DTU Library

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

Pedersen, Kristine B.; Jensen, Pernille Erland; Ottosen, Lisbeth M.; Barlindhaug, John

Accepted Manuscript

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

Kristine B. Pedersen, Pernille E. Jensen, Lisbeth M. Ottosen, John Barlindhaug

Please cite this article as: Kristine B. Pedersen, Pernille E. Jensen, Lisbeth M. Ottosen, John Barlindhaug, Influence of electrode placement for mobilising and removing metals during electrodialytic remediation of metals from shooting range soil, *Chemosphere* (2018), doi: 10.1016/j. chemosphere.2018.07.063

1 **Influence of electrode placement for mobilising and removing metals during electrodialytic**

2 **remediation of metals from shooting range soil**

3 *Kristine B. Pedersen[a], Pernille E. Jensen[b], Lisbeth M. Ottosen[b], John Barlindhaug[,c]*

4 * corresponding author: e-mail: kristine.pedersen@akvaplan.niva.no, tel. +47 928 799 28

5 [a] Akvaplan-niva AS, Fram Centre - High North Research Centre for Climate and the Environment,

6 Hjalmar Johansens gate 14, 9007 Tromsø, Norway

7 [b] Arctic Technology Centre, Department of Civil Engineering, Technical University of Denmark,

8 Building 118, 2800 Lyngby, Denmark

9 [c] Perpetuum AS, Stakkevollvegen 41, 9010 Tromsø, Norway

10

11 **Abstract**

12 Electrodialytic remediation was applied to a shooting range soil to investigate the influence of

13 electrode placement on the removal and binding of metals during the treatment. The set-up

14 was based on a 2-compartment cell, in which the cathode was separated from the soil by a

15 cation exchange membrane and the anode was placed directly in the soil, thereby introducing

16 protons and oxygen directly in the soil. Mobilisation of metals from less available fractions

17 (oxidisable and residual) in the soil occurred, due to oxidation/dissolution of insoluble/soluble

18 organic matter and possibly metal oxides in the residual fraction.

19 The transport via electromigration out of the soil and/or re-precipitation in other fractions of

20 the soil (oxidisable, reducible, exchangeable) depended on the metal. More than 30% of the

21 initial content of Mn, Cd, Cu, Pb and Zn and less than 20% of the initial content of Al, Fe, K, Mg,

22 As, Cr and Ni was transported out of the soil. By decreasing the distance between the

23 electrodes from 3.0 to 1.5 cm, the removal of the targeted metal for remediation, Pb, was

24 improved by more than 200%, from 14 to 31%. A similar removal could be achieved in

25 experiments with long distance between electrodes (3.0 cm) by increasing the current intensity

26 from 4 to 10 mA and/or the remediation time from 7 to 35 d. The experiments showed that the

27 design and optimisation of electrodialytic remediation depends on the targeted metal and

28 metal partitioning.

29

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

31

32 **1. Introduction**

33 The in-situ remediation of polluted fine-grained soils remains a challenge due to the low

34 hydraulic conductivity. Electrokinetics has for the past 30 y been recognized to deal with this

35 specific challenge along with the site-specific conditions related to local geochemical processes,

36 pollutant composition and concentration (Virkutyte et al., 2002; Alshawabkeh, 2009). The

37 principle of electrokinetic remediation is to apply a DC electric field of low intensity to the

38 polluted soil, thereby forming an acidic front at the anode and an alkaline front at the cathode

39 due to electrolysis reactions at the electrodes. The acidic front prevails, desorbing metals along

40 its path towards the cathode. Electromigration has been recognized as the most important

41 transport pathway of metals in electrokinetic remediation and charged metals and complexes

42 are transported to the electrode of opposite charge (Acar and Alshawabkeh, 1993). In the zone

43 between the acidic and alkaline fronts, precipitation of metals occurs. Accordingly some early

44 optimization efforts to increase the removal of metals were related to preventing the alkaline

45 front from forming, for instance by adding agents to the catholyte to neutralize hydroxyl ions

46 produced at the cathode (Puppala et al., 1997; Zhou et al., 2004, 2005), or by using ion

47 exchange membranes (electrodialytic remediation) (Hansen et al., 1997). By applying ion

48 exchange membranes instead of passive membranes, the transport of ions between the

49 electrolytes/electrodes and the soil matrix can be controlled. In the traditional 3- compartment

50 set-up, ion exchange membranes have been applied to prevent protons from the anode and

51 hydroxyl ions from the cathode from entering the soil matrix (Ottosen et al., 1997). Water

52 splitting at ion-exchange membranes occur at a limiting current at which there are not enough

53 ions in the immediate vicinity of the membranes to carry the current. Due to the negative

54 charge of clay, there is an abundance of cations compared to anions in soils and for this reason,

55 depletion of anions adjacent to the anion-exchange membrane will occur at a lower current

56 than depletion of cations at the cation-exchange membrane. The limiting current density

57 depends on the membrane and solution properties. In electrodialytic remediation the limiting

58 current has been exploited to ensure acidification of the soil, by water splitting at the anion

59 exchange membrane (Ottosen et al., 2000), adjacent to the anode, and by proton leakage from

60 the cation exchange membrane (Nystroem et al., 2005).

61 In recent years, optimisation efforts in electrodialytic remediation have included the

62 development of the 2-compartment cell design, in which the anode is placed directly in the soil

63 compartment, introducing protons directly in the compartment. A cation exchange membrane

64 separating the soil- and cathode compartment prevents hydroxyl ions produced at the cathode

65 from entering the soil (Fig. 1a) (Ebbers et al., 2015). In comparison with the traditional 3-

66 compartment cell design, faster acidification and energy efficiency are among the advantages

67 observed in the 2-compartment cell design (Ebbers et al., 2015; Pedersen et al., 2015b). In

68 addition, it has been speculated whether metals bound in organic matter are more readily

69 released by oxidation in the 2-compartment cell due to the introduction of oxygen from the

70 electrolysis reaction (Pedersen et al., 2015a). The 2-compartment cell has been tested in a

71 stirred set-up, but has yet to be tested in a stationary set-up. The latter is relevant for in-situ

72 remediation when minimal physical disturbance to the land at a given site is desirable,

73 providing that the site conditions allow time and space for the remediation.

74 In previous stationary electrokinetic set-ups, the anode has been separated from the soil

75 compartment and the influence of placing the anode directly in the soil on the metal

76 mobilisation has not yet been tested. Metal speciation has previously been found to affect the

77 extent to which metals desorb from the soil matrix under the influence of an electric field (Kim

78 and Kim, 2001; Suèr et al., 2003; Zhou et al., 2005; Jensen et al., 2007), the effect of introducing

79 oxygen directly into the soil via electrolysis reactions on the anode, has however not been

80 investigated.

81 In this study, lab-scale experiments were performed to investigate the influence of the

82 placement of electrode, on the mobilisation of metals near the anode as well as the

83 perpendicular distance from the anode was studied and related to important variables in the

84 electrokinetic remediation process, i.e. current density and remediation time. This also included

85 an assessment of the influence on metal fractionation before and after the electrodialytic

86 treatment. To obtain an understanding of the changes in the binding of metals in the soil,

87 environmental priority metals as well as selected trace elements were included.

88 **2. Methods and materials**

89   *2.1 Soil*

90   The soil used in this study was sampled from the top 10 cm of the earthen backstop from a

91   former military shooting range in Lygna, Norway. Prior to analysis and electrodialytic

92   experiments, the soil was sieved and particles larger than 4 mm were separated and disposed

93   of.

94   The soil characteristics have been analysed in a previous study (Pedersen et al., 2018) and are

95   summarised in table 1. The concentrations of the priority metals (As, Cd, Cr, Cu, Ni, Pb and Zn)

96   were compared to the Norwegian quality criteria for soil of good environmental quality (Class

97   2). The only metal exceeding the criteria was Pb with a concentration in the range of Norwegian

98   quality class 4 soil (300-700 mg kg^{-1} of Pb). Quality Class 4 soils are characterised as 'poor

99   environmental quality', with potential adverse effects on human health and risk of dispersion

100   into the environment.

101   **Table 1**

102   *2.2 Analysis*

103   Metal concentrations (Al, Fe, K, Mg, Mn, As, Cd, Cr, Cu, Ni, Pb, Zn) were measured before and

104   after the electrodialytic remediation by Inductively Coupled Plasma - Optical Emission

105   Spectrometry (ICP-OES) after digestion (Norwegian standard NS4770). The sampled soil was

106   dried at 105°C and crushed. 1.0 g of the soil and HNO_3 (9 M, 20 mL) were autoclaved (200 kPa,

107   120 °C, 30 min). Solid particles were subsequently removed by vacuum filtration through a 0.45

108   μm filter and the liquid was diluted to 100mL. Triple determination were made.

109   *Sequential extraction* was made in four steps based on the improvement of the three-step

110   method (Rauret et al., 1999) described by Standards, Measurements and Testing Program of

5

111   the European Union. Air-dried soil (0.5 g) was first extracted with acetic acid (0.11 M, 20 mL,

112   pH3) for 16 h; secondly with hydroxylammonium chloride (0.1 M, 20 mL; pH2) for 16 h; thirdly

113   with hydrogen peroxide (8.8 M, 5 mL) for 1 h, followed by extraction at 85 $^{\circ}$C for 1 h,

114   evaporation of liquid at 85°C, and subsequent extraction of the cooled solid fraction with

115   ammonium acetate (1 M, 25 mL, pH 2) for 16 h; and fourthly the remaining solid particles were

116   analysed for metal content after digestion. Liquids were measured for metals by ICP-OES. Triple

117   determination was made.

118   *2.3 Electrodialytic remediation*

119   *2.3.1 Electrodialytic cell design*

120   The set-up and principles of the 2-compartment electrodialytic cell used in this study is

121   illustrated in fig. 1. The cell design consisted of an electrolyte compartment (catholyte) and a

122   compartment containing the soil. The cell compartments were manufactured from Plexiglas®

123   and the dimensions were: length of electrolyte compartment 3.5 cm; length of soil

124   compartment 1.5 or 3.0 cm; inner diameter of all compartments 8 cm. Ionics supplied the

125   cation exchange membrane (CR67 HUY N12116B). The catholyte was NaNO$_3$ (0.01 M) adjusted

126   to pH 2 by HNO$_3$ (5 M). The catholyte (500 mL) was circulated (Pan World pumps) through a 500

127   mL glass bottle at flow rates of 30 mL min^{-1}. Circulation of the catholyte allows for the removal

128   of gasses generated at the electrode, ensures low polarization at the electrode and minimizes

129   concentration gradients (Sun et al., 2012). Platinum coated titanium electrode was used as a

130   cathode, a titanium coated mesh (height 4 cm; width 8 cm) was used as anode and a power

131   supply (Hewlett Packard E3612A) maintained a constant DC current.

132   **Fig. 1**

133   After the electrodialytic experiments, the soil was cut longitudinal into three slices (Fig. 1b).

134   Slice 1 included the top section of the cell, not in direct contact with the anode (25% of the

135   total amount of soil). Slice 2 included the middle part of the cell, in contact with the anode

136   mesh in the left side of the cell (50% of the total amount of soil). Slice 3 included the bottom

137   section of the cell, not in direct contact with the anode (25% of the total amount of soil). Soil

138   from each slice was homogenised by the use of a mortar. Subsequently soil was sampled for

139   total metal concentration analysis by ICP-OES and sequential extraction analysis (section 2.2).

140   The membrane and electrodes were rinsed in HNO_3 (5M) overnight and the heavy metal

141   concentrations in the rinsing liquids as well as in the catholyte were measured by ICP-OES.

142   *2.3.2 Electrodialytic experiments*

143   The variables tested were distance between electrodes, current density and remediation time.

144   The distance between the electrodes was measured as the distance between the cation

145   exchange membrane and the anode mesh (i.e. the length of the soil compartment). The

146   objective of the study was to investigate the influence of the anode placement, with the focus

147   of analysing effects on the metal partitioning, a short distance between the electrodes was

148   chosen (1.5/3.0 cm). The experimental settings are given in table 2.

149   The removal percentages of metals were calculated as the fraction of metal removed compared

150   to the total amount of metal at the end of the experiments. The calculation of metals removed

151   were based on the metal concentrations in the rinsing liquids after the electrodialytic

152   experiments (cathode, catholyte and membrane).

153   The power consumption in Wh (E) was calculated as:

7

154 $$\int_{t=0}^{t} E = VI\,dt$$

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

156 time (h).

157 **3. Results and discussion**

158 *3.1 Influence of experimental settings on the removal of metals*

159 Pb is the primary component in bullets (ca. 90%) and co-contaminants due to shooting range

160 activities include As, Cd, Cu, Ni, Sb and Zn (Sorvari, 2011; Sanderson et al., 2012; Seshadri et al.,

161 2017). Metallic fragments from bullets were not observed in the soil from the shooting range

162 and the low standard deviations of analysed potential pollutants (As, Cd, Cu, Pb and Zn)

163 confirmed this observation. The concentrations of As, Cd, Cu, Ni and Zn were low in relation to

164 the soil quality criteria, but may be elevated compared to the natural background conditions.

165 Anthropogenic metal sources can change the metal partitioning in the soil (Wuana and

166 Okieimen, 2011). Based on the pollutant sources at the site, the metal concentrations and

167 partitioning of Al, Fe, K, Mg, Mn and Cr are not expected to be impacted by the previous

168 activities.

169 The percentage of metals removed after the electrodialytic treatment depended on the metal.

170 The lowest percentages removed (<5%) were As, Cr and Fe and the highest observed removal

171 (>40%) was Cd and Cu (table 2). This is in line with previous findings showing that As and Cr are

172 less mobile than Cd and Cu under the influence of an electric field (Hansen et al., 1997; Ottosen

173 et al., 2009; Lu et al., 2012; Yang et al., 2014). Within the experimental space studied, the

8

174　influence of variables on the removal percentages varied with the metal (table 2). For most of

175　the metals, changing the experimental settings did not significantly influence the removal

176　percentage. Considerably deviating from this trend, a higher current density increased the

177　removal of Cu and Pb by 270% and 220% (exp. 1 and exp. 3). Increasing the distance between

178　the electrodes from 1.5 to 3.0 cm halved the removal of Cu and Pb (exp. 1 and 2). Similar

179　removal of Cu and Pb was observed in exp. 3 (low current density, short distance between the

180　electrodes), and exp. 2 (high current density, long distance between the electrodes). Likewise,

181　by increasing the remediation time from 7 to 35 d it was possible to increase removal

182　percentages.

183　The experimental settings did not influence the final pH levels, and could be due to a high

184　buffer capacity related to Al/Fe oxides/hydroxides and high content of organic matter in the soil

185　at this pH level (Wang et al., 2015; Wang et al., 2017). The reason, that the metals, except Cu

186　and Pb, had similar removal percentages in all experiments could be related to the same final

187　pH levels (table 2). The deviating trend for Cu and Pb suggests a difference in binding pattern

188　and possibly indication of anthropogenic impact. The solid-solution partitioning (Kd) of metals

189　in soils vary with metal concentration, e.g. Kd for Pb increases while Kd for Zn decreases with

190　increasing anthropogenic impact (Sauvé et al., 2000).

191　**Table 2**

192　The consumption of energy per mass of soil was lowest in exp. 2 (table 2). Consumption of

193　energy per mass of soil increased with higher current density (exp. 1 vs. exp. 3) and with a

194　longer remediation time (exp. 2 vs. exp. 4). Doubling the amount of soil to be remediated did

195　not increase the energy consumption per mass of soil (exp. 1 vs. exp. 2). For the targeted metal

9

196   for remediation, Pb (table 1), highest removal was in exp. 1 and 4. Despite the higher

197   consumption of energy, the energy required to remove Pb was however lowest in exp. 1 and

198   exp. 4. If the design of the electrodialytic removal of Pb includes energy consumption, optimal

199   conditions (high removal, low energy consumption) can be achieved by either applying short

200   distance between electrodes or applying high current density and remediation time in designs

201   with long distance between electrodes.

202   *3.2 Removal of metals in different fractions in soil*

203   Electrodialytic treatment and experimental settings influenced the metal fractionation of the

204   potential pollutant metals. The naturally occurring metals (Al, Fe, K, Mg, Mn, Cr and Ni)

205   displayed some differences in metal fractionation after the electrodialytic treatment (Fig. 2).

206   The fractionation of Al, Fe and Mg was similar in exp. 1-3, with some differences in exp.4

207   indicating that a long remediation time (35 d) at high current (10 mA) changed the mobilisation

208   in the studied soil. For K, the removal was similar in the four experiments, while the biggest

209   alteration to the metal binding was observed in exp. 2 and exp. 4 with higher quantities of the

210   metal mobilised from the residual fraction and precipitating in the more available fractions of

211   the soil.

212   The removal of Mn was not influenced by the experimental design, the electrodialytic

213   treatment was however observed to influence metal fractionation. The partitioning in the soil

214   after all electrodialytic treatments was however similar, indicating that the experimental

215   settings did not influence the removal or mobilisation of Mn in the soil. The amount of Mn

216   bound in the residual fraction was reduced by a third and the exchangeable fraction halved

217   during the treatment, suggesting that Mn released from the residual fraction, either from

10

218 insoluble organic matter or well-crystalline oxides, was largely transported by electromigration

219 out of the soil. Less than 1% of Cr was removed from the soil during the electrodialytic

220 remediation, it was however observed that 7-17% of the Cr originally bound in the residual

221 fraction was transferred to more available fractions, especially the oxidisable fraction. For both

222 Cr and Mn, re-adsorption from the residual fraction of the soil could be related to the high

223 content of organic matter in the soil. Previous studies have found that organic acids increase

224 metal mobility at low pH (<4) (Renella et al., 2004; Wang et al., 2013; Vítková et al., 2015) and

225 could have desorbed Cr and Mn bound in insoluble organic matter or stable minerals, present

226 in the residual fraction (Tessier et al., 1979). Depending on the metal mobility and affinity to

227 compounds in the soil, the metals could be transported through the soil with limited re-

228 precipitation, as Mn, or re-precipitated, as was observed for Cr in the oxidisable fraction. Humic

229 acids are known to form stable Cr complexes and is insoluble, immobile and unreactive in the

230 pH ranges 2.7-4.5, while other organic acids such as citric acid and fulvic acid form soluble Cr

231 complexes (Kotaś and Stasicka, 2000).

232 **Fig. 2**

233

234 For Cd, the fractionation was similar in exp. 1-3, with some differences in exp. 4, indicating that

235 a long remediation time at a high current, to a higher degree influenced the metal

236 fractionation. Less Cd was bound in the oxidisable fraction in exp. 4 suggesting higher oxidation

237 of Cd-organic complexes, increasing the desorption of Cd from the soil (Zhao et al., 2014).

238 The electrodialytic remediation influenced the removal and fractionation of Cu in the soil. The

239 original partitioning of 90% of the Cu in the oxidisable and residual fractions was reduced to 45-

240 70% during the electrodialytic treatments. This is an indication of oxidation of soluble as well as

241 insoluble organic matter releasing Cu in the process, and potential oxidation of Cu minerals in

242 the residual fraction. The Cu sulphides chalcopyrite and bornite are for instance found in the

243 residual rather than oxidisable fraction of the sequential extraction regime (Dold, 2003). Some

244 of the released Cu from insoluble organic matter was likely re-precipitated in the oxidisable

245 fraction due to the high affinity of Cu to organic matter (Kinniburgh et al., 1999), and adsorbed

246 to clay minerals in the exchangeable fraction.

247 After the electrodialytic remediation experiments, the initial content of Pb in the oxidisable and

248 residual fractions was reduced from 60% to 22-30%. Release of Pb could take place by oxidation

249 of soluble and insoluble organic matter. Due to the high affinity of Pb to organic matter

250 (Eggleton and Thomas, 2004) some of the Pb in solution may have re-precipitated in the

251 oxidisable fraction. More than 30% of the Pb was bound in the reducible fraction after the

252 experiments, indicating that substantial reduction of Mn/Fe oxides during the treatment did

253 not occur and that some of the released Pb from the oxidisable and residual fractions may have

254 re-precipitated in the reducible fraction. Pb has high affinity to be adsorbed to Fe, Mn and Al

255 oxides, and co-precipitated with Fe and Mn oxides (Bradl, 2004; Favas et al., 2011).

256   The reduction of Zn bound in the oxidisable and residual fractions was not as pronounced as

257   observed for Cu and Pb (Fig. 2). Most of the removal observed during the electrodialytic

258   remediation originated from the residual and oxidisable fractions indicating oxidation of Zn-

259   organic complexes and potential dissolution of stable Zn minerals. In exp. 4 re-precipitation of

260   Zn occurred in the exchangeable fraction and could be related to Zn in acidic medium adsorbing

261   to clay minerals by cation exchange processes (Fotovat and Naidu, 1998).

262   Previous studies have shown that electrokinetic remediation of soil and sediments enhances

263   natural weathering processes (Kirkelund et al., 2010). Electrodialytic treatment has also been

264   shown to remove naturally occurring metals in soil and sediment, the removal percentages

265   depend on the mobility of the metal and how the metal is bound in the soil minerals (Jensen et

266   al., 2006; Pedersen et al., 2016). In this study, low removal percentages (<15%) as well as low

267   influence of experimental settings on metal fractionation was observed for most of the

268   naturally occurring metals Al, Fe, K, Mg, Cr, Ni. An exception to this was Mn, which had higher

269   removal percentages (31-38%) and metal fractionation changed after electrodialytic treatment.

270   This indicates that Mn desorbed/dissolved and that the electrodialytic conditions increased the

271   mobility of Mn compared to the other trace metals. This observation is in line with other

272   studies showing that under the influence of an electric field, Mn is mobilised to a higher degree

273   than other trace metals (Jensen et al., 2006; Pedersen et al., 2017).

274   The metals Cd, Cu, Pb and Zn had the highest removal percentages (table 2). The initial

275   concentrations of Cd, Cu and Zn (table 1) were below levels considered as pollution. However,

276   since the metals constitute part of bullets, the concentrations may be elevated compared to

277   the natural background concentrations at the site. The initial metal fractionation of Cd, Cu and

278   Zn was comparable to that reported in literature (Tipping et al., 2003). Metal fractionation of

279   Cd and Zn was not significantly affected by the experimental settings indicating that pH rather

280   than the electrodialytic conditions controlled the mobilisation in the studied experimental

281   space. The metal fractionation of Cu was affected by the experimental settings indicating that

282   electrodialytic conditions, e.g. acidification and redox affected the mobilisation. Based on the

283   observed trends for Cd, Cu and Zn, it is not possible to assess whether the initial concentrations

284   are background concentrations or affected by the shooting range activities. The high initial

285   concentration of Pb was a clear indication of anthropogenic impact.

286   In this study, most of the removal of Cu and Pb originated from the labile fractions of the soil

287   (oxidisable and residual). This could be due to the electrodialytic cell design and the soil

288   characteristics. As an effect of placing the anode directly in the soil, oxidation of insoluble and

289   soluble organic compounds could occur, thereby increasing the mobilisation of Cu and Pb. The

290   soil characteristics (high content of clay/silt and organic matter) may have enhanced the re-

291   precipitation of released metals, thereby preventing the electromigration of metals out of the

292   soil. This is in line with previous studies in which metals concentrations in the exchangeable

293   fraction increased during electrokinetic remediation, due to re-precipitation of metals from

294   dissolution of organic matter and minerals (Ribeiro and Mexia, 1997; Peppicelli et al., 2018).

295   *3.3 Influence of anode placement*

296   To evaluate the effect of the anode placement, the soil was sliced in three at the end of the

297   experiments. In the traditional 3-compartment set-up it was shown that the horizontal

298   transport of protons and metals through the soil during electrodialysis decreases with the

299   horizontal distance from the anode (Hansen et al., 1997). In this study, the anode was,

14

300 however, placed directly in the soil and instead of the usual practice of slicing the soil vertically,

301 perpendicularly to the electric field to assess the transport across the cell, the soil was sliced

302 longitudinal. This was done in order to investigate the possible influence of the direct contact of

303 anode with the soil (slice 2), on metal removal and partitioning in the soil, e.g. more

304 mobilisation due to electrolysis reactions. The pH was lowest in the middle part of the cell (slice

305 2, Fig. 3) with similar pH levels in other parts of the cell. The water content did not vary

306 significantly between the different parts of the cell. For this reason, slices 1 and 3 are expected

307 to show similar patterns in removal percentages of metals.

308 **Fig. 3**

309 For the metals Al, Mn, Cu and Pb differences in the removal percentages from different parts of

310 the cell were observed (Fig. 4). For Al, higher removal was observed from the middle part of the

311 cell (soil in direct contact with anode) and it is speculated whether this was due to dissolution

312 of the stable mineral aluminium hydroxide oxide, as electrolysis is a well-established technique

313 for extracting Al from bauxite (Gow and Lozej, 1993) and would occur adjacent to the anode.

314 The difference in removal of Mn from different parts of the cell is especially apparent in the two

315 experiments with short distance between the electrodes (exp. 1 and 3). Mn is known to be

316 among the more mobile metals in soil (Violante et al., 2010) and has low affinity for clay

317 minerals (Fijałkowski et al., 2012) compared to the other metals. The biggest difference in

318 removal from different parts of the cell was observed for Cu and Pb, with the highest removal

319 from the middle part of the cell. This could be related to the slightly lower pH observed in the

320 middle part of the cell (Fig. 4) or different redox conditions due to electrolysis reactions on the

321 anode.

15

322   **Fig. 4**

323   In order to evaluate the potential effect of the electrolysis reactions on the release of Cu and Pb

324   in the different parts of the cell, metal fractionation was used (Fig. 5). There was an observed

325   difference in the removal and mobilisation of Cu and Pb from the different parts of the cell,

326   most noticeable for Cu. There was more removal and desorption from the oxidisable and

327   residual fractions in slice 2 (anode directly in contact with soil) indicating more dissolution and

328   release of Cu/Pb due to a lower pH, redox conditions (oxidation) or that the electric field was

329   more efficient in this part of the soil. More re-precipitation in the reducible and exchangeable

330   fractions were observed in slices 1 and 3, and could be an indication of more efficient

331   electromigration in the middle part of the cell. The effect of experimental settings on the metal

332   fractionation in different parts of the soil was most obvious in exp. 1 and exp. 4, the

333   experiments for which the highest removal of Cu and Pb was observed (table 2). These

334   experiments had the highest charge transfer per quantity of soil, with the highest observed

335   effect on the metal fractionation as well as on the removal of Cu and Pb. As a reference to

336   these observations, the metal fractionation of Zn, known to be mobile under the influence of an

337   electric field, was used. More removal of the metal was observed in slice 2 (exp. 1 and exp. 4)

338   and the difference in metal fractionation between the different parts of the cell was mainly

339   related to the residual fraction. This could indicate dissolution of Zn minerals in the residual

340   fraction. Similar amounts of Zn were bound in the exchangeable, reducible and oxidisable

341   fractions in the different parts of the cell (Fig. 5). This indicates similar re-precipitation of Zn

342   across different parts of the soil and the electric field, the higher removal of Zn from the middle

343   part of the cell however indicating higher efficiency of the electric field. The placement of the

344   anode hence appears to influence the efficiency of electrodialytic remediation, affecting the

345   oxidation of minerals and organic matter, thereby influencing the mobilisation of metals bound

346   in the oxidisable and residual fractions and in addition affecting the efficiency of transport

347   through the cell.

348   **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.

References

373   Acar, Y.B., Alshawabkeh, A.N., 1993. Principles of electrokinetic remediation. Environ. Sci. Technol27,
374   2638-2647.
375   Alshawabkeh, A.N., 2009. Electrokinetic Soil Remediation: Challenges and Opportunities. Separ. Purif.
376   Technol. 44, 2171-2187.
377   Bradl, H.B., 2004. Adsorption of heavy metal ions on soils and soils constituents. J. Colloid Interf. Sci 277,
378   1-18.
379   Dold, B., 2003. Speciation of the most soluble phases in a sequential extraction procedure adapted for
380   geochemical studies of copper sulfide mine waste. J. Geochem. Explor. 80, 55-68.
381   Ebbers, B., Ottosen, L.M., Jensen, P.E., 2015. Comparison of two different electrodialytic cells for
382   separation of phosphorus and heavy metals from sewage sludge ash. Chemosphere 125, 122-129.
383   Eggleton, J., Thomas, K.V., 2004. A review of factors affecting the release and bioavailability of
384   contaminants during sediment disturbance events. Environ. Int. 30, 973-980.
385   Favas, P., Pratas, J., Gomes, M., Cala, V., 2011. Selective Chemical Extraction of Heavy Metals in Tailings
386   and Soils Contaminated by Mining Activity: Environmental Implications. J. Geochem. Explor. 111, 160-
387   171.
388   Fijałkowski, K., Kacprzak, M., Grobelak, A., Placek, A., 2012. The influence of selected soil parameters on
389   the mobility of heavy metals in soils. Inż. i Ochrona środowiska 15, 81-92.
390   Fotovat, A., Naidu, R., 1998. Changes in composition of soil aqueous phase influence chemistry of
391   indigenous heavy metals in alkaline sodic and acidic soils. Geoderma 84, 213-234.
392   Gow, N.N., Lozej, G.P., 1993. Bauxite. Geosci. Can. 20.
393   Hansen, H.K., Ottosen, L.M., Kliem, B.K., Villumsen, A., 1997. Electrodialytic remediation of soils polluted
394   with Cu, Cr, Hg, Pb and Zn. J. Chem. Technol. Biot.70, 67-73.
395   Jensen, P.E., Ottosen, L.M., Ferreira, C., Villumsen, A., 2006. Kinetics of electrodialytic extraction of Pb
396   and soil cations from a slurry of contaminated soil fines. J. Hazard. Mater.138, 493-499.
397   Jensen, P.E., Ottosen, L.M., Harmon, T.C., 2007. The effect of soil type on the electrodialytic remediation
398   of lead-contaminated soil. Environ. Eng. Sci.24, 234-244.
399   Kim, S.-O., Kim, K.-W., 2001. Monitoring of electrokinetic removal of heavy metals in tailing-soils using
400   sequential extraction analysis. J. Hazard. Mater.85, 195-211.
401   Kinniburgh, D.G., van Riemsdijk, W.H., Koopal, L.K., Borkovec, M., Benedetti, M.F., Avena, M.J., 1999. Ion
402   binding to natural organic matter: competition, heterogeneity, stoichiometry and thermodynamic
403   consistency. Colloids and Surfaces A: Physicochem. Eng. Aspects 151, 147-166.
404   Kirkelund, G.M., Ottosen, L.M., Villumsen, A., 2010. Investigations of Cu, Pb and Zn partitioning by
405   sequential extraction in harbour sediments after electrodialytic remediation. Chemosphere 79, 997-
406   1002.
407   Kotaś, J., Stasicka, Z., 2000. Chromium Occurrence in the Environment and Methods of Its Speciation.
408   Lu, P., Feng, Q., Meng, Q., Yuan, T., 2012. Electrokinetic remediation of chromium- and cadmium-
409   contaminated soil from abandoned industrial site. Separ. Purif. Technol. 98, 216-220.
410   Nystroem, G.M., Ottosen, L.M., Villumsen, A., 2005. Acidification of Harbor Sediment and Removal of
411   Heavy Metals Induced by Water Splitting in Electrodialytic Remediation. Separ. Purif. Technol. 40, 2245-
412   2264.

413   Ottosen, L.M., Hansen, H.K., Hansen, C.B., 2000. Water splitting at ion-exchange membranes and
414   potential differences in soil during electrodialytic soil remediation. J. Appl. Electrochem. 30, 1199-1207.
415   Ottosen, L.M., Hansen, H.K., Laursen, S., Villumsen, A., 1997. Electrodialytic Remediation of Soil Polluted
416   with Copper from Wood Preservation Industry. Environ. Sci. Technol. 31, 1711-1715.
417   Ottosen, L.M., Jensen, P.E., Hansen, H.K., Ribeiro, A., Allard, B., 2009. Electrodialytic Remediation of Soil
418   Slurry–Removal of Cu, Cr, and As. Separ. Purif. Technol. 44, 2245-2268.
419   Pedersen, K.B., Jensen, P.E., Ottosen, L.M., Barlindhaug, J., 2018. The relative influence of electrokinetic
420   remediation design on the removal of As, Cu, Pb and Sb from shooting range soils. Eng. Geol.238, 52-61.
421   Pedersen, K.B., Jensen, P.E., Ottosen, L.M., Evenset, A., Christensen, G.N., Frantzen, M., 2017. Metal
422   speciation of historic and new copper mine tailings from Repparfjorden, Northern Norway, before and
423   after acid, base and electrodialytic extraction. Miner. Eng.107, 100-111.
424   Pedersen, K.B., Jensen, P.E., Ottosen, L.M., Lejon, T., 2015a. An optimised method for electrodialytic
425   removal of heavy metals from harbour sediments. Electrochim. Acta 173, 432-439.
426   Pedersen, K.B., Lejon, T., Jensen, P.E., Ottosen, L.M., 2016. Applying multivariate analysis as decision
427   tool for evaluating sediment-specific remediation strategies. Chemosphere 151, 59-67.
428   Pedersen, K.B., Ottosen, L.M., Jensen, P.E., Lejon, T., 2015b. Comparison of 2-compartment, 3-
429   compartment and stack designs for electrodialytic removal of heavy metals from harbour sediments.
430   Electrochim. Acta 181, 48-57.
431   Peppicelli, C., Cleall, P., Sapsford, D., Harbottle, M., 2018. Changes in metal speciation and mobility
432   during electrokinetic treatment of industrial wastes: Implications for remediation and resource
433   recovery. Sci. Total Environ. 624, 1488-1503.
434   Puppala, S.K., Alshawabkeh, A.N., Acar, Y.B., Gale, R.J., Bricka, M., 1997. Enhanced electrokinetic
435   remediation of high sorption capacity soil. J. Hazard. Mater.55, 203-220.
436   Rauret, G., Lopez-Sanchez, J.F., Sahuquillo, A., Rubio, R., Davidson, C., Quevauviller, P., 1999.
437   Improvement of the BCR three step sequential extraction procedure prior to the certification of new
438   sediment and soil reference materials. J. Environ. Monitor. 1, 57-61.
439   Renella, G., Landi, L., Nannipieri, P., 2004. Degradation of low molecular weight organic acids complexed
440   with heavy metals in soil. Geoderma 122, 311-315.
441   Ribeiro, A.B., Mexia, J.T., 1997. A dynamic model for the electrokinetic removal of copper from a
442   polluted soil. J. Hazard. Mater.56, 257-271.
443   Sanderson, P., Naidu, R., Bolan, N., Bowman, M., McLure, S., 2012. Effect of soil type on distribution and
444   bioaccessibility of metal contaminants in shooting range soils. Sci. Total Environ. 438, 452-462.
445   Sauvé, S., Hendershot, W., Allen, H.E., 2000. Solid-Solution Partitioning of Metals in Contaminated Soils:
446   Dependence on pH, Total Metal Burden, and Organic Matter. Environ. Sci. Technol. 34, 1125-1131.
447   Seshadri, B., Bolan, N.S., Choppala, G., Kunhikrishnan, A., Sanderson, P., Wang, H., Currie, L.D., Tsang,
448   D.C.W., Ok, Y.S., Kim, G., 2017. Potential value of phosphate compounds in enhancing immobilization
449   and reducing bioavailability of mixed heavy metal contaminants in shooting range soil. Chemosphere
450   184, 197-206.
451   Sorvari, J., 2011. Shooting Ranges: Environmental Contamination A2 - Nriagu, J.O. Encyclopedia of
452   Environmental Health. Elsevier, Burlington, pp. 41-50.
453   Suèr, P., Gitye, K., Allard, B., 2003. Speciation and Transport of Heavy Metals and Macroelements during
454   Electroremediation. Environ. Sci. Technol37, 177-181.
455   Sun, T.R., Ottosen, L.M., Jensen, P.E., Kirkelund, G.M., 2012. Electrodialytic remediation of suspended
456   soil – Comparison of two different soil fractions. J. Hazard. Mater.203-204, 229-235.
457   Tessier, A., Campbell, P.G., Bisson, M., 1979. Sequential extraction procedure for the speciation of
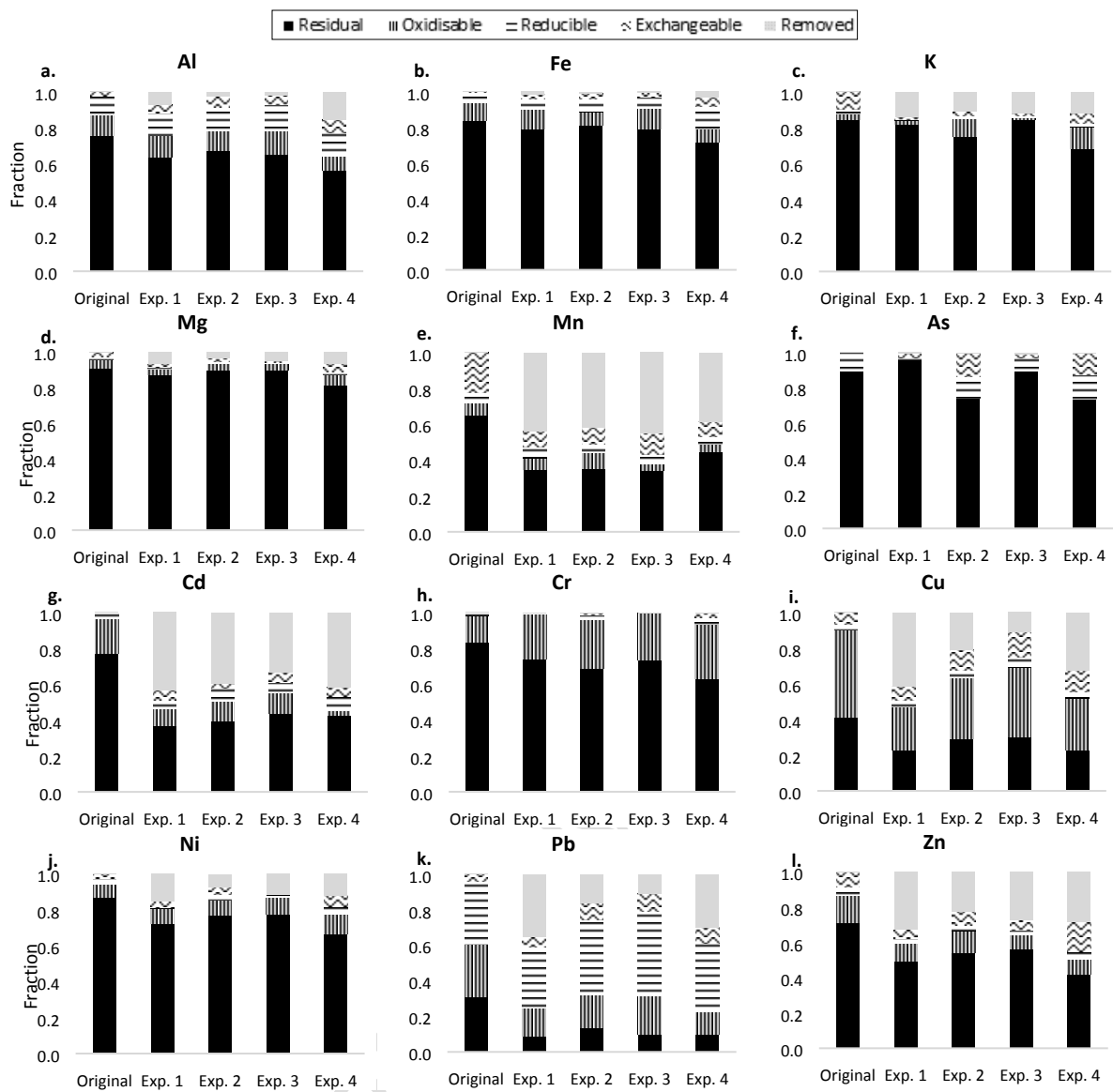458   particulate trace metals. Anal. Chem. 51, 844-851.

459 Tipping, E., Rieuwerts, J., Pan, G., Ashmore, M.R., Lofts, S., Hill, M.T.R., Farago, M.E., Thornton, I., 2003.
460 The solid–solution partitioning of heavy metals (Cu, Zn, Cd, Pb) in upland soils of England and Wales.
461 Environ. Pollut. 125, 213-225.
462 Violante, A., Cozzolino, V., Perelomov, L., Caporale, A., Pigna, M., 2010. Mobility and bioavailability of
463 heavy metals and metalloids in soil environments. J. Soil Sci. Plant Nut. 10, 268-292.
464 Virkutyte, J., Sillanpää, M., Latostenmaa, P., 2002. Electrokinetic soil remediation — critical overview.
465 Sci. Total Environ. 289, 97-121.
466 Vítková, M., Komárek, M., Tejnecký, V., Šillerová, H., 2015. Interactions of nano-oxides with low-
467 molecular-weight organic acids in a contaminated soil. J. Hazard. Mater. 293, 7-14.
468 Wang, J., Lv, J., Fu, Y., 2013. Effects of organic acids on Cd adsorption and desorption by two anthropic
469 soils. Front. Env. Sci. Eng. 7, 19-30.
470 Wang, X., Tang, C., Mahony, S., Baldock, J.A., Butterly, C.R., 2015. Factors affecting the measurement of
471 soil pH buffer capacity: approaches to optimize the methods. Eur. J. Soil Sci. 66, 53-64.
472 Wang, Y., Cheng, P., Li, F., Liu, T., Cheng, K., Yang, J., Lu, Y., 2018. Variable charges of a red soil from
473 different depths: Acid-base buffer capacity and surface complexation model. Appl. Clay Sci. 159 107-115.
474 Wuana, R.A., Okieimen, F.E., 2011. Heavy metals in contaminated soils: a review of sources, chemistry,
475 risks and best available strategies for remediation. Isrn Ecol. 20 pp.
476 Yang, J.-S., Kwon, M.J., Choi, J., Baek, K., O'Loughlin, E.J., 2014. The transport behavior of As, Cu, Pb, and
477 Zn during electrokinetic remediation of a contaminated soil using electrolyte conditioning. Chemosphere
478 117, 79-86.
479 Zhao, X., Jiang, T., Du, B., 2014. Effect of organic matter and calcium carbonate on behaviors of cadmium
480 adsorption–desorption on/from purple paddy soils. Chemosphere 99, 41-48.
481 Zhou, D.-M., Deng, C.-F., Cang, L., 2004. Electrokinetic remediation of a Cu contaminated red soil by
482 conditioning catholyte pH with different enhancing chemical reagents. Chemosphere 56, 265-273.
483 Zhou, D.-M., Deng, C.-F., Cang, L., Alshawabkeh, A.N., 2005. Electrokinetic remediation of a Cu–Zn
484 contaminated red soil by controlling the voltage and conditioning catholyte pH. Chemosphere 61, 519-
485 527.

486

487

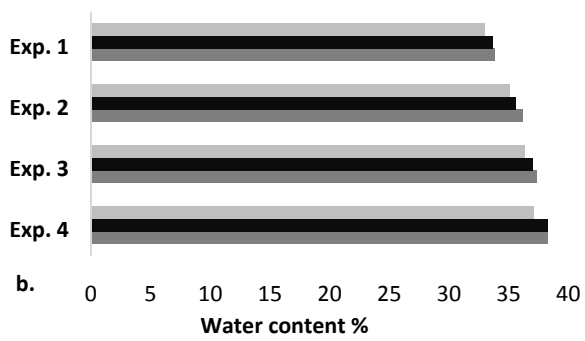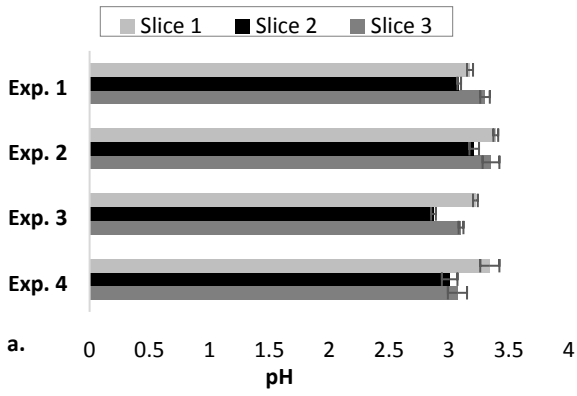Legend: ■ Residual   ⦀ Oxidisable   ⹀ Reducible   ⌇ Exchangeable   ▨ Removed

a. **Al**

b. **Fe**

c. **K**

d. **Mg**

e. **Mn**

f. **As**

g. **Cd**

h. **Cr**

i. **Cu**

j. **Ni**

k. **Pb**

l. **Zn**

a.

b.

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.

Characteristic	Unit	Value	Standard deviation	Norwegian quality criteria for soil class 2
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