CL:AIRE

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EiCLaR bulletin

CL:AIRE's EiCLaR bulletins describe *in situ* bioremediation technology developments and tools created within the EiCLaR project. This bulletin describes the development of a new soil remediation technology which combines three individual techniques: phytoremediation, chemical immobilization, and electrochemical oxidation.

Enhanced phytoremediation of soil with complex contamination

1. INTRODUCTION

A novel soil remediation technology has been developed to immobilize arsenic and simultaneously degrade polycyclic aromatic hydrocarbons (PAHs) *in situ*. The technology synergistically combines three individual techniques: phytoremediation, chemical immobilization, and electrochemical oxidation. Individually, each method serves a specific purpose, but together they leverage their unique strengths to effectively address complex soil contamination. Phytoremediation utilizes plants to stabilize and degrade contaminants, chemical immobilization binds arsenic to reduce its mobility, and electrochemical oxidation breaks down PAHs. Additionally, the technology enhances soil health and promotes microbial activity, providing an integrated electrochemical-biological solution for complex soil contamination. Such complex mixtures of contaminants are often found in wood treatment facilities where creosote oil and Boliden salt (chromated copper arsenate or CCA) have been used. Most importantly, the technology can be applied *in situ*, that is, without the need to excavate the soil, which is quite complicated when soil is silty or clayey and free phase creosote is still present in soil.

Initially the method was called enhanced phytoremediation, but to reflect the complexity of the overall technology, the entire approach has been named Integrated Contaminant Degradation and Stabilization (ICoDeS) Technology.

In this bulletin the theory and rationale behind the integrated technology are described providing details of the on-going research and development work and some of the so far obtained results. Several bench-scale and small-scale outdoor experiments were implemented to test and further optimise the technology for soils with mixed contaminants (metals, PAH). Further, the technology is being tested at pilot scale *ex situ* and *in situ* in Sweden and France.

2. BACKGROUND TO THE TECHNOLOGY

2.1 Combining Individual Techniques

Combining phytoremediation, chemical immobilization of arsenic, and electrochemical oxidation of PAHs involves a coordinated effort to leverage the strengths of each method. Furthermore, innovation of specific processes has been implemented to advance the overall technology.

- **Phytoremediation** employs plants that only absorbs low levels of arsenic into their above ground biomass whilst stabilising the soil surface and simultaneously above ground biomass, stimulating the degradation of PAHs. Certain grasses and legumes, such as ryegrass, alfalfa, and reed canary grass, can aid in PAH degradation. These plants have the ability to tolerate arsenic and absorb low levels of this metalloid into their above ground biomass. The limited mobilization and translocation of contaminants once absorbed by the plant roots make these species attractive for phytostabilization and phytodegradation of soils with mixed contaminants. That is, this dual-purpose approach aims at stimulating degradation of organic contaminants and avoiding metal(loid) uptake thereby mitigating the impact of contaminants on the soil environment. The selected plants are established in the contaminated area for the management of shallow contamination. Plant health and contaminant levels are monitored to ensure that contaminants are not spreading from soil to above ground biomass of plants.
  Over the past three decades, phytoremediation has been considered as a cost-effective and environmentally friendly alternative to traditional physicochemical remediation methods. Initially, the focus was on phytoextraction of metals, a relatively slow and incomplete process that often results in problematic biomass disposal in many regulatory jurisdictions (Bardos *et al.*, 2011). A more successful

Enhanced and Innovative *In Situ* Biotechnologies
for Contaminated Land Remediation

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approach leverages the synergistic interactions between plants, microorganisms, and mycorrhizae to either completely degrade organic contaminants or immobilize metals *in situ*. The use of soil amendments that bind metals and reduce their toxicity, or the inoculation with arbuscular mycorrhizal fungi (AMF) to enhance plant performance, can significantly increase the efficiency of phytoremediation for both organic and inorganic pollutants (e.g. Coninx *et al.*, 2017). Additionally, innovative methods for applying soil amendments *in situ* are needed to further enhance the effectiveness of this technology in field applications.

- **Chemical Immobilization of Arsenic** involves the addition of stabilizing agents or amendments that bind arsenic, reducing its mobility. The goal is to stabilize arsenic, preventing it from leaching into groundwater or being taken up by plants beyond safe levels.

  Soil amendments are essential for improving conditions in contaminated soil, as they help reduce contaminant toxicity and bioavailability, allowing plants and microorganisms to establish more easily. The most common and highly effective amendments for arsenic immobilization are iron oxides (Cundy *et al.*, 2008; Mench *et al.*, 2010, Komarek *et al.*, 2013). Iron oxides are universal soil scavengers and, due to their amphoteric nature, are capable of sorbing both cations and anions. In the context of soil remediation, metallic or zero-valent iron is usually applied, which then oxidises to iron oxides in the soil.

  The usual way of amending soil is to first excavate it, mix it with amendments and then return it to the ground. Spreading amendments on the top layer and tilling in is also performed. However, if the contaminants are located deeper than deep ploughing depth (50 cm) and the soil is silty or clayey, mixing in amendments becomes very difficult.

  In this research the introduction of soil amendments to soil has been optimized by applying our innovation – the dispersive force of an electrical field. Here, iron electrodes are used as a source of iron in soil. The corroding electrodes provide iron, while electricity helps to spread iron ions through the soil towards contaminants. Electric current is provided using EkoGrid technology, where pulsing voltage and polarity is switched regularly, so that all electrodes serve as both cations and anions, and equally corrode over time. In this way the use of electrodes is maximized, while the contaminant plume is trapped on site. Iron ions spread from the corroding electrodes and upon contact with arsenic immobilize it in the soil. This leads to lower concentrations of dissolved and bioavailable arsenic in soil and better chances for plants and microorganisms to survive and degrade organic contaminants. Switching polarity also helps to overcome one of the main limitations of electrokinetic remediation - the soil acidification by the acid front generated at the anode and alkalinization at the cathode. Using our approach, iron amendments are distributed through the soil using corroding electrodes and a low intensity electric field instead of excavating soil and mixing with iron particles or injecting nanoparticles through wells. The latter two methods have limited success to spread iron homogenously through the soil and are practically unfeasible in silty and clayey soils (Bennett *et al.*, 2010; Su *et al.*, 2013).

- **Electrochemical Oxidation of PAHs** is used to oxidatively degrade these compounds in the soil. This process involves installing electrodes in a grid pattern across the contaminated site to ensure uniform treatment. The electrodes are connected to a power source, with voltage and current settings optimized to promote the oxidation of PAHs through generation of reactive oxygen species (i.e. free radicals) capable of initiating degradation processes in soil. Studies have shown that even at a very low electric field strength (0.15 V cm^{-1}), organic contaminants (e.g. phenols) can be simultaneously desorbed, mobilised and degraded *in situ* (Proietto *et al.*, 2023).

  Continuous monitoring of electrical parameters and soil conditions (such as pH and redox potential) is carried out and used to further optimize the electrochemical process.

  Degradation of PAHs in soil subjected to an electric field is a complex process that can occur directly by the transfer of electrons from the organic molecule to anode or indirectly by splitting water molecules induced by the electric field and formation of reactive oxygen species that react with organic pollutants (Ajab *et al.*, 2020). Moreover, the rapid degradation of PAHs may be facilitated by alternating the polarity of the electrodes during the electrochemical treatment. Alternating the polarity has previously been shown to increase PAH degradation compared to using a constant one-directional direct current flow (Li *et al.*, 2012). By periodically reversing the current flow, the direction of movement of water, colloids and ions frequently changes, increasing the contact and interaction opportunities between soil microorganisms, nutrients and contaminants (Li *et al.*, 2012).

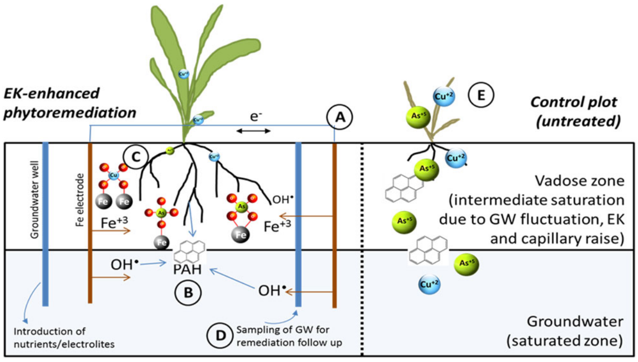
  EkoGrid technology utilizes a process known as Pulsed Electroosmosis (PEO), which involves the application of specific constant voltage pulses with continuously changing polarity (direction of the current). EkoGrid has refined this technology based on observations of how PEO alters physicochemical conditions in soil pores, recognizing that all electrokinetic phenomena are driven by electrochemical reactions at the soil particle/water interface. The most important reaction products formed are free radicals and oxygen. Hydrocarbon degradation then occurs through two primary mechanisms: electrochemical oxidation and PEO-enhanced bioremediation. The use of pulses keeps the system active for longer periods without creating issues such as pH imbalances. The change in polarity is important for triggering reactions throughout all pores within the entire treatment area.

2.1 Integration and Coordination

By modifying the enhanced phytoremediation approach, an added value process has been created that overcomes limitations of the traditional electrokinetic soil remediation technique and leverages the benefits of each individual method, reaching technology demonstration phase (TRL 6).

Successful integration of these remediation methods does not require any specific synchronization. Phytoremediation, chemical immobilization and electrochemical oxidation can proceed simultaneously as the electrochemical treatment does not antagonize any of the processes. On the contrary, the low intensity electric field is expected to facilitate biologically-enhanced degradation of organic contaminants without the need of additional bacterial inoculation, by this further decreasing soil toxicity. Low intensity electric fields have previously been shown to have a positive effect on enhancing soil biological activity of indigenous microorganisms and increasing cell mobility (Beretta *et al.*, 2020; Li *et al.*, 2020). Mycorrhizal inoculum can be injected to further promote plant establishment. Site irrigation and nutrient injection can be added to further stimulate soil bacteria and support plant growth while maintaining soil conditions favourable for electrochemical processes, contaminant oxidation and immobilization.

Regular monitoring is implemented to track groundwater contamination levels, soil chemistry and plant health. Based on monitoring results, adjustments to the treatment strategies are made to ensure ongoing effectiveness. This dynamic approach ensures that all three methods work in harmony, enhancing the overall remediation outcome.



(A) Electrodes are inserted through the vadose zone into the groundwater layer. (B) Organic contaminants will get degraded due to the reactive oxygen species formed by electricity and through excretion of fatty acids (e.g. linoleic acid) by plant roots. Reduced soil toxicity would stimulate indigenous microbial population, which will further contribute to contaminant degradation and promotion of plant colonization. (C) Mobile and bioavailable fractions of metal(loid)s will come in contact with iron oxides originating from corroding electrodes leading to reduced soil toxicity. (D) Groundwater quality will be monitored and soil remediation success evaluated. Untreated site (E) is used as a control for comparison of the remediation success. GW – groundwater; EK- electrokinetics.

Figure 1. Principles of the enhanced phytoremediation approach - ICoDeS Technology - applied in the EiCLaR project.

3. DEVELOPMENT OF THE TECHNOLOGY AT SMALL AND MEDIUM-SCALE

The aim of testing the technology in laboratory- and medium-scale settings was to observe the soil remediation processes in a controlled environment before scaling up the test to field pilot scale.

The impact of electrically-distributed iron amendments was evaluated for arsenic immobilisation and simultaneous electrochemical oxidation of PAHs in contaminated soil by i) analysing the supply of iron amendments to soil from corroding electrodes operated with a low voltage electric current, ii) evaluating iron dispersion through soil and consequent immobilisation of arsenic, and iii) evaluating the extent of simultaneous PAH degradation in soil. Furthermore, impact of the treatment on arsenic uptake by plants and degradation of PAH by plants was evaluated. The plant that was selected for these tests was reed canary grass (*Phalaris arundinacea*).

Organic soil contaminated with PAHs and arsenic was collected at a former wood impregnation site in Limmared, south Sweden, which was later used for a pilot demonstration. The method was tested at two scales: i) in 6 L plexiglas cells, each filled with 4 kg of contaminated soil, ii) in 1 m^3 high-density polyethylene containers, each filled with ca 200 kg soil. All cells and containers were equipped with a pair of iron electrodes (Ø 5 mm). The electrodes were connected to a power control unit (EkoGrid, Finland). Experiments were run in various configurations with a voltage potential of 0.5 – 2.4 V/cm, without pulses and only changing current direction, and with pulses at frequencies varying from 500 – 1000 pulses/second.

The results showed that for the iron electrodes to corrode and provide soil with additional iron, higher voltage potential is needed. But when applied, 2.4 V/cm voltage potential was able to rapidly corrode electrodes (Fig. 2) and spread iron through the soil.

Figure 2. Corroded electrodes compared to an unused electrode after 1 week of the lab experiment.

The results of these studies showed that the amount of poorly crystalline iron oxides in soil substantially increased, enabling 76-89% of arsenic to be bound to this most reactive iron fraction. Due to the corrosion of the iron electrodes, the concentration of iron and abundance of poorly crystalline iron oxides were largest close to the electrodes. Nevertheless, over 10% of arsenic was still present in the most soluble and available fraction (exchangeable), which needs to be reduced further.

Furthermore, the electrochemical treatment resulted in a decrease of the total 16-PAH concentration in soil by 56-68% during a two month-laboratory experiment. All PAH fractions in the soil and solution degraded simultaneously, but low molecular weight PAHs in soil decreased the most (on average by 84%), followed by high molecular weight PAH fractions (by 66%) and then medium molecular weight PAHs (by 55%).

The degradation of PAH was slightly higher in soil containing plants, while the uptake of arsenic into the aboveground biomass in the treated soil decreased by 71% compared to the untreated soil, coinciding with the decreased arsenic availability in soil porewater and the exchangeable soil fraction caused by the soil treatment.

The microbiological tests showed that Gammaproteobacteria were the most common bacteria in all soil samples throughout the treatment, confirming that they can thrive in highly contaminated soil. Overall, the amount of bacteria identified did not change much during the treatment.

4. DEMONSTRATION OF THE TECHNOLOGY AT PILOT FIELD-SCALE *IN SITU*

The technology has been tested in Sweden and France. In this section, pilot scale field tests implemented in Sweden at the Limmared former wood impregnation site are described in more detail.

A hot-spot with high concentrations of arsenic (>1000 mg/kg) and PAH (ca 39 g/kg) was selected from the reports of previously implemented site investigations. A plot of 30 m x 15 m (450 m^2) was used for the pilot. Iron electrodes (3.5 cm in diameter) were inserted to 2 m depth in a 5 m x 5 m electrode grid (in total 28 electrodes) and connected to an EkoGrid control unit. Four groundwater wells inside the grid were installed at 2.2-2.5 m depth for groundwater monitoring. Two wells were installed outside the treated grid for control. The total volume of treated soil was 900 m^3.

The concentrations of PAH and arsenic were measured once a month during the first year and every third month during the second year.

Concentrations of PAH rapidly decreased, but fluctuated in all wells inside the treated plot. Nevertheless, concentrations of dissolved PAH during periodic increases were smaller than the initial concentrations measured at the beginning of the experiment. An example of variations of PAH concentrations in one of the wells with very high initial values is given in Figure 3.

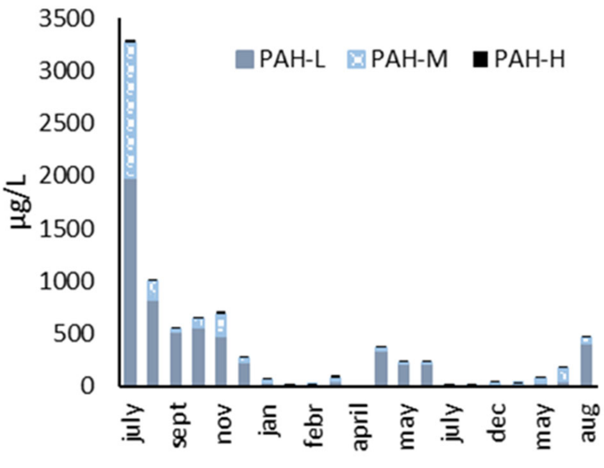


Figure 3. Variation of dissolved PAH concentrations in one of the groundwater wells inside of the treated grid.

The other wells had similar trends. The total decrease in PAH concentration in groundwater depends on when the calculations are done in time, but the validation of the remediation success can only be done by analysing soil samples, which will be done at the end of the pilot tests by the end of the second year.

Concentration of dissolved arsenic in the treated plot decreased by 74 – 98% compared with the initial concentrations.

Besides dissolved arsenic and PAH, arsenic speciation and PAH degradation intermediates – oxyPAHs – were measured during the second year. Analysis of bacterial community structure and fungus in groundwater, as well as analysis of arsenic uptake in reed canary grass planted on site is still on-going. Preliminary results indicate that the dominant arsenic species is As(V), which is less toxic than the As(III) form. Several oxyPAHs were identified (e.g. 1-indanone, acridine, carbazole), but their concentrations were close to the instrument detection limits and can be considered as negligible compared to the concentrations of PAHs.

5. APPLICATION OF THE TECHNOLOGY

The above-described ICoDeS Technology has a potential for full-scale field use, as it has been demonstrated on a small and medium scale and in ongoing pilot scale with very promising results. This technology, combining three distinct methods, can be successfully applied to treat organic and inorganic contaminants simultaneously, at any depth and in most soil types *in situ*. For the electricity to be conducted, the soil must be humid. Thus, the method works best in groundwater and soils with high water holding capacity. Furthermore, the electrodes and connecting cables can be installed in the sub-ground making the site surface completely unhindered for industrial activities during the soil treatment. The spacious electrode positioning at 5 m distance means that treatment of large areas is technically feasible and at reasonable costs. The geometry of the electrode placement is flexible and can be adjusted to the existing infrastructure and site-specific conditions. The cables collected at the end of the treatment can be reused at other sites.

Considering the climate impact of associated CO_2 emissions, calculations were made comparing the site treatment *in situ* using the developed technology with soil excavation and transportation to the nearest waste management facility that has a permit to handle hazardous waste. The consumption of electricity in the pilot test was 27-36 kWh/month, which corresponds to 6.5 – 8.6 kg CO_2/year[1] to treat ca 1440 tons of soil; which in turn corresponds to 4.5 - 6 g CO_2/t of treated soil/year. If the soil had been excavated and transported to the nearest waste management facility (ca 100 km away), the total transportation distance to take away the contaminated soil and replace it with the clean soil would correspond to a cumulative distance of 20 000 km. This would equate to ca 13 000 kg CO_2 emissions. This does not consider emissions during the soil excavation and is already substantially higher than the impact of the soil treatment *in situ*.

The developed ICoDeS Technology does not have side effects that are normally associated with traditional electrokinetic soil remediation, such as acidification of soil at the anode and alkalinization at the cathode. No acidifying chemicals are injected either as the purpose of the technology is not to transport arsenic or other metals towards electrodes, but to precipitate them in the soil for long-term immobilization.

6. CONCLUSIONS

Individual soil remediation technologies based solely on chemical or biological processes are no longer capable of providing satisfactory results for complex soil pollution problems. A smart combination of purpose-fit methods is required to effectively address these challenges. The enhanced phytoremediation approach, tested for the first time in the EiCLaR project shows that it is possible to treat mixed contaminants *in situ* by combining three remediation methods. That is, an electrical current is used to electrochemically degrade organic compounds and concurrently disperse iron amendments to immobilise arsenic in soil. Plants further enhance PAH degradation and all these methods stimulate microbiological activity, adding an additional dimension to this technology. Thus, this integrated approach provides a comprehensive solution for complex soil contamination without the need for excavation. Since clean-up methods with minimal or zero external energy input are preferred, this technology can be powered by solar energy. Using solar power as the energy source enhances the sustainability and environmental friendliness of the remediation process and enables the treatment of remote areas.

The technology is still in its early stages and requires further development to speed-up remediation and ensure long-term stability of immobilised arsenic. However, the results obtained so far on small, medium, and pilot scales indicate that it could become a competitive soil remediation method for complex contamination in challenging soil matrices, such as silty and clayey soils, and at varying depths of contamination.

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