Performance Assessment and Monitoring of a Permeable Reactive Barrier for the Remediation of a Contaminated Site

Valerio Zolla, Rajandrea Sethi, Antonio Di Molfetta
DITAG – Dipartimento del Territorio, dell'Ambiente e delle Geotecnologie
Politecnico di Torino – C.so Duca degli Abruzzi 24, 10129 - Torino, Italy

Abstract: The present study illustrates the long-term monitoring plan carried out in order to investigate the performance of a zero-valent iron permeable reactive barrier (PRB) at a chlorinated solvents' site. The cleanup intervention has been undertaken at an industrial landfill located near the city of Turin (Italy) and represents the first full-scale application of this technology in Italy. The monitoring plan started in November 2005 with the aim to verify the attainment of the cleanup goals and to evaluate the efficiency status of the PRB. Controls focuses not only on contaminant monitoring but also on the hydraulic and chemical conditions created by the barrier, in order to evaluate potential long term effects of secondary biogeochemical processes (e.g. mineral precipitation, microbially-mediated redox transformation, gas accumulation) on PRB performance. The monitoring plan provides controls on groundwater chemistry (target contaminants and geochemical indicators) and core sampling for mineralogical analysis of zero-valent iron by X-ray diffraction and scanning electron microscopy. The first, partial results of the monitoring activity are illustrated. Monitoring data clearly indicate that the plume is being adequately captured and treated in order to accomplish the clean-up goals with a good safety margin. However, it results that mineral precipitation and gas phase accumulation could determine, over time, a decreasing in hydraulic conductivity and porosity of the barrier, thus modifying the flow field through the reactive cell. Besides the monitoring controls, further investigations will be performed to assess the occurring microbial process and to evaluate their impact on PRB performance.
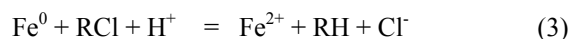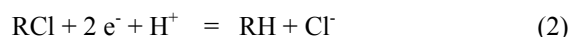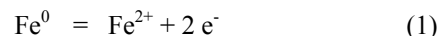
Keywords: zero valent iron, permeable reactive barrier, long-term performance, mineral precipitation, chlorinated hydrocarbons.

INTRODUCTION

The concept of PRBs is relatively simple: reactive material is placed in the subsurface to intercept a contaminated plume that moves through it under natural gradient. As the groundwater passes through the reactive media, the occurring physical and chemical processes transform the contaminants to less harmful or immobile species[1]. This passive type of remediation results in reduced costs due to the semi-permanent installation, lack of external energy input, reduced monitoring requirements, conservation of clean water, and continued productive use of the site almost immediately after installation.

PRB are generally backfilled with high permeability coarse grained materials. Although a variety of reactive media are available, the most commonly used is zero-valent iron (ZVI). The prevalent use of ZVI is mainly due to its demonstrated effectiveness against a wide variety of contaminants and particularly chlorinated aliphatic hydrocarbons (CAHs), against which conventional clean-up methods are almost useless.

The process is based on a series of redox reactions generated by the high reductive potential of ZVI: as the iron corrodes, the resulting electron activity reduces the chlorinated compounds to potentially non-toxic products; by the transfer of electrons from the solid iron to the CAH molecules, the chloride is separated as an anion dissolving in the water phase, according to the following chemical reactions:

$$Fe^0 \quad = \quad Fe^{2+} + 2\ e^- \tag{1}$$

$$RCl + 2\ e^- + H^+ \quad = \quad RH + Cl^- \tag{2}$$

$$Fe^0 + RCl + H^+ \quad = \quad Fe^{2+} + RH + Cl^- \tag{3}$$

Zero-valent iron not only plays a role in reactions that involve contaminant species, but also affects the main chemical processes that regulate the biogeochemical behaviour of the groundwater system, thus significantly altering its original conditions. These processes are of particular concern because over time they can negatively affect the properties of the PRB, by leading to changes in its reactivity, porosity, and hydraulic conductivity.

Corresponding Author: Valerio Zolla DITAG (Dipartimento del Territorio, dell'Ambiente e delle Geotecnologie) Politecnico di Torino, c.so Duca degli Abruzzi 24, 10129 - Torino, Italy

Over the past 10 years, the use of PRBs has evolved from innovative to accepted standard practice for the treatment of a variety of groundwater contaminants. Worldwide, there have been nearly 120 applications of iron-based PRBs, 83 of which are considered full scale[2]. Yet, being this a relatively recent technology, there are still a few available studies on the long-term performance of these systems. Generally, all the studies agree that the biogeochemical conditions inside the reactive cell have a fundamental role in determining how the efficiency of a PRB evolves over time: in other words, the common opinion is that it is not possible to predict the longevity of a PRB without considering the biogeochemical processes actually or potentially being in progress.

In Italy, the first full-scale iron-based PRB has been built during 2004 in Avigliana, near the city of Turin, to remediate a chlorinated solvents plume at an old industrial landfill site[3-5]. In November 2005 a monitoring plan has been started, with the aim to verify the attainment of the cleanup goals, evaluate the current efficiency status of the PRB and collect chemical and physical data to make predictions about long-term performance. This study, after a brief description of the site, illustrates the monitoring plan and shows the first results, focusing on the biogeochemical processes that can affect the performance of the PRB.

SITE DESCRIPTION

The contaminated site is located between Avigliana and Buttigliera Alta, near the city of Torino, Italy. The area was used in the past as an industrial landfill for the disposal of wastes coming from metal working factories.

The most superficial part of the lithostratigraphic sequence contains an unconfined aquifer whose impermeable bottom layer consists of muddy clayey drifts found 11–20 m below the ground surface. The saturated thickness of this aquifer ranges from 9 to 11 m showing a progressive reduction towards the Dora River, thus representing the drainage axis of the groundwater. The average flow direction in the area is SSW-NNE, the hydraulic gradient is 1.1% and the average hydraulic conductivity is $1.4 \cdot 10^{-4}$ m/s.

Chemical analyses of site groundwater revealed the presence of two contaminated plumes with a concentration of perchloroethylene (PCE, maximum concentrations of 40 μg/L), trichloroethylene (TCE, 130 μg/L) and 1,2-dichloroethilene (1,2-DCE, 135 μg/L) higher than Italian maximum concentration levels (Fig. 1). A detailed risk assessment analysis was performed leading to a remediation goal of 30 μg/L of total carcinogenic CAHs.

The most suitable technologies to remediate the contaminated plumes were found to be a zero-valent iron permeable reactive barrier for the main plume and a capping with monitored natural attenuation for the less contaminated zone.

The dimensioning phase required definition of the configuration, position, orientation, capture area, geometry of the PRB and was supported by numerical flow, particle tracking and multispecies contaminant transport simulations[3, 4]. The degradation kinetics of chlorinated hydrocarbons were derived from a column test performed by University of Tuebingen on contaminated water sampled from the site.

The site assessment led to the choice of a 120 m long continuous reactive barrier configuration[5]. The reactive barrier was designed to penetrate 0.6 m into the loamy-clayey bottom, thus the average depth of the excavation is 13 m, whereas the average reactive height of the barrier is 10.5 m. Although numerical modelling indicated that a 0.5 m wide PRB was sufficient, the final width of the barrier was chosen as 0.6 m, due to the standard dimensions of commercial excavation grabs. The trench was planned to be filled with a mixture of five parts of Gotthart Maier Metallpulver iron and one part sand.

The trench excavation was performed using a crawler crane equipped with an hydraulic grab. The excavation was divided into 17 panels and biopolymer slurry was used as shoring fluid. Each panel has been filled with ZVI-sand mix containing 83% by volume of iron. A total amount of 1,700 metric tons of iron were used to backfill the trench. Finally, a sand layer overlain by an impermeable clay cap was placed on the top of the permeable reactive barrier to prevent oxidation of the iron.

OBJECTIVES OF PRB MONITORING

Once a PRB has been designed and constructed, the system must be monitored as long as the plume exists. The primary objective of a monitoring program is to assure that the plume is being adequately captured and treated, so that downgradient concentrations of the target contaminants (and any byproduct) are below the established cleanup levels. Monitoring activity involves watching for[6]:

1. potential contaminant bypass around, over, or beneath the barrier;
2. potentially deleterious effects on groundwater quality due to the reactive medium itself;
3. potential breakthrough of contaminants (PCE, TCE, 1,2-DCE) or environmentally deleterious byproducts through the reactive cell. In fact, incomplete dechlorination of TCE may generate a series of compounds as vinyl chloride (VC) or 1-1-DCE, which are considered more dangerous to human health than the original contaminants.
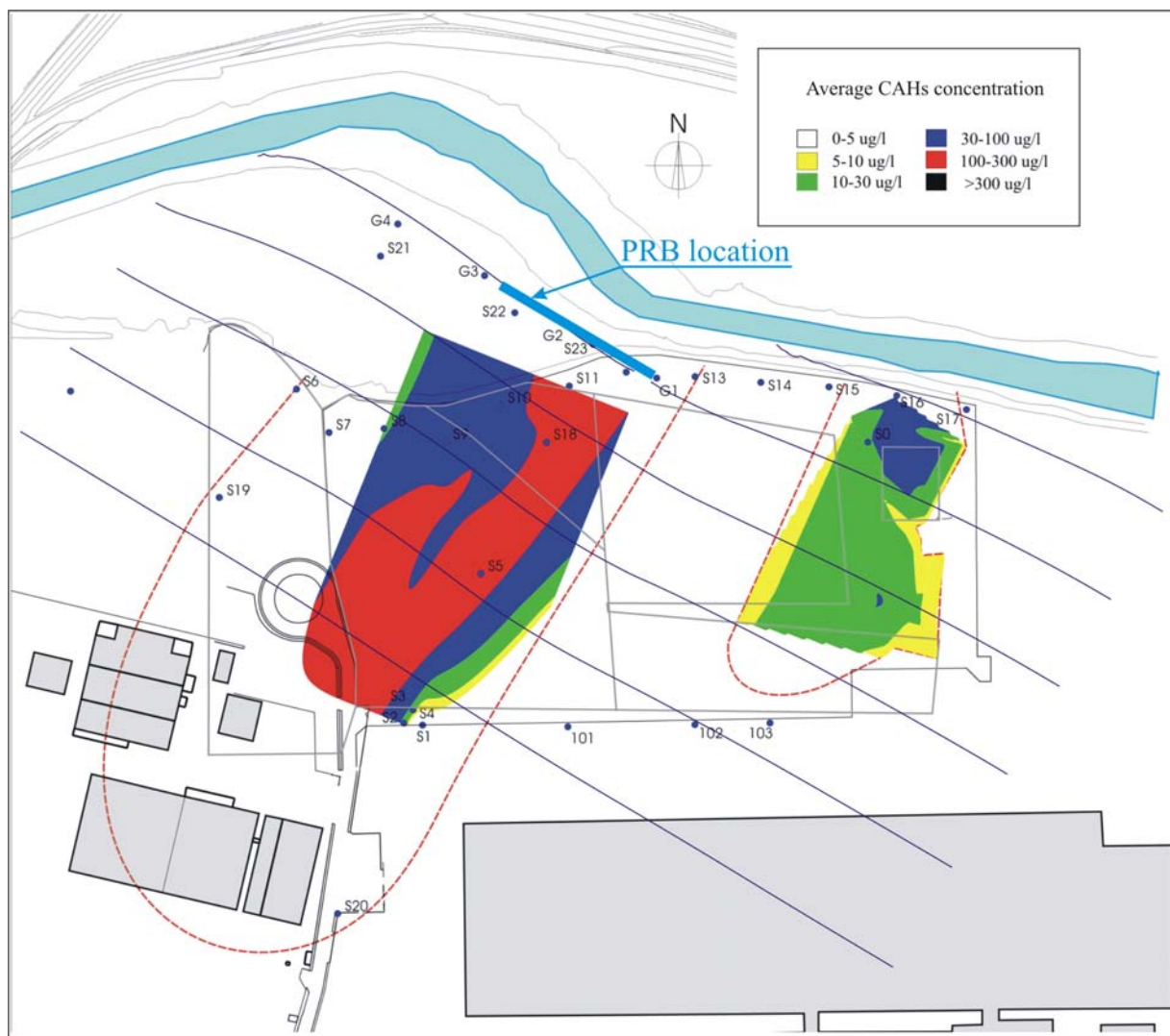
Fig. 1: Delimitation of the contaminated area.

Besides contaminant removal and hydraulic performance monitoring, further controls have to be periodically accomplished to investigate the efficiency status of the barrier: these additional investigations usually are usually called geochemical performance monitoring.

Potential long-term performance problems are mainly due to the biogeochemical conditions developing in the reactive cell. In fact, the kinetics and the pathways of iron corrosion, mineral precipitation, microbial activity, and gas production within and around the reactive media are governed by a variety of reaction processes that involve ZVI and the major anionic (e.g. Cl^-, SO_4^{2-}, HCO_3^-) and cationic (e.g., Ca^{2+}, Mg^{2+}) groundwater constituents[7]. The action of these processes will lead the physical and chemical properties of the PRB to change with time as a result of the "aging" of the zero-valent iron. It is important to underline that this does not generally compromise the effectiveness of the remediation technique: however, biogeochemical processes certainly play a fundamental role in determining the lifetime and the long-term performance of the PRB[8].

Geochemical performance monitoring is used to identify the occurring processes and to forewarn if they could create any problem in the future, before it is evidenced by ordinary contaminant monitoring. The next section briefly illustrates the chemical and microbial reactions that usually occur within a ZVI cell and that could potentially affect its performance.

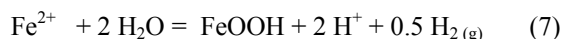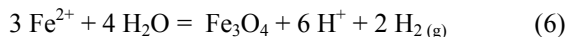## BIOGEOCHEMICAL PROCESSES AFFECTING PRB PERFORMANCE

Anaerobic iron corrosion: At the studied site, before entering the PRB the groundwater is anaerobic, with dissolved oxygen concentrations lower than 0.5 mg/l. Therefore, the oxidation of ZVI is expected based on the reaction of anaerobic corrosion:

$$Fe^0 + 2\,H_2O \;=\; Fe^{2+} + H_{2\,(g)} + 2\,OH^- \qquad (4)$$
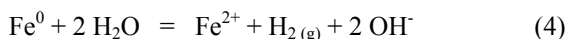
According to Eq. 4, reduction of water occurs, leading to an increase of pH and to the production of hydrogen gas. The resulting rise of pH can lead to the precipitation of ferrous precipitates, e.g. ferrous hydroxide, according to Eq. (5):
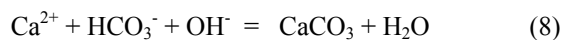
$$Fe^{2+} + 2\,OH^- \;=\; Fe(OH)_2 \qquad (5)$$
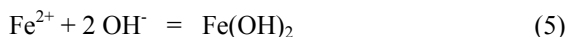
Ferrous hydroxide is thermodynamically unstable and may be further oxidized[9] to magnetite (6) or goethite (7):

$$3\,Fe^{2+} + 4\,H_2O = Fe_3O_4 + 6\,H^+ + 2\,H_{2\,(g)} \qquad (6)$$

$$Fe^{2+} + 2\,H_2O = FeOOH + 2\,H^+ + 0.5\,H_{2\,(g)} \qquad (7)$$

Many dissolved species can enhance iron corrosion, e.g. chloride, carbonate and sulfate, by increasing the dissolution rate of iron and eventually leading to the formation of unstable green rust minerals[10]. As the corrosion process proceeds, iron hydroxides will form a passivating layer over the surface of ZVI grains; as the thickness of the passivating layer grows, ZVI reactivity will be gradually reduced.

Moreover, hydrogen gas that is formed as a product of iron corrosion may temporarily passivate the iron surface; if hydrogen gas cannot escape from the subsurface, it may also accumulate inside the PRB, leading to the progressive clogging of the system. However, this phenomenon is quite unusual, because hydrogen gas is generally consumed as electron donor in a variety of microbial processes.

Carbonate reactions: In carbonate-containing waters, the rise of pH due to anaerobic corrosion of iron will shift the carbonate–bicarbonate equilibrium and lead to the precipitation of various carbonate minerals[11], e.g. calcite (8) or the polymorph aragonite, magnesite (9), siderite (10):

$$Ca^{2+} + HCO_3^- + OH^- \;=\; CaCO_3 + H_2O \qquad (8)$$

$$Mg^{2+} + HCO_3^- + OH^- \;=\; MgCO_3 + H_2O \qquad (9)$$

$$Fe^{2+} + HCO_3^- + OH^- \;=\; FeCO_3 + H_2O \qquad (10)$$

The accumulation of carbonates precipitates onto ZVI surface will gradually reduce the pore volume of the granular iron, and could decrease its porosity and permeability.

Microbial reactions: In presence of nutrients and electron acceptors, dissolved hydrogen that is produced by iron corrosion can be used as electron donor for the microbial metabolism of various anaerobic bacteria. The role of hydrogen as primary growth-substrate for groundwater bacteria has been widely studied[12]. In ZVI barriers, under anaerobic conditions, the most relevant microbial processes that potentially may occur are nitrate reduction (11), sulfate reduction (12) and methanogenesis (13):

$$2\,NO_3^- + 5\,H_2 + 2\,H^+ \;=\; N_{2\,(g)} + 6\,H_2O \qquad (11)$$

$$SO_4^{2-} + 4\,H_2 + H^+ \;=\; HS^- + 4\,H_2O \qquad (12)$$

$$HCO_3^- + 4\,H_2 + H^+ \;=\; CH_{4\,(g)} + 3\,H_2O \qquad (13)$$

In natural groundwaters, the above described microbial processes are believed to consume a great amount of hydrogen generated by ZVI oxidation. However, these processes may lead to negative consequences on the PRB performance: in fact, hydraulic conductivity could be reduced both by the proliferation of bacteria in the pore volumes of the ZVI grains, and by nitrogen and methane gas accumulation.

Moreover, at high pH and negative redox potential the microbial reduction of sulfates to sulfides will lead to the precipitation of insoluble ferrous sulfides, e.g. pyrite, or mackinawite (14):

$$Fe^{2+} + HS^- \;=\; FeS + H^+ \qquad (14)$$

The accumulation of sulfide minerals over the ZVI surface could also have secondary long-term effects on PRB performance.

Reactions with silica: Field evidence indicates that dissolved silica is removed by ZVI barriers. Forms of SiO_2 are not likely precipitating in iron walls because of their slow precipitation kinetics and because the growing pH increases rather than decreases SiO_2 solubility. One possibility is that silica is associated with magnesium in the clay mineral sepiolite, $Mg_4(OH)_2Si_6O_{15}\bullet6H_2O$[7]. However, the role that silica might play in passivated iron surfaces is not clear at present.

MATERIALS AND METHODS

Groundwater sampling and analysis: Figure 2 shows the configuration of the monitoring network that has been installed at the site. Considering the homogeneity and the small saturated thickness of the aquifer, only full-screened, PVC monitoring well were installed. Four piezometers were drilled to monitor the water quality after the PRB in order to verify the complete degradation of contaminants. On the same flowlines four wells were placed upgradient, to verify the inlet concentrations and to evaluate the degradation kinetics of the barrier. Two additional 2-inch-diameter monitoring wells are placed inside the reactive medium, and another couple of wells is placed at the two ends of the barrier to monitor for contaminant bypass.

When collecting groundwater samples from the reactive cell, traditional methods that involve purging several well-casing volumes of water prior to collection should be avoided, because such practices may capture water that represents a significantly lower residence

time in the reactive cell. For this reason, "Low flow purging" and "low flow sampling" methods are adopted to minimize chemical and hydrological disturbances in and around the well, in order to yield representative water samples[13]. Eight monitoring wells have been provided with submersible bladder pumps for groundwater sampling at low flowrates, whereas the wells that are located at greater distance from the PRB are sampled with submersible centrifugal pumps. Purging and sampling rates range from 0.5 to 1.0 L/min with bladder pumps and from 0.1 to 0.15 L/s with centrifugal pumps.
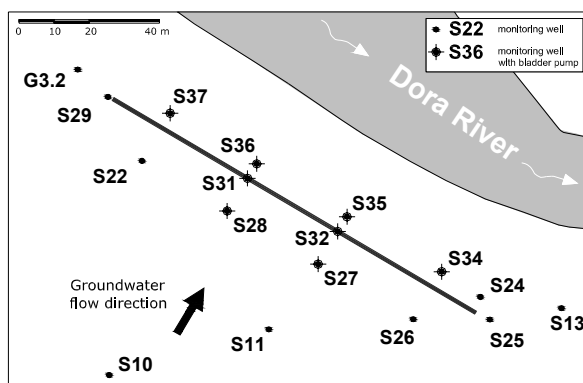

Fig. 2: Monitoring wells configuration.

Once collected, water samples are filtered and preserved at 4°C. Chemical monitoring involves the determination of both target contaminants and geochemical indicators, e.g. groundwater field parameters (Eh, pH, dissolved oxygen, temperature and conductivity), inorganic chemicals (through ICP-MS and HPLC analysis) and chlorinated organic compounds (GC-MS analysis). Samples collection is conducted on a quarterly basis to indicate any seasonal changes in contaminant distribution or geochemistry. Appropriate quality control procedures are followed to ensure that valid data are collected and analyzed.

Core sampling and analysis: Continuous core samples of the ZVI barrier were collected by Carsico S.r.l. using a direct push device (Geoprobe system), equipped with a 2 inch inner diameter core barrel with plastic sleeves. Both vertical and 25° angled cores were collected to evaluate geochemical changes occurring at the upgradient and downgradient portions of the permeable wall.

It is known that samples collection and preparation have a significant impact on the mineralogical analysis of ZVI[14]. Therefore, particular care was adopted to preserve the samples from the contact with air, by minimizing the air content inside the sleeves and by sealing them with plastic caps. The samples were preserved at 4°C and shipped to the laboratory, where they were dried using acetone and subjected to magnetic separation to divide ZVI grains from sand. ZVI samples were subjected to the following analyses: quantitative determination of soluble carbonates, sulfides and metals (HPLC, ICP-MS); field emission scanning electron microscopy (FESEM) with EDS analysis; X-ray diffraction (XRD).

HPLC and ICP-MS determinations were made to quantitatively define the fraction of carbonates, sulfides and non-iron metals into core samples of ZVI. SEM analyses allowed to make a high-resolution visual and elemental characterization of ZVI grains and to identify the morphology and the composition of precipitates and corrosion products. XRD were made to qualitatively investigate the crystalline phases and to identify the composition of the precipitates.

RESULTS AND DISCUSSION

This section illustrate the most relevant results that were obtained during the first year of application of the above described monitoring plan.

Contaminant behaviour: The average concentration of groundwater contaminants after PRB installation is shown in Table 1. These results indicate that the groundwater quality downgradient of the PRB is in compliance with the target cleanup objectives.

The concentration of CAHs entering the PRB is greater in the middle portion, near S27 (TCE = 158 μg/l; 1,2-DCE = 68.3 μg/l) and S28 (TCE = 89.4 μg/l; 1,2-DCE = 60.4 μg/l), than at both the two sides of the reactive cell.

Output concentrations are largely below the limit of 30 μg/l of total carcinogenic compounds; indeed carcinogenic CAHs are below 1.0 μg/l in almost every water sample taken from downgradient wells.

The percent reduction of TCE concentrations, representing the only relevant chlorinated mother product, varies from 86% to 98%. Reaction byproducts (VC, 1,1-DCE, 1,2-DCE) are absent or at negligible concentrations both inside and downgradient the PRB and these evidences prove that the barrier is able to perform a complete dehalogenation of the contaminants.

TCE and 1,2-DCE average distributions in proximity to the barrier are illustrated in Figure 3. This representation highlights the absence of contaminant bypass or breakthrough and the complete capture of the plume.

To conclude, monitoring data clearly show that the plume is being adequately captured and treated. At present, no critical situations are found and the PRB appears to be able to accomplish the clean-up goals.

Table 1: Average concentration of chlorinated solvents and by-products at the PRB of Avigliana (Nov. 05 – Oct. 06).

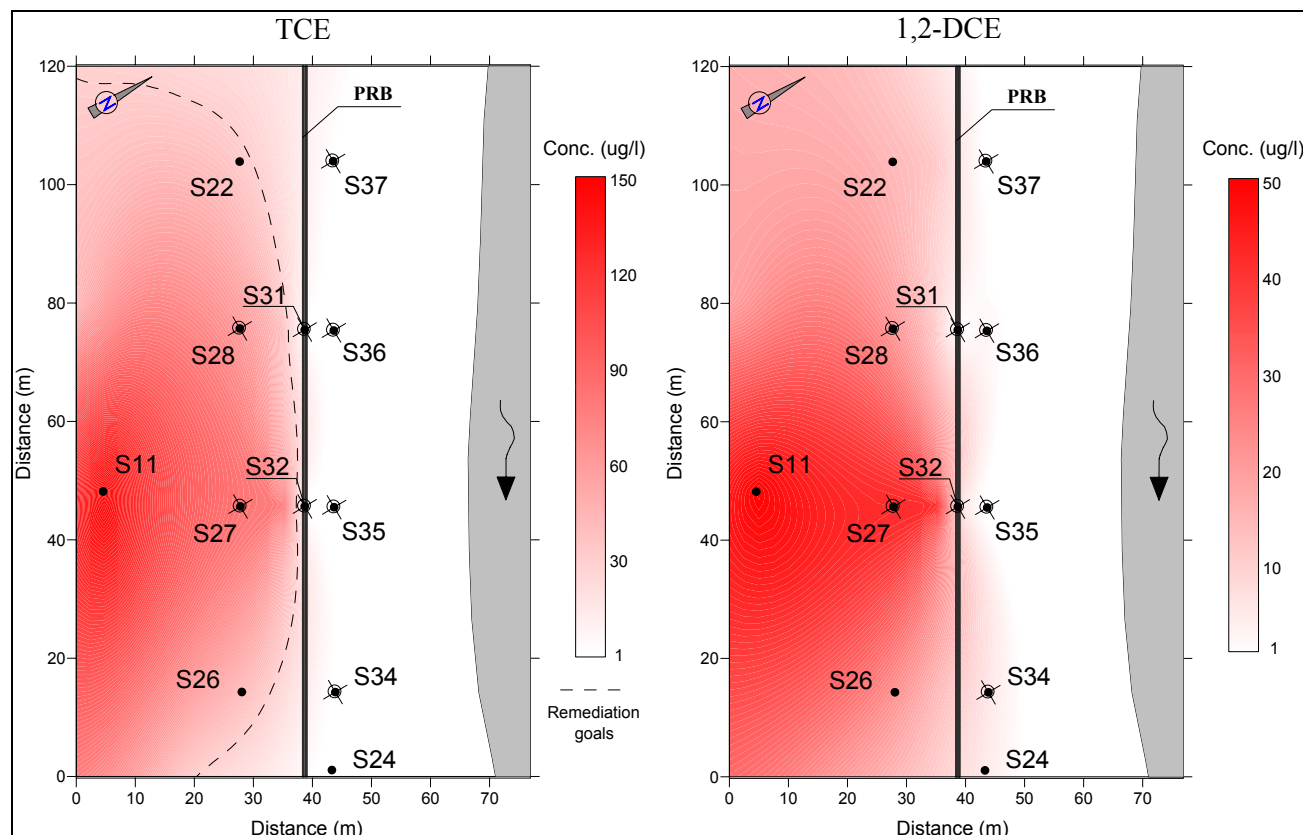| ANALYTE		Upgradient aquifer				PRB		Downgradient aquifer			
		S22	S26	S27	S28	S31	S32	S34	S35	S36	S37
PCE	µg/L	0.62	0.85	1.01	0.47	<0.05	0.3	0.2	<0.05	<0.05	<0.05
TCE	µg/L	13.2	13.9	158.0	89.4	0.96	0.4	0.39	0.84	0.51	2.11
1,1-DCE	µg/L	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
1,2-DCE	µg/L	19.7	39.6	68.3	60.4	27.3	32.1	3.82	3.66	2.41	5.94
VC	µg/L	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
CF	µg/L	<0.05	0.89	<0.05	0.28	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05

Fig. 3: TCE and 1,2-DCE average distribution in proximity to the barrier.

Biogeochemical assessment: A comparison of groundwater chemistry between upgradient and downgradient wells (Table 2) indicates that the iron wall is a long-term sink for various inorganic constituents, including sulfur, carbonate, calcium, magnesium, silica and manganese. These compounds are expected to be involved in geochemical or microbial processes and to form mineral precipitates while crossing the PRB. The assessment of the occurring processes was supported by core samples analyses on ZVI samples.

The loss of Ca and Mg between the influent and the effluent is due to the formation of carbonate minerals, e.g. calcite, aragonite and magnesite, whose presence was detected by SEM microscopy (Fig. 4a) and XRD analyses. The loss of Mn is probably caused by the precipitation of rhodochrosite ($MnCO_3$) also.

EDS mapping confirmed an overlay between the distribution of Mg and Si: therefore, it is likely that a fraction of Mg precipitates as the clay mineral sepiolite, in association with silica. Some XRD analyses also revealed the presence of quartz: however, the high intensity of the peaks suggests that the presence of quartz is due to non-magnetic residues (sand) in the sample.

Table 2: Groundwater chemistry at the Avigliana PRB (Nov. 05 – Oct. 06).

ANALYTE		S27 Upgradient	S35 Downgradient	% Change	S28 Upgradient	S36 Downgradient	% Change
pH	-	6.8	7.5	+10.9	6.8	7.2	+6.5
Eh	mV	-87.0	-215	-147	-87.1	-221	-153
O_2	mg/L	1.1	1.0	-1.9	1.6	1.2	-24.2
Alkalinity	meq/L	7.7	4.6	-39.4	7.2	5.3	-25.9
Nitrate	mg/L	1.5	1.4	-6.7	1.4	1.2	-15.5
Chloride	mg/L	17.0	10.7	-37.1	18.8	15.2	-19.3
Sulfate	mg/L	190	83.2	-56.3	193	75.2	-61.0
Sulfide	mg/L	< 0.01	< 0.01	-	< 0.01	< 0.01	-
Silica	mg/L	5.2	4.8	-7.8	5.1	4.9	-3.5
Ca	mg/L	101	36.4	-63.8	119	42.4	-64.4
Mg	mg/L	37.2	16.0	-57.0	42.6	23.0	-46.0
K	mg/L	5.5	3.8	-29.7	5.7	3.2	-42.8
Na	mg/L	43.8	32.0	-26.9	44.0	28.4	-35.5
Fe (0.45 μm)	μg/L	31.4	176	+459	16.0	99.8	+523
Mn (0.45 μm)	μg/L	224	30.4	-86.4	268	42.6	-84.1

According to the analytical results, the most relevant microbial processes for the studied PRB are sulfate-reduction and methanogenesis. Nitrate concentration does not decrease through the barrier at all, probably because the influent concentration are too low to allow the growth of a population of nitrate-reducing bacteria. On the contrary, sulfate concentration decreases from high influent values of about 200 mg/L to less than 90 mg/L in downgradient wells. The reducing, alkaline environment of the PRB is not favourable to the precipitation of sulfate salts: therefore, the decline in sulfate levels is due to the activity of sulfate-reducing bacteria, which give sulfide ion as a by-product (13). Sulfur eventually precipitates as ferrous sulfide minerals, e.g. mackinawite, as it was demonstrated by SEM (Fig. 4b) and XRD analyses.

Methanogenesis is also an important microbial process in our case study: in fact, groundwater analyses indicate that the decline in inorganic carbon (as bicarbonates or dissolved CO_2) is not fully compensated by the loss of cations (see Table 2). This suggests that the loss of dissolved inorganic carbon is due to a microbial methanogenesis process, which results in the production of methane gas. Unlike hydrogen, methane gas is not consumed by microbial activity; when it is produced within permeable materials in the subsurface, it naturally volatilizes to the surface. However, if ZVI permeability decreased, methane gas could not find the way out to the surface and it would accumulate within the PRB, rapidly causing system clogging and failure. We retain this process of great concern for its impact on PRB performance and for this reason it will be thoroughly studied and investigated.
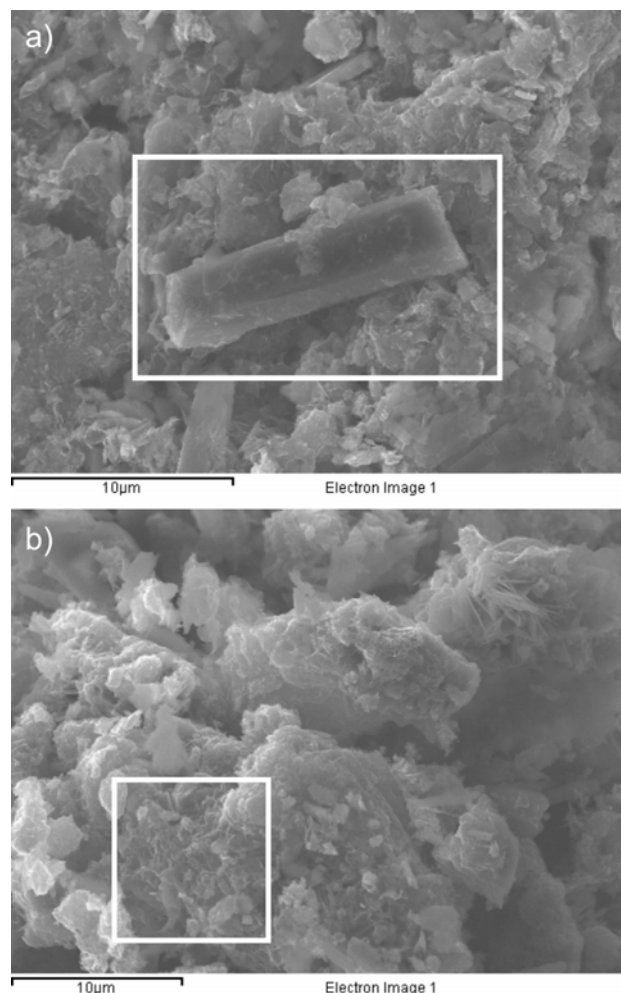

Fig. 4: FESEM images of ZVI samples showing the presence of (a) calcite crystals and (b) ferrous sulfides.

CONCLUSIONS

The monitoring results show that the studied PRB is able to intercept and treat the contaminated plume largely attaining the remediation goals. The output concentrations of the parent contaminants and of their by-products are frequently below 1.0 μg/L, to indicate the complete degradation of chlorinated organic compounds.

Groundwater and core samples analyses indicate that mineral precipitation and gas phase accumulation could determine, over time, a decreasing in hydraulic conductivity and porosity of the barrier, thus modifying the flow field inside the reactive cell.

Periodical in situ permeability tests within the PRB will be conducted in order to evaluate any variation of hydraulic conductivity. Besides, a detailed investigation of the microbiological processes that could lead to the production and accumulation of gases inside the PRB will be performed.

Furthermore, the acquired geochemical data will be used to perform equilibrium simulations and multi-component reactive transport models in order to make reliable predictions on the effects that biogeochemical processes could have on the efficiency of the PRB.

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