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Influence of electrode placement for mobilising and removing metals during electrodynamic remediation of metals from shooting range soil

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Abstract

Electrodialytic remediation was applied to a shooting range soil to investigate the influence of electrode placement on the removal and binding of metals during the treatment. The set-up was based on a 2-compartment cell, in which the cathode was separated from the soil by a cation exchange membrane and the anode was placed directly in the soil, thereby introducing protons and oxygen directly in the soil. Mobilisation of metals from less available fractions (oxidisable and residual) in the soil occurred, due to oxidation/dissolution of insoluble/soluble organic matter and possibly metal oxides in the residual fraction.

The transport via electromigration out of the soil and/or re-precipitation in other fractions of the soil (oxidisable, reducible, exchangeable) depended on the metal. More than 30% of the initial content of Mn, Cd, Cu, Pb and Zn and less than 20% of the initial content of Al, Fe, K, Mg, As, Cr and Ni was transported out of the soil. By decreasing the distance between the

electrodes from 3.0 to 1.5 cm, the removal of the targeted metal for remediation, Pb, was improved by more than 200%, from 14 to 31%. A similar removal could be achieved in experiments with long distance between electrodes (3.0 cm) by increasing the current intensity from 4 to 10 mA and/or the remediation time from 7 to 35 d. The experiments showed that the design and optimisation of electrodialytic remediation depends on the targeted metal and metal partitioning.

Keywords: Electrokinetic remediation, heavy metals, shooting range soil, metal fractionation

1. Introduction

The in-situ remediation of polluted fine-grained soils remains a challenge due to the low hydraulic conductivity. Electrokinetics has for the past 30 y been recognized to deal with this specific challenge along with the site-specific conditions related to local geochemical processes, pollutant composition and concentration (Virkutyte et al., 2002; Alshawabkeh, 2009). The principle of electrokinetic remediation is to apply a DC electric field of low intensity to the polluted soil, thereby forming an acidic front at the anode and an alkaline front at the cathode due to electrolysis reactions at the electrodes. The acidic front prevails, desorbing metals along its path towards the cathode. Electromigration has been recognized as the most important transport pathway of metals in electrokinetic remediation and charged metals and complexes are transported to the electrode of opposite charge (Acar and Alshawabkeh, 1993). In the zone between the acidic and alkaline fronts, precipitation of metals occurs. Accordingly some early optimization efforts to increase the removal of metals were related to preventing the alkaline

front from forming, for instance by adding agents to the catholyte to neutralize hydroxyl ions produced at the cathode (Puppala et al., 1997; Zhou et al., 2004, 2005), or by using ion exchange membranes (electrodialytic remediation) (Hansen et al., 1997). By applying ion exchange membranes instead of passive membranes, the transport of ions between the electrolytes/electrodes and the soil matrix can be controlled. In the traditional 3- compartment set-up, ion exchange membranes have been applied to prevent protons from the anode and hydroxyl ions from the cathode from entering the soil matrix (Ottosen et al., 1997). Water splitting at ion-exchange membranes occur at a limiting current at which there are not enough ions in the immediate vicinity of the membranes to carry the current. Due to the negative charge of clay, there is an abundance of cations compared to anions in soils and for this reason, depletion of anions adjacent to the anion-exchange membrane will occur at a lower current than depletion of cations at the cation-exchange membrane. The limiting current density depends on the membrane and solution properties. In electrodialytic remediation the limiting current has been exploited to ensure acidification of the soil, by water splitting at the anion exchange membrane (Ottosen et al., 2000), adjacent to the anode, and by proton leakage from the cation exchange membrane (Nystroem et al., 2005).

In recent years, optimisation efforts in electrodialytic remediation have included the development of the 2-compartment cell design, in which the anode is placed directly in the soil compartment, introducing protons directly in the compartment. A cation exchange membrane separating the soil- and cathode compartment prevents hydroxyl ions produced at the cathode from entering the soil (Fig. 1a) (Ebberts et al., 2015). In comparison with the traditional 3-compartment cell design, faster acidification and energy efficiency are among the advantages

observed in the 2-compartment cell design (Ebberts et al., 2015; Pedersen et al., 2015b). In addition, it has been speculated whether metals bound in organic matter are more readily released by oxidation in the 2-compartment cell due to the introduction of oxygen from the electrolysis reaction (Pedersen et al., 2015a). The 2-compartment cell has been tested in a stirred set-up, but has yet to be tested in a stationary set-up. The latter is relevant for in-situ remediation when minimal physical disturbance to the land at a given site is desirable, providing that the site conditions allow time and space for the remediation.

In previous stationary electrokinetic set-ups, the anode has been separated from the soil compartment and the influence of placing the anode directly in the soil on the metal mobilisation has not yet been tested. Metal speciation has previously been found to affect the extent to which metals desorb from the soil matrix under the influence of an electric field (Kim and Kim, 2001; Suèr et al., 2003; Zhou et al., 2005; Jensen et al., 2007), the effect of introducing oxygen directly into the soil via electrolysis reactions on the anode, has however not been investigated.

In this study, lab-scale experiments were performed to investigate the influence of the placement of electrode, on the mobilisation of metals near the anode as well as the perpendicular distance from the anode was studied and related to important variables in the electrokinetic remediation process, i.e. current density and remediation time. This also included an assessment of the influence on metal fractionation before and after the electrodialytic treatment. To obtain an understanding of the changes in the binding of metals in the soil, environmental priority metals as well as selected trace elements were included.

2. Methods and materials

2.1 Soil

The soil used in this study was sampled from the top 10 cm of the earthen backstop from a former military shooting range in Lygna, Norway. Prior to analysis and electrochemical experiments, the soil was sieved and particles larger than 4 mm were separated and disposed of.

The soil characteristics have been analysed in a previous study (Pedersen et al., 2018) and are summarised in table 1. The concentrations of the priority metals (As, Cd, Cr, Cu, Ni, Pb and Zn) were compared to the Norwegian quality criteria for soil of good environmental quality (Class 2). The only metal exceeding the criteria was Pb with a concentration in the range of Norwegian quality class 4 soil (300-700 mg kg⁻¹ of Pb). Quality Class 4 soils are characterised as 'poor environmental quality', with potential adverse effects on human health and risk of dispersion into the environment.

Table 1

2.2 Analysis

Metal concentrations (Al, Fe, K, Mg, Mn, As, Cd, Cr, Cu, Ni, Pb, Zn) were measured before and after the electrochemical remediation by Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-OES) after digestion (Norwegian standard NS4770). The sampled soil was dried at 105°C and crushed. 1.0 g of the soil and HNO₃ (9 M, 20 mL) were autoclaved (200 kPa, 120 °C, 30 min). Solid particles were subsequently removed by vacuum filtration through a 0.45 µm filter and the liquid was diluted to 100mL. Triple determination were made.

Sequential extraction was made in four steps based on the improvement of the three-step method (Rauret et al., 1999) described by Standards, Measurements and Testing Program of

the European Union. Air-dried soil (0.5 g) was first extracted with acetic acid (0.11 M, 20 mL, pH3) for 16 h; secondly with hydroxylammonium chloride (0.1 M, 20 mL; pH2) for 16 h; thirdly with hydrogen peroxide (8.8 M, 5 mL) for 1 h, followed by extraction at 85 °C for 1 h, evaporation of liquid at 85°C, and subsequent extraction of the cooled solid fraction with ammonium acetate (1 M, 25 mL, pH 2) for 16 h; and fourthly the remaining solid particles were analysed for metal content after digestion. Liquids were measured for metals by ICP-OES. Triple determination was made.

2.3 Electrodialytic remediation

2.3.1 Electrodialytic cell design

The set-up and principles of the 2-compartment electrodialytic cell used in this study is illustrated in fig. 1. The cell design consisted of an electrolyte compartment (catholyte) and a compartment containing the soil. The cell compartments were manufactured from Plexiglas® and the dimensions were: length of electrolyte compartment 3.5 cm; length of soil compartment 1.5 or 3.0 cm; inner diameter of all compartments 8 cm. Ionics supplied the cation exchange membrane (CR67 HUY N12116B). The catholyte was NaNO₃ (0.01 M) adjusted to pH 2 by HNO₃ (5 M). The catholyte (500 mL) was circulated (Pan World pumps) through a 500 mL glass bottle at flow rates of 30 mL min⁻¹. Circulation of the catholyte allows for the removal of gasses generated at the electrode, ensures low polarization at the electrode and minimizes concentration gradients (Sun et al., 2012). Platinum coated titanium electrode was used as a cathode, a titanium coated mesh (height 4 cm; width 8 cm) was used as anode and a power supply (Hewlett Packard E3612A) maintained a constant DC current.

Fig. 1

After the electrodialytic experiments, the soil was cut longitudinal into three slices (Fig. 1b). Slice 1 included the top section of the cell, not in direct contact with the anode (25% of the total amount of soil). Slice 2 included the middle part of the cell, in contact with the anode mesh in the left side of the cell (50% of the total amount of soil). Slice 3 included the bottom section of the cell, not in direct contact with the anode (25% of the total amount of soil). Soil from each slice was homogenised by the use of a mortar. Subsequently soil was sampled for total metal concentration analysis by ICP-OES and sequential extraction analysis (section 2.2). The membrane and electrodes were rinsed in HNO_3 (5M) overnight and the heavy metal concentrations in the rinsing liquids as well as in the catholyte were measured by ICP-OES.

2.3.2 Electrodialytic experiments

The variables tested were distance between electrodes, current density and remediation time. The distance between the electrodes was measured as the distance between the cation exchange membrane and the anode mesh (i.e. the length of the soil compartment). The objective of the study was to investigate the influence of the anode placement, with the focus of analysing effects on the metal partitioning, a short distance between the electrodes was chosen (1.5/3.0 cm). The experimental settings are given in table 2. The removal percentages of metals were calculated as the fraction of metal removed compared to the total amount of metal at the end of the experiments. The calculation of metals removed were based on the metal concentrations in the rinsing liquids after the electrodialytic experiments (cathode, catholyte and membrane). The power consumption in Wh (E) was calculated as:

$$\int_{t=0}^t E = VI dt$$

where V is the voltage between the electrodes (V), I is the current (A) and t is the remediation time (h).

3. Results and discussion

3.1 Influence of experimental settings on the removal of metals

Pb is the primary component in bullets (ca. 90%) and co-contaminants due to shooting range activities include As, Cd, Cu, Ni, Sb and Zn (Sorvari, 2011; Sanderson et al., 2012; Seshadri et al., 2017). Metallic fragments from bullets were not observed in the soil from the shooting range and the low standard deviations of analysed potential pollutants (As, Cd, Cu, Pb and Zn) confirmed this observation. The concentrations of As, Cd, Cu, Ni and Zn were low in relation to the soil quality criteria, but may be elevated compared to the natural background conditions. Anthropogenic metal sources can change the metal partitioning in the soil (Wuana and Okieimen, 2011). Based on the pollutant sources at the site, the metal concentrations and partitioning of Al, Fe, K, Mg, Mn and Cr are not expected to be impacted by the previous activities.

The percentage of metals removed after the electrodialytic treatment depended on the metal. The lowest percentages removed (<5%) were As, Cr and Fe and the highest observed removal (>40%) was Cd and Cu (table 2). This is in line with previous findings showing that As and Cr are less mobile than Cd and Cu under the influence of an electric field (Hansen et al., 1997; Ottosen et al., 2009; Lu et al., 2012; Yang et al., 2014). Within the experimental space studied, the

influence of variables on the removal percentages varied with the metal (table 2). For most of the metals, changing the experimental settings did not significantly influence the removal percentage. Considerably deviating from this trend, a higher current density increased the removal of Cu and Pb by 270% and 220% (exp. 1 and exp. 3). Increasing the distance between the electrodes from 1.5 to 3.0 cm halved the removal of Cu and Pb (exp. 1 and 2). Similar removal of Cu and Pb was observed in exp. 3 (low current density, short distance between the electrodes), and exp. 2 (high current density, long distance between the electrodes). Likewise, by increasing the remediation time from 7 to 35 d it was possible to increase removal percentages.

The experimental settings did not influence the final pH levels, and could be due to a high buffer capacity related to Al/Fe oxides/hydroxides and high content of organic matter in the soil at this pH level (Wang et al., 2015; Wang et al., 2017). The reason, that the metals, except Cu and Pb, had similar removal percentages in all experiments could be related to the same final pH levels (table 2). The deviating trend for Cu and Pb suggests a difference in binding pattern and possibly indication of anthropogenic impact. The solid-solution partitioning (K_d) of metals in soils vary with metal concentration, e.g. K_d for Pb increases while K_d for Zn decreases with increasing anthropogenic impact (Sauvé et al., 2000).

Table 2

The consumption of energy per mass of soil was lowest in exp. 2 (table 2). Consumption of energy per mass of soil increased with higher current density (exp. 1 vs. exp. 3) and with a longer remediation time (exp. 2 vs. exp. 4). Doubling the amount of soil to be remediated did not increase the energy consumption per mass of soil (exp. 1 vs. exp. 2). For the targeted metal

for remediation, Pb (table 1), highest removal was in exp. 1 and 4. Despite the higher consumption of energy, the energy required to remove Pb was however lowest in exp. 1 and exp. 4. If the design of the electrodialytic removal of Pb includes energy consumption, optimal conditions (high removal, low energy consumption) can be achieved by either applying short distance between electrodes or applying high current density and remediation time in designs with long distance between electrodes.

3.2 Removal of metals in different fractions in soil

Electrodialytic treatment and experimental settings influenced the metal fractionation of the potential pollutant metals. The naturally occurring metals (Al, Fe, K, Mg, Mn, Cr and Ni) displayed some differences in metal fractionation after the electrodialytic treatment (Fig. 2). The fractionation of Al, Fe and Mg was similar in exp. 1-3, with some differences in exp.4 indicating that a long remediation time (35 d) at high current (10 mA) changed the mobilisation in the studied soil. For K, the removal was similar in the four experiments, while the biggest alteration to the metal binding was observed in exp. 2 and exp. 4 with higher quantities of the metal mobilised from the residual fraction and precipitating in the more available fractions of the soil.

The removal of Mn was not influenced by the experimental design, the electrodialytic treatment was however observed to influence metal fractionation. The partitioning in the soil after all electrodialytic treatments was however similar, indicating that the experimental settings did not influence the removal or mobilisation of Mn in the soil. The amount of Mn bound in the residual fraction was reduced by a third and the exchangeable fraction halved during the treatment, suggesting that Mn released from the residual fraction, either from

insoluble organic matter or well-crystalline oxides, was largely transported by electromigration out of the soil. Less than 1% of Cr was removed from the soil during the electrodynamic remediation, it was however observed that 7-17% of the Cr originally bound in the residual fraction was transferred to more available fractions, especially the oxidisable fraction. For both Cr and Mn, re-adsorption from the residual fraction of the soil could be related to the high content of organic matter in the soil. Previous studies have found that organic acids increase metal mobility at low pH (<4) (Renella et al., 2004; Wang et al., 2013; Vítková et al., 2015) and could have desorbed Cr and Mn bound in insoluble organic matter or stable minerals, present in the residual fraction (Tessier et al., 1979). Depending on the metal mobility and affinity to compounds in the soil, the metals could be transported through the soil with limited re-precipitation, as Mn, or re-precipitated, as was observed for Cr in the oxidisable fraction. Humic acids are known to form stable Cr complexes and is insoluble, immobile and unreactive in the pH ranges 2.7-4.5, while other organic acids such as citric acid and fulvic acid form soluble Cr complexes (Kotaś and Stasicka, 2000).

Fig. 2

For Cd, the fractionation was similar in exp. 1-3, with some differences in exp. 4, indicating that a long remediation time at a high current, to a higher degree influenced the metal fractionation. Less Cd was bound in the oxidisable fraction in exp. 4 suggesting higher oxidation of Cd-organic complexes, increasing the desorption of Cd from the soil (Zhao et al., 2014).

The electrodialytic remediation influenced the removal and fractionation of Cu in the soil. The original partitioning of 90% of the Cu in the oxidisable and residual fractions was reduced to 45-70% during the electrodialytic treatments. This is an indication of oxidation of soluble as well as insoluble organic matter releasing Cu in the process, and potential oxidation of Cu minerals in the residual fraction. The Cu sulphides chalcopyrite and bornite are for instance found in the residual rather than oxidisable fraction of the sequential extraction regime (Dold, 2003). Some of the released Cu from insoluble organic matter was likely re-precipitated in the oxidisable fraction due to the high affinity of Cu to organic matter (Kinniburgh et al., 1999), and adsorbed to clay minerals in the exchangeable fraction.

After the electrodialytic remediation experiments, the initial content of Pb in the oxidisable and residual fractions was reduced from 60% to 22-30%. Release of Pb could take place by oxidation of soluble and insoluble organic matter. Due to the high affinity of Pb to organic matter (Eggleton and Thomas, 2004) some of the Pb in solution may have re-precipitated in the oxidisable fraction. More than 30% of the Pb was bound in the reducible fraction after the experiments, indicating that substantial reduction of Mn/Fe oxides during the treatment did not occur and that some of the released Pb from the oxidisable and residual fractions may have re-precipitated in the reducible fraction. Pb has high affinity to be adsorbed to Fe, Mn and Al oxides, and co-precipitated with Fe and Mn oxides (Bradl, 2004; Favas et al., 2011).

The reduction of Zn bound in the oxidisable and residual fractions was not as pronounced as observed for Cu and Pb (Fig. 2). Most of the removal observed during the electrodialytic remediation originated from the residual and oxidisable fractions indicating oxidation of Zn-organic complexes and potential dissolution of stable Zn minerals. In exp. 4 re-precipitation of Zn occurred in the exchangeable fraction and could be related to Zn in acidic medium adsorbing to clay minerals by cation exchange processes (Fotovat and Naidu, 1998). Previous studies have shown that electrokinetic remediation of soil and sediments enhances natural weathering processes (Kirkelund et al., 2010). Electrodialytic treatment has also been shown to remove naturally occurring metals in soil and sediment, the removal percentages depend on the mobility of the metal and how the metal is bound in the soil minerals (Jensen et al., 2006; Pedersen et al., 2016). In this study, low removal percentages (<15%) as well as low influence of experimental settings on metal fractionation was observed for most of the naturally occurring metals Al, Fe, K, Mg, Cr, Ni. An exception to this was Mn, which had higher removal percentages (31-38%) and metal fractionation changed after electrodialytic treatment. This indicates that Mn desorbed/dissolved and that the electrodialytic conditions increased the mobility of Mn compared to the other trace metals. This observation is in line with other studies showing that under the influence of an electric field, Mn is mobilised to a higher degree than other trace metals (Jensen et al., 2006; Pedersen et al., 2017). The metals Cd, Cu, Pb and Zn had the highest removal percentages (table 2). The initial concentrations of Cd, Cu and Zn (table 1) were below levels considered as pollution. However, since the metals constitute part of bullets, the concentrations may be elevated compared to the natural background concentrations at the site. The initial metal fractionation of Cd, Cu and

Zn was comparable to that reported in literature (Tipping et al., 2003). Metal fractionation of Cd and Zn was not significantly affected by the experimental settings indicating that pH rather than the electrodialytic conditions controlled the mobilisation in the studied experimental space. The metal fractionation of Cu was affected by the experimental settings indicating that electrodialytic conditions, e.g. acidification and redox affected the mobilisation. Based on the observed trends for Cd, Cu and Zn, it is not possible to assess whether the initial concentrations are background concentrations or affected by the shooting range activities. The high initial concentration of Pb was a clear indication of anthropogenic impact.

In this study, most of the removal of Cu and Pb originated from the labile fractions of the soil (oxidisable and residual). This could be due to the electrodialytic cell design and the soil characteristics. As an effect of placing the anode directly in the soil, oxidation of insoluble and soluble organic compounds could occur, thereby increasing the mobilisation of Cu and Pb. The soil characteristics (high content of clay/silt and organic matter) may have enhanced the re-precipitation of released metals, thereby preventing the electromigration of metals out of the soil. This is in line with previous studies in which metals concentrations in the exchangeable fraction increased during electrokinetic remediation, due to re-precipitation of metals from dissolution of organic matter and minerals (Ribeiro and Mexia, 1997; Peppicelli et al., 2018).

3.3 Influence of anode placement

To evaluate the effect of the anode placement, the soil was sliced in three at the end of the experiments. In the traditional 3-compartment set-up it was shown that the horizontal transport of protons and metals through the soil during electrodialysis decreases with the horizontal distance from the anode (Hansen et al., 1997). In this study, the anode was,

however, placed directly in the soil and instead of the usual practice of slicing the soil vertically, perpendicularly to the electric field to assess the transport across the cell, the soil was sliced longitudinal. This was done in order to investigate the possible influence of the direct contact of anode with the soil (slice 2), on metal removal and partitioning in the soil, e.g. more mobilisation due to electrolysis reactions. The pH was lowest in the middle part of the cell (slice 2, Fig. 3) with similar pH levels in other parts of the cell. The water content did not vary significantly between the different parts of the cell. For this reason, slices 1 and 3 are expected to show similar patterns in removal percentages of metals.

Fig. 3

For the metals Al, Mn, Cu and Pb differences in the removal percentages from different parts of the cell were observed (Fig. 4). For Al, higher removal was observed from the middle part of the cell (soil in direct contact with anode) and it is speculated whether this was due to dissolution of the stable mineral aluminium hydroxide oxide, as electrolysis is a well-established technique for extracting Al from bauxite (Gow and Lozej, 1993) and would occur adjacent to the anode. The difference in removal of Mn from different parts of the cell is especially apparent in the two experiments with short distance between the electrodes (exp. 1 and 3). Mn is known to be among the more mobile metals in soil (Violante et al., 2010) and has low affinity for clay minerals (Fijałkowski et al., 2012) compared to the other metals. The biggest difference in removal from different parts of the cell was observed for Cu and Pb, with the highest removal from the middle part of the cell. This could be related to the slightly lower pH observed in the middle part of the cell (Fig. 4) or different redox conditions due to electrolysis reactions on the anode.

Fig. 4

In order to evaluate the potential effect of the electrolysis reactions on the release of Cu and Pb in the different parts of the cell, metal fractionation was used (Fig. 5). There was an observed difference in the removal and mobilisation of Cu and Pb from the different parts of the cell, most noticeable for Cu. There was more removal and desorption from the oxidisable and residual fractions in slice 2 (anode directly in contact with soil) indicating more dissolution and release of Cu/Pb due to a lower pH, redox conditions (oxidation) or that the electric field was more efficient in this part of the soil. More re-precipitation in the reducible and exchangeable fractions were observed in slices 1 and 3, and could be an indication of more efficient electromigration in the middle part of the cell. The effect of experimental settings on the metal fractionation in different parts of the soil was most obvious in exp. 1 and exp. 4, the experiments for which the highest removal of Cu and Pb was observed (table 2). These experiments had the highest charge transfer per quantity of soil, with the highest observed effect on the metal fractionation as well as on the removal of Cu and Pb. As a reference to these observations, the metal fractionation of Zn, known to be mobile under the influence of an electric field, was used. More removal of the metal was observed in slice 2 (exp. 1 and exp. 4) and the difference in metal fractionation between the different parts of the cell was mainly related to the residual fraction. This could indicate dissolution of Zn minerals in the residual fraction. Similar amounts of Zn were bound in the exchangeable, reducible and oxidisable fractions in the different parts of the cell (Fig. 5). This indicates similar re-precipitation of Zn across different parts of the soil and the electric field, the higher removal of Zn from the middle part of the cell however indicating higher efficiency of the electric field. The placement of the

anode hence appears to influence the efficiency of electrodialectic remediation, affecting the oxidation of minerals and organic matter, thereby influencing the mobilisation of metals bound in the oxidisable and residual fractions and in addition affecting the efficiency of transport through the cell.

Fig. 5

4. Conclusions

By placing the anode directly in the soil, mobilisation of metals from less available fractions in the soil during electrodialytic remediation was observed. This was suggested to be due to oxidation/dissolution of insoluble/soluble organic matter and metal oxides in the residual fraction on account of electrolysis reactions at the anode. The transport via electromigration out of the soil and re-precipitation in other fractions of the soil (oxidisable, reducible, exchangeable) depended on the metal. More than 30% of the original content of Mn, Cd, Cu, Pb and Zn was removed from the soil while less than 20% of the initial content was transported out of the soil for the metals Al, Fe, K, Mg, As, Cr and Ni. From the middle part of the cell, in which the anode was in direct contact with the soil, higher mobilisation and removal was observed, especially for Cu and Pb. Metal fractionation after the electrodialytic remediation showed more removal from the oxidisable/residual fractions.

Optimal settings for the removal of metals depended on the metal. For the targeted metal for remediation, Pb, the removal increased by applying short distance between the electrodes (1.5 cm). Similar removal efficiency in experiments with long distance between the electrodes (3.0 cm) could be achieved by increasing the current density and the remediation time. The findings of this study demonstrated that the design and optimisation of electrodialytic remediation should take into regard the targeted metal(s) and the metal fractionation.

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Figure captions

Fig. 1: a). The electrodialytic cell scheme. b). The sampling regime after the electrodialytic experiments.

Fig. 2: The partitioning of metals, based on the total amount of metal in the electrodialytic cell after the experiments. 'Removed' is the fraction of metal mobilised and transported to the cathode compartment during the electrodialytic treatment, 'exchangeable' is the fraction of metals available by ion exchange or weak acid in the soil, 'reducible' is the fraction of metals bound in Fe/Mn oxides in the soil, 'oxidisable' is the fraction of metals bound to soluble organic matter in the soil and 'residual' is the fraction of metals bound in insoluble organic matter and stable minerals in the soil.

Fig. 3: pH and water content in the different parts of the soil compartment after the electrodialytic remediation experiments. Slice 1 is the top part of the soil (25% of the total amount of soil), slice 2 is the middle part of the soil (50% of the total amount of soil) and slice 3 is the bottom part of the soil (25% of the total amount of soil) in the electrodialytic cell.

Fig. 4: Removal of metals in the different parts of the soil compartment in the electrodialytic remediation experiments. Slice 1 is the top part of the soil (25% of the total amount of soil), slice 2 is the middle part of the soil (50% of the total amount of soil) and slice 3 is the bottom part of the soil (25% of the total amount of soil) in the electrodialytic cell.

Fig. 5: Metal speciation of Cu, Pb and Zn in the different parts of the soil compartment before and after the electrodialytic remediation experiments. Slice 1 is the top part of the soil (25% of the total amount of soil), slice 2 the middle part of the soil (50% of the total amount of soil) and slice 3 is the bottom part of the soil (25% of the total amount of soil) in the electrodialytic cell.

Highlights

Electrodialysis was applied to mobilise and remove metals from a shooting range soil

The anode placement in the soil ensured introduction of protons and oxygen

Oxidation and dissolution of organic matter and metal oxides, mobilized metals

Electromigration and re-precipitation in other soil fractions depended on the metal

Optimisation depends on the targeted metal, metal speciation and soil characteristics

Table 1: Soil characteristics and metal concentrations, compared to the Norwegian quality criteria class 2 (predicted no effects), where these are available.

<i>Characteristic</i>	<i>Unit</i>	<i>Value</i>	<i>Standard deviation</i>	<i>Norwegian quality criteria for soil class 2</i>
Carbonate	%	0.2	20%	-
Organic matter	%	12.6	8%	-
Total carbon	%	13.6	14%	-
pH		3.7	1%	-
Conductivity	mS cm ⁻¹	0.3	8%	-
Grain size distribution				
Clay (<2µm)	%	12.9		-
Silt (2-63µm)	%	35.5		-
Sand (63µm-1mm)	%	25.7		-
Gravel (>1mm)	%	25.9		-
Metal concentrations				
Al	mg kg ⁻¹	10,280	4%	-
Fe	mg kg ⁻¹	15,760	6%	-
K	mg kg ⁻¹	1090	9%	-
Mg	mg kg ⁻¹	2070	4%	-
Mn	mg kg ⁻¹	270	15%	-
As	mg kg ⁻¹	3.0	7%	20
Cd	mg kg ⁻¹	0.2	15%	10
Cr	mg kg ⁻¹	15	6%	200
Cu	mg kg ⁻¹	47	8%	200
Ni	mg kg ⁻¹	11	7%	135
Pb	mg kg ⁻¹	450	9%	100
Zn	mg kg ⁻¹	46	7%	500

Table 2: Experimental settings and results of the electrodialytic remediation experiments. The removal of metals (%), the final pH and energy consumption per kg treated soil in the four experiments. Pb was the targeted metal for remediation and calculation of the energy required for removing Pb is also provided.

	Exp. 1	Exp. 2	Exp. 3	Exp. 4
Experimental settings				
Distance between electrodes (cm)	1.5	3.0	1.5	3.0
Current density (mA cm ⁻²)	0.2	0.2	0.08	0.2
Remediation time (d)	7	7	7	35
Removal of metals (%)				
Al	7	2	2	14
Fe	1	1	1	3
K	14	10	11	12
Mg	7	4	5	7
As	1	1	1	1
Cd	43	39	34	42
Cr	<1	<1	<1	<1
Cu	41	21	16	33
Ni	13	8	11	12
Pb	31	14	14	30
Zn	34	23	28	29
pH				
Final pH	3.2	3.3	3.0	3.1
Energy consumption				
kWh kg ⁻¹ soil	0.48	0.29	0.38	0.44
kWh g ⁻¹ Pb removed	3.0	5.8	9.0	3.1