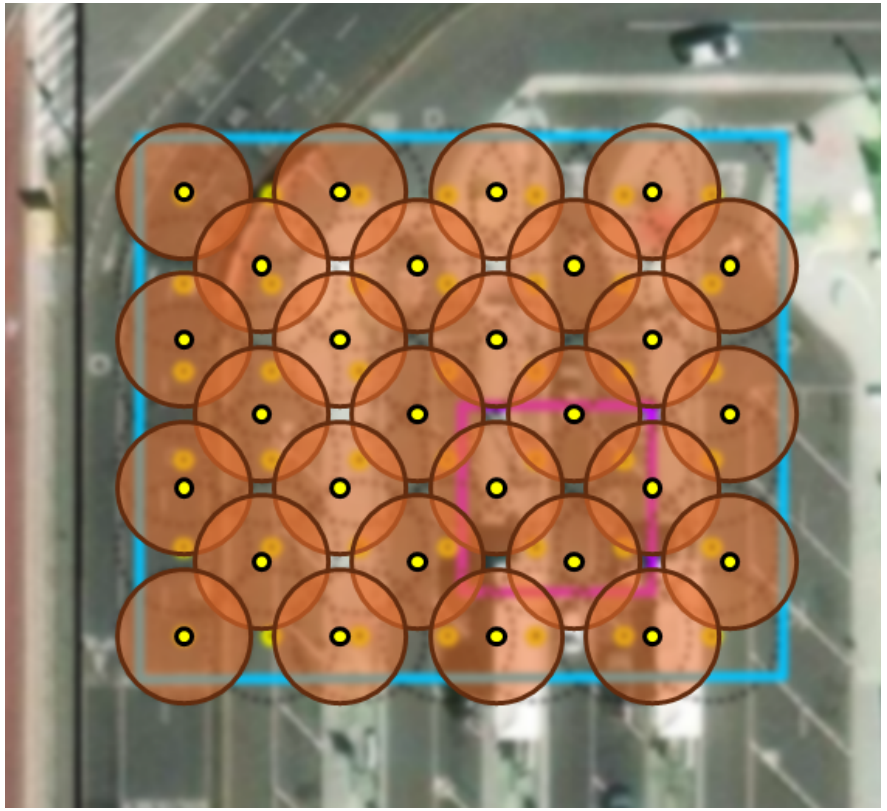




FRx

# Technology Overview – Controlled Hydraulic Fracturing



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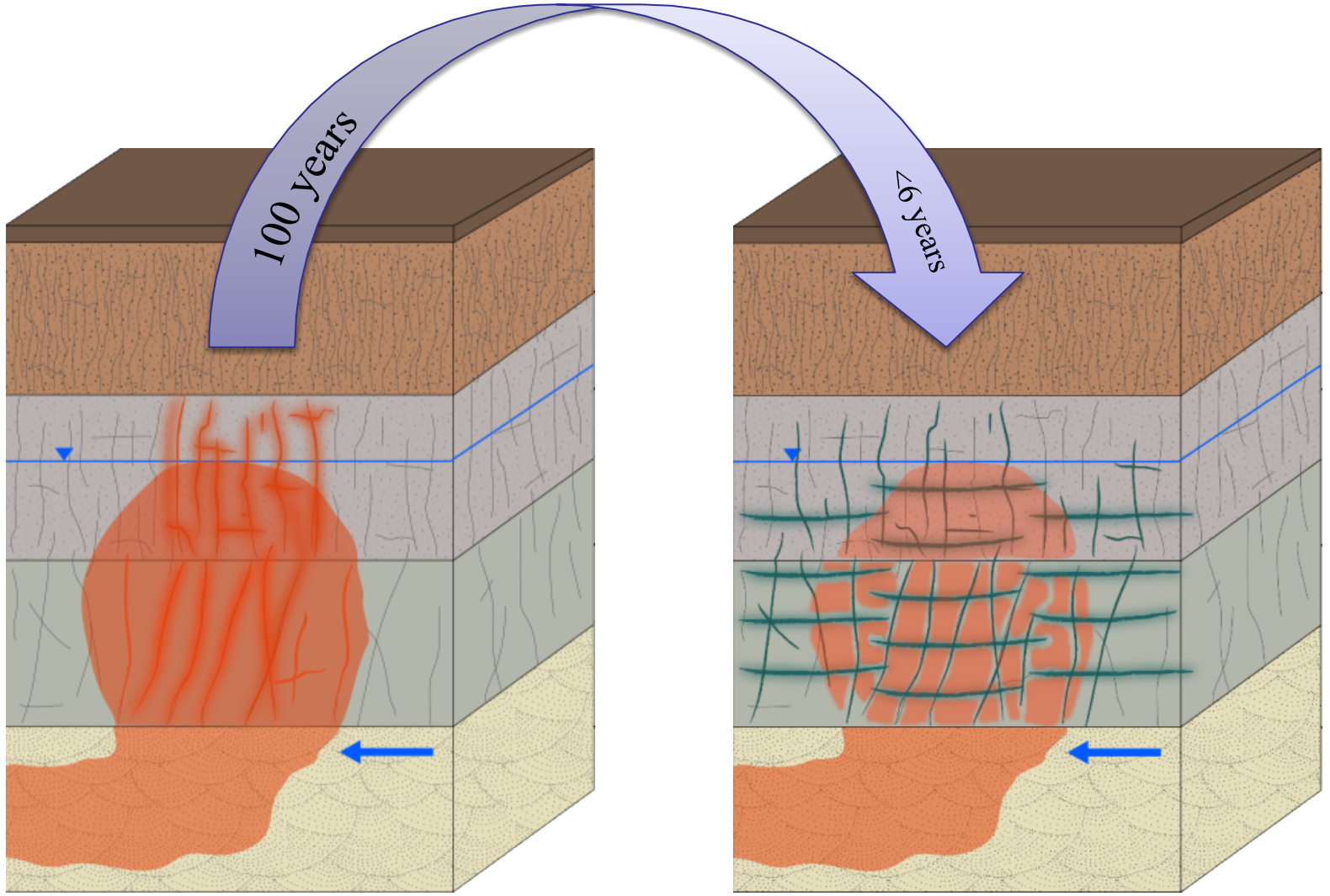


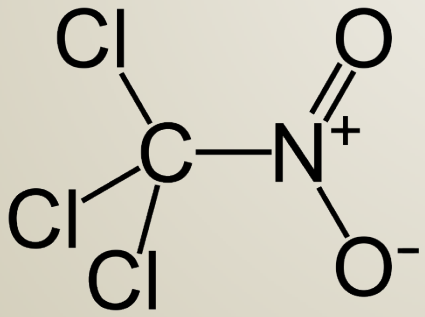
# Acknowledgements


- Chris Martin, Rhiannon Scott, and Chris Greene – MA

# Case Study: Northeastern US

# Case Study – Former Chemical Plant in Northeastern US

- Contaminant of concern: Chloropicrin ($CCl_3NO_2$)
- Manufactured for agricultural use as a soil fumigant
- Strong irritant to eyes, nose, and lungs
- Historically used in some military applications as a tear gas




**RESTRICTED USE PESTICIDE**
**Due To Acute Toxicity**
For retail sale to and use by certified applicators or persons under their direct supervision and only for those uses covered by the certified applicator's certification.

## Chloropicrin 100 Fumigant

**ACTIVE INGREDIENT:**
Chloropicrin ..... 99%
**OTHER INGREDIENTS:** ..... 1%
**TOTAL:** ..... 100%

*This product weighs 13.88 lbs./gal. @ 68°F (20°C).*

**KEEP OUT OF REACH OF CHILDREN**

**DANGER** **PELIGRO**

**POISON**

*Si Usted no entiende la etiqueta, busque a alguien para que se la explique a Usted en detalle.*
*(If you do not understand the label, find someone to explain it to you in detail.)*

**IN ALL CASES OF OVEREXPOSURE, GET MEDICAL ATTENTION IMMEDIATELY.**
**TAKE PERSON TO A DOCTOR OR TO AN EMERGENCY TREATMENT FACILITY.**

**FIRST AID**

| | |
|---|---|
| **IF INHALED:** | • Move person to fresh air.<br>• If person is not breathing, call 911 or an ambulance; then give artificial respiration, preferably by mouth-to-mouth, if possible.<br>• Call a poison control center or doctor for further treatment advice. |
| **IF ON SKIN OR CLOTHING:** | • Take off contaminated clothing.<br>• Rinse skin immediately with plenty of water for 15-20 minutes.<br>• Call a poison control center or doctor for treatment advice. |
| **IF IN EYES:** | • Hold eye open and rinse slowly and gently with water for 15-20 minutes.<br>• Remove contact lens, if present, after the first 5 minutes; then continue rinsing eye.<br>• Call a poison control center or doctor for treatment advice. |

**NOTE:** Have the product container or label with you when calling a poison control center or doctor, or going for treatment. Do not give anything by mouth to an unconscious person.

**NOTE TO PHYSICIAN**
Chloropicrin is a volatile liquid that is the active ingredient in tear gas. As a gas it is a powerful lachrymator. Early symptoms of overexposure are lachrymation, respiratory distress, and vomiting. Pulmonary edema may develop later. Treatment is symptomatic.

**EMERGENCY PHONE NUMBER:** Chemtrec, 1-800-424-9300

*[See inside of label booklet for additional Precautionary Statements and complete Directions for Use.]*

EPA Reg. No. 8536-2
☐ EPA Est. 11220-CA-4
☐ EPA Est. 11220-CA-8

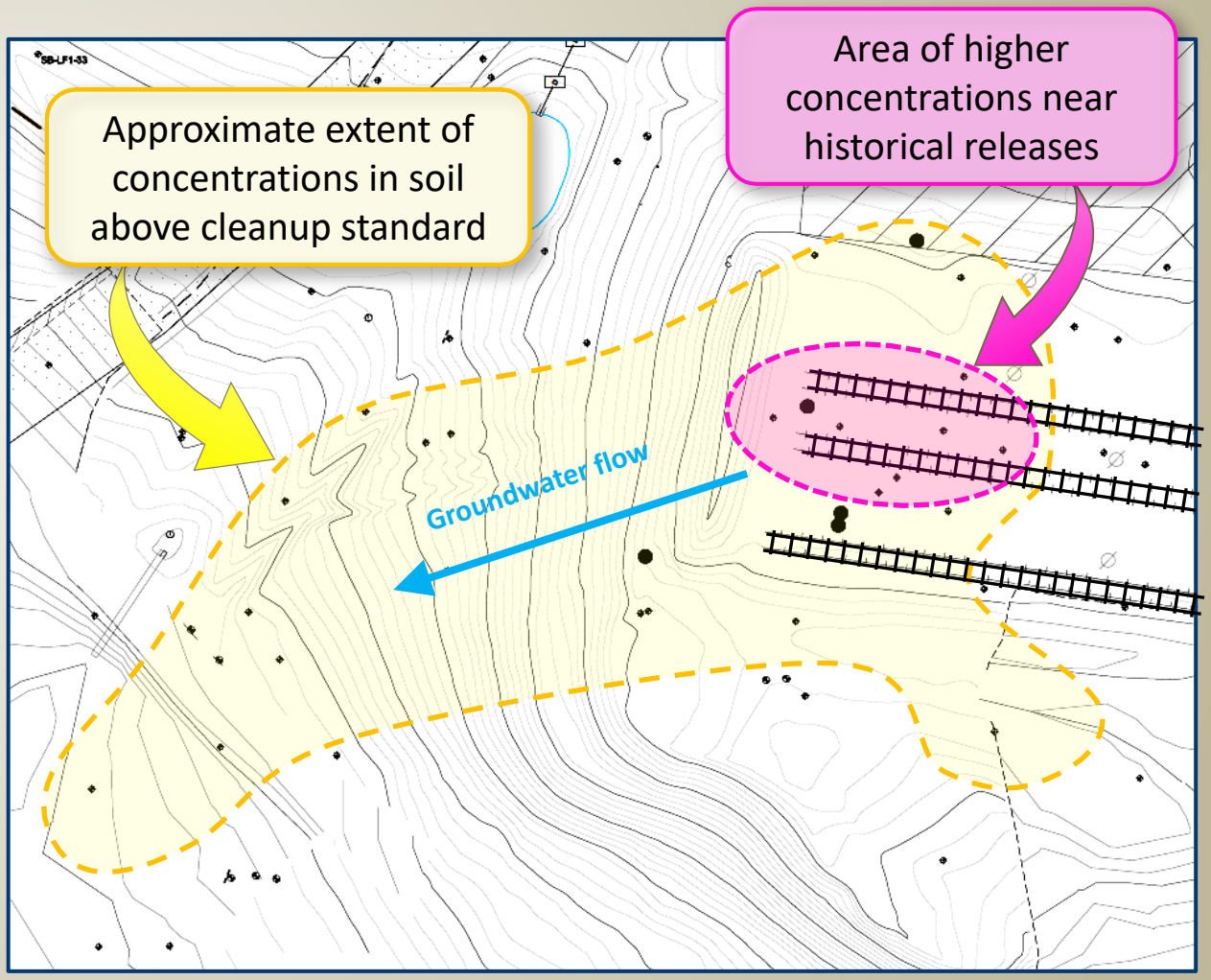
*Produced for:*
**Soil Chemicals Corporation D/B/A Cardinal Professional Products**
**8100 Arroyo Circle • Gilroy, CA 95020**
**(831) 637-0195**

Net Contents:
☐ 50 LBS
☐ 150 LBS
Other____ LBS

*[Date of Labeling: November 6, 2017]*

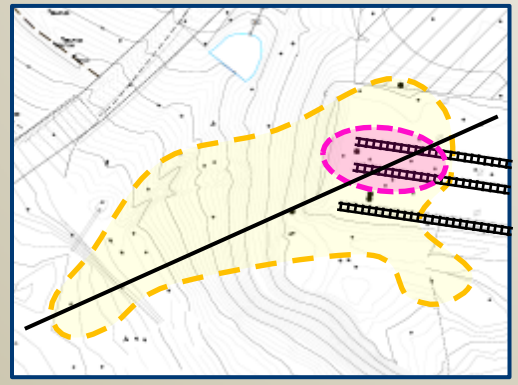
# Background and Site History – Northeastern US Site

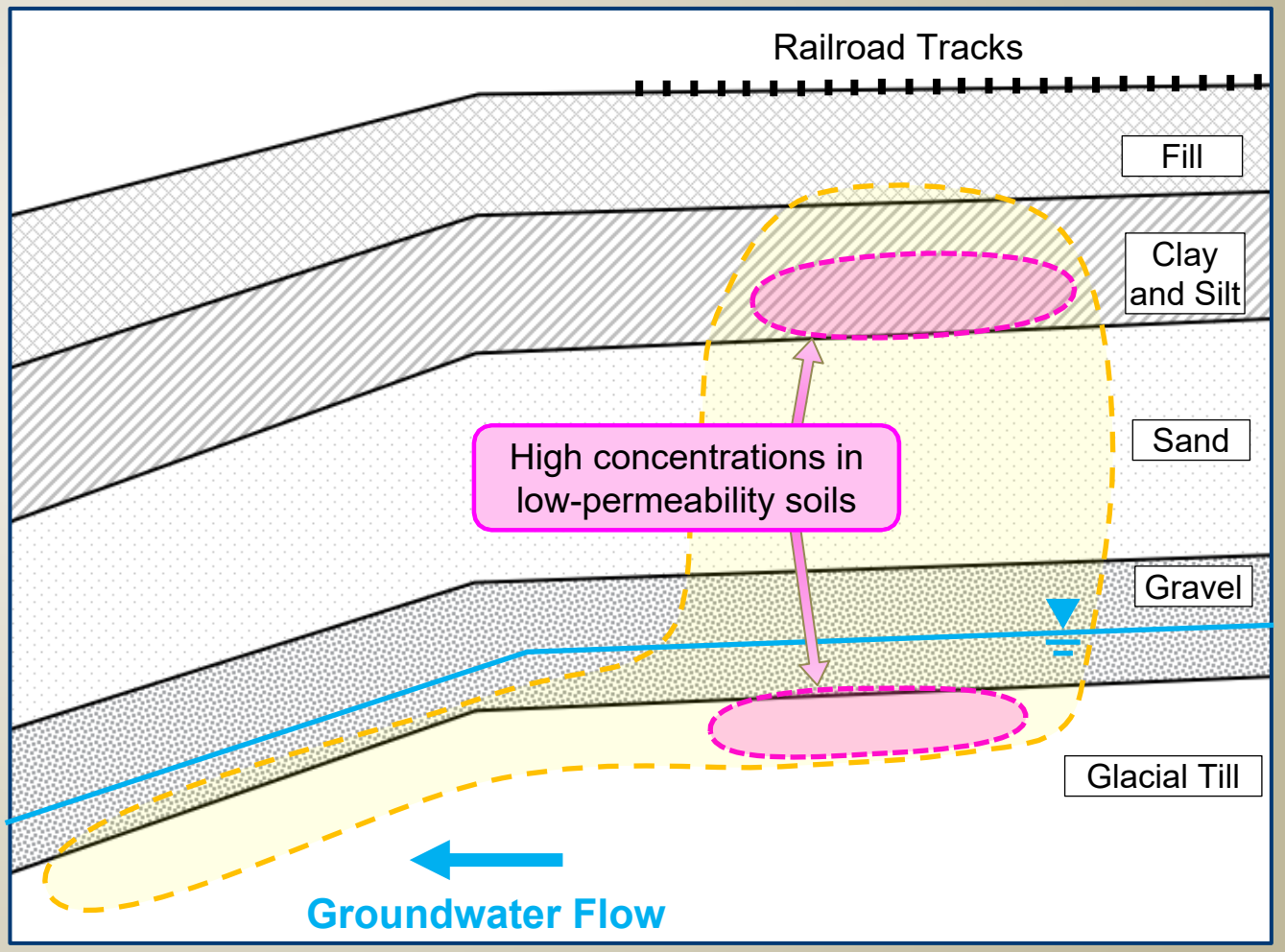
- Chloropicrin was formerly manufactured on site and loaded in railroad tank cars, and historical releases occurred in the loading area
- Detected above soil cleanup standard (0.125 mg/kg) at depths up to 40 ft bgs
- Concentrations in soil up to 19,000 mg/kg
- Excavation of impacted soil was not a feasible remedy due to active railroad operations and safety concerns related to potential chloropicrin air emissions



# Background and Site History – Northeastern US Site

- Complex glacial geology with widely variable permeability
- Target treatment zone includes several distinct strata above and below water table
- High concentrations of chloropicrin >10,000 mg/kg were identified in low-permeability soils





# Bench-Scale Treatability Testing

- Limited data was available in literature or from other sites regarding feasibility of treating chloropicrin in-situ
- Bench-scale testing was conducted using soil and groundwater from the site
  - 1st round of testing screened 6 different amendments using batch reactor tests
  - 2nd round of batch testing further evaluated 2 of these amendments to optimize the amendment dose over a wide range of chloropicrin concentrations

# Bench-Scale Treatability Testing

## Study #1: Remedial Technology Screening

| Treatment Technology | Amendments |
|---|---|
| In-Situ Chemical Oxidation (**ISCO**) | Base activated persulfate |
| | Matrix activated persulfate |
| | Temperature activated persulfate |
| In-Situ Chemical Reduction (**ISCR**) | Zero-valent iron (ZVI) |
| | Potassium thiosulfate |
| Enhanced In-Situ Bioremediation (**EISB**) | Newman Zone® and KB-1® Plus |

**Outcome:**

- All amendments effectively degraded chloropicrin
- 2 amendments were retained for further evaluation

## Study #2: Amendment Dosing and Optimization

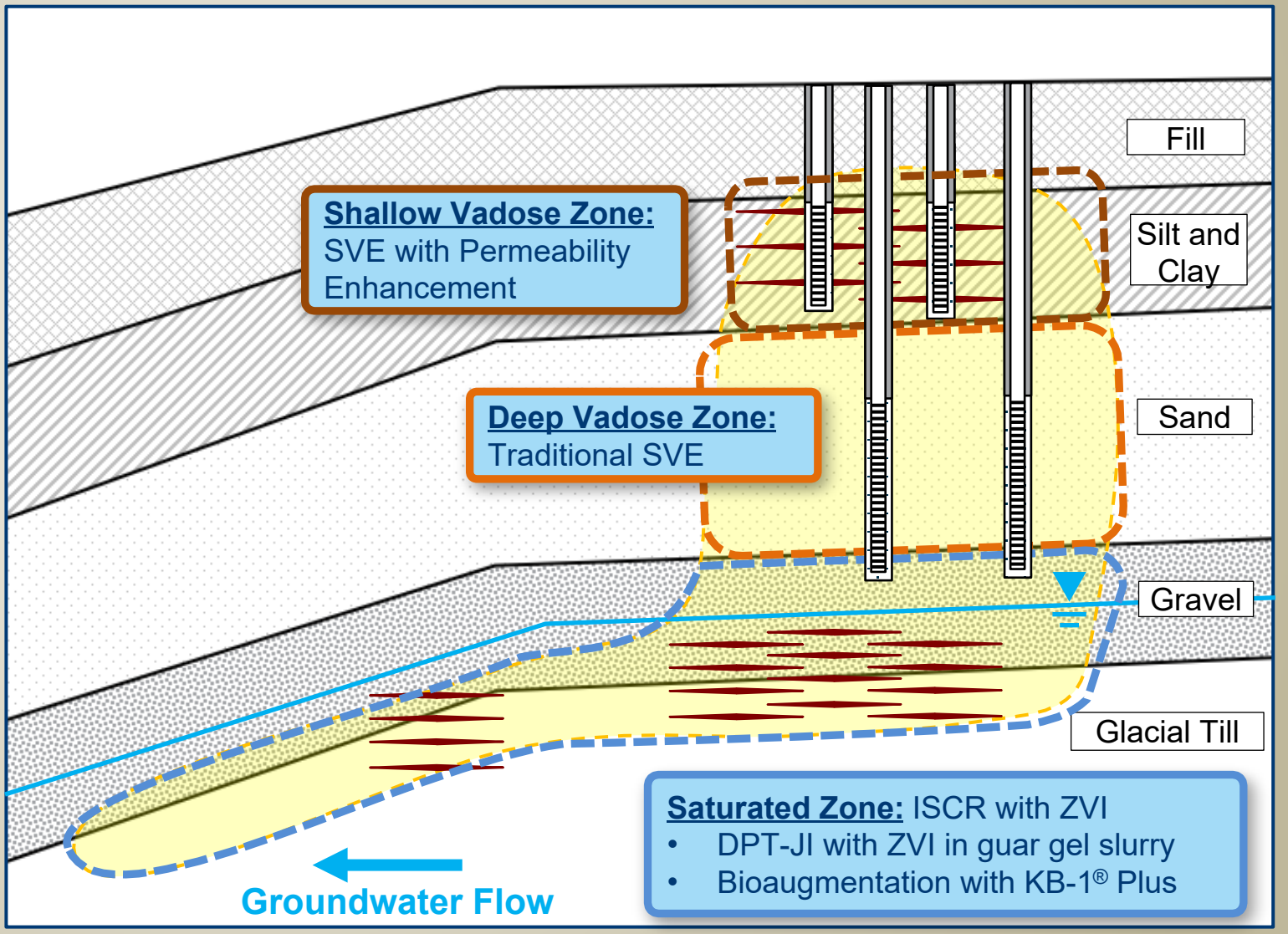
| Treatment Technology | Amendments |
|---|---|
| In-Situ Chemical Oxidation (**ISCO**) | Base activated persulfate |
| | Matrix activated persulfate |
| | Temperature activated persulfate |
| In-Situ Chemical Reduction (**ISCR**) | Zero-valent iron (ZVI) |
| | Potassium thiosulfate |
| Enhanced In-Situ Bioremediation (**EISB**) | Newman Zone® and KB-1® Plus |

**Outcome:**

- ISCR with ZVI treated chloropicrin to below cleanup standard at all chloropicrin concentrations tested
- EISB was inhibited at higher chloropicrin concentrations
- ZVI injection combined with KB-1® Plus bioaugmentation was selected for field pilot testing

# Remedial Design – Northeastern US Site

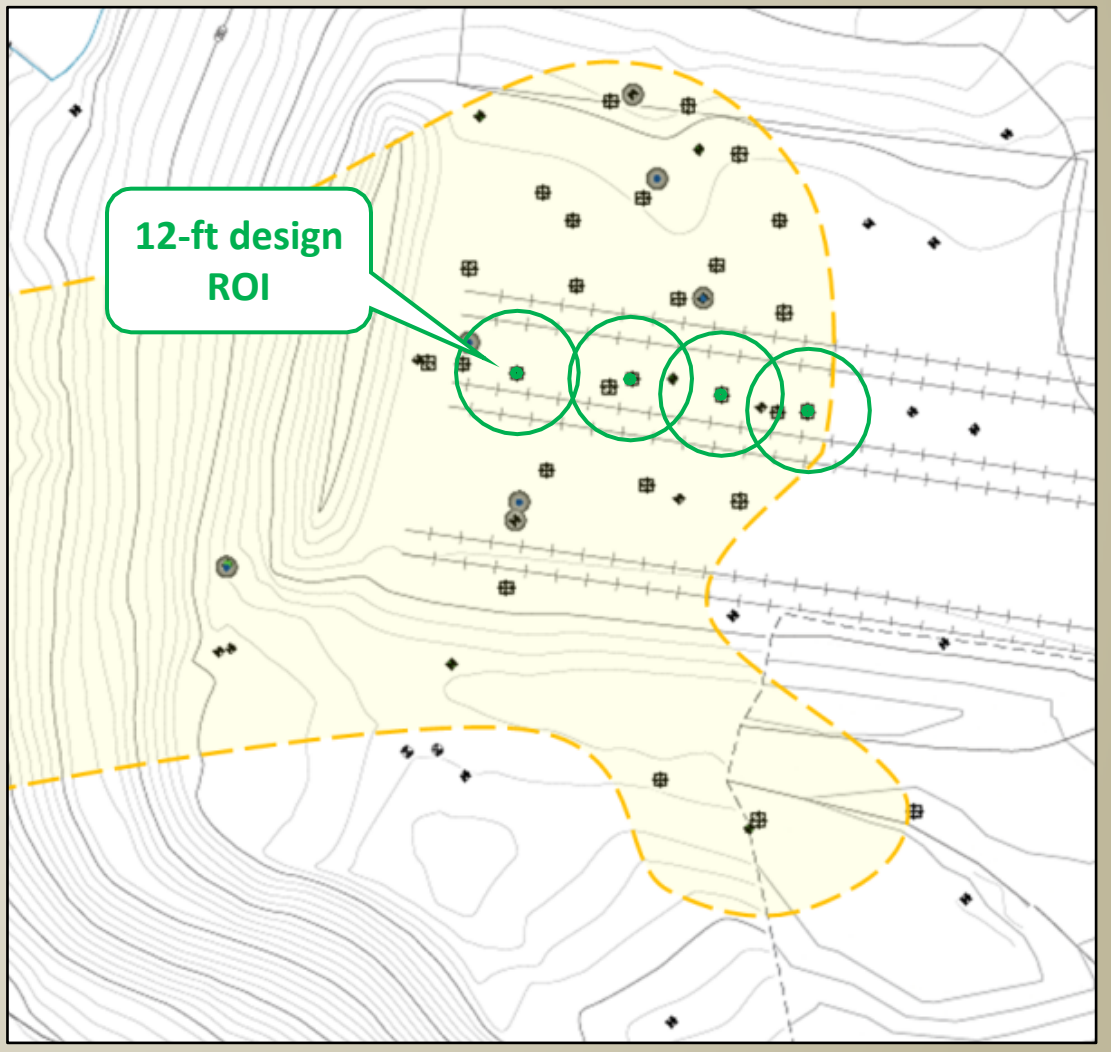
- Treatment approach utilized DPT-JI to enhance treatment in low-permeability soil strata:
- Increase permeability of silt and clay layer to facilitate SVE
- Increase control over ZVI injection in glacial till
- Reduce the number of injection points and SVE wells needed for treatment due to larger and more predictable radius of influence (ROI) compared to traditional SVE and DPT injection



# Remedy Implementation


# Remedy Implementation – Enhanced SVE in Vadose Zone

- Pilot Test
  - 4 locations with 14 individual injections
  - 8,400 lbs. sand
  - 4,200 lbs. ZVI
  - 4 SVE wells installed with screens in contact with fractures



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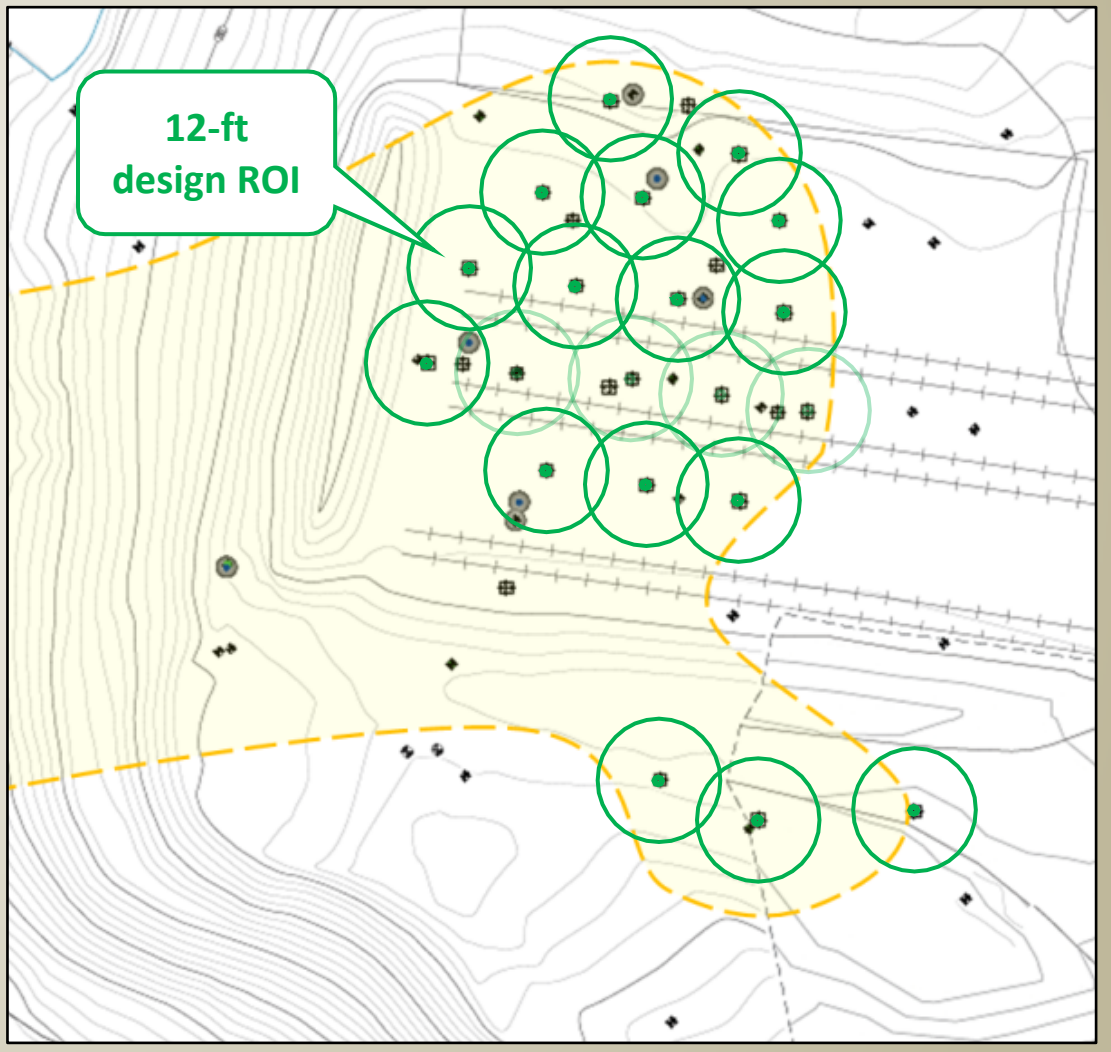
- Pilot Test
  - 4 locations with 14 individual injections
  - 8,400 lbs. sand
  - 4,200 lbs. ZVI
  - 4 SVE wells installed with screens in contact with fractures
- Full Scale
  - 16 locations with 42 individual injections
  - 25,025 lbs. sand
  - 11,480 lbs. ZVI
  - 16 SVE wells installed with screens in contact with fractures



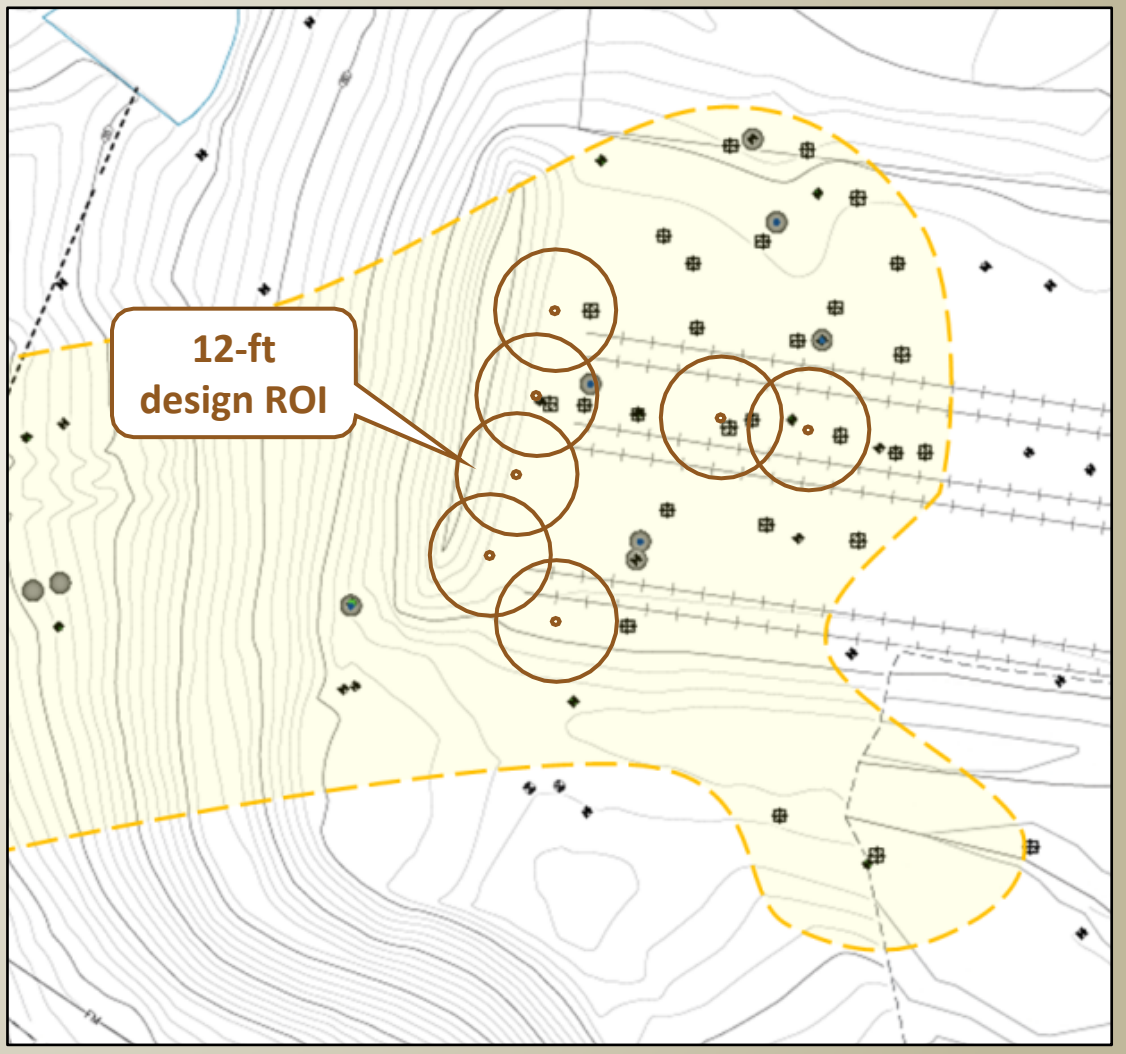
# Remedy Implementation – SVE System

Full scale SVE system

- 20 shallow fracture enhanced SVE wells targeting clay and silt stratum
- 7 deep traditional SVE wells in sand and gravel stratum

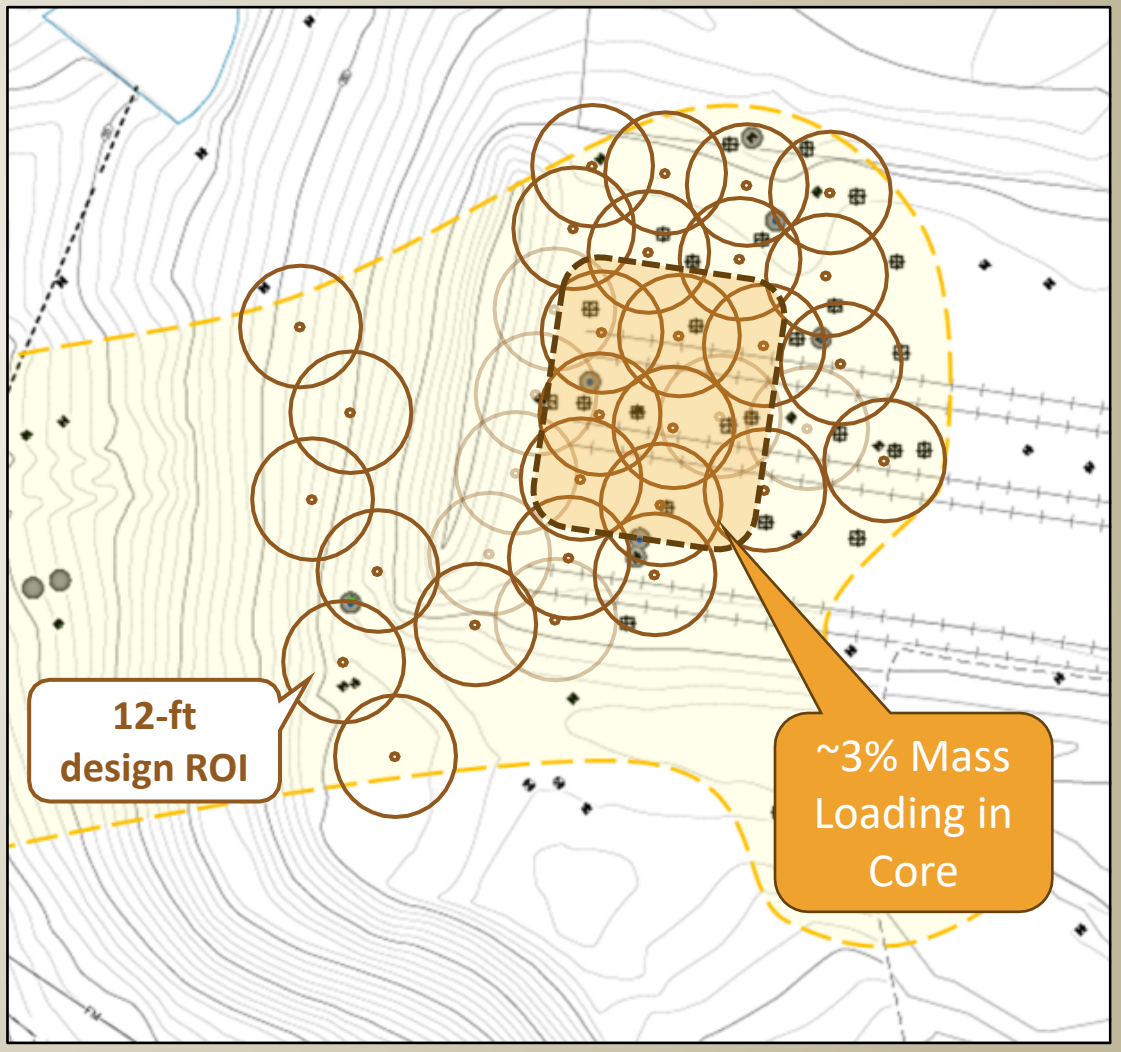
# Remedy Implementation – ZVI in Saturated Zone

- Pilot Test
  - 7 locations with 24 individual injections
  - 37,100 lbs. ZVI (~2% dosing by weight)
  - 42 L KB-1® Plus



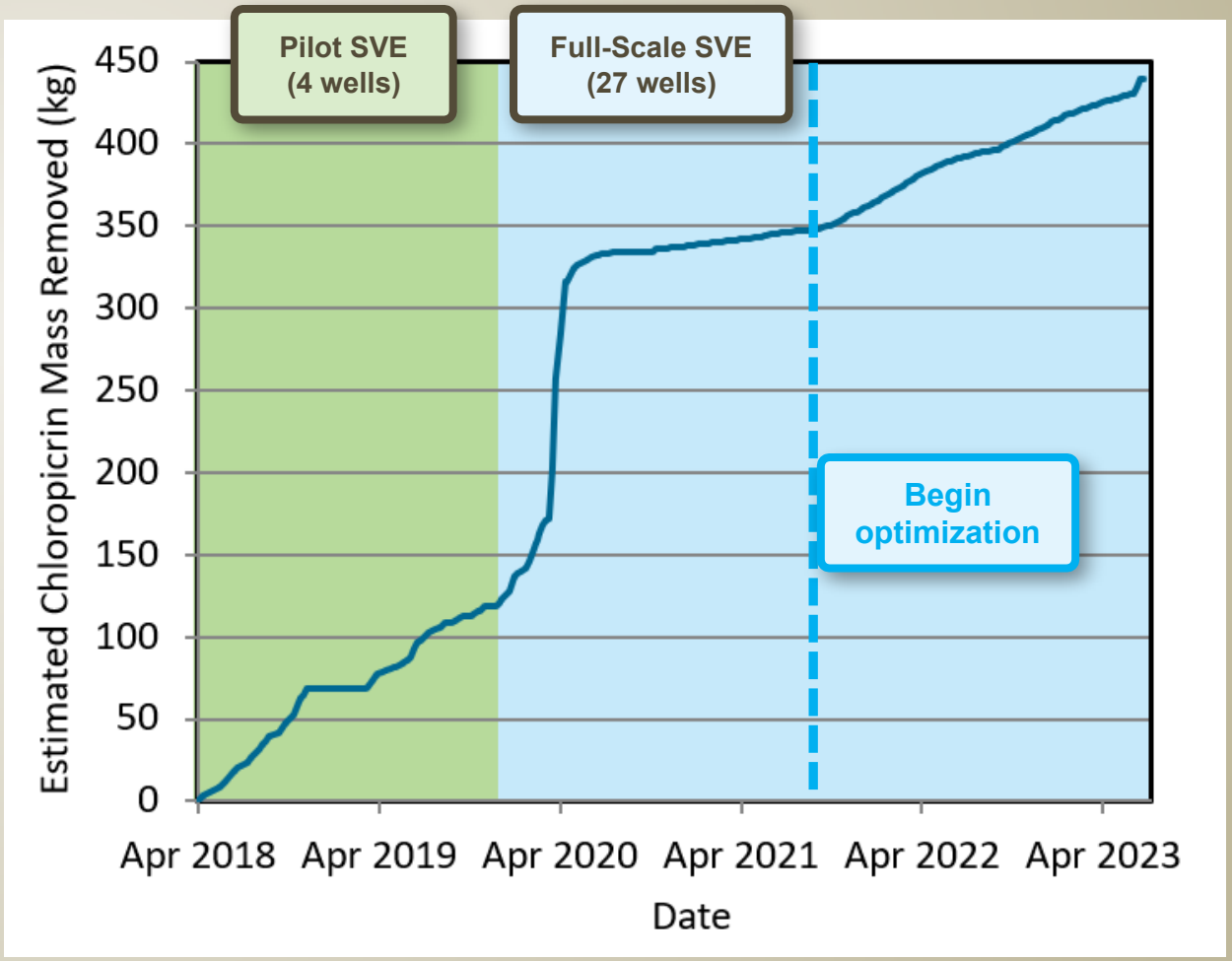
# Remedy Implementation – ZVI in Saturated Zone

- Pilot Test
  - 7 locations with 24 individual injections
  - 37,100 lbs mZVI (~2% dosing by weight)
  - 42 L KB-1® Plus
- Full Scale
  - 27 locations with 80 individual injections
  - 163,600 lbs mZVI (2.5% dosing by weight)
  - 180 L KB-1® Plus



# Performance Monitoring – Vadose Zone – SVE

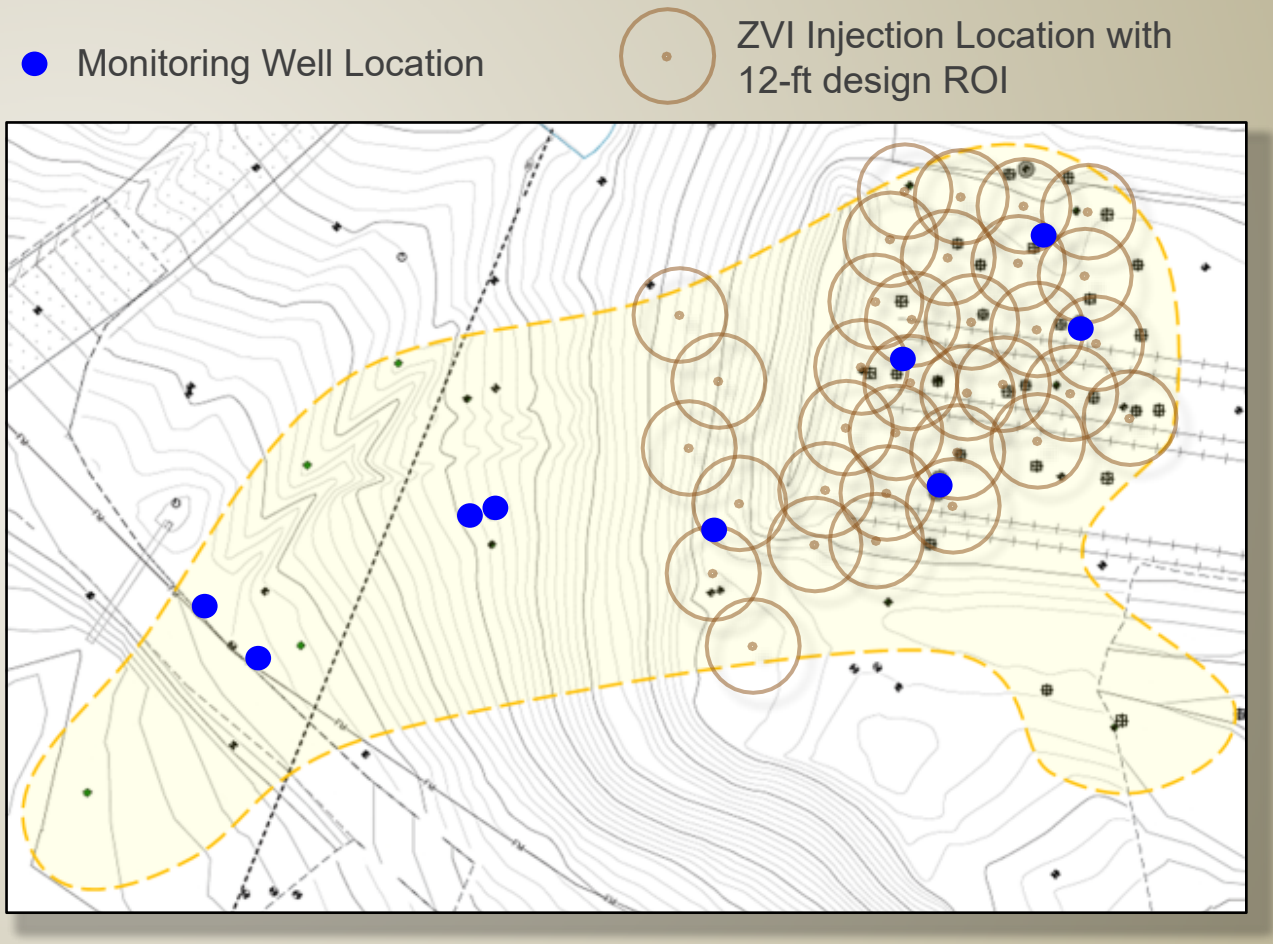
- Chloropicrin mass removal is estimated from PID measurements and SVE system flow rates
- 119 kg removed by pilot system in first 19 months
- Full-scale system brought online
- Optimization began after 3 years of operation with low concentration wells being eliminated
- 440 kg removed after 5 years



# Performance Monitoring – Groundwater – ZVI

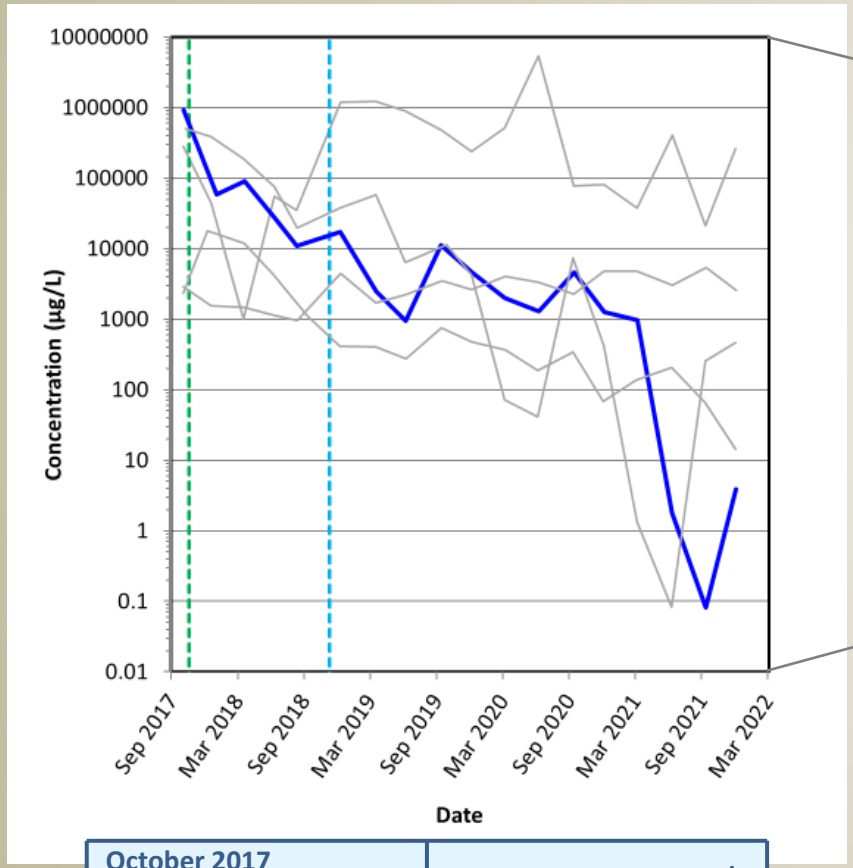
Groundwater monitoring objectives:

- Monitor concentration trends in ZVI treatment area (5 wells)
- Assess downgradient influence of source treatment (4 wells)
- Decide when to collect post-treatment soil samples

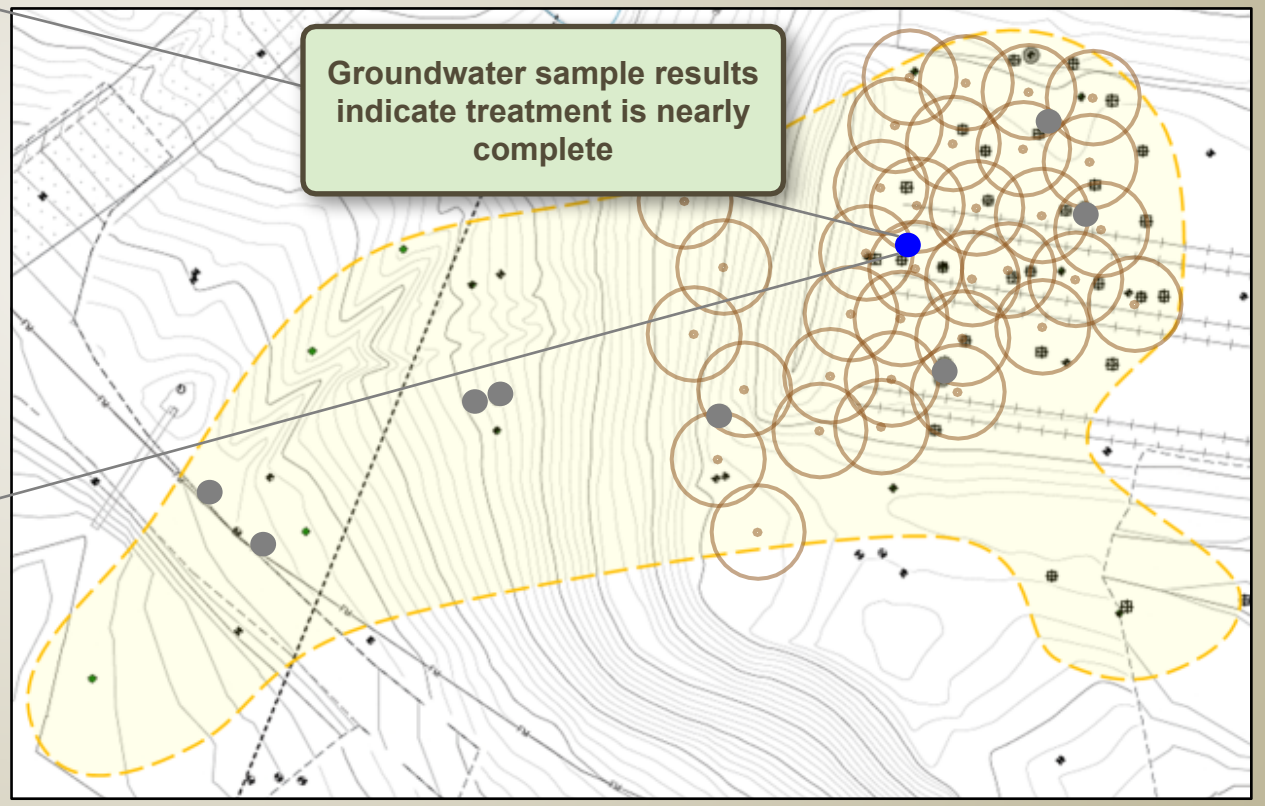


# Performance Monitoring – Groundwater – ZVI

Groundwater monitoring results 3 years after full-scale treatment:




| | |
|---|---|
| October 2017 (Pre-Treatment) | 930,000 µg/L |
| December 2021 | 3.86 µg/L |
| **% Change** | **-99.999%** |



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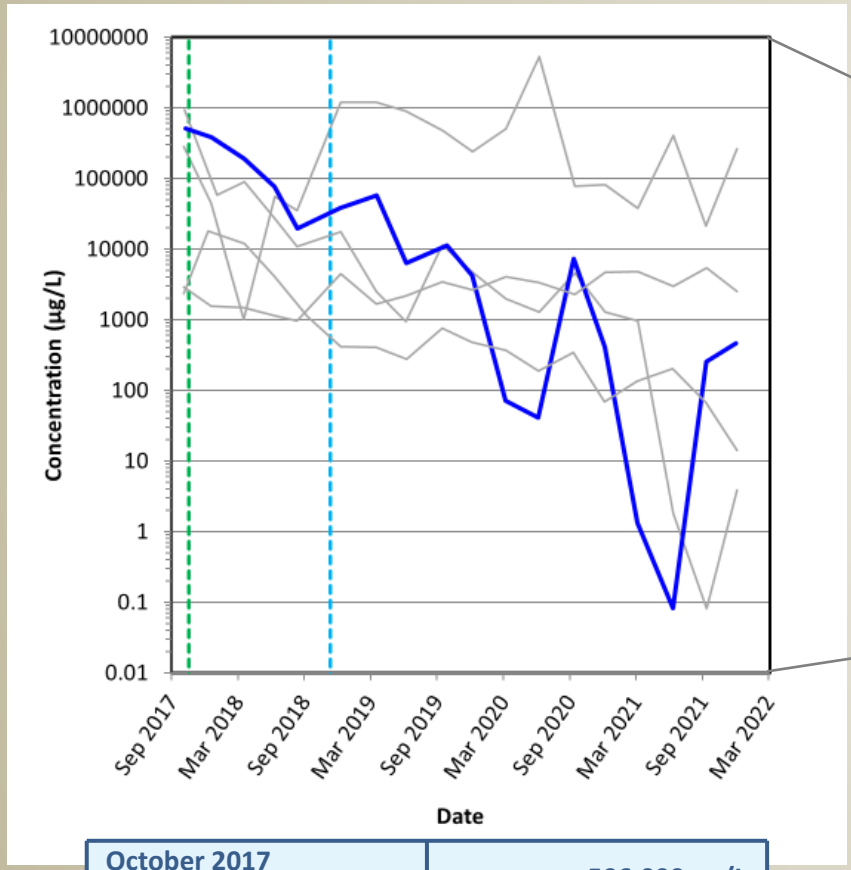
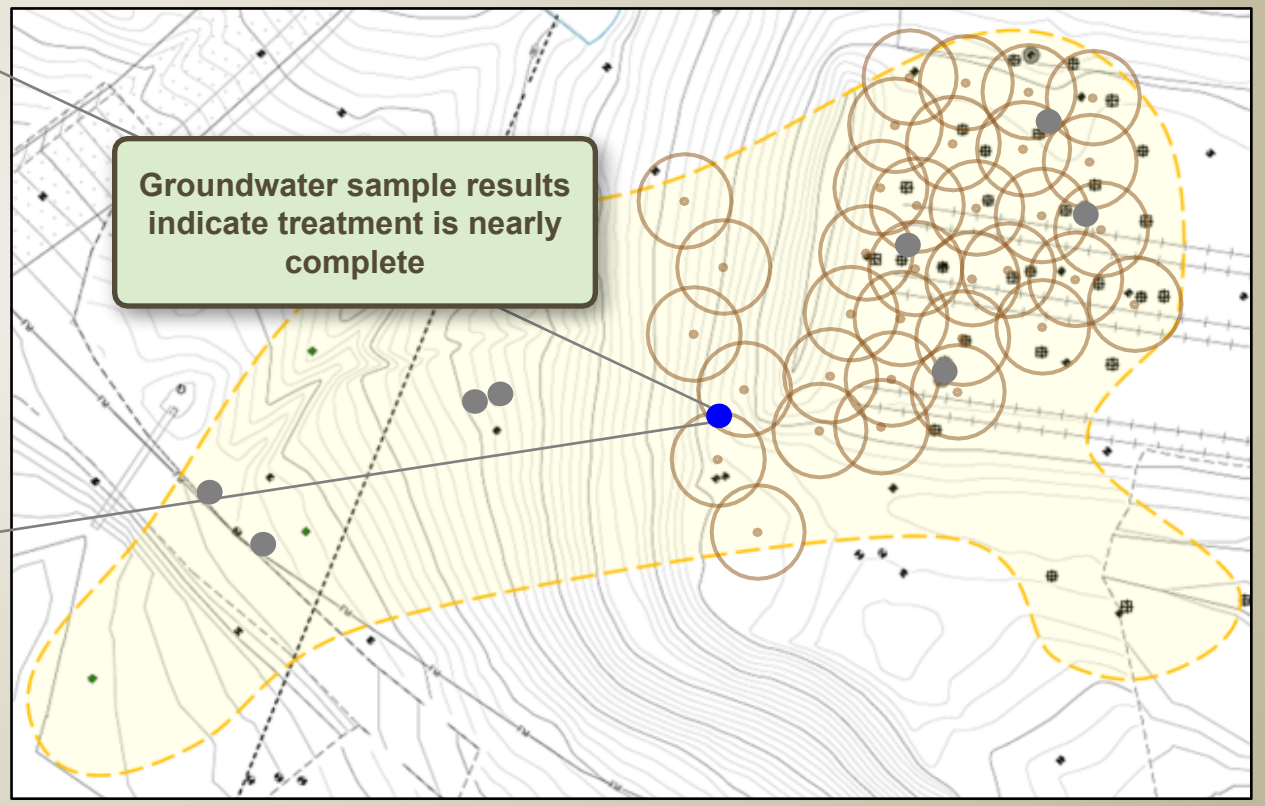
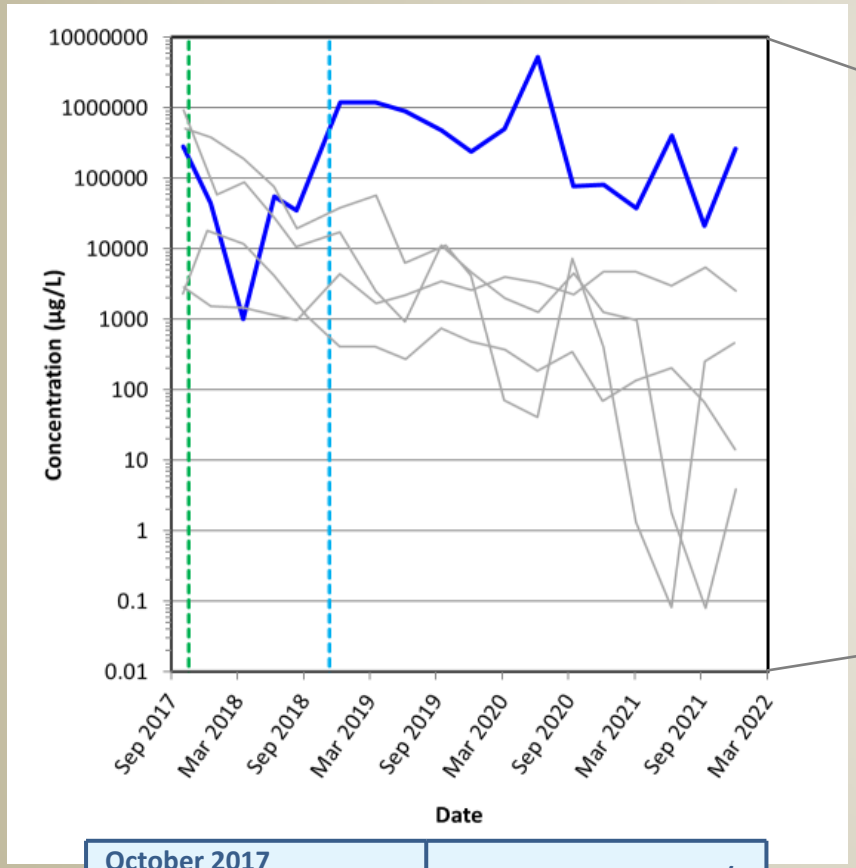



| | |
|---|---|
| October 2017 (Pre-Treatment) | 506,000 µg/L |
| December 2021 | 465 µg/L |
| **% Change** | **-99.91%** |

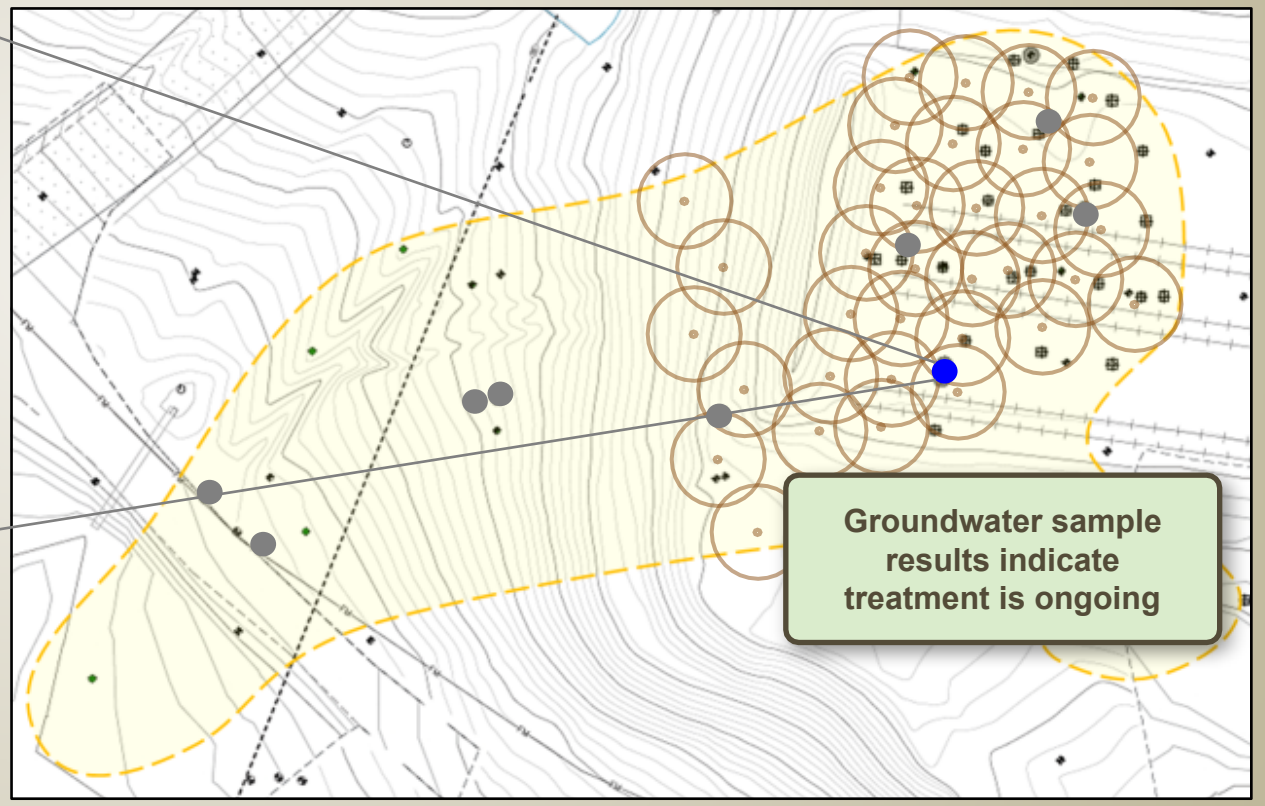


# Performance Monitoring – Saturated Zone Treatment – ZVI

Groundwater monitoring results 3 years after full-scale treatment:

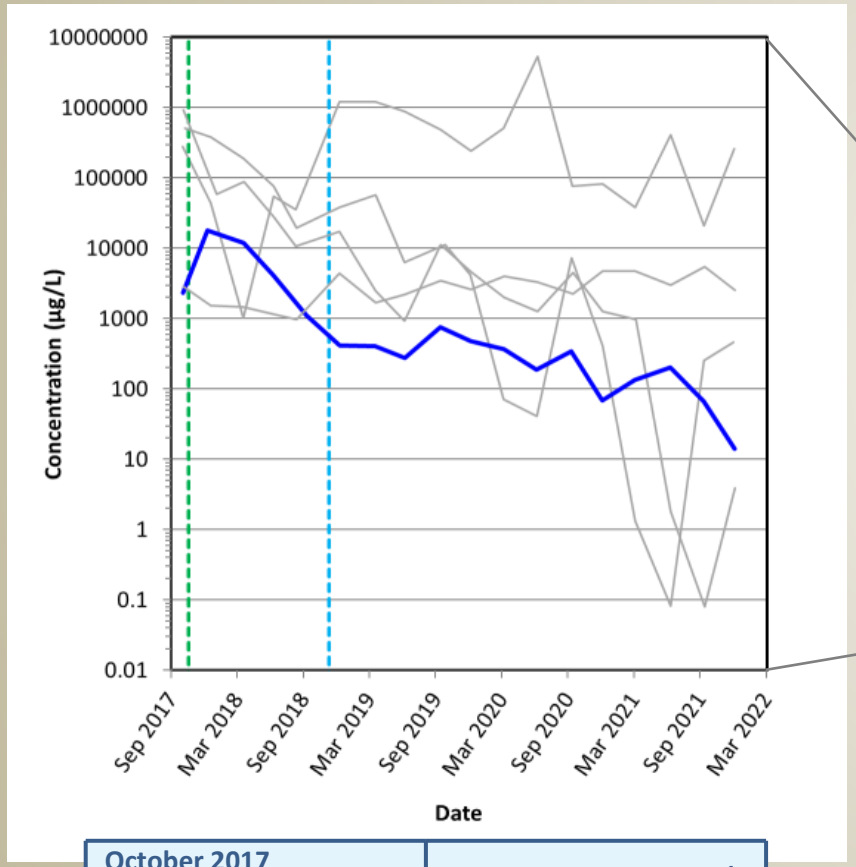



| | |
|---|---|
| October 2017 (Pre-Treatment) | 282,000 µg/L |
| December 2021 | 262,000 µg/L |
| **% Change** | **-7%** |

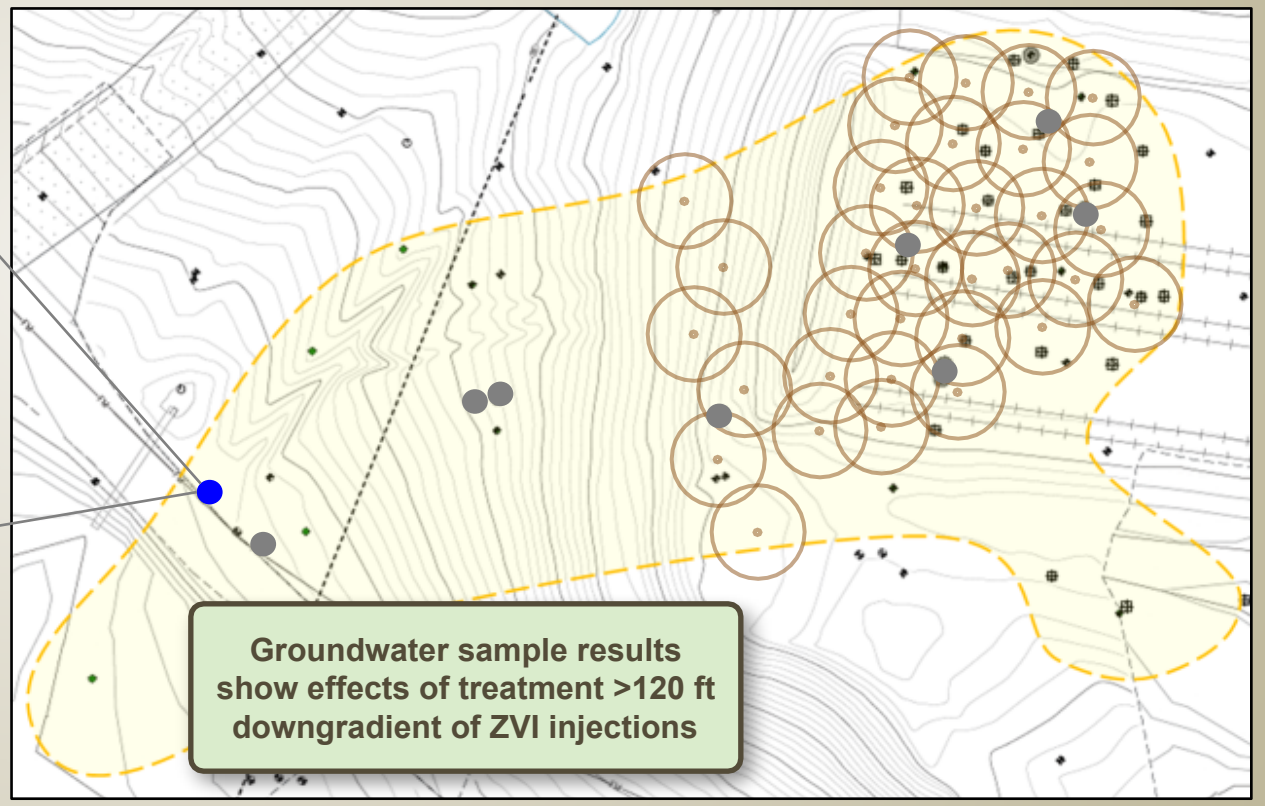


# Performance Monitoring – Groundwater – ZVI

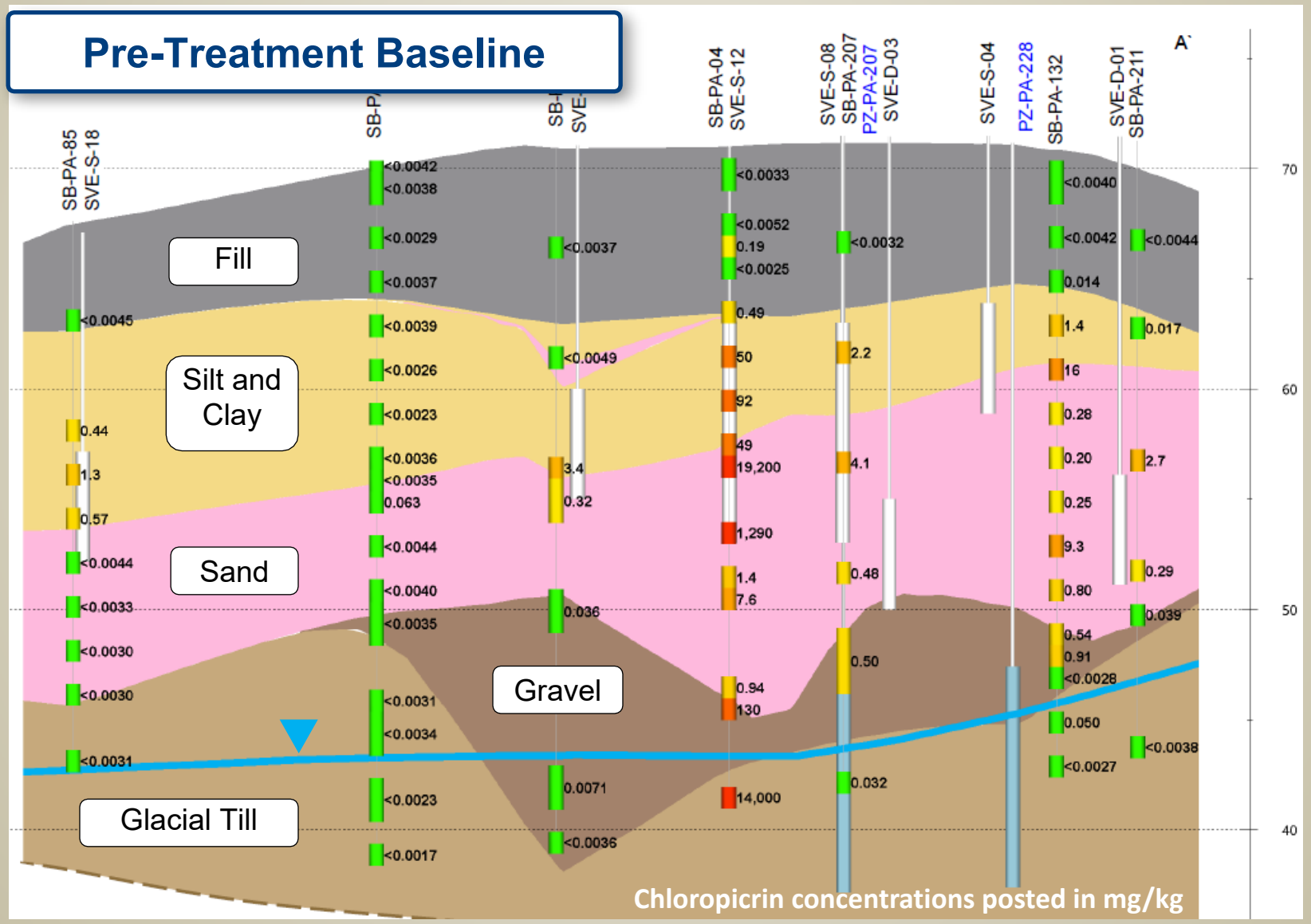
Groundwater monitoring results 3 years after full-scale treatment:




| | |
|---|---|
| October 2017 (Pre-Treatment) | 2,330 µg/L |
| December 2021 | 14 µg/L |
| **% Change** | **-99.4%** |



# Performance Monitoring – Soil – ZVI



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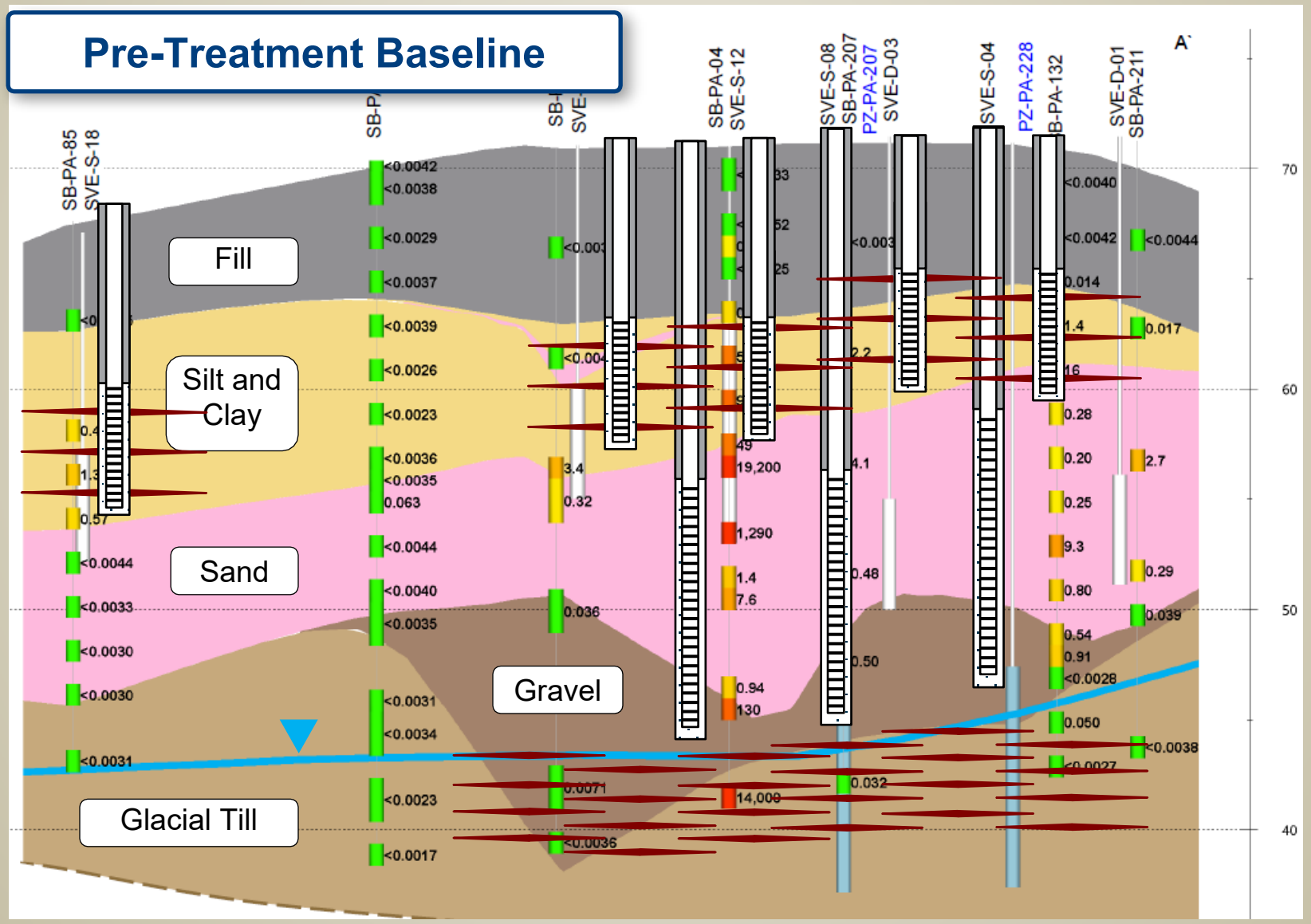
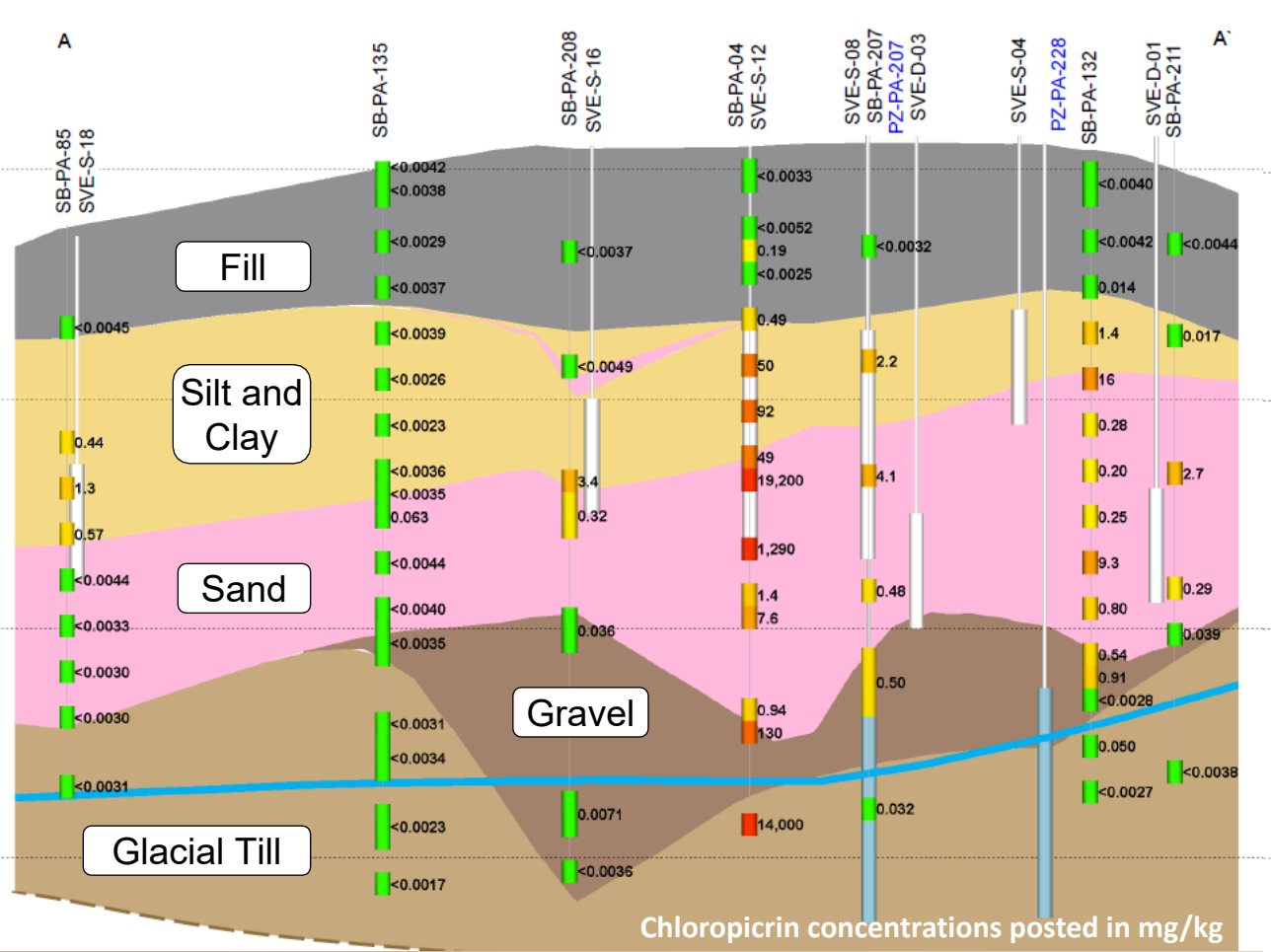
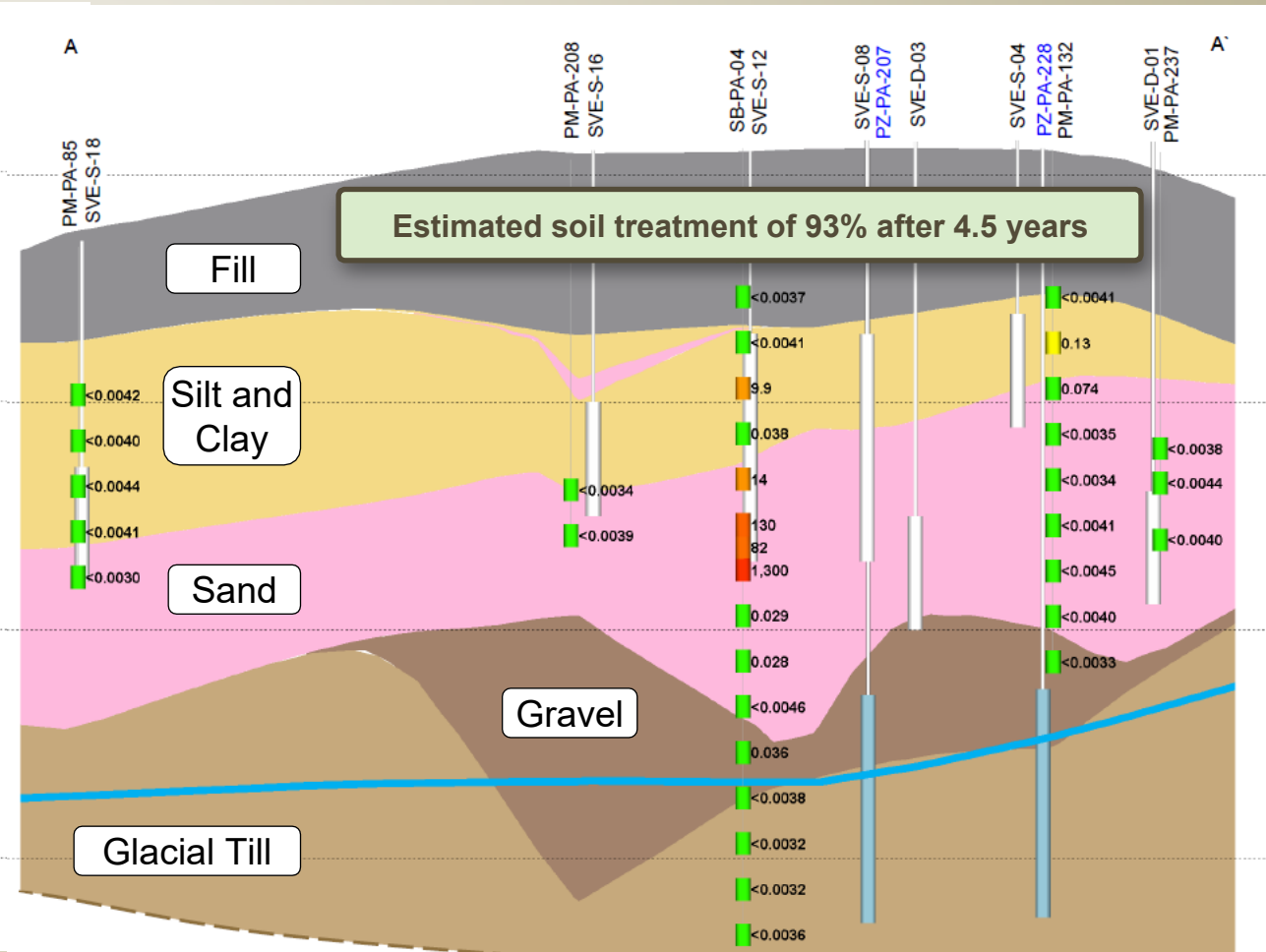


# Performance Monitoring – Soil – ZVI

## Pre-Treatment Baseline




## Sept 2022 – After 4.5 years



# Conclusions

- Bench-scale and pilot testing provided a measured approach to achieving treatment for an unfamiliar contaminant in a challenging geologic setting.
- Sand-filled fractures enhanced SVE efficiency in clay and silt soils where conventional SVE would have been ineffective.
- As of June 2023 (5 years after treatment), concentration decreases in groundwater range from 63% to more than 99%, with an average decrease of 89%.
- The estimated mass of chloropicrin in soil decreased by more than 93% by 4.5 years after the start of treatment based on EVS modeling.


Questions?