Application of novel amendment via forced advection delivery for rapid anaerobic dechlorination of TCE impacted groundwater

2022 Battelle Chlorinated Remediation Conference

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Bright ideas.
Sustainable change.

Presentation outline

- Key site features
- Remedial approach
- Remedial design and implementation
- Results
- Takeaways and Conclusions

Key site features

Former metal parts manufacturing facility from 1919 to 1996, where cVOC-impacted soil and groundwater was detected in 2004.

Site impacts

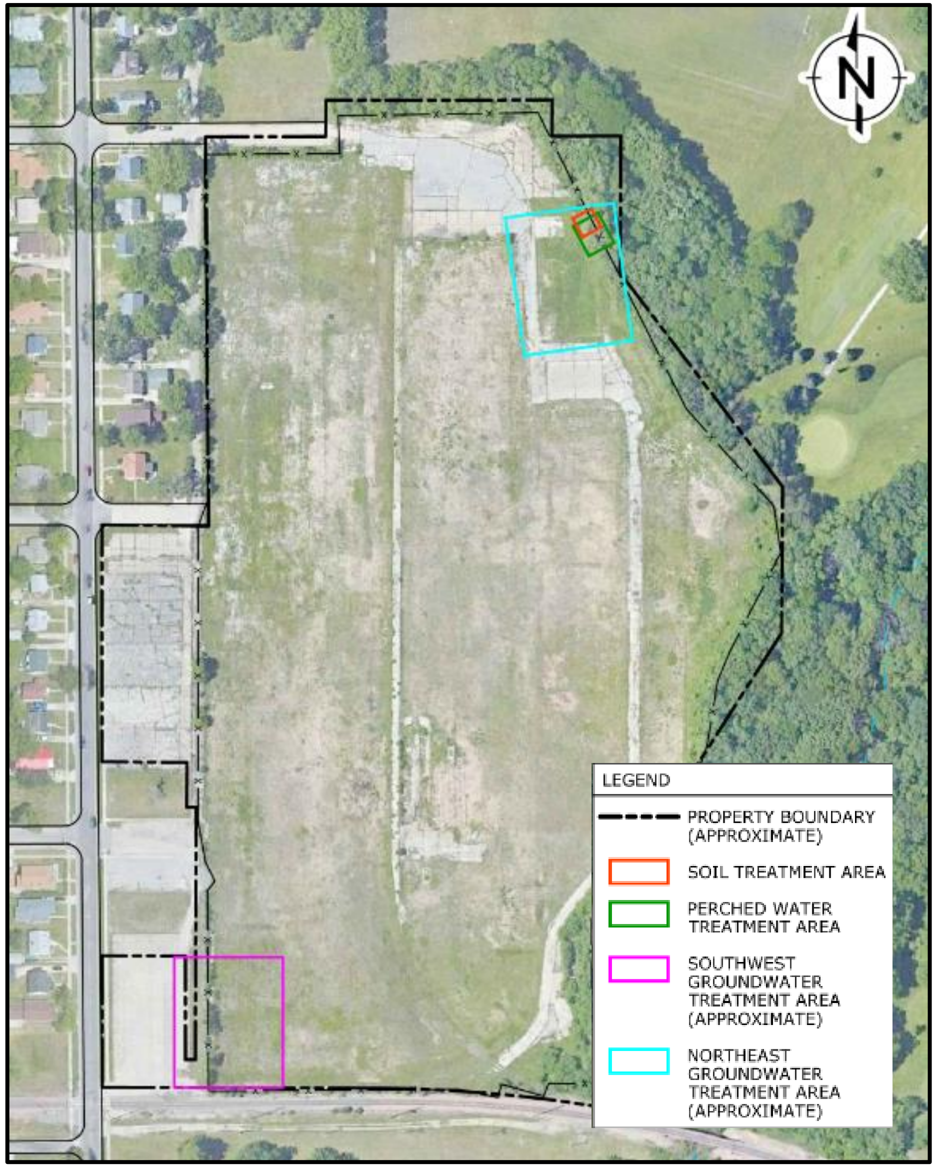
- Source area vadose zone soil impacted with up to 24,000 µg/kg TCE
- Source area perched water impacted with up to 420,000 µg/L TCE
- Site-wide TCE-impacted groundwater with two embedded 1-acre areas of groundwater up to 11,000 µg/L TCE to ~45 feet below grade

Water table

- Depth: ~20 ft below grade, in sandy soils
- Groundwater flow to the west-southwest

Objective

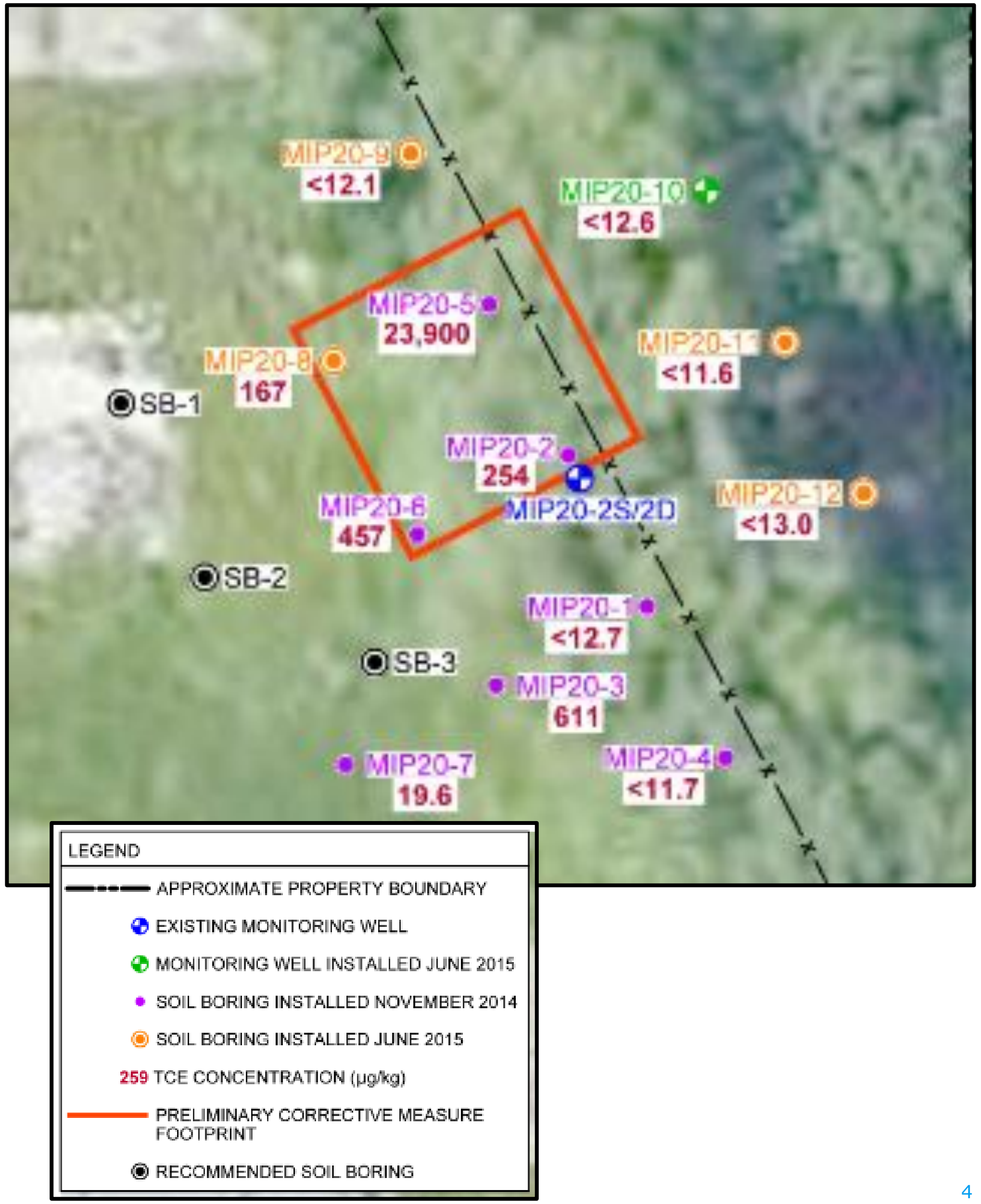
- Interim Remedial Measures (IRMs) to support long-term monitoring



Remedial approach

Vadose zone soil

- Based on cost evaluation, ISCO via soil mixing was selected over SVE or excavation and offsite landfill disposal
- Sandy vadose zone soils likely to facilitate rapid drainage of reagent, such that rapid-reacting oxidant was preferred
- Modified Fenton’s Reagent (MFR) selected
  - MFR is hydrogen peroxide catalyzed with ferrous iron.



Remedy implementation
Vadose zone soil

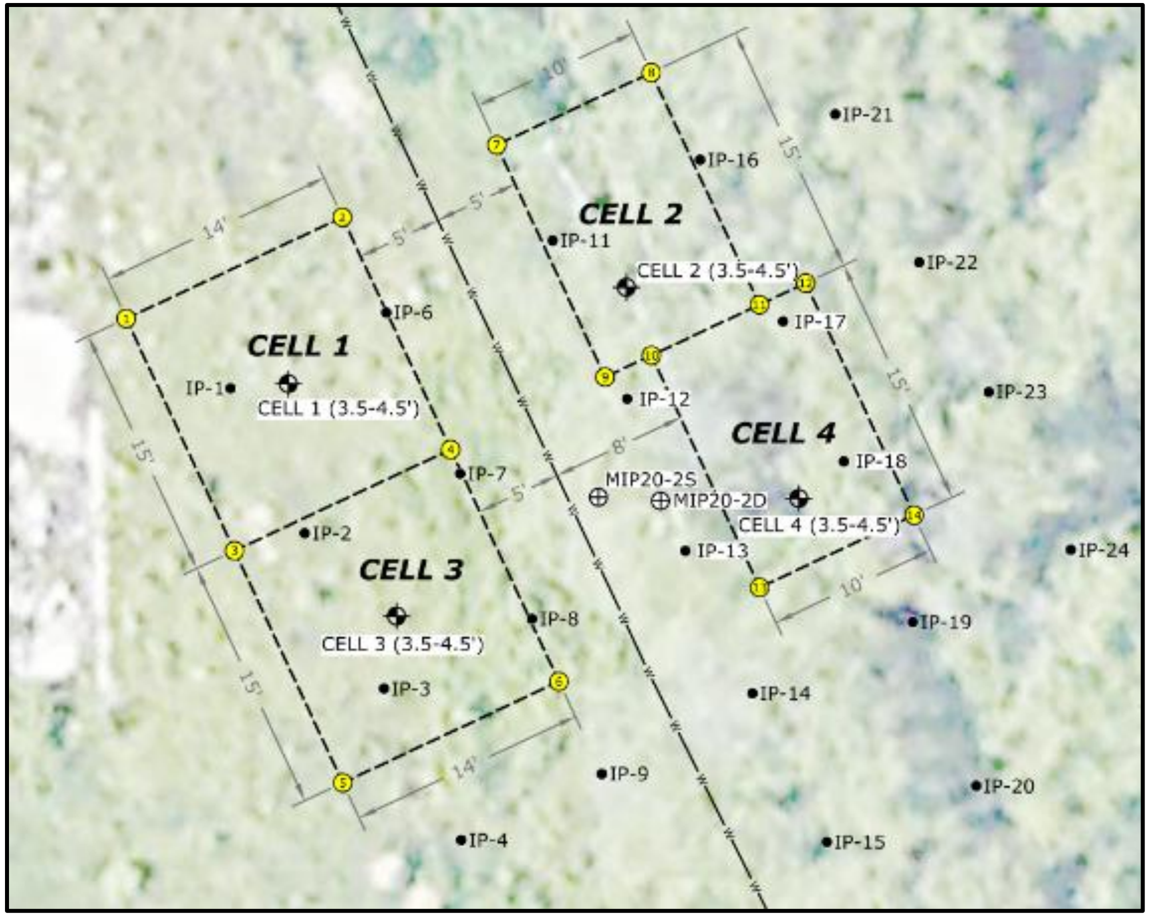
- In situ soil mixing completed in April 2018
- Based on PNOD of 1 g/kg and safety factor of 3, treatment zone was dosed with 2,300 gallons of 8.8% solution of MFR to target 20% of the available pore volume
- MFR spray-applied into soil vadose zone as conventional excavator mixed soil
- Soil mixed using the excavator until a homogenous consistency achieved

Results of remedial action

Vadose zone soil

- Post-remediation soil sampling conducted in August 2018 (4 months after treatment)
- One soil boring completed within each treatment cell
- Concentration reductions exceeded 99%

Parameter	Baseline average	Cell 1	Cell 2	Cell 3	Cell 4
TCE (µg/kg)	6,200	12.1	11.7	8.96	<2
cDCE (µg/kg)	10,090	33.0	117	93.0	<2
VC (µg/kg)	<134	<2	<2	<2	<2



Remedial approach

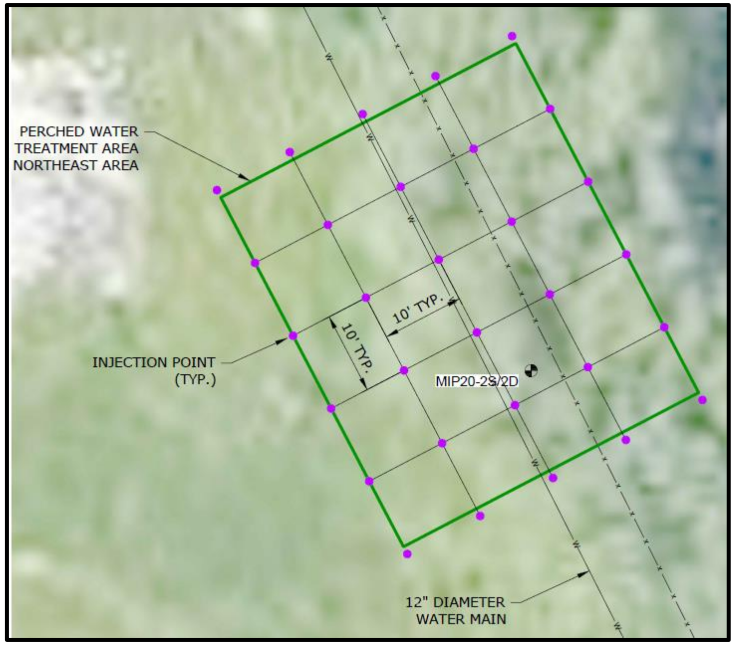
Perched water

- Perched groundwater impacted with cVOCs
- Perched monitoring well contained:
  - TCE: 419,000 µg/L
  - cDCE: 77,800 µg/L
  - VC: 4,950 µg/L
- Goal was to substantially reduce mass flux from perched water to groundwater
- Treatment zone depth interval of 8 to 15 feet below ground surface

Remedy implementation

Perched water

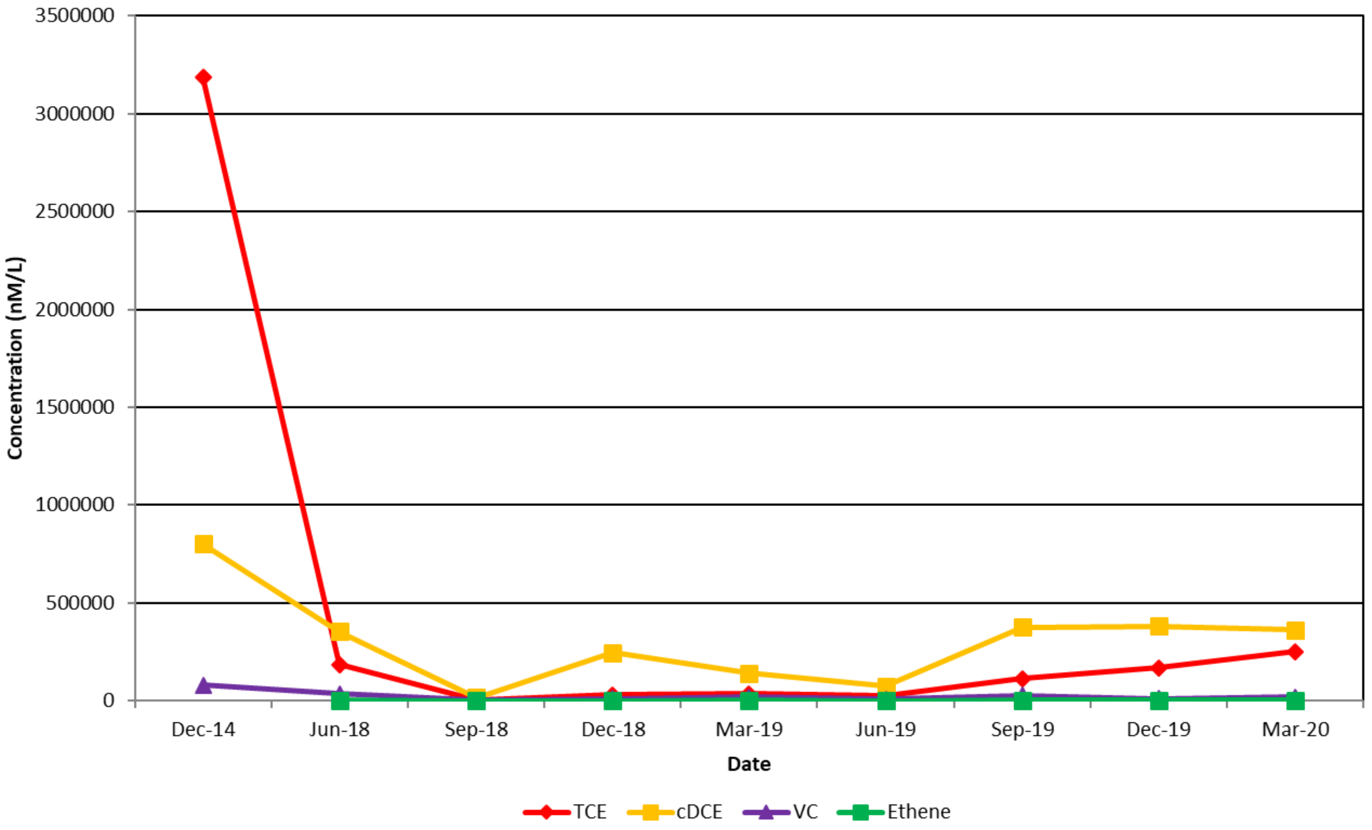
- Perched water injection conducted April 2018
- Volume of reagent injected targeted 7% of pore space in the treatment zone
- 1,400 gallons of reagent with micro-scale ZVI injected on 10-foot centers
- Based on high CVOC concentrations, used robust reagent dose (0.2 lb per cubic foot)
- The injected reagent was composed of 3,000 lbs of 50% ZVI and 50% carbon amendment (lactates and fatty acids)



Results of remedial action

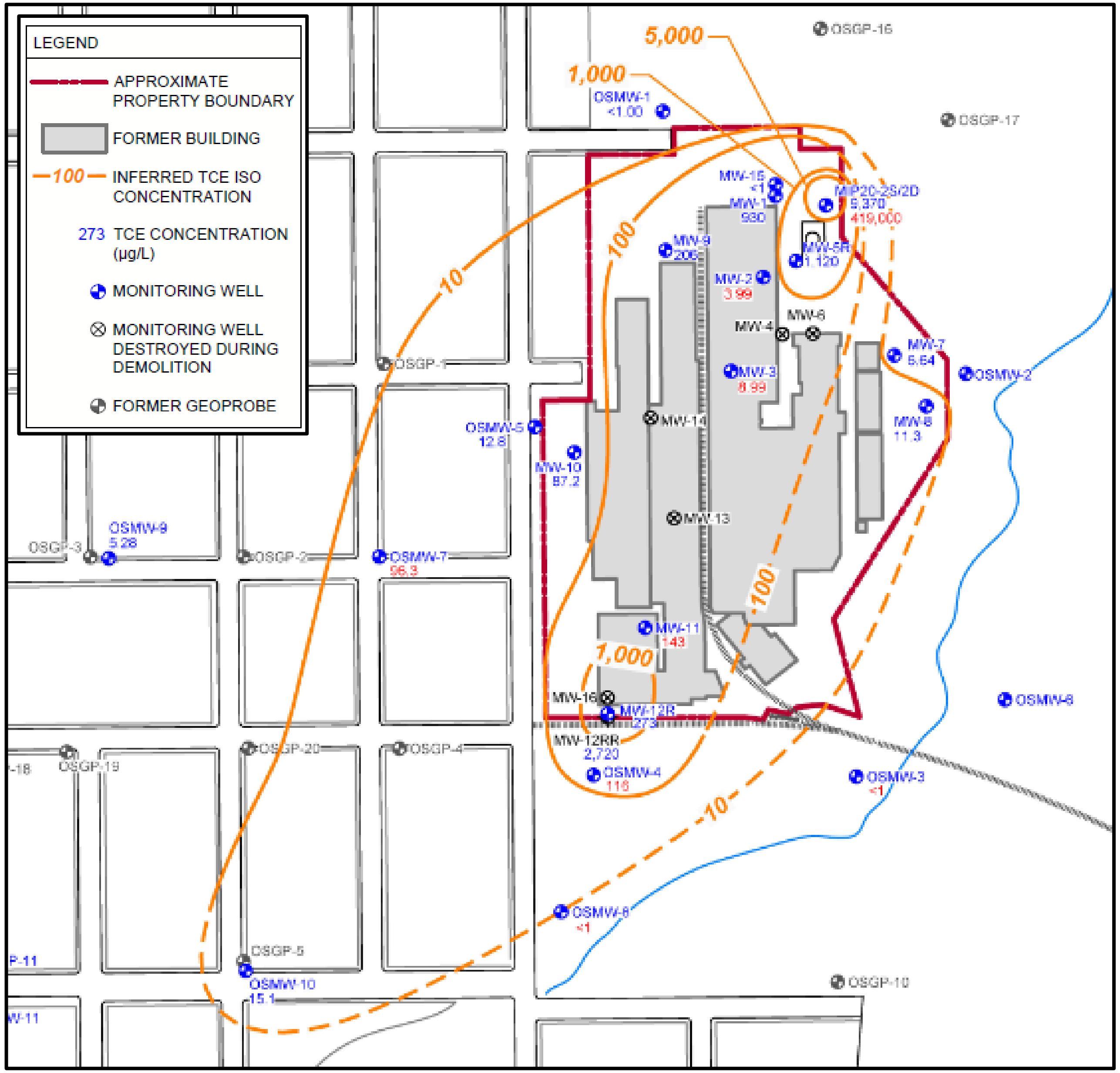
Perched water

- Pre-treatment TCE concentrations indicated likely DNAPL, posing significant challenges to remediation given the common stagnant nature of perched water
- Post-treatment groundwater monitoring data reveal 92% reduction in TCE and 85% reduction in total chlorinated ethenes.
- Geochemical results indicate continued dechlorination of residual CVOCs in perched zone likely. Two years post-injection:
  - 47.4 mg/L TOC
  - 4.37 mg/L methane
  - 23.7 mg/L ferrous iron
  - 1.92 mg/L sulfate



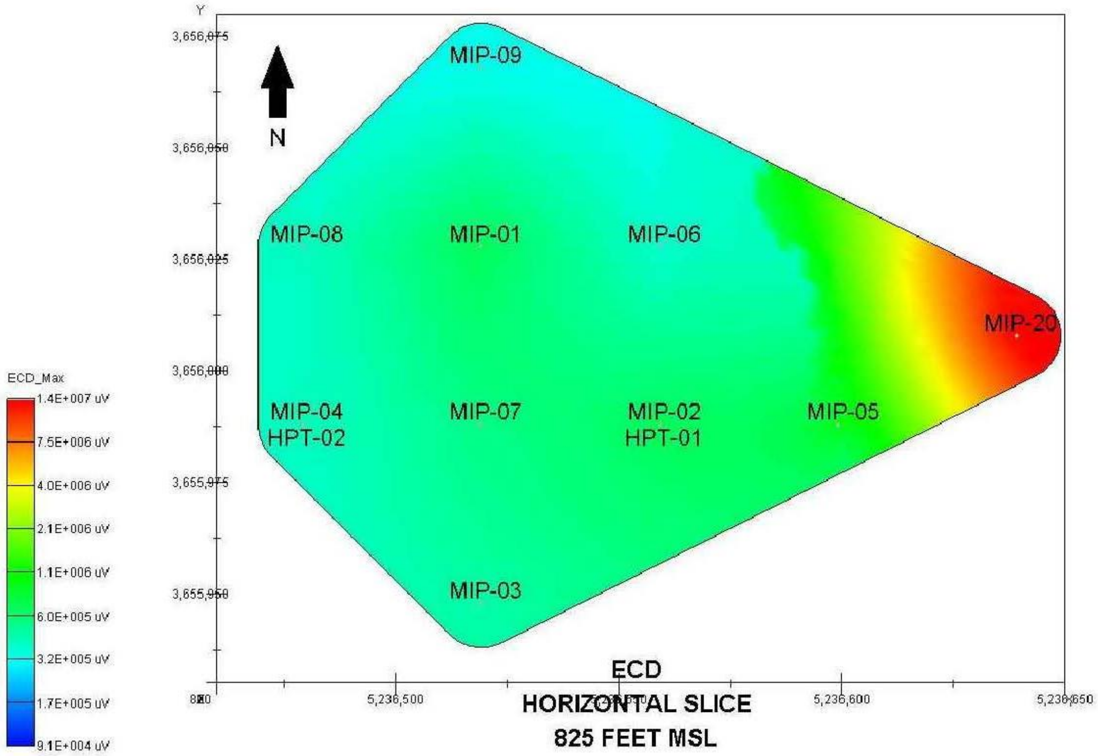
Remedial approach

Groundwater

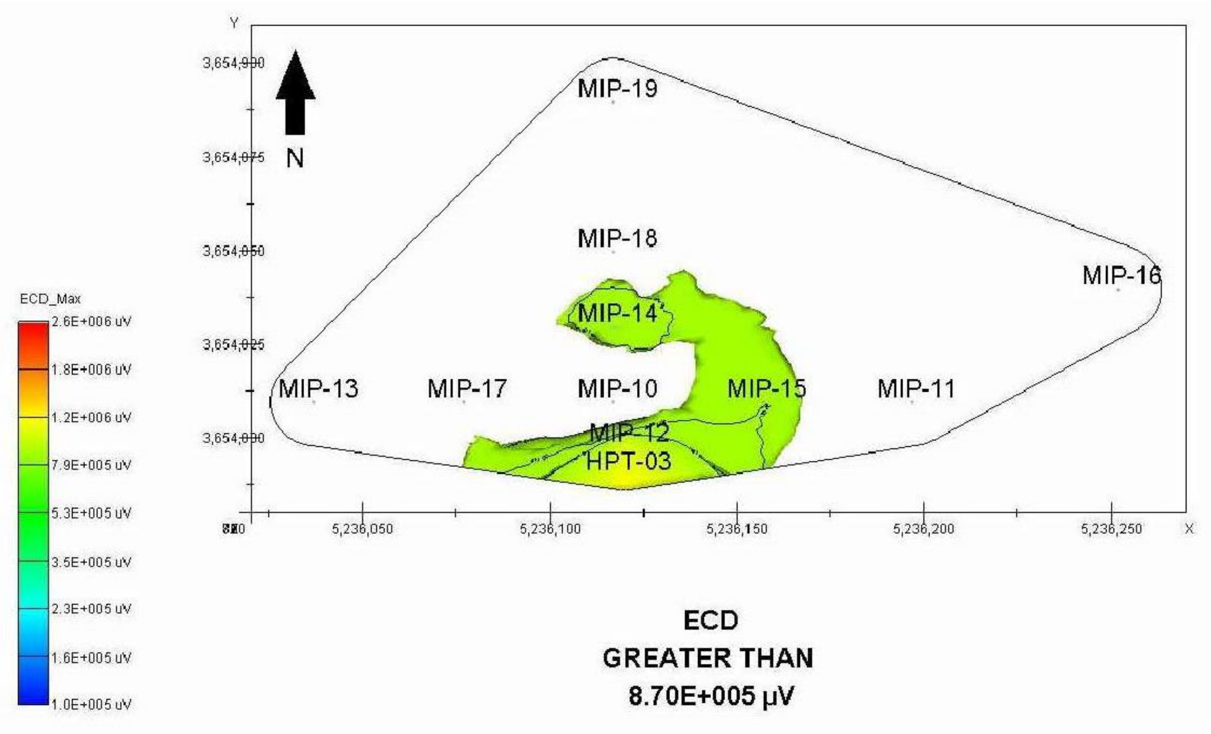


MIP electron capture detector results

Northeast treatment area



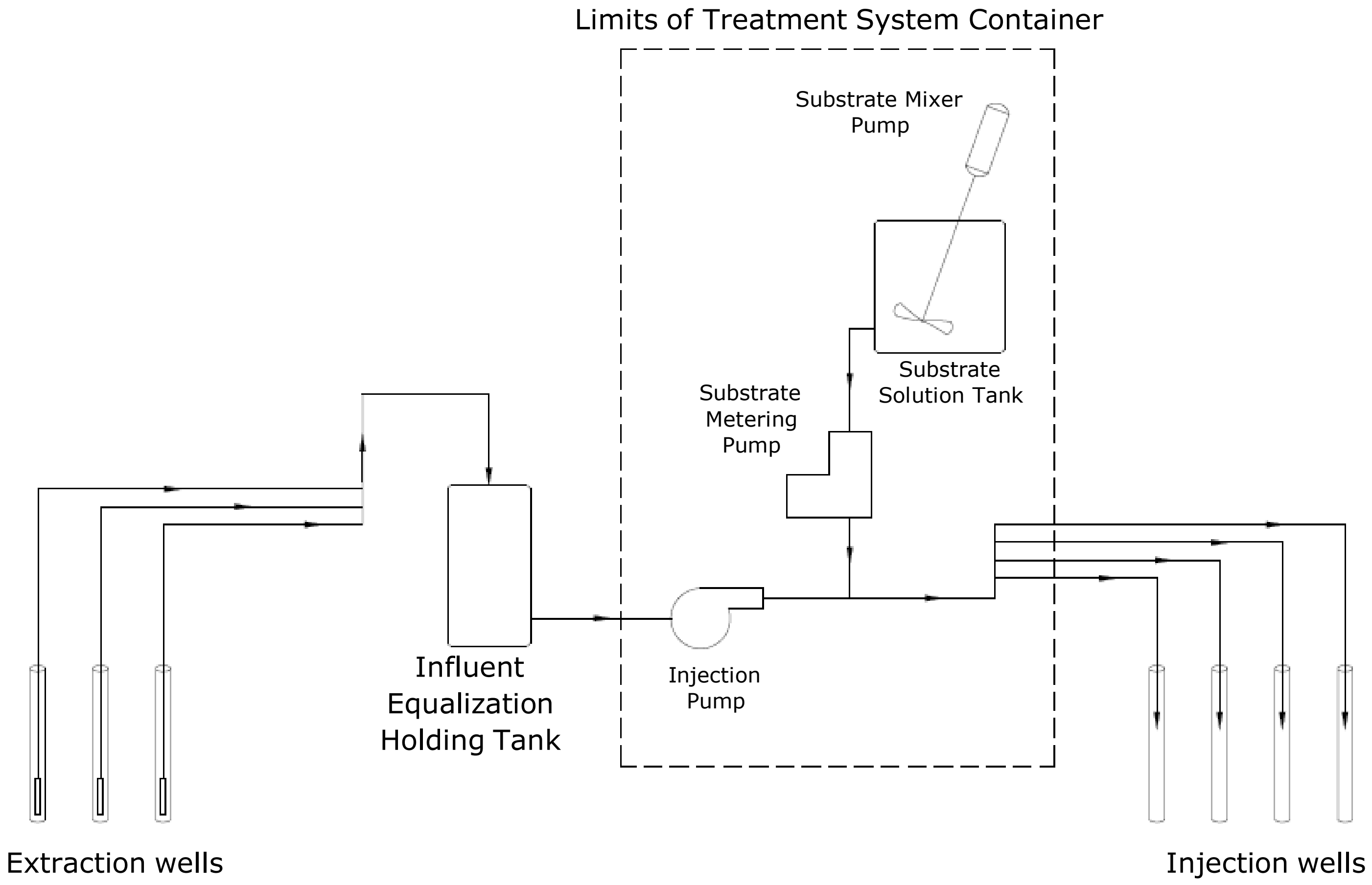
Southwest treatment area



Remedial approach

Groundwater

- Based on large treatment footprints and depths, low hydraulic gradients and permeable soils, we selected a forced advection (groundwater recirculation) amendment delivery approach
- Additives travel under increased gradients and degrade primarily within the recirculation cell
- Can promote better flushing and desorption of high cVOC concentrations than batch injection approaches



Remedial approach

Groundwater: Carbon amendment selection

Ethanol: $C_2H_6O + 5H_2O \rightarrow 2HCO_3^- + 2H^+ + 6H_2$ (12.10/46.1 = 0.26 gH_2/g)

Methanol: $CH_4O + 2H_2O \rightarrow HCO_3^- + H^+ + 3H_2$ (6.05/32.0 = 0.19 gH_2/g)

Glycerol: $C_3H_5(OH)_3 + 6H_2O \rightarrow 3HCO_3^- + 3H^+ + 7H_2$ (14.11/92.1 = 0.15 gH_2/g)

Sucrose/lactose (whey): $C_{12}H_{22}O_{11} + 25H_2O \rightarrow 12HCO_3^- + 12H^+ + 24H_2$ (48.38/342 = 0.14 gH_2/g)

Fructose/glucose (molasses): $C_6H_{12}O_6 + 12H_2O \rightarrow 6HCO_3^- + 6H^+ + 12H_2$ (24.19/180 = 0.13 gH_2/g)

These equations show that:

1. The highest theoretical yield of hydrogen is from ethanol (0.26 g H_2/g) and methanol (0.19 g H_2/g)
2. The lowest acid-producing fermentions are from ethanol and methanol (1 mole acid/3 moles H_2)

Remedial approach

Groundwater: carbon Amendment selection

- Based on evaluation of several electron donors, selected a new product that contains glycerol and ethanol as 90% fermentable material
- Also contains inorganic N&P nutrients and vitamin B12 (2.5 mg/kg) for rapid microbial growth
- Efficient electron donor in terms of cost per pound of hydrogen produced (3X sodium lactate)
- Ethanol reduces amendment viscosity to enhance pumpability under cold weather conditions (63 Centipoise at 0 degrees C)
- Ethanol inhibitory at high concentrations, reducing fouling of injection wells while stimulating microbial development at distance from the injection wells

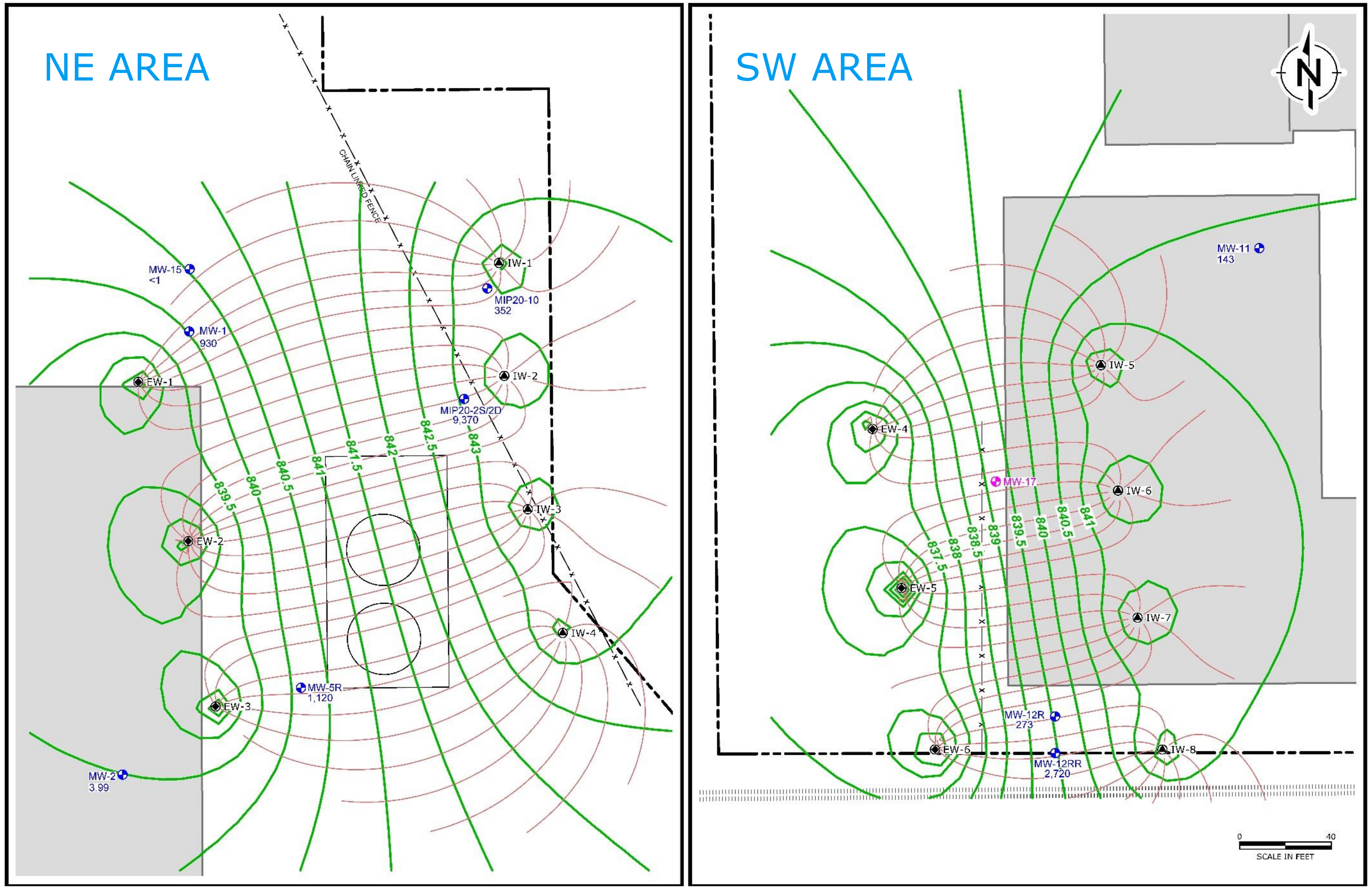
Remedial design

Groundwater: Estimated carbon Amendment dosage

Parameter	Value
Impacted groundwater volume	1.6 M gallons
Groundwater seepage velocity	130 feet/year
Safety factor	5
Hydrogen demand for reduction of aqueous electron acceptors	1,720 lbs
Hydrogen demand for reduction of sorbed electron acceptors	52 lbs
Total hydrogen demand	1,770 lbs
Carbon substrate required	24,900 lbs

Remedial design

Groundwater capture zones



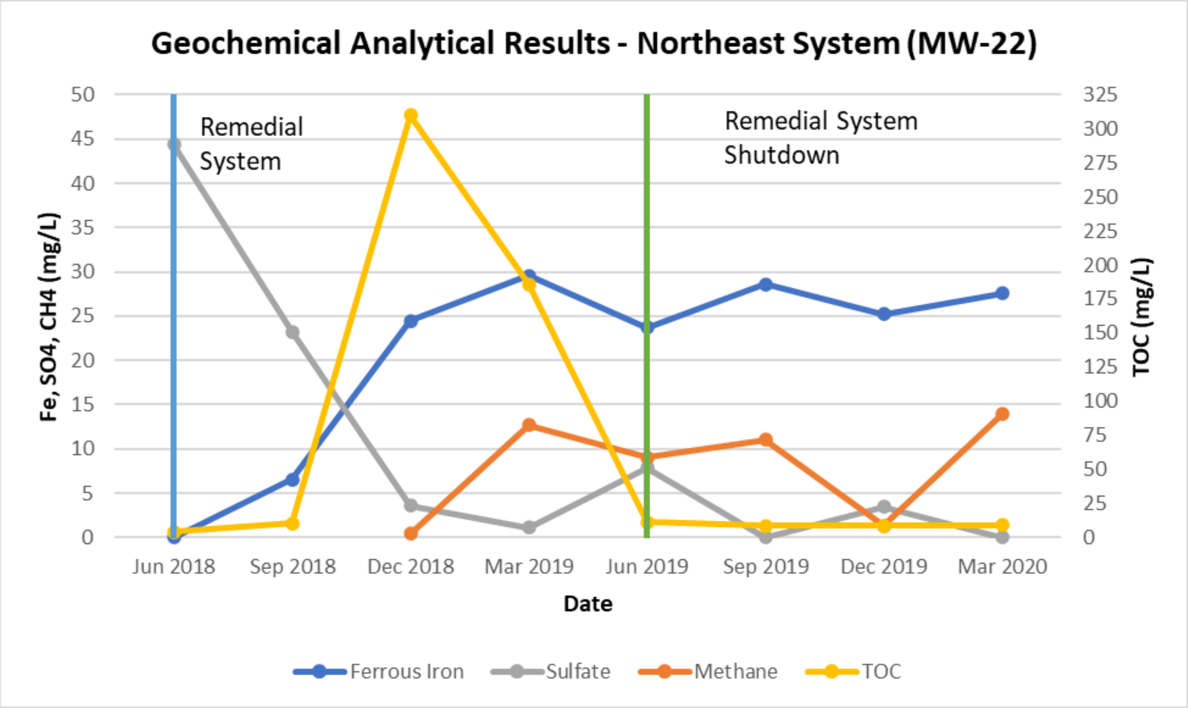
Remedy implementation

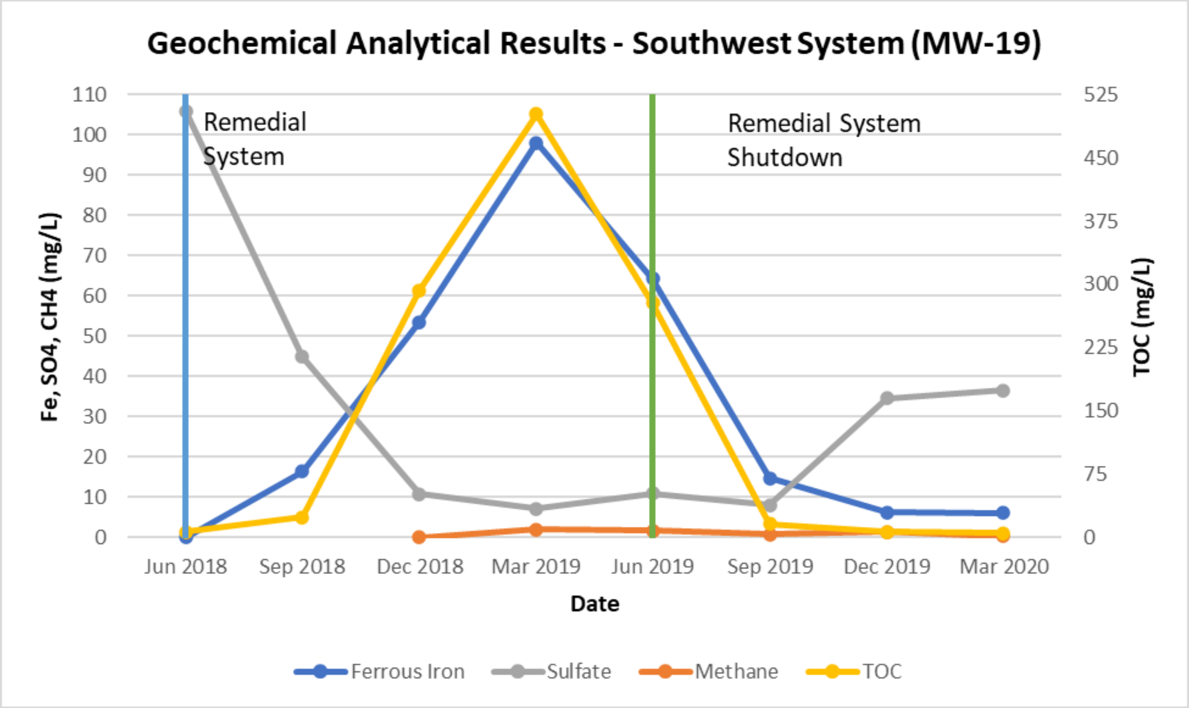
Groundwater: injection program

- Injected solution: glycerol, ethanol, vitamin B12, inorganic nutrients, water
- Monthly injection program:
  - 3,000 lb per month
  - 4 days injection/recirculation
  - 26 days recirculation only to reduce injection well biofouling
- Pumping rate: ~11.2 gallons per minute, based on previous pumping tests, groundwater capture zone analysis and post-startup groundwater elevations

Results of remedial action

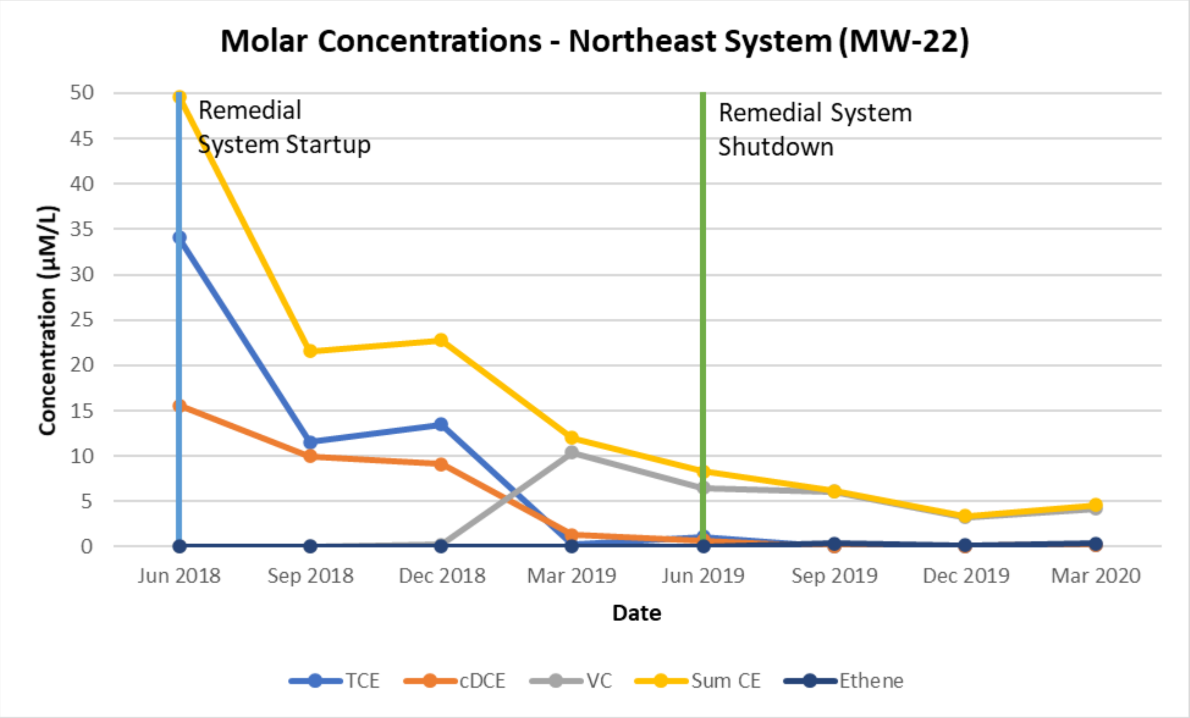
Groundwater

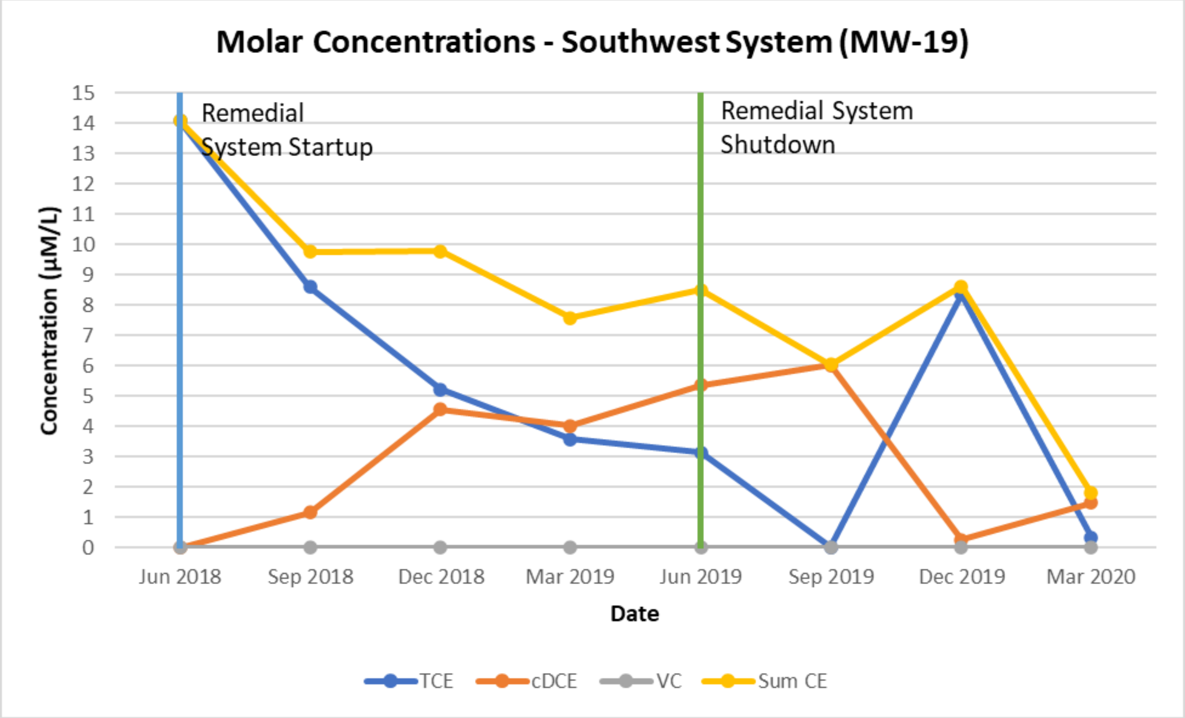




Results of remedial action

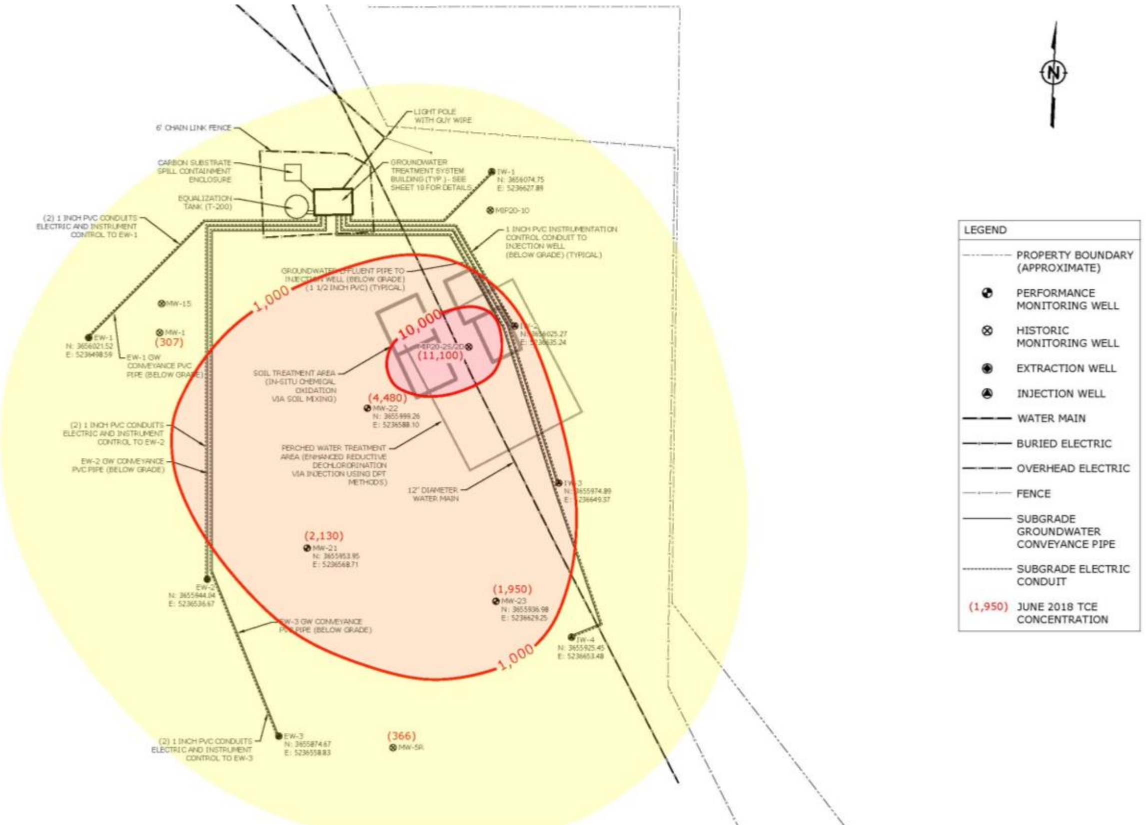
Groundwater



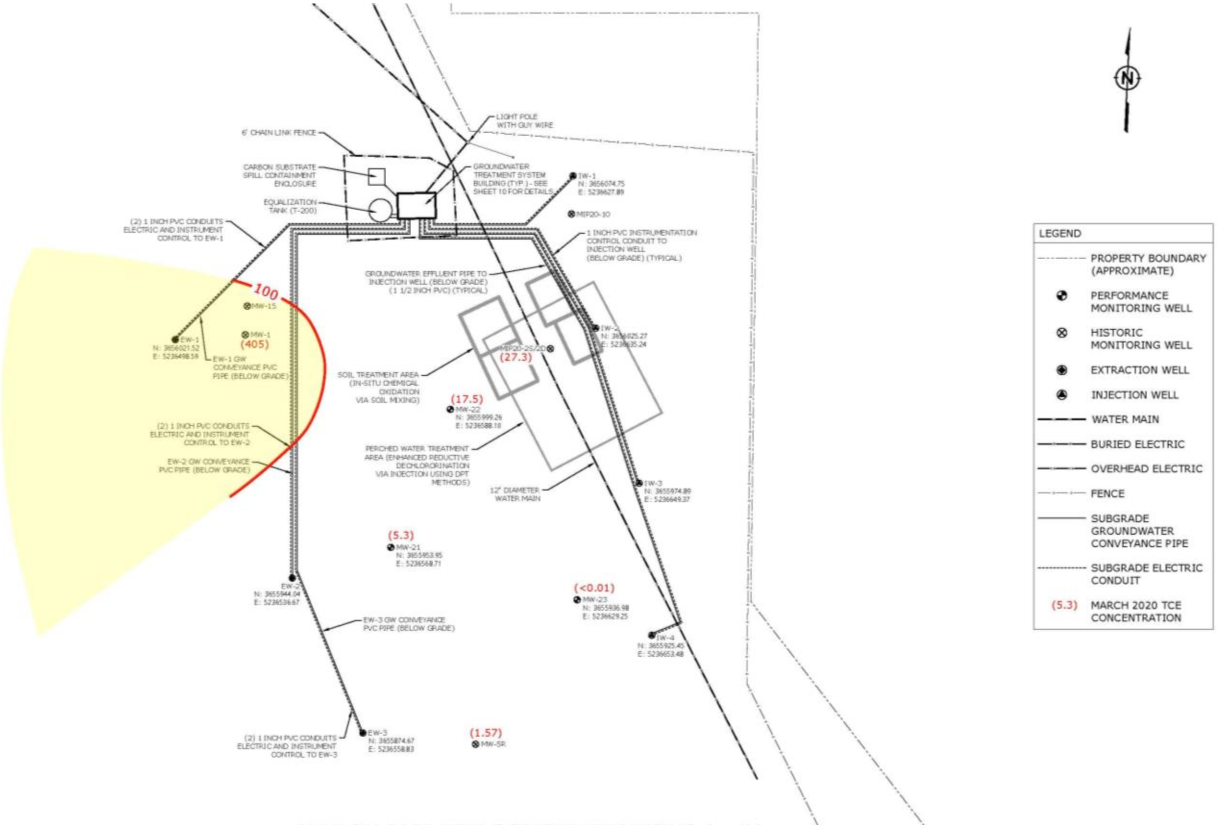


Results of remedial action

Groundwater



JUNE 2018 TCE CONCENTRATIONS (µg/L)



MARCH 2020 TCE CONCENTRATIONS (µg/L)

Results of remedial action

Groundwater

- Most impacted well (NE area) contained 11,000 µg/L TCE at system startup in June 2018 but declined to 47 µg/L within 3 months (September 2018)
- Rebound has not been observed as the TCE concentration at this well 9 months after system shutdown (March 2020) was 27 µg/L
- Detected presence of ethene in both areas starting 9 months after system startup indicates development of *Dehalococcoides (Dhc)* without bioaugmentation
- Methane concentrations remain high at this well (18,000 ug/L) 9 months after system shutdown
- Based on these favorable findings, the USEPA granted approval of a probationary shutdown of both systems in June 2019 (12 months after system start-up)

Takeaways
Groundwater

- Addition of ethanol/glycerol-based electron donor via forced advection resulted in rapid and widespread anaerobic conditions at an otherwise aerobic site
- Based on the favorable post-shutdown groundwater data, USEPA granted approval of final remedial system shutdown in May 2020, after completion of only 1 year of the initially-estimated 3-year operational timeframe
- Both remedial systems have been removed, and 2 downgradient property boundary wells remain to monitor any residual CVOC concentrations via periodic sampling
- We used rapid-release electron donors; however, enhanced anaerobic dechlorination can result in sustained treatment, likely due to accumulation of biomass and reduced iron minerals that support future dechlorination
- Such sustained treatment reduces the likelihood of rebound in CVOC concentrations

Acknowledgments

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Thank you

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