

Application of an All-In-One ISCO Technology for the Treatment of Monochlorobenzene, BTEX and Chloroform in Groundwater at a Former Pharmaceutical Facility in Italy

2024 Chlorinated Conference
June 4, 2024

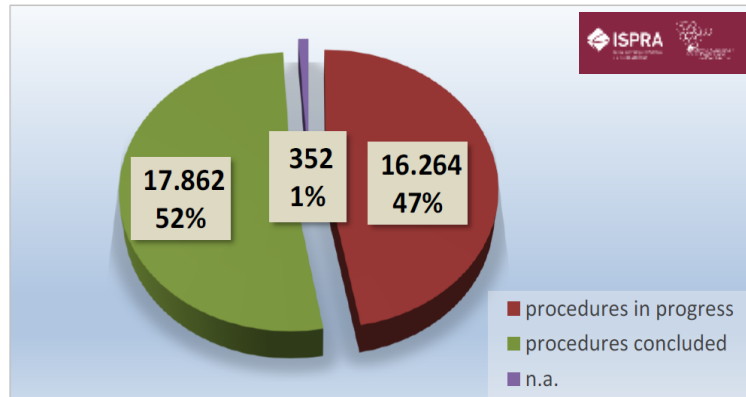
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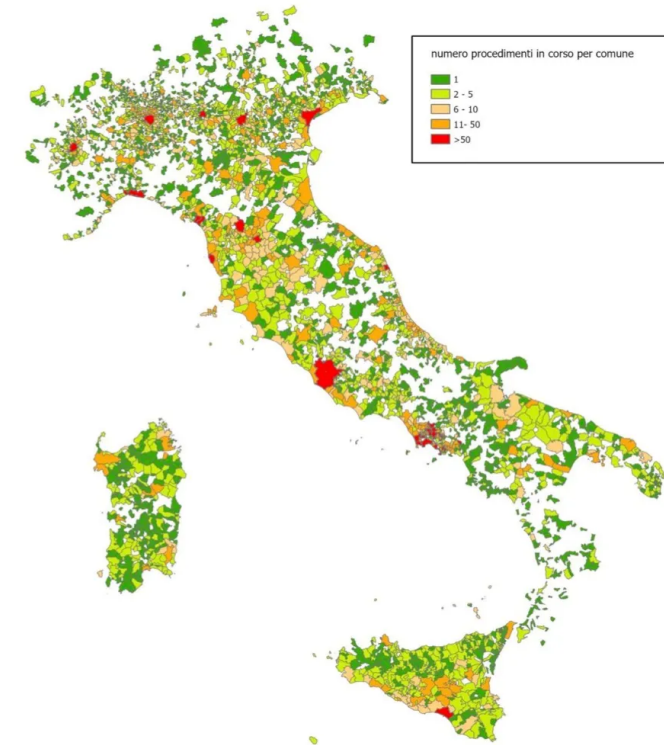


Discussion of Contaminated Sites in Italy

- 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.



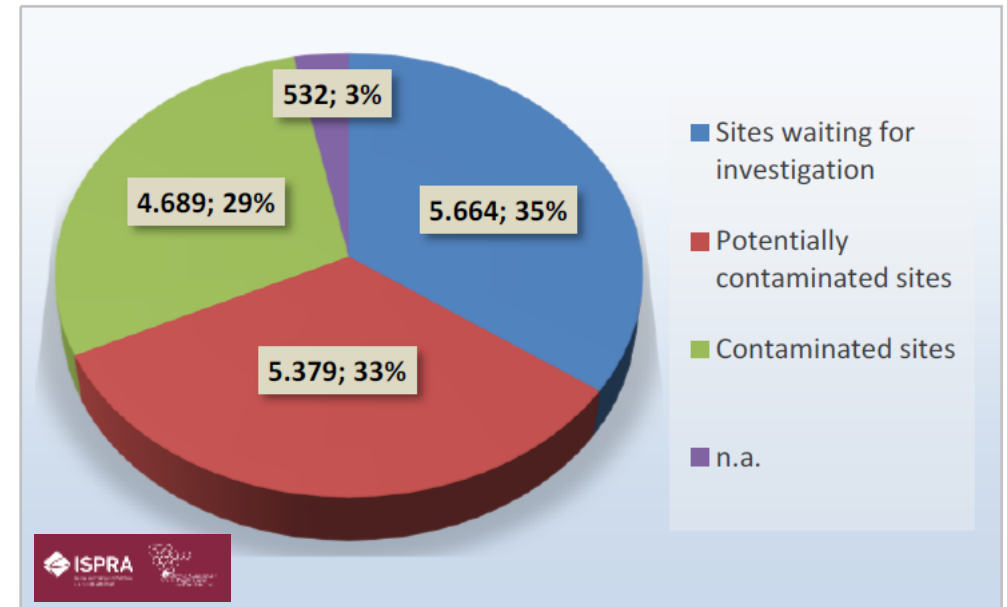
Number of OPEN contaminated site proceedings for each IT Municipality

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

Discussion of Contaminated Sites in Italy

Procedures in progress - The information on the contamination status is reported for 15,733 equal to 97% of the sites.

- Substantial balance between sites waiting for preliminary investigations (contamination not known – 35%), potentially contaminated sites (screening values exceeded – 33%) and contaminated sites (*unacceptable risks* – 29%).
- Where the contamination risk is not acceptable, remediation actions have been implemented or planned.
- Very typical of having *low remedial goals* (Legislative Decree n. 152/06) in GW for...
 - ✓ *TPH* = 0.35 mg/L
 - ✓ *MTBE, ETBE* = 0.04 mg/L
 - ✓ *Benzene* = 0.001 mg/L
 - ✓ *PAHs* = 0.0001 mg/L



Type of OPEN contaminated site proceedings

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

Petroleum Hydrocarbons Site Remediation Activities

Demand for an in-situ remedy for many reasons

- Need for solution in areas that cannot be excavated – *i.e., active gas stations and/or oil deposits*
- 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 KLOZUR® CR on site in order to address the following main concerns:
 - ✓ Other common treatment reagents completely failed with MTBE and ETBE in groundwater treatment
 - ✓ Request of a reagent with a very high standard quality (*i.e., low-metals powder formula*)
 - ✓ No disruption of the daily site activities (*i.e., gas station services*)
 - ✓ Effective in several site conditions, low-cost, safe, and easy to apply

KLOZUR® CR – Combined Remedy

- Released in 2006 – over 15 years of experience
- “CR” = Combined Remedy
 - In situ chemical oxidation (ISCO)
 - Aerobic bioremediation
 - Anaerobic oxidation
- KLOZUR® CR is a blend of KLOZUR® SP and PERMEOX® Ultra
 - Typical blend is 50:50 ratio
 - PERMEOX® Ultra activates the sodium persulfate

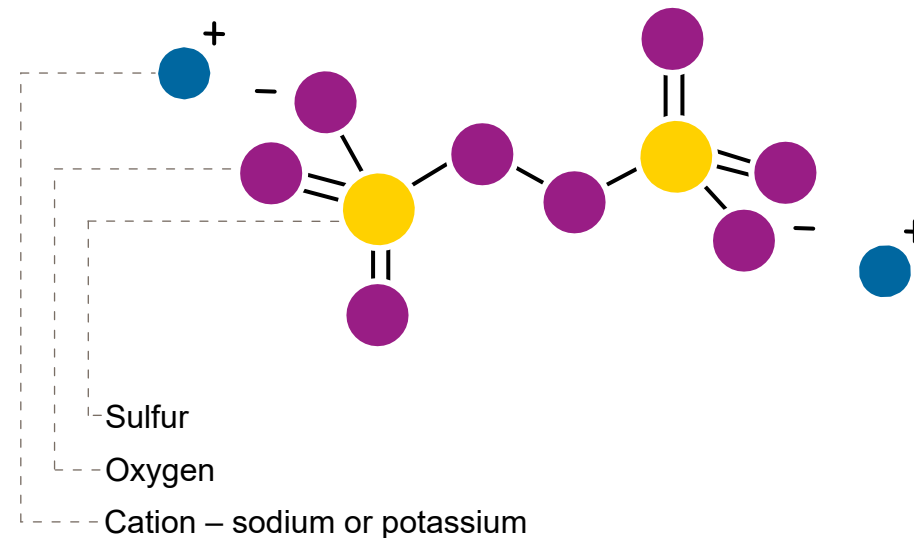
Three remedial pathways
in a single application



KLOZUR®

Persulfates Chemistry

- Sodium and potassium persulfate are used in environmental remediation applications
- A strong oxidant
- Activation results in the formation of oxidative and reductive radicals
- Applicable across a broad range of contaminants
- Extended subsurface lifetime (weeks to months)
- Little to no gas evolution



Free Radical Chemistry:

Persulfates produce free radicals in many diverse reaction situations



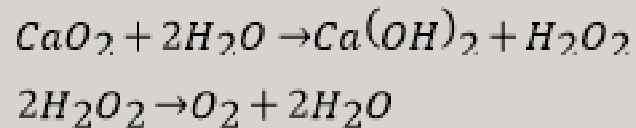
Activation produces a radical which is more powerful and kinetically fast

PERMEOX® Ultra Chemistry

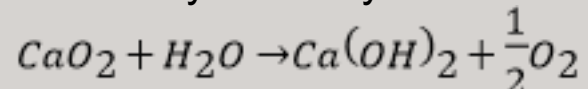
- PERMEOX® Ultra

- Calcium peroxide
- Proprietary stabilizer
- Hydrated lime

Primary Pathway:



Secondary Pathway:



- Key Characteristics:

- >18% active oxygen is typical
 - Higher or highest AO of calcium peroxide products
 - ~180 mg O₂ formed per g PERMEOX® Ultra applied
 - ~90 mg O₂ formed per g KLOZUR® CR applied
- pH 10.2 to 10.6 (1% slurry at 25 C)
- PERMEOX® Ultra has a very low solubility
 - Applied as a solid-slurry
 - Persistence of many months typical
- Rate of solid slurry dissolution increases with decreasing pH

Wang et al, 2016, Chem Eng J, 303, 450-457

Combined Chemistry: Three Treatment Methods

Method	Description	Treatment Pathways	Contaminants Treated	Expected Persistence
ISCO	Alkaline and hydrogen peroxide activated persulfate	Oxidative and reductive pathways	Treats most organic contaminants	2 to 8 weeks
Bioremediation	Aerobic	Oxidative	Treats most petroleum hydrocarbons	Up to 9 months
Bioremediation	Anaerobic oxidation (sulfate reduction)	Weaker oxidative	Treats easily oxidizable compounds	Years

KLOZUR® CR Applications in Italy (2017-2023)

- Up to 186 sites have been treated using KLOZUR® CR technologies in the last couples of years in all the main provinces of Italy.
- About 65% sites have reached closure with the first KLOZUR® CR injection campaign.
- Additional 25% sites have reached closure with more than one injection campaign.
- Additional 10% sites required more treatment actions due to recalcitrant contamination and/or rebound effects.
- KLOZUR® CR technology has been successful in the IT market due to
 - ✓ Safe and easy to apply
 - ✓ Not exothermic
 - ✓ Cost competitive
 - ✓ Efficient (multiple mechanisms of degradation)
 - ✓ Very high standard quality



Number of KLOZUR® CR site applications in the main Italian provinces. In red up to 10 sites per area, in yellow 5-10 sites per area, in green <5 sites per area.

KLOZUR® blend leads to site closure in urban Vicenza, Italy

Site:
Former pharmaceutical facility

Location:
Vicenza City Center, Italy

Contaminants:
Monochlorobenzene, BTEX and chloroform in groundwater

Remedial Approach:
Injection of a KLOZUR® blend to treat source area and plume



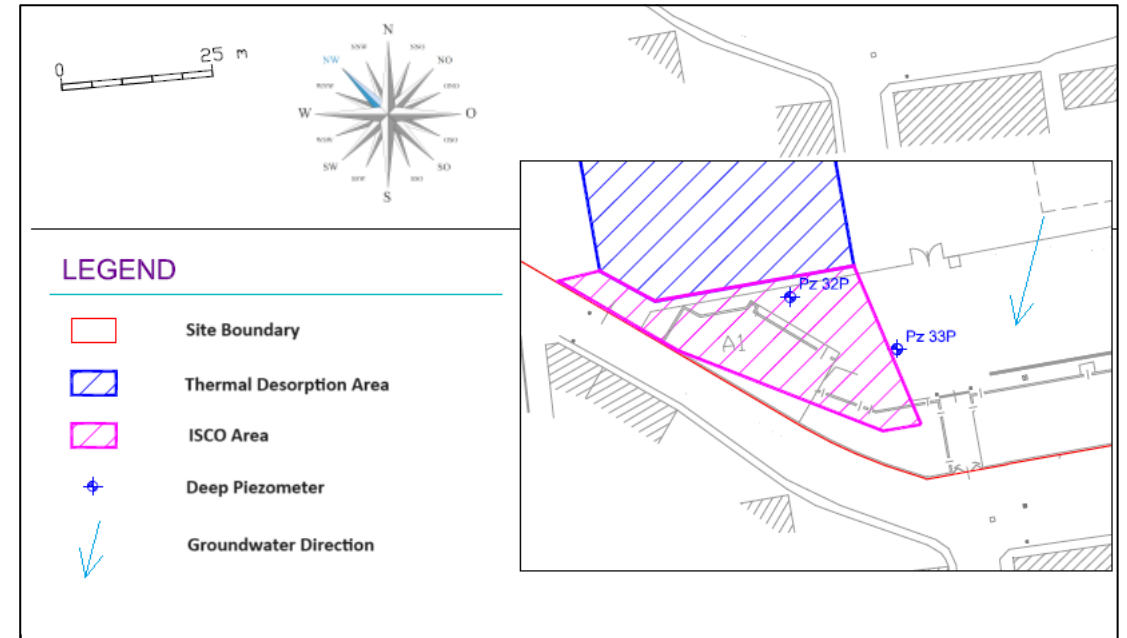
Early Pilot Test – ISCO Commercial Additives via Pressured Injections

- In 2018-2021, injections of other commercial ISCO reagents in the main contaminated zones.
- No evidence of treatment in the following monitoring campaigns.
- Local authorities required to evaluate ISCO alternatives such as persulphate (AAP - Alkaline Activated Persulfate).
- KLOZUR® CR along with KLOZUR® KP potassium persulfate have been selected for injection into the impacted groundwater and capillary fringe.
- Manchette tub technology has been selected as injection methodology due to the heterogenous saturated soil matrix.



Site Details – ISCO Area

- Treatment area: **> 700 m²** (> 7535 ft²)
- Treatment interval: **2 to 15 m bgs** (6.5 to 49 ft bgs)
- GW table: **2 m bgl** (6.5 ft)
- Saturated soil matrix: **sand, silty sands to silty clays**
- Depth to bottom of shallow aquifer: **15 m** (clay layer)
- Soil bulk density $\approx$ **1500 kg / m³**
- Seepage velocity $\approx$ **1 to 5 m/yr** (3 to 15 ft / yr)
- GW direction : **NO-SW**
- Fraction organic carbon $\approx$ **0.01**
- GW natural geochemical conditions: **moderate anaerobic, neutral pH**



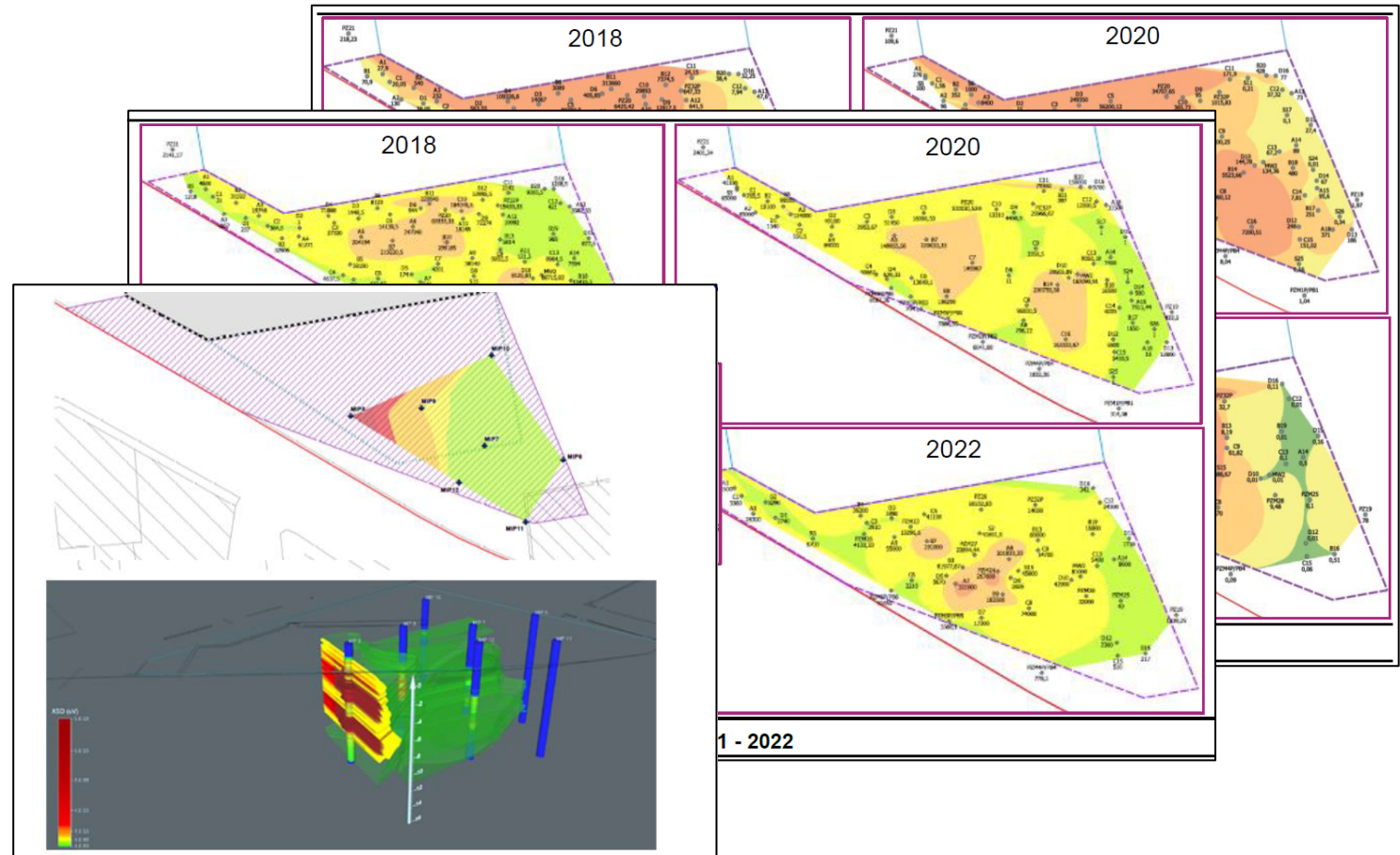
Baseline Concentrations and Remedial Goals

- **Contaminant of concerns:**

- TCM > 25 mg/l
- MCB > 112 mg/l
- BTEX > 16 mg/l

- **Cleanup goals: regulatory limits**

- TCM = 0.0015 mg/L
- MCB = 0.04 mg/L
- BTEX = 0.001 mg/L



KLOZUR® Pilot in ISCO area (July 2022)



- A total of 5,460 kg KLOZUR® CR along with 1,670 kg KLOZUR® KP injected over one injection events via manchette tubs:
 - 5 injection points (IP1, IP2, IP3, IP4, IP5) with ROI ≈ 3 m
 - 5,800 liters (1,532 gallons) per point at 25% by weight aqueous slurry
 - Bottom-up pressured Injections

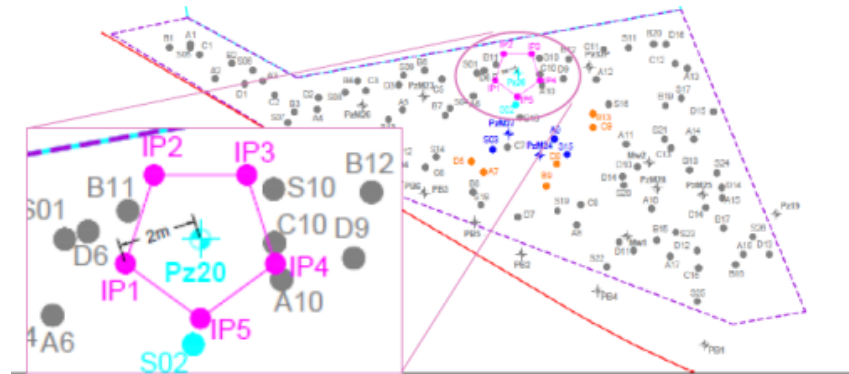
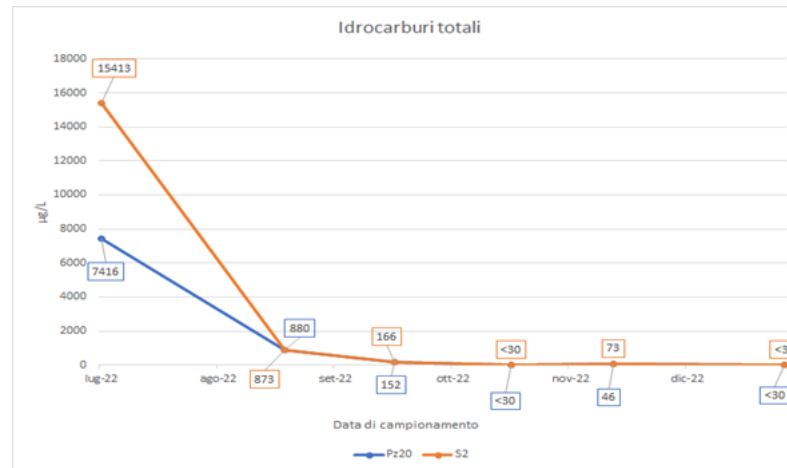
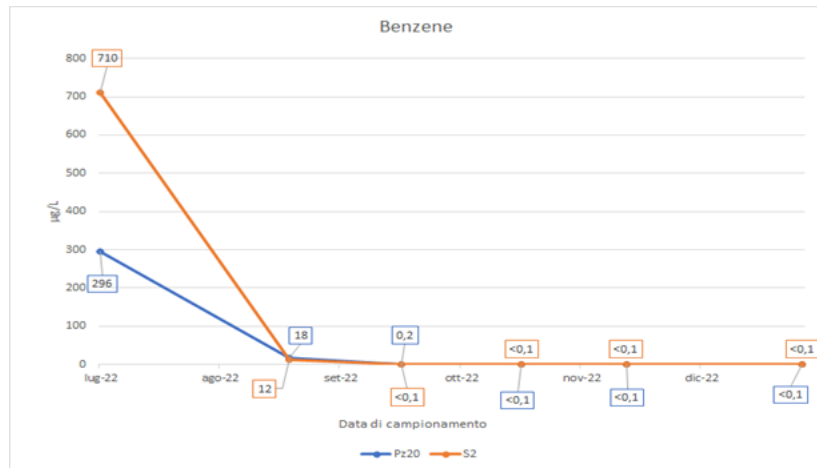
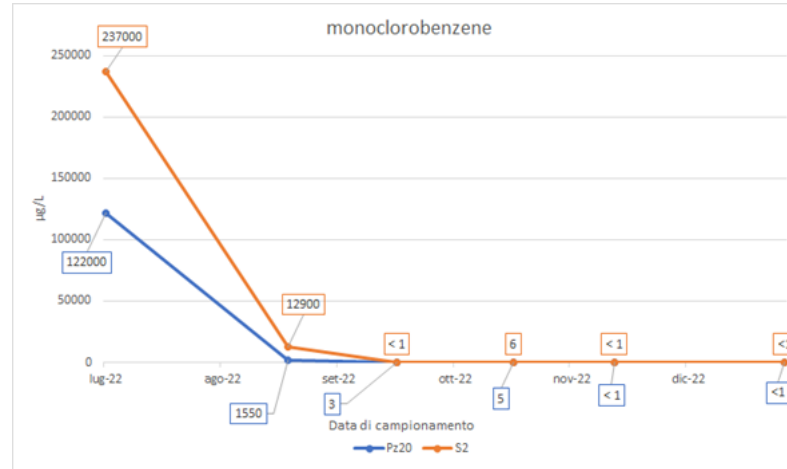
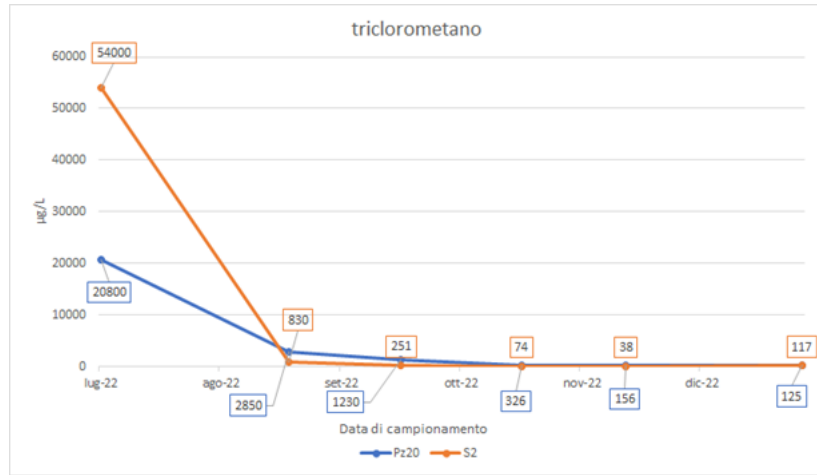


Figura 5.1 : Ubicazione e geometria del test pilota

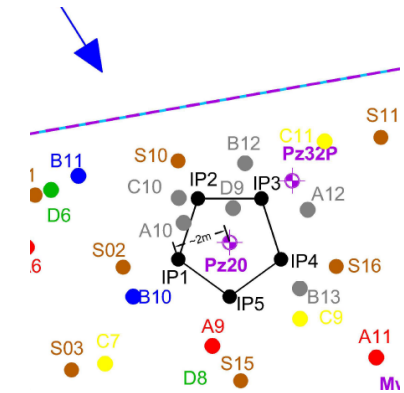
Results - Post Application Data (6 Months) in the Pilot Area



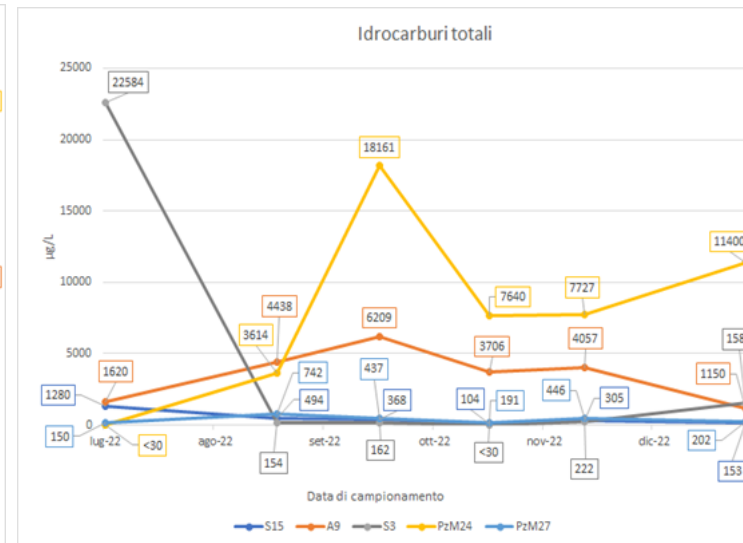
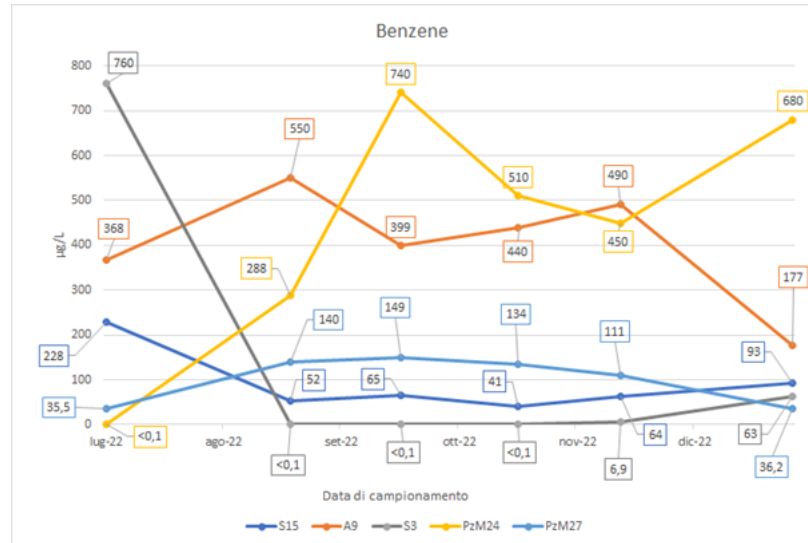
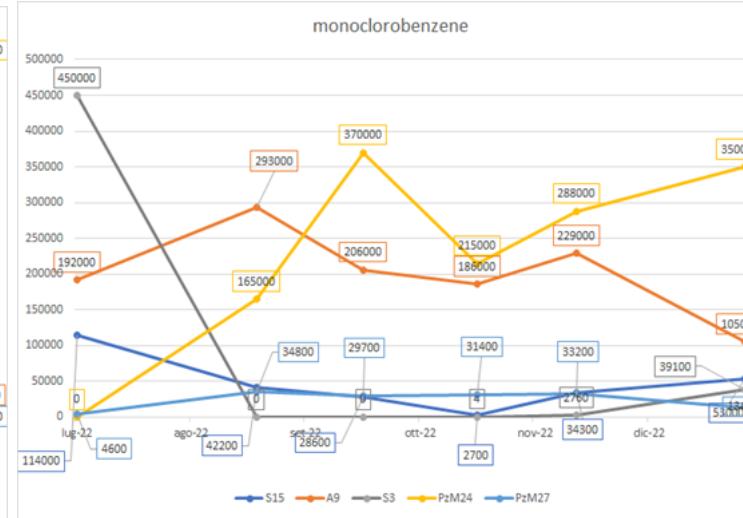
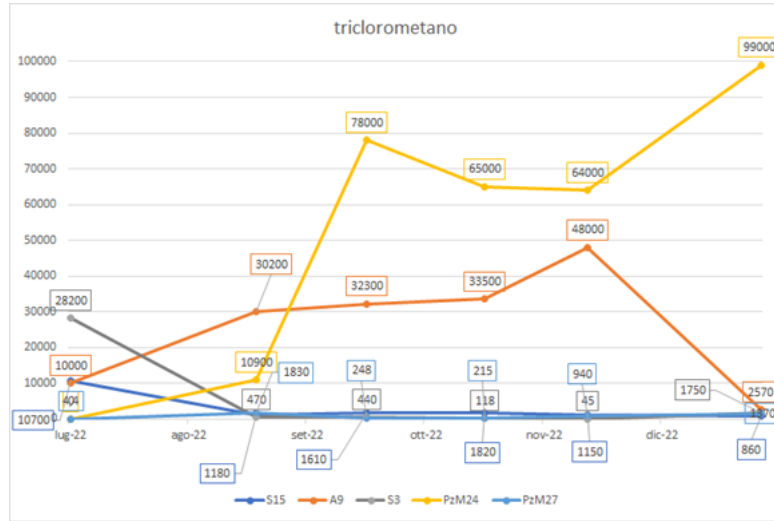
Results:

Remedial goals obtained for all contaminants in the pilot area

- TCM > 90% reduction
- MCB > 90% reduction
- BTEX > 90% reduction



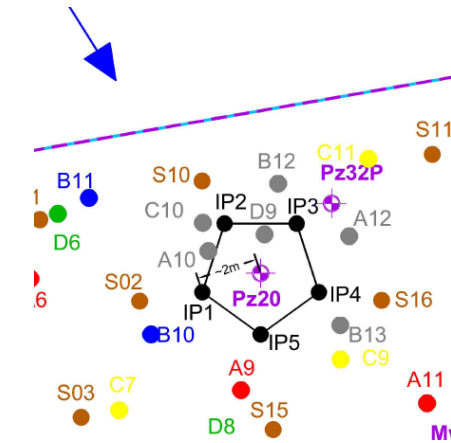
Results - Post Application Data (6 Months) outside the Pilot Area



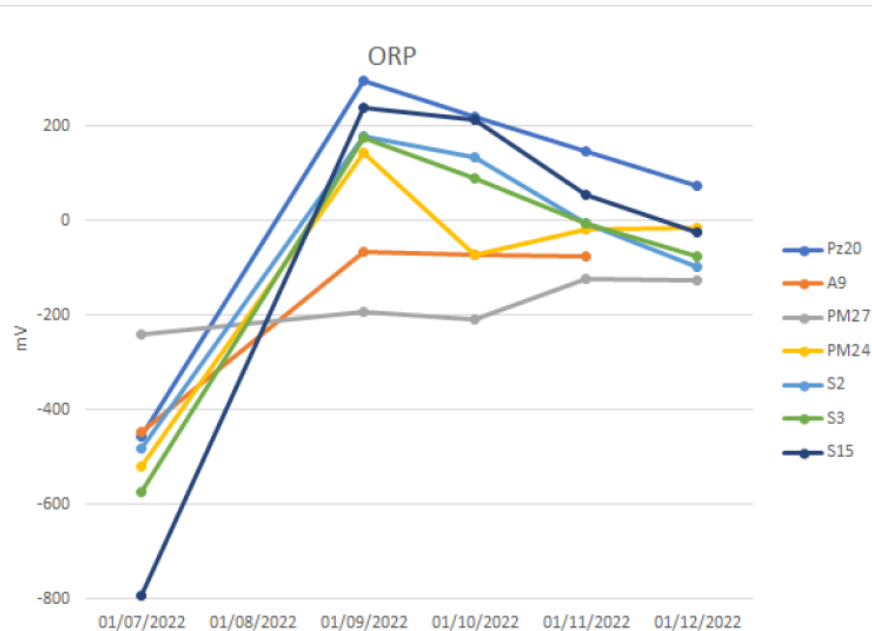
Results:

Fluctuating results obtained for all contaminants in piezometers outside pilot area

- Partial degradation due to the lower KLOZUR[®] dosage
- Desorption of COCs due to high pH

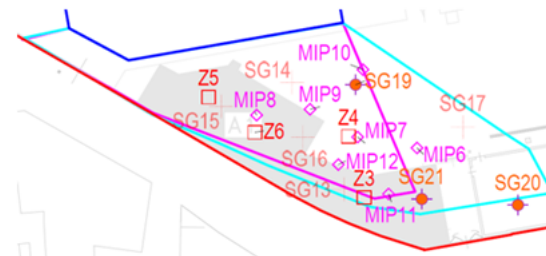
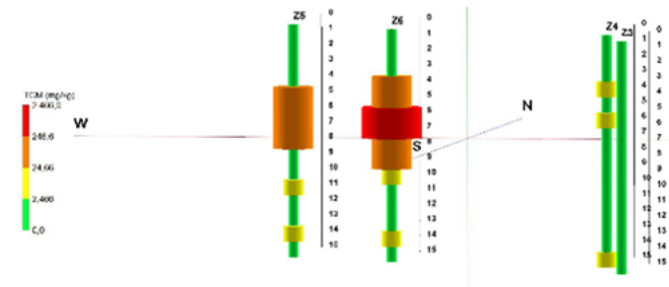


Geochemical Response - Post Application Data (6 Months)



An increase in oxidative reductive potential (ORP) was observed at all monitoring points in the treatment area, as well as higher dissolved oxygen (DO) concentrations.

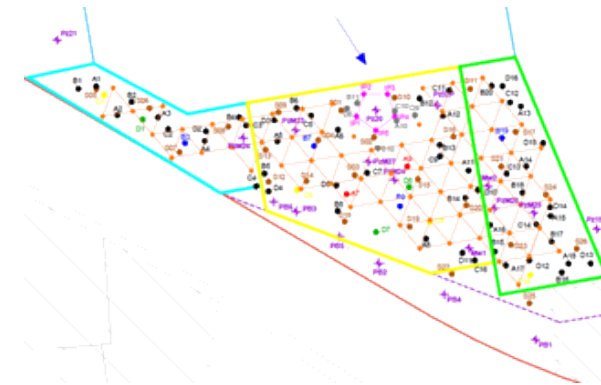
This data confirmed that KLOZUR® CR was effective in creating and maintaining the parameters necessary to remediate the contaminants found at this site. Residual TCM contaminants have been detected in saturated soils in 2022 (samples Z3, Z4, Z5 e Z6 – outside pilot area).



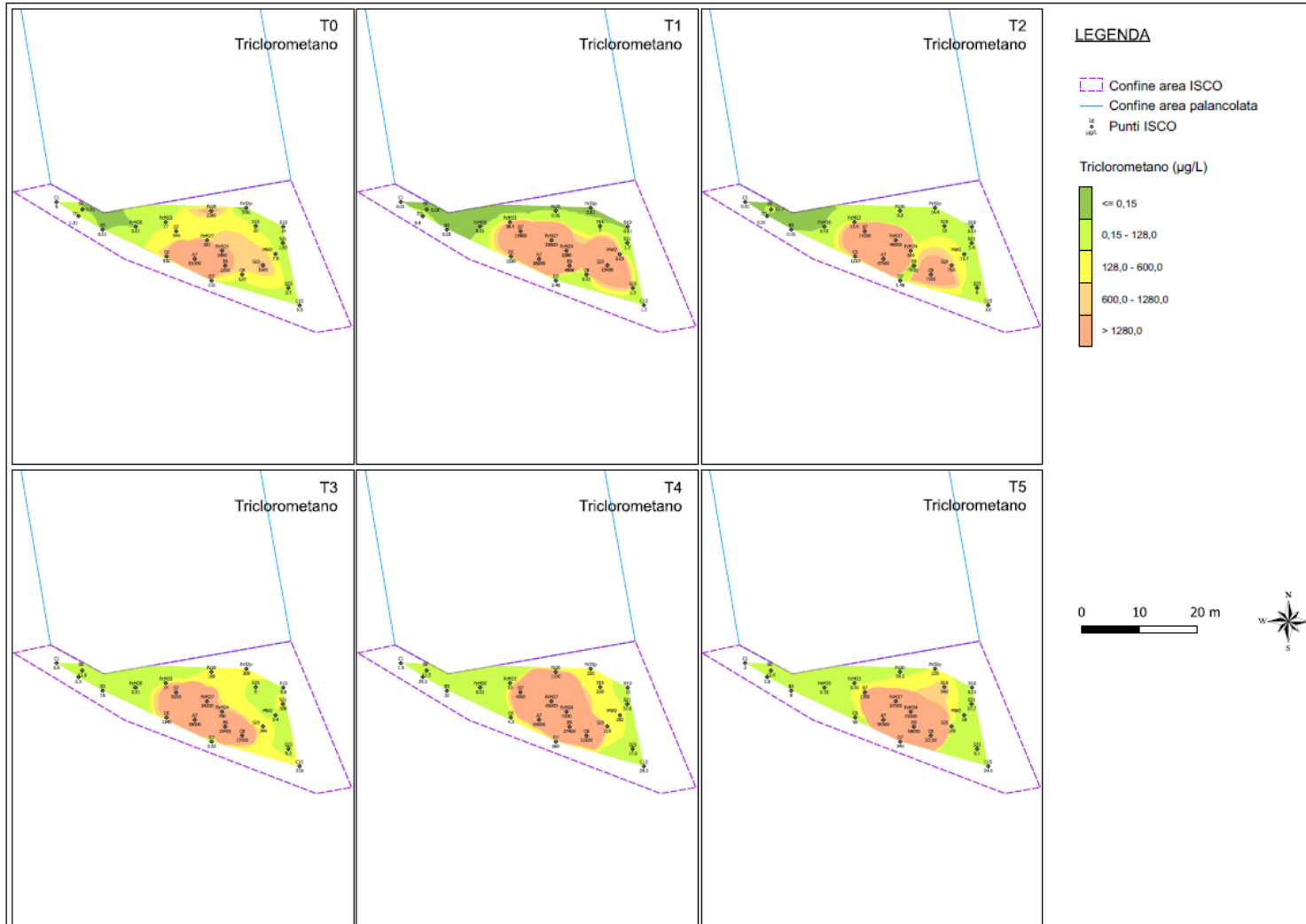
KLOZUR® Full-Scale in ISCO Area (June 2023)



- A total of 29.1 MT KLOZUR® CR along with 9.2 MT KLOZUR® KP injected over one injection events via manchette tubs:
 - 71 injection points with ROI $\approx$ 3 m
 - 2200 liters (582 gallons) per point at 20% by weight aqueous slurry
 - Bottom-up pressured injections



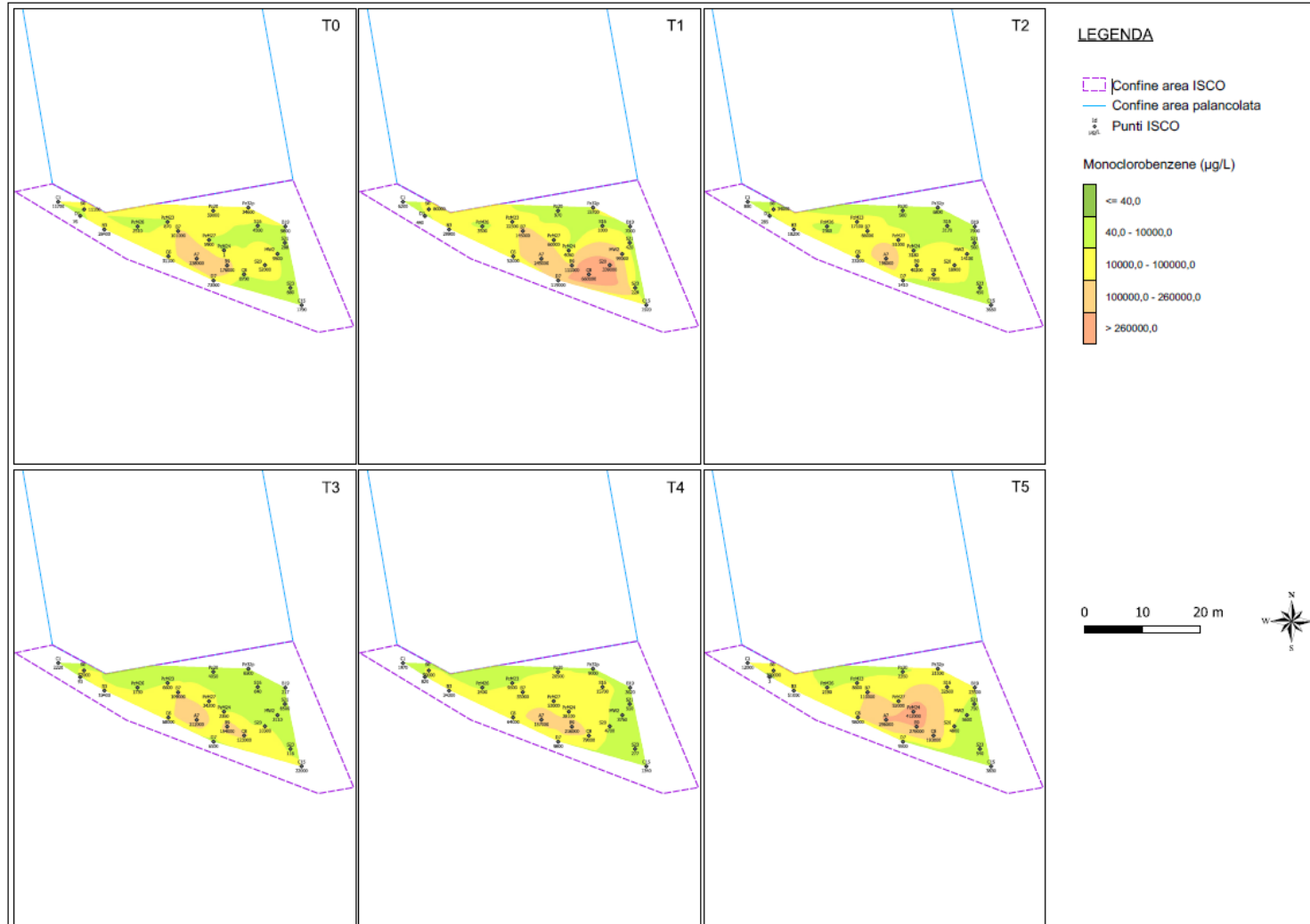
TCM Results – Full-Scale Post Application Data (6 Months)



TCM Results:

- Remedial goals obtained in the light-contaminated zones (> 90% reduction)
- Evidence of rebound in the most contaminated (source) zone demonstrating adsorbed contamination
- Ongoing treatment – possible polishing step after 1 year from the first full-scale injection campaign

MCB Results – Full-Scale Post Application Data (6 Months)



MCB Results:

- Remedial goals obtained in the light-contaminated zones (> 90% reduction)
- Evidence of rebound in the most contaminated (source) zone demonstrating adsorbed contamination
- Ongoing treatment – possible polishing step after 1 year from the first full-scale injection campaign

Summary

- Client has been happy with approach combining ISCO with aerobic bioremediation; approach continues to be used by client
- Multiple sites planned for 2024 and 2025

**Remedial goals achieved.
Polishing ongoing!**

- KLOZUR® CR is ideal for low to moderate levels of petroleum hydrocarbon contamination
 - Three possible treatment pathways from a single application:
 - In-situ chemical oxidation with activated persulfate and hydrogen peroxide
 - Aerobic bioremediation with extended release PERMEOX® Ultra
 - Anaerobic biological oxidation (with specific geochemical conditions)
- Highly contaminated sites would favor more classic ISCO applications

Questions?

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





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