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Case study

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Large-scale Application of Klozur® CR for the Treatment of an Aquifer Contaminated with Heavy Hydrocarbons and MTBE in Southern Italy

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Summary

Klozur® CR is a combined remedy treatment technology consisting of Klozur® SP and PermeOx® Ultra. Klozur CR is a single, all-in-one formulated product that can be readily applied to either source areas or plumes with mixed petroleum and chlorinated solvents contamination. Klozur CR destroys contaminants in soil and groundwater by promoting three modes of action: Klozur activated persulfate chemical oxidation, aerobic bioremediation and anaerobic bioremediation. This technology was successfully applied to a site in southern Italy, contaminated by the storage and sale of fuels. The groundwater was contaminated by heavy chain hydrocarbons (TPH> 2500 µg / l) and MTBE (> 150 µg / l) in proximity to the reservoir park. During the site maintenance activities, the qualitative status of adjacent coastal waters was also verified, which, however, were found to be compliant. Previously the site used a pump and treat system, but it was unable to achieve remedial goals. Klozur CR was injected and within 4 months, the concentrations of the contaminants were found to have reached the remedial goals. In addition, monitoring data also confirmed enhanced ISCO conditions and enhanced aerobic bioremediation were present at the site.

The Approach

2016 monitoring data suggested that the total contaminated area of the site was approximately 700 m^2.

Figure 1: Site location (via Google Earth)

During the first phase of hydraulic containment (P & T), the trend over time of TPH and MTBE concentrations in the groundwater of the area showed a significant reduction in the first months of operation; however, in 2017 the values still higher than the remedial goals. To obtain remedial goals Klozur CR was applied for an *in situ* chemical oxidation ISCO and an enhanced bioremediation approach to contaminant destruction. The distribution of contaminant concentrations, in the source area, before the treatment activity is shown in Figure 2 for heavy hydrocarbons and in Figure 3 for MTBE.

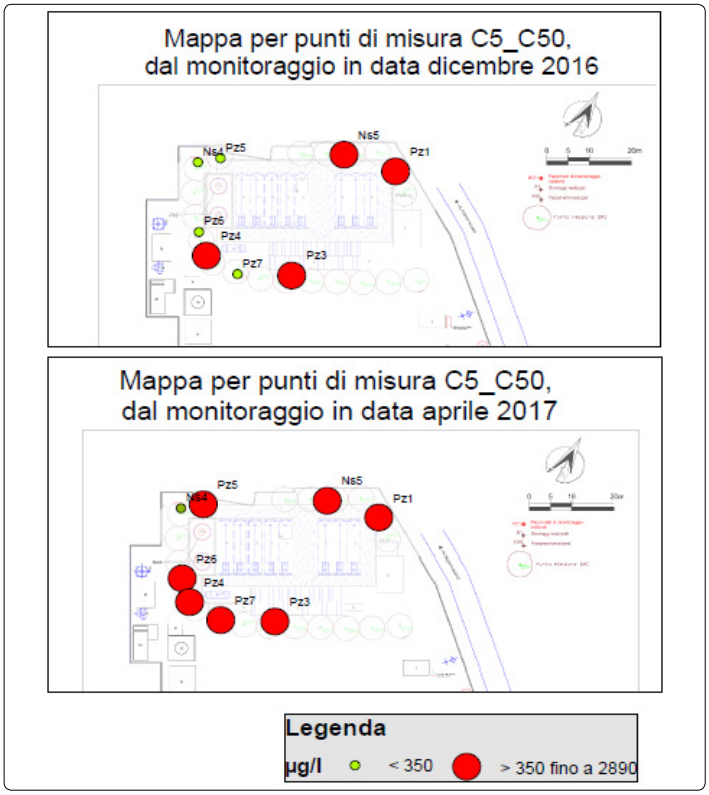

Figure 2: Concentrations of heavy hydrocarbons in the source area before treatment.

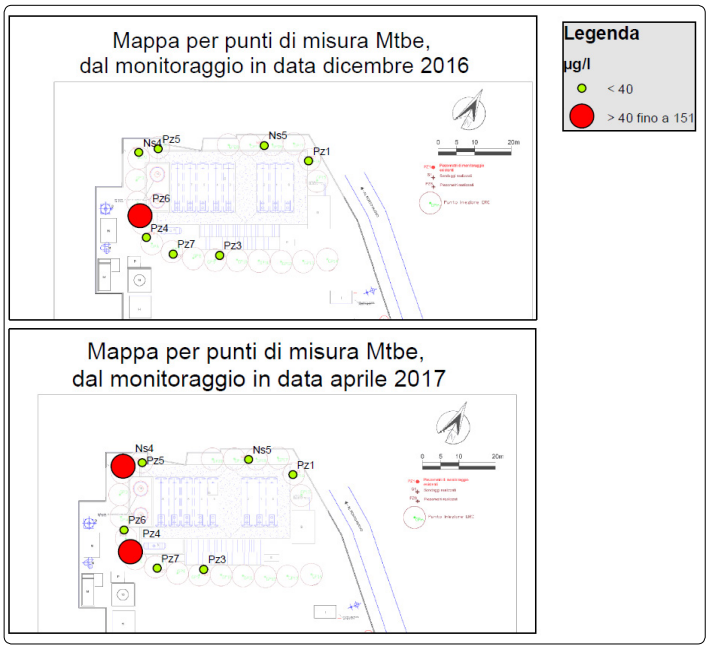

Figure 3: MTBE concentrations in the source area before treatment

The contaminated surface aquifer consists of pyroclastic deposits and massive lavas whose hydraulic conductivity is approximately 6 x 10^{-5} m / s; consequently, the linear velocity of the groundwater flow is equal to about 126 m / year, considering a hydraulic gradient of about 2% and an effective porosity of the saturated medium of about 30%. The piezometric surface is located about 5 meters below ground surface, while the base of the aquifer, represented by a compact lava, about 9 m from the ground. Furthermore, before treatment, the aquifer showed naturally anaerobic conditions (Eh ≈ -20 mV, DO ≈ 1 mg / L), an average sulfate content of about 42 mg / L and pH values in the range of neutrality (pH ≈ 7). To help determine proper dosing of Klozur CR for the site, a Soil Oxidant Demand (SOD) value of 1g of Klozur / Kg of soil and a base buffering capacity (BBC) of 3 grams of 25% NaOH / Kg of soil were assumed.

The Science of KLOZUR CR

Klozur® CR, a Combined Remedy technology, is comprised of a specially formulated mixture of Klozur® SP and PermeOx® Ultra. Klozur CR is a single, all-in-one formulated product that can be readily applied to either source areas or plumes with mixed petroleum and chlorinated solvents contamination. Klozur CR destroys contaminants in soil and groundwater by promoting three modes of action: Klozur activated persulfate chemical oxidation, aerobic bioremediation and anaerobic bioremediation. Klozur CR provides self-activating Klozur persulfation oxidation technology, utilizing the alkalinity generated by calcium peroxide to achieve a pH in the range of 11. In addition, the calcium peroxide will slowly generate hydrogen peroxide allowing for peroxide activation of persulfate. High pH activated persulfate is capable of destroying a wide range of contaminants, including petroleum hydrocarbons and chlorinated solvents. Following the initial chemical oxidation phase, Klozur CR will continue to release oxygen to be used as an electron receptor for aerobic bioremediation for up to a year, as a result of the slow hydration of the engineered calcium peroxide. Diffusion and transport of oxygen downgradient will support contaminant reductions in plume areas, treating BTEX, PAH's and petroleum hydrocarbons. As a result of the persulfate oxidation with organic compounds, generated sulfate ions can be utilized by sulfate reducting bacteria as an electron acceptor under anaerobic conditions to degrade BTEX, PAH's and petroleum hydrocarbons.

Field Application

In May 2017, about 2300 kg of Klozur CR as a 25% slurry was injected under pressure (≈ 4 bar) between depths of 5 m and 7.5 m below ground surface (bgs) through 20 fixed injection points (Figure 4) distributed in the source area. The remedial goals were TPH = 350 µg / L, and MTBE = 40 µg / L for the treatment area (PZ3, PZ4, PZ5, PZ6, PZ7 and NS5).

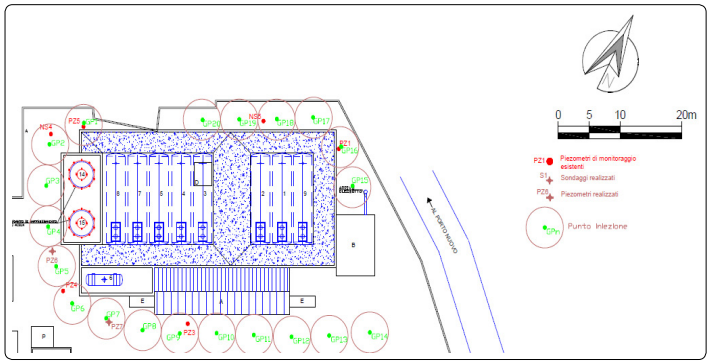

Fig. 4: Grid of the injection points n ° 20 (in green) and monitoring points n ° 8 (in red) together with the direction of flap NE.

Results

In less than 6 after the Klozur CR injections, the remediation objectives were achieved. Figure 5 shows the concentrations of TPH and MTBE in groundwater have decreased to be below the remedial goals.

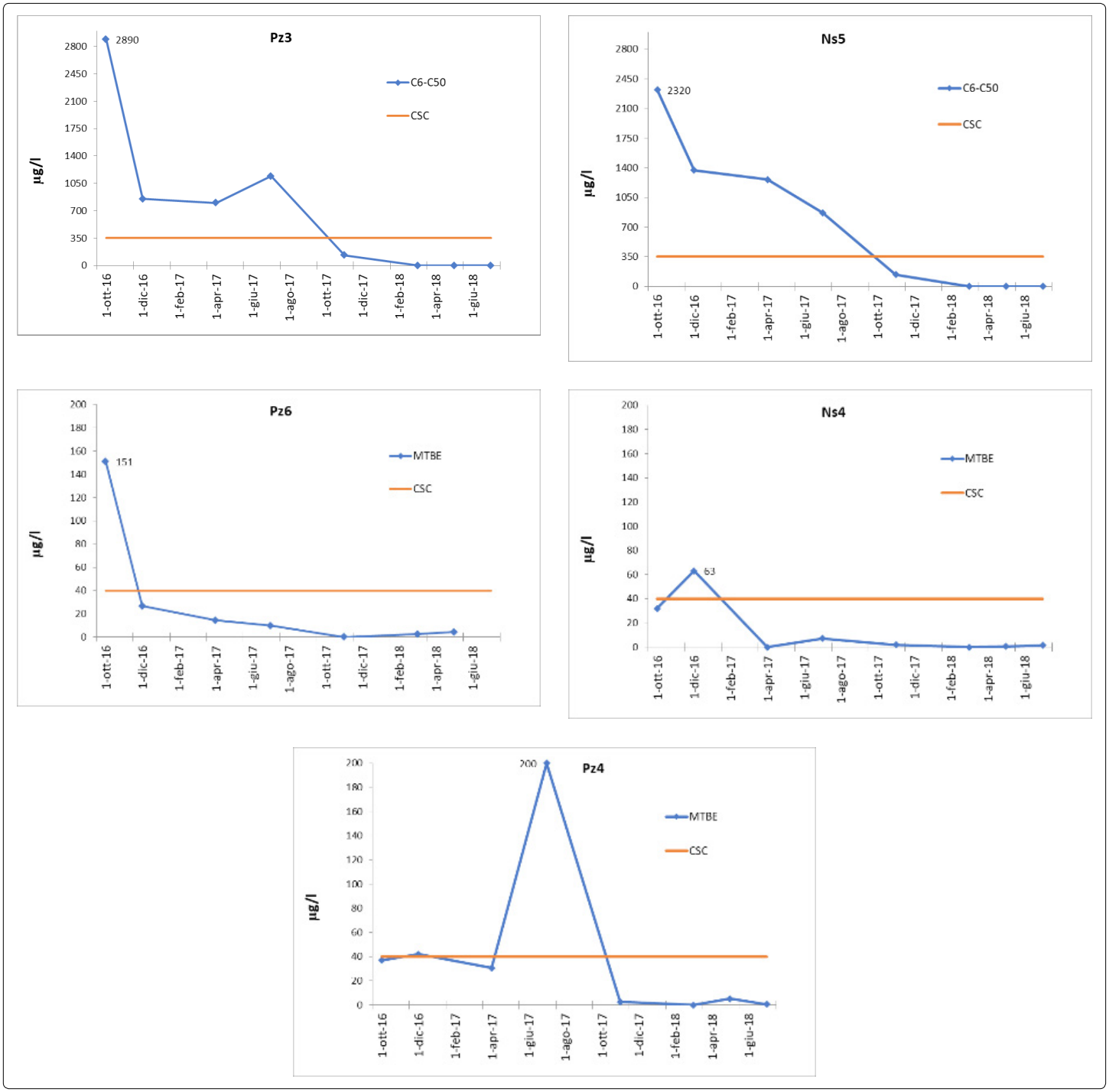

Fig. 4: TPH and MTBE concentration monitoring data in the treated groundwater before and after the application of Klozur® CR

No subsequent rebound phenomena of the solution contamination were observed, demonstrating the complete degradation of the present contaminant mass. In any case, a second injecting campaign, for the final cleaning of the aquifer, was performed in January 2019 and consisted of an application equal to the previous one in terms of both Klozur CR reagent quantities and operating methods. During the application activities and subsequently, alterations of the qualitative status of the coastal waters adjacent to the site have never been observed.

Secondary Monitoring Parameters for Klozur CR

To determine that the treatment ware was under the influence of the applied reagents and to demonstrate the extent of distribution, parameters including Fe (II) and Mn were monitored. A significant decrease in Fe (II) and Mn concentrations in all the monitoring piezometers present in the treatment area was observed, confirming the correct distribution of the reagent in the stratum and the establishment of enhanced aerobic conditions.

In addition, an increase in the oxidation-reduction potential (ORP) was also observed at all treatment site monitoring points, as well as an increase in dissolved oxygen concentrations [1-6].

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