



Applying multivariate analysis as decision tool for evaluating sediment-specific remediation strategies

Pedersen, Kristine B.; Lejon, Tore; Jensen, Pernille Erland; Ottosen, Lisbeth M.

Published in:
Chemosphere

Link to article, DOI:
[10.1016/j.chemosphere.2016.02.063](https://doi.org/10.1016/j.chemosphere.2016.02.063)

Publication date:
2016

Document Version
Peer reviewed version

[Link back to DTU Orbit](#)

Citation (APA):
Pedersen, K. B., Lejon, T., Jensen, P. E., & Ottosen, L. M. (2016). Applying multivariate analysis as decision tool for evaluating sediment-specific remediation strategies. *Chemosphere*, 151, 59-67.
<https://doi.org/10.1016/j.chemosphere.2016.02.063>

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

1 Applying multivariate analysis as decision tool for evaluating 2 sediment-specific remediation strategies

3
4 Kristine B. Pedersen^{a,c}, Tore Lejon^{*a} Pernille E. Jensen^b and Lisbeth M. Ottosen^b

5 *Corresponding author: e-mail tore.lejon@uit.no; tel. +47 776 44736; fax. +47 776 44765

6 ^a Department of Chemistry, University of Tromsø, The Arctic University of Norway, Postbox
7 6050 Langnes, 9037 Tromsø, Norway.

8 ^b Arctic Technology Centre, Department of Civil Engineering, Technical University of
9 Denmark, Building 118, 2800 Lyngby, Denmark

10 ^c Akvaplan-Niva AS, Framsenteret, Postbox 6606 Langnes, 9296 Tromsø, Norway

11 12 **Abstract**

13 Multivariate methodology was employed for finding optimum remediation conditions for
14 electrodialytic remediation of harbour sediment from an Arctic location in Norway. The parts of the
15 experimental domain in which both sediment- and technology-specific remediation objectives were
16 met were identified. Objectives targeted were removal of the sediment-specific pollutants Cu and
17 Pb, while minimising the effect on the sediment matrix by limiting the removal of naturally occurring
18 metals while maintaining low energy consumption.

19 Two different cell designs for electrochemical remediation were tested and final concentrations of
20 Cu and Pb were below background levels in large parts of the experimental domain when operating
21 at low current densities (<0.12 mA/cm²). However, energy consumption, remediation times and the
22 effect on naturally occurring metals were different for the 2- and 3-compartment cells.

23 **Keywords:** Electrodialytic remediation, PLS, heavy metals, harbour sediments

24

25

26 Introduction

27 Human activities have always affected the environment but with the industrial revolution, this has
28 been accentuated and in contrast to early human activity, the problem reaches far beyond our local
29 environment. Despite efforts to develop technology that will minimize pollution, there is still a need
30 for treatment of already polluted water, soils, and sediments.

31 Sediments may contain complex mixtures of organic contaminants and/or heavy metals as pollution
32 originates from different sources, e.g. shipping, shipyards, discharge of sewage, spills and from land-
33 based activities. Depending on the nature of contamination and the location, it is sometimes
34 possible to immobilize contaminants by capping. However, if sediments result from dredging, ex situ
35 treatment will be necessary and to this end deep-sea dumping, aquatic containment and dumping at
36 landfills have been employed. By treatment of sediments it is possible to minimize the amount of
37 polluted material needing to be deposited (e.g. by removing coarser, less contaminated fractions) or
38 even to be able to reuse the sediments for other purposes (e.g. as construction material). The
39 selection of the most appropriate technology for the remediation of sediments/soils thus depends
40 on site-specific conditions, types of pollutants, pollutant concentrations and the end use of the
41 treated sediment (Rulkens et al., 1998; Mulligan et al., 2001).

42 Organic pollutants are effectively destroyed by thermal remediation techniques but certain heavy
43 metals (Hg, As and Cd) may be volatilized in the process and others (Mo and V) may become more
44 leachable due to oxidation (Rulkens, 2005). Bioremediation (Guevara-Riba et al., 2004; Tabak et al.,
45 2005) is one possible option, in which microorganisms are employed for immobilizing (White et al.,
46 1997) or mobilizing (Erüst et al., 2013) metals that are part of natural biochemical cycles. Water
47 soluble pollutants that are loosely bound to sediment particles may be solubilized before washing
48 (Löser et al., 2007; Bing et al., 2008) and heavy metals have also been removed by extraction with
49 strong acids (Dermont et al., 2008). Electrokinetic remediation offers another possibility that has
50 been employed for both organic contaminants (Gomes et al., 2012; Méndez et al., 2012; Fan et al.,
51 2016) and heavy metals (Gent et al., 2004; Kim et al., 2011; Iannelli et al., 2015).

52 Applying electrodialysis, removal efficiencies of >90 % of heavy metals have been achieved for waste
53 materials such as soil, sediments, fly ash, wood and sewage sludge (Ottosen et al., 1995; Ribeiro et
54 al., 2000; Ferreira et al., 2002; Jakobsen et al., 2004; Nystroem et al., 2005a) while maintaining low
55 energy consumption (Sun and Ottosen, 2012). Electrodialysis is based on the principles of
56 electrokinetic remediation and relies on an electric field of low current being applied to the polluted
57 material. Ion-exchange membranes are employed to control the transport of ions to and from the
58 polluted material. In this way acidification of the contaminated material causing mobilization of
59 metals bound in the sediment is ensured by either water splitting at the anion exchange membrane
60 (Ottosen et al., 2000) or by direct introduction of protons produced at the anode.

61 The need for developing tools for selecting the most appropriate remediation technology and
62 identifying the optimal site-specific remediation conditions is apparent. For this, different statistical
63 tools may prove valuable and in a recent report the use of factorial design in optimizing the
64 remediation of uranium polluted soils was reported (Radu et al., 2015). Another method is
65 projections onto latent structures (PLS) which has been extensively used in chemical synthesis
66 (Carlson and Carlson, 2005a) and also in studies of the influence of soil properties on PAH oxidation

67 (Jonsson et al., 2007) and for identifying the most relevant variables for electrochemical treatment
68 of sediments (Pedersen et al., 2015b; Pedersen et al., 2015c; Pedersen et al., 2015d).

69 PLS is a method suited for handling large data sets by calculating the quantitative relationship
70 between independent variables and responses. By arranging the observations (e.g. experimental
71 settings, sediment characteristics) in an X-matrix and the responses (e.g. removal of contaminants,
72 energy consumption) in a Y-matrix, the correlation may be calculated and optimal experimental
73 settings, within the experimental domain studied, may be identified. In contrast to regression
74 methods, PLS is based on projections, making it a robust method that tolerates missing data.

75 The focus of this study was demonstrating the applicability of PLS to a sediment-specific remediation
76 strategy for harbour sediment, exemplified by electrochemical remediation. PLS was employed to
77 determine optimal experimental settings in regard to the remediation objectives and was also used
78 to evaluate energy consumption in the different parts of the experimental domain.

79 **2 Methods and materials**

80 *2.1 Sediment analyses*

81 The sediment from Hammerfest harbour (40.17°N, 41.32°E), located in Norway, used in this study,
82 has previously been found to contain levels of Cu and Pb above background levels according to the
83 Norwegian sediment quality criteria (Pedersen et al., 2015a).

84 The sediment was from the top 10 cm of the seabed using a Van Veen grab in Hammerfest harbour,
85 Norway. The samples were kept cool during transport and stored in a freezer (-18°C) until analysed
86 or treated.

87 *Major elements and heavy metal concentrations* (Al, Fe, K, Mg, Mn, As, Cr, Cu, Ni, Pb, Zn) were
88 measured based on digestion (Norwegian standard NS4770). Sediment dried at 105°C (1.0g) and
89 HNO₃ (9M, 20mL) were autoclaved (200kPa, 120°C, 30 minutes). Solid particles were subsequently
90 removed by vacuum filtration through a 0.45 µm filter and the liquid was diluted to 100mL. Metal
91 concentrations in the liquid were measured by Inductively Coupled Plasma - Optical Emission
92 Spectrometry (ICP-OES).

93 *Carbonate* content was measured by treating dried sediment (5.0g) with HCl (3M; 20mL) and the
94 developed CO₂ was measured volumetrically in a Scheibler apparatus, calibrated with CaCO₃.

95 *Organic content* was based on loss of ignition on dried sediment (2.5g) being heated at 550°C for an
96 hour.

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

99 *Grain size distribution* was measured by wet sieving and dry sieving. Wet sediment (75g), distilled
100 water (350mL) and Na₄P₂O₇·10H₂O (0.1M, 10mL) was agitated for 24 hours. The slurry was then
101 sieved through a 63µm sieve and the fraction above 63µm was subsequently dried and sieved for 15
102 minutes in a mechanical shaker using sieves with screen openings of 0.063, 0.080, 0.125, 0.25, 1.0
103 and 2.0mm. The slurry fraction below 63µm was transferred to Andreasen pipette for gravitational

104 sedimentation. Stoke's law was used for measuring time required for particles to settle 20cm and
105 samples representing the sizes 40, 32, 16, 8, 4, 2 and 1µm were sampled.

106 *Sequential extraction* was made in four steps based on the improvement of the three-step method
107 (Rauret et al., 1999) described by Standards, Measurements and Testing Program of the European
108 Union. Air-dried sediment (0.5g) was first extracted with acetic acid (0.11M, 20mL, pH3) for 16
109 hours; secondly extracted with hydroxylammonium chloride (0.1M, 20mL; pH2) for 16 hours; thirdly
110 extracted with hydrogen peroxide (8.8M, 5mL) for 1 hour, followed by extraction at 85°C for 1 hour,
111 followed by evaporation of liquid at 85°C, subsequently the cooled solid fraction was extracted with
112 ammonium acetate (1M, 25mL, pH2) for 16h; and fourthly digestion on the remaining solid particles
113 was made, following the description above.

114 *2.3 Electrodialytic remediation experiments*

115 *2.3.1 Materials and procedure*

116 Two different electrodialytic remediation (EDR) cells were employed in the study. The set-up and
117 principles of the cell designs are illustrated in figure 1. The difference between the two is the
118 insertion of an anode compartment in the extensively used 3-compartment cell. Acidification has
119 been shown to occur faster in the 2-compartment cell and with a lower energy consumption. The
120 faster mobilisation of metals may result in relatively higher release of naturally occurring metals into
121 the liquid phase and for this reason the 3-compartment cell has in this study been used as a
122 reference. Stirring has proven more efficient than a stationary set-up (Pedersen et al., 2003; Ottosen
123 et al., 2012) and appears appropriate to apply for remediating dredged sediments. Other variables of
124 importance to the efficiency of EDR include sediment, cell design, current density and time
125 (Pedersen et al., 2015d; Pedersen et al., 2015e).

126 **Figure 1: EDR cell designs – the 3-compartment cell and the 2-compartment cell.**

127 The 2-compartment and 3-compartment cells used in the study were designed using the same
128 materials and sizes; the 3-compartment cells consisted of two electrolyte compartment and
129 between these a compartment containing the sediment suspension. The 2-compartment cell
130 consisted of one electrolyte compartment (catholyte) and a compartment containing the sediment
131 suspension. The cell compartments were manufactured from Plexiglas and the dimensions were:
132 length of electrolyte compartments 3.5 cm; length of sediment suspension compartment 10 cm;
133 inner diameter of all compartments 8 cm. Ion exchange membranes from Ionics (anion exchange
134 membrane 204 SZRA B02249C and cation exchange membrane CR67 HUY N12116B). The electrolyte
135 was NaNO₃ (0.01M) adjusted to pH 2 by HNO₃ (5M). The electrolyte liquids (350 mL) were circulated
136 via Pan World pumps with flow rates of 30mL/min. Platinum coated titanium electrodes were used
137 in each electrolyte compartment and a power supply (Hewlett Packard E3612A) maintained a
138 constant DC current. The sediment suspension was stirred by a RW11 Basic lab-egg (IKA 2830001)
139 with a stirrer consisting of plastic flaps (4cm x 0.5cm) fastened to a glass rod.

140 After the EDR experiments the sediment suspensions were filtered and the heavy metal
141 concentration in both the suspension liquid and solids were measured. The stirrer, membranes and
142 electrodes were rinsed in HNO₃ (5M) overnight and the heavy metal concentrations in the rinsing
143 liquids as well as with the electrolyte liquids were measured by ICP-OES.

144 2.3.2 Remediation objectives

145 The remediation objectives were related to achieving background concentrations of the two
146 targeted heavy metals, Cu and Pb as well as limiting the removal of naturally occurring metals. The
147 latter objective partly due to mobilised metals reducing the removal of targeted metals during
148 electrokinetic remediation (Kim et al., 2009) as well as ensuring that disposing of the suspension
149 liquid after treatment does not create an environmental issue. Inorganic Al is for instance toxic to
150 many aquatic species (Hindar and Lydersen, 1995; WHO, 1998; ATSDR, 2008; Pedersen et al., 2015e).
151 Even though it has been shown that metals bound in both available and stable fractions of the
152 sediment are removed during electrokinetic remediation (Kirkelund et al., 2010; Kim et al., 2011),
153 the objective of limiting removal of metals was quantified to the amounts bound in the most
154 available fraction (exchangeable). The means of determining amount of metal bound in the different
155 fractions of the sediment was done by the BCR sequential extraction scheme in which the
156 approximate distribution of metals in soils/sediments in the fractions exchangeable (including acid
157 soluble), reducible, oxidisable and residual fractions (Rauret et al., 1999) is determined. Drawbacks
158 of the method include potential readsorption and redistribution of metals during the sequential
159 extraction; the method has, however, been found to be sufficiently repeatable and reproducible to
160 be applied (Filgueiras et al., 2002).

161 2.3.3 Experimental design

162 The experimental variables varied in this study were current density and remediation time after
163 acidification. A previous study revealed that excluding the acidification time (lag phase) improved
164 model predictability (Pedersen et al., 2015d). Time after acidification in this study was calculated as
165 time after the sediment suspension reached pH 4.

166 For determining optimal experimental settings, two experimental designs for each cell were applied,
167 based on fractional factorial designs of two variables resulting in two experiments in each design.
168 These were supplemented with 1-2 experiments representing the centre point of the experimental
169 domains. Due to the structure of the experimental designs, two of the experiments (no. 1 and 6)
170 were included in two designs. Experiments 13-18 were conducted to test the predictability of the
171 PLS models of the four experimental designs. The experimental settings are given in table 1.

172 **Table 1: The experimental designs**

Experiment	Cell design	Time after acidification	Current density	Exp. design
		(h)	(mA/cm ²)	
1	3-compartment	48	0.04	1.1, 1.2
2	3-compartment	246	0.28	1.1
3	3-compartment	444	0.52	1.1
4	3-compartment	278	0.20	1.2
5	3-compartment	163	0.12	1.2

6	2-compartment	48	0.04	2.1, 2.2
7	2-compartment	246	0.28	2.1
8	2-compartment	444	0.52	2.1
9	2-compartment	48	0.20	2.2
10	2-compartment	163	0.12	2.2
11	2-compartment	163	0.12	2.2
12	2-compartment	278	0.04	2.2
13	3-compartment	246	0.36	
14	3-compartment	48	0.52	
15	3-compartment	444	0.20	
16	2-compartment	246	0.36	
17	2-compartment	48	0.52	
18	2-compartment	444	0.20	

173 ¹ Previously published in (Pedersen et al., 2015e)

174 ² Previously published in (Pedersen et al., 2015c)

175

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

177
$$\int_{t=0}^t E = VI dt$$

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

180 2.4 Multivariate modelling

181 PLS was used for calculating the quantitative relation between a descriptor matrix (the experimental
182 variables) and a response matrix (final metal concentrations; energy consumption).

183 2.4.1 PLS modelling

184 In this study SimcaP11 software was used for PLS modelling based on the 18 experiments in table 1.
185 A quantitative relationship between a descriptor matrix containing the experimental variables
186 (arranged by experiments in the rows and settings in the columns) and a response matrix (final
187 concentrations of metals; energy consumption) was calculated. PLS models quantitative relations
188 between a descriptor matrix, X, and a response matrix, Y and can subsequently be used to calculate
189 expected responses by entering new data into the X-matrix. If the number of independent variables
190 in the X-matrix is given by K and the number of dependent variables in the Y-matrix is M, the objects
191 (e.g. experiments) will be represented as points in the K-dimensional X space (descriptors/variables)

192 and the M -dimensional Y space (responses) (Wold et al., 2001; Carlson and Carlson, 2005b). Objects
193 in each space are projected down to PLS components that describe the variation in each space with
194 the constraint that for each PLS dimension, the PLS scores of the Y -matrix (u) should have a
195 maximum correlation to the scores of the X -matrix (t) (Carlson and Carlson, 2005b; Eriksson et al.,
196 2014). New PLS components are iteratively introduced until all the systematic variation in the Y -
197 matrix has been exhausted and only noise remains. Advantages of PLS are that it provides plots of
198 the data compressed to fewer dimensions than the original dataset, it can simultaneously model
199 several responses and it copes with colinearity between variables, noise in both the X and Y matrices
200 and moderate amounts of missing data (<20%) (Wold et al., 2001; Trygg and Wold, 2002; Carlson
201 and Carlson, 2005b). Moreover, since PLS is based on projections, it is possible to have more
202 variables than objects (Carlson and Carlson, 2005b).

203 R^2Y is a measure of the fraction of the Y matrix explained by the model and the predictive power,
204 Q^2 , is an estimate of the reliability of the model calculated by cross-validation. Sweet spot plots of
205 the calculated PLS models were used as foundations for development of remediation strategies.

206 A sweet spot plot is essentially contour plots of all the responses as a function of two variables in
207 one plot, and is based on the site-specific remediation objectives. The sweet spot plot thus highlights
208 the areas of the experimental domain in which the different objectives are met. The number of
209 objectives met are illustrated in different shades and the sweet spot is the part of the experimental
210 domain in which all remediation objectives are met.

211 **3 Results and discussion**

212 **3.1 Sediment characteristics and EDR results**

213 Selected sediment characteristics are summarised in table 2, for more characteristics including
214 conductivity and contents of chloride, carbon, phosphorous and sulphur, please refer to (Pedersen
215 et al., 2015a). As is apparent in the table, the sediment used for experiments in this study has low
216 contents of carbonate as well as organic matter, resulting in a low buffer capacity. Lower removal
217 efficiencies of heavy metals from carbonaceous sediments during EDR treatment applying the same
218 experimental settings have been reported (Nystroem et al., 2005a, b; Nystrom et al., 2005; Ottosen
219 et al., 2007). The clay and silt fractions only constitute 25% of the sediment; none the less metal
220 concentrations in each grain size fraction (clay, silt, sand, gravel) revealed that approximately 50-
221 65% of the total metal content was found in these fractions (<63 μ m).

222 **Table 2: Sediment characteristics, metal-binding patterns and metal removal during the EDR experiments.**

223 The concentrations of heavy metals of environmental concern are compared to the sediment quality
224 criteria of the Norwegian Environment Agency as well as OSPAR (ratified by Norway) in table 2.
225 OSPAR operates with two sets of criteria for background levels; background concentrations (BC) and
226 background assessment concentrations (BAC). The latter are based on statistical calculations in
227 which there is a 90% probability that the observed mean concentration will be below the BAC when
228 the true mean concentration is equivalent to BC (OSPAR, 2009). The Norwegian sediment criteria for
229 background levels (class 1) are based on similar calculations; the assessments of levels that pose low
230 risks of adverse biological effects are based on national conditions (SFT, 2007). Cu and Pb exceed the
231 BAC and Norwegian class 1 levels and are hence the targeted heavy metals in this study. The other

232 analysed heavy metals As, Cd, Cr, Ni and Zn have concentrations well below the sediment quality
233 criteria and are equivalent to naturally occurring levels.

234 A previous study revealed a correlation between the concentrations of Al, Fe, K, Mg, Mn, Cr and Ni
235 bound in the residual fraction of the sediment indicating similar binding of these elements in the
236 stable minerals of the sediment (Pedersen et al., 2015a). Cu, Pb and Zn were found to have different
237 binding patterns and this was in part attributed to anthropogenic sources rather than natural
238 occurrence. This study supported this observation in that Al, Fe, K, Mg, Mn, Cr and Ni were mainly
239 bound in the residual and to a lesser degree the exchangeable fractions in the sediment (table 2),
240 while Cu was mostly bound in the exchangeable and oxidisable fractions; Pb in the exchangeable
241 fraction and Zn in the exchangeable and reducible fractions.

242 **3.2 Preliminary assessment of EDR experiments**

243 During EDR, removal from all fractions of the sediment has been reported in a previous study,
244 initially relatively higher removal from the exchangeable, reducible and oxidisable fractions
245 (Kirkelund et al., 2010). Comparing the removal of metals during EDR with the amounts bound in the
246 different fractions of the sediment can hence provide foundation for assessing the approximate
247 disturbance to the sediment, albeit not providing indications of possible accelerated weathering of
248 the sediment during the EDR process.

249 For both cell designs the highest observed removal of metals exceeded the amounts bound in the
250 available fractions (i.e. exchangeable, reducible and oxidisable) for Al, Fe, Mg, Mn, Cr and Ni
251 indicating that regardless of design, EDR influences the stable minerals in the sediment. Higher
252 removal of the naturally occurring metals were observed in the 2-compartment cell compared to the
253 3-compartment cell, possibly due to the lower final pH levels detected in the 2-compartment cell
254 experiments. These observations are indications that the sediment matrix is affected to a larger
255 degree in the 2-compartment than the 3-compartment cell. The 2-compartment cell was however
256 more efficient regarding energy consumption (figure 1) while removal of the targeted heavy metals
257 was similar for both cell types (table 2).

258 In the following multivariate analysis is applied to explore the experimental domain of both the 2-
259 compartment and 3-compartment cell designs and ultimately determine optimal settings for the
260 studied sediment, depending on the most appropriate design in relation to the remediation
261 objectives identified in the next section.

262 **3.3 Determining optimal experimental settings**

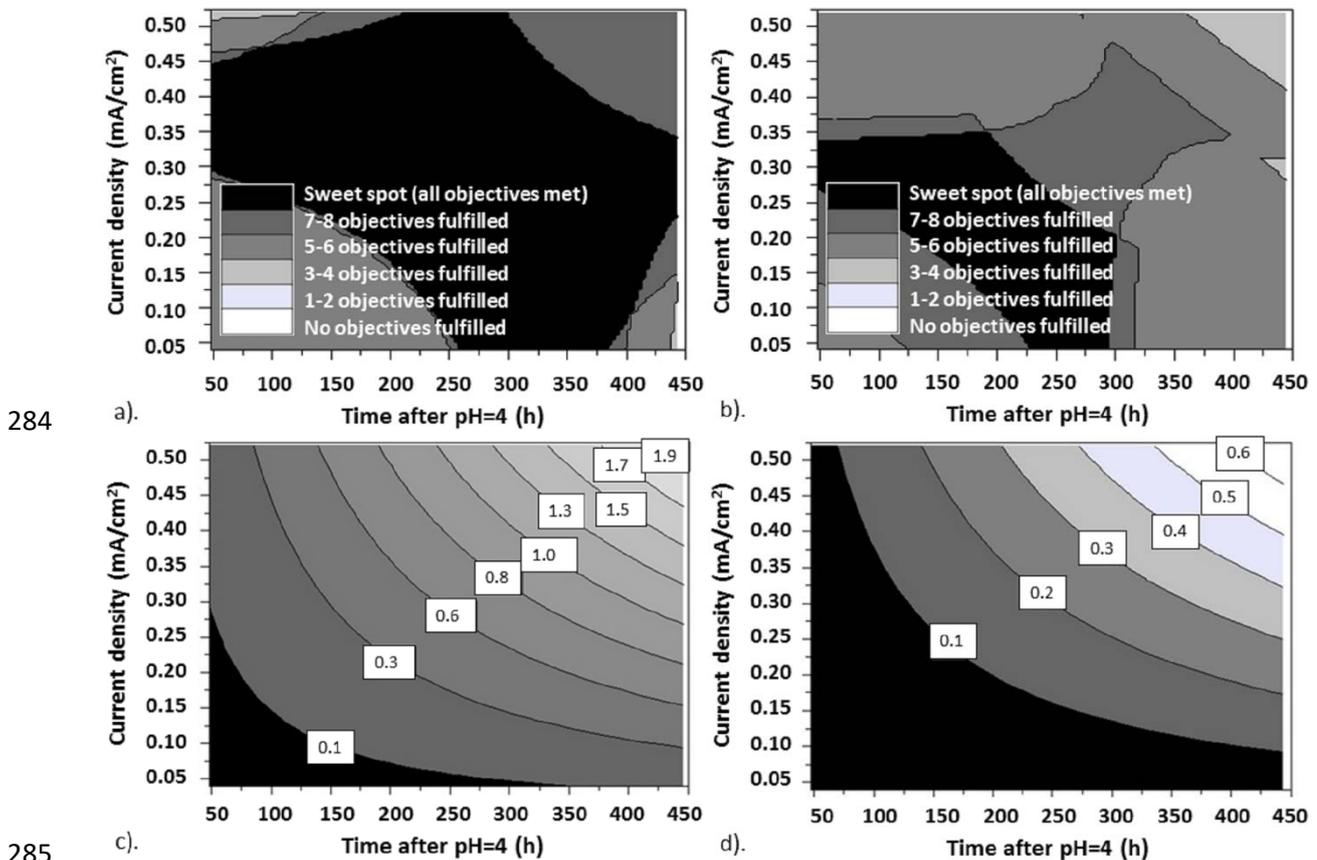
263 *3.3.1 Remediation objectives*

264 The remediation objectives in this study were to achieve final concentrations of the targeted metals,
265 Cu and Pb equivalent to background concentrations as determined by the Norwegian sediment
266 quality criteria (table 2), while maintaining removal of Al, Fe, K, Mg, Mn, Cr and Ni below amounts
267 bound in the exchangeable fractions (table 2). In addition, a low energy consumption objective was
268 set so that the contribution of electricity for the EDR process to the total cost was low, €20/m³ dry
269 sediment (see section 2.1 for details).

270 *3.3.2 Preliminary assessment of experimental domain*

271 A previous study showed that the EDR process in the two cell designs applied in this study differ
 272 from in each other with respect to acidification and metal mobilisation and should be modelled
 273 separately as they constitute entirely different experimental approaches. The first designs were
 274 based on obtaining overviews of the total studied experimental domain and the PLS models were
 275 calculated based on 3-4 experiments for each cell design (design 1.1 and 2.1 in table 1). Model 1.1 of
 276 the 3-compartment cell had a correlation factor, R2Y, of 0.72 and a predictive power, Q2, of 0.45 and
 277 model 2.1 of the 2-compartment cell had correlation factor R2Y of 0.88 and predictive power of
 278 0.66. The models for both designs were considered good and stable, and hence suitable for further
 279 evaluation of the experimental domain.

280 Remediation objectives for metal removal with regards to the targeted heavy metals (Cu and Pb) as
 281 well as the metals Al, Fe, K, Mg, Mn, Cr and Ni (see section 2.3.2) were inserted into a sweet spot
 282 plot to evaluate in which parts of the experimental domain the remediation objectives in relation to
 283 the metal removal were met.

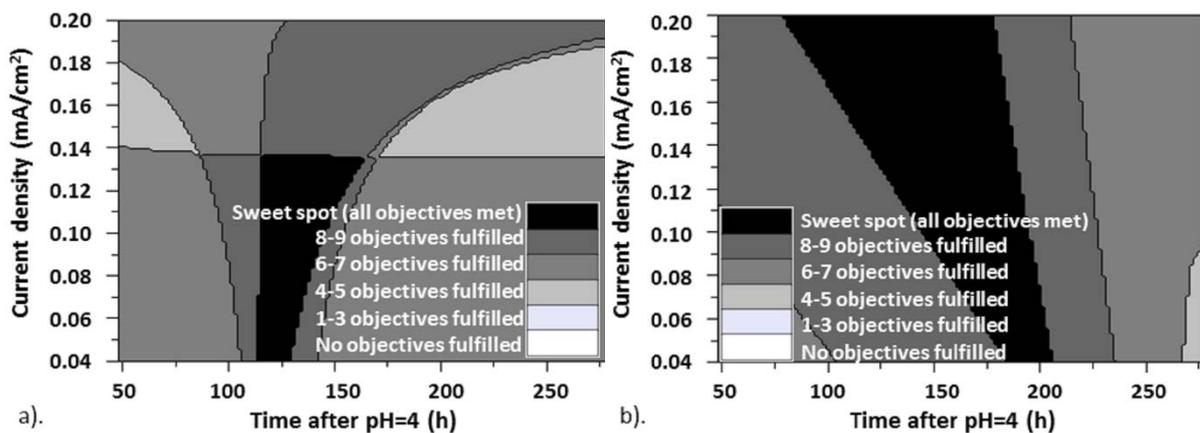


286 **Figure 2: a) Sweet spot plot of the 3-compartment cell b). Sweet spot plot of the 2-compartment**
 287 **cell. For both cell designs, the remediation objectives were achieving final concentrations of Cu**
 288 **and Pb equivalent to background concentrations (Norwegian Class 1) and for Al, Fe, Mg, Mn, Cr**
 289 **and Ni less removal than the amounts bound in the exchangeable fractions of the untreated**
 290 **sediment. Figures a) and b) illustrate the parts of the experimental domain in which all the**
 291 **remediation objectives were met (sweet spot). Contour plots of energy consumption (kWh/kg dry**
 292 **sediment) for the c). 3-compartment cell and d). the 2-compartment cell. The PLS models for c)**
 293 **and d) are based on design 1.1 (3-compartment cell) and 2.1 (2-compartment cell) with R2Y 0.80-**
 294 **0.84 and Q2 0.60-0.77.**

295 The sweet spots (dark shading) in figure 2, illustrate the experimental settings to operate within for
 296 meeting the specified remediation objectives for the removal of metals during EDR in both cell
 297 designs. The experimental domain to operate within in the 2-compartment cell (figure 2b) is
 298 significantly reduced compared to the 3-compartment cell (figure 2a) indicating a higher risk of
 299 removing metals from some of the more stable minerals in the sediment during EDR in the 2-
 300 compartment cell design.

301 *3.3.3 Developing sediment specific remediation strategy*

302 Based on the sweet spot plots and energy consumption contour plots in figure 2, it was decided to
 303 further explore the part of the experimental domain of lower current densities and remediation
 304 times. Since the sweet spot plots revealed that remediation objectives might be achieved at current
 305 densities below 0.20mA/cm² and time after acidification below 300h, the second designs were
 306 developed in the domain of 0.04-0.20mA/cm² and 48-278h. The calculated PLS models 1.2 and 2.2
 307 for the 3- and 2-compartment cells, respectively yielded correlation factors, R_{2Y}, of 0.62-0.77 and
 308 predictive powers, Q₂, of 0.40-0.67. The models were hence assessed as good, stable and suitable
 309 for evaluating this part of the experimental domain further.



310 a). b).
 311 **Figure 3: Sweet spot plots of a). model 1.2 (3-compartment cell) and b). model 2.2 (2-compartment**
 312 **cell) in the reduced experimental domain 48-278 h; 0.04-0.20mA/cm². Both models include**
 313 **remediation objectives for metal removal of Al, Fe, Mg, Mn, Cr, Ni, Cu and Pb as well as energy**
 314 **consumption (<0.1kWh/kg dry sediment).**

315 In order to meet the remediation objectives in the 3-compartment cell, the difference in possible
 316 experimental settings is relatively small, but can be important in relation to the cost of electricity.
 317 Operating at 0.12mA/cm² and 125hours results in an energy consumption of 0.05kWh/kg dry
 318 sediment giving an electricity cost per m³ dry sediment of 67NOK (€7.0) while operating at
 319 0.04mA/cm² and 110 hours results in a cost per m³ of 36NOK (€3.5). The latter settings provide the
 320 lowest cost of electricity in the shortest time within the experimental domain of the 3-compartment
 321 cell.

322 The difference in possible experimental settings for meeting the remediation objectives are larger in
 323 the 2-compartment cell and will depend on whether time or cost is more vital. Performing the
 324 experiments at 0.20mA/cm² and 100h (shortest possible time) results in an electricity cost of
 325 approximately 54NOK/m³ (€5.5) while operating at 0.04mA/cm² and 180h would result in cubic

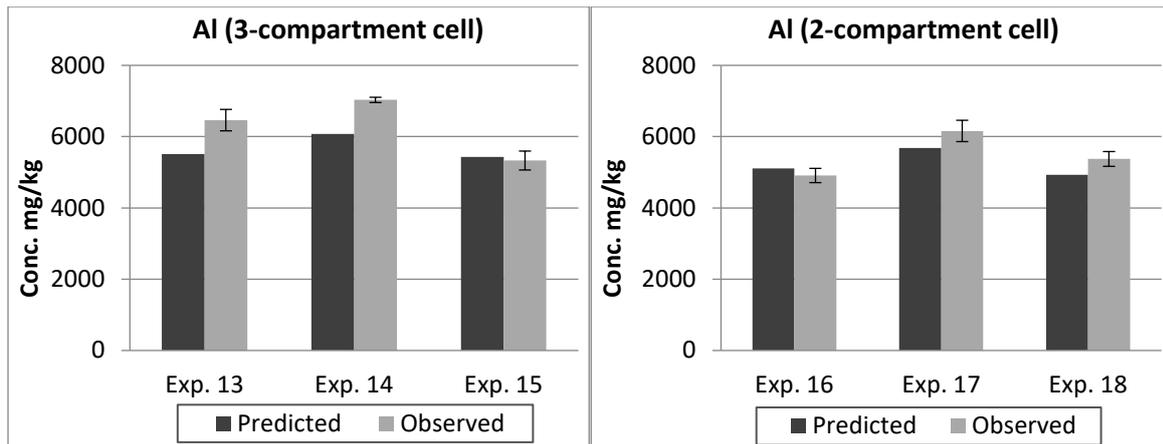
326 meter price of 25NOK/m³ (€3.0), the latter providing the lowest cost of electricity in the
327 experimental domain of the 2-compartment cell. In comparison, dredging followed by disposal or
328 treatment on land has a more than twenty-fold estimated cost in Norway.

329 *3.3.4 Model predictability*

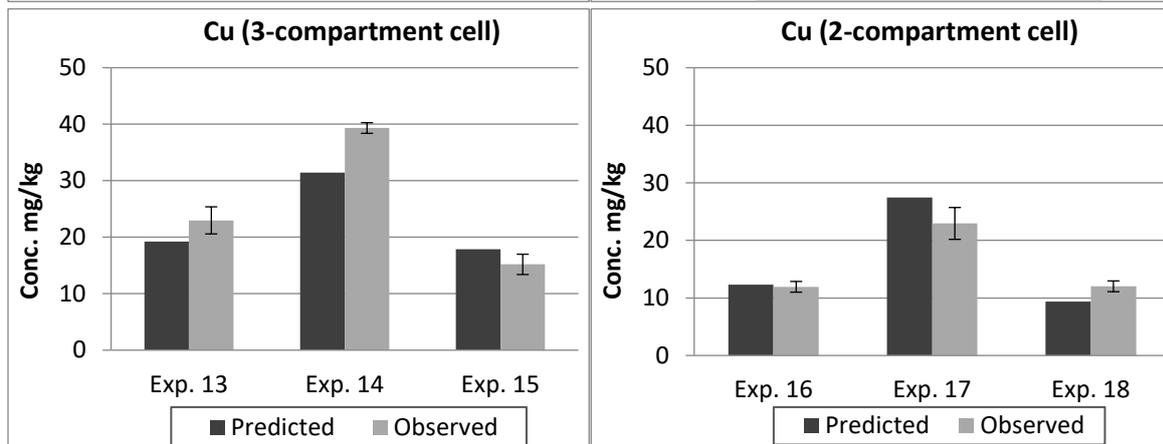
330 In order to evaluate the predictability of the calculated PLS models, a comparison of model predicted
331 final concentrations and observed final concentrations of metals in experiments 13-18 (not
332 previously included in the PLS models). A previous study illustrated that PLS models that included
333 several sediments might be applied for predicting starting points of remediation tests for new
334 sediments (Pedersen et al., 2015c). In this study the PLS models only included one sediment and the
335 predictions of final concentrations are more accurate. Figure 3 illustrates the trends of the metals Al,
336 Cu and Pb – Al was chosen as a representative of the naturally occurring metals due to the potential
337 toxic effects upon mobilisation.

338 The largest deviation between the model predictions and measured concentrations are found in
339 experiments 14 and 17 and is not surprising when considering that they were conducted in one of
340 the outer points of the experimental domain (48h and 0.52mA/cm²) for each of the cell designs. At
341 this point, the predictions of Al and Cu are within a deviation of 25%, which can be conceived as a
342 reasonable deviation when taking into account that the sediment is heterogeneous and that initial
343 metal concentration analysis standard deviations were up to 32%. The deviation between predicted
344 and observed final concentrations of Pb is however not within this deviation and may be due to
345 different binding patterns in the sediment resulting in larger deviations in the initial mobilisation
346 occurring at pH levels 3-4 achieved in experiments 14 and 17.

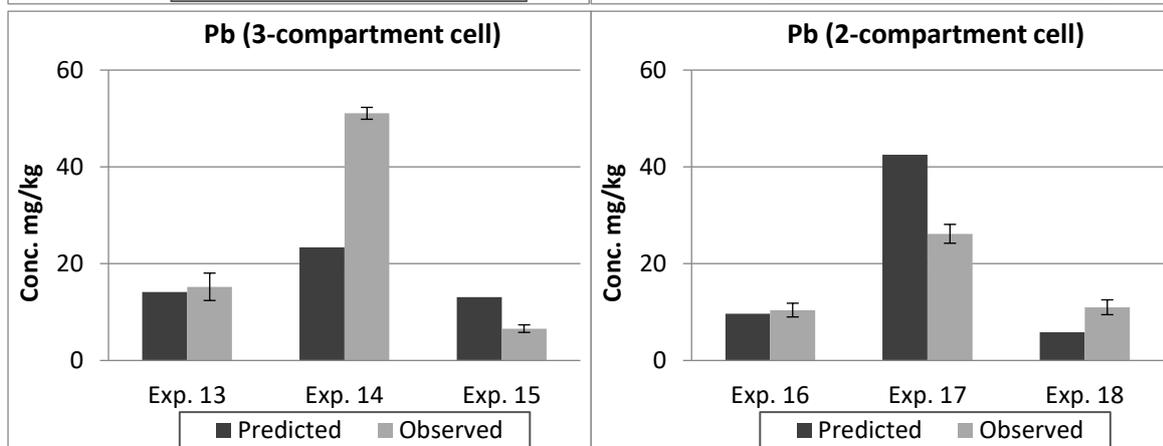
347



348



349



350 **Figure 4: PLS models' (R2Y 0.6-0.7; Q2 0.5-0.6) predicted and observed concentrations of Al, Cu**
351 **and Pb in experiments 13-15 for the 3-compartment cell and experiments 16-18 for the 2-**
352 **compartment cell. Standard deviations of the observed concentrations have been included in the**
353 **figures.**

354 The other experiments 13, 15, 16 and 18 represent parts of the experimental domain closer to the
355 model experiments and lower deviations between the predicted and registered final concentrations
356 were observed. It is hence clear that model stability and predictability will improve with the number
357 of experiments, as will any statistical method. However, the level of deviation in this study is
358 reasonable for applying the models for determining remediation designs, when taking into account
359 metal analysis standard deviations and the heterogeneous sediment.

360

361 As evidenced from the above experiments, PLS proves a more efficient method for the rapid
362 identification of remediation conditions than presented in other one-variable-at-a-time studies and
363 with comparable or better results (Akciil et al., 2015). The results also provide a good foundation for
364 later scaling up ((Pedersen et al., 2015e).

365 **4 Conclusions**

366 Multivariate analysis as a decision tool was effectively applied for evaluating remediation strategies
367 for specific remediation technology (EDR) and sediment from the Arctic region of Norway in this
368 study. The calculated PLS models were able to deal with sediment-specific clean-up level goals for
369 the targeted pollutants as well as objectives specific to EDR, i.e. minimising removal of naturally
370 occurring metals and maintaining a low energy consumption (<0.1 kWh/kg treated sediment)
371 throughout the remediation.

372 The removal of the targeted heavy metals, Cu and Pb reached final concentrations equivalent to
373 background levels as defined by the Norwegian authorities in large parts of the experimental domain
374 for the two tested EDR cell designs. With the 2-compartment cell, higher removal rates of heavy
375 metals and minimised use of energy was achieved in shorter time, while disturbance to the sediment
376 matrix was lower in the 3-compartment cell. Optimising with regards to all parameters were
377 however possible in both cell designs for the specific sediment. In the 3-compartment cell the lowest
378 approximate electricity cost for meeting the remediation objectives was estimated to be 36NOK/m³
379 dry sediment (€3.5), while being approximately 25NOK/m³ dry sediment (€3.0) in the 2-
380 compartment cell.

381 An evaluation of the model predictability showed good correspondence between model predicted
382 and observed final metal concentrations. Based on the results in this study, the use of multivariate
383 analysis is encouraged for other remediation studies, independent of method of choice.

384

385 **Acknowledgements**

386 The Northern Environmental Waste Management (EWMA) project, funded by the Research Council
387 of Norway through NORDSATSNING (grant number 195160) and Eni Norge AS, is acknowledged for
388 funding. Hammerfest municipality is acknowledged for providing boat and assistance in sampling of
389 sediments.

390 **References**

391 Akciil, A., Erust, C., Ozdemiroglu, S., Fonti, V., Beolchini, F., 2015. A review of approaches and
392 techniques used in aquatic contaminated sediments: metal removal and stabilization by chemical
393 and biotechnological processes. *Journal of Cleaner Production* 86, 24-36.
394 ATSDR, 2008. Toxicological Profile for Aluminum. Agency for toxic substances and disease registry
395 (ATSDR), US Department of Health and Human Services, Atlanta, pp. 175-227.
396 Bing, P., GAO, H.-m., CHAI, L.-y., SHU, Y.-d., 2008. Leaching and recycling of zinc from liquid waste
397 sediments. *Transactions of Nonferrous Metals Society of China* 18, 1269-1274.

398 Carlson, R., Carlson, J.E., 2005a. Chapter 1 Introduction: Strategies on different levels in organic
399 synthesis. in: Rolf, C., Johan, E.C. (Eds.). *Data Handling in Science and Technology*. Elsevier, pp. 1-13.
400 Carlson, R., Carlson, J.E., 2005b. Chapter 18 Quantitative relations: Observed responses and
401 experimental variations. in: Rolf, C., Johan, E.C. (Eds.). *Data Handling in Science and Technology*.
402 Elsevier, pp. 425-469.

403 Dermont, G., Bergeron, M., Mercier, G., Richer-Lafleche, M., 2008. Soil washing for metal removal: a
404 review of physical/chemical technologies and field applications. *Journal of Hazardous Materials* 152,
405 1-31.

406 Eriksson, L., Trygg, J., Wold, S., 2014. A chemometrics toolbox based on projections and latent
407 variables. *Journal of Chemometrics* 28, 332-346.

408 Erüst, C., Akcil, A., Gahan, C.S., Tuncuk, A., Devenci, H., 2013. Biohydrometallurgy of secondary metal
409 resources: a potential alternative approach for metal recovery. *Journal of Chemical Technology and*
410 *Biotechnology* 88, 2115-2132.

411 Fan, G., Cang, L., Gomes, H.I., Zhou, D., 2016. Electrokinetic delivery of persulfate to remediate PCBs
412 polluted soils: Effect of different activation methods. *Chemosphere* 144, 138-147.

413 Ferreira, C., Ribeiro, A.B., Ottosen, L.M., 2002. Study of different assisting agents for the removal of
414 heavy metals from MSW fly ashes. *Waste Management and the Environment*, 171-179.

415 Filgueiras, A.V., Lavilla, I., Bendicho, C., 2002. Chemical sequential extraction for metal partitioning in
416 environmental solid samples. *J Environ Monitor* 4, 823-857.

417 Gent, D.B., Bricka, R.M., Alshwabkeh, A.N., Larson, S.L., Fabian, G., Granade, S., 2004. Bench-and
418 field-scale evaluation of chromium and cadmium extraction by electrokinetics. *Journal of Hazardous*
419 *Materials* 110, 53-62.

420 Gomes, H.I., Dias-Ferreira, C., Ribeiro, A.B., 2012. Electrokinetic remediation of organochlorines in
421 soil: enhancement techniques and integration with other remediation technologies. *Chemosphere*
422 87, 1077-1090.

423 Guevara-Riba, A., Sahuquillo, A., Rubio, R., Rauret, G., 2004. Assessment of metal mobility in
424 dredged harbour sediments from Barcelona, Spain. *Science of the Total Environment* 321, 241-255.

425 Hindar, A., Lydersen, E., 1995. Er utfelt/sedimentert aluminium etter vassdragskalking et mulig
426 miljøproblem? (Norwegian). NIVA, Oslo, Norway.

427 Iannelli, R., Masi, M., Ceccarini, A., Ostuni, M., Lageman, R., Muntoni, A., Spiga, D., Poletti, A.,
428 Marini, A., Pomi, R., 2015. Electrokinetic remediation of metal-polluted marine sediments:
429 experimental investigation for plant design. *Electrochimica Acta* 181, 146-159.

430 Jakobsen, M.R., Fritt-Rasmussen, J., Nielsen, S., Ottosen, L.M., 2004. Electrodialytic removal of
431 cadmium from wastewater sludge. *J Hazard Mater* 106, 127-132.

432 Jonsson, S., Persson, Y., Frankki, S., van Bavel, B., Lundstedt, S., Haglund, P., Tysklind, M., 2007.
433 Degradation of polycyclic aromatic hydrocarbons (PAHs) in contaminated soils by Fenton's reagent:
434 A multivariate evaluation of the importance of soil characteristics and PAH properties. *Journal of*
435 *Hazardous Materials* 149, 86-96.

436 Kim, K.-J., Kim, D.-H., Yoo, J.-C., Baek, K., 2011. Electrokinetic extraction of heavy metals from
437 dredged marine sediment. *Separation and purification technology* 79, 164-169.

438 Kim, K.-W., Lee, K.-Y., Kim, S.-O., 2009. *Electrokinetic Remediation of Mixed Metal Contaminants.*
439 *Electrochemical Remediation Technologies for Polluted Soils, Sediments and Groundwater.* John
440 Wiley & Sons, Inc., pp. 285-313.

441 Kirkelund, G.M., Ottosen, L.M., Villumsen, A., 2010. Investigations of Cu, Pb and Zn partitioning by
442 sequential extraction in harbour sediments after electrodialytic remediation. *Chemosphere* 79, 997-
443 1002.

444 Löser, C., Zehnsdorf, A., Hoffmann, P., Seidel, H., 2007. Remediation of heavy metal polluted
445 sediment by suspension and solid-bed leaching: estimate of metal removal efficiency. *Chemosphere*
446 66, 1699-1705.

447 Méndez, E., Pérez, M., Romero, O., Beltrán, E., Castro, S., Corona, J., Corona, A., Cuevas, M., Bustos,
448 E., 2012. Effects of electrode material on the efficiency of hydrocarbon removal by an electrokinetic
449 remediation process. *Electrochimica Acta* 86, 148-156.

450 Mulligan, C.N., Yong, R.N., Gibbs, B.F., 2001. Remediation technologies for metal-contaminated soils
451 and groundwater: an evaluation. *Engineering Geology* 60, 193-207.

452 Nystroem, G.M., Ottosen, L.M., Villumsen, A., 2005a. Acidification of harbor sediment and removal
453 of heavy metals induced by water splitting in electro-dialytic remediation. *Separ Sci Technol* 40, 2245-
454 2264.

455 Nystroem, G.M., Ottosen, L.M., Villumsen, A., 2005b. Electro-dialytic removal of Cu, Zn, Pb, and Cd
456 from harbor sediment: Influence of changing experimental conditions. *Environ Sci Technol* 39, 2906-
457 2911.

458 Nystrom, G.M., Ottosen, L.M., Villumsen, A., 2005. Test of experimental set-ups for electro-dialytic
459 removal of Cu, Zn, Pb and Cd from different contaminated harbour sediments. *Eng Geol* 77, 349-357.

460 OSPAR, 2009. CEMP assessment report: 2008/2009 Assessment of trends and concentrations of
461 selected hazardous substances in sediments and biota. OSPAR, www.ospar.org.

462 Ottosen, L., Jensen, J.B., Villumsen, A., Laursen, S., Hansen, H.K., Sloth, P., 1995. Electrokinetic
463 remediation of soil polluted with heavy metals - Experiences with different kinds of soils and
464 different mixtures of metals. *Contaminated Soil '95, Vols 1 and 2* 5, 1029-1038.

465 Ottosen, L.M., Hansen, H.K., Hansen, C.B., 2000. Water splitting at ion-exchange membranes and
466 potential differences in soil during electro-dialytic soil remediation. *Journal of Applied*
467 *Electrochemistry* 30, 1199-1207.

468 Ottosen, L.M., Jensen, P.E., Kirkelund, G.M., Ferreira, C.D., Hansen, H.K., 2012. Electro-dialytic
469 Remediation of Heavy Metal Polluted Soil - treatment of water saturated or suspended soil.
470 *Chemical Engineering Transactions* 28, 103-108.

471 Ottosen, L.M., Nystrom, G.M., Jensen, P.E., Villumsen, A., 2007. Electro-dialytic extraction of Cd and
472 Cu from sediment from Sisimiut Harbour, Greenland. *J Hazard Mater* 140, 271-279.

473 Pedersen, A.J., Ottosen, L.M., Villumsen, A., 2003. Electro-dialytic removal of heavy metals from
474 different fly ashes - Influence of heavy metal speciation in the ashes. *J Hazard Mater* 100, 65-78.

475 Pedersen, K., Lejon, T., Jensen, P., Ottosen, L., 2015a. Chemometric Analysis for Pollution Source
476 Assessment of Harbour Sediments in Arctic Locations. *Water Air Soil Pollut* 226, 1-15.

477 Pedersen, K.B., Jensen, P.E., Ottosen, L.M., Lejon, T., 2015b. An optimised method for electro-dialytic
478 removal of heavy metals from harbour sediments. *Electrochimica Acta* 173, 432-439.

479 Pedersen, K.B., Kirkelund, G.M., Ottosen, L.M., Jensen, P.E., Lejon, T., 2015c. Multivariate methods
480 for evaluating the efficiency of electro-dialytic removal of heavy metals from polluted harbour
481 sediments. *Journal of Hazardous Materials* 283, 712-720.

482 Pedersen, K.B., Lejon, T., Ottosen, L.M., Jensen, P.E., 2015d. Screening of variable importance for
483 optimizing electro-dialytic remediation of heavy metals from polluted harbour sediments.
484 *Environmental Technology* 36, 2364-2373.

485 Pedersen, K.B., Ottosen, L.M., Jensen, P.E., Lejon, T., 2015e. Comparison of 2-compartment, 3-
486 compartment and stack designs for electro-dialytic removal of heavy metals from harbour sediments.
487 *Electrochimica Acta* 181, 48-57.

488 Radu, A., Panturu, E., Woinaroschy, A., Isopescu, R., 2015. Experimental Design and Process
489 Optimization for Uranium Polluted Soils Decontamination by Acid Washing. *Water Air Soil Pollut* 226,
490 1-11.

491 Rauret, G., Lopez-Sanchez, J.F., Sahuquillo, A., Rubio, R., Davidson, C., Quevauviller, P., 1999.
492 Improvement of the BCR three step sequential extraction procedure prior to the certification of new
493 sediment and soil reference materials. *J Environ Monitor* 1, 57-61.

494 Ribeiro, A.B., Mateus, E.P., Ottosen, L.M., Bech-Nielsen, G., 2000. Electro-dialytic removal of Cu, Cr,
495 and As from chromated copper arsenate-treated timber waste. *Environ Sci Technol* 34, 784-788.

496 Rulkens, W., 2005. Introduction to the treatment of polluted sediments. *Reviews in Environmental*
497 *Science and Bio/Technology* 4, 213-221.

498 Rulkens, W.H., Tichy, R., Grotenhuis, J.T.C., 1998. Remediation of polluted soil and sediment:
499 perspectives and failures. *Water Science and Technology* 37, 27-35.
500 SFT, 2007. Guidelines for classification of environmental quality in fjords and coastal waters
501 (Norwegian). in: Agency), S.n.N.E. (Ed.). SFT.
502 Sun, T.R., Ottosen, L.M., 2012. Effects of pulse current on energy consumption and removal of heavy
503 metals during electro-dialytic soil remediation. *Electrochim Acta* 86, 28-35.
504 Tabak, H.H., Lens, P., van Hullebusch, E.D., Dejonghe, W., 2005. Developments in bioremediation of
505 soils and sediments polluted with metals and radionuclides—1. Microbial processes and mechanisms
506 affecting bioremediation of metal contamination and influencing metal toxicity and transport.
507 *Reviews in Environmental Science and Bio/Technology* 4, 115-156.
508 Trygg, J., Wold, S., 2002. Orthogonal projections to latent structures (O-PLS). *Journal of*
509 *Chemometrics* 16, 119-128.
510 White, C., Sayer, J., Gadd, G., 1997. Microbial solubilization and immobilization of toxic metals: key
511 biogeochemical processes for treatment of contamination. *FEMS microbiology reviews* 20, 503-516.
512 WHO, 1998. Aluminium in drinking water - Background document for development of WHO
513 Guidelines for Drinking-water Quality. Health criteria and other supporting information, Geneva.
514 Wold, S., Sjöström, M., Eriksson, L., 2001. PLS-regression: a basic tool of chemometrics.
515 *Chemometrics and Intelligent Laboratory Systems* 58, 109-130.

516