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*Published in:*  
Engineering Geology

*Link to article, DOI:*  
[10.1016/j.enggeo.2018.03.005](https://doi.org/10.1016/j.enggeo.2018.03.005)

*Publication date:*  
2018

*Document Version*  
Peer reviewed version

[Link back to DTU Orbit](#)

*Citation (APA):*  
Pedersen, K. B., Jensen, P. E., Ottosen, L. M., & Barlindhaug, J. (2018). The relative influence of electrokinetic remediation design on the removal of As, Cu, Pb and Sb from shooting range soils. *Engineering Geology*, 238, 52-61. <https://doi.org/10.1016/j.enggeo.2018.03.005>

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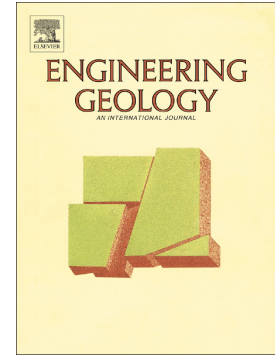
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## Accepted Manuscript

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PII: S0013-7952(17)31403-5  
DOI: doi:[10.1016/j.enggeo.2018.03.005](https://doi.org/10.1016/j.enggeo.2018.03.005)  
Reference: ENGEO 4783  
To appear in: *Engineering Geology*  
Received date: 25 September 2017  
Revised date: 5 February 2018  
Accepted date: 11 March 2018

Please cite this article as: Kristine B. Pedersen, Pernille E. Jensen, Lisbeth M. Ottosen, John Barlindhaug , The relative influence of electrokinetic remediation design on the removal of As, Cu, Pb and Sb from shooting range soils. The address for the corresponding author was captured as affiliation for all authors. Please check if appropriate. Enggeo(2018), doi:[10.1016/j.enggeo.2018.03.005](https://doi.org/10.1016/j.enggeo.2018.03.005)

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# The relative influence of electrokinetic remediation design on the removal of As, Cu, Pb and Sb from shooting range soils

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**Abstract**

Electrodialytic remediation was applied for remediation of shooting range soils from two sites in Norway for which the targeted metals were As, Cu, Pb and Sb. Up to 75% Cu and 78% Pb was removed in the treatment, while low removal of As (<3%) and Sb (14%) was observed suggesting low mobility and bioavailability of these two metals in the studied soils. Removal of metals from the natural soil matrix (Al, Fe, K, Mg and Mn) were with the exception of Mn generally low (<20%) making it possible to target the removal of Cu and Pb while limiting the disturbance to the natural soil matrix. Multivariate design and analysis was applied for assessing the efficiency of electro-dialytic remediation treatment and variable importance varied for each of the studied metals. In general, applying a stirred set-up improved the metal removal, acidification time and reduced the energy consumption. The placement of the anode directly in the soil did not significantly influence the removal of Al, Mg, Mn, As and Pb, while moderately influencing the removal of Cu. Multivariate analysis (projections onto latent structures) revealed similar variable importance and optimal settings for removal of Cu and Pb. It is hence possible to simultaneously optimise the removal by applying a stirred set-up, placement of the anode directly in the soil suspension, sieving the soil (<2mm fraction) and long treatment time (35 days). The study showed that multivariate analysis is a valuable tool for evaluating remediation measures depending soil characteristics and this way be used for selection of site-specific best available remediation methods.

**Keywords:** Heavy metals, electrokinetic remediation, polluted soil, metal speciation, projections onto latent structures

## 1 Introduction

Heavy metal contamination in soil is of concern due to the risks it may pose on human health and the environment. The sources span a wide range of human and industrial activities such as mining, agriculture, industrialisation and urbanisation (e.g. traffic run-off) [1-4]. Shooting ranges are amongst sources of heavy metal pollution due to deposition of bullets, which are weathered over time and the metals/metalloids from bullets can be mobilised and dispersed into the environment via pore, surface or ground water [5, 6]. The main concern at shooting range sites has historically been Pb, and elevated soil concentrations of minor components of bullets such as As, Cu, Ni, Sb and Zn, have also been observed [7]. The risk of being exposed to heavy metals is linked to direct contact with the soil or dispersion from the polluted site into the environment. The dispersion depends on how well metals are retained in the soil, the adsorption mechanisms depending on the soil characteristics and the given metal [7-9].

To mitigate and/or minimise the risks that heavy metal pollution poses to human health and the environment, various biological, chemical and physical remediation techniques are applied. The choice of technology depends on the soil properties, pollutant quantity and composition, binding of pollutants in soil as well as considerations regarding cost-effectiveness and site-specific conditions [10]. Most of the technologies are based on decreasing the bioavailability and risk of exposure through the immobilisation of heavy metals, e.g. by application of a topsoil to prevent leaching [8, 11], addition of phosphate, lime or MgO to chemically stabilise the metals [12, 13] or phytoremediation to stabilise the metals in soil or in plants/vegetation [14-16]. These technologies are relevant in areas for which future risk of exposure to the soil is minimal, but may fall short for sites situated in present/future sensitive land areas, e.g. residential areas, or when there is a need for re-using the soil as an unpolluted material. In these cases methods developed to mobilise and remove metals from the soil are more appropriate. Soil washing, in which metals are separated from the soil by mixing with reagents and extractants, affords such a method [17, 18] and has been vastly used. One of the disadvantages of soil washing is that it requires excavation of the soil and hence cannot be applied in-situ.

Electrokinetic remediation has proved a viable method to separate metals from soil either in-situ or ex-situ, designed according to site-specific conditions, including clean-up goals. It is based on applying a low intensity electric field at the electrodes and due to electrolysis reactions on the electrodes, an acidic front develops from the anode [19]. The acidification of the soil ensures mobilisation of metals/metal complexes that under the influence of the electric field are transported to the electrode of opposite charge and thus separated from the soil. The efficiency of the method in regards to removal of metals depends on the soil properties and experimental settings [20]. Early enhancement techniques involved preventing or limiting the alkaline front, emerging from the cathode. By applying ion-exchange membranes protons and hydroxides produced on the electrodes are prevented from entering the soil and acidification is ensured by water splitting at the anion-exchange membranes (figure 1), the method referred to as electrodialytic remediation [21]. Further developments in the optimisation of electrokinetic remediation have been related to site-specific conditions. It has for instance been demonstrated that stirring the soil suspension significantly reduces the treatment time for removing metals [22, 23] and is relevant for ex-situ treatments as well as providing a fast evaluation of whether the method is appropriate for a specific soil, regardless of whether in-situ or ex-situ treatment is preferred. Amongst newer developments is application of the anode directly in the soil, which has shown to decrease the acidification time and electric energy consumption [24, 25]. The relative influence of these different designs (stationary/stirred, placement

of anode) and experimental settings on the electrodynamic removal of metals from soil have not yet been evaluated.

Multivariate design and analysis can be used as a tool for assessing the relative importance of variables in a remediation design [26]. Factorial designs are constructed to independently determine both the effects of each factor and interaction effects [27, 28]. This is achieved by simultaneously varying the factors and investigating all possible combinations of the levels of factors. Most commonly two-level designs are used, accordingly a two-level factorial design with  $k$ -factors contains  $2^k$  experiments. Each factor is investigated at two fixed levels, continuous variables have a low and high value, determined by the experimental domain and discrete variables have two alternatives (e.g. stirred or stationary set-up). Two-level factorial designs of 4-7 factors entail conducting 32-128 experiments, however by assuming that interaction effects between three or more variables are low compared to the main effects, the number of experiments can be reduced by constructing designs that are fractions of factorial designs,  $1/2^p$  of a complete factorial design, resulting in a total of  $2^{k-p}$  experiments [29]. In a fractional factorial design the experiments are widely distributed to cover a maximum variation over the experimental domain. The fractional factorial designs are constructed in a way to control confounding of main and interaction effects. The resolution of a design describes the degree to which main effects are confounded with two-variable, three-variable and higher order interaction effects. In a Resolution III design, e.g.  $2^{6-3}$ , main effects are confounded with two-variable interaction effects. In a Resolution IV design, e.g.  $2^{5-2}$ , main effects are confounded with three-variable interaction effects and two-variable interaction effects are confounded with each other. In a Resolution V design, e.g.  $2^{4-2}$ , main effects are confounded with four-variable effects and two-variable interaction effects are confounded with three-variable interaction effects [29]. Supplementing a fractional factorial design with experiments in the centre of the experimental domain provides an estimate of the experimental error variance as well as the possibility of assessing potential curvature of the response surface.

Projections onto latent structures (PLS) is a multivariate tool for evaluating the quantitative relations between a descriptor matrix,  $X$  and a response matrix,  $Y$  [30, 31]. Objects in each space are projected down to PLS components that describe the variation in each space with the constraint that for each PLS dimension, the PLS scores of the  $Y$  matrix should have a maximum correlation to the scores of the  $X$ -matrix [32]. New PLS components are iteratively introduced until all the systematic variation in the  $Y$ -matrix has been exhausted. Advantages of PLS include simultaneous modelling of several responses, coping with collinearity between variables, coping with noise in the  $X$  and  $Y$  matrices, coping with moderate amounts of missing data (<20%) and since it is based on projections, it is possible to have more variables than objects [30, 31]. The use of PLS in studies of pollution has been scarce and besides limited use for optimisation of remediation [33-35], it has been employed for identifying important factors for formation of toxic compounds in waste combustion [36, 37].

In this study multivariate design and analysis has been employed for identifying significant variables in the electrodynamic remediation of shooting ground soil from two sites in Norway. The focus has been on the influence of conducting the experiments in stirred and stationary set-ups as well as the placement of the anode directly/indirectly in the soil. By using multivariate analysis the influence of the set-up on the remediation efficiency has been compared to other important variables (current, treatment time, sieving the soil, soil characteristics).

## 2 Materials and methods

### 2.1 Soil

The soil used in this study was sampled from the top 10 cm of the earthen backstop of a shooting range and from a clay pigeon shooting ground from two former military sites in Norway – respectively Lygna and Gimlemoen. Prior to analysis and electro-dialytic experiments, the soil was sieved and particles larger than 4 mm were separated and disposed of. To investigate the influence of metal fragments in the size range 2-4 mm present in the soil on the remediation efficiency, for selected experiments the soil was sieved and particles larger than 2 mm were disposed of (table 1).

## 2.2 Analysis

**2.2.1 Major elements and heavy metal concentrations** (Al, Fe, K, Mg, Mn, As, Cd, Cr, Cu, Ni, Pb, Zn) were measured based on digestion (Norwegian standard NS4770). Sediment dried at 105°C (1.0g) and HNO<sub>3</sub> (9M, 20mL) were autoclaved (200kPa, 120°C, 30 minutes). Solid particles were subsequently removed by vacuum filtration through a 0.45µm filter and the liquid was diluted to 100mL. Metal concentrations in the liquid were measured by Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-OES).

**2.2.2 Carbonate content** was measured by treating dried sediment (5.0g) with HCl (3M; 20mL) and the developed CO<sub>2</sub> was measured volumetrically in a Scheibler apparatus, calibrated with CaCO<sub>3</sub>.

**2.2.3 Organic content** was based on loss on ignition of dried sediment (2.5g) heated to 550°C for one hour.

**2.2.4 pH (KCl)**. Dried sediment (5.0g) was agitated with KCl (1M, 12.5mL) for one hour and pH was subsequently measured using a radiometric analytical electrode.

**2.2.5 Conductivity**. Dried sediment (5.0g) was agitated with distilled water (25 mL) for one hour and the conductivity was measured using a radiometric analytical electrode.

**2.2.6 Total Carbon (TC)** was measured by high temperature combustion. Dried sediment (0.5g) was combusted (1,350°C) to convert all carbon into CO<sub>2</sub>. The gas was passed through scrubber tubes to remove interferences and the CO<sub>2</sub> was measured by infrared detector.

**2.2.7 Grain size distribution** was measured by wet sieving and dry sieving. Wet sediment (75 g), distilled water (350 mL) and Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub>·10H<sub>2</sub>O (0.1 M, 10 mL) were agitated for 24 hours. The slurry was then sieved through a 63µm sieve and the fraction above 63µm was subsequently dried and sieved for 15 minutes in a mechanical shaker using sieves with screen openings of 0.063, 0.080, 0.125, 0.25, 1.0 and 2.0 mm. The slurry fraction below 63 µm was transferred to Andreasen pipette for gravitational sedimentation. Stoke's law was used for estimating the time required for particles to settle 20 cm and samples representing the sizes 40, 32, 16, 8, 4, 2 and 1 µm were measured.

**2.2.8 Metal concentrations in different fractions of the soil** was measured by dry sieving the soil in the fractions <63µm; 63µm-1mm and 1mm-4mm and analysing the soil fractions for metals by digestion as described in 2.2.1.

**2.2.9 Sequential extraction** was made in four steps based on the extension of the three-step method [38] described by Standards, Measurements and Testing Program of the European Union. Air-dried sediment (0.5g) was first extracted with acetic acid (0.11M, 20mL, pH3) for 16 hours; secondly with hydroxylammonium chloride (0.1M, 20mL; pH2) for 16 hours; thirdly with hydrogen peroxide (8.8M, 5mL) for 1 hour, followed by extraction at 85°C for 1 hour, evaporation of liquid at 85°C, and subsequent extraction of the cooled solid fraction with ammonium acetate (1M, 25mL, pH2) for 16h; and fourthly the remaining solid particles were analysed for metal content by digestion, as described in 2.2.1.

## 2.3 Electrodialytic remediation

### 2.3.1 Electrodialytic cell design

The design and principles of the four set-ups of the electrodialytic cell used in this study are illustrated in figure 1. The design of the cells was based on stirred/stationary set-ups and testing the influencing of placing the anode directly in the soil (2-compartment set-up). In order to ensure comparison between the different set-ups, the cells were designed according to treating an equivalent quantity of soil (dry matter), i.e. the soil compartment in the stirred and stationary cells were different in volume. The length of the soil compartment in the stationary set-up was 3.0 cm and 10 cm in the stirred set-up and all had an inner diameter of 8 cm. The length of each electrolyte compartments was 3.5 cm. The cell compartments were manufactured from Plexiglas®. In all set-ups a cation-exchange membrane from Ionics (CR67 HUY N12116B) was used to separate the soil compartment from the electrolyte compartment on the right hand side. In the 3-compartment cells, an anion exchange membrane from Ionics was used to separate the soil compartment from the electrolyte compartment on the left hand side.

Platinum coated electrodes were used as cathode in all set-ups, and as anode in the 3-compartment cell. A titanium coated mesh (height 4 cm; width 8 cm) was used as anode in the stationary 2-compartment cell. A power supply (Hewlett Packard E3612A) maintained a constant DC current. The electrolyte was NaNO<sub>3</sub> (0.01M) adjusted to pH 2 by HNO<sub>3</sub> (5M). The electrolyte liquid (500 mL) was circulated (Pan World pumps) at flow rates of 30mL/min.

After the electrodialytic experiments, the soil suspensions in the stirred set-ups were filtered and both soil and liquid fractions were analysed for metals. Metal concentrations of soil from the stirred and stationary set-ups were analysed by digestion (2.2.1). The membranes and electrodes were rinsed in HNO<sub>3</sub> (5M) overnight and the heavy metal concentrations in the rinsing liquids as well as in the electrolyte liquid were measured by ICP-OES.

### 2.4 Experimental design

For the purpose of an initial screening to evaluate the relative influence of experimental variables and determine which variables to exclude in future experiments and optimisation efforts, a Resolution III design was employed. The main effects were thus confounded with two-variable interaction effects and the results can be used as foundation for separating specific effects in future designs and experiments. A 2<sup>6-3</sup> fractional factorial design of 8 experiments (1-8) and three experiments (9-11) representing the centre of the continuous experimental domain to validate the PLS model was used for evaluating the comparative influence of the six experimental variables (table 1). The continuous variables were *current* and *treatment time*. The discrete variables were *stirring/stationary*, *sorted (<2mm)/non sorted (<4mm)*, *type of soil (Lygna/Gimlemoen)* and *cell design (2-compartment or 3-compartment)*. The responses of the experiments included removal efficiencies of metals, the final pH and the electric energy consumption in the experiments.

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).

### 2.5 Multivariate analysis

SimcaP11 software was used for the multivariate modelling, by projections onto latent structures (PLS). The X-matrix consisted of the experimental variables. For the comparison of soils with different initial metal concentrations, the Y matrix consisted of the removal efficiencies of metals, calculated as the final quantities found in the catholyte and anolyte compartments and precipitated on the electrodes, compared to the final quantities of metals in the treated soil. For the models to evaluate the influence of variables on acidification and energy consumption, the Y matrix consisted of the final pH of the soil and the energy consumption per remediated amount of soil (kWh/g).

To assess viability and stability of the calculated PLS models, correlation coefficients, R2Y (the fraction of the Y-matrix explained by the model) and predictive powers, Q2 (an estimate of the reliability of the model calculated by cross-validation) were used. In order to obtain a high predictive power, R2Y should be high. A value of Q2>0.9 is excellent, while a value above 0.5 is good. The difference between R2Y and Q2 should be as low as possible and a difference larger than 0.2-0.3 may indicate outliers or the presence of irrelevant variables in the X block. Variable Importance in the Projection (VIP) values present the absolute importance of each parameter in the model with respect to its correlation to all the responses (Y) and to the projection (X). The VIP values are calculated for each X variable by summing the squares of the PLS loading weights, weighted by the amount of sum of squares explained in each model component. The sum of squares of all VIP's is equal to the number of terms in the model, accordingly the average VIP is equal to 1. High VIP values (>1) represent high influence of the variable(s) in the model, and VIP values <0.5 indicate low influence of the variable(s) on the model. VIP plots were used to assess the variable importance in the calculated models. To evaluate if the variables had positive or negative impacts on the model responses, coefficient plots were used.

### 3 Results and discussion

#### 3.1 Soil characteristics

The buffer capacity of soil has been shown to retard the acidification process during electrodiolytic remediation [39]. The content of carbonate in the two soils (table 2) are low (<1%), but the high content of organic matter in both soils may retard metal removal due to re-adsorption to insoluble organic matter [40]. Both soils are acidic; the pH of the Lygna soil is however, a magnitude lower than the soil from Gimlemoen, potentially increasing the initial mobility of metals in the soil. Grain size analysis revealed a difference in texture between the two soils (table 2); the Lygna soil has a higher fraction of finer fractions (clay and silt) and has texture as a loam, while the soil from Gimlemoen has a texture of a sandy loam.

The metal concentrations varied between the two soils (table 2), with higher concentrations of Fe, K and Mg in the Gimlemoen soil and higher concentration of Al in the Lygna soil, an indication of different composition of minerals in the two soils. For the environmentally prioritised metals (As, Cd, Cu, Cr, Ni, Pb and Zn) the concentrations have been compared to the Norwegian soil quality criteria and in the Lygna soil it was only Pb (Class 4, very polluted) that exceeded background level concentrations (non-polluted). For the Gimlemoen soil, As and Cu had elevated concentrations, however below levels of adverse effect, and the Pb concentrations were above Class 5 levels, defined as hazardous waste. There is no environmental quality criteria for Sb in Norway, it has however been acknowledged of being potentially toxic and given special focus for polluted soil from shooting ranges. The Dutch environmental authorities operate with an environmental quality criteria of 3 mg/kg for non-polluted soils. Concentrations of Sb in both soils exceed this level.

In the following the focus will be on the priority metals exceeding non-polluted concentration levels, i.e. As, Cu, Pb and Sb. In addition, results of the metals Al, Fe, K, Mg and Mn have been included to investigate changes to the natural soil matrix.

Electrodialytic remediation has been shown to be most efficient for fine soil materials (clay and silt, <63 $\mu$ m) [22] and the binding of metals in the different soil textures provides a potential for extraction and removal. For both soils it is observed that a higher fraction of As, Cu, Pb and Sb are bound in the clay and silt fraction of the soil, compared to the metals Al, Fe, K, Mg and Mn (figure 2). This could indicate that it is possible to mobilise the prioritised metals while limiting the removal of naturally occurring metals in the soil matrix. For the Lygna soil the binding of Al, Fe, K, Mg and Mn in clay and silt (figure 2) is in fact in the same range as the grain size distribution of this fraction (table 2).

During electro-dialytic remediation, dissolution of carbonates and oxidation of organic matter has been observed [41-43], subsequently desorbing metals bound in the exchangeable and oxidisable fractions of the soil. Electro-dialytic remediation has been shown to accelerate weathering of soil, making metals in all soil fractions more available [44] and removal from both the available and less available fractions of harbour sediment has been observed [42]. Metal speciation of the soil provides a preliminary assessment of the potential of desorption of metals from the different fractions of the soil.

In both soils the majority of the metals Al, Fe, K, Mg, Mn, As and Sb are bound in the residual fraction (figure 3) indicating that these metals may be more challenging to desorb and remove during electro-dialytic remediation compared to Cu and Pb. In both soils, 40-50% of the Cu is bound in the oxidisable fraction, and could potentially desorb under oxidizing conditions (e.g. aeration through stirring of the soil slurry or by production of oxygen on the anode in the 2-compartment cell, figure 1). 75-90% of Pb is bound in the exchangeable, reducible and oxidisable fractions of the soils. The larger fractions of Cu and Pb in the more available fractions of the soil may facilitate the desorption and subsequent removal during electro-dialytic treatment, compared to the other metals bound in stable minerals and for Al, Fe, K, Mg and Mn also in the coarser fractions of the soil.

### *3.2 Electro-dialytic remediation experiments*

#### *3.2.1 Influence of experimental settings on acidification*

pH is an important factor for desorption of metals from soil and pH values below 4 are, in general necessary to achieve significant mobilisation of the targeted metals Cu and Pb [45-47]. Even though other factors are known to influence the removal rate of metals during electrokinetic treatment including the geochemical characteristics of the soil [19, 48] and the experimental settings [22, 49-51], the acidification rate is among the more important parameters to ensure sufficient desorption of Cu and Pb.

There appears to be a distinct difference in the final pH of the experiments with stirred set-up (pH 1.4-2.6, table 3) and the experiments with a stationary set up (pH 3.1-3.6, table 3), indicating that stirring ensures a faster acidification of the soil. The influence of other experimental settings on the acidification is not as distinct and a PLS model was used for evaluating variable importance in the 11 experiments. The model correlation was good ( $R^2$  0.97) and the model was stable ( $Q^2$  0.81), enabling solid interpretations of the model results. As was initially observed, the stirred/stationary set-up had the highest influence on acidification in the electro-dialytic remediation experiments ( $VIP \gg 1$ , figure 4). All other variables apart from cell design had a medium influence on the acidification in the studied experimental domain. Variable coefficients revealed that the stirred set-

up, high current (albeit below the limiting current for the cation exchange membrane), long time and sieving of the soil (<2mm) increased the acidification, in line with observations of previous electrodiolytic remediation studies [22, 23, 49].

The cell design has a low influence on the acidification, compared with the other parameters (figure 4). Previous electrodiolytic remediation studies of fly ash and harbour sediments [24, 33] showed that acidification in the 2-compartment cell was more efficient than in the 3-compartment cell, this is however not necessarily in contrast to the findings in this study. The experimental domain in the previous studies was different (e.g. current of up to 50mA) and the relative influence of stationary/stirred set-up, current and time on the acidification was not included. In addition, it is important to note that the three studies have dealt with different materials with other properties for which introducing protons directly into the soil in the 2-compartment cell could have a higher significance.

### 3.2.2 Energy consumption

To assess the relative influence of variables on the energy consumption per quantity of treated soil (kWh/g), a PLS model was calculated. The model was good ( $R^2Y$  0.80), but unstable ( $Q^2 < 0$ ), accordingly with some caution overall trends can be retracted from the model. VIP values of the variables (figure 4) revealed that stirring, current and time had the highest influence on the energy consumption. Coefficients in the model revealed that low energy consumption was promoted by stirring, low current and low time. It is also important to note that applying a stirred set-up to ensure low levels of energy produced in the electrodiolytic remediation cell could potentially be counteracted by energy necessary for doing the stirring. Previous electrodiolytic remediation studies found that energy consumption was generally lower in the 2-compartment than the 3-compartment cell design [24, 25]. This study however showed that other parameters are more important for optimising energy consumption within the studied experimental domain.

To assess the electric energy efficiency in the treatments in relation to metal removal, the energy consumption per removed quantity of the targeted metals for remediation, As, Cu, Pb and Sb in this study, were calculated (figure 5). The energy consumption levels for Cu and Pb are comparable to removal of metals from soil during ED with similar experimental settings [52] and for both metals experiment 4 was most energy efficient in relation to quantity of metal removed (figure 5). The reason for the very high energy levels for removing As and Sb is related to the low concentrations and low removal of these metals during the treatments (table 3).

### 3.2.3 Variable importance for the removal of metals

For the targeted metals for remediation in this study, the highest removal efficiencies were observed for Cu (up to 75%) and Pb (up to 78%), while the removal of As was low (<3%) and the removal of Sb was generally below 6% except experiment 5, where 14% was removed (table 3). For the other metals the removal of Fe, K and Mg was below 20% as were the removal of Al, apart from experiment 4 with a removal efficiency of 35%. The removal of Mn was in the range 31-47% (table 3). The highest removal of each metal was observed in different experiments, e.g. Al, Fe and Cu in experiment 4, K in experiment 6, Sb in experiment 5 and As, Mn and Pb in experiment 8, indicating that variable importance varies between the metals. In addition this indicates that removal of Cu and Pb is possible while maintaining limited disturbance to the natural soil matrix.

For an assessment of variable importance for the removal of metals during the electrodiolytic treatment, a PLS model, was calculated. The model had a good correlation ( $R^2Y$  0.84) and the model was fairly stable ( $Q^2$  0.50), making it possible to make a preliminary evaluation of the difference in

variable importance between the different metals. In general, the variables stirring and time had the strongest influence on electro dialytic removal of metals from the soil (figure 6). For all metals apart from K and Mg, stirring increased the removal of metals, suggesting different binding and re-precipitation binding patterns of K and Mg compared to the other metals. This may also be the reason for K and Mg having a positive correlation to soil (in the first weighted component,  $pc(corr)_1$  in figure 6), while the remaining metals have a negative correlation to soil. K and Mg are more easily removed from Gimlemoen soil (assigned -1 in the X-matrix of the PLS model) than Lygna soil, corresponding to the higher fractions bound in exchangeable fractions of the Gimlemoen soil (figure 3). Al, Mn, As, Cu, Pb and Sb also had relative higher quantities bound in the exchangeable fractions of Gimlemoen soil, the higher removal efficiencies in the Lygna soil, however, suggests that other variables than metal binding, such as stirring and time, are more important for increasing mobilisation of these metals.

In general, time has a positive correlation with all metals apart from K and Mg in the first weighted component and all metals apart from Sb in the second weighted component (figure 6) indicating that time is an essential variable for designing the electro dialytic removal of targeted metals from the soils. The vicinity of Cu and Pb indicate a correlation between the variations in the removal efficiencies with the variation in the experimental settings for these two metals. Their location in the plot, close to the variable time suggests that time has the highest influence of all variables on the electro dialytic removal of Cu and Pb from the soils.

Due to the difference in variable importance for the metals, PLS models for each of the metals were calculated. The models were good and stable ( $R^2Y 0.60-0.99$ ;  $Q^2 0.3-0.8$ ) and the VIP values of each model revealed differences in the influence of variables on the different metals (table 4). The treatment time had a high influence on most metals, with the exception of Fe, K and Sb for which increasing the treatment time from 7 to 35 days did not significantly increase the removal. This is an indication of the changes in soil properties (e.g. pH) during the electro dialytic treatment does not affect desorption and removal of these three metals.

Current has previously been found to have a high influence on the electro dialytic removal of metals from soil [22]. The reason for current having a low-medium influence on the removal of metals in this study is due to the limit in the range of current (4-10 mA). For the stationary experiments running at higher currents than 10mA was not viable due to high resistance across the cell. For the targeted metals As, Cu and Pb changing the electric intensity did not affect the removal. For Fe and Mg the highest current increased the removal. Applying a stirred set-up improved the electro dialytic removal of Al, Fe, Mn, As, Cu, Pb and Sb from the soils, in line with previous findings [22, 23]. For K and Mg applying a stationary set-up however significantly improved the removal and this may be related to the binding of these metals in the soils as well as the redox conditions and re-precipitation during the experiments. Sorting the soil by removing particles >2mm improved the removal efficiencies of Fe, Cu and Pb and this could be related to the removal of metal fragments of disintegrated bullets/cartridges. Larger metal fragments have previously been shown to influence the removal rate of metals [53, 54].

The two types of soil applied in this study had similar characteristics (table 2), nonetheless they still influenced the removal of most metals. For K and Mg, the highest removal efficiencies were observed for the Gimlemoen soil and could be related to metal speciation with a higher fraction bound in the more available fractions of the soil, compared to the Lygna soil (figure 3). This was also the case for Al, Fe, Mn and As, however for these metals the highest removal efficiencies were observed in the Lygna soil, accordingly other characteristics influenced the mobilisation. The pH in the soils was different making the treatment time at a lower pH longer for the Lygna than the Gimlemoen soil. It

could also be related to the composition and concentration of elements affecting the removal efficiencies, known to depend on the ionic mobility, concentration and total electrolyte concentration under the influence of an electric field [19, 55]. Cu and Pb also had similar binding patterns in the two soils, and the difference in removal from the two soils is hence related to other parameters.

Compared to the other variables, the cell design generally had a low influence on the removal of metals. The cell design did however have a medium influence on the removal of Fe, K, Cu and Sb. The 3-compartment cell increased the removal of Fe and Sb and it is speculated whether this is related to re-precipitation of the two metals under oxidising conditions in the 2-compartment cell, thus retarding the removal. The higher removal of K in the 2-compartment cell could be related to more desorption occurring at a faster acidification and a higher ionic mobility of K compared to the other measured metals. The higher removal of Cu is related to the relatively higher binding in the oxidisable fraction (figure 3), released during oxidation of soil due to the introduction of oxygen via electrolysis reactions at the anode (figure 1), as observed in previous studies [33, 42]. Applying the 2-compartment cell for optimising the removal of Cu would increase the removal of K, while maintaining or limiting the removal of other metals in the soil matrix.

In regards to the Norwegian quality criteria for soil, the targeted metals in the shooting range soils used in this study were As, Cu, Pb and Sb. Very low removal efficiencies were observed for As and Sb and is due to the strong retainment in the soils, and could be attributed to the oxidation state (III or V) of the metals, the high content of organic matter in the soils (binding to humic acids) and/or the high fraction of Sb bound in finer fractions (figure 2), since solubility of Sb has been shown to decrease with increasing content of clay [45, 56]. Because of the moderate concentrations of As and Sb and the limited mobilisation during the electrodynamic remediation experiments, a strategy to ensure immobilisation rather than optimise the removal, e.g. through addition of reducing and chelating agents [57] is suggested in the cases of the soils from Gimlemoen and Lygna.

From the PLS results, it is apparent that the specific soil characteristics (e.g. carbonate, metal binding patterns in the soil, organic matter content) and the targeted metal are decisive for the choice of cell design. Due to the medium influence of cell design on the removal of Cu in this study, the 2-compartment cell would provide the most optimal conditions for simultaneous removal of Cu and Pb. If the influence of cell design was low for all targeted metals, the cell design would depend more on site-specific conditions and economic/practical considerations for identifying the most soil-appropriate cell design. Apart from the cell design, the optimal conditions for mobilisation and removal of Cu and Pb were similar – 35 day treatment, stirred set-up and sieving the soil <2mm (table 4). Based on the multivariate analysis results (table 4) it is apparent that employing these conditions would also increase the removal of other metals, however applying a low current would limit the removal of Fe and Mg. Applying a stirred set-up could increase the mobilisation of As and Sb, albeit still low removal efficiencies. To ensure the immobilisation of these two metals in the soils, iron based amendments could be added to the soil [58, 59] after sufficient electrodynamic removal of Cu and Pb.

The PLS models of this study can be used as a foundation for optimising the remediation of metals from the two sites studied. Taking into account the site-specific conditions, such as the type of soil, whether in-situ or ex-situ methods are most relevant and environmental goals of the given site, this will result in PLS models with reduced amounts of variables and higher resolution design. The advantage of applying a multivariate design is that existing experiments do not need to be repeated; supplementing with 4-8 experiments will provide the possibility of separating confounding effects by

increasing the resolution design. In this way it will be possible to focus on optimising the removal of targeted metals while maintaining low removal of metals in the natural soil matrix.

### **Conclusion**

Multivariate design and analysis was applied for assessing the efficiency of electrodynamic remediation of shooting range soils from two sites and identifying the most important experimental variables. Variable importance for removing the studied metals (Al, Fe, K, Mg, Mn, As, Cu, Pb and Sb) varied for each metal. In general, the setting that increased the metal removal most was applying a stirred rather than a stationary set-up. This also had the highest influence on increasing acidification and decreasing the electric energy consumption in the remediation. Accordingly ex-situ treatment under stirred conditions is more efficient.

For the metals of environmental concern (As, Cu, Pb, Sb) up to 75% of Cu and 78% of Pb was removed, while the treatment was not effective for As and Sb with removal of less than 20% of the original metal content in the soils. The final concentrations of As and Sb were however below levels of adverse effects and due to the low mobilisation during the electrodynamic treatment are not expected to pose a risk for human health and the environment. Since variable importance of Cu and Pb were similar it is possible to simultaneously optimise the removal by the same experimental settings (stirred set-up, sieving the soil and applying the 2-compartment cell) for the two studied soils. Applying these settings would limit the removal of Fe, K and Mg ensuring minimal disturbance to the natural soil matrix.

The application of electrodynamic remediation of shooting range soils from two sites showcased how multivariate design and analysis can be used for evaluating remediation measures depending on site specific conditions, including remediation objectives, soil characteristics and type of pollutants. In this way it was illustrated that multivariate analysis can be a valuable tool in the evaluation and selection of remediation method as well as optimisation efforts in accordance to environmental goals of the specific site.

### **Acknowledgements**

The Norwegian Defense Estates Agency and the Environmental Waste Management (EWMA), funded by the Research Council of Norway (grant no. 195160) and ENI Norway are acknowledged for funding. The laboratory technicians Ebba Schnell, Malene Grønvold and Sabrina June Hvid are acknowledged for their help with the electrodynamic experiments and chemical analyses.

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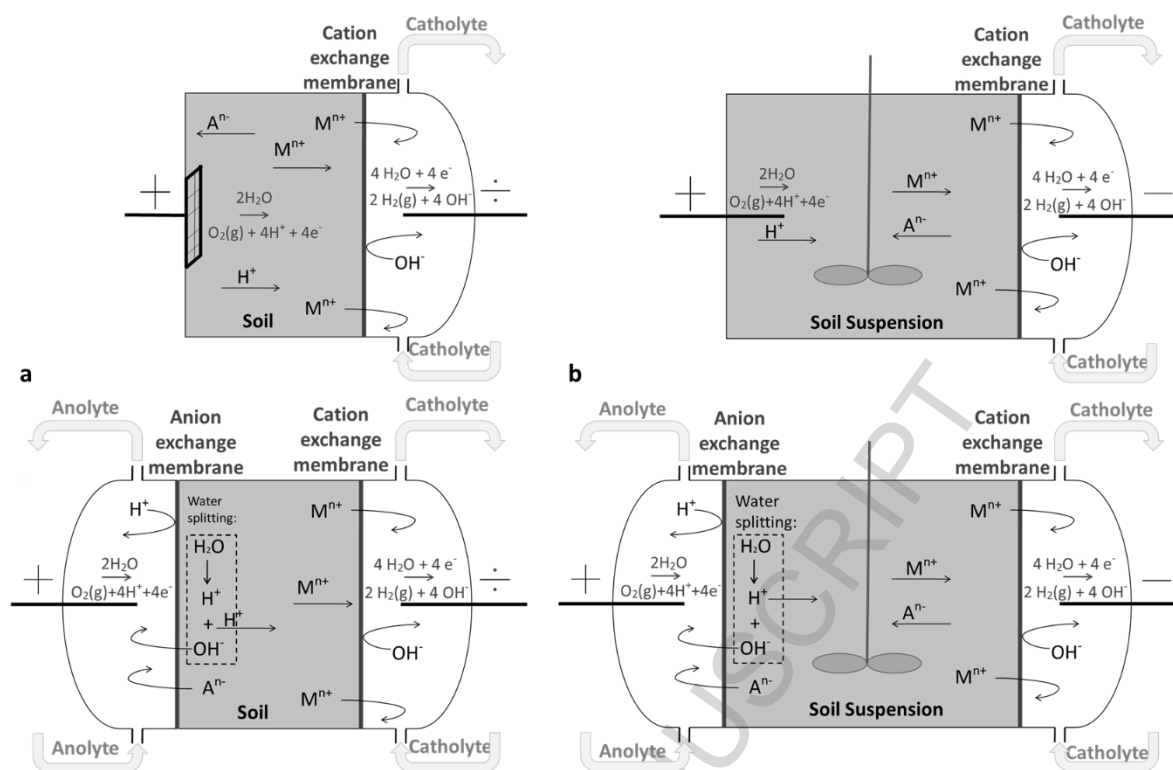
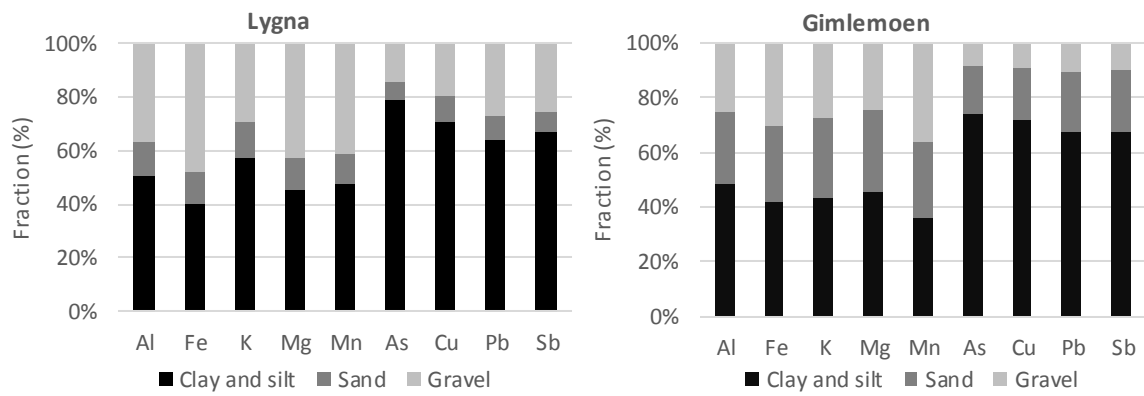
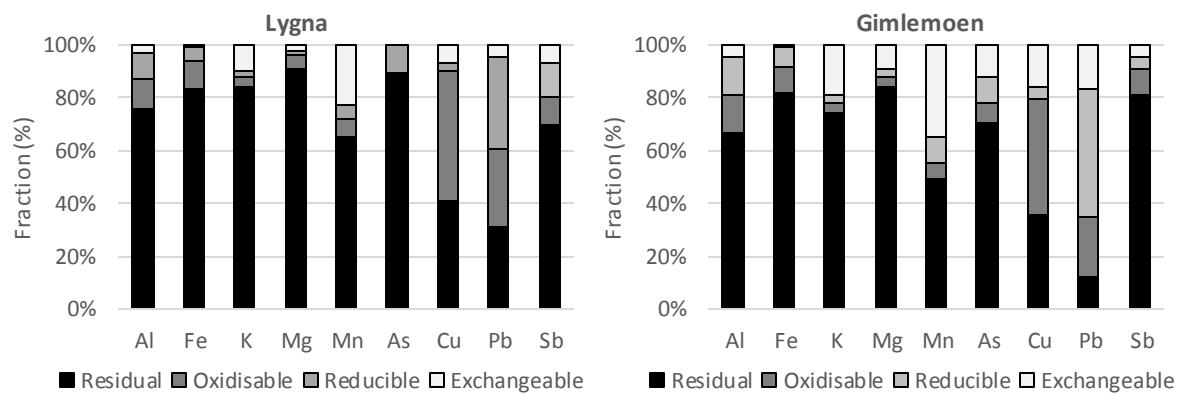


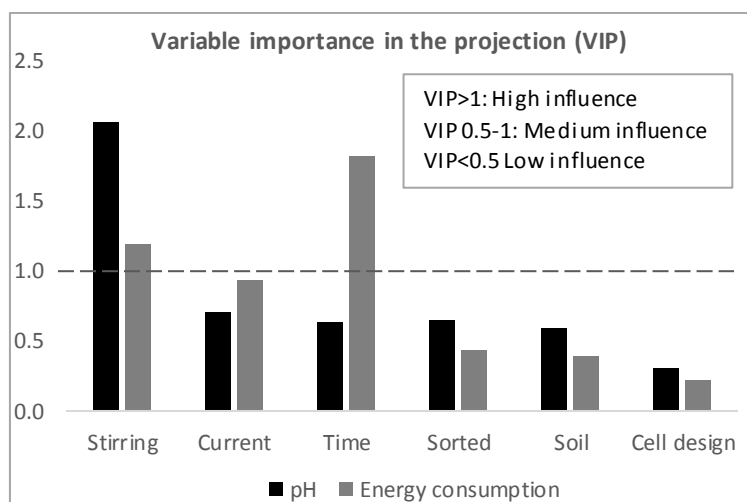
Figure 1: The four set-ups of the electrochemical cell: a). Stationary 2-compartment cell; b). Stirred 2-compartment cell; c). Stationary 3-compartment cell; d). Stirred 3-compartment cell.



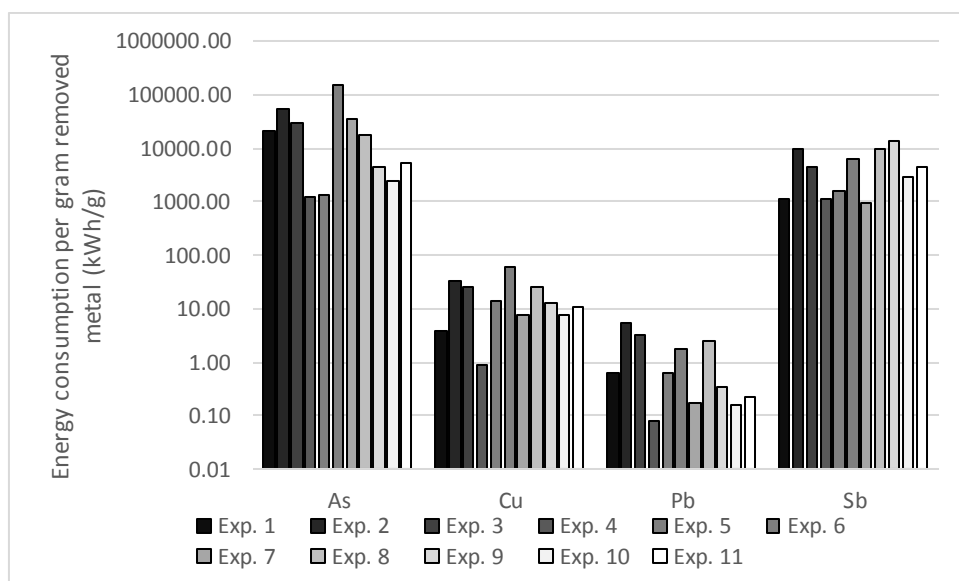
**Figure 2: The fraction of metal bound in the soil textures clay and silt, sand and gravel for the two experimental soils from Lygna and Gimlemoen shooting grounds, respectively.**



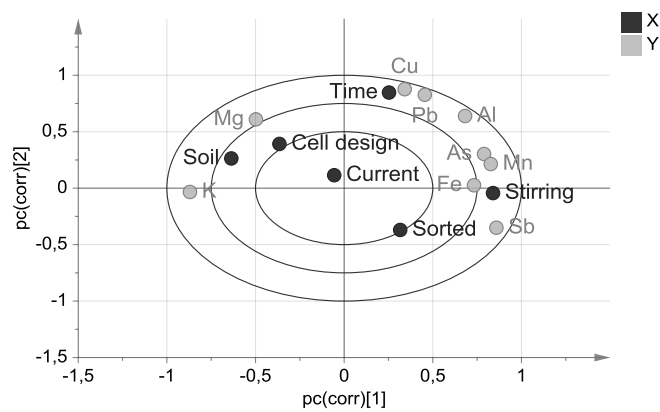
**Figure 3: Metal speciation for the two experimental soils from Lygna and Gimlemoen shooting grounds, respectively.**



**Figure 4: Variable importance in the projections (VIP) values for models of pH (R<sup>2</sup><sub>Y</sub> 0.97; Q<sup>2</sup> 0.81) and energy consumption (R<sup>2</sup><sub>Y</sub> 0.80; Q<sup>2</sup> -0.1). The VIP values (unitless) were calculated for each variable by summing the squares of the PLS loading weights. High VIP values (>1) represent high influence of the variable(s) in the model, and VIP values <0.5 indicate low influence of the variable(s) on the model.**



**Figure 5: Energy consumption per quantity of removed As, Cu, Pb and Sb in the electrochemical remediation experiments. Logarithmic scale.**



**Figure 6: Weight plot of the PLS model (R2Y 0.84; Q2 0.50) of all metals. The weight vectors have been scaled and are plotted against each other. The plot illustrates the independent contribution of X matrix variables to the systematic variation in the responses (here the metals). Metals located close to one another are correlated. Metals and variables located in the same quadrant are positively correlated.**

Table 1: Experimental settings for the EDR experiments.

Experiment	Current (mA)	Treatment time (days)	Stirred/Stationary	Cell design	Sorting	Soil
1	4	7	Stirred	2-compartment	<2 mm	Gimlemoen
2	10	7	Stationary	2-compartment	<4 mm	Lygna
3	4	35	Stationary	2-compartment	<2mm	Lygna
4	10	35	Stirred	2-compartment	<4 mm	Gimlemoen
5	4	7	Stirred	3-compartment	<4 mm	Lygna
6	10	7	Stationary	3-compartment	<2mm	Gimlemoen
7	4	35	Stationary	3-compartment	<4 mm	Gimlemoen
8	10	35	Stirred	3-compartment	<2mm	Lygna
9	7	21	Stationary	2-compartment	<4 mm	Gimlemoen
10	7	21	Stationary	2-compartment	<4 mm	Gimlemoen
11	7	21	Stationary	2-compartment	<4 mm	Gimlemoen

**Table 2: Soil characteristics and metal concentrations compared to the Norwegian soil quality criteria [39], where these are available. Class 1 – non-polluted (background concentrations); Class 2 – low pollutant concentrations (no adverse effects level); Class 3 – medium pollutant concentrations (Probable effects level); Class 4 – high pollutant levels (risk of adverse effects at long-term exposure); Class 5 – very high pollutant levels (risk of adverse effects at short-term exposure). Soil with concentrations higher than class 5 criteria is considered hazardous waste.**

Characteristic	Unit	Lygna	Gimlemoen	Standard deviation	Norwegian soil quality criteria (mg/kg)				
					Class 1	Class 2	Class 3	Class 4	Class 5
Carbonate	%	0.2	0.4	20%					
Organic matter	%	12.6	12.7	8%					
Total carbon	%	13.6	17.3	14%					
pH		4.5	5.5	1%					
Conductivity	mS/cm	69.4	77.6	8%					
Grain size distribution									
Clay (<2 $\mu$ m)	%	12.9	8.7						
Silt (2-63 $\mu$ m)	%	35.5	22.5						
Sand (63 $\mu$ m-1mm)	%	25.7	41.8						
Gravel (>1mm)	%	25.9	27.1						
Metal concentrations									
Al	mg/kg	10,280	7,700	4%					
Fe	mg/kg	15,760	19,800	20%					
K	mg/kg	1090	1,460	14%					
Mg	mg/kg	2070	2,370	7%					
Mn	mg/kg	270	271	20%					
As	mg/kg	3.0	14	7%	8	20	50	600	1000
Cd	mg/kg	0.2	0.40	15%	1.5	10	15	30	1000
Cr	mg/kg	15	14	20%	50	200	500	2800	25000
Cu	mg/kg	47	140	13%	100	200	1000	8500	25000
Ni	mg/kg	11	17	17%	60	135	200	1200	25000
Pb	mg/kg	450	3,200	9%	60	100	300	700	2500
Sb	mg/kg	5	17	9%					
Zn	mg/kg	46	150	13%	200	500	1000	5000	25000

**Table 3: Removal efficiencies, final pH and energy consumption in the electrodynamic remediation experiments. For the replicate experiments 9-11, average values and standard deviations are given. A single factor ANOVA analysis (n=3) indicated that there are no significant differences in the metal removals in experiment 9-11.**

Experiment	Removal efficiencies (%)									Final pH	Energy consumption kWh/kg
	Al	Fe	K	Mg	Mn	As	Cu	Pb	Sb		
1	8	2	12	6	43	1	17	8	5	2.5±0.03	0.04
2	2	1	10	4	34	<1	21	14	1	3.3±0.03	0.29
3	14	3	12	7	38	1	33	30	2	3.1±0.03	0.44
4	35	10	6	12	43	2	75	69	2	1.4±0.01	0.22
5	12	5	4	2	45	2	9	16	14	2.6±0.03	0.04
6	1	2	19	11	31	<1	4	6	<1	3.3±0.03	0.30
7	9	1	18	13	36	<1	32	38	<1	3.6±0.04	0.38
8	20	6	4	9	47	3	56	78	6	1.7±0.02	0.58
9-11	5±0.8	1±0.8	14±2.0	13±1.2	37±3	<1	24±1	24±0.5	<1	3.5±0.04	0.37±0.07

**Table 4: Variable importance based on individual PLS models for each metal (R<sup>2</sup><sub>Y</sub> 0.60-0.99; Q<sup>2</sup> 0.3-0.8). The relative importance is presented as 'high' (VIP>1), 'medium' (VIP 0.5-1.0) and 'low' (VIP <0.5). For variables of medium-high influence, regression coefficients were used to assign the influence as positive/negative sign on the PLS models. For the discrete variables, stirring, sorting (<2mm), the Gimlemoen soil and 3-compartment cell were assigned (+1) in the models and stationary set-up, sorting (<4mm), the Lygna soil and 2-compartment cell were assigned (-1) in the models. Based on the sign of the regression coefficients, the experimental settings that achieve the highest removal of each metal during electrochemical remediation are given for variables of medium-high influence.**

<i>Metal</i>	<i>Time</i>	<i>Current</i>	<i>Stirred/stationary set-up</i>	<i>Sorted</i>	<i>Soil</i>	<i>Cell design</i>
Al	<b>High (+)</b>	Medium (-)	<b>High (+)</b>	Low	Medium (-)	Low
	<i>35 days</i>	<i>4 mA</i>	<i>Stirred</i>		<i>Lygna</i>	
Fe	Low	Medium (+)	<b>High (+)</b>	Medium (+)	Medium (-)	Medium (+)
		<i>10 mA</i>	<i>Stirred</i>	<i>&lt;2mm</i>	<i>Lygna</i>	<i>3-C</i>
K	Low	Low	<b>High (-)</b>	Low	<b>High (+)</b>	Medium (-)
			<i>Stationary</i>		<i>Gimlemoen</i>	<i>2-C</i>
Mg	<b>High (+)</b>	Medium (+)	Medium (-)	Low	<b>High (+)</b>	Low
	<i>35 days</i>	<i>10 mA</i>	<i>Stationary</i>		<i>Gimlemoen</i>	
Mn	Medium (+)	Low	<b>High (+)</b>	Low	Medium (-)	Low
	<i>35 days</i>		<i>Stirred</i>		<i>Lygna</i>	
As	<b>High (+)</b>	Low	<b>High (+)</b>	Low	<b>High (-)</b>	Low
	<i>35 days</i>		<i>Stirred</i>		<i>Lygna</i>	
Cu	<b>High (+)</b>	Low	Medium (+)	Medium (+)	Low	Medium (-)
	<i>35 days</i>		<i>Stirred</i>	<i>&lt;2mm</i>		<i>2-C</i>
Pb	<b>High (+)</b>	Low	Medium (+)	Medium (+)	Low	Low
	<i>35 days</i>		<i>Stirred</i>	<i>&lt;2mm</i>		
Sb	Low	Medium (-)	<b>High (+)</b>	Low	<b>High (-)</b>	Medium (+)
		<i>4 mA</i>	<i>Stirred</i>		<i>Lygna</i>	<i>3-C</i>

**Highlights**

- 75-78% Cu and Pb were removed from shooting range soil by electrodialectic remediation
- Removal of other metals in the natural soil matrix was low during the treatment
- A stirred set-up improved the metal removal and reduced the energy consumption
- Remediation can be designed to target Cu and Pb, and limit removal of other metals

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