

Application of an All-in-One ISCO Technology for the Treatment of Hydrocarbons, BTEX and MTBE at a Former Retail Petrol Station in Italy

Battelle Bioremediation Symposium, May 9, 2023

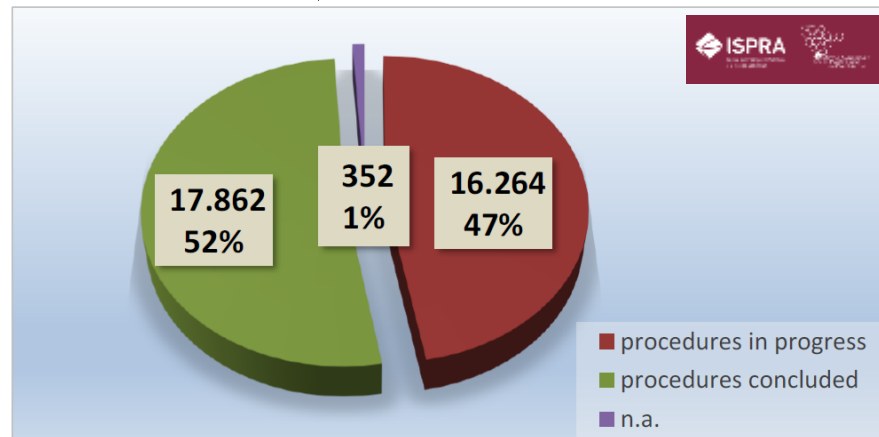
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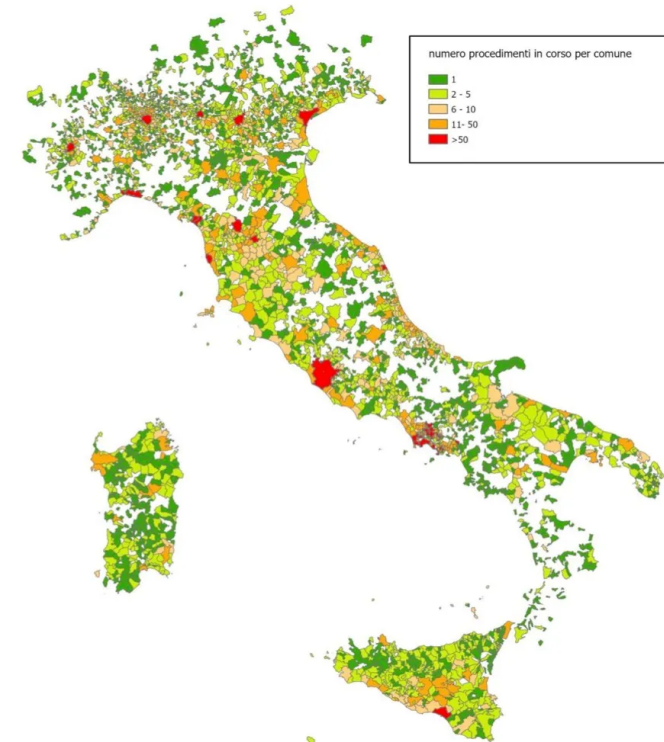


Discussion of Petroleum Hydrocarbons in Italy

- 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 34.478,00. In particular, 16.264,00 sites had ongoing procedures, and 17.862,00 ones reached the Site Closure.



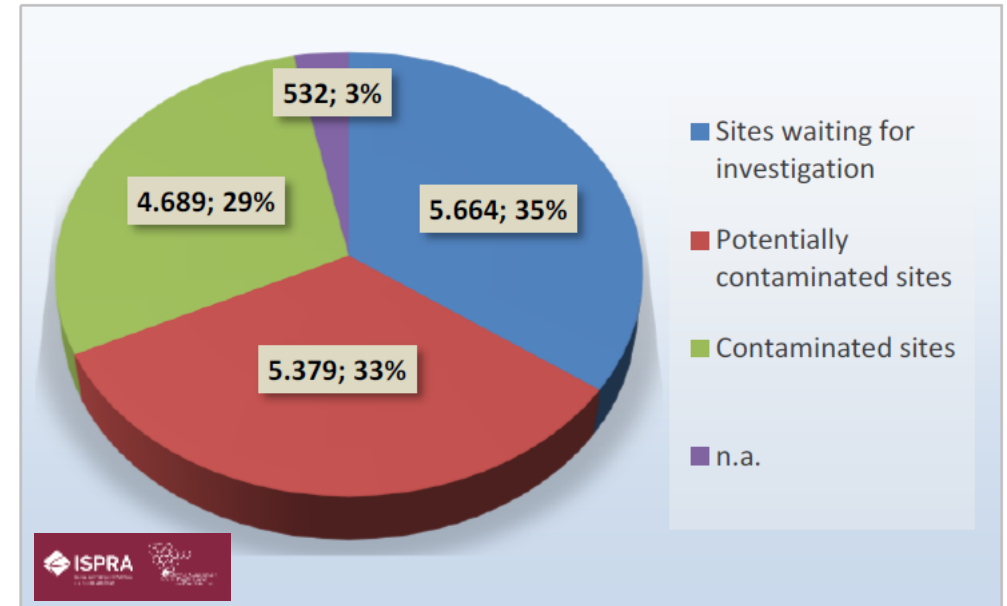
Number of OPEN contaminated site proceedings for each IT Municipality

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

Discussion of Petroleum Hydrocarbons in Italy

Procedures in progress - The information on the contamination status is reported for 15.733,00 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 a *in-situ* remedy for many reasons,

- Need to solution in areas that cannot be excavated – *i.e. Active Gas Stations and/or Oil Deposits*
- Existing *In-situ* remedies had been unsuccessful – *i.e. Physical Remedial Approach such as P&T, SVE etc., Other common reagents etc.*
- Large portfolio of sites needed a safe and cost-effective approach that could be implemented throughout the country

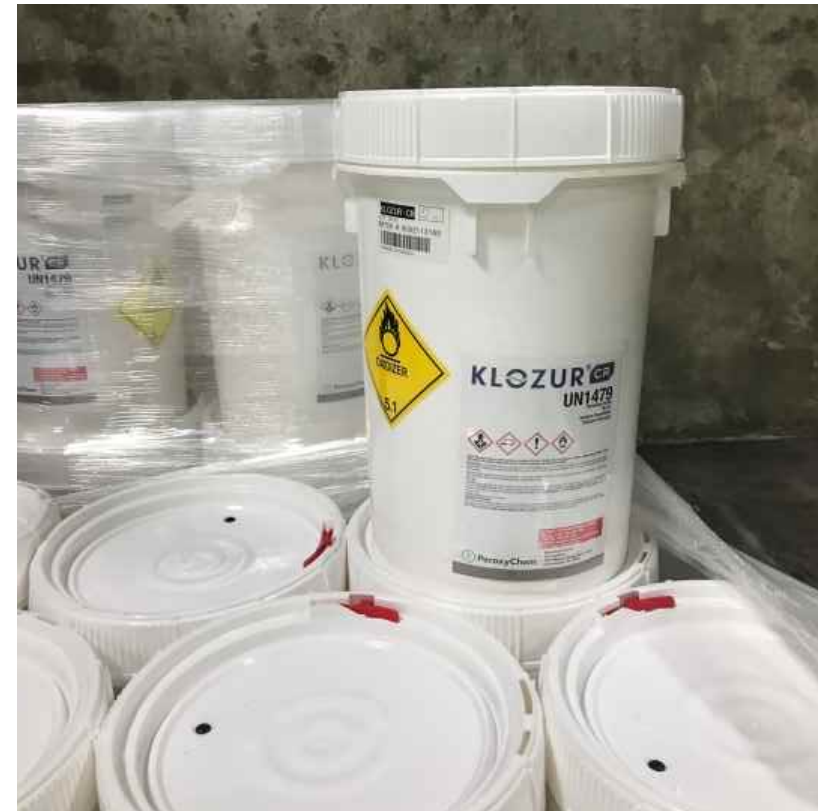
In 2017, Evonik was contacted from several firms regarding our technologies

- Considering typical concentrations and characteristics of sites we reviewed, we generally recommended then test 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

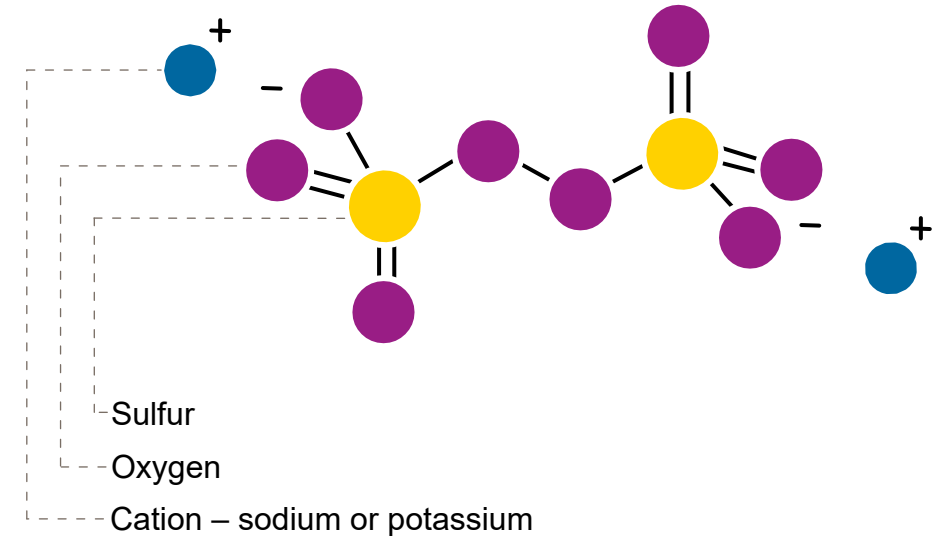
- Released in 2006 – Over 15 years of experience
- “CR” = Combined Remedy
 - In situ chemical oxidation (ISCO)
 - Aerobic bioremediation
 - Anaerobic oxidation
- Klozur® CR is a blend of Klozur® SP and PermeOx® Ultra
 - Typical blend is 50:50 ratio
 - PermeOx® Ultra activates the sodium persulfate

Three remedial pathways in 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

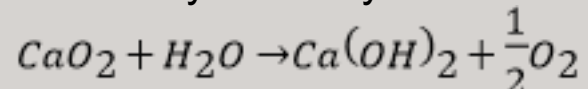
- PermeOx[®] Ultra

- 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 (2017-2022)

- Up to 150 sites have been treated using Klozur® CR technologies in the last couples of years in all the main provinces of Italy.
- About 60% sites have reached closure with the first Klozur® CR injection campaign.
- Additional 30 % 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 have 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 IT provinces. In Red up to 10 sites per area, In Yellow 5-10 sites per area, in green <5 sites per area.

Klozur® CR Leads to Site Closure in Urban Bologna, Italy Gas Station

Site: Confidential Former Petroleum Station

Location: Bologna City Center, Italy

Contaminants: Petroleum hydrocarbons
(benzene, ethylbenzene, MTBE) in
groundwater

Remedial Approach: Injection of Klozur CR to
treat source area and plume



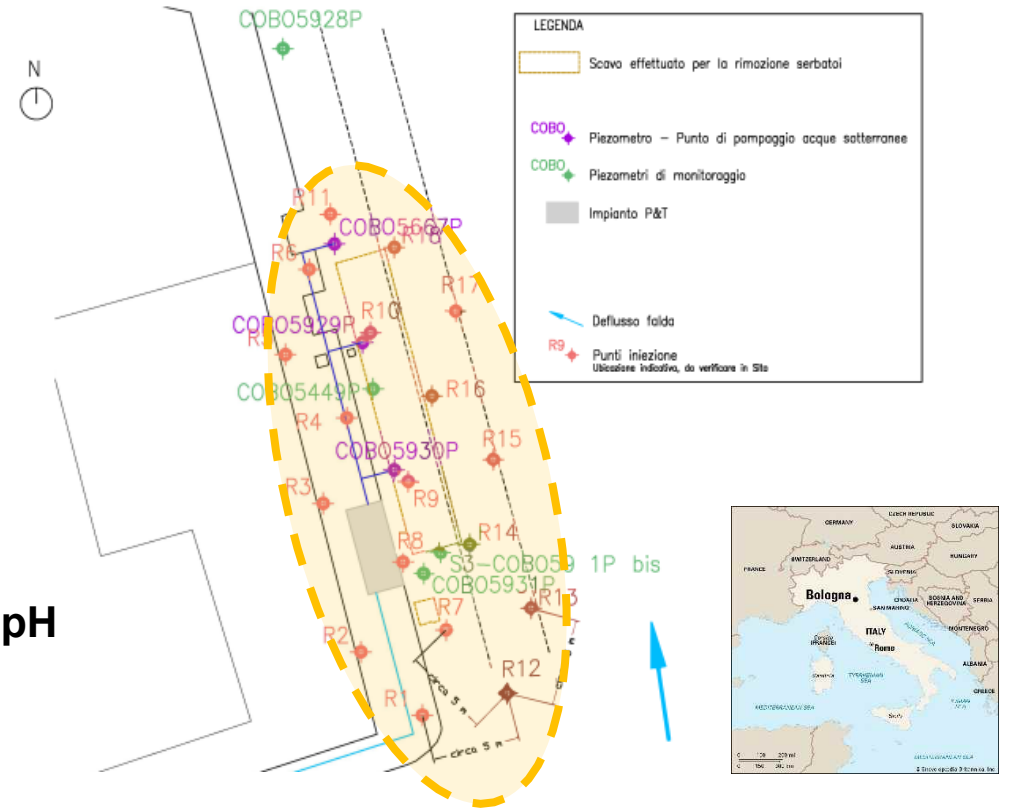
Early Pilot Test – PermeOx® Ultra application via Soil Mixing

- In 2016, Excavation of the main contaminated zones and PermeOx Ultra application via *Soil Mixing* at the bottom of the pit have been proposed.
- Local regulators have evaluated that Full-Scale Dig & Dump followed by Soil Mixing could have affected the local traffic system in the city center of Bologna for months.
- Local Authorities required Petrol Company to evaluate alternative such as Direct Push Injection of reagents.
- Klozur® CR has been selected for injection into the impacted groundwater and capillary fridge.



Site Details

- Treatment area: > **350 m²** (3,800 ft²)
- Treatment interval: **4 to 9 m bgs** (13 to 30 ft bgs)
- GW table: **4 m bgl** (13 ft)
- Saturated soil matrix: **Silty sands to silty clays**
- Seepage velocity ≈ **4÷ 5 m/yr**
- GW natural geochemical conditions: **Moderate Anaerobic, Neutral pH**



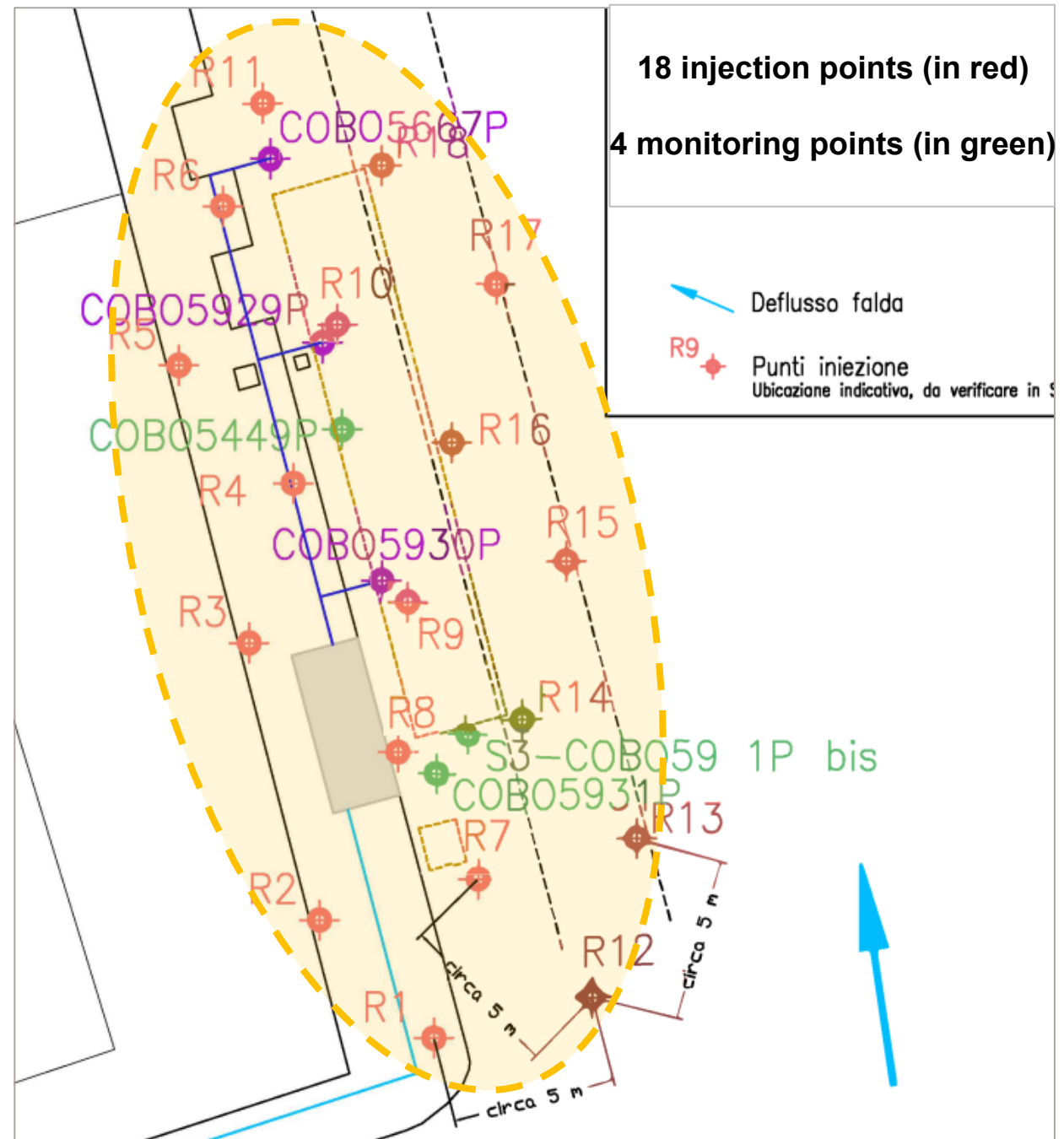
Baseline Concentrations and Remedial Goals

Contaminant of Concerns:

- Total Petroleum Hydrocarbons (TPH) \approx 2 mg/l
- Benzene \approx 0.5 mg/l
- Ethylbenzene $>$ 0.4 mg/l
- MTBE $>$ 13 mg/l

Cleanup goals: Regulatory limits

- TPH = 0.35 mg/L
- MTBE = 0.04 mg/L
- Benzene = 0.001 mg/L

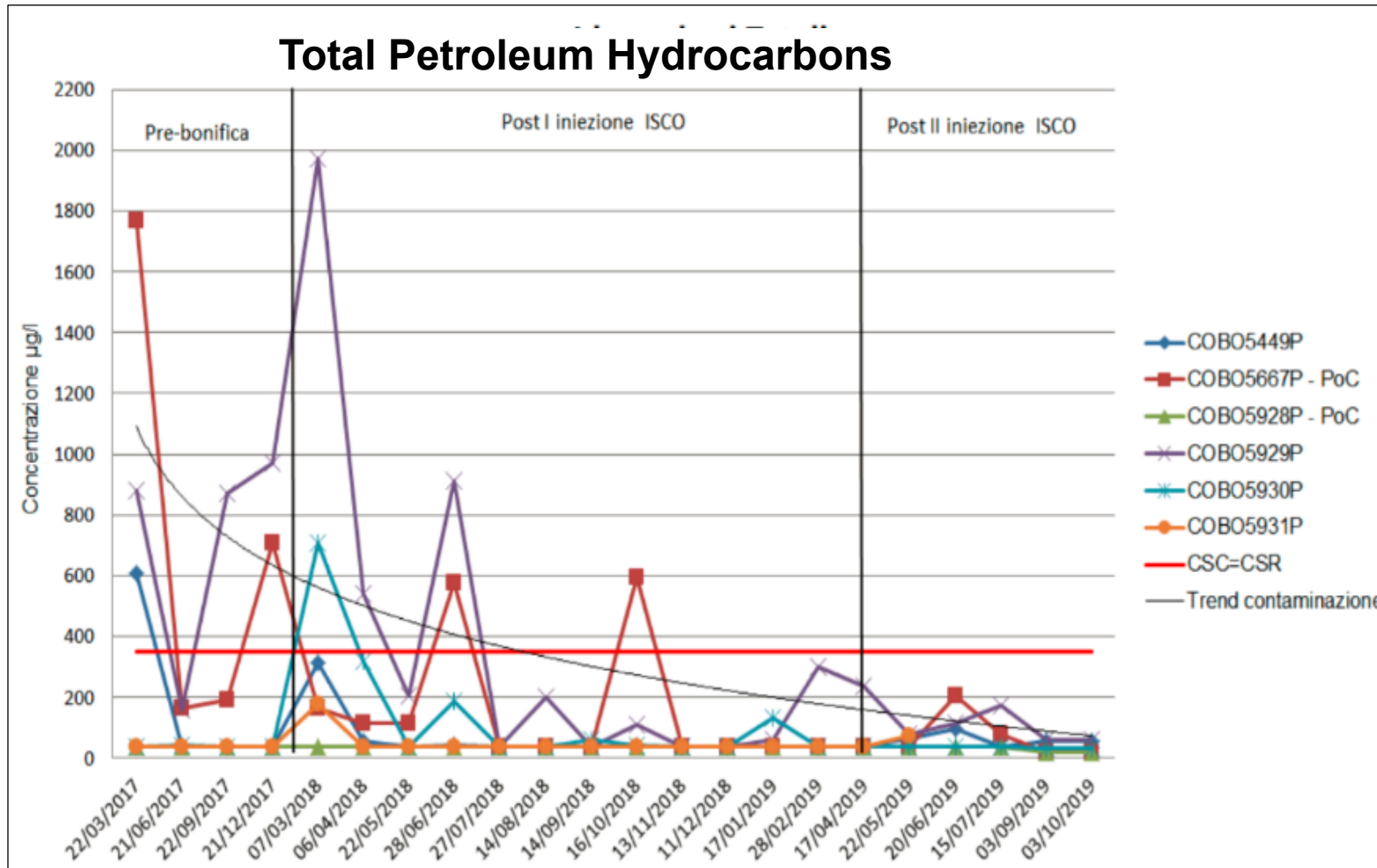


Klozur® CR Applied in Two Injection Events (2018 -2019)



- A total of 6300 kg Klozur CR injected over two injection events via DPT:
 - First Injection event (February 2018):
 - 18 Injection points
 - 190 kg (419 lbs) of Klozur CR per point
 - 25% by weight aqueous slurry
 - Second Injection event (April 2019):
 - 18 Injection points
 - 160 kg (353 lbs) of Klozur CR per point
 - 25% by weight aqueous slurry

Results - Post Application Data (24 Months)



Results:

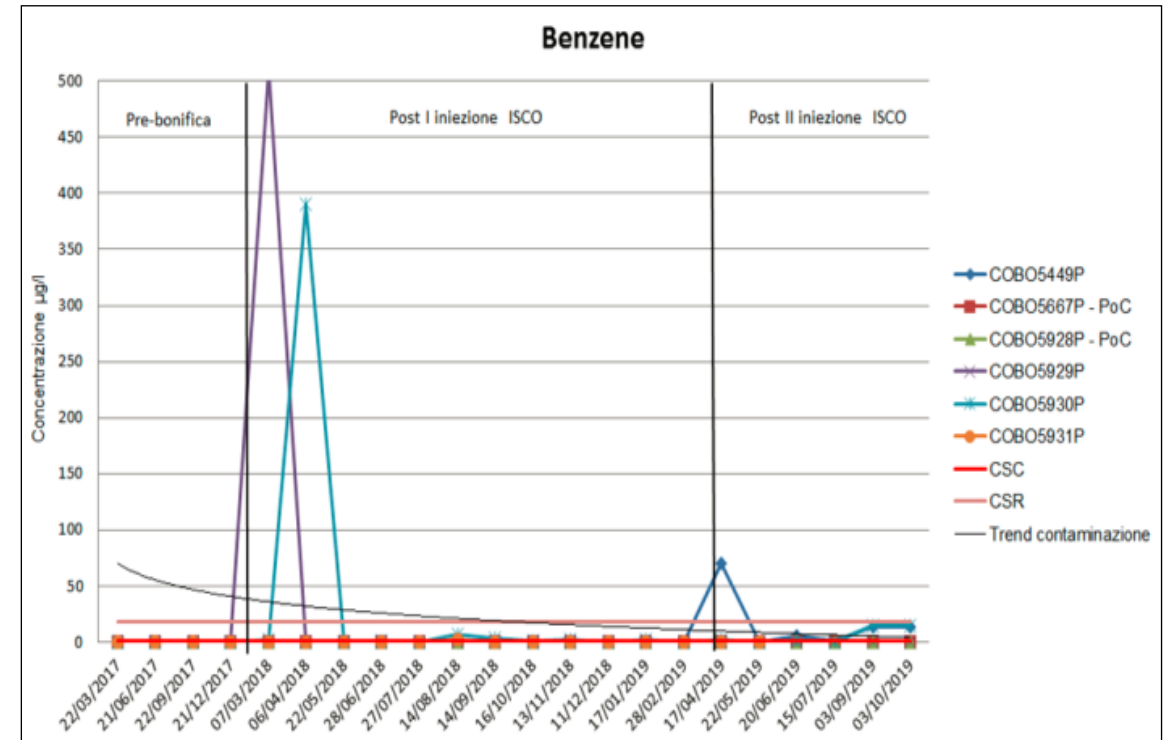
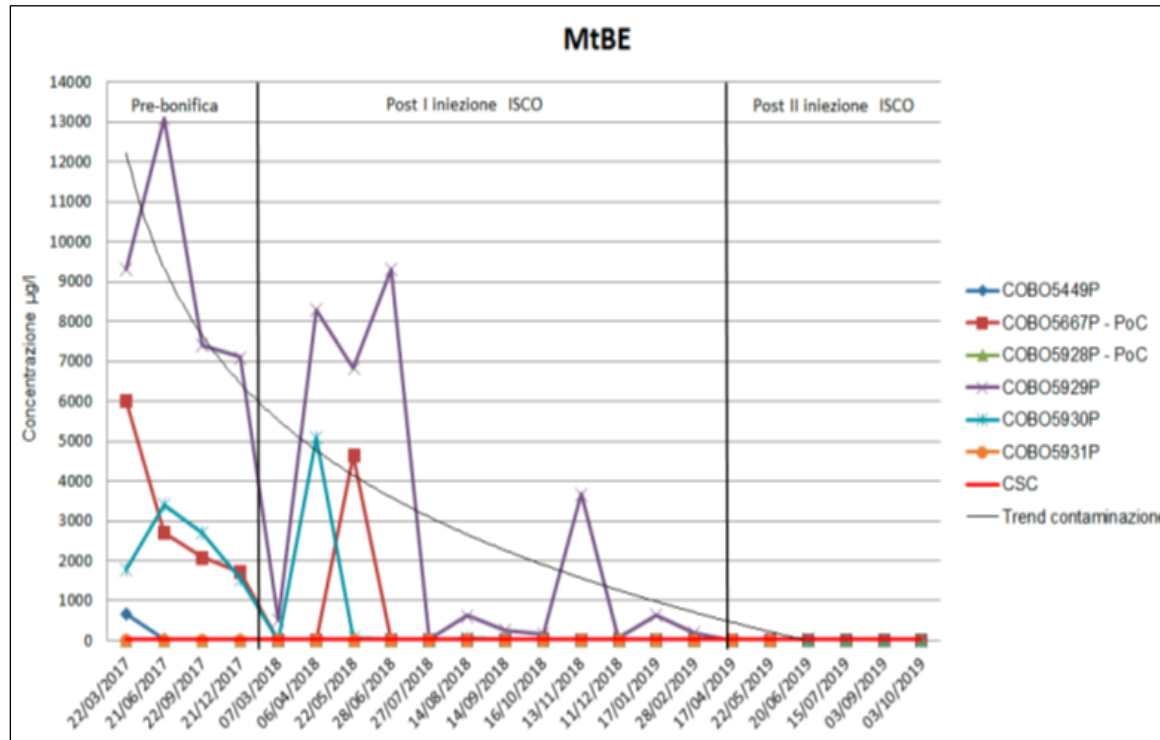
Remedial goals obtained for all contaminants

TPH > 80% Reduction

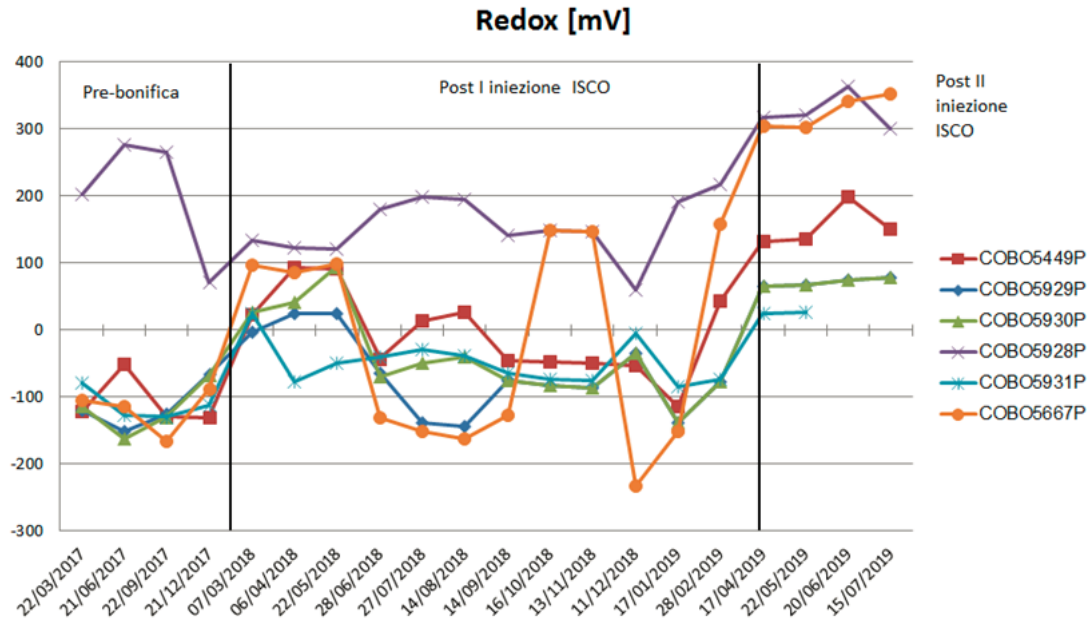
MTBE > 90% Reduction

Benzene > 90% Reduction

Results - Post Application Data (24 Months)

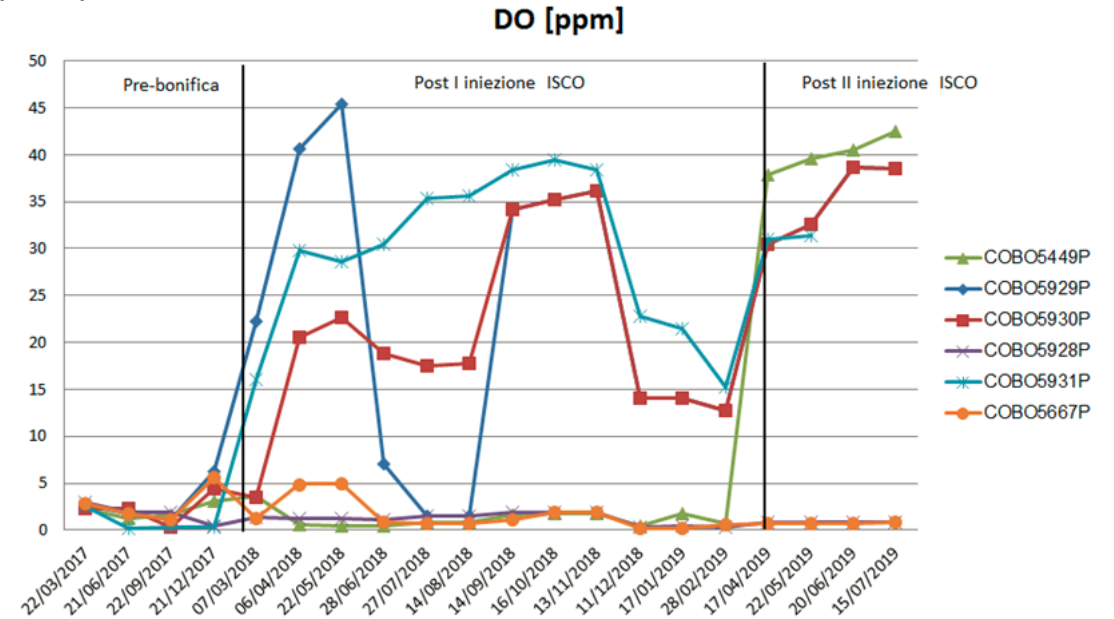


Geochemical Response - Post Application Data (24 Months)



This data confirmed that Klozur CR was effective in creating and maintaining the parameters necessary to remediate the contaminants found at this site.

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.



Summary

- Client has been happy with approach combining ISCO with aerobic bioremediation approach is continuing to be used by client
 - *Multiple sites planned for 2023 and 2024*

**Remedial goals achieved
Site Closed !**

- 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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