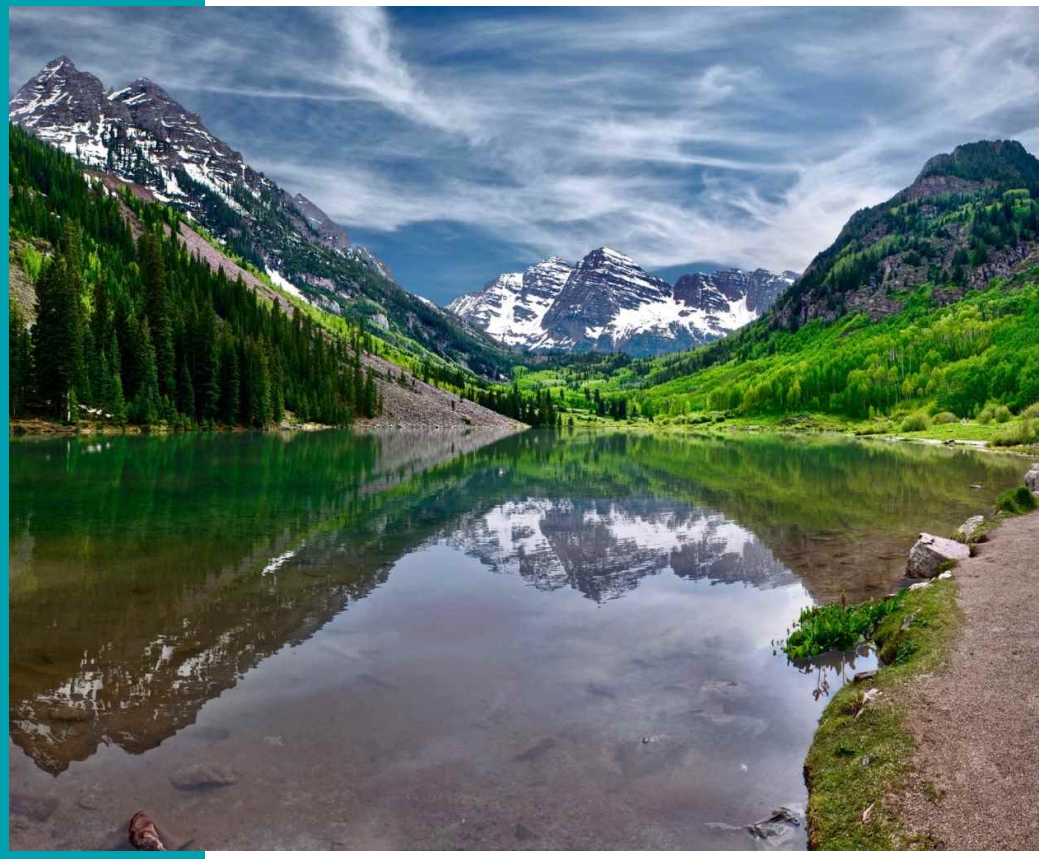
Geosyntec consultants

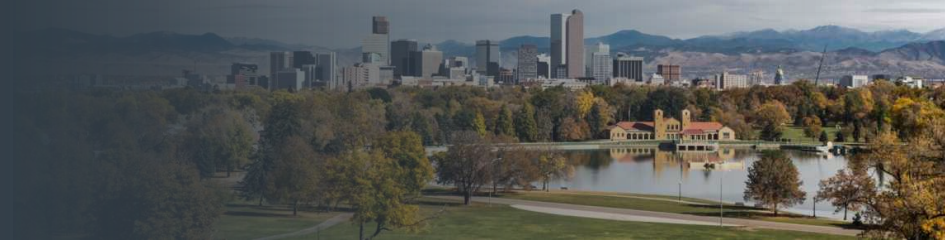
CREATIVE THINKING
EXCEPTIONAL SOLUTIONS

Full Scale Application of ERD following ISCO/S-ISCO® for Treatment of NAPL Pharmaceutical Waste Mixture

Leah MacKinnon



Authors



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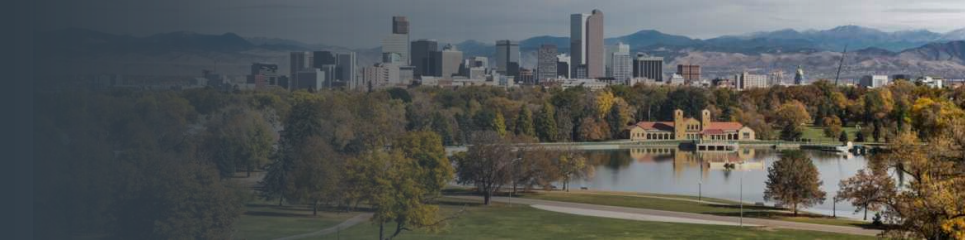
KÆRGÅRD PLANTAGE – WASTE RELEASED



286,000 m^3 of wastewater legally released into 6 waste pits

60,000 metric tons of salts and organics

Complex mixture of contaminants in soil and groundwater, including residual NAPL

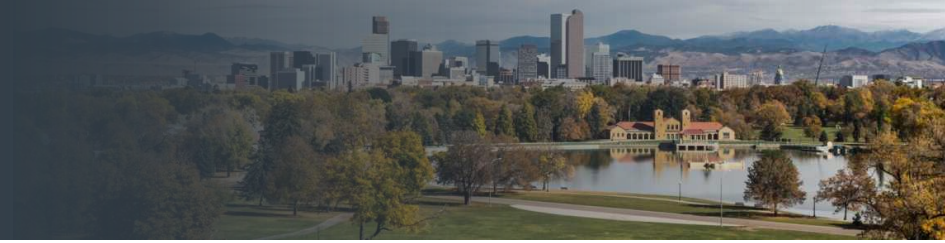
Site contaminants: sulfonamides, barbiturates, aniline, pyridine, chlorinated solvents, fuel hydrocarbons, mercury, cyanide, lithium and other compounds.

Goal:

Reduce risk to ecological and human receptors from groundwater discharging into the North Sea, by reducing contaminant mass flux from waste pits

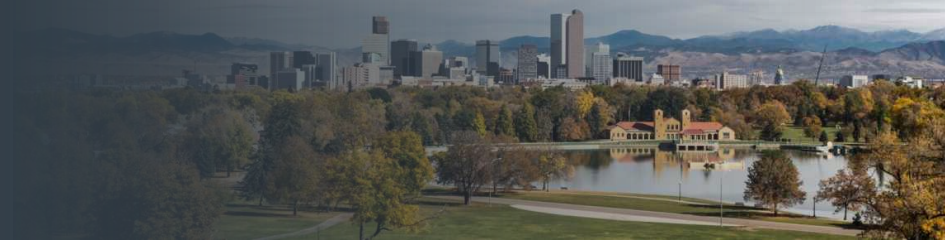
Figure: COWI, 2020

Conceptual Site Model



Core Pit 3 – Layer 2 – geology is beach sand and gravels, with some silt/clay
Very low buffer capacity and natural organic carbon content

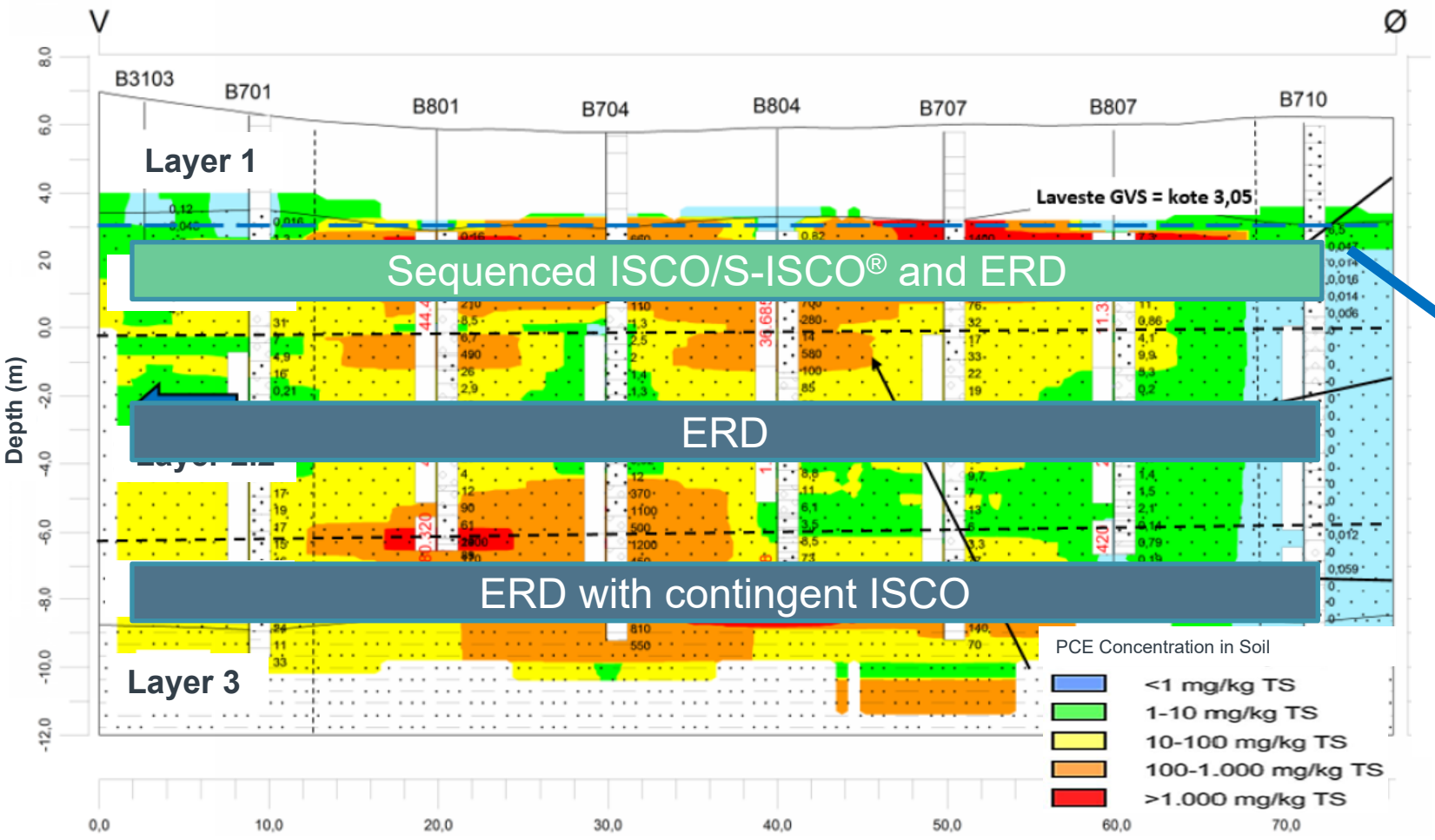
Staged Approach for Remedy



1. 2008-2011 – Treatability and Field Pilot tests of ISCO and ERD
2. 2017- Current – Full-Scale Demonstration Project (Pit 3) and Remedy Implementation (Pit 1, 2, and 4)
    - 2017-2019: CSM update in each Pit
    - Pit 3: 2018 – 2020: ISCO application & Optimization → 6 Events
    - Pit 3: 2021 – Transition to S-ISCO® → 2 Events
    - Pit 3: Late 2021/Early 2022 – Current: ERD
    - Pits 1, 2 and 4 - 2019 – Current: ISCO/S-ISCO®

1 - S-ISCO, E-Mulse 3 and 145 as proprietary, patented technologies owned by Ethical Solutions, LLC (dba EthicalChem)

CSM Update and Remedy Strategy – Pit 3



Pit 3 Treatment Zone:

- Layer 2 Volume: 11,615 m^3
- PCE Mass: ~ 4.1 ton
- TPH Mass: ~ 11 ton
- Groundwater velocity: ~1 m/day
- VOC Flux: 180-475 kg/yr
- TPH Flux: 85-220 kg/yr

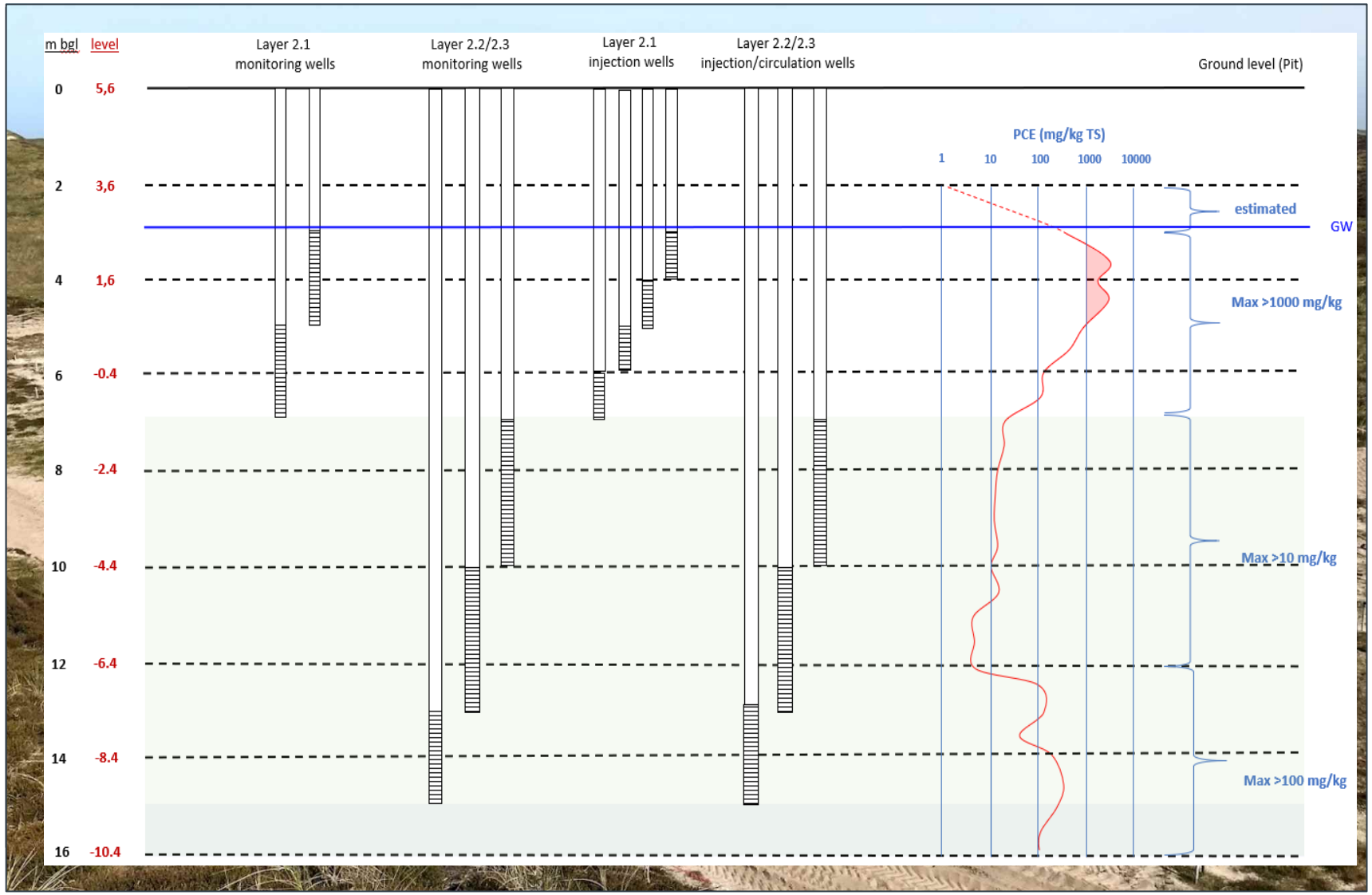
Design Basis:

- Mixed NAPL in layer 2.1
- Lower concentrations layers 2.2 and 2.3
- Limited NAPL Layer 2.2

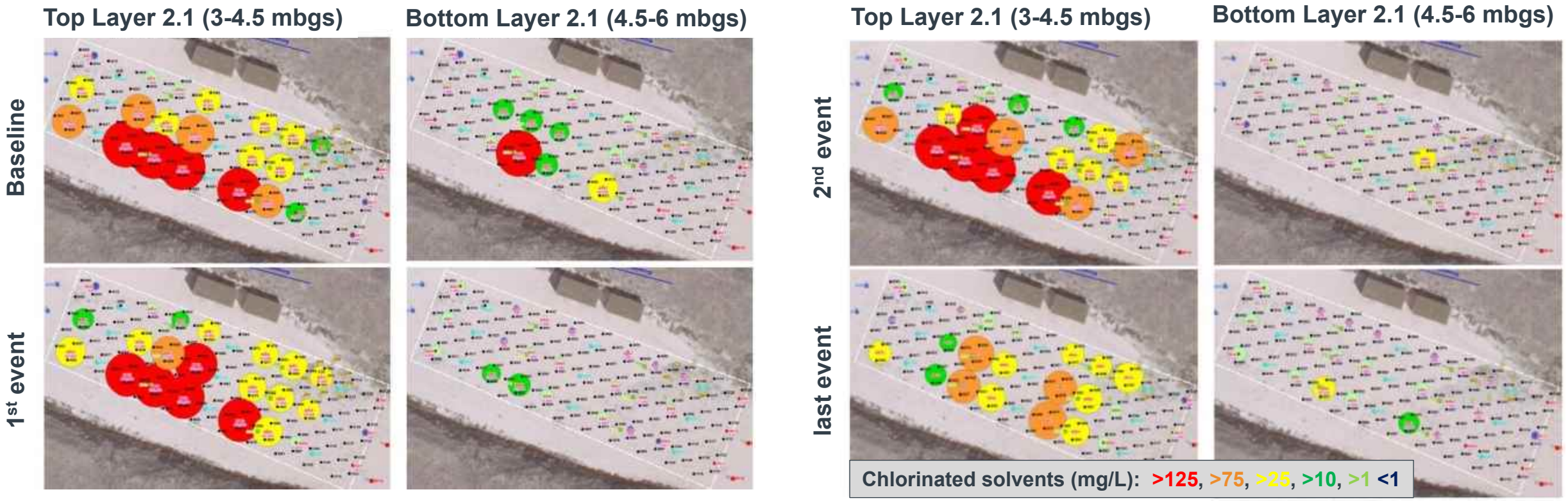
Full-Scale Field Demonstration – Pit 3

Pit 3

~250 wells



ISCO/S-ISCO® RESULTS - PIT 3

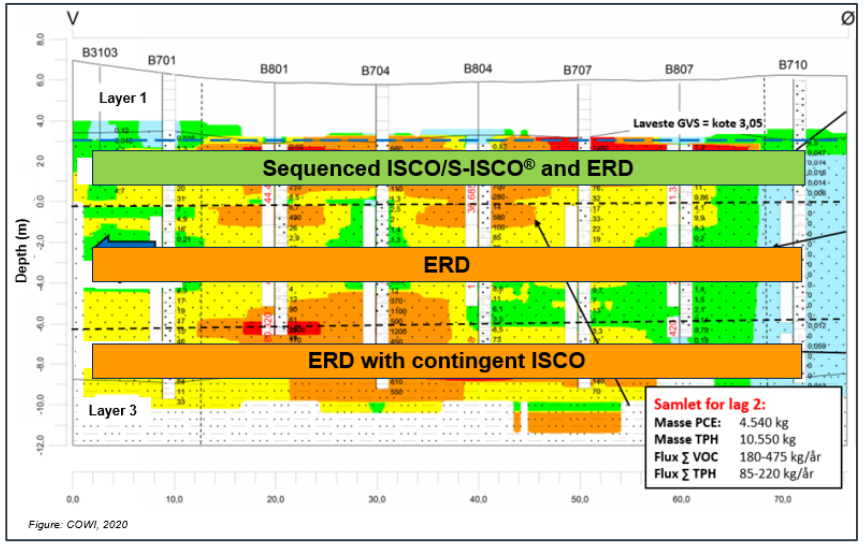


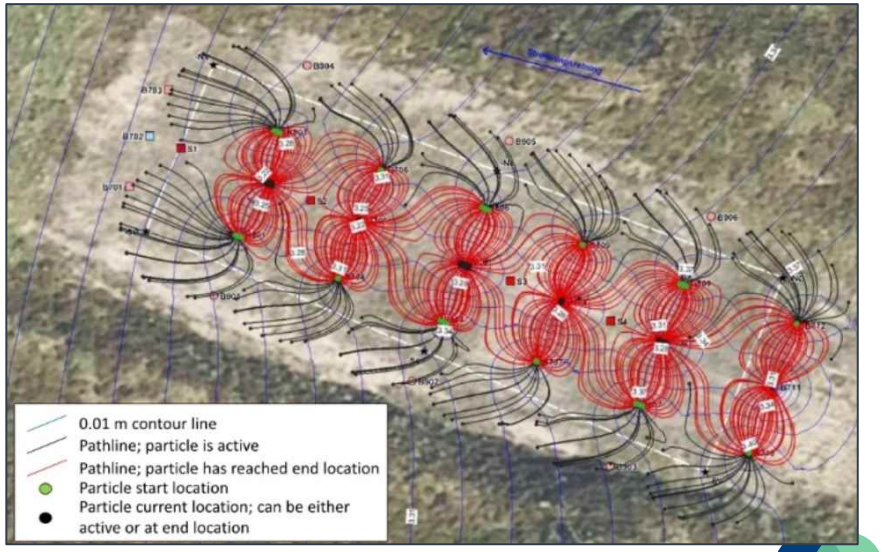
Significant decrease in TPH and PCE aqueous concentrations, especially deeper interval

ISCO alone not effective where significant NAPL is present → S-ISCO®

Enhanced Reductive Dechlorination (ERD)

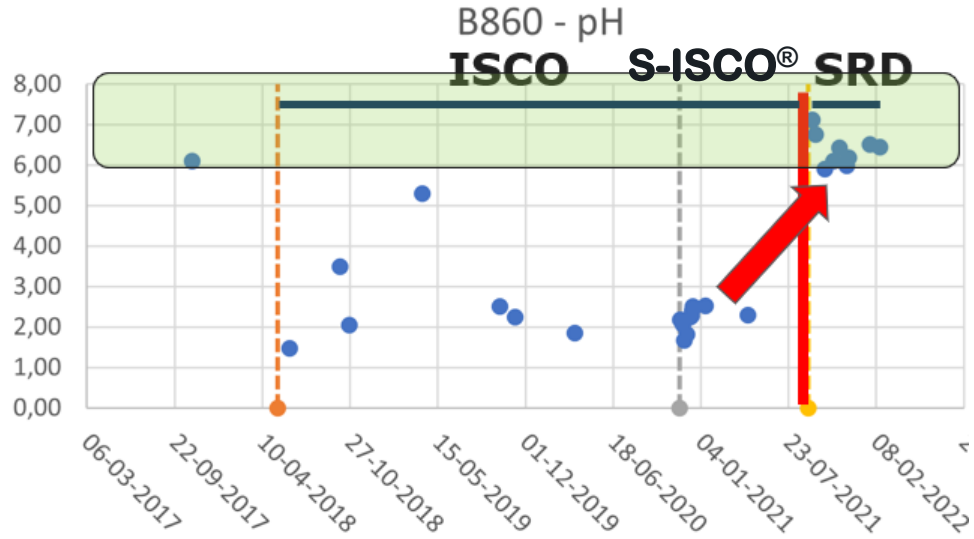
- Polishing step following ISCO/S-ISCO® injections in Layer 2.1 (passive, batch injection)
- Stand alone remedy in Layers 2.2 (recirculation) and 2.3 (passive)
- Design questions for ERD:
  - Effect of low pH, high ORP, surfactant?
  - Is residual NAPL treated?
  - How are amendment delivery, retention and longevity effected by high groundwater velocity?
- Implementation involved two stages:
  1. Conditioning aquifer after ISCO with pH buffer, soluble electron donors, before bioaugmentation
  2. Addition of long-term electron donors, buffers, bioaugmentation using KB-1® Plus (low pH culture)

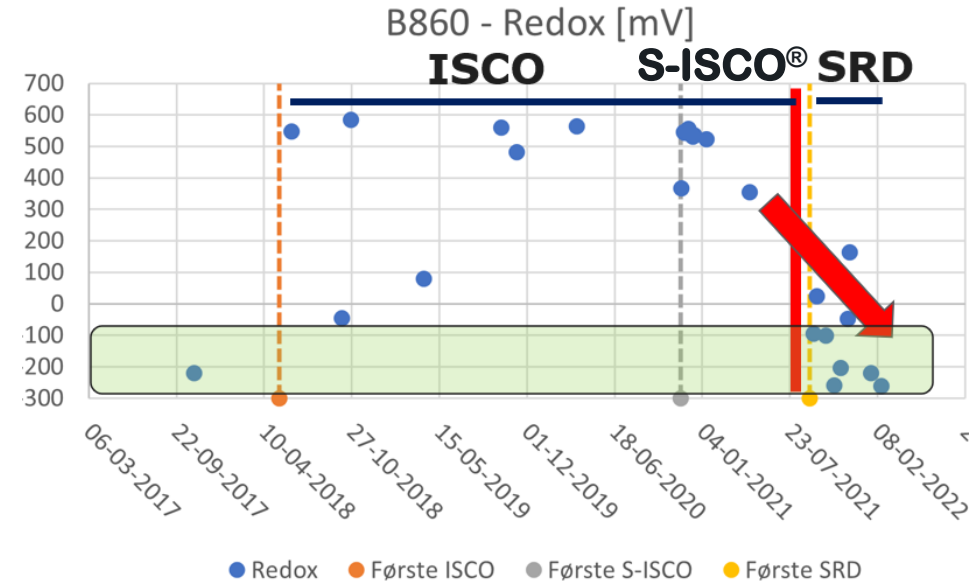




ERD Transition - Post ISCO/S-ISCO® - Pit 3

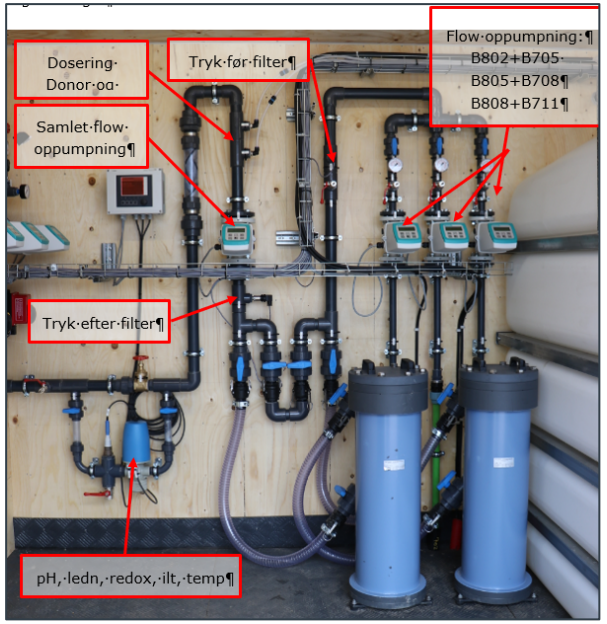
Initial Post-ISCO Conditions	Solutions
pH <2	Successfully raised to neutral using soluble buffer (bicarbonate) and maintained with long-term buffer (Neutral Zone)
Redox >500 mV	Effectively decreased redox and maintained anaerobic conditions by adding soluble (lactate) and long-term electron donors (EVO)
Sulfate >1,000 mg/L	Time interval between ISCO/S-ISCO® and ERD of ~ 6 months to flush sulfate out of the ERD zone. Electron donor creates sulfate reducing conditions.
Residual NAPL	ERD using KB-1® Plus (low pH) was effective to degrade relatively high concentrations of PCE, TCE and cDCE within months, followed by full degradation to ethene.





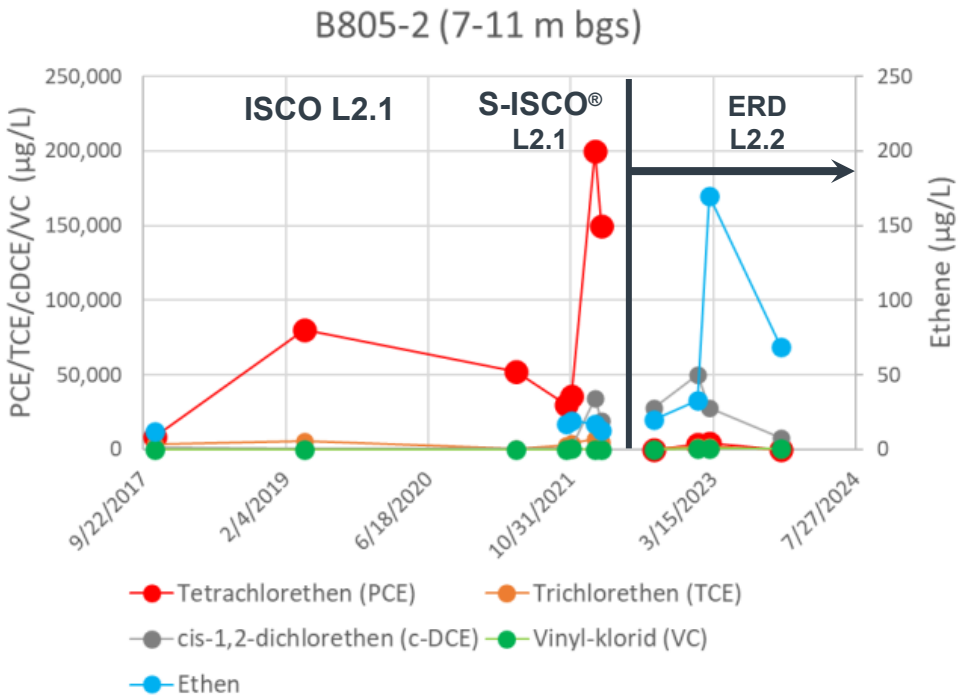
Layer 2.2 – Operation

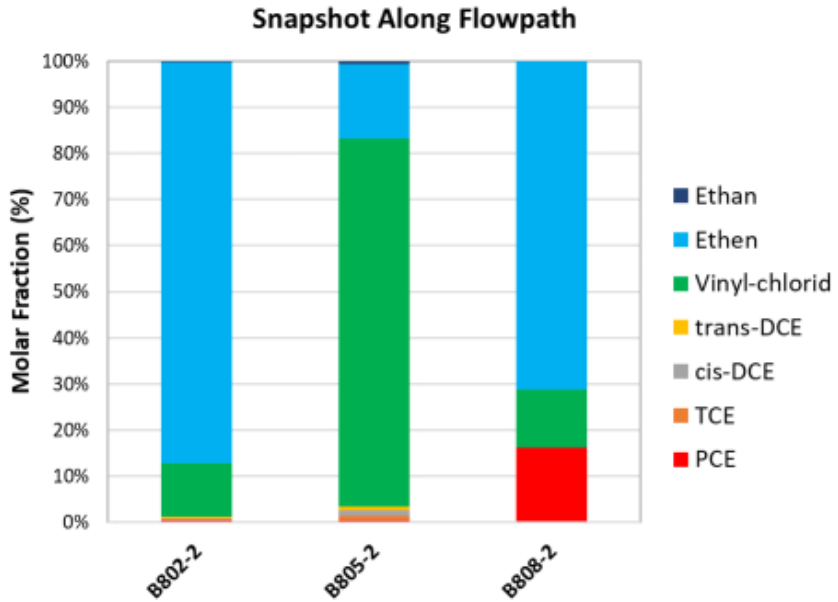
- Recirculation used in Layer 2.2 to transition to anaerobic / near-neutral pH before transition to passive operations
- Note - high sulfate from persulfate and naturally present iron
  - Reduced minerals → abiotic reduction pathways
  - Some geochemical fouling of recirculation equipment and wells
  - To manage fouling, completed periodic operation



ERD Results – Pit 3 – Layer 2.2

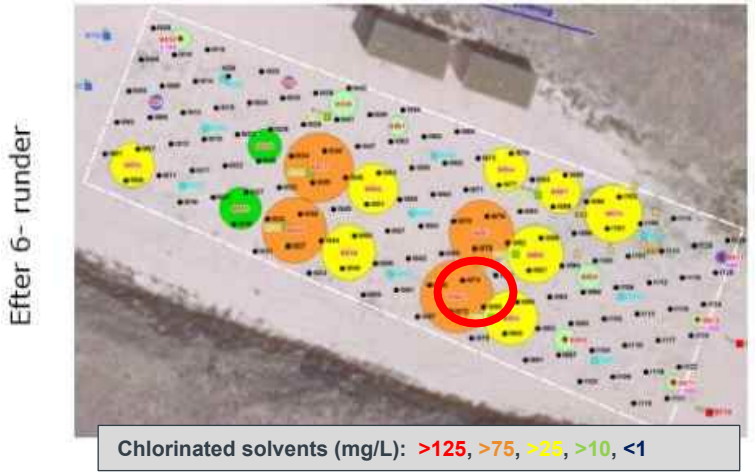
- Complete degradation of PCE to ethene observed within 8 months
- cis-DCE becomes dominant degradation product, followed by ethene concentration
- General increase in daughter products along flow path

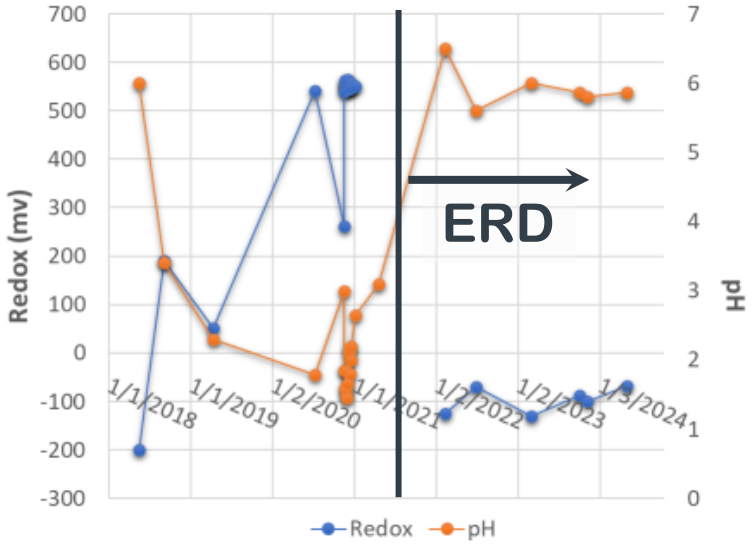


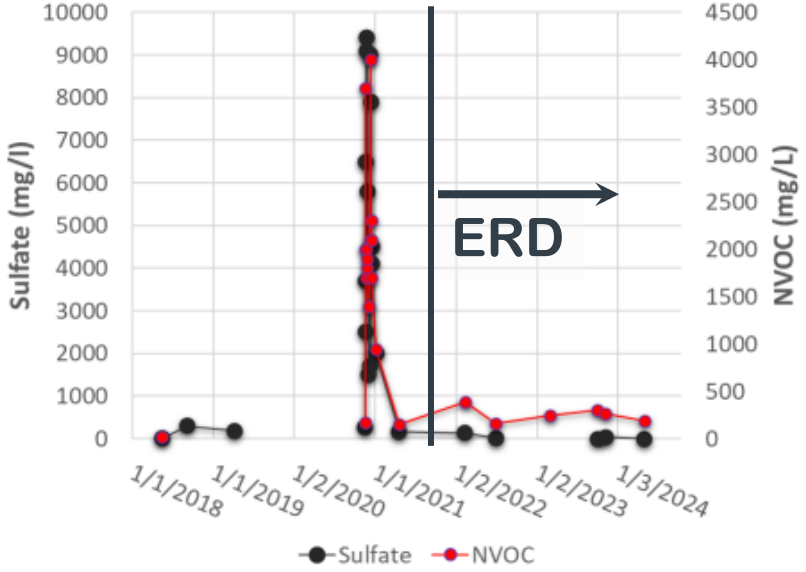


Layer 2.1 - Geochemical Conditions

- Initial injection - 126 m3 lactate and bicarbonate solution
- Second injection - 90 m3 3% EVO solution with 1.4 ton Neutral Zone, 0.5 ton bicarbonate and KB-1® Plus (low pH culture)
- pH increases above 6, ORP decreases to ~-100 mV
- Sulfate (donor demand) reduction
- High TOC/NVOC during S-ISCO in part from surfactant – food source?
    - Remained between >250 mg/L during ERD



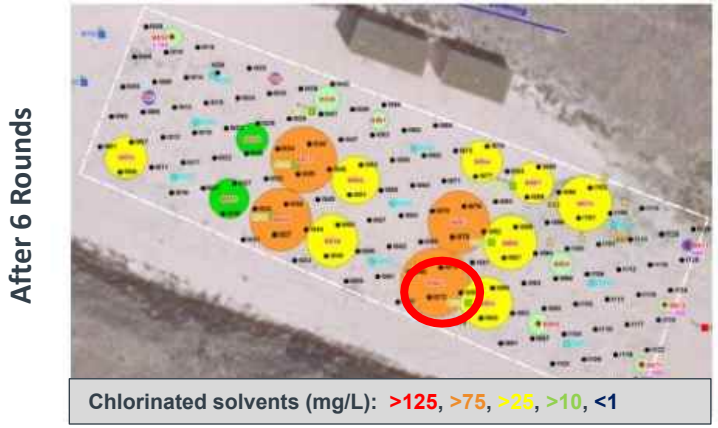


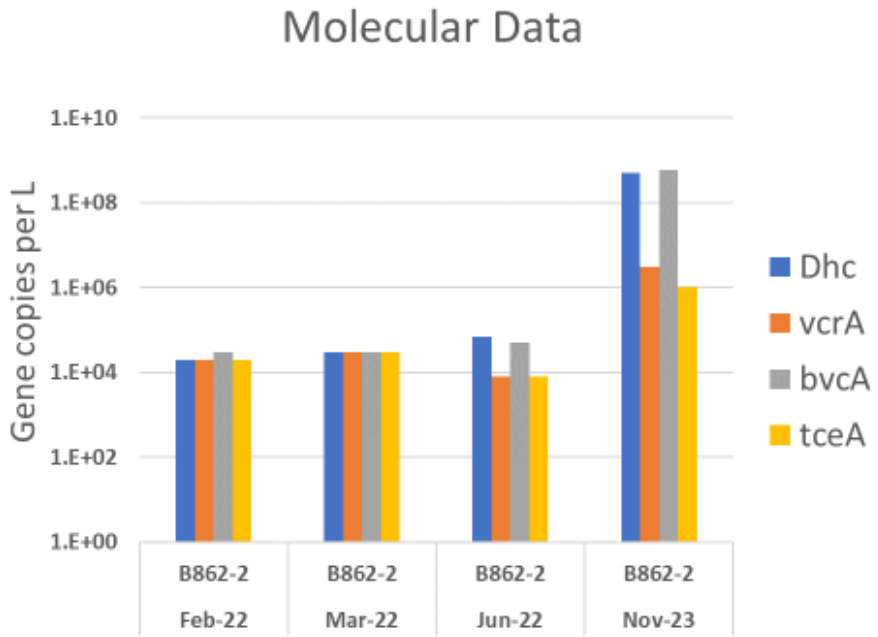


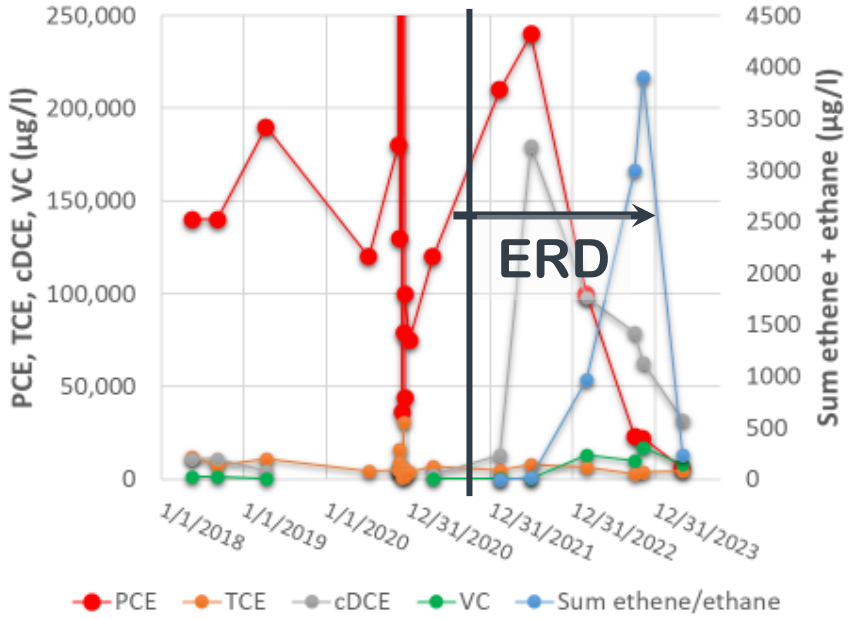
Layer 2.1 - Molecular Growth, CVOC Treatment

With establishment of anaerobic conditions

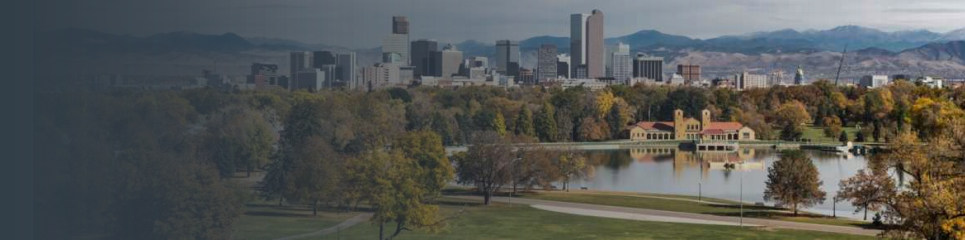
- Dhc, vcrA, bvcA, tceA increase over time at multiple wells
- Complete degradation observed





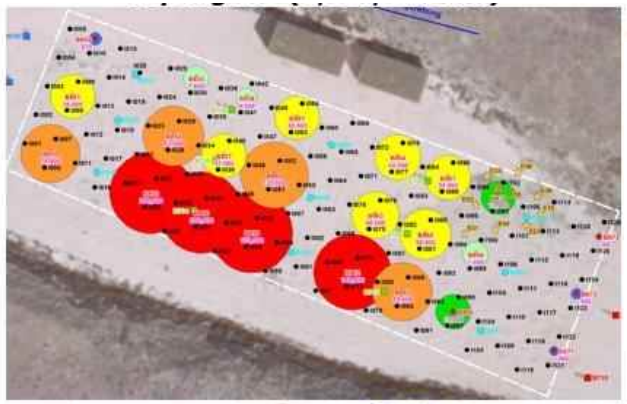


Overall Treatment – Top Layer 2.1

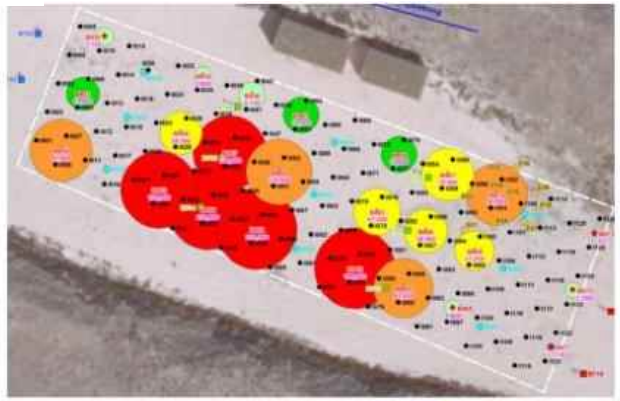


Top Layer 2.1 (3-4.5 mbgs) ISCO/S-ISCO

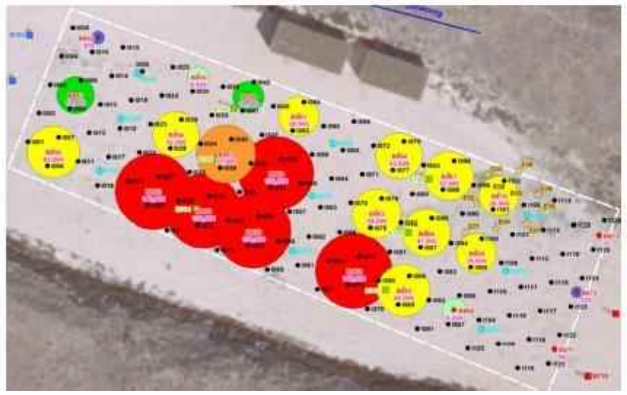
Baseline



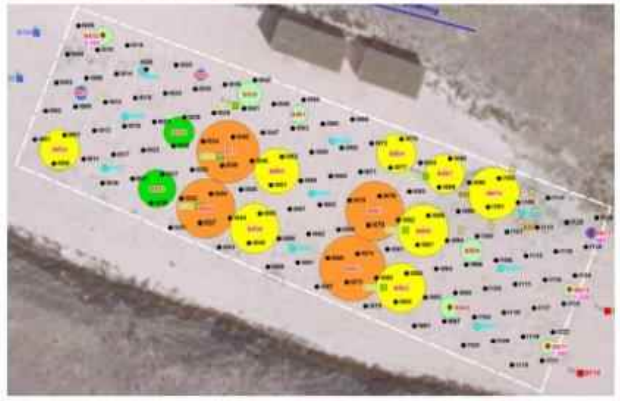
After 2 Rounds



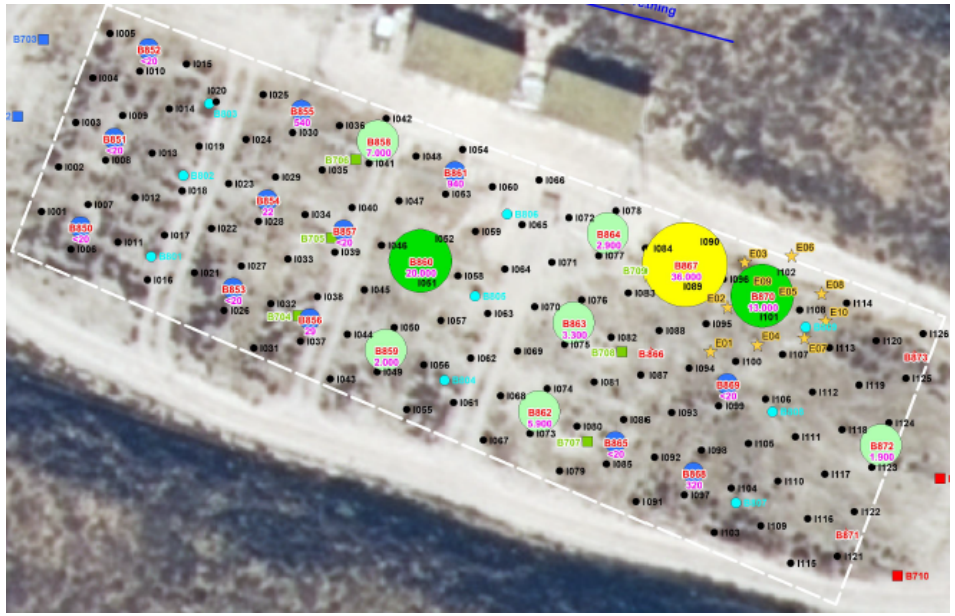
1st event



After Last Event

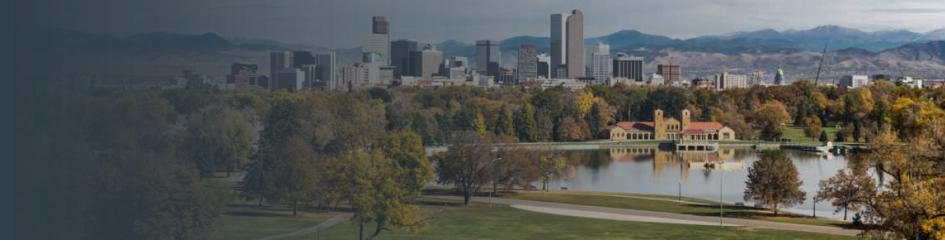


May 2024: Top Layer 2.1, After 2.5 Years of ERD



Chlorinated solvents (mg/L): >125, >75, >25, >10, >1, <1

Final Considerations



- Importance of staged approach and flexibility

  → Allows for refinement to technical approach and optimization as you go

- Low pH, redox and high sulfate concentrations following ISCO/S-ISCO ® must be managed to implement subsequent ERD
- Establishment of ERD after ISCO/S-ISCO® achieved within 6-12 months after last injection of oxidants, 2.5 years later conditions are still favorable although some local buffer/donor addition spot addition possible in 2024
- ERD can treat very high concentrations of PCE /residual mass under ideal conditions
- The demonstration project has provided important input for the final design of the full-scale remediation in the other Pits

Questions?

Region Syddanmark

Geosyntec consultants

COWI