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Opportunities and critical issues related to the use of amendments as sustainable remediation techniques

Opportunità e criticità legate all'uso di ammendanti come tecniche di bonifica sostenibili

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Riassunto

Questo studio mira ad analizzare le opportunità e le criticità legate all'uso degli ammendanti come tecniche di bonifica. Le prestazioni degli ammendanti (Biorisanamento aerobico, Ossidazione chimica in situ e Surfattanti) sono state confrontate con quelle di altre tecnologie di bonifica delle acque sotterranee (*Air Sparging, Pump&Treat, Multi-Phase Extraction, Pump&Reinjection, Monitoring Natural Attenuation*) sulla base di un dataset di 180 siti contaminati. I fattori considerati sono: efficacia della bonifica; costo di bonifica; tempo necessario per la bonifica; sostenibilità ambientale.

La frequenza e le tipologie di criticità legate agli ammendanti sono state studiate sui 40 siti in cui sono stati applicati gli ammendanti. Le criticità si sono verificate nel 20% dei 40 casi analizzati e consistevano in: a) occlusione parziale o totale dei pozzi di monitoraggio e formazione di sottoprodotti, per esempio metalli pesanti (5%); b) aumento incontrollato delle concentrazioni di contaminanti e potenziale migrazione a valle (8%); c) formazione di sottoprodotti senza ostruzione dei pozzi (7%). Per ogni criticità è stata condotta un'analisi approfondita per comprendere i processi (equilibri di pH-Eh, desorbimento dei contaminanti, riduzione della conducibilità idraulica), per evidenziare le lacune progettuali e procedurali (eccesso di ammendante, selezione del metodo di iniezione, rimozione dei contaminanti mediante spurgo). Tuttavia, è stato osservato che le criticità possono essere evitate o mitigate con una progettazione accurata, con l'esecuzione di test pilota, con l'applicazione di protocolli di applicazione del prodotto ammendante e protocolli di monitoraggio, e se necessario, con una risposta tempestiva adottando un piano di azione correttivo. L'uso di ammendanti si rivela una soluzione efficace: nel 64% dei siti analizzati, ha portato a una riduzione significativa della contaminazione entro un anno dall'applicazione. Il costo è circa un terzo rispetto alla media delle altre tecnologie. Il tempo di funzionamento è circa la metà della media del tempo operativo delle altre tecnologie. In base ai risultati dell'analisi di sostenibilità, le tecnologie mediante ammendanti riducono la produzione di rifiuti, il consumo di energia e di acqua, e minimizzano le emissioni in atmosfera. Considerando la sostenibilità in senso lato (ambientale, economica e temporale), è possibile affermare che la bonifica tramite ammendanti è la più sostenibile e potrebbe soddisfare l'interesse di tutti gli *stakeholders*.

Abstract

This study aims to analyze the opportunities and critical issues related to the use of amendments as remediation techniques. The performance of amendments (Aerobic Bioremediation, In Situ Chemical Oxidation and Surfactants) was compared with the performance of other groundwater remediation technologies (Air Sparging, Pump&Treat, Multi-Phase Extraction, Pump&Reinjection, Monitoring Natural Attenuation) based on a dataset of 180 contaminated sites. The considered factors are: effectiveness of the remediation; cost to remediate; operational time; environmental sustainability.

The occurrence and types of amendment-related issues analyzed were studied on the 40 sites where the amendments had been applied. Issues occurred in 20% of the 40 analyzed cases and consisted of: a) partial or total occlusion of the monitoring wells and by-product formation, for example heavy metals (5%); b) uncontrolled increase in contaminant concentrations and potential downstream migration (8%); c) by-product formation without well obstruction (7%). For each critical event, a detailed analysis was conducted to understand the processes (pH-Eh equilibria, contaminant desorption, hydraulic conductivity reduction), to highlight the design and procedural gaps (surplus of amendment, injection method selection, contaminant removal by purge). However, it has been observed that the issues can be avoided or mitigated with an accurate design, pilot tests performance, with the application of delivery and monitoring protocols, and at least with a prompt response adopting a corrective action plan, if necessary. The use of amendments turns out to be an effective solution: in 64% of the analyzed sites, it led to a significative reduction of the contamination within one year from the application. The cost is about one third if compared to the average of the other technologies. The operational time is about half the average operational time of the other technologies. Based on the results of sustainability analysis, amendments technologies reduce the production of waste, energy and water consumption, and they minimize air emissions. Considering the sustainability in its broadest sense (environmental, economic, and temporal), it is possible to state that the remediation by amendments is the most sustainable and would meet the interest of all the stakeholders.

Introduction

Amendments used for groundwater remediation are part of the group of remediation technologies defined as in-situ technologies. These technologies do not involve the extraction of the contaminated matrix for remediation, but they treat and reduce the mass of the contaminants directly within the site where it was detected. Amendments are used to treat a large quantity of both organic and inorganic compounds such as petroleum hydrocarbons, chlorinated solvents, heavy metals, and pesticides. The processes promoted by different typologies of amendments can be biological, for example for aerobic or anaerobic biodegradation; chemical, for chemical oxidation or chemical reduction and chemical-physical processes for surfactant products that favor the desorption of contamination adsorbed to the solid matrix. Since the products must be injected into the aquifer, it is essential to assess and ensure the distribution of the amendment in the aquifer. As with other remediation technologies, geological heterogeneity and low hydraulic conductivities can significantly reduce the radius of influence. However, by preparing a thick injection mesh, it is possible to act even with conductivities of 10^{-5} m/s, as tested in three case studies analyzed and included in this study.

In order to assess the progress of the remediation and to have full control of the system, the technologies by amendments require specific and frequent monitoring including chemical analysis and chemical-physical parameters measurement on the field.

In Situ Chemical Oxidation has been applied in the field of groundwater remediation for almost 10-15 years in Italy, and for even longer periods abroad. According to the study carried out on more than 180 contaminated sites (Dal Santo et al. 2019), during the last 5 years there has been a significant growth in the adoption of remediation amendments technologies. Using amendments has become more and more appreciated by the designers and by Public Authorities because in some cases, in particular in presence of residual and recalcitrant contamination, they turn out to be more effective, sustainable and cheaper.

This study analyzed the opportunities and critical issues related to the use of amendments with the aim to better understand how to effectively apply them. This study is part of a research effort to promote the maturation and increase the reliability of these technologies, which are very promising in terms of sustainability.

Materials and Methods

The contaminated sites were analyzed to elaborate a statistical analysis for a comparison among the different technologies. They were also analyzed as case studies. The selected sites have the following characteristics, also summarized visually in Figure 1:

- located in Italy;
- areal extension from 1000 to 10000 m^2;
- presence of an unconfined aquifer;
- petroleum-hydrocarbon-related contamination into groundwater, from 1 to 100 times the Italian threshold limits (Repubblica Italiana 2006) for one or more of the following parameters: Total hydrocarbon expressed as n-hexane, benzene, toluene, xylene, ethylbenzene, styrene (BTEXS) Methyl tert-butyl ether (MTBE), Ethyl tert-butyl ether (ETBE);
- point source contamination or multi-point contamination.

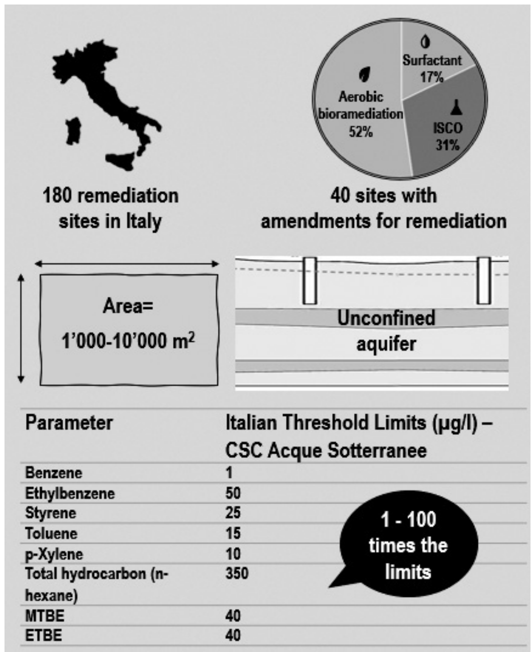

Fig. 1 - Characteristics of the sites selected for the study.

Fig. 1 - Caratteristiche dei siti selezionati per lo studio.

The amendments used for the remediations and selected for this study can be classified into three main families.

- Enhanced aerobic bioremediation (abbreviated to Biorem in the following graphs and pictures). The enhanced aerobic bioremediation increases the number and activity of microorganisms capable to degrade oil-related contaminants. This technology is driven mainly by a biological process and the products consist of slow-release oxygen compounds, for example CaO_2 or H_2O_2. (Gieg et al. 1999).
- In Situ Chemical Oxidation (in the following ISCO). These products allow to generate radicals with an extremely high oxidation potential, which can rapidly oxidize the contaminant molecules and break the chemical carbon bond. They are, for example, persulphate products properly activated with other compounds. (Siegrist et al. 2011).
- Surfactants (in the following Surfact). These compounds temporarily desorb the organic pollutants adhering to the solid matrix, thus making them more available to subsequent removal by groundwater purge. These compounds are made up of amphiphilic molecules acting indeed as surfactants (Harwell et al. 1999).

Based on a dataset of 180 contaminated sites, the performance of the amendments was compared with the performance of other groundwater remediation technologies such as:

- Air Sparging (AS);
- Monitoring Natural Attenuation (MNA);
- Multi-Phase Extraction (MPE);
- Pump&Reinjection (P&R);
- Pump&Treat (P&T).

Figure 2 shows the distribution of the selected technologies, 25% of the statistical population are amendments application technologies.

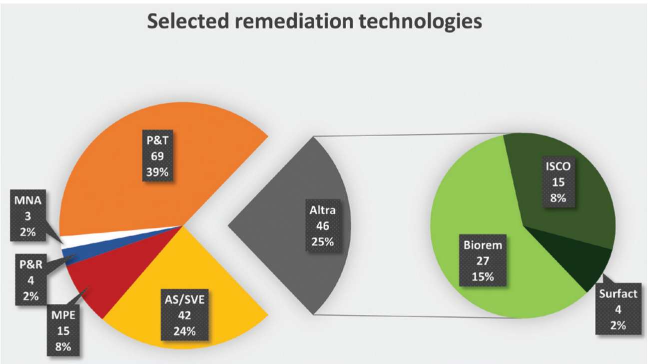

Fig. 2 - Distribution of the selected remediation technologies, 25% is based on amendments application. Lables indicate type of remediation technology, number of investigated cases and percentage.

Fig. 2 - Distribuzione delle tecnologie di bonifica selezionate, il 25% è basato sull'applicazione di ammendanti. Le etichette indicano il tipo di tecnologia di risanamento, il numero di casi indagati e la percentuale.

A statistical analysis was carried out considering the following factors:

- **cost to remediate the contaminated site.** Since the installation of the plant or the application of the amendments on site considering: the cost of installation/ application, operation - and - maintenance costs, monitoring costs;
- **time to remediate the contaminated site.** It considers the time since the installation/application to the achievement of the remediation goals.

A semi-quantitative and relative sustainability analysis was carried out considering the entire remediation life cycle and by analyzing the following indicators:

- **energy consumption**. It takes into account the energy to feed the remediation plant or to run the pump to inject the amendments;
- **waste production**. Here we included the exhausted carbons of the treatment plant. The plants including water treatment are P&T and P&R, while MPE includes treatment both for water and air. With amendments application the only produced waste is the packaging containing the product (drums and pallets). For surfactants, there is also a water waste production. In fact, after the application, the surfactant and the contaminated groundwater must be removed by purging and disposed as waste water;
- **emission to air**. Here we included the emission to air after the plant treatment (MPE; AS/SVE) and/or the emission related to the transport of the plant or of the amendments during the installation/application. It takes into account also the mobility to the site for the operation and maintenance activities, waste disposal, field and monitoring activities;
- **water consumption**. Here we included water discharge into the sewage or into surface water after treatment in the treatment plant (P&T, MPE). Another water-consuming activity is the amendment mixing with water supply before the injection (Bioremediation, ISCO, Surfactant) and groundwater extraction after surfactant treatment. In this case groundwater was disposed off-site as a waste;
- **raw materials use**. Here we included the material, mechanical and electrical components of a plant or the material used to produce the amendments, for example calcium peroxide, persulfates, surfactants.

Another statistical analysis was carried out on 40 sites where the amendments were applied. Also in this case, the 40 sites were used both for statistics and as case studies. In detail we analyzed:

- **effectiveness of the remediation.** This analysis considered the reduction of contamination compared to the initial values and to remediation targets;
- **the occurrence and types of amendments-related issues.** For each issue reported (by-product formation; occlusion of the monitoring wells; increase of contaminant concentrations), a detailed investigation was carried out to understand the related complex processes.

Results

This chapter discusses the opportunities and critical issues which emerged, and the obtained results.

Opportunities

Use of amendments brings opportunities in terms of a) effectiveness of the remediation, b) cost, c) time to remediate and d) sustainability as described below.

a) *Effectiveness of remediation by amendments*

The remediation by amendments led to a reduction in contaminant concentrations within one year in 64% of the 40 analyzed cases. 48% of the sites had a remarkable decrease of contamination and are near to the closure of the environmental case. These evaluations were carried out one year after product application because the effectiveness of the product is expected to last for 9-12 months for aerobic bioremediation, 3-6 months for ISCO and 7-15 days for surfactants. Consequently, we assumed the effectiveness of the remediation can already be assessed within one year. A further assessment of the remediation effectiveness can be made after the remediation completion.

Figure 3 shows the effectiveness of the remediation. Five classed were distinguished considering contaminant concentration variation since the application to one year.

These 5 classes are so described:

- **Remarkable decrease:** concentrations are two orders of magnitude lower than initial contaminant concentrations. They are close to or below the set remediation targets;
- **Average decrease:** concentrations are one order of magnitude lower than initial contaminant concentrations;
- **Minor decrease:** concentrations are in the same order of magnitude, but there is a decrease trend recognizable;
- **No variation:** monitoring data recorded concentration values similar to those before the injection. No variation occurred since the application, no increasing or decreasing trend can be identified;
- **Increase:** augmentation of the contaminant concentrations is detected if compared to the initial ones. This is an undesirable effect that needs to be kept under control, although it may be determined by a desorption effect due to the injection activities.

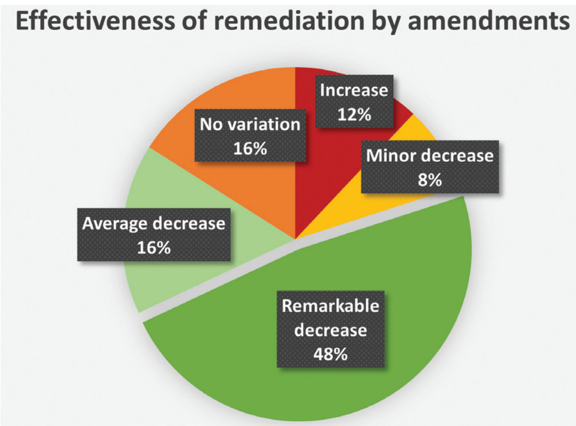

Fig. 3 - Effectiveness of remediation by amendments within one year. In 64% of the analyzed cases they led to a reduction in contaminant concentrations within one year.

Fig. 3 - Efficacia della bonifica tramite ammendanti. Il 64% dei casi analizzati hanno portato a una riduzione delle concentrazioni di contaminanti entro un anno.

Technologies by amendments have therefore a proven effectiveness and can be considered a valid alternative to the plant solutions for the remediation. Within this process of maturation of the technologies we observed that with the introduction of procedures and best practices it is possible to enhance the effectiveness of these kinds of remediation.

b) *Remediation Costs*

Figure 4 shows the average costs for each remediation technology. The costs include the plant start-up or the amendments application, the operation and maintenance, if necessary, and the monitoring of the groundwater quality to assess the remediation. The proposed cost for each technology is the average cost calculated between sites where the same remediation technology has been applied. As the analyzed sites have a certain variability in terms of areas, site specific characteristics and initial concentrations, we arbitrarily assumed an uncertainty of ± 20% the average values. From a comparison between the technologies, it is observed that when using amendments, the cost is about one third. In fact, the remediation techniques with amendments do not require a plant installation but only a temporary system to inject the products, for example with a mixing box and a pump and, if necessary, the drilling of dedicated injection wells. There are no operational and maintenance activities and monitoring costs are concentrated in few years.

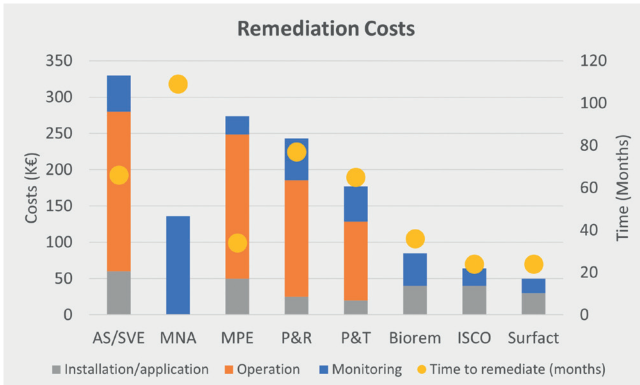

Fig. 4 - Remediation costs based on the analized dataset. Each cost includes the installation/application cost; the operational cost if any and the monitoring cost.

Fig. 4 - Costi di bonifica basati sul set di dati analizzati. Ogni costo include il costo di installazione/applicazione; l'eventuale costo operativo e il costo di monitoraggio.

c) *Time to remediate*

Figure 5 shows the time needed to remediate for each remediation technology since the plant start-up/application to the achievement of the remediation objectives. As for costs, since the analyzed sites have a certain variability in terms of areas, site specific characteristics and initial concentrations, we arbitrarily assumed an uncertainty of ± 20% the average values. The results show that, when amendments are used, the time needed for remediation is around one half compared to the average of the other systems. It is worthy of note that MPE's have remediation times comparable to bioremediation (34 months and 36 months). This makes the MPE a good solution in terms of time to remediate and it is also applicable to sites with high contamination concentrations, as opposed to bioremediation (API 1996; ISPRA 2018). However, an MPE solution is not comparable to the use of amendments in terms of costs and environmental sustainability.

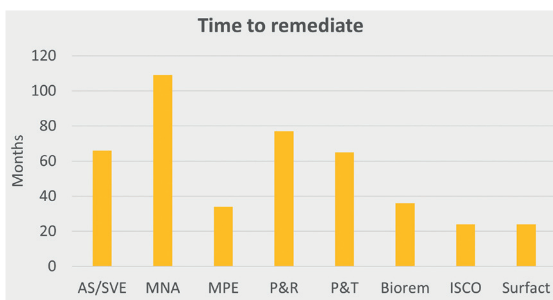

Fig. 5 - Time to remediate the site based on the analized dataset. It goes since the start up of the plant or since the injection to the achievement of the remediation objectives.

Fig. 5 - Tempo necessario per bonificare il sito basato sul set di dati analizzati. Si considera dall'avvio dell'impianto o dall'iniezione al raggiungimento degli obiettivi di bonifica.

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d) ***Sustainability***

The carried out sustainability analysis is a semi-quantitative analysis where remediation technologies were compared on a relative basis. It considers all the life cycle of the remediation since the installation/application to the achievement of remediation objectives.

A score from 1 to 5 was assigned for each category (Table 1) to evaluate environmental impact for each indicator, where 5 represents the maximum environmental impact. In the following, for each considered indicator, there is a dissertation of the identified semi-quantitative criteria as well as further considerations applied to assign the scores.

- **energy consumption**. It takes into account energy needed to feed the plant. We assigned score 4 for MPE, P&T and P&R, and score 3 for AS/SVE, assuming it is a less energivorous plant. For the injection of amendments, the only energy needed is related to the pump for the injection and it is time-limited to the weeks of application activities (score 1);
- **waste production**. We assigned 5 to MPE, considering the exhausted carbons of treatment plant both for water and air treatment; 4 to P&R and P&T considering the exhausted carbons for water treatment only; 3 to AS/SVE, considering the lower amount of exhausted carbons used for air treatment; 3 for surfactants, due to water purge and waste produced by the package of the amendments; Score 1 to Bioremediation and ISCO, related to the waste package of the amendments (pallets and drums);
- **emission to air**. Here we included emission to air after the plant treatment for MPE and AS/SVE, the emission related to the transport of the plant or of the amendments, the movement related to the operation and maintenance activities (for MPE; AS/SVE; P&T; P&R) or monitoring activities (MNA; bioremediation; ISCO; surfactant). For MNA we consider a long-time monitoring while the monitoring is very short in time and less in number for remediation technics using amendments (score 1);
- **water consumption**. after treatment in the treatment plant (P&T, MPE plants) water was discharged into the sewage or into surface water. We attributed score 5 to P&T because it usually has higher water discharges then MPE (score 4). Another activity consuming water is the mixing of the amendments with water supply essential for injection (score 1 because it is only for the week of injection activities) and the extraction of impacted groundwater for the disposal as a waste using surfactant (score 2: 1 for water mixing and 1 for water purging);
- **raw material use**. Here we included the mechanical and electrical components of a plant (metal, plastics, concrete etc.). MPE needs more raw material (score 4) in comparison to other plant solutions (score 3), because it is a bigger plant (double system), which treats both water and air. Raw materials are also used to produce amendments. This resulted in the assignment of score 2 for Bioremediation and ISCO, which use a higher amount of product and 1 for surfactants, which use less product.

Total impact of a technology was calculated as the sum of the scores attributed to each indicator and total sustainability was calculated considering the maximum value of the environmental impact score (25) minus the impact score obtained for each technology.

$$\text{Enviromental Impact (EI)}=\sum_{n=1}^{5}(\textit{Indicator Score})_n$$

$$\text{Sustainability index (SI)}= \max EI - EI$$

Figure 6 shows the results as percentage of environmental impact. It is appreciable how each indicator (energy, waste, emission to air, water and raw material consumption) weighs with respect to the total impacts for each remediation technology.

The results show that MNA is the most sustainable choice in terms of environmental impact. It is always necessary, however, to consider the applicability of the remediation technology (API 1996; ISPRA 2018) in relation to the initial contaminant concentrations and site-specific conditions, the potential migration of contaminants out of the site and reaching a vulnerable target, and the time required to complete the remediation.

Tab. 1 - Environmental sustainability analysis on applicable technologies.

Tab. 1 - Analisi di sostenibilità ambientale delle tecnologie applicabili.

ENVIRONMENTAL SUSTAINABILITY ANALYSIS ON APPLICABLE TECHNOLOGIES							
	Energy	Waste	Emissions to air	Water consumption	Raw materials	Total Impact	Total sustainability
AS/SVE	3	3	4	0	3	13	12
MNA	0	0	2	0	0	2	23
MPE	4	5	5	4	4	22	3
P&R	4	4	2	0	3	13	12
P&T	4	4	2	5	3	18	7
Biorem	1	1	1	1	2	6	19
ISCO	1	1	1	1	2	6	19
Surfact	1	3	1	2	1	8	17

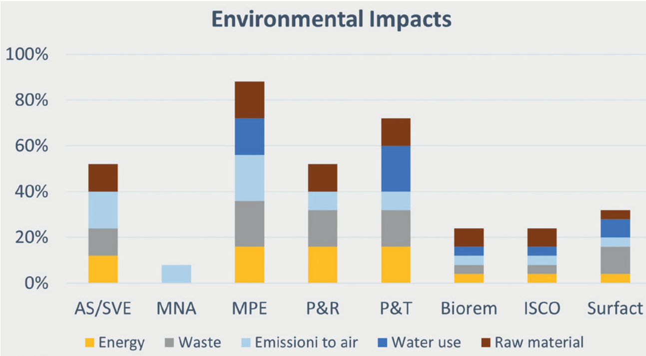

Fig. 6 - Percentage of impact for single remediation technique in terms of energy, waste production, air emission, water and raw material consumption. MNA, if applicable, has low impact on environment constituting a natural-based solution.

Fig. 6 - Percentuale di impatto per singola tecnica di bonifica in termini di energia, produzione di rifiuti, emissioni in aria, uso di acqua e consumo di materie prime. L'MNA, se applicabile, ha un basso impatto sull'ambiente costituendo una soluzione a base naturale.

Among the plant solutions, the recirculation of groundwater into the wells (P&R) allows to significantly reduce the water consumption because the water extracted after treatment is reinjected into the aquifer. In this way there is essentially a net balance from the extraction to the reinjection without extra water consumption.

The use of amendments succeeds in reducing all factors compared to plant solutions. The energy required for the injection is not comparable to that required to power a fixed plant. The waste production is exclusively related to the packaging of the amendments (drums and pallets). In the case of P&T, MPE, AS/SVE the waste production is related to the filters for the treatment. There are no emissions to air, except for those related to travel to the site to perform field monitoring activities. The use of water is due to the mixing of the amendments to allow injection into the groundwater. In the case of P&T, on the contrary, the extracted and treated water does not return to the aquifer but is discharged into the sewage system or into a surface water body. For surfactant the desorbed contamination must be recovered but this water consumption and waste generation will only last a few weeks related to surfactant application activities. There is no need of plant box, mechanical or electrical components, or of carbon filters for treatment but only the raw material to produce the amendant product.

To make the technologies by amendments even more sustainable some actions were identified:

- **A careful design of the remediation** to identify an appropriate dosage minimizing the amount of amendments to be applied. Consequently, raw material consumption for the production of the amendment, water consumption used for mixing, packaging (drums and pellets to disposed as a waste) were reduced using less amendment quantities if compared to a non-appropriate dosage;
- The use of **natural products** from **circular economy**. For example, biosurfactants can derive from olive oil or wine production residues. As regards the synthesis of ISCO products, Sulphur from by-production in crude oil refining processes could be used;
- **short supply chain** of amendments could help reduce the air emissions related to the transport.

Critical Issues

During the application of amendments as remediation techniques issues occurred in 20% of the 40 analyzed cases and consisted of: a) occlusion of monitoring wells, b) by-product formation, c) increase in contaminant concentrations (Fig. 7).

a) *Occlusion of the monitoring wells*

This issue consists of partial or total occlusion of the monitoring wells. The main factors leading to the occlusion are the product solubility, the method of application and the dosage. This issue was detected when bioremediation and ISCO products, less soluble than surfactant, were used direct into the monitoring wells and not into a dedicated injection well. On 7% of the studied cases part of the product remained in the well as immiscible solid occluding the screen of the monitoring well. Also, hydrogeochemical processes as pH-Eh variations, presence of swelling clays or biofouling can concur to occlusion. Biofouling has not been taken into account, it is not excluded that also this process contributes to the obstruction of the monitoring wells.

b) *By-product formation*

By-product formation consists of the formation of unwanted products during the interaction between the amendment and the aquifer. When applying bioremediation and ISCO, in 12% of the analyzed cases, heavy metals, characterized by high toxicity, were detected in the monitoring wells dissolved into the groundwater. It is essentially related to the hydrogeochemical processes as variation in the pH-Eh equilibria and dissolution of new components. In 7% of cases, problems related to clogged wells and by-product formation occurred together.

c) *Increase in contaminant concentrations*

In 8% of 40 cases, increases in contaminant concentrations were recorded with potential downstream migration of the contamination using surfactant but also ISCO. The surfactant remediation technology is based on contaminant desorption processes and an initial increasing of the contamination is the desired effect. Therefore, the contaminant desorbed must be totally and promptly removed to avoid downgradient migration. There is also a physical process results in increasing the contamination due to the displacement of contamination from the soil matrix or from any sacs in the aquifer to the monitoring wells.

Detailed investigation of the processes

A deep investigation on the processes leading to amendment-related issues are carried out. Some are related to hydrogeochemical processes while others are related to design and procedural gaps.

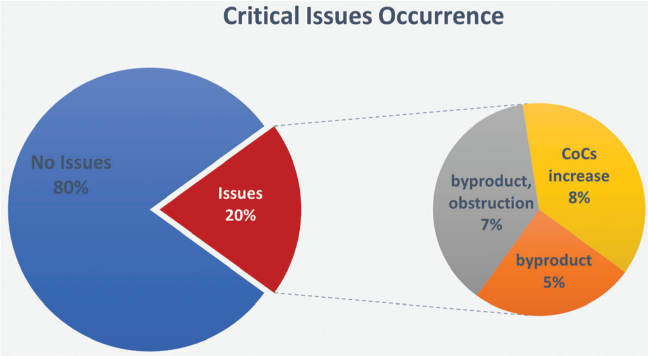

Fig. 7 - Amendment-related issues occurred in 20% of the 40 sites. 7% shows by-product formation such as heavy metals and partial or total occlusion of the monitoring wells; 5% by-product formation without occlusion and 8% an increasing of the contaminant concentrations.

Fig. 7 - Si sono verificati nel 20% dei 40 siti criticità legate agli ammendanti. Il 7% mostra la formazione di sottoprodotti come metalli pesanti e l'occlusione parziale o totale dei pozzi di monitoraggio; il 5% la formazione di sottoprodotti senza occlusione e l'8% un aumento delle concentrazioni di contaminanti.

pH-Eh variations

pH and Eh variations modify the chemical equilibria and result in the solubilization of pH and Eh-sensitive compounds such as heavy metals (Brookins 1988). The aquifer usually has a buffering effect due to, for example, iron minerals and organic matter. For example, in an unbuffered system, high pH values up to 13 and high redox potential values (100 mV) were measured, promoting dissolution of Chromium and the speciation of Chromium VI.

Hydraulic conductivity reduction

The change in pH can lead to a reduction in hydraulic conductivity if clay minerals are present in the aquifer (Ishiguro, 2003). The swelling of clays significantly changes and reorganizes the grain structure of the entire aquifer, reducing the hydraulic conductivity. The aquifer may no longer be suitable for injection or other technologies that require good hydraulic conductivity.

Contaminant desorption

As mentioned before, it is related to the desorption of the contamination and its dissolution into the aquifer enhanced by a chemical driver (for example oxidant product or surfactant).

Design and procedural gaps

The occurrence of critical issues during the use of amendments can highlight design flaws and procedural gaps. These are listed below.

- Surplus of amendment. The excess of amendment could cause well obstructions and variations of pH-Eh equilibria causing by-product formation;
- Application method selection. The use of monitoring network for the amendment injection, instead of a dedicated injection network, could damage the monitoring wells causing obstruction or it could make the local condition of the monitoring wells not representative of the aquifer;
- Contaminant removal by purge. In case of surfactant use, the desorbed contaminant must be totally and promptly removed. If the desorbed contaminant were not removed totally, it would result in an increase of the contaminant concentrations and a potential migration of the contamination.

The observed critical issues related to design and procedural gaps can be avoided or mitigated with the application of specific protocols (Dal Santo et al. 2020; ITRC 2020; IMPEL 2021).

Conclusions

The use of amendments turns out to be an effective solution compered to plant solutions: in 64% of the analyzed sites, it led to a significative reduction of the contamination within one year from the application.

The cost is about one third compared to the average of the other technologies, the operational time is about half compared to the average of the other technologies.

Based on the results of the environmental sustainability analysis, the amendments technologies reduce the production of waste, the energy, water and raw material use and have no direct emissions to air except by the transport.

The observed critical issues (occlusion of the well, by-product formation and contaminant concentration increase) can be avoided or mitigated with an accurate design, the execution of pilot tests, the application of delivery and monitoring protocols, and at least with a prompt response adopting a corrective action plan, if necessary.

Figure 8 shows an aggregate analysis normalized from 0 to the maximum value for each of the three factors and finally expressed in percentage. Each of the three factors has the same weight. The figure shows that the remediation techniques by amendments can minimize the time of remediation, the cost

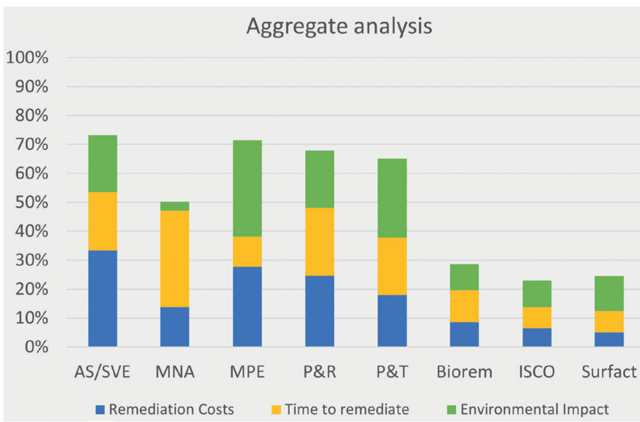

Fig. 8 - Aggregate analysis: cost, time and environmental impact normalized from 0 to the maximum value for each of the three factors and finally reported as percentage. Each of the three has the same weight.

Fig. 8 - Analisi aggregata: costi, tempi e impatto ambientale normalizzati da 0 al valore massimo per ciascuno dei tre fattori e infine riportati come percentuale. Ognuno dei tre ha lo stesso peso.

of remediation and the environmental impact compared to all the others. The remediation techniques by amendments vary from 25% to 29%, the plant solutions from 65% to 73% and MNA has a value of 50%.

Considering the sustainability in its broadest sense it is possible to state that the remediation by amendments is the most sustainable. In fact, in a balance of the cost-benefits, not only environmental, but also economic and time-related sustainability can be considered. In fact, short-term remediation means to return the land to the community more quickly. A remediation technology that ensures this kind of sustainability would meet the interest of all the stakeholders.

Competing interest
The authors declare no competing interest.

Author contributions
Mara Dal Santo: Conceptualization, Methodology, Formal analysis, Investigation and Writing.
Giuseppe Alberto Prosperi: Materials, Acquisition, Methodology, Investigation, validation, Supervision

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