

# Remediation of groundwater contamination from an old, non-functional landfill in Hořkovec open cast mine, Czech Republic

Adyl Anvarov, Adelaida Pelaez Angel, Beatriz Felices Rando and Jimena Lazaro Gil

## ABSTRACT

The main aim of this work was to assess different suitable strategies for the remediation of groundwater contaminated with the leachate from an old, not functional landfill located next to Hořkovec open cast mine, in the Czech Republic. The leachate consisted of mainly chlorinated aliphatic compounds and aromatic volatile compounds. The site, that had already been treated, was observed to show rebounding effects after the first remediation treatment. This article analyses the possibilities of using different types of remediation technologies that include *in-situ* chemical oxidation (ISCO) with different oxidants (potassium permanganate, sodium permanganate and sodium persulfate), as well as *in-situ* bioremediation (ISB), and the combination of both types of treatment. From the results of the analysis it was concluded that the best option for this case was to carry out a pre-treatment of the area by ISCO with sodium persulfate as the oxidant agent and then a further biological treatment.

**Key words** | bioremediation, BTEX, groundwater remediation, *in-situ* chemical oxidation, landfill leachate, petroleum hydrocarbons

Adyl Anvarov (corresponding author)  
Adelaida Pelaez Angel  
Beatriz Felices Rando  
Jimena Lazaro Gil  
Department of Water Technology and  
Environmental Engineering,  
University of Chemistry and Technology,  
Technická 5, Dejvice, 166 28 Praha 6,  
Czech Republic  
E-mail: adylanvar@gmail.com

## INTRODUCTION

Contamination of groundwater resources as a result of inappropriate construction and management of municipal and industrial waste landfills is a common problem worldwide. In the Czech Republic, the number of active landfills (for industrial, municipal and inert waste storage) increased drastically after the breakup of Czechoslovakia. However, the number of active landfills decreased over time as a result of the development of new legislation. In detail, the number of active landfills decreased from a total of 10,000 in 1990 to 380 in 1996 (Fagin 2001). Moreover, the entry of the Czech Republic into the European Union in 2004 entailed the entry into force of new environmental laws and regulation. Consequently, a total number of 178 waste disposal sites are currently under operation in the country,

while the rest have been closed and are under post-closure operations (Martinát *et al.* 2016). Within the post-closure operations, the Council Directive 1999/31/EC of 26 April 1999 states the requirement to perform a monitoring plan for at least 25 years in order to ensure the absence of adverse effects on the environment and people. Therefore, research into suitable soil and water remediation techniques is essential to avoid the negative impact of the landfills into the environment.

The studied landfill was established on January 22nd, 1968 and it was used as a storage of wastes from paint and varnish industries, as well as pharmaceutical and personal care products. The groundwater in the contaminated site was isolated from the leachate coming from the

aquifer and received further treatment in 1990. However, the monitoring of the treated area showed a rebounding effect, and therefore, an increment in contaminants' concentration during the last years. The concentration of the groundwater contaminants, characterized by a monitoring well, is presented in Table 1. The most abundant compounds found were chlorinated aliphatic compounds (CACs) and

aromatic volatile compounds – benzene, toluene, ethylbenzene and xylenes (BTEX).

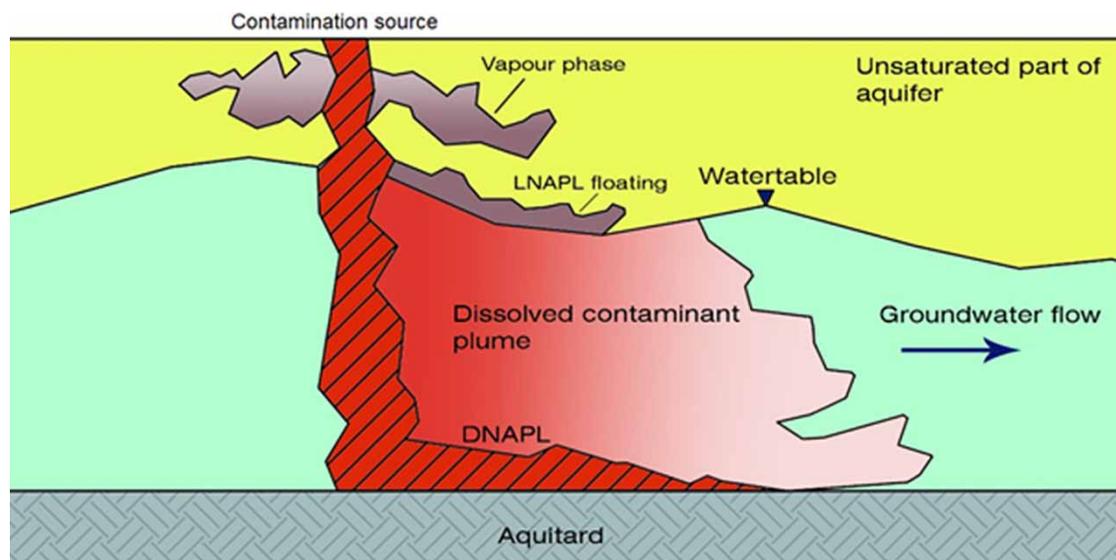
Regarding the distribution of the contaminants within the aquifer, aromatic volatile compounds and chlorinated hydrocarbons can be present in four different states (Figure 1): dissolved in water, adsorbed on solid particles, vapour and free phase (when solubility limit of pollutant in water is exceeded). The free phase, known as non-aqueous phase liquid (NAPL), can be divided into two different subdivisions according to their specific gravity – specific weight higher than water (dense – DNAPLs) and specific weight lower than water (light – LNAPLs). The vast majority of petroleum hydrocarbons belongs to LNAPLs (Bouchard 1989).

Numerous methods and techniques have been developed for groundwater remediation during the last decades. However, the differences in the nature of the contamination, the water properties, and the aquifer soil properties do not allow the use of identical remediation approaches at different sites.

Wasay *et al.* (1999) studied the efficiency of using granular activated carbon, ferric chloride (coagulation agent) and granular activated alumina for heavy metals' removal from a contaminated groundwater reservoir. Results showed that the maximum cation separation of Cd (II), Cu (II), Cr (III), Mn (II), Pb (II) and Zn (II) was achieved by granular

**Table 1** | Concentration of detected contaminants in the monitoring well; Czech Republic standards and pollution indicator concentration

Compound	Czech Republic standards [ $\mu\text{g/L}$ ]	Pollution indicator [ $\mu\text{g/L}$ ]	Monitoring well [ $\mu\text{g/L}$ ]
Benzene	1	0.39	597
Toluene	0.2	860	187
Ethylbenzene	0,2	1.3	64.3
o-xylene	0.2	–	54.5
1,2-dichlorethane	3	0.15	1,960
Chloroform	2.5	0.19	19,400
Tetrachlorethane	10	9.7	21.1
Trichlorethane	10	0.44	664
cis-1,2-dichlorethane	0.1	28	73.2
Vinylchloride	0.5	0.015	<100
Dichlormethane	0.1	9.9	1,620



**Figure 1** | Petroleum hydrocarbons' distribution through unsaturated and saturated part of the aquifer profile.

activated carbon at neutral pH. By using this technique, heavy metals' removal percentages between 80% and 96% were obtained. Liang & Liu (2008) investigated the possibilities for treating leachate from a municipal solid waste landfill by means of anammox microorganisms. This technique showed a removal capacity of 97% for ammonia nitrogen, 87% for total nitrogen and 89% for chemical oxygen demand (COD). Moreover, Li *et al.* (2009) studied the performance of a field-scale aged refuse biofilter for treating a landfill leachate. Results showed that the continuous operation of the biofilter can decrease the amount of ammonia and COD content in the leachate. The average COD concentration dropped from 5,478 mg/L to 267 mg/L and the mean ammonia concentration from 811 mg/L to 6 mg/L. Liang *et al.* (2008) researched the possibility of treating groundwater and soil slurries contaminated with gasoline and diesel fuels by oxidative degradation. To this aim, activated persulfate was used as the main oxidizing agent. The treatment efficiency was considered to be dependent on the activation method (thermal or chemical), the oxidizing agent dose and the presence of chelating agents. Moreover, membrane technologies have also been studied for separating wastewater from petroleum hydrocarbons. In this paper, an analysis of the advantages, disadvantages and limitations of different remediation technologies is presented. In view of their suitability for the treatment of the studied leachate, a combination of different technologies is proposed. Additionally, a financial assessment and an environmental impact assessment of the proposed treatment are also included.

## MATERIALS AND METHODS

Different methods for *in-situ* chemical oxidation (ISCO) and *in-situ* bioremediation (ISB) were reviewed in order to assess their suitability for contamination removal.

### *In-situ* chemical oxidation

ISCO is a technology that consists of the introduction of chemical oxidants into the groundwater subsurface with the aim of destroying organic pollutants. ISCO is feasible when the pollutants can be mineralized to carbon dioxide and water or when they can be oxidized into a less harmful

sub-product that can be treated afterwards. The main limitation of ISCO technologies is to deliver the oxidant agent in the sense that it can be physically in contact with the target contaminant. Another important limitation is that the oxidant agent is consumed by subsurface chemical reactions that are not related to the degradation of the target pollutants. This loss of oxidant is called natural oxidant demand (NOD) (Haselow *et al.* 2003).

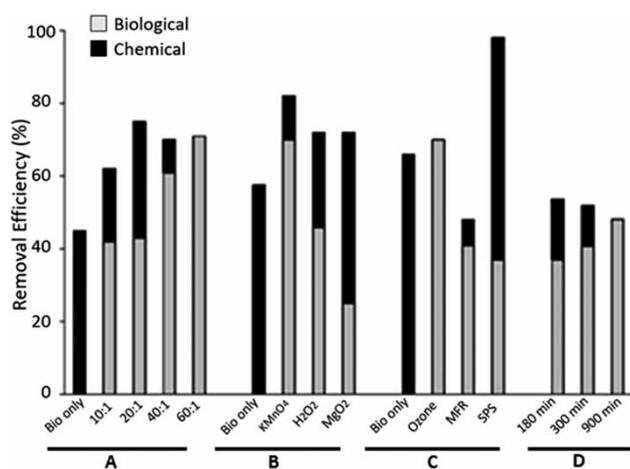
The suitability of using potassium permanganate, sodium permanganate, and sodium persulfate as oxidants was assessed with regard to the characteristics of the contaminants and the treatment area. In this sense, several factors need to be considered when selecting the most appropriate oxidant: (a) delivery and distribution of the oxidant; (b) rate and extent of NOD; (c) rate and extent of reaction with the contaminant; and (d) geochemical effects from the oxidation.

Potassium and sodium permanganate are the most common forms of permanganate ( $\text{MnO}_4^-$ ). Both of them are used for ISCO of chlorinated solvents, as they produce  $\text{MnO}_2$  and  $\text{CO}_2$  when reacting with organic compounds, as well as other intermediate organic products (Yin & Allen 1999). They are non-specific oxidizers with a low oxidation potential and high NOD that can be used within a wide range of pH values and they do not require a catalyst (Environmental Protection Agency). The main advantages of using permanganate as an oxidant are: (i) no exothermic reactions; (ii) catalysts are not required; (iii) pH control is not required; and (iv) bioremediation can accompany oxidation because neither the oxidants nor the by-products are toxic for the microbial population (Kluck & Achari 2004). However, some drawbacks must be taken into account as well: (i) manganese remains dissolved in the area, as well as unreacted permanganate, that leaves a purple colour in groundwater (Interstate Technology Regulatory Council 2005); and (ii)  $\text{MnO}_2$  can precipitate, occupying pore space, reducing soil permeability and creating a coating that would reduce the contact surface between the oxidant and the NAPL (Environmental Security Technology Certification Program 1999). However, there is not an exact approach to quantify to what extent this drawback affects contaminant oxidation (Interstate Technology Regulatory Council 2005).

However, permanganate can have an adverse effect on bioremediation if used in large amounts (Major *et al.* 2002). Figure 2 shows the percentages of removal efficiency of bioremediation and different oxidation techniques when combined (Sutton *et al.* 2011). It is observed that the best results are obtained for sodium persulfate (SPS) and permanganate, and that the percentage of bioremediation efficiency for the last one is noticeably reduced.

Regarding SPS, it is considered as an emerging oxidant for ISCO technology for the treatment of organic pollutants in groundwater, soils and sediments (Brown *et al.* 2002). Persulfate is a strong oxidant with relatively high stability under normal subsurface conditions, thus being able to reach the contaminated zone. In comparison with permanganate, persulfate has lower NOD, so less quantity of persulfate is needed in order to treat pollutants, which is an important factor in terms of cost-effectiveness and sustainability (Petri *et al.* 2011).

Regarding its reaction chemistry, it can react by direct electron transfer (direct oxidation) or by its decomposition into free radicals that can degrade target organic compounds. Persulfate decomposition into free radicals requires previous activation by: heat, chelated or non-chelated transition metals (especially iron), hydrogen peroxide, and alkaline pH conditions. Activated persulfate



**Figure 2** | Summary of removal efficiency for combined chemical and biological remediation in instances where a variety of *in-situ* chemical oxidation treatments were tested (sodium persulfate and permanganate were used as an oxidation agent). Labels indicate what follows: A: H<sub>2</sub>O<sub>2</sub>/Fe ratio used for treatment; B: type of chemical oxidant used prior to incubation for 134 days; C: type of chemical oxidant, including modified Fenton's reagent and iron-activated SPS, and data are for the first 20 days of experimentation; and D: duration of ozone treatment (Sutton *et al.* 2011).

reaction is more rapid and less selective than direct oxidation. However, persulfate is consumed more rapidly and it could be less productive (Petri *et al.* 2011).

Different types of persulfate activation were reviewed with the aim of assessing the most suitable one. In the case of heat activation, it may result in very aggressive oxidizing conditions; reaction mechanisms may shift with increasing temperature, affecting the overall reaction efficiency. Installation of a parallel heating system to heat the aquifer matrix to the desired temperature implies high operational costs. Regarding its effectiveness against DNAPL contamination, the increasing temperature may produce volatilization and dissolution of contaminants, enhancing further treatment of dissolved DNAPL and contaminant desorption. Another degradation process that also occurs at high temperatures is hydrolysis. However, chlorinated ethenes are generally resistant to hydrolysis (Jeffers *et al.* 1989).

Oxidant activation by special metal compounds is another option to generate strong radicals. Several studies show that iron-chelated complexes improve the effectiveness of treatment compared to non-chelated iron systems (Block *et al.* 2004). The reason is that the oxidant/iron/chelator molar ratio appears to have a strong impact on the overall effectiveness. Another advantage of chelated activation in comparison to the non-chelated one is that the first one occurs at neutral pH conditions, while the last one requires acid pH (Petri *et al.* 2011).

Finally, in terms of its potential efficiency, several studies have demonstrated that persulfate is able to degrade all CAC present in this study area (Waldemer *et al.* 2007). Block *et al.* (2004) developed an investigation about the degradation of these compounds in aqueous systems under a variety of persulfate activation methods: Fe (II) and Fe (III), chelated Fe (III), hydrogen peroxide, alkaline pH, and without activation. The results showed that in the case of activation methods, the concentrations of chloroethene were substantially lower in comparison to the inactivated ones, proving to be more effective (Petri *et al.* 2011).

### Determining dosing requirements

A sufficient amount of oxidant injection into the targeted treatment area is one of the most important factors in the

ISCO process. In order to calculate the oxidant dosing requirement, the sum of three different factors has to be performed: (1) the stoichiometric demand, (2) the reaction with reduced species in the soil matrix (NOD) or soil oxidant demand and (3) the loss due to decomposition.

In the case of persulfate, the only component of NOD that reacts with this compound is reduced metals, as it does not react with natural organic material (NOM) (Brown *et al.* 2004). In this sense, the reaction with reduced metals is rapid and near stoichiometric, and the reaction with NOM is very slow and indistinguishable from decomposition, which is the most important non-beneficial reaction. For this reason, persulfate dose is a function of the stoichiometric demand and of the quantity required to compensate the amount lost by decomposition (Brown 2010).

The stoichiometric demand is the stoichiometric requirement times the mass of the contaminant, and is calculated using the equivalent weight of persulfate and the equivalent weight of the contaminant being oxidized (Equation (1)). The equivalent weight is the molecular weight divided by the number of electrons transferred (usual valence).

$$\text{Stoichiometric requirement} = \frac{\text{Equivalent weight oxidant}}{\text{Equivalent weight contaminant}} \quad (1)$$

Persulfate, as peroxygen compound, will decompose to oxygen and sulfate. The decomposition test carried out by Brown (2010) suggests that persulfate losses continue to occur over time for all concentrations of persulfate, and decomposition increases with increasing levels of added persulfate and with experiment duration time. A pilot test can be developed in order to calculate the amount of persulfate to be decomposed. Moreover, several titration procedures by potassium permanganate can estimate the amount of oxidant lost due to the decomposition.

In order to calculate the decomposition of persulfate by titration, the following procedure is used:

- Preparation of 50% (wt-wt) slurries of persulfate and soil from the site. Persulfate concentrations should be 50, 100 and 150 g/L (5, 10 and 15%).
- Take a 5 mL aliquot of the liquid, add 25 mL of 25% of sulfuric acid, and stir for 2 minutes.

- Add dried (105 °C for 24 hours) ferrous sulfate heptahydrate ( $\text{FeSO}_4 \times \text{H}_2\text{O}$ ). Add 0.75 g for the 5%, 1.4 g for the 10% and 2.0 g for 15%. Stir for 10 minutes.
- Titrate to a persistent pink colour with 0.1 N  $\text{KMnO}_4$ .
- Calculate the concentration of persulfate by Equation (2):

$$\text{Na}_2\text{S}_2\text{O}_8 \left( \frac{\text{g}}{\text{L}} \right) = \left[ \frac{((\text{Weight FeSO}_4 \times \text{H}_2\text{O})/278.01) - ((\text{mL KMnO}_4/1000) \times N \text{ KMnO}_4)}{\text{mL sample}/1000} \right] \times 119 \quad (2)$$

This procedure needs to be done every 2–5 days for a total of 10–20 days of time. The length of time between samples depends on the rate of decomposition of the persulfate.

### *In-situ* bioremediation (ISB)

ISB is a biological treatment employing microorganisms such as bacteria and fungi to transform organic pollutants into non-toxic compounds or mineralize them to inorganic compounds like carbon dioxide, methane, water and inorganic salts (Farhadian *et al.* 2008; Wolicka *et al.* 2009; Perelo 2010). In this sense, considering the literature review performed, Table 2 presents the most suitable bacteria strains capable of degrading the pollutants present in the aquifer.

ISB has two major advantages: the first is the reduction of cost while the second one is that it can lead to a complete mineralization of the pollutants (Farhadian *et al.* 2008; Perelo 2010). However, it is important to emphasize that bioremediation is not always suitable; this depends on such factors as the pollutant biodegradability and the geophysical conditions of the aquifer to be treated. That includes soil structure and stratification, pH, temperature, hydraulic conductivity, presence of nutrients, etc. (National Research Council 1993). Especially important for ensuring microbial growth is the presence of elements such as nitrogen, phosphorus and potassium, which can be provided as additional nutrients (Henry 2010).

**Table 2** | Bacteria used for biodegradation of target contaminants (Aulenta et al. 2006; Farhadian et al. 2008; Pérez-de-Mora et al. 2014)

Pollutant	Microorganisms
BTEX	<i>Rhodococcus rhodochrous</i> , <i>Rhodococcus</i> sp., <i>Pseudomonas</i> sp., <i>Pseudomonas putida</i> , <i>Pseudomonas fluorescens</i> , <i>Cladophialophora</i> sp., <i>Achromobacter xylosoxidans</i>
BTX	<i>Geobacteraceae</i> , <i>Rhodococcus pyridinovorans</i>
BTE, TCE	<i>Pseudomonas putida</i>
Toluene	<i>Ralstonia pickettii</i> , <i>Burkholderia cepacia</i> , <i>Pseudomonas putida</i> , <i>Blastochloris sulfoviridis</i> , <i>Geobacter</i> sp., <i>Thauera aromatica</i> , <i>Desulfobacula toluolica</i> , <i>Dechloromonas</i> sp.
Benzene	<i>Pseudomonas aeruginosa</i> , <i>Dechloromonas</i> sp.
Ethylbenzene	<i>Azoarcus</i> sp. strain EB1
Aromatic compounds and chloroaliphatics	<i>Pseudomonas putida</i>
PCE, TCE, DCE, VC	<i>Dehalococcoides ethenogenes</i> , <i>Dehalococcoides</i> sp.
PCE, TCE	<i>Desulfitobacterium</i> sp., <i>Clostridium bifermentans</i> , <i>Dehalobacter restrictus</i> , <i>Enterobacter agglomerans</i> , <i>Desulfuromonas chloroethenica</i> , <i>Desulfuromonas michiganensis</i> , <i>Dehalospirillum multivorans</i> , <i>Sulfurospirillum halorespirans</i> , <i>Desulfomonile tiedjei</i>

PCE, perchloroethene; TCE, trichloroethene; DCE, dichloroethene; VC, vinylchloride.

### Rapid impact assessment matrix

The rapid impact assessment matrix (RIAM) method was developed by Pastakia & Madsen (1996) and consists of evaluating each scenario within the following categories of impacts: (i) physical and chemical impacts, (ii) ecological and biological impacts, (iii) sociological and cultural impacts and (iv) economical and operational impacts. These categories of impacts were subdivided into specific impacts that were further evaluated one by one in terms of their severity. The evaluation was done by considering a previously defined criteria. Two main groups were distinguished: (A) criteria related to the condition, which can affect individually the score obtained; (B) criteria related to the situation that should not affect individually the score obtained. These groups are composed of the following criteria: importance (A1), magnitude (A2), permanence (B1), reversibility (B3) and cumulation (B3). Thus, a score was assigned to each impact and for each of the four different criteria related to the performance and scope of the project.

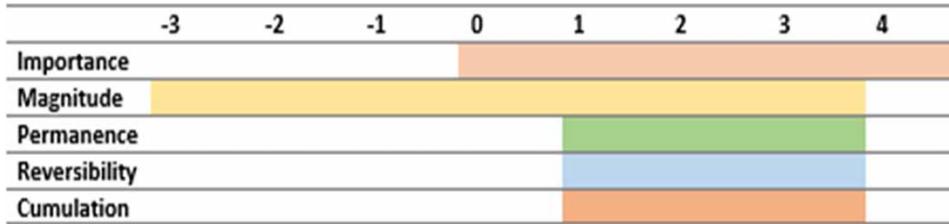
The aim was to categorize all the identified impacts as positive or negative. To achieve this, the scores for the criteria (group B) were summed together, which helps to account for all factors and create an overall, joint result. The sum of the B group criteria was multiplied by the

product of the group A criteria to obtain a final environmental score (ES) for each of the impacts (Equation (3)):

$$ES = (A1 \times A2) \times (B1 + B2 + B3) \quad (3)$$

In group A, the importance (A1) refers to the degree of significance of a particular impact, taking into consideration the spatial boundaries of the project. The score ranges from +4 (important to national/international interests) to -4 (no importance). The magnitude (A2) is stated as a measure of the scale of benefit/disbenefit of an impact; it can take values in the range of +3 (major positive benefit) to -3 (major disbenefit or change) (Figure 3).

Regarding group B, permanence (B1) defines if an impact is temporary or permanent, describing the temporal status of the condition. The values range from 1 (no change/not applicable) to 3 (permanent). Reversibility (B2) refers to the possibility of reconstruction of the factor affected by the project, i.e., the possibility of returning to the initial conditions prior to the action by natural means. The values range from 1 (no change/not applicable) to 3 (irreversible). Finally, cumulation is a measure of whether the impact will have a single direct impact or whether cumulative effects will take place over time, or a synergistic effect with other impacts. The value ranges from 1 (no change/not applicable) to 3 (cumulative/synergistic) (Figure 3). The ES



**Figure 3** | Range of environmental impact values assigned to each factor.

values can be further classified according to the bands shown in [Table 3](#).

### Financial analysis

The cost for each remediation technique is highly dependent on the specific conditions of each site. Therefore, adequate approximation of the costs were used based on the values proposed in the literature ([Harkness & Farnum 2010](#)).

Additionally, the cost categories were also divided according to the protocol given by [Harkness & Farnum \(2010\)](#). According to the authors, the cost information of each remediation technique can be classified into four general categories (design, capital, operation and maintenance; and monitoring) and in turn each category is divided into other sub-categories as shown in [Figure 4](#).

The total investment required for the proposed scenario was obtained by calculating the net present value (NPV), according to Equation (4), where  $NC_t$  is the net cost at

time  $t$ ,  $r$  is the discount rate and  $T$  is the time horizon of the project. In this study, the value for  $r$  was taken as 4.5%, the average discount rate for the Czech Republic in the past 24 years ([Trading Economics 2019](#)).

$$NPV = \sum_{t=0}^T \frac{NC_t}{(1+r)^t} \quad (4)$$

## RESULTS AND DISCUSSION

### *In-situ* chemical oxidation (ISCO)

After the analysis of the properties of the site pollutants and the different possible technologies for their remediation, as well as the experience of scientists in the field ([Table 4](#)), two scenarios were proposed: (1) ISB combined with ISCO using sodium persulfate or (2) ISB combined with

**Table 3** | Range bands used for ES score of the environmental impact assessment

RIAM environmental score (ES)	Range value (RV) (Alphabetical)	Description of range band
108 to 72	E	Major positive change/impact
71 to 36	D	Significant positive change/impact
35 to 19	C	Moderate positive change/impact
10 to 18	B	Positive change/impact
1 to 9	A	Slight positive change/impact
0	N	No change/status quo/not applicable
-1 to -9	-A	Slight negative change/impact
-10 to -18	-B	Negative change/impact
-19 to -35	-C	Moderate negative change/impact
-36 to -71	-D	Significant negative change/impact
-72 to -108	-E	Major negative change/impact

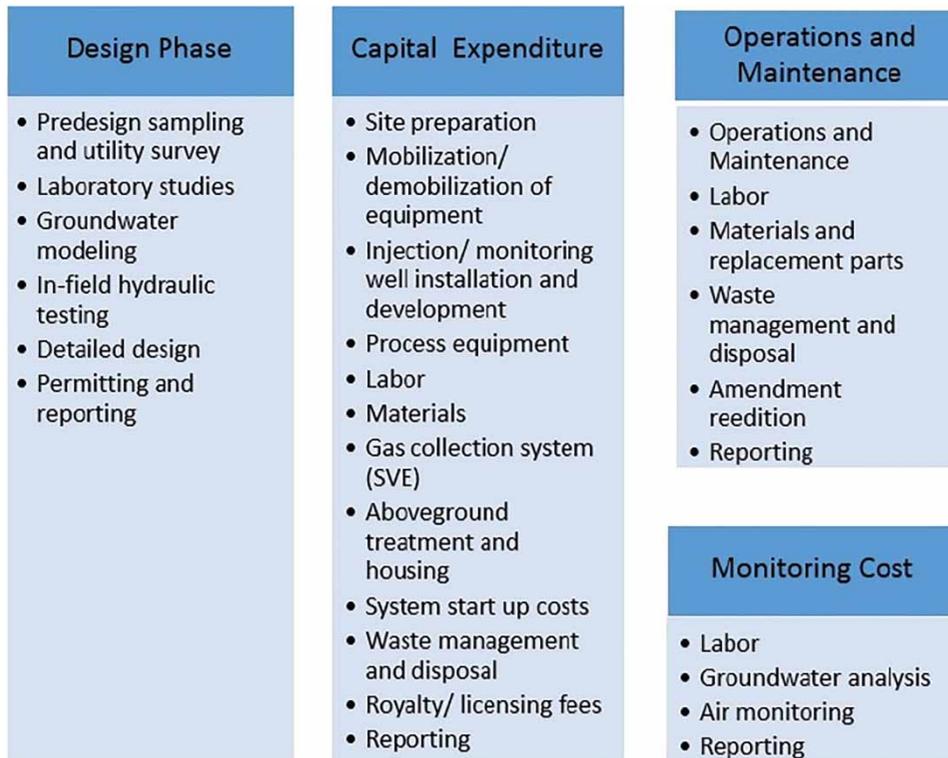


Figure 4 | Categories and sub-categories for cost analysis (adapted from Harkness & Farnum 2010).

ISCO using permanganate. ISB was the preferred method due to all its advantages: it is a natural process that provides the possibility of a complete mineralization of the pollutants, and the cost of the treatment and equipment needed are very low. However, the high concentration and toxicity of the pollutants found in the site requires the use of additional chemical treatment of the contaminated area. This additional treatment includes the previously exposed ISCO methods prior to ISB by means of the oxidants already presented: potassium/sodium permanganate or sodium persulfate. Since the intention is to use this technology together with bioremediation, the preferred oxidant is sodium persulfate because, as shown in Figure 2, the efficiency of biological treatment when using sodium persulfate is much higher than using permanganate, and the global removal efficiency using biological treatment combined ISCO with sodium persulfate appears to be the highest. The success of the treatment relies on two factors: (a) the site characterization and (b) the ability to deliver an adequate amount of oxidant (Henry 2010).

### Pilot test and injection plan

In order to characterize the site and the contaminants present a pilot test is necessary. In this sense, the pilot test is an important phase in every type of remediation study in order to understand how the targeted site will respond to the specified remediation strategy. In addition, it provides information to assess the geological conditions and geochemical properties of the aquifer (Brown 2010). Pilot tests are carried out at the site, under *in-situ* conditions, by monitoring wells and soil borings, so they provide an accurate insight about what to expect during full-scale application. They also provide insight into design parameters such as achievable radius of influence (ROI) and field injection rates for full-scale applications. In addition, information about oxidant dosage and its distribution within the aquifer, NOD, and NADP and metals' presence can also be obtained. Finally, initial phase characterization provides information regarding geological conditions and geochemical properties of the aquifer (Table 5) (Brown 2010).

**Table 4** | Scientific experience on the treatment of leachate plume from different types of landfill

Author	Target contaminants	Methodology	Results
Chellam & Clifford (2002)	Leachate from uranium mining and milling sites (molybdenum, selenium, uranium and radium)	Coagulation with iron ions ( $\text{Fe}^{3+}$ ) at different pH values (low, neutral and high)	Efficiency of coagulation process directly depends on the type of chemical compound. For instance, radium was successfully removed at both high and low pH, while molybdenum was removed only at low pH
Zhong <i>et al.</i> (2017)	Recalcitrant chemicals present in leachate	Physico-chemical operations (coagulation-flocculation, chemical precipitation, filtrations, adsorption and ion exchange)	It was assessed that different methods have both advantages and disadvantages. For instance, coagulation and precipitation have a high sludge production rate that must undergo further treatment; Different type of filtrations (microfiltration, ultrafiltration and reverse osmosis) typically costly and required pre-treatment operation; Ion exchange and adsorption has high efficiency but typically used as a polishing step in the end of treatment train
Jun <i>et al.</i> (2009)	Leachate from industrial landfill containing mostly ammonium, heavy metals and organic contaminants	Sequence of permeable reactive barrier filled by zeolites and granular zero valent iron as a reactive media	Reactor used in the pilot-scale operation showed that it has potential to decompose highly recalcitrant chemical compounds and convert them to easily biodegradable substances. As a result of the research it was investigated that BOD to COD ratio rapidly increased. Reactive media were acting as a reducing agent and consequently performed redox reactions
Christensen <i>et al.</i> (2000)	Leachate plume from an old non-functional landfill (petroleum hydrocarbons and chlorinated solvents)	Natural attenuation	Results showed that application of cost-effective strategy (natural attenuation) can provide mass reduction of the target contaminants. However, it is suggested to use such approach only in sites where conventional treatment (pump and treat, physico-chemical operations, etc.) were already performed

Regarding the injection of the required oxidant, an injection plan has to be previously designed. This design should ensure an appropriate contact between the ISCO reagents and the target contaminant. Due to the fact that the distribution of the reagent depends on the characteristics of the site, the injection plan needs to be based on the pilot test results and model development. In this sense, hydraulic data are crucial, and can be obtained from pump tests, dipole test and conventional slug tests conducted in specific areas of the contaminant plume (Naval Facilities Engineering Command-NAVFAC 2013).

Attending to the characteristics of the studied area, the 'direct injection method' is selected as the preferred one,

as it is less equipment intensive and quicker in comparison to other methods such as recirculation. It consists of the direct injection of the reagent into the subsurface in a determined volume of water from an external source, consequently displacing groundwater according to the volume of reagent injected.

In order to design the layout and spacing of the injection wells, a key design parameter is the ROI around a treatment well. The ROI determines the lateral area of the aquifer that can be impacted by the treatment well over the duration of the remediation treatment. In order to accurately calculate it, it is necessary to develop a groundwater model, using the design pumping rate to

**Table 5** | Site characterization parameters and design implications (based on pilot test)

Parameters	Description	Design impact
Nature and extent of contamination	Horizontal and vertical distribution of contaminants Presence of NAPLs	Horizontal or vertical locations to introduce oxidants Impact oxidant demand
Human and ecological health risks	Determination of contaminants and their ecotoxicology	Influence on treatment goals
Fate and transport of contaminants	Movement of contaminants within the aquifer (flow rate)	Location of injection wells Concentration of oxidants and their introduction
Hydrogeology	Lithology (heterogeneities, grain size, permeability) Gradients Confined or unconfined aquifer  Saturated thickness Hydraulic conductivities Darcy velocity Mineralogy Groundwater flow	Approach to introduce oxidants into aquifer  Metal mobilization (mineralogy) Low conductivity regions might need additional injections Radius of influence NOD (persulfate reacts with reduced metals)
Hydrogeochemistry	Distribution coefficients (Kd) pH Buffering capacity Dissolved oxygen (DO) Oxidation reduction potential	Approach to introduce oxidants into aquifer
Plume size		Oxidant dosification Well layout
Depth to groundwater		Well design

determine the expected hydraulic gradients and imparted groundwater flow field.

### Environmental impact assessment (EIA) and financial analysis

Regarding the EIA, the ES values obtained from the RIAM matrix were classified according to Table 6. No values belonging to E or –E categories were found, meaning that there will not be any extremely strong impact from any of the factors (neither positive nor negative). Table 6 shows all the factors included in the categories D and –D which are defined as significant positive and negative impacts, respectively, while Table 7 shows the most significant impacts. Finally, a bubble diagram (Figure 5) was used as an alternative technique to represent environmental impact magnitude.

For the purposes of financial analysis, the treatment train proposed (ISCO + ISB) is expected to last four years with a monitoring plan for 30 years. Table 8 shows the

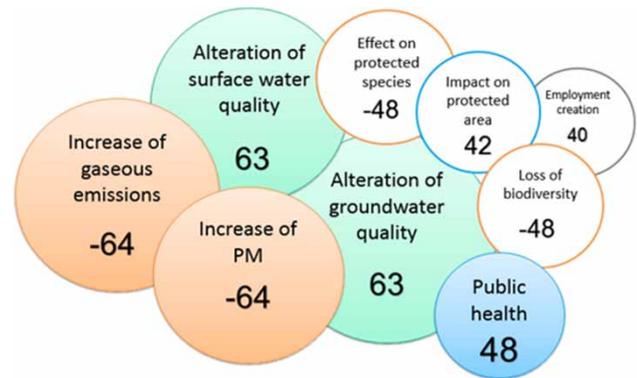
site characteristic values obtained from the literature, own calculations, preliminary design and other reliable sources. Table 9 summarizes the cost for the treatment train proposed, where it was assumed that a crew of four people will be hired to perform the injection of the treatments and this strategy will be done annually (up to four years) over 3 weeks. Thus, practically for the first two years, persulfate for ISCO treatment will be injected, while during the last two years, lactic acid will be injected as substrate for the microorganism in order to stimulate ISB. It was also assumed that the wells installed will be suitable for both ISCO and ISB, where the injection plan was also assumed to be through a manifold using a dosing pump connected to the river that passes nearby. As additional analysis, monitoring was ascertained as the category with the highest cost. Indeed, this category consumes a great deal of time, monitoring instruments and labour. Operation and maintenance is the second most expensive category.

**Table 6** | Summary of RIAM results

		ES	RB	A1 Importance (0 → 4)	A2 Magnitude (-3 → 3)	B1 Performance (1 → 3)	B2 Reversibility (1 → 3)	B3 Cumulation (1 → 3)
<b>Physical and chemical</b>								
Environmental quality	Increase of gases emissions level	-64	-D	4	-2	2	3	3
	Increase of particular matter emissions level	-64	-D	4	-2	2	3	3
Hydrogeology	Groundwater quality alternation	63	D	3	3	2	2	3
	Surface water quality alternation	63	D	3	3	2	2	3
<b>Ecological and biological</b>								
Flora and fauna	Loss of biodiversity	-48	-D	3	-2	2	3	3
	Affectation to protected species	-48	-D	3	-2	2	3	3
<b>Economical and operational impacts</b>								
Demographic system	Direct or indirect employment creation	40	D	4	2			
	Public health	48	D	2	3	2	3	3
<b>Sociological and cultural impacts</b>								
Cultural and historical heritage	Impact on the value of the protected area	42	D	3	2	2	2	3

**Table 7** | Most significant positive (+D) and negative (-D) impacts

Significant negative impacts (-D)	Significant positive impacts (+D)
Increase of gaseous emissions levels	Alteration of groundwater quality
Increase of particulate matter levels	Alteration of surface water quality
Risk of loss of biodiversity	Direct or indirect employment
Effect on the protected species	Public health
	Impact on the value of the protected area



**Figure 5** | Bubble diagram showing the magnitude of impacts from the project.

## CONCLUSIONS

The composition of the contaminants present in the leachate from the landfill was analysed and, according to it, the suitability of ISCO (with either  $KMnO_4$ ,  $NaMnO_4$  or SPS as the main oxidants) and ISB was evaluated as

a remediation treatment, showing that the best option encountered was to perform a pre-treatment by ISCO with SPS and a following treatment using bioremediation. Since the variety of contaminants present in the leachate is very complex, difficulties were faced during the literature review due to the lack of similar case studies.

**Table 8** | Summary of site parameters and values used to calculate the treatment costs

Parameter	Value
Length of the landfill (m)	125
Width of landfill (m)	75
Area of the landfill (m <sup>2</sup> )	9,375
Injection rate (L/min)	15
Natural oxidant demand-NOD (persulfate) (g/kg solids)	3
Substrate adsorption (g/kg solids)	1.5
Well ROI (m) <sup>a</sup>	12
Length between wells (m)	24
Number of wells needed	21

<sup>a</sup>Value from Krembs *et al.* (2011).

**Table 9** | Summary of costs for the treatment done by ISCO + ISB

Summary of costs (€)	
Total design	71,100
Total capital	75,690
Total operation and maintenance (4 yr NPV)	110,800
Total monitoring (30 yr NPV)	376,218
<b>Overall total (30 yr NPV)</b>	<b>633,808</b>

Moreover, the geology and geochemistry of the area is another important factor while evaluating the suitability of different technologies, such as the presence of chelating agents, etc. In this sense, the performance of a pilot test is highly required before designing the remediation treatment in order to characterize the pollutants present and the characteristics of the treated area. Moreover, key parameters needed for designing the oxidant injection method can also be obtained. Pilot tests also provide an insight about the future performance and efficiency of the selected remediation technology.

Finally, performing a financial assessment is an important part of assessing the economical feasibility of the proposed remediation project. Moreover, an environmental impact assessment also needs to be carried out in order to identify the negative impacts of the remediation project. In this sense, mitigation activities can be assessed in order to reduce these impacts.

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