Pump&Treat versus bioremediation: a comparative test for Sulfates treatment in groundwater

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Summary

The green-remediation options allow sustainable-environmental solutions, the reduction of remediation times and not negligible economic benefits. In the present study case, it has made it possible to accelerate the redevelopment of a disused industrial area, one of the largest sugar refineries in Italy, that operated the cycle of processing sugar beet into refined sugar and other secondary products.
The characterization of the subsoil and the analysis of health and environmental risk have shown unacceptable levels of risk for surface soils and groundwater for the Sulfates parameter.
The redevelopment of the site included the permanent securing of surface soils through a stabilization intervention with lime and an intervention for groundwater through a system of Pump & Treat implemented with bioremediation.

Riassunto

Le opzioni di green-remediation consentono soluzioni ambientali sostenibili, la riduzione dei tempi di bonifica e non trascurabili vantaggi economici. Nel caso in esame, ha consentito di accelerare la riqualificazione di un'area industriale dismessa, uno delle maggiori raffinerie di zucchero di Italia che operava il ciclo di trasformazione della barbabietola da zucchero in zucchero raffinato ed altri prodotti secondari.
La caratterizzazione del sottosuolo e l'Analisi del Rischio Sanitario ed ambientale hanno evidenziato livelli di rischio inaccettabili per i terreni superficiali ed acque sotterranee per il parametro solfati.
Le attività di riqualificazione del sito hanno incluso la messa in sicurezza permanente dei terreni superficiali mediante un intervento di stabilizzazione a calce e un intervento per le acque sotterranee mediante un sistema di Pump & Treat implementato con biorisanamento.

1. Introduction

The sugar refinery area was dismantled about ten years ago, together with 13 sugar refineries in Italy above the total of 19, due to the *"Council Regulation (EC) No 320/2006 of 20 February 2006 establishing a temporary scheme for the restructuring of the sugar industry in the Community and amending Regulation (EC) No 1290/2005 on the financing of the common agricultural policy"*.

The site occupies a surface area of approx. 400 000 m^2 (see figure 1) located in an industrial/commercial/services zone located few meters from the nearest residential area and surrounded by plots of agricultural land. A minor river is located about 150 m from the plant and a small channel on the border.

The underground lithology of the first 15 meters of this site can be summarized as follows:

- 0.0 – 1.5 m bgs[1]: surface material consisting of gravel and sand;
- 1.5 – 4.0 m bgs: clayey silt and silty clay;

[1] Bgs: below ground surface

- 4.0 – 9.0 m bgs: sand and silty sand and/or gravel in sandy matrix;
- 9.0 – 15.0 m bgs: prevailing clay with low permeability.

The following Figure indicates the topographic map of the site containing the location of the former sugar refinery area and the remediation wells.

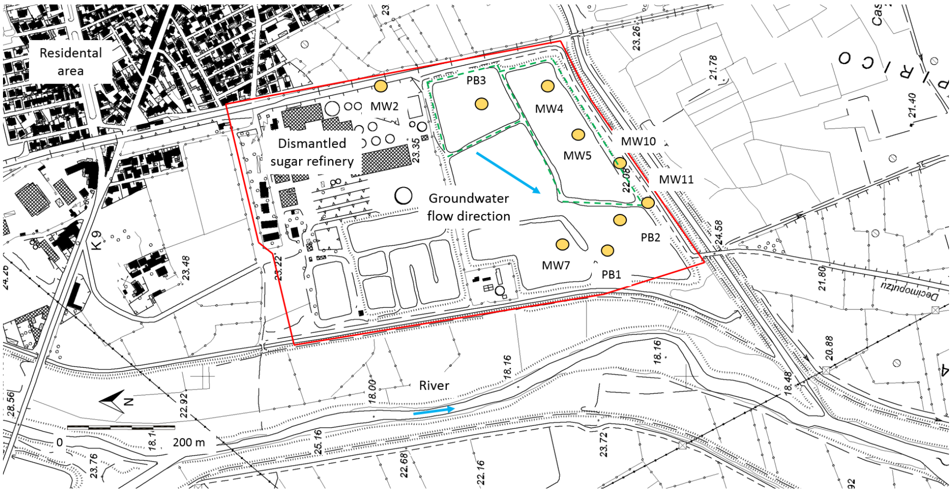

Figure 1 – Topographic map with the location of the former sugar refinery area.

The aquifer is located at a depth from 2 to 9 m below ground surface and the groundwater level is between 2 and 3 m. The average permeability (K) is about $1{,}83E^{-4}$ m/s, the hydraulic gradient under static conditions is about 0.005 with flow direction from PB3 to PB1-PB2 (see Figure 1).

The main critical area identified at the sugar refinery involves a part of the former wastewater treatment plant WWTP basins (green lines in Figure 1), used to treat and re-cycle the industrial-process water. The following substances were used: hypochlorite, sulphuric acid, caustic soda, flocculants (metal based and organic polyelectrolyte), hydrochloric acid, sulphur dioxide and other surfactants.

A performed soil and groundwater survey and risk analysis [2] highlighted unacceptable environmental risks to sub-soils and groundwater for the parameter Sulfates found in the WWTP basins.

2. Activities

Site redevelopment included the permanent safety commissioning by soils lime stabilization of basins area and a Pump & Treat (P&T) plant to cleanup groundwater.

From 2013 to 2017, the P&T system reached a reduction on the Sulfates concentration from 7 800 mg/l to 5 700 mg/l. In addition, other non-target anomalies were removed as follow: 39 kg of Aluminium, 14 kg of Arsenic, 33 kg of Manganese, 34 kg of Nitrites and 1.3 kg of Copper.

After 4 years of P&T the Sulfates concentrations remained significantly high more then 20 times above the legislative limit of 250 mg/l.

Considering that the source of contamination was removed and the former basis areas stabilized, an average estimated Sulfates extraction rate of 500 mg/l was obtained in the first 4 years with the P&T system. After a cost-effective analysis, this extraction rate was considered not reasonable, due the excessive to necessary to reach the law limit of 250 mg/l of Sulfates.

The speed up of the remediation proposed for Sulfates (SO_4^{2-}) in groundwater is the target of the following pilot test based on the bioremediation technique. The bioremediation was reached stimulating the autochthonous Sulphur Reducing Bacteria (SRB) already present at site. Bacteria are capable to degrade the dissolved Sulfates (SO_4^{2-}) into hydrogen sulphide (H_2S) at gaseous state. The oxidized compounds are susceptible to reduction under anaerobic conditions by biotic (biological) processes [3]. Enhanced anaerobic bioremediation is intended to exploit primarily biotic anaerobic processes to degrade oxidized compounds in groundwater using H_2 as electron donor [4]. An organic enhancer can be added to provide the H_2 and Carbon source to the native bacteria community. The sequential reduction performed by bacteria in the environment is schematized in Figure 2.

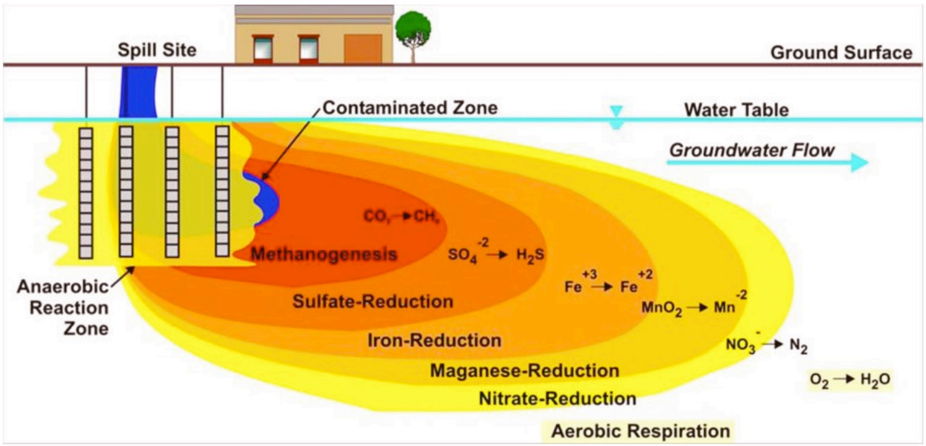

Figure 2 – Reducing zones established down-gradient of substrate injection.

Moreover, in the typical conditions of aquifers (neutral or alkaline pH,) sulphide (S_2^-) reacts with the metals present (Zn^{2+}, Cu^{2+}, Pb^{2+}, Ni^{2+}, Fe^{2+} e As^{2+}) to form insoluble sulphides (E.g. FeS_2) [5].

This approach to accelerate the remediation results was tested on site by a pilot test:

- shutdown the existing groundwater extraction activities;
- a single direct injection of approx. a ton of organic enhancer consisting of glycerol (from 45% to 60%) and mixed triglycerides and soybean oil (from 3% to 10%);
- groundwater monitoring before pilot test and after 30, 60, 90 and 120 days from the initial single injection;
- groundwater analysis for chemical-physical parameters (OD, conductivity, pH and Eh), geochemical parameters (aluminium, arsenic, cadmium, total organic carbon (TOC), total chromium, nickel, mercury, lead, copper, iron, selenium, fluorides, sulphides and Sulfates), microbiological parameters (reducing sulphite clostridium spores).
- soil gas tests to reveal the H_2S concentrations in field and laboratory.

3. Results

The main monitoring results of the bioremediation pilot test are summarized in the following paragraphs and are focused on PB3 pilot test area with the maximum concentration of Sulfates.

3.1 Redox potential (Eh)

The trend of redox potential in groundwater observed during the pilot test activities, from June to December 2017, shows a significant decrease (see Figure 3) derived from the transition from original oxidation conditions before the pilot test [approx. 200 mV] to reducing conditions provoked by the pilot test [approx. -400 mV].

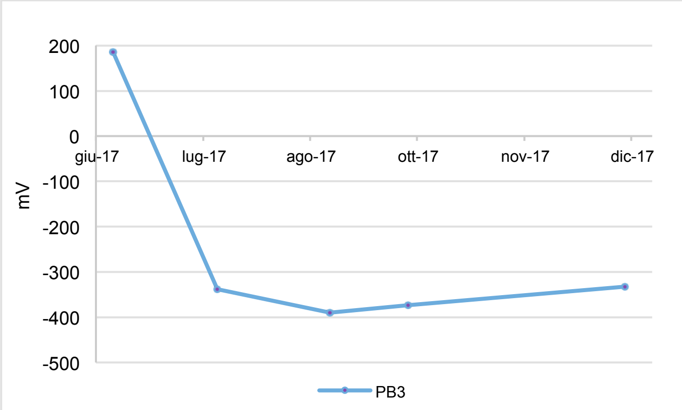

Figure 3 – Trend of Redox Potential in the pilot test area (PB3).

3.2 Total Organic Carbon (TOC)

The trend of the TOC concentration in groundwater observed during the pilot test activities, from June to December 2017, shows the increase of concentration from the initial value of 24 mg/l in June 2017 to 1 753 mg/l in August 2017 and the subsequent decrease until 417 mg/l at the end of pilot test, in December 2017. The increase of the TOC is due to the injection of the organic enhancer and indicate the carbon source bio-available in pilot test area.

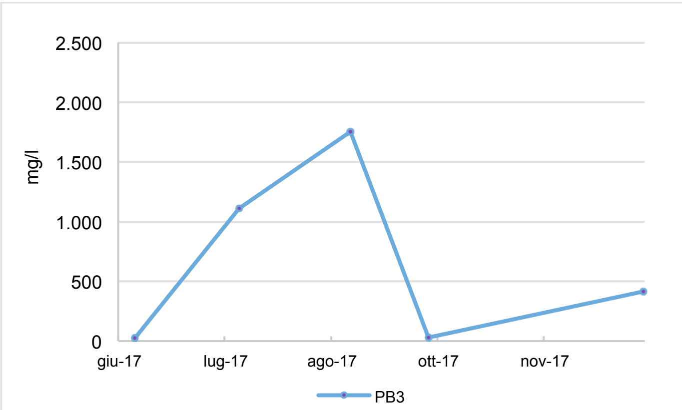

Figure 4 - Trend of Total Organic Carbon in the pilot test area (PB3).

3.3 Reducing sulphite clostridium spores [SRB]

The trend of SRB concentrations in groundwater observed during the pilot test activities, from June to December 2017, shows an increase from the initial value of 21 UCF/100ml and the final concentration of 860 UCF/100ml. The increase of SRB is due to the stimulation of the autochthonous spores.

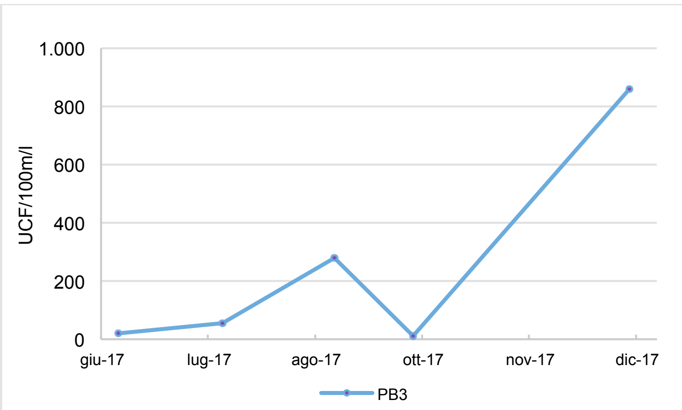

Figure 5 – Trend of SRB in the pilot test area (PB3)

3.4 Sulfates

The trend of the Sulfates concentration in groundwater, from 7 800 mg/l to 5 800 mg/l was observed during the first 4 years of P&T activities. Under pilot test conditions, from June to December 2017, it shows the reduction of about 96% in the concentration of the dissolved Sulfates from the initial value of 5 700 mg/l to 232 mg/l, **below the threshold limit.** The decrease of the Sulfates is due to microbial degradation in pilot test area.

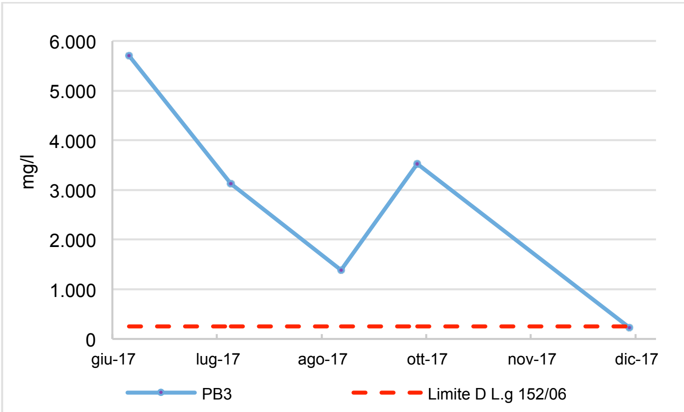

Figure 6 – Trend of Sulfates concentration in the pilot test area (PB3).

4. Conclusions

In 4 years of P&T, from 2013 to 2017, the Sulfates concentration in groundwater decreased from 7 800 mg/l to 5 700 mg/l. During the six months of biorem pilot test activities the Sulfates concentration decreased from 5 700 mg/l to 232 mg/l (figure 6).

The remediation efficiency in the reduction of Sulfates concentration values measured in groundwater is shown in Figure 7 from an average of 525 mg/l/y (or 43.75 mg/l by month) (*concentration from 7 800 to 5 700 mg/l*) with P&T to and average of 10 935 mg/l/y (or 911.3 mg/l by month) (*concentration from 5 700 to 525 mg/l)* with bioremediation.

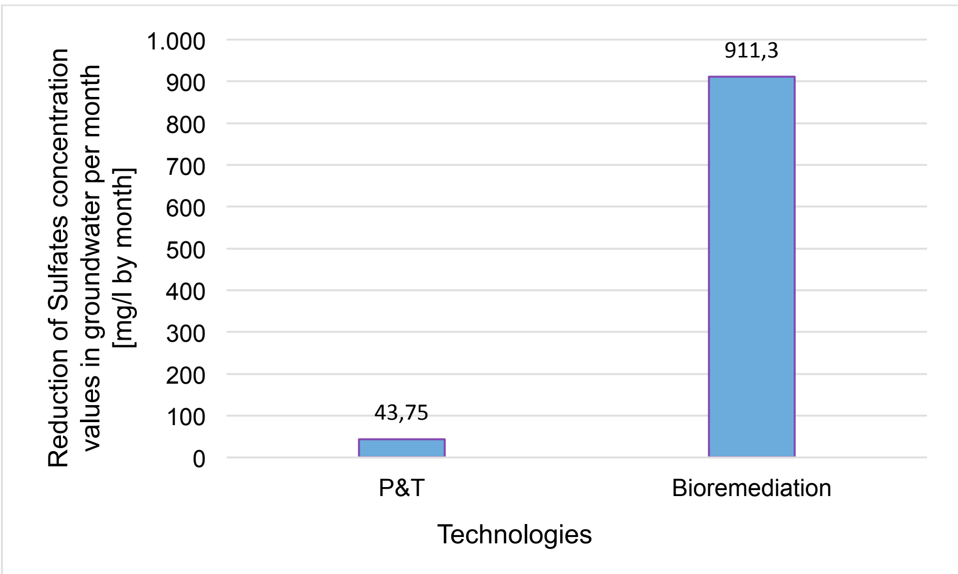

Figure 7 - Comparison of the Sulfates reduction of concentrations in groundwater per month (P&T vs Biorem)

P&T comparison vs Bioremediation looks impressive and should direct the cleanup strategies for the full scale Biorem activities also in relation to the following issues:

- H_2S: emissions could be significant into the injection wells, near groundwater level, but during this pilot test, H_2S was not detected in the manhole well or in the surrounding area of the injection point.
- Metals mobilization: at the initial state it is expected for example for Fe, As, Al and Cu depending of the local chemistry, moreover the metal mobilization is expected to be stabilized.
- Rebound: it is possible to consider rebound phenomena that can interfere in the continuous degradation of the Sulfates.
- Volume of treated water: estimate of groundwater treated with Biorem and comparison with P&T.

Moreover, the following main benefits were obtained in the pilot test area:

- approx. 20 000 m^3 of groundwater preserved by the 6 months turn off of P&T;
- approx. 30 000 kW/h of energy saving by the 6 months turn off of P&T;
- no maintenance activities on P&T equipment;
- increase the efficiency in the reduction of contaminants concentration in groundwater.

References

[1] D. Lgs. n° 152 del 03.04.06. Testo unico in materia ambientale.

[2] Criteri metodologici l'applicazione dell'analisi assoluta di rischio ai siti contaminati. APAT 2008.

[3] **Parsons.** 2004. Principles and Practices of Enhanced Anaerobic Bioremediation of Chlorinated Solvents. AFCEE, NFEC, ESTCP 457 pp, August 2004.

[4] **Aulenta, M. Beccari, M. Majone, M.Petrangeli Papini, V. Tandoi,** Competition for H2 between sulfate reduction and dechlorination in butyrate-fed anaerobic cultures, Process Biochemistry, 43(2) 161-168, 2008.

[5] **Francis H. Chapelle e Derek R. Lovley** (1992). Competitive Exclusion of Sulfate Reduction by Fe(lll)-Reducing Bacteria.