Science of the Total Environment 918 (2024) 170656

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Immobilisation of arsenic in contaminated soil by electrokinetics in an outdoor experiment

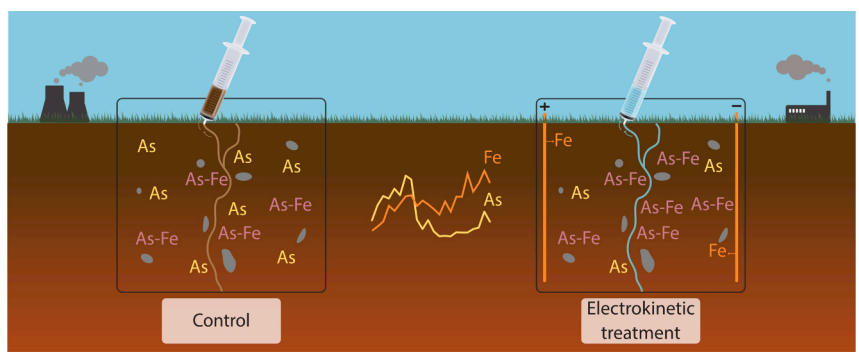
Kim Johansson *, Ivan Carabante, Jurate Kumpiene

Waste Science and Technology, Luleå Technical University, 971 87 Luleå, Sweden

HIGHLIGHTS

- Electrokinetic remediation can treat soil and porewater simultaneously *in situ*.
- Arsenic concentration in sand porewater decreased.
- Iron-bound As fraction increased after stabilisation with corroding Fe electrodes.
- Plants showed lower As uptake after electrokinetic treatment.
- Redox conditions need to be controlled to further enhance As immobilisation.

GRAPHICAL ABSTRACT



ARTICLE INFO

Guest Editor: Michael Komárek

Keywords:
Iron(oxyhydr)oxides
Stabilisation
Electrokinetic remediation
Reed canary grass
Phalaris arundinacea

ABSTRACT

Although landfilling is environmentally and economically unsustainable, it is the dominant soil remediation method in EU member states. This paper describes part of a study on mixed contaminants that investigated the stabilisation of arsenic (As) in contaminated soil in an outdoor box experiment with electrokinetic treatment (EK). The experiment was conducted in two 1 m^3 boxes, each containing a 20 cm bottom layer of sand, overlaid with 20 cm of peat. In EK, a pulsating, low-voltage current was applied with the intention of corroding the zerovalent iron (Fe) electrodes, migrating ionic Fe species, and forming secondary iron minerals, thereby immobilizing As. Porewater samples were collected over two seasons to determine whether the treatment decreased the concentration of dissolved As. Sequential extraction was performed on the soil samples to determine whether the fraction of Fe-bound As increased. Reed canary grass was planted in one of the boxes during the second season and analysed for As uptake. The results showed that the treatment decreased the porewater As concentration in sand by 50–54 %, while the concentration of Fe increased. The sequential extraction of sand showed that the fraction of As bound to poorly crystalline Fe oxides increased during this time. This treatment effect was less visible in the peat. Moreover, the exchangeable As fraction increased in both peat and sand, most likely because of the decrease in redox potential at the end of the experiment. The plants grown in treated soil accumulated less As than those grown in untreated soil, indicating that the phytoavailable As fraction decreased. This study showed that EK remediation can be a suitable *in situ* remediation technique, mostly in sand. Future research should focus on redox control to further optimise EK remediation and ensure long-term As stability in treated soils.

* Corresponding author.
E-mail addresses: kim.johansson@ltu.se (K. Johansson), ivan.carabante@ltu.se (I. Carabante), jurate.kumpiene@ltu.se (J. Kumpiene).

https://doi.org/10.1016/j.scitotenv.2024.170656
Received 28 November 2023; Received in revised form 30 January 2024; Accepted 1 February 2024
Available online 4 February 2024
0048-9697/© 2024 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

1. Introduction

One of the reasons why excavation is still the dominant remediation technique in the EU is that many decision-makers base their implementation of remediation techniques on guidelines on contaminant concentrations instead of on the risks posed by those contaminants in the soil. These risks ultimately depend on the chemical speciation of the contaminant, leading to different mobility, bioavailability, and toxicity of the contaminant (Mohan and Pittman, 2007; Smedley et al., 2002). In the EU alone, the number of contaminated sites is estimated to be approximately 2.8 million (Pérez and Rodríguez Eugenio, 2018). Transporting and landfilling all that soil would be unsustainable, both economically and environmentally. If contaminant speciation and the risks associated with the contaminants are considered, in addition to their total concentration, the development of soil remediation techniques *in situ* would lead to more sustainable remediation practices.

Creosote and chromated copper arsenate (CCA) have been commonly used as wood preservatives. Creosote is a persistent bioaccumulative and toxic/very persistent and very bioaccumulative (PBT/vPvB) substance with high concentrations of polycyclic aromatic hydrocarbons (PAH), whereas CCA contains metal(loid) contaminants. Both PAH and metal(loid)s are persistent and highly toxic in the environment (Guha Mazumder, 2008; Sakshi et al., 2019; Wares et al., 2014). Although the use of these chemicals has been restricted for wood-impregnation purposes in the EU, inappropriate industrial practices in the past have left many metal(loid)/PAH-contaminated sites to be dealt with in the present.

Zerovalent iron (ZVI) has been proposed as an effective chemical amendment that decreases the mobility of metal(loid)s in soil (Jain et al., 1999; Kumpiene et al., 2012; Kumpiene et al., 2021; Warren et al., 2003; Yeung and Gu, 2011). The rapid oxidation of ZVI in soils could lead to the formation of iron (Fe) secondary minerals, *i.e.*, iron oxyhydroxides, that can adsorb both cations (*e.g.*, Cu^{2+}) and anions (*e.g.*, AsO_4^{3-}). A study on historically contaminated soil showed that the bioavailable fractions of As can be reduced by up to 99 % in soil porewater by stabilisation with ZVI (Kumpiene et al., 2006). Amendment with ZVI can increase the amount of poorly crystalline Fe oxides in soil, which, in turn, leads to an increase in the immobilisation of arsenic (As) in soil, up to 82–99 % (Cundy et al., 2008; Komárek et al., 2013; Kumpiene et al., 2021).

Electrokinetic remediation (EK) is an environmental technique that has been studied and used since the 1980s, mostly at laboratory scale (Ren et al., 2014). Traditionally, an electric field is applied between two electrodes, generating an electroosmotic flow of metal-polluted soil porewater towards the cathode, where the contaminants are either pumped out and treated or precipitated on the electrode, which is then removed (Alshawabkeh, 2009); Virkutyte et al., 2002). This is an energy-demanding process that often requires chemical additives to improve the mobilisation of metals and prevent pH changes. Another common problem in electrochemistry is the corrosion of electrodes and the need to exchange them. However, in this study, this problem was addressed and used as an asset by choosing to introduce ZVI electrodes in the EK treatment setup with the purpose of intentionally corroding them in soil and using the corrosion products to immobilise As *in situ*. It is expected that, by applying a pulsating low-voltage current, the EK treatment could spread ionic Fe species throughout the soil profile *via* electromigration, electroosmosis, and electrophoresis (Acar et al., 1995). Since electrodes are easily inserted into the soil, this technique is intended to be applied *in situ*, without soil excavation, for immobilisation of inorganic contaminants (Chu et al., 2022; Kumpiene et al., 2023).

In this study, the effects of EK treatment on As immobilisation in soils contaminated with wood-impregnation chemicals were investigated. The aim of this study was to use EK treatment to amend soil with Fe from intentionally corroding electrodes and to evaluate the impact of this treatment on As immobilisation by following changes in the dissolved As concentration in porewater, As fractionation in soil constituents by means of sequential extractions, and phytoavailability to reed canary grass in an outdoor box experiment.

2. Materials and methods

2.1. Experimental setup and sampling

2.1.1. Soil

Sandy soil and soil rich in organic matter (hereafter referred to as sand and peat, respectively) were sampled in May 2021 from a former wood-impregnation industrial site in Limmared, Sweden. The site was previously used for the impregnation of railway sleepers, first with creosote, and later with CCA. Approximately 400 kg of each soil type was excavated from the hotspot and transported to the laboratory. Prior to the experiment, the sand and peat were homogenised separately using a rotating cement blender, and rocks and coarse particles >10 cm were removed. Two 1 m^3 boxes (polyethylene, 1 × 1 × 1 m), *Treated 1* and *Treated 2*, were filled with soil so that a 20 cm bottom layer of sand was formed at the bottom and a 20 cm layer of peat was placed on top. This design was selected to simulate the field conditions at the sampling site, where peat soil was overlaying sand soil (Fig. 1).

Soil samples (10 g) were collected by hand at three times during the experiment: at the start of the first season, at the end of the first season/beginning of the second season, and at the end of the second season. In the treatments the samples were taken from the centre of the boxes, and from the areas around each of the electrodes. In the controls, samples were taken from the centre of the containers. Samples were placed in diffusion-tight soil sampling bags and stored at 4 °C prior sequential extraction.

2.1.2. Groundwater

A polyethylene groundwater tube was installed in the middle of each box to sample the simulated groundwater and monitor the groundwater levels, which were maintained at 10 cm below the soil surface by adding the required amount of fresh tap water to the soil. Groundwater samples were collected with a high density polyethene bailer (Unoson Environmental AB) twice a week during the first season, and every second or third week during the second season. The pH (WHT pH 340/SET-1), electrical conductivity (EC) (radiometer Copenhagen PHM 95 pH/ion meter), and redox potential (Radiometer Copenhagen CDM 210 conductivity meter) of the samples were analysed immediately.

2.1.3. Porewater

Rhizon samplers were installed in each soil layer to sample the porewater. The samplers were distributed in a manner that followed the pH development and Fe distribution in the soil (Fig. 1). The porewater was extracted by creating vacuum with pulled up syringes. Sampling was performed twice a week during the first season, resulting in 22 sampling occasions. In the second season, sampling was performed once every second or third week for a total of four sampling occasions. The sampling intensity was lower during the second season due to the observed changes in the porewater concentrations during the first season.

The porewater samples were immediately analysed for pH, EC, and redox potential. The remaining samples were acidified with concentrated nitric acid and stored at 4 °C prior to element analysis by inductively coupled plasma – optical emission spectrometry (ICP-OES, PerkinElmer optima 8300, detection limits in mg L^{-1} first season; As: 0.0128, Fe: 0.004, and second season; As: 0.014, Fe: 0.003).

During the first season, it was not always possible to extract porewater from all 24 porewater samplers (pw) on all sampling occasions, probably because of temporary clogging of the pw. Consequently, no porewater was extracted from pw3 and pw23 throughout the experiment. During the second season, an additional porewater sampler was clogged (pw24) and excluded from further analyses. The samplers were not replaced to avoid soil disturbance and soil layer mixing.

2.1.4. Electrokinetic soil treatment

Two ZVI electrodes (from the local hardware store) were inserted into the soil, placed at opposite corners of the boxes, and connected to a power control unit (Ekogrid, Finland). A low pulsating voltage (3 V) with a varying pulse frequency of 500–1000 pulses/s was constantly applied throughout the experiment, and the direction of the electric direct current (DC) was switched once per week so that each electrode could interchangeably act as both the anode and cathode. The first part of the experiment (first season) was performed for 4.5 months (June–October) outdoors under natural light and temperature conditions in Luleå, Sweden, but with a controlled water supply. The treatments and controls were loosely covered with a plastic film/vapour barrier to prevent precipitation from entering the boxes while allowing airflow. The boxes were kept idle during winter.

The second part of the experiment (second season) was performed under the same conditions, but ran for 2.5 months (July–September). During the winter between the first and second seasons, Treated 2 accidentally took in some snow, which delayed the start of sampling waiting for the excess water to evaporate.

2.1.5. Plants

During the second season, reed canary grass (*Phalaris arundinacea*) was pre-cultivated indoors. Prior to planting, the seeds were placed in a refrigerator for 24 h, after which they were planted in soil in small pots. The plants were watered regularly and maintained under specific light conditions (23 W) from 7 am to 7 pm. After 40 d, the plants were placed outdoors for 72 h to acclimatise to the outdoor conditions. They were then cut to approximately 4 cm and planted in one of the boxes (hereafter called *Treated 2 + plant*) and in untreated soil (*Untreated 2 + plant*). At the end of the experiment, plant shoots were cut at approximately 4 cm from the soil surface, washed with distilled water, and dried in the dark at 22 °C for 8 months. The dried grass was subsequently milled and extracted in hydrogen peroxide and nitric acid at 195 °C for 10 min using a microwave digestion system, with three replicates from the treated soil and one replicate from the untreated soil (due to limited biomass).

2.1.6. Control

Controls were set up in two 10 L containers, *Untreated 1* and *Untreated 2*, filled with a 10 cm bottom layer of sand and a 10 cm top layer of peat without applying any electricity. In the controls, twelve Rhizon samplers (three in each soil layer) were placed to sample the porewater every other week to monitor the pH, redox potential, and EC. The remaining samples were acidified with concentrated nitric acid and stored at 4 °C prior to element analysis by ICP-OES.

2.1.7. Sequential extraction of soil

To determine the changes in As and Fe fractionation in the treated and untreated soils, sequential extraction was performed on samples collected at the beginning and end of each season from several locations, namely near the electrodes and in the middle of the boxes further away from the electrodes. Separate samples were collected from sand and

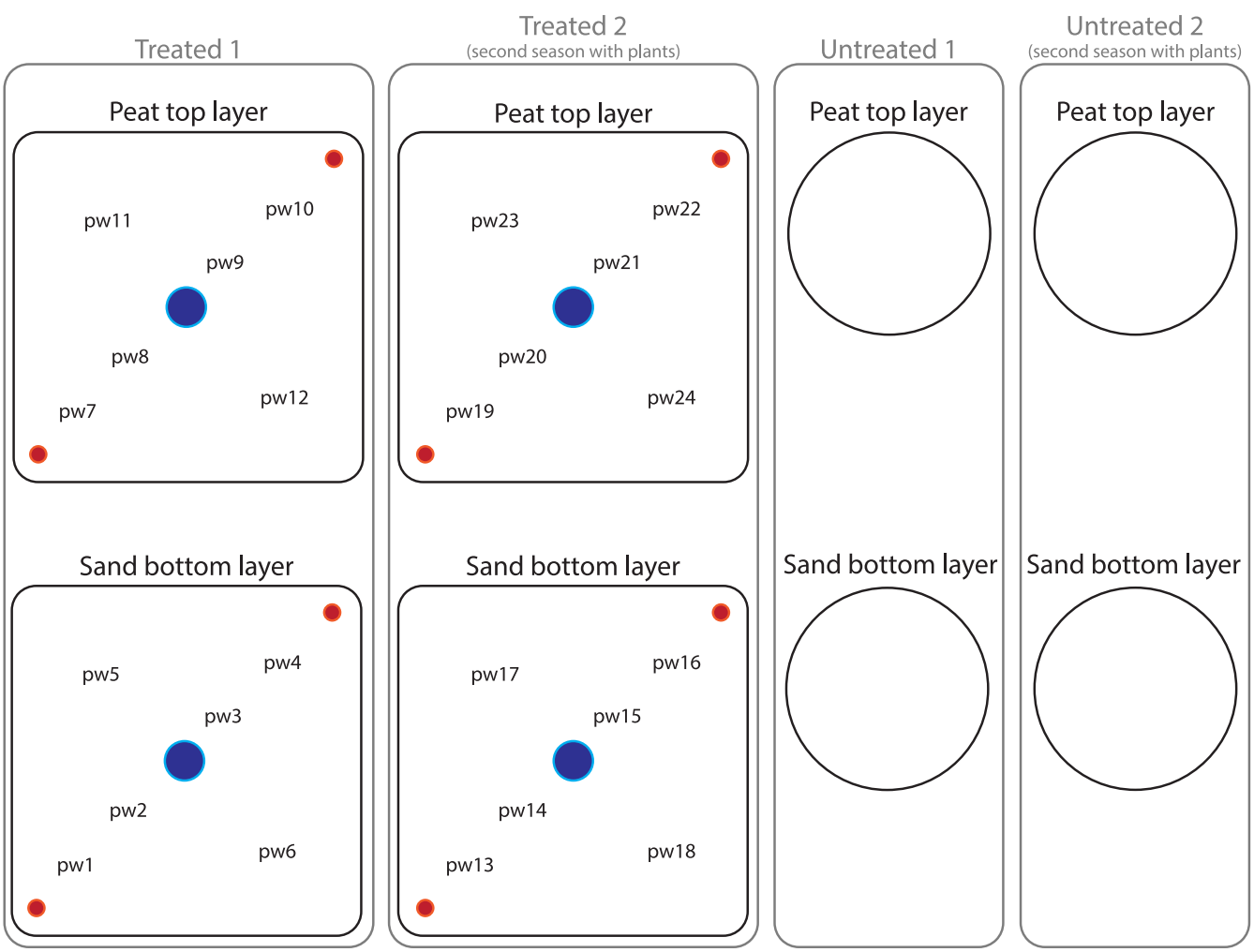


Fig. 1. Experimental setup over the two seasons and placement of the 24 porewater samplers (pw1 – pw24) in the treatments. Six porewater samplers were placed in each treated soil layer, yielding a total of twelve samplers in sand and twelve in peat, totally in the two treatments.

peat. The method described by (Kumpiene et al., 2012) was used. Six fractions were extracted: (I) exchangeable, (II) Fe(*III*)oxyhydroxide, (III) Fe(*II*)oxide, (IV) Fe—Mn oxide, (V) organic matter and secondary sulphur, and (VI) residual fractions. Extracts from all fractions were analysed with ICP-OES. The total element concentrations in sand and peat were calculated as the average sum of all fractions of the soil samples collected at the different locations in the boxes after the first season.

2.2. Statistics

IBM SPSS 28 software was used for statistical analyses. A two-sample independent *t*-test ($p < 0.05$) was performed to discriminate between sample means.

3. Results and discussion

3.1. Soil properties

The main properties of sand and peat are summarised in Table 1. Total dissolution in aqua regia showed that peat contained higher concentrations of As than sand, and both soils exceeded the Swedish guideline value for As in soils with less sensitive land use of 25 mg kg^{-1} (Swedish EPA, 2022). The peat also contained higher concentrations of Fe than the sand (Table 1).

3.2. Changes in soil solution pH and electrical conductivity

To prevent the common problem in EK remediation with acidic conditions at the anode and alkaline conditions at the cathode, the polarity was switched weekly (Chilingar et al., 1997; Saichek and Reddy, 2005) to attempt to overcome the need to use additives to prevent pH changes.

The results from the first season showed that the pH did not vary in the treatments depending on the sampling location of the pw ($p < 0.01$). This was observed for both sand and peat in both treatments and is in line with the aim of preventing a pH gradient in the soil by alternating which electrode acted as the anode and cathode (Fig. 2a and b). This was also in line with a study on EK remediation in phenol-contaminated soil, which showed that the pH remained constant over time due to polarity switching (Luo et al., 2005). In both treatments and controls, the pH remained relatively constant over time, which indicates that it was unaffected by EK.

The second season also showed that the pH did not vary in the treatments depending on the pw location in any of the soil layers ($p < 0.01$) (Fig. 2c and d). This further supports the idea that switching the polarity could have had a positive effect on achieving even pH levels in the soil. This result further indicates that switching the polarity is a successful option instead of using chemical additives for pH control. The pH remained relatively constant over time in both the treatment and controls.

The electrical conductivity of pw remained relatively constant throughout both seasons (Fig. A1a–d). The same pattern was observed in the controls, indicating that it was not affected by the treatment.

Table 1
Main properties of the two studied soils.

Soil	pH	EC, μS cm^{-1}	Organic matter[a], %	As, mg kg^{-1}	Fe, mg kg^{-1}
Sand	5.35 ± 0.07	82 ± 10	2.21 ± 0.18	150 ± 65	21,267 ± 5812
Peat	5.09 ± 0.03	409 ± 119	88.89 ± 2.07	438 ± 86	29,380 ± 6276

[a] Measured as loss on ignition at 550 °C.

3.3. Changes in soil redox conditions

Simultaneously, as the outdoor temperature decreased in the first season, the porewater redox potential decreased to negative values for most pw, and an increase in As concentration was observed. Due to these effects, the first season was divided into a "high-redox" period, taking place from sampling occasions 1 to 17, and a "low-redox" period, taking place from sampling occasions 18 to 21, and is hereafter referred to as such (Fig. 2 e and f). High redox is defined as the majority of pw having positive redox values. Low redox is defined as the majority of pw having negative values. On sampling occasion 22, the redox started to increase again, resulting in positive redox values for most pw, and was hence excluded from the "low-redox" period.

Despite attempts to control the water level in the boxes, the soil water content was heavily influenced by the outdoor temperature, meaning that, at the end of the first season when the temperature decreased, around sampling occasions 17–18, the evaporation of soil water decreased. Consequently, less water was added and the soil became saturated over longer periods.

The second season ended with plant harvesting, which occurred earlier in the fall than that in the previous year. In the second season, the redox values remained positive most of the time for most of the pw; hence, this season was not divided into high- or low-redox periods (Fig. 2g and h).

3.4. Impact of EK on As in soil porewater

During the first season, the As concentration in the pw in sand decreased with time (Fig. 3a). This was observed in both Treated 1 (50 % decrease, $p < 0.01$) and Treated 2 (54 % decrease, $p = 0.018$) samples. At the end of the experiment, the concentration of dissolved As began to increase again, probably because of a simultaneous decrease in the redox potential. The As concentrations have been shown to increase under water-saturated and reducing conditions in soil solutions (Kumpiene et al., 2009; Mitsunobu et al., 2006). This also highlights the challenge of the *in situ* stabilisation of redox-dependent metal(loid)s, such as As, and the need to maintain oxic conditions to ensure long-term stability (Kumpiene et al., 2021). Cycles of anoxic and oxic soil conditions can increase the risk of As release into soil solution (Park et al., 2022). Since the redox potential naturally fluctuates in soil over time, dependent on for example temperature, rainfall and microbial activity, the extent of As remobilisation needs to be further studied (Chari et al., 2021). Alternating redox cycles in As contaminated soil, Han et al. (2019) has observed an increased release of As to groundwater in response to repeated anoxic conditions, probably due to dissolution of Fe minerals and simultaneous microbial reduction of As (Han et al., 2019).

However, the decrease in the As concentration in peat over time was not statistically significant (Fig. 3b), which indicates that the stabilisation of As in organic soil might be more difficult than that in sandy soil. The interactions among As, Fe, and organic matter (OM) are complex and not fully understood. It is believed that soluble OM–cationic metal complexes can strongly bind to dissolved anions, where cationic metals act as bridging complexes (Lin et al., 2004; Ritter et al., 2006). At the same time, it has been suggested that OM competes with As for the sorption sites on the Fe oxide surface and hinders As sorption in the presence of dissolved OM (Kim et al., 2015; Sharma et al., 2010). Spectroscopic studies on the interactions between Fe, As, and OM in natural stream water by Sundman et al. (2015) found no clear evidence of the formation of As(V)–Fe(III)–natural OM complexes (Sundman et al., 2015). This was indicated by the coexistence of Fe(III)–OM and free As(V), even at high As (V) concentrations. These latter studies suggest that complexation between Fe(III) and OM can result in higher levels of free As(V) because Fe(III) can become unavailable for As sorption, which might be the reason for the less evident stabilisation of As in peat compared with that in sandy soil in this study.

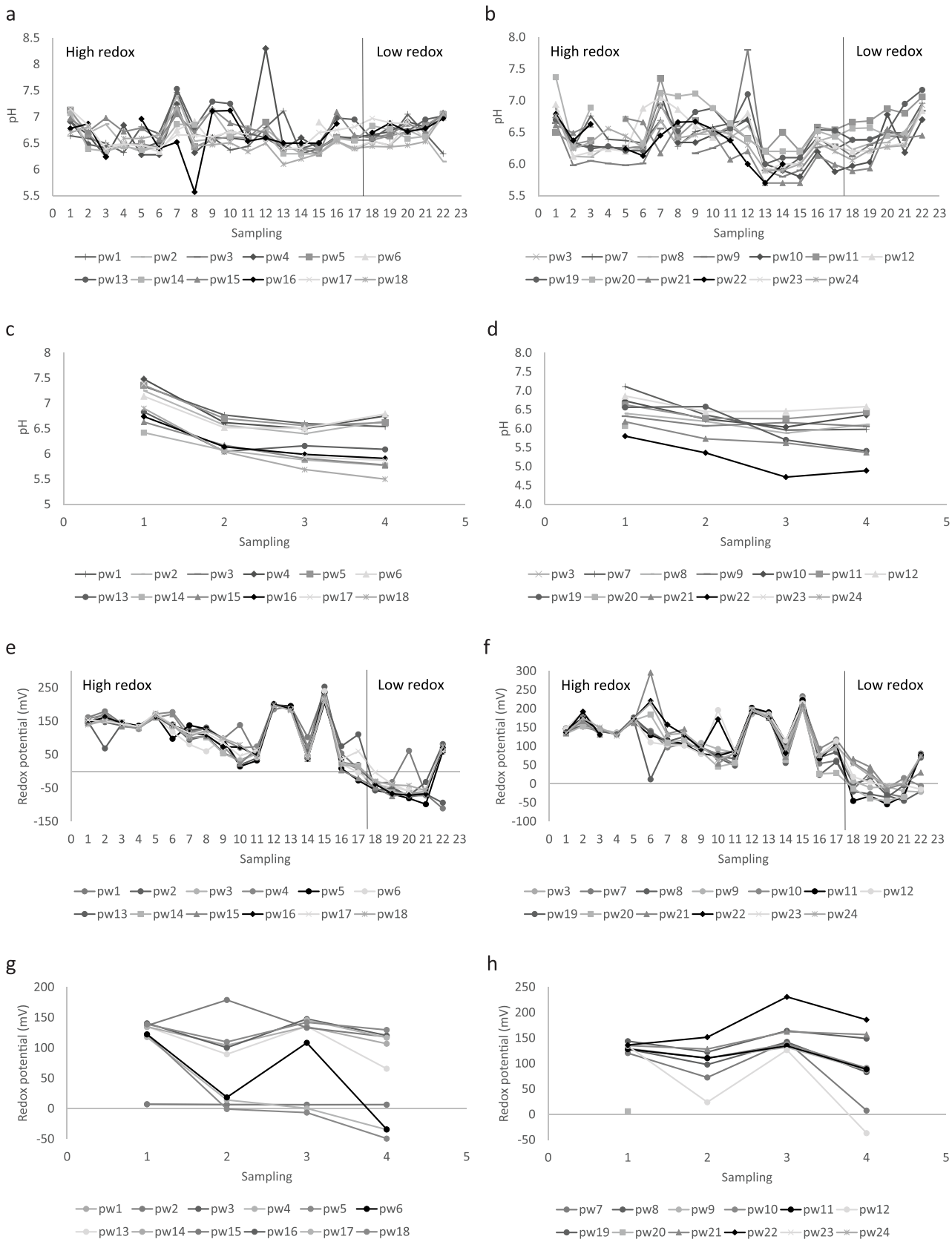


Fig. 2. Variations in pH and redox potential in porewater sampled in (a, e) sand in Treated 1 from porewater samplers pw1-pw6 and in Treated 2 from pw13-pw18 the first season, (b, f) peat in Treated 1 from pw7-pw12 and Treated 2 from pw19-pw24 the first season, (c, g) in Treated 1 from pw1-pw6 and in Treated 2 from pw13-pw18 the second, and (d, h) peat in Treated 1 from pw7-pw12 and Treated 2 from pw19-pw24 the second season.

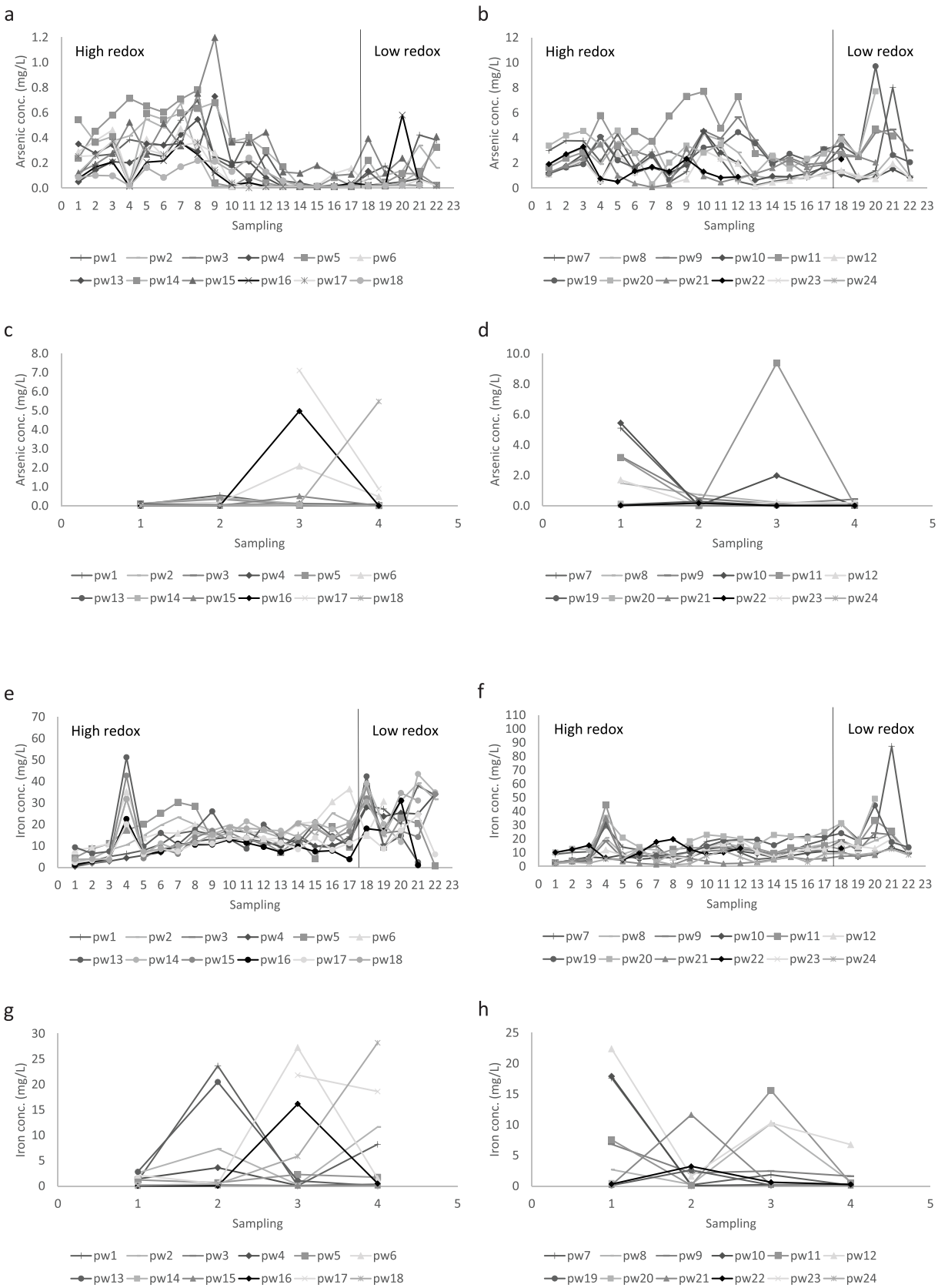


Fig. 3. Variations in arsenic and iron concentration in porewater sampled in (a, e) sand in Treated 1 from porewater samplers pw1-pw6 and in Treated 2 from pw13-pw18 the first season, (b, f) peat in Treated 1 from pw7-pw12 and Treated 2 from pw19-pw24 the first season, (c, g) in Treated 1 from pw1-pw6 and in Treated 2 from pw13-pw18 the second, and (d, h) peat in Treated 1 from pw7-pw12 and Treated 2 from pw19-pw24 the second season.

In contrast with these results, the observations during the second season were reversed; that is, the As concentration increased in sand and decreased in peat in both boxes (Treated 1: 96 % decrease, $p = 0.010$; Treated 2 + plant: 80 % decrease, $p = 0.05$) (Fig. 3c and d). This might be the outcome of the experimental design, in which peat was placed on top of sandy soil to simulate field conditions. As the boxes were left to stand over winter and faced snowmelt without any treatment, porewater had a chance to move downwards, thus affecting the As concentrations in the deeper (sand) layers. When comparing the results from the start of the first season to the end of the second season, there was an overall decrease in the As concentration in all soil layers, except for the sand in Treated 2 + plant (second season). Moreover, at the end of the second season, 55 % of the pw reached As concentrations lower than WHO guidelines for drinking water (0.01 mg L^{-1}). Before treatment, the As concentrations exceeded the guidelines at all sampling points, indicating that EK could be used to immobilise As in contaminated soil.

3.5. Impact of EK on Fe distribution in soil and As binding

The concentration of dissolved Fe in the porewater increased over time during the first season (Fig. 3e and f). This was observed for porewater in the sand in Treated 1 (90 % increase, $p = 0.0323$), sand in Treated 2 (70 % increase, $p = 0.002$), peat in Treated 1 (99 % increase, $p = 0.017$), and peat in Treated 2 (72 % increase, $p = 0.043$), which could be due to the corrosion of the electrodes, but also due to the dissolution of the indigenous Fe that was already present in soil as affected by EK treatment (Zhang et al., 2023). There was no significant difference ($p = 0.01$) in the dissolved Fe concentration close to or far from the electrodes in any of the soil layers, except for the peat in Treated 2. As the polarity of the current flow was alternated regularly and soil water was repeatedly replenished during the experiment, the soil solution and dissolved ions were able to move both horizontally (through electromigration and electroosmosis) and vertically (gravitational movement), probably leading to the observed equalisation of the dissolved Fe concentrations. During the second season, the dissolved Fe concentration increased in pw in sand but not in peat; the reason for this could be the same as that for the changes in As distribution, that is, the downward migration of the soil solution over time (Fig. 3g and h).

The distribution of Fe between the operationally defined soil fractions during the first season indicated that the fraction of poorly crystalline Fe oxides increased slightly in the sand in the centre of the box and at one of the electrodes compared with that in the untreated soil, but not in peat. Interestingly, the concentration of this Fe fraction at the opposite electrode in both soils nearly disappeared (Fig. 4b). As the current flow was supplied in the pulsating mode with varying pulse frequencies towards the cathode and anode, it is possible that this affected the precipitation of secondary Fe oxides differently at different electrodes, causing the observed differences in the accumulation of poorly crystalline Fe oxides in the soil. In contrast, the fraction of these Fe oxides increased in the vicinity of one of the electrodes during the second season in both sand treatments and in peat without plants compared with the other sampling locations and the control (Fig. 4d). It is likely that the same reason for the depletion of this fraction during the first season at one of the electrodes also caused Fe accumulation during the second season, namely the varying pulse frequencies towards different electrodes. This could have caused stronger migration of Fe towards one of the electrodes, resulting in an uneven distribution of newly formed Fe oxides. The impact of direct current with varying pulse frequencies and alternating polarity on the dissolution and precipitation of secondary Fe oxides in EK-treated soils is not fully understood and requires more detailed studies with specifically designed experiments. The Fe fractions present as the sum of poorly crystalline and crystalline Fe oxides (fractions II–IV) in treated soils were similar during both seasons, but the fraction of the residual Fe increased significantly in the second season, on average from 30 to 50 % to 67–91 % of the total soil Fe. A significant increase in the residual Fe fraction was observed in earlier studies where Fe amendments were used for As immobilisation, which was attributed to newly formed precipitates (Kumpiene et al., 2012).

The exchangeable fraction (fraction I) was not present in the untreated sand, but increased to 296–441 mg kg^{-1} after the EK-treatment. Similarly, an increase in this Fe fraction was also observed in peat (to 767–932 mg kg^{-1}). The exchangeable fraction is the most labile, but over time might recrystallize into more stable Fe oxides, by this, contributing to new sorption sites for As. Indeed, this fraction decreased during the second year, although it is not clear whether it recrystalised to other fractions or got desorbed (exchanged). The sequential extraction of As after the first season showed that, in the EK-treated sandy soil, a higher As fraction (by 58 %) was bound to Fe oxides (fractions II and III combined) compared with the control (Fig. 4a). However, this was not observed in the peat, confirming earlier reports that dissolved organic matter can prevent reactions between As and secondary Fe oxides (Kim et al., 2015).

At the end of the second season, the distribution of As among the soil fractions of the treated soils was similar to that observed during the first season, except for an increase in the organic matter-bound As fraction at several sampling locations (fraction V, Fig. 4c), the reasons for which are unclear. Usually, sorption of As to organic matter is hindered by electrostatic repulsion between negatively charged arsenates and organic molecules, but formation of ternary complexes of As-cationic metal-OM in solution were suggested to be the principle mechanisms describing the association between OM and As (Redman et al., 2002). Indeed, a significant increase in Fe concentration bound to organic matter (fraction V) was observed in the treated soils, which might have acted as a bridge for As binding. Nevertheless, as discussed earlier, Sundman et al. (2015) had raised doubts about the formation of such complexes, although their study was conducted in solutions.

A decrease in the exchangeable fraction was observed at the end of the experiment compared with the first season (on average from 13 to 21 % to 7–12 % of the total soil As). Overall, the decreased As concentration in the exchangeable soil fraction, as well as in soil porewater indicate that EK-enhanced As immobilisation in soil could have occurred. Decreased concentration of As in soil solution and the exchangeable fraction, along with the decreased plant uptake, are often used among indicators of the soil remediation success in Fe-amended soils (Moor et al., 2000; Kumpiene et al., 2006; Chen et al., 2015; Kim et al., 2016).

3.6. Effect of EK on As uptake in plants

The *P. arundinacea* harvested from control soil showed higher As concentrations (51.85 mg kg^{-1}) than grass harvested from the EK-treated soil (14.88 mg kg^{-1}), in line with the suggestion that EK treatment can reduce As mobility (Fig. 5). Uptake of As by reed canary grass in this study only reflects the effects of EK on peat because the plant roots were located in this soil layer.

Plants are often used as one of the main bioassays for the evaluation of impact of soil amendments on changes in metal(loid) bioavailability in treated soils (Vangronsveld et al., 2009; Chen et al., 2015; Kim et al., 2015). In many such studies, decreased plant uptake of As in Fe amended soils has been observed, although not always (Hartley and Lepp, 2008; An et al., 2019), indicating that other factors than reduced concentration of dissolved metal(loid)s (*e.g.* nutrient deficiency) can affect plant growth and contaminant accumulation.

4. Conclusions

An attempt to apply electrokinetic soil treatment for the immobilisation of As *in situ* showed promising results in terms of decreased dissolved, exchangeable, and phytoavailable As in the soil. During the two seasons of the outdoor experiment, the dissolved As concentration decreased in both peat samples and one sand sample, and 55 % of the

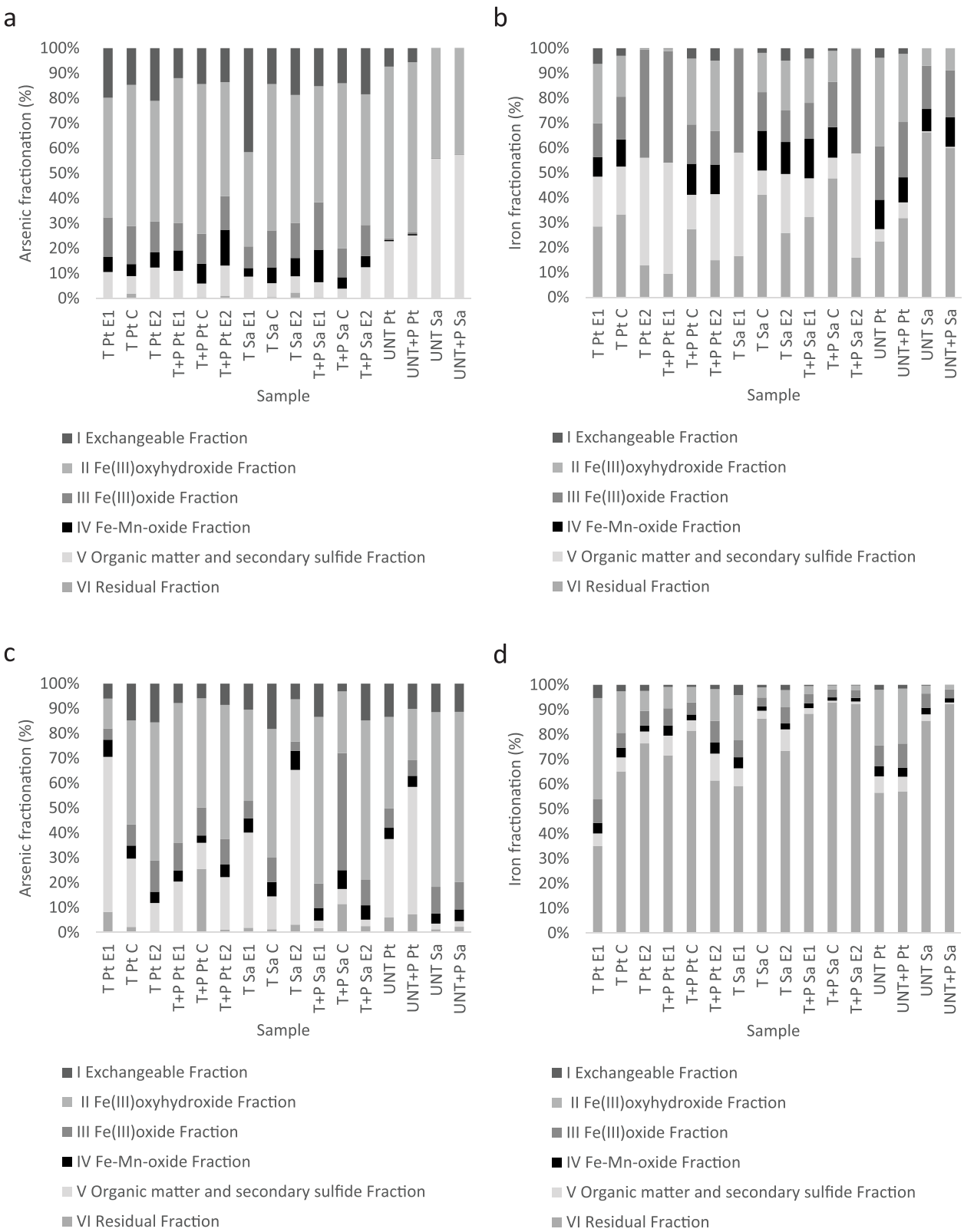


Fig. 4. Fractionation of (a) arsenic the first season (b) iron the first season (c) arsenic the second season (d) iron the second season, after EK treatment (T and T + P) compared to control (UNT and UNT + P) in peat (Pt) and sand (Sa) on samples taken from the centre of the box (C), and from the areas around the electrodes (E1 and E2).

porewater samples reached As concentrations below the WHO guidelines for drinking water (0.01 mg L^{-1}). Simultaneously, the exchangeable As concentration in all treated soils decreased over time. Reed canary grass (*Phalaris arundinacea*) transplanted into the peat soil layer in one of the experimental boxes accumulated considerably lower concentrations of As in shoots compared with the untreated soil, coinciding

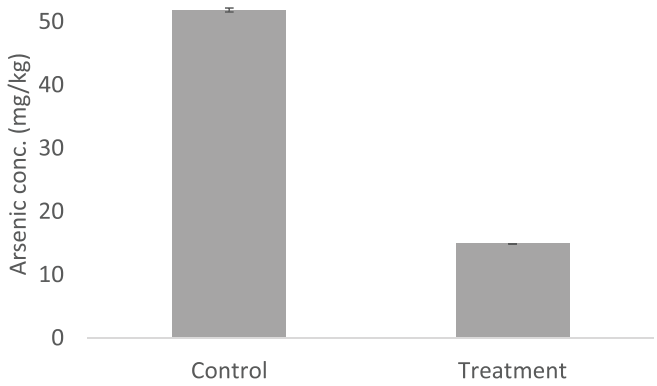


Fig. 5. Arsenic concentrations in grass harvested from EK treated soil compared to control.

with decreased As availability in soil porewater and the exchangeable soil fraction.

However, a prolonged period of soil saturation caused a redox drop and consequent remobilisation of the previously bound As in the second sandy soil sample. This demonstrates, once again, the importance of maintaining soil redox values in the positive range for the stability of bound As, and when using EK for stabilisation, further method optimisation is necessary to avoid redox fluctuations during soil treatment.

Overall, this study shows that EK treatment induced chemical changes in the soil, leading to the immobilisation of As despite the minor corrosion of Fe oxides and limited supply of additional Fe to the treated soil. Further studies are required to clarify the role of additional Fe in As immobilisation in soil *versus* the activation of indigenous Fe by electrokinetics.

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2024.170656.

CRediT authorship contribution statement

Kim Johansson: Writing – original draft, Visualization, Validation, Resources, Methodology, Investigation, Formal analysis, Conceptualization. **Ivan Carabante:** Writing – review & editing, Visualization, Validation, Supervision, Resources, Methodology, Investigation, Formal analysis, Conceptualization. **Jurate Kumpiene:** Writing – review & editing, Visualization, Validation, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Jurate Kumpiene reports financial support was provided by Horizon 2020 European Innovation Council Fast Track to Innovation. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

This project received funding from the European Union's Horizon 2020 Research and Innovation Program under Grant Agreement No. 965945. All EiCLaR partners are acknowledged for their contributions to this discussion. Ekogrid are acknowledged for their contribution to the power units. Dr. Mariusz Gusiatin and Tanise Yang are acknowledged for their assistance with sampling and monitoring.

References

Acar, Y.B., et al., 1995. Electrokinetic remediation: basics and technology status. J. Hazard. Mater. 40 (2), 117–137. https://doi.org/10.1016/0304-3894(94)00066-P.

Alshawabkeh, A.N., 2009. Electrokinetic soil remediation: challenges and opportunities. Sep. Sci. Technol. 44 (10), 2171–2187. https://doi.org/10.1080/01496390902976681.

An, J., Jeong, B., Nam, K., 2019. Evaluation of the effectiveness of in situ stabilization in the field aged arsenic-contaminated soil: Chemical extractability and biological response. J. Hazard. Mater. 367, 137–143. https://doi.org/10.1016/j.jhazmat.2018.12.050.

Chari, N.R., et al., 2021. Interactive effects of temperature and redox on soil carbon and iron cycling. Soil Biol. Biochem. 157 (February), 108235 https://doi.org/10.1016/j.soilbio.2021.108235.

Chen, X.-P., Zhou, J., Lei, Y., He, C., Liu, X., Chen, Z., Bao, P., 2015. The fate of arsenic in contaminated paddy soil with gypsum and ferrihydrite amendments, pp. 48–62. https://doi.org/10.1504/IJEP.2014.067675.

Chilingar, G.V., et al., 1997. Electrobioremediation of soils contaminated with hydrocarbons and metals: progress report. Energy Sources 19 (2), 129–146. https://doi.org/10.1080/00908319708908838.

Chu, L., et al., 2022. A novel electrokinetic remediation with in-situ generation of H2O2 for soil PAHs removal. J. Hazard. Mater. 428 (71), 128273 https://doi.org/10.1016/j.jhazmat.2022.128273.

Cundy, A.B., Hopkinson, L., Whitby, R.L.D., 2008. Use of iron-based technologies in contaminated land and groundwater remediation: A review. Sci. Total Environ. 400 (1–3), 42–51. https://doi.org/10.1016/j.scitotenv.2008.07.002.

Guha Mazumder, D.N., 2008. Chronic arsenic toxicity & human health. Indian J. Med. Res. 128 (4), 436–447.

Han, Y.S., et al., 2019. Redox transformation of soil minerals and arsenic in arsenic-contaminated soil under cycling redox conditions. J. Hazard. Mater. 378, 120745 https://doi.org/10.1016/j.jhazmat.2019.120745.

Hartley, W., Lepp, N.W., 2008. Effect of in situ soil amendments on arsenic uptake in successive harvests of ryegrass (Lolium perenne cv Elka) grown in amended As-polluted soils. Environ. Pollut. 156 (3), 1030–1040. https://doi.org/10.1016/j.envpol.2008.04.024.

Jain, A., Raven, K.P., Loeppert, R.H., 1999. Arsenite and arsenate adsorption on ferrihydrite: surface charge reduction and net OH- release stoichiometry. Environ. Sci. Technol. 33 (8), 1179–1184. https://doi.org/10.1021/es980722e.

Kim, E.J., Hwang, B.R., Baek, K., 2015. Effects of natural organic matter on the coprecipitation of arsenic with iron. Environ. Geochem. Health 37 (6), 1029–1039. https://doi.org/10.1007/s10653-015-9692-1.

Komárek, M., Vaněk, A., Ettler, V., 2013. Chemical stabilization of metals and arsenic in contaminated soils using oxides - a review. Environ. Pollut. 172, 9–22. https://doi.org/10.1016/j.envpol.2012.07.045.

Kumpiene, J., et al., 2006. Assessment of zerovalent iron for stabilization of chromium, copper, and arsenic in soil. Environ. Pollut. 144 (1), 62–69. https://doi.org/10.1016/j.envpol.2006.01.010.

Kumpiene, J., et al., 2009. Impact of water saturation level on arsenic and metal mobility in the Fe-amended soil. Chemosphere 74 (2), 206–215. https://doi.org/10.1016/j.chemosphere.2008.09.068.

Kumpiene, J., Fitts, J.P., Mench, M., 2012. Arsenic fractionation in mine spoils 10 years after aided phytostabilization. Environ. Pollut. 166, 82–88. https://doi.org/10.1016/j.envpol.2012.02.016.

Kumpiene, J., et al., 2021. LONG-TERM stability of arsenic in iron amended contaminated soil. Environ. Pollut. 269, 116017 https://doi.org/10.1016/j.envpol.2020.116017.

Kumpiene, J., et al., 2023. Arsenic immobilisation in soil using electricity-induced spreading of iron in situ. J. Environ. Manag. 325 (June 2022) https://doi.org/10.1016/j.jenvman.2022.116467.

Lin, H.T., Wang, M.C., Li, G.C., 2004. Complexation of arsenate with humic substance in water extract of compost. Chemosphere 56 (11), 1105–1112. https://doi.org/10.1016/j.chemosphere.2004.05.018.

Luo, Q., et al., 2005. The use of non-uniform electrokinetics to enhance in situ bioremediation of phenol-contaminated soil. J. Hazard. Mater. 121 (1–3), 187–194. https://doi.org/10.1016/j.jhazmat.2005.02.007.

Mitsunobu, S., Harada, T., Takahashi, Y., 2006. Comparison of antimony behavior with that of arsenic under various soil redox conditions. Environ. Sci. Technol. 40 (23), 7270–7276. https://doi.org/10.1021/es060694x.

Mohan, D., Pittman, C.U., 2007. Arsenic removal from water/wastewater using adsorbents-a critical review. J. Hazard. Mater. 142 (1–2), 1–53. https://doi.org/10.1016/j.jhazmat.2007.01.006.

Park, S., et al., 2022. Effect of organic substrate and Fe oxides transformation on the mobility of arsenic by biotic reductive dissolution under repetitive redox conditions. Chemosphere 305 (January), 135431. https://doi.org/10.1016/j.chemosphere.2022.135431.

Pérez, A.P., Rodríguez Eugenio, N., 2018. Status of Local Soil Contamination in Europe - Revision of the Indicator "Progress in the Management Contaminated Sites in Europe", Eur 29124 En. https://doi.org/10.2760/093804.

Ren, L., et al., 2014. Enhanced electrokinetic technologies with oxidization-reduction for organically-contaminated soil remediation. Chem. Eng. J. 247, 111–124. https://doi.org/10.1016/j.cej.2014.02.107.

Ritter, K., et al., 2006. Evidence for the aquatic binding of arsenate by natural organic matter-suspended Fe(III). Environ. Sci. Technol. 40 (17), 5380–5387. https://doi.org/10.1021/es0519334.

Saichek, R.E., Reddy, K.R., 2005. Electrokinetically enhanced remediation of hydrophobic organic compounds in soils: a review. Crit. Rev. Environ. Sci. Technol. 35 (2), 115–192. https://doi.org/10.1080/10643380590900237.

Sakshi, Singh, S.K., Haritash, A.K., 2019. Polycyclic aromatic hydrocarbons: soil pollution and remediation. Int. J. Environ. Sci. Technol. 16 (10), 6489–6512. https://doi.org/10.1007/s13762-019-02414-3.

Sharma, P., Ofner, J., Kappler, A., 2010. Formation of binary and ternary colloids and dissolved complexes of organic matter, Fe and As. Environ. Sci. Technol. 44 (12), 4479–4485. https://doi.org/10.1021/es100066s.

Smedley, P.L., et al., 2002. Hydrogeochemistry of arsenic and other inorganic constituents in groundwaters from La Pampa, Argentina. Appl. Geochem. 17 (3), 259–284. https://doi.org/10.1016/S0883-2927(01)00082-8.

Sundman, A., Karlsson, T., Persson, P., 2015. Reactivity of Fe from a natural stream water towards As(V). Appl. Geochem. 61, 185–191. https://doi.org/10.1016/j.apgeochem.2015.05.023.

Vangronsveld, J., Herzig, R., Weyens, N., Boulet, J., Adriaensen, K., Ruttens, A., Thewys, T., Vassilev, A., Meers, E., Nehnevajova, E., van der Lelie, D., Mench, M., 2009. Phytoremediation of contaminated soils and groundwater: lessons from the field. Environ. Sci. Pollut. Res. Int. 16 (7), 765–794. https://doi.org/10.1007/s11356-009-0213-6.

Virkutyte, J., Sillanpää, M., Latostenmaa, P., 2002. Electrokinetic soil remediation - critical overview. Sci. Total Environ. 289 (1–3), 97–121. https://doi.org/10.1016/S0048-9697(01)01027-0.

Wares, M., et al., 2014. Environmentally persistant toxicant arsenic affects uterus grossly and histologically. Bangladesh Journal of Veterinary Medicine 11 (1), 61–68. https://doi.org/10.3329/bjvm.v11i1.13175.

Warren, G.P., et al., 2003. Field trials to assess the uptake of arsenic by vegetables from contaminated soils and soil remediation with iron oxides. Sci. Total Environ. 311 (1–3), 19–33. https://doi.org/10.1016/S0048-9697(03)00096-2.

Yeung, A.T., Gu, Y.Y., 2011. A review on techniques to enhance electrochemical remediation of contaminated soils. J. Hazard. Mater. 195, 11–29. https://doi.org/10.1016/J.JHAZMAT.2011.08.047.

Zhang, C., et al., 2023. Effect of biogas slurry and sucrose addition on electrokinetic removal of arsenic from paddy soil. Int. J. Environ. Sci. Technol. 20 (1), 703–714. https://doi.org/10.1007/s13762-022-04006-0.