Application of a Combined Technology for the Treatment of an Aerobic Aquifer Impacted with Carbon Tetrachloride and Chloroform

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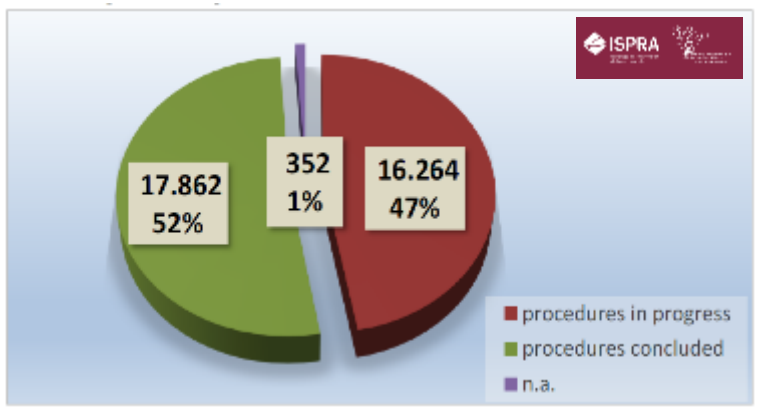
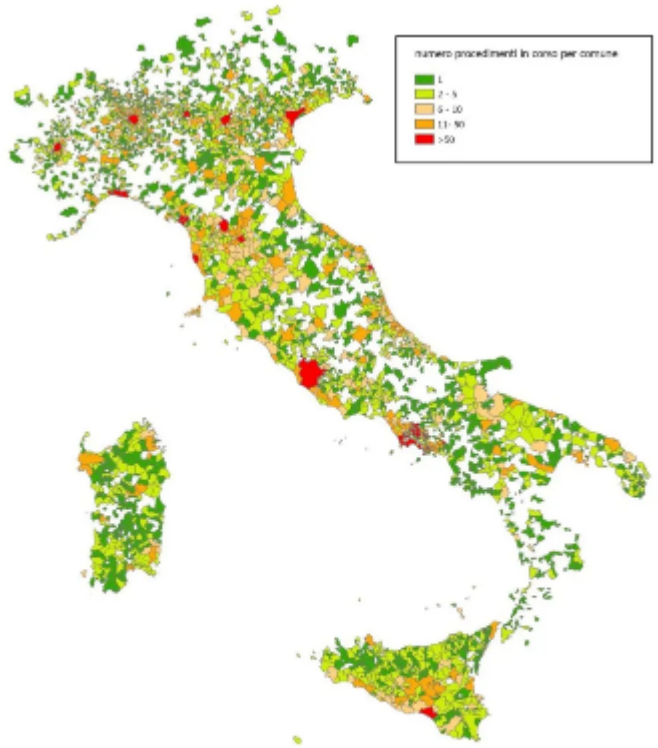
Discussion of Contaminated Sites in Italy

- Below the total number of sites subjected to an administrative procedure of local contamination management according to Legislative Decree n. 152/06.
  - The dataset covers all the procedures collected in regional registers in the period up to 2020, including those started and/or completed under the previous legislation (DM 471/99).



- Total number of contaminated sites was 34,478.
- In particular, 16,264 sites had ongoing procedures, and 17,862 ones reached the site closure.



Number of OPEN contaminated site proceedings for each IT Municipality

(*ISPRA - Italian Institute for Environmental Protection and Research, 2020*)

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Chlorinated Compound Site Remediation Activities

Demand for an in-situ remedy for many reasons

- Need for solution in areas that cannot be excavated – *i.e., active chemical plant*
- Existing in-situ remedies unsuccessful – *i.e., physical remedial approach such as P&T, SVE, other common* reagents, etc.
- Large portfolio of sites needed a safe and cost-effective approach that could be implemented throughout the country

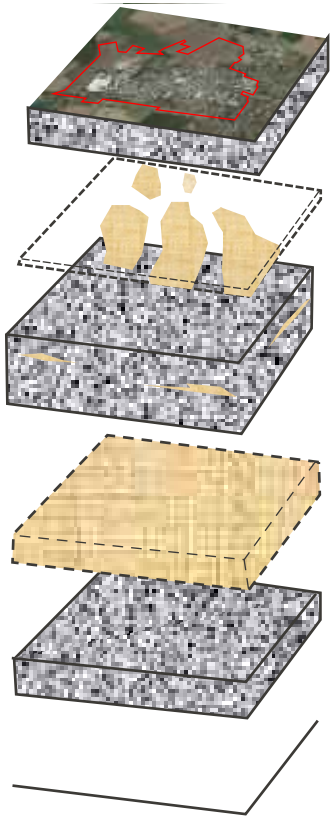
In 2017, Evonik was contacted by several firms regarding our technologies

- Considering typical concentrations and characteristics of sites we reviewed, we generally recommended testing a combined ISCR & ERD approach on site, such as EHC® Liquid, in order to address the following main concerns:
  - ✓Other common treatment reagents completely failed with CT, CF and DCA in groundwater treatment
  - ✓Request of a reagent with a *very high stable molecule and long-lasting release profile*
  - ✓Minimal formation of daughter products thanks to the combined ISCR & ERD approach
  - ✓No disruption of daily site activities *(i.e., chemical plant)*
  - ✓Effective in several site conditions, low-cost, safe, and easy to apply

IT Case Study Background

- Site located in Northern Italy, an active chemical plant with numerous facilities.
- Ramboll has been supporting the client at this site for site solutions and litigation issues since 2007.
- Heavy contamination due to CHCs (mainly carbon tetrachloride and chloroform) and, secondarily, CrVI for both vadose and saturated zones.
- Hydrogeological setting consisting of three main sand and gravel aquifers separated by clay levels. The phreatic aquifer has been shown as the most contaminated.

Geology – Site Conceptual Model



Shallow level
(Level A)
Intermediate permeability

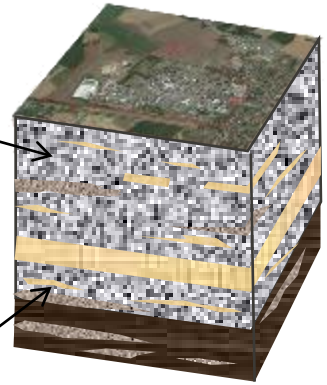
Aquitard
(non-contiguous)

Intemediate level
(Level B)
High permeability

Aquitard
(For the most part contiguous)

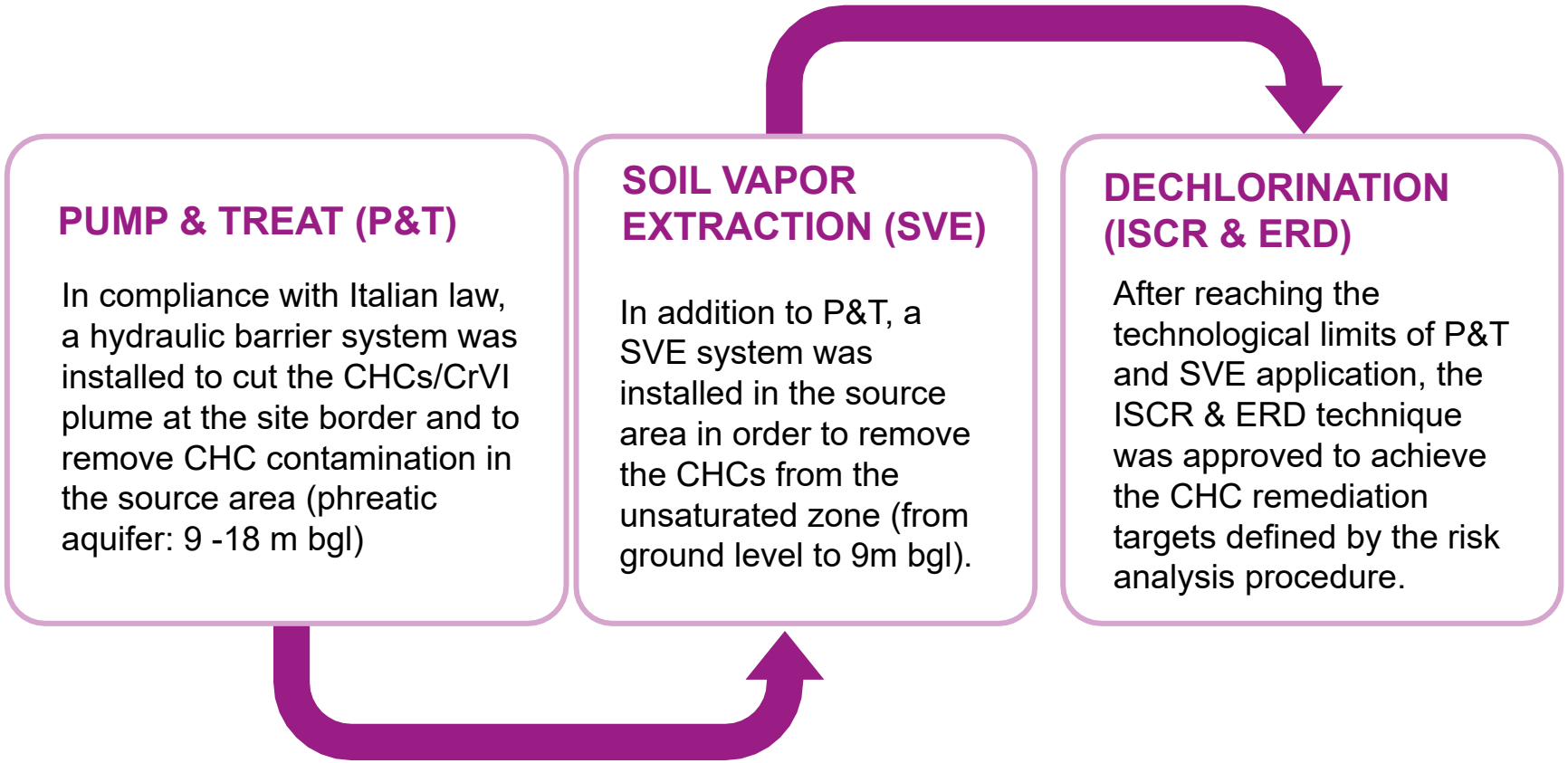
Deep level
(Level C)
Intermediate – high permeability

Depositional unit 'Villafranchiano'
(Grey clay)



- Sandy gravel
- Sand / silty sand
- Clay / silty clay
- Lacustrine or brackish dep. clay

Treatment Train Application

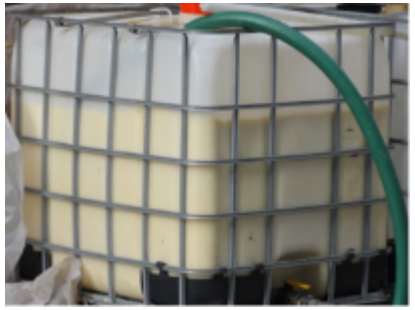


EHC® Liquid Overview

- Cold-water soluble ISCR & ERD product - injection via existing wells or hydraulic injection networks
- Composition: controlled-release organic carbon with an organo-iron compound, all food grade

- Delivered in two parts:
  1. ELS® Microemulsion or Concentrate
  2. EHC® Liquid Mix, an organo-iron powder (pH buffer, if needed, delivered as powder)

- Water content will vary with desired injection volume and physical conditions – typically 10% dilution in water



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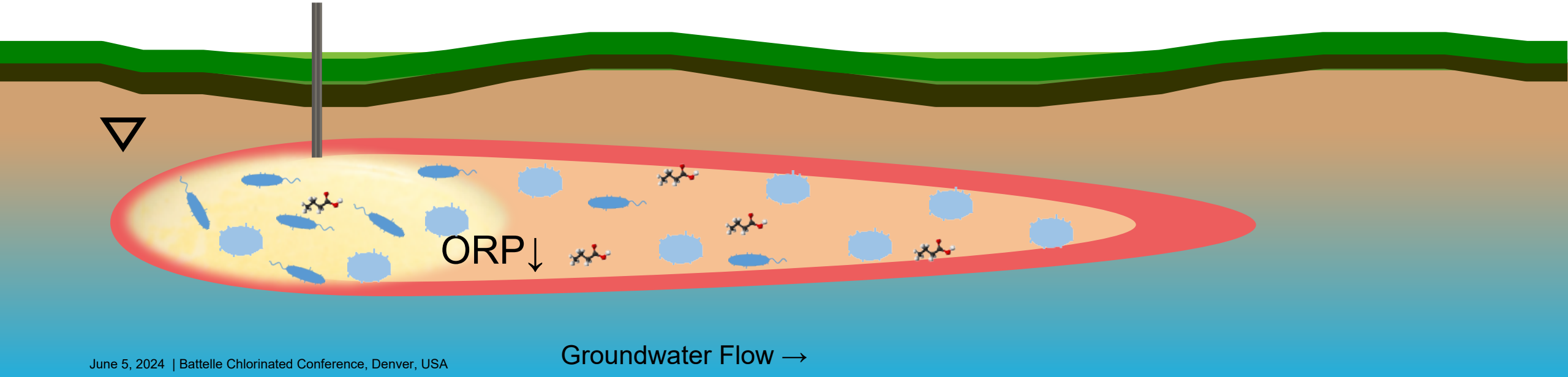
Overview of Reductive Mechanisms

Enhanced Reductive Dechlorination
After the addition of organic carbon (liquid or solid) to the subsurface:

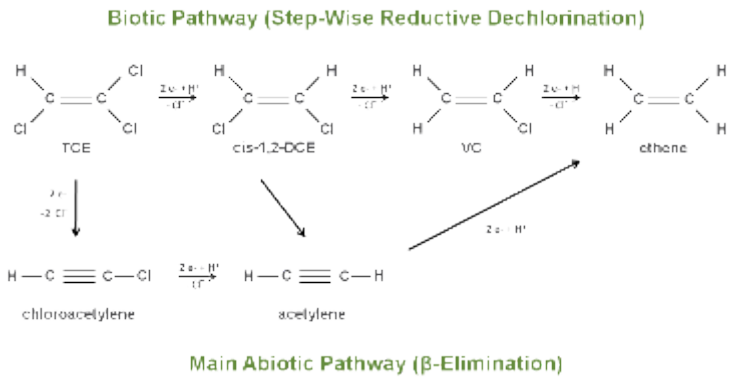
- Heterotrophic bacteria feed on the organic carbon as an electron acceptors reducing the redox potential
- Volatile fatty acids (VFAs) are generated through fermentation and released into the treatment area
- Dehalogenators utilize the VFAs as electron donors and feed on the chlorinated organics

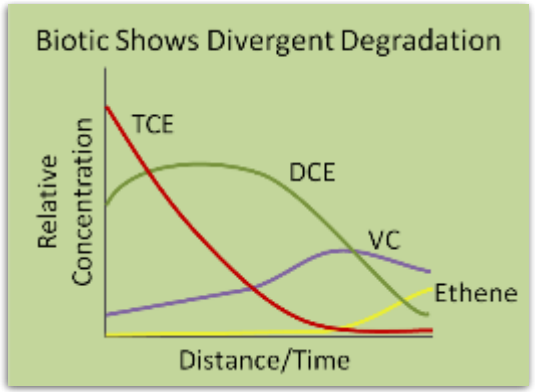


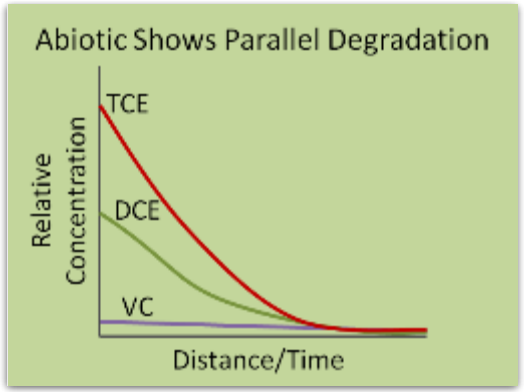
Overview of Reductive Mechanisms and Pathways

Indirect Chemical Reduction

- Occurs when soluble ferrous iron precipitates out of solution as reduced iron minerals
  - Iron sulfides: pyrite, mackinawite, greigite
  - Iron oxides: magnetite, iron hydroxide / green rust
- These iron minerals support abiotic dichlorination
- Since soluble ferrous iron can migrate, indirect chemical reduction can occur beyond the placement zone







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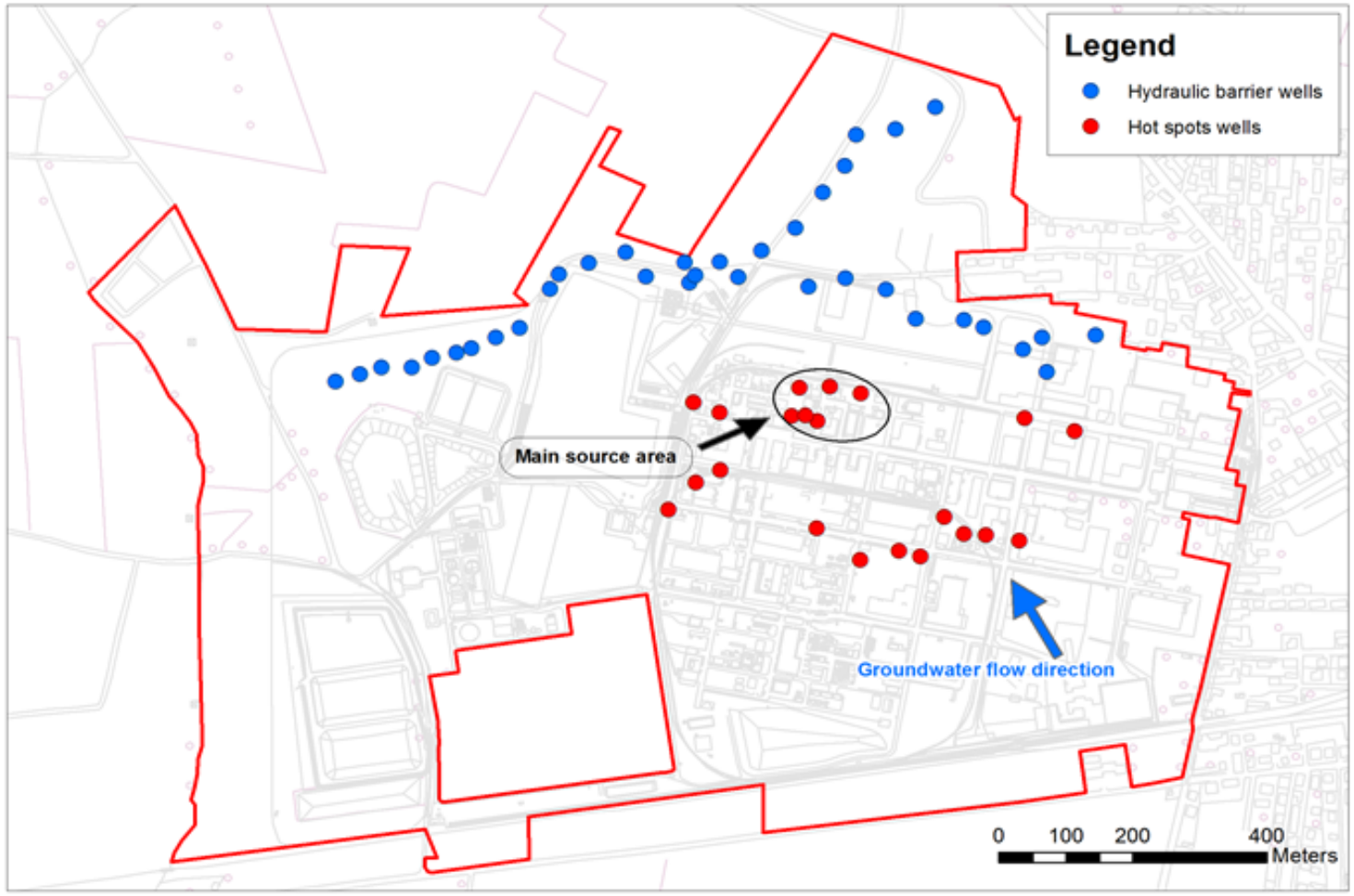
ERD & ISCR Reagent Applications



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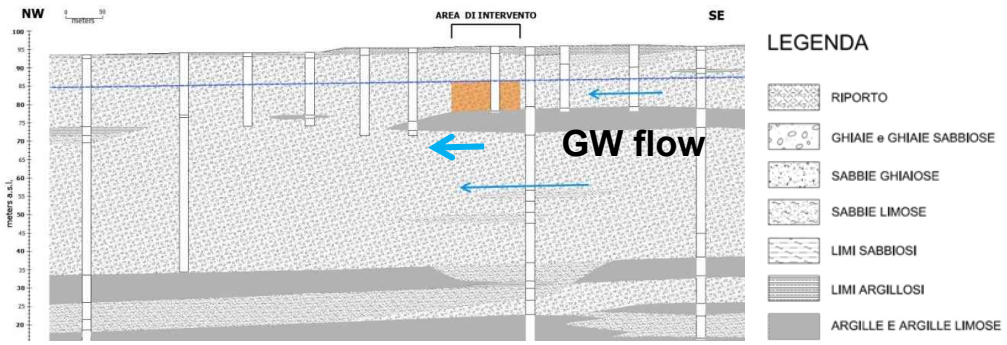
Phase 1 - Main Source Area Treatment

- Treatment area: **> 2.250 m²** (24219 ft²)
- Treatment area thickness: **9 m** (29.5 ft)
- GW table: **8 m bgL** (26.2 ft)
- Saturated soil matrix: **gravelly sand**
- Seepage velocity **≈ 280 m/yr** (918.6 ft/y)
- GW natural geochemical conditions: **aerobic, neutral pH**
- COCs: **CT > 5 mg/L, CF > 3 mg/L, TCE > 0.5 mg/L, CrVI > 2 mg/L**
- Cleanup goals: **regulatory limits (CT = 0.066 mg/L, CF = 0.065 mg/L)**



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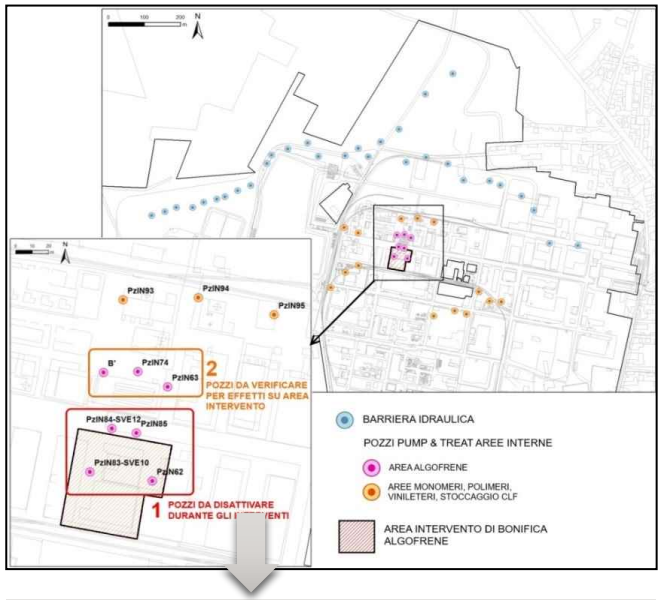
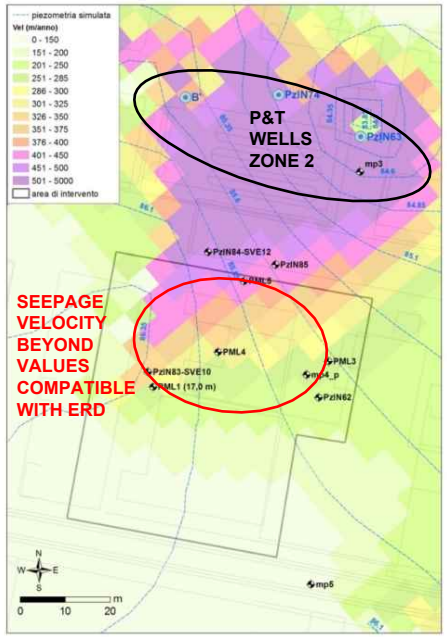
Remodeling P&T System Effects on EHC® Liquid Treatment Area



To protect effectiveness of the ISCR & ERD treatment, active P&T wells in the injection area have been switched off.

Effective ROI of the P&T wells located in Zone 2 was verified using MODFLOW2000 (USGS); a mathematical flow model.



Results of the model showed how wells located in Zone 2, at current flow rates, could have modified local groundwater flow conditions, causing an increase in flow velocities beyond values compatible with the ERD treatment design (300 meters/year).

Through use of the mathematical model, optimal flow rates were defined for each well in Zone 2 to keep seepage velocity < 300 m/year in the ISCR & ERD treatment area.

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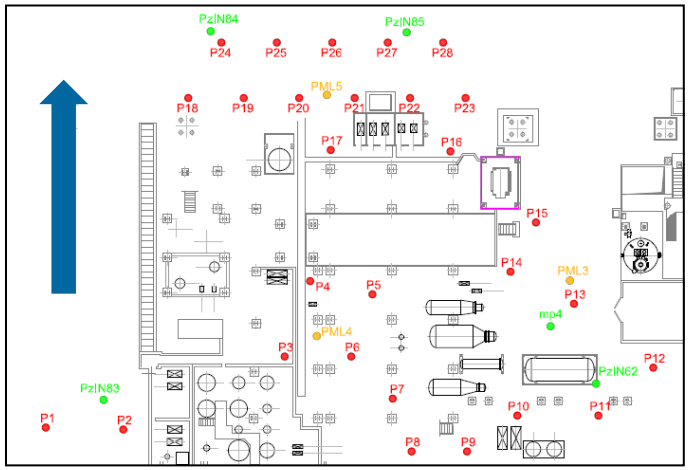
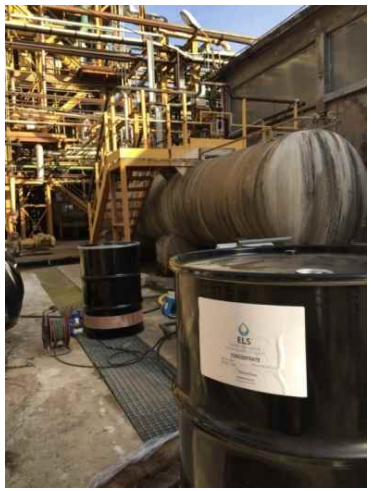
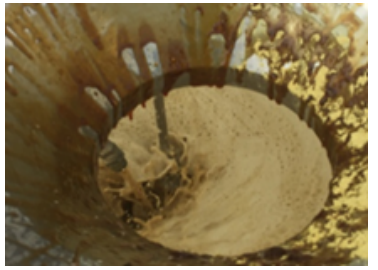
Phase 1 - ISCR / ERD Field Activity





- Application: **direct injection through 28 fixed manchette tubes**
- Injection campaign **≈ 306 kg of ELS® Concentrate per point, plus 70 kg of organo-iron powder (EHC® Liquid Mix)**
- Total injection volume: **96 m³ of EHC® Liquid emulsion, in 10% solution**
- Average injection pressure: **≈ 17 Bar**
- Average injection flow rate: **≈ 17 L/minute**
- Field activities start date: **December 2017**



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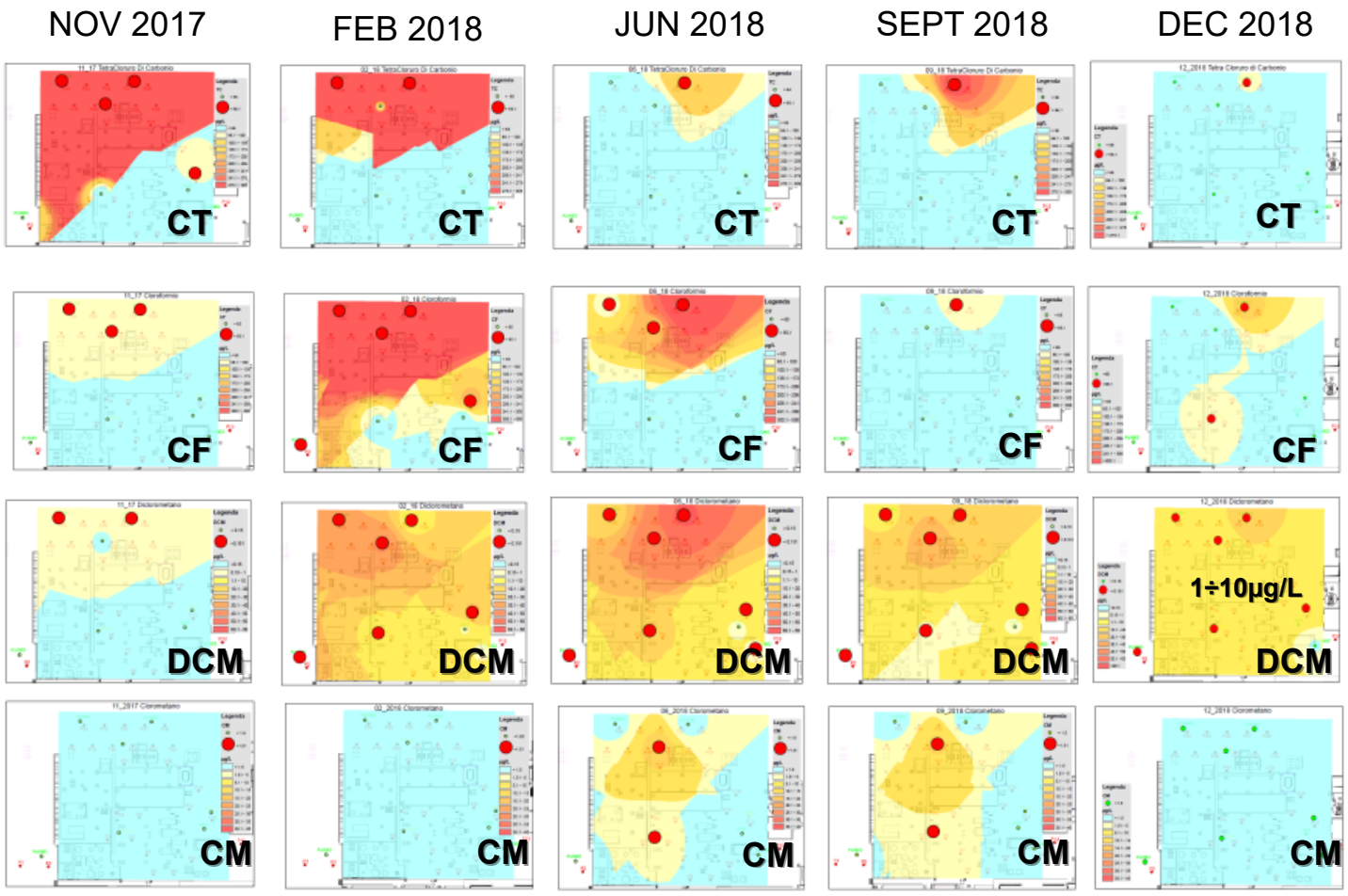
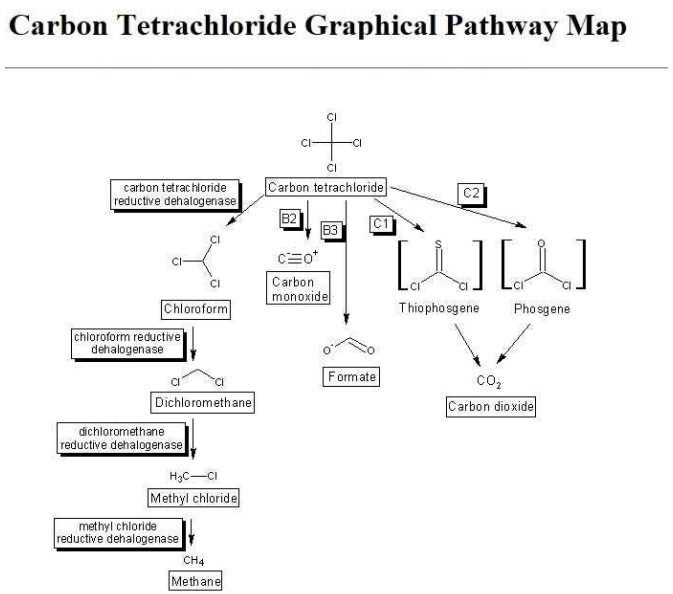
Post-Application Results (12 months) in µg/L





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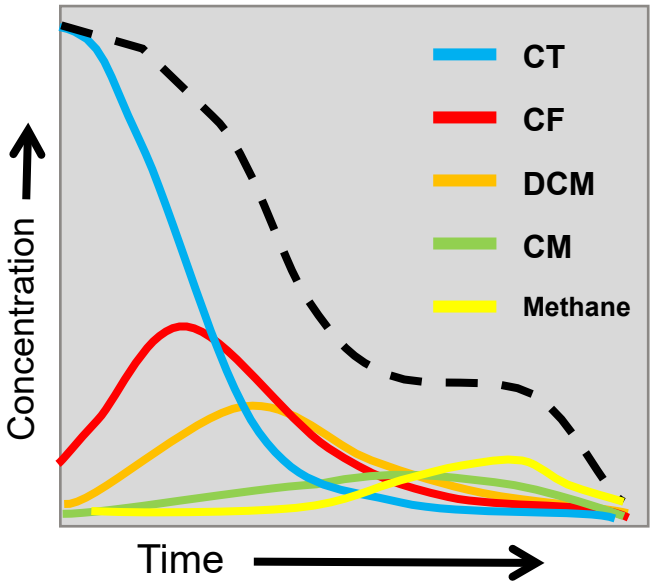
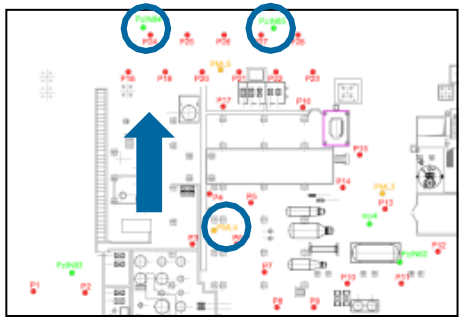
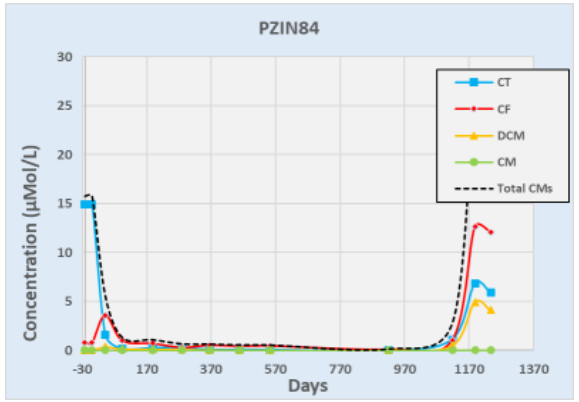
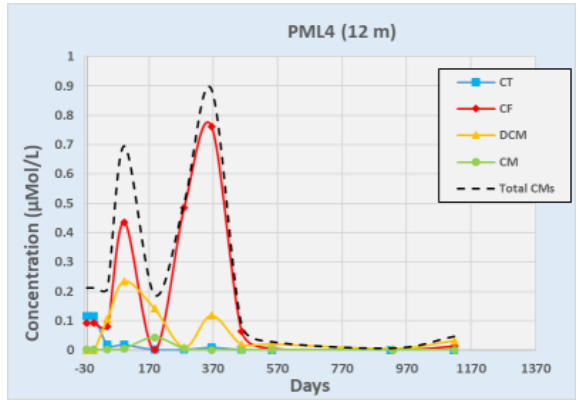
Post-Application Results (3.5 years) in µMol/L

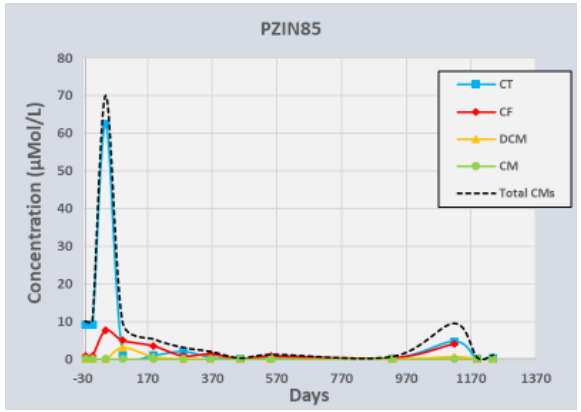
ISCR & ERD Degradation Performance Curves

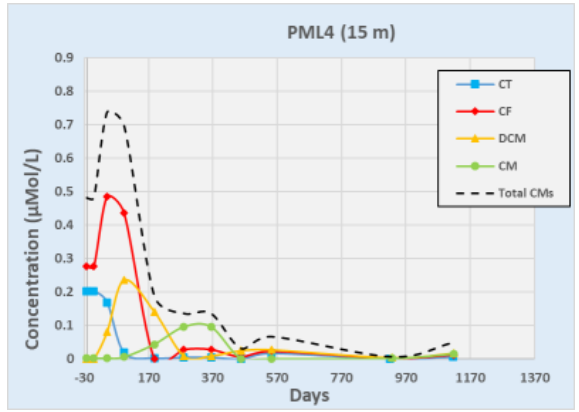












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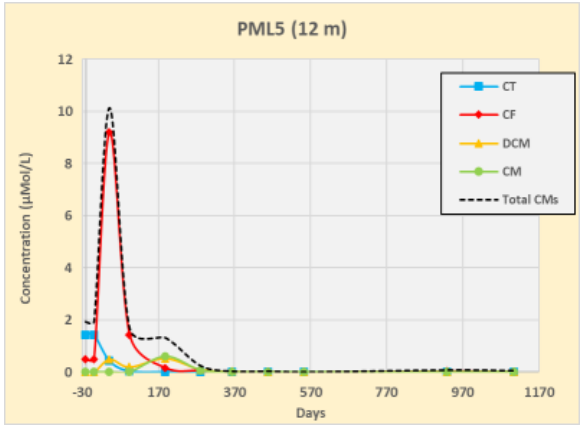
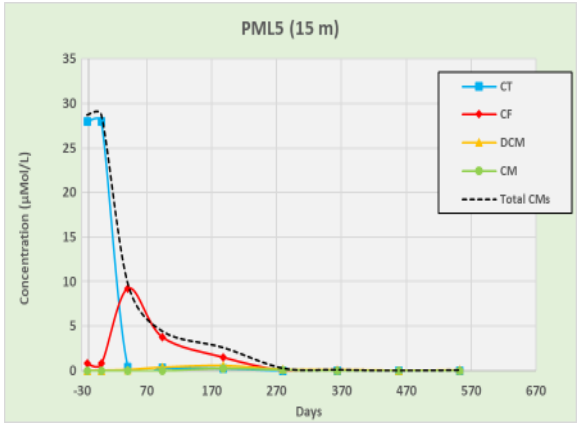
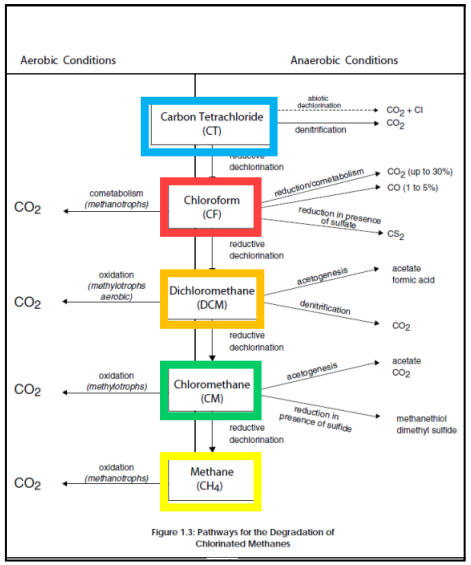
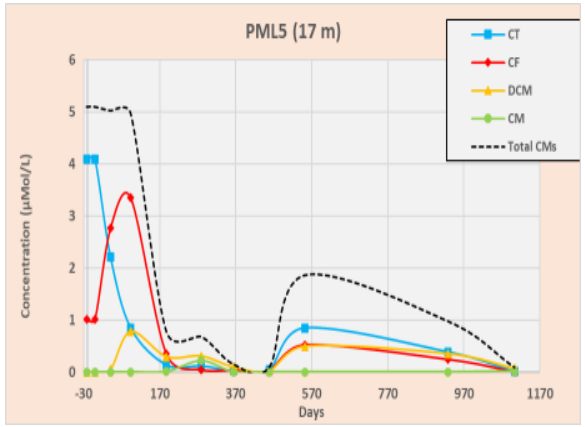
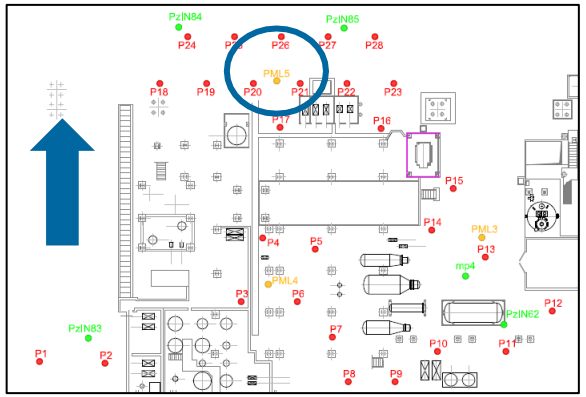
Post-Application Results (3.5 years) in µMol/L











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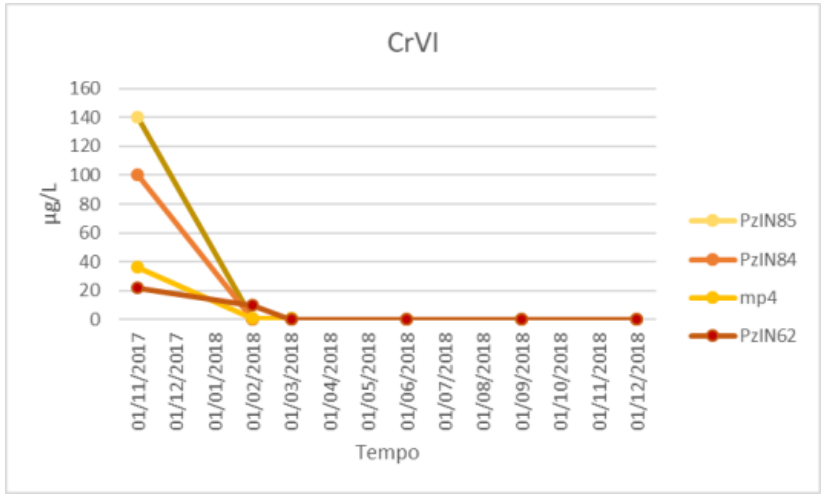
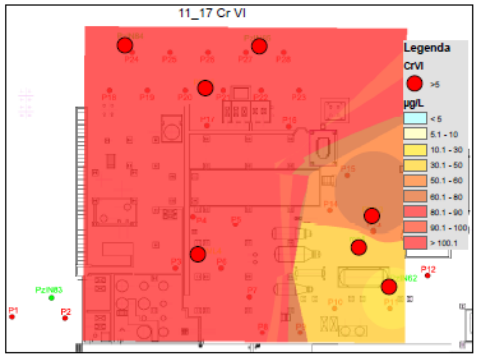
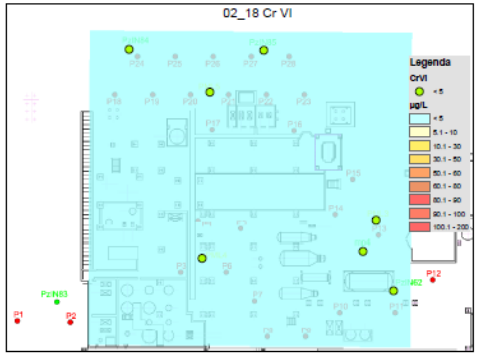
Post-Application Field Parameters

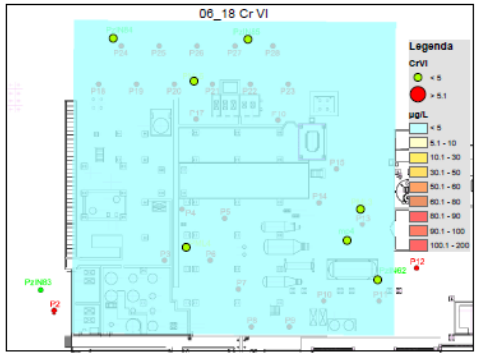
Main field parameters in the ISCR & ERD treatment areas:

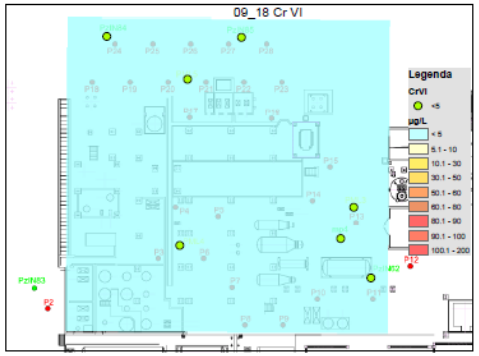
- Increase of Mn & Fe(II) in solution as **anaerobic cometabolites**
- Decrease of DO (mg/L) and sulphate (mg/L) – **competing electron acceptors**
- pH stable in the **neutral range**
- **Negative redox** around -50 to -150 mV











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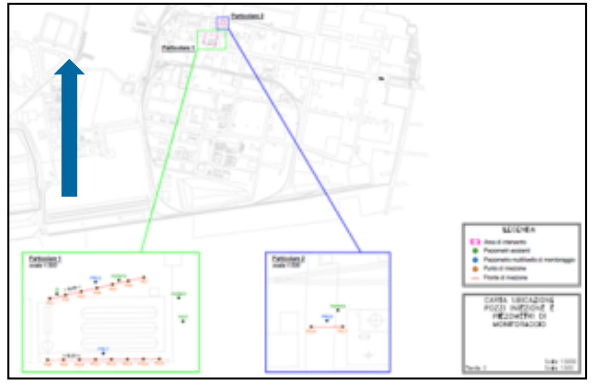
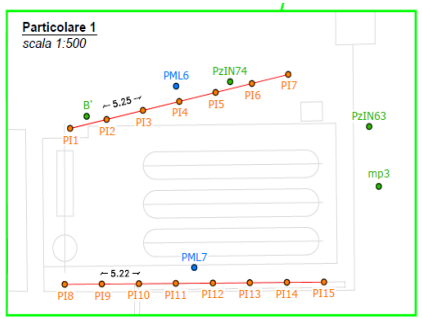
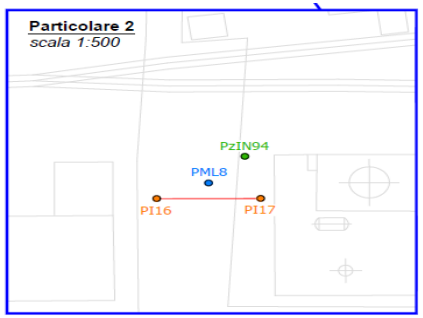
Phase 2 - Plume Area Treatment

- Treatment area: **> 1.554 m²** (16727 ft²)
- Treatment area thickness: **7-8 m** (22.9-26.2 ft)
- GW table: **11 m bgl** (36 ft)
- Saturated soil matrix: **gravelly sand**
- Seepage velocity **≈ 280 m/yr** (918.6 ft/y)
- GW natural geochemical conditions: **aerobic, neutral pH**
- COCs: **CT > 0.8 mg/l, CF > 0.2 mg/l**
- Cleanup goals: **CT = 0.066 mg/L, CF = 0.065 mg/L**

- Application: **direct injection through 17 fixed manchette tubes**
- Injection per point **≈ 462 kg ELS® Conc. + 106 kg EHC® L Mix**
- Total injection volume: **108 m³ of EHC® Liquid solution (10%)**
- Field activities start date: **February 2020**







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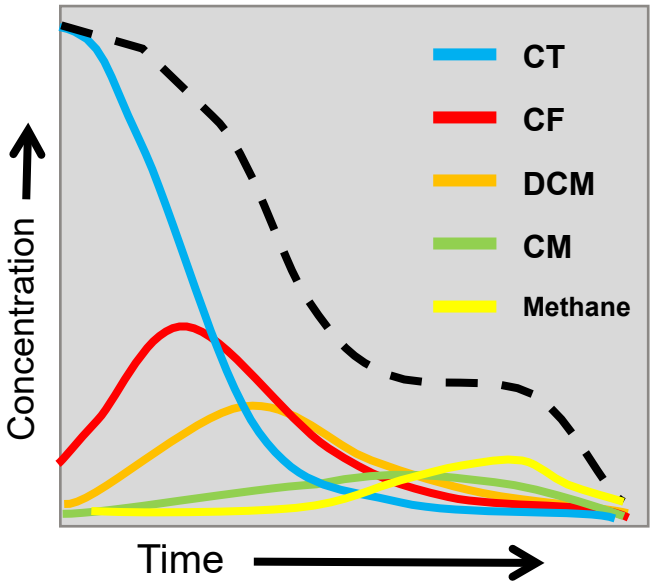
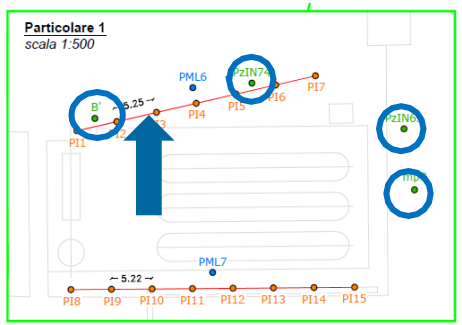
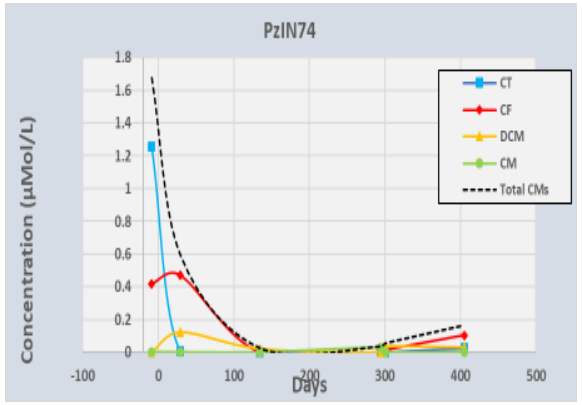
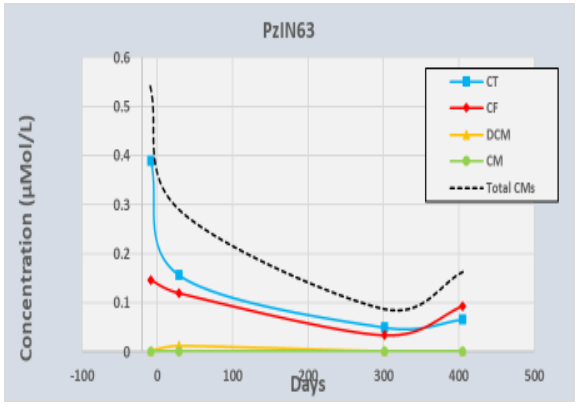
Post-Application Results (3.5 years) in µMol/L

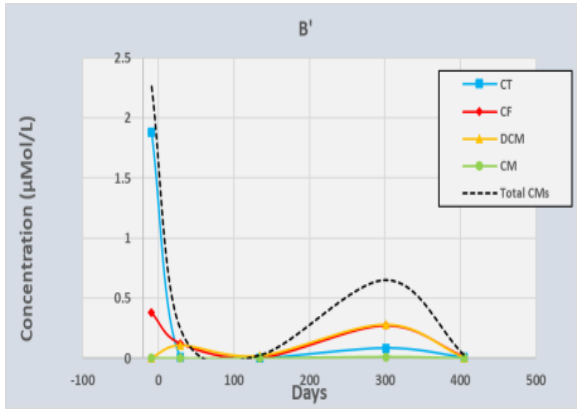
ISCR & ERD Degradation Performance Curves

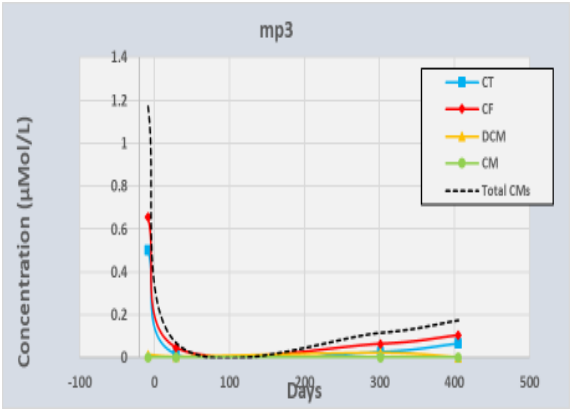












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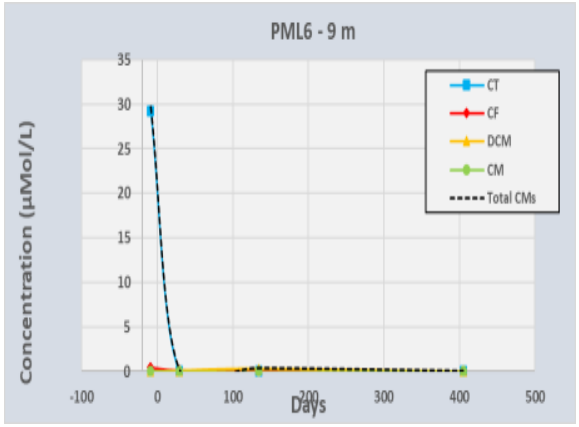
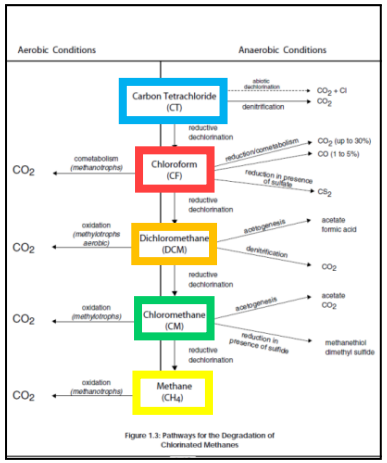
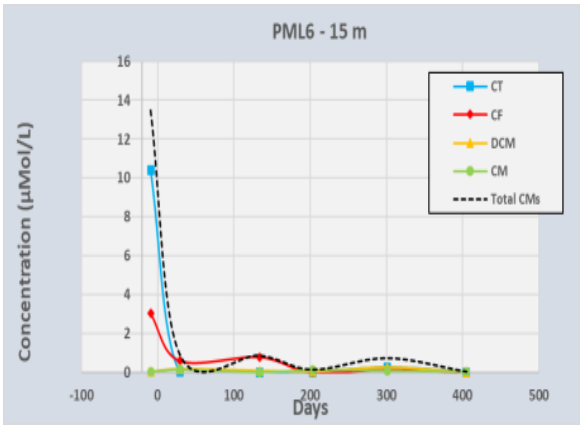
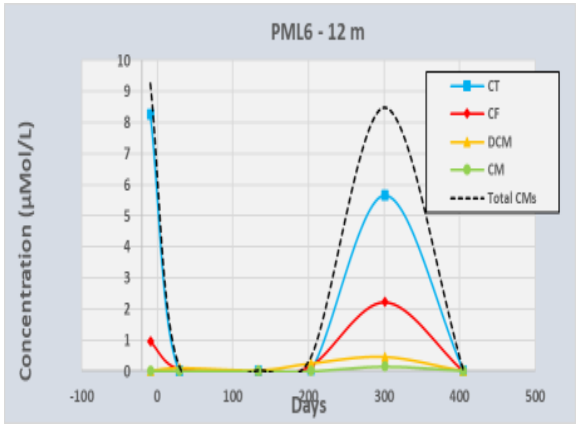
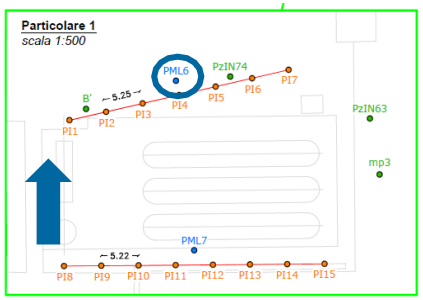
Post-Application Results (1.5 years) in µMol/L

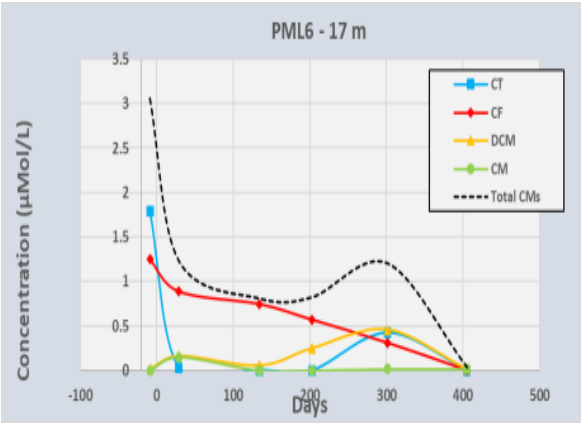












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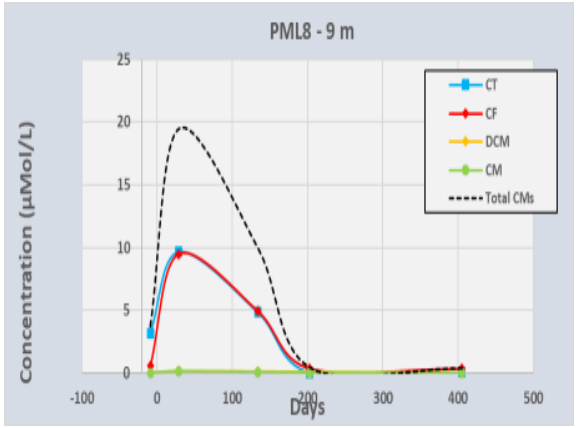
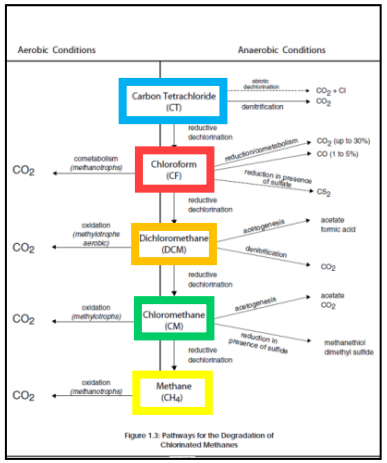
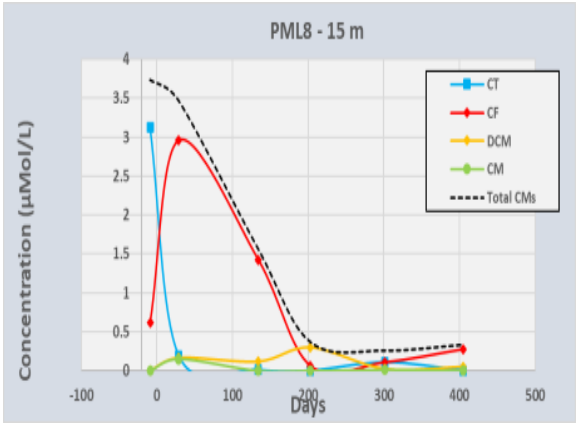
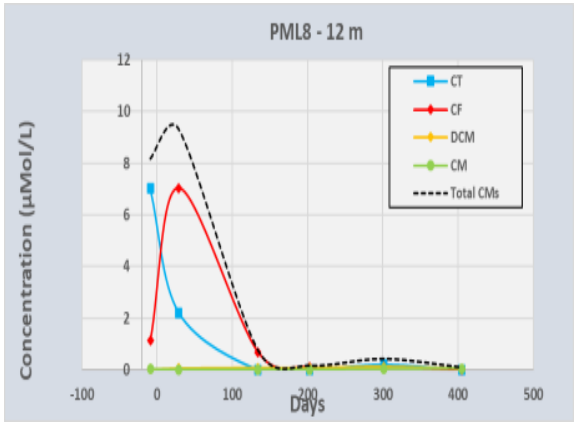
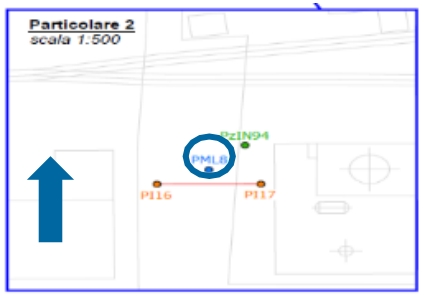
Post-Application Results (1.5 years) in µMol/L

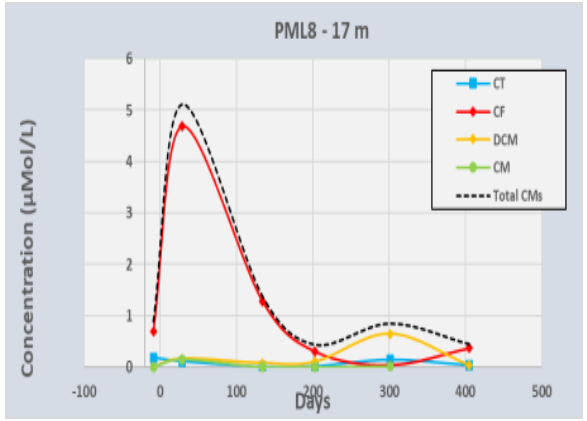












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Phase 3 – Hot Spot PzIN1 Treatment

- Treatment area: **> 1.750 m²** (18837 ft²)
- Treatment area thickness: **13 m** (42.65 ft)
- GW table**: 8 m bgl** (26.2 ft)
- Saturated soil matrix: **gravelly sand**
- Seepage velocity **≈ 630 m/yr** (2067 ft/y)
- GW natural geochemical conditions: **aerobic, neutral pH**
- COCs: **CT > 0.01 mg/l, CF > 0.3 mg/l**
- Cleanup goals: **CT = 0.066 mg/L, CF = 0.065 mg/L**

- Application: **direct injection through 22 fixed manchette tubes**
- Injection per point **≈ 732 kg ELS® Conc. + 168 kg EHC® L Mix**
- Total injection volume: **182 m³ of EHC® Liquid solution (10%)**
- Field activities start date: **July 2021**

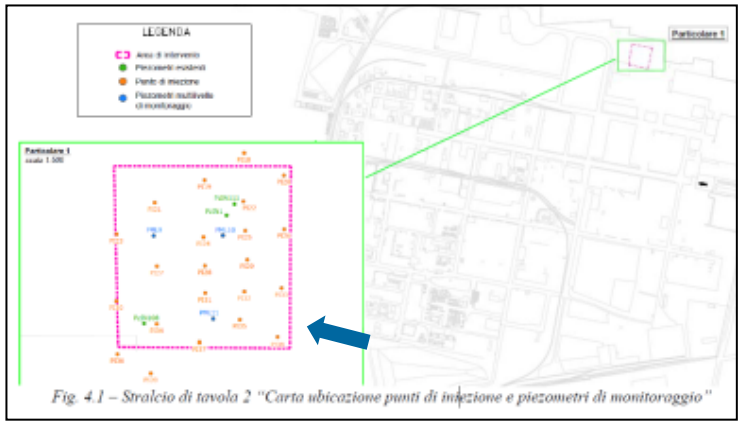

Fig. 4.1 – Stralcio di tavola 2 "Carta ubicazione punti di iniezione e piezometri di monitoraggio"

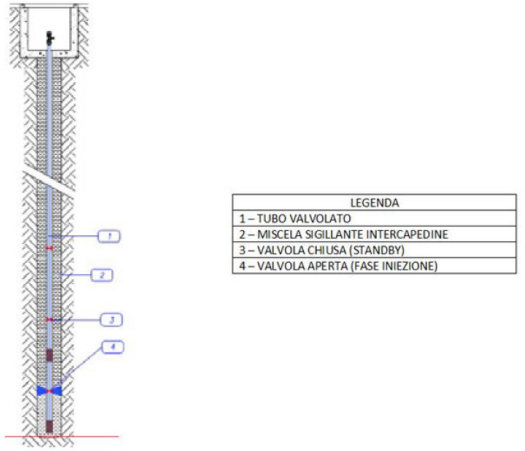

Fig. 4.2 – Schema costruttivo di un punto di iniezione con tubazione valvolata

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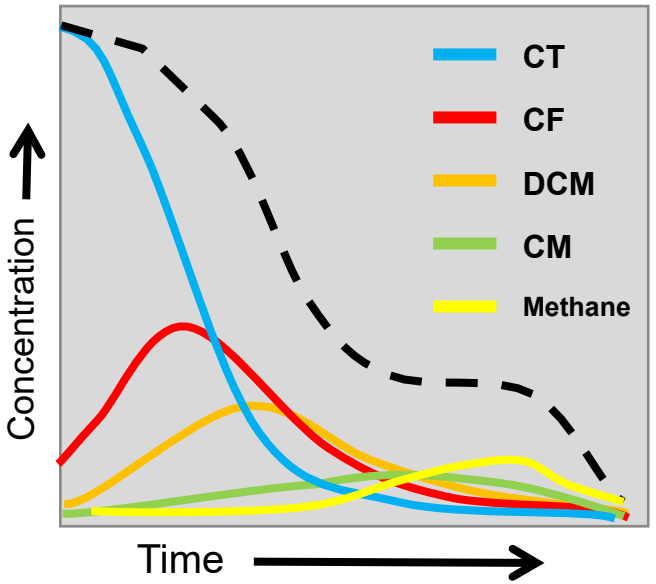
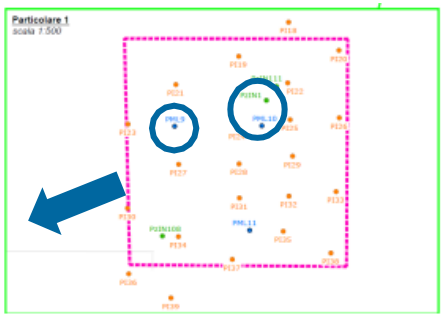
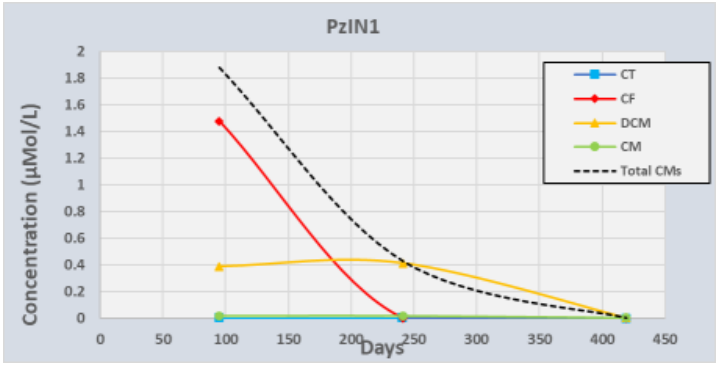
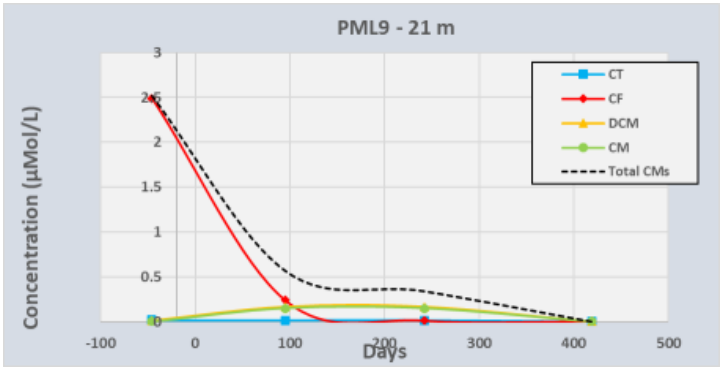
Post-Application Results (1.5 years) in µMol/L

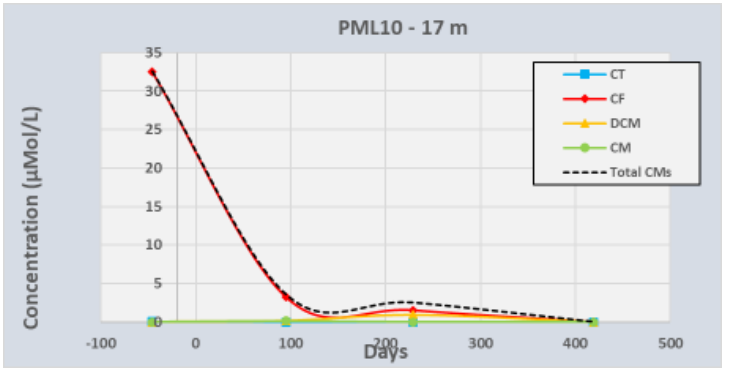
ISCR & ERD Degradation Performance Curves











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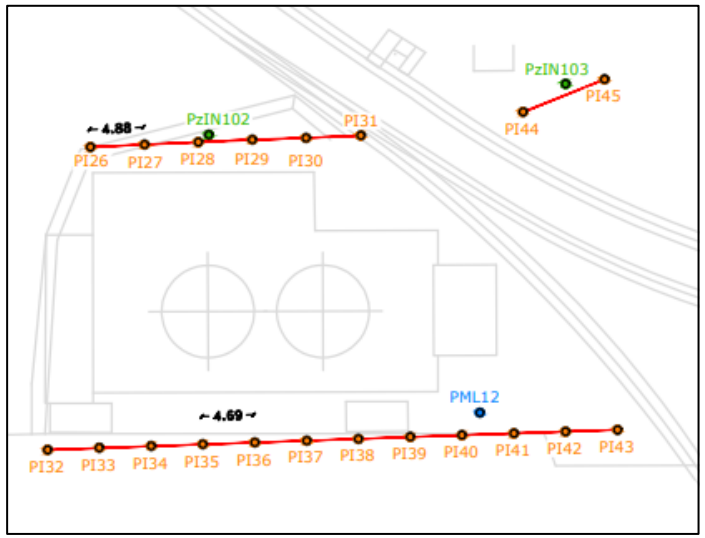
Phase 4 – Hot Spot PzIN102 Treatment

- Treatment area: **> 2.000 m²** (21528 ft²)
- Treatment area thickness: **7 m** (22.96 ft)
- GW table: **8 m bgl** (26.24 ft)
- Saturated soil matrix: **gravelly sand**
- Seepage velocity **≈ 526 m/yr** (1726 ft/y)
- GW natural geochemical conditions: **aerobic, neutral pH**
- COCs: **CT > 0.14 mg/l, CF > 0.41 mg/l**
- Cleanup goals: CT = 0.066 mg/L, CF = 0.065 mg/L
- Application: **direct injection through 20 fixed manchette tubes**
- Injection per point **≈ 745 kg ELS® Conc. + 171 kg EHC® L Mix**
- Total injection volume: **168 m³ of EHC® Liquid solution (10%)**
- Field activities start date: **2022 – 2023**



Monitoring Point	Ante Operam (FEB '23)	Post Operam (JUL '23)	Post Operam (SEPT '23)	Post Operam (DEC '23)	Post Operam (MARCH'24)	CLEAN UP GOALS (CT = 66 µg/L, CF= 65 µg/L)
PzIN102	CT = 4000 µg/L, CF = 100 µg/L	CT = 10 µg/L, CF = 51 µg/L	CT = 580 µg/L, CF = 1110 µg/L	CT = 3.9 µg/L, CF = 14.2 µg/L	CT = 50 µg/L, CF = 54 µg/L	YES
PzIN103	CT = 620 µg/L, CF = 161 µg/L	CT = 0.058 µg/L, CF = 9 µg/L	CT = 7.1 µg/L, CF = 90 µg/L	CT = 0.062 µg/L, CF = 1.3 µg/L	CT = 12 µg/L, CF = 51 µg/L	YES
PzIN112	CT = 93 µg/L, CF = 175 µg/L	CT = 95 µg/L, CF = 151 µg/L	CT = 93 µg/L, CF = 176 µg/L	CT = 79 µg/L, CF = 121 µg/L	CT = 65 µg/L, CF = 108 µg/L	NOT INJECTED
PML12 (11 m)	N/A	CT = 0.02 µg/L, CF = 0.02 µg/L	CT = 0.027 µg/L, CF = 0.082 µg/L	CT = 0.027 µg/L, CF = 0.0418 µg/L	CT = 0.223 µg/L, CF = 5 µg/L	YES
PML12 (14 m)	CT = 450 µg/L, CF = 58 µg/L	CT = 0.02 µg/L, CF = 0.02 µg/L	CT = 0.236 µg/L, CF = 7.1 µg/L	CT = 0.027 µg/L, CF = 0.23 µg/L	CT = 0.027 µg/L, CF = 0.56 µg/L	YES
PML12 (16 m)	CT = 710 µg/L, CF = 57 µg/L	CT = 0.18 µg/L, CF = 5.4 µg/L	CT = 0.64 µg/L, CF = 11 µg/L	CT = 0.027 µg/L, CF = 0.2 µg/L	CT = 0.027 µg/L, CF = 0.29 µg/L	YES
PML12 (18 m)	CT = 1300 µg/L, CF = 107 µg/L	CT = 6.8 µg/L, CF = 148 µg/L	CT = 4.9 µg/L, CF = 44 µg/L	CT = 0.027 µg/L, CF = 1.4 µg/L	CT = 0.027 µg/L, CF = 0.43 µg/L	YES

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Summary

- Client has been happy with approach combining ISCR with ERD – Enhanced Reductive Dichlorination; approach continues to be used by the client
- Multiple sites planned for 2024 and 2025

Remedial goals achieved
Polishing ongoing!

- EHC® Liquid is ideal for low to moderate levels of chlorinated compound contamination
- Three possible treatment pathways from a single application:
  - In-situ chemical reduction with organo-iron powder
  - Anaerobic bioremediation with extended-release ELS® Microemulsion
  - Biogeochemical Dichlorination with reduced iron minerals
- Highly contaminated sites would favor more classic ISCR applications such as EHC®

Questions?

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Thank you for your attention. We look forward to working with you!

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