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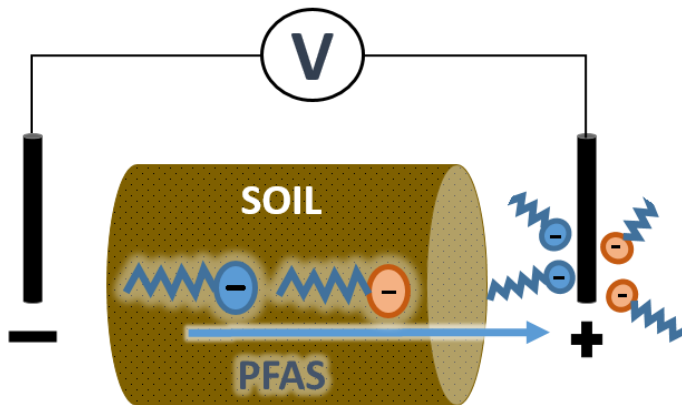
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1 Electrodialytic per- and polyfluoroalkyl
2 substances (PFASs) removal mechanism
3 for contaminated soil
4

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13 Graphical abstract



14

15 Abstract

16 Contamination of soils with per- and polyfluoroalkyl substances (PFASs) is a global problem, in
17 particular at fire-fighter training sites due to the usage of PFAS-containing aqueous fire-fighting foams
18 (AFFFs). In this study, an electrodialytic remediation method was applied for the first time to remove
19 PFASs from contaminated soil. The electrodialytic remediation system was evaluated in a laboratory-
20 scale experiment with current densities of 0.19 mA cm^{-2} and 0.38 mA cm^{-2} over 21 days, using PFAS-
21 contaminated soil from a fire-fighter training site at Stockholm Arlanda Airport, Sweden. Of the 23
22 PFASs targeted, significant ($p < 0.05$) PFAS electromigration towards the anode was observed for C₃-C₇
23 perfluoroalkyl carboxylates (PFCAs) (PFBA, PFPeA, PFHxA, PFOA) and C₄, C₆, and C₈ perfluoroalkane
24 sulfonates (PFSAs) (PFBS, PFHxS, PFOS) since these PFASs were predominantly negatively charged. In
25 contrast to the electromigration of the charged PFASs, *N*-methyl perfluorooctane sulfonamide
26 (MeFOSA), perfluorooctane sulfonamidoacetic acid (FOSAA) and ethyl FOSAA (EtFOSAA) showed
27 significant ($p < 0.05$) transport towards the cathode, which is probably attributed due to electro-osmotic
28 flow of these predominantly neutral PFASs. Mass balance calculations showed that for the shortest-
29 chained PFASs (i.e., PFBA, PFPeA, PFHxA, PFBS, and PFHxS), up to 20% was extracted from the soil to
30 the anolyte, which showed that electrodialytic is a possible *in-situ* remediation technique for PFAS-
31 contaminated soil.

32 1. Introduction

33 Contamination of soil and groundwater with per- and polyfluoroalkyl substances (PFASs) can
34 eventually impact drinking water delivery systems, posing a risk to human health (Ahrens, 2011).
35 Recently, several water sources in Japan (Murakami et al., 2009), Germany (Gellrich et al., 2013) and
36 Sweden (Li et al., 2018) have had to be restricted or even shut down because of PFAS residues entering
37 the groundwater and contaminating wells. Particularly high concentrations of PFASs in the aqueous
38 environment and in drinking water have been attributed to the use of PFAS-containing aqueous fire-
39 fighting foams (AFFF) at fire-fighter training facilities (Baduel et al., 2015), resulting in long-term
40 contamination of the immediate environment originating from contaminated soils (Ahrens et al., 2015;
41 Filipovic et al., 2015). Thus, there is an urgent need to develop treatment techniques for remediation
42 of soil and groundwater. To date, very few studies have focused on innovative remediation methods
43 for PFAS-contaminated soil. Two studies have shown that PFASs can be stabilized in soil by mixing
44 activated carbon (AC) or cementitious materials into the soil (Kupryianchyk et al., 2016; Hale et al., 2017;
45 Söregård et al., 2019). However, short-chain PFASs have been shown to desorb from AC over time
46 (McCleaf et al., 2017), and long-term studies on stabilization remediation methods are lacking. Another
47 reported remediation method is phytoremediation, where PFASs are extracted from contaminated soil
48 and groundwater through plants (Gobelius et al., 2017), but this method mainly extracts water-soluble
49 shorter-chain PFASs and extraction rates are low, resulting in time-consuming remediation.

50 A promising remediation method is electrokinetic extraction, a non-interruptive *in situ* remediation
51 technique that involves applying an electric field to the soil (Acar and Alshwabkeh, 1993; Virkutyte et
52 al., 2002; Yeung and Gu, 2011). Under the induced low current, positively charged ions are transported
53 by electric force and migrate towards the cathode, while negatively charged ions migrate to the anode
54 (i.e., electromigration) (Fig. 1). Electrokinetic extraction has been applied to soil to remove various
55 pollutants, such as heavy metals (Jensen et al., 2007) and various neutral, cationic, and anionic organic
56 contaminants (Guedes et al., 2014; López-Vizcaíno et al., 2017a; Yusni and Tanaka, 2015) (see Table S1
57 in Supporting Information (SI)). However, to our knowledge, the technology has not previously been

58 evaluated for PFASs. PFASs have unique characteristics, being amphiphilic, and most PFASs are charged
59 at typical environmental pH. For example, the acid dissociation constant (pK_a) value of perfluoroalkyl
60 carboxylates (PFCAs) and perfluoroalkane sulfonates (PFASs) is generally <2 (Du et al., 2014; Rayne et
61 al., 2009), which makes PFASs ideal candidates for electromigration. This is in contrast to most other
62 regulated persistent organic pollutants of concern for soil remediation, which most are neutral under
63 environmental pH (Ren et al., 2018) and therefore not subjectable to electromigration (Chung and Lee,
64 2007; Ruiz et al., 2014; Gholami et al., 2014).

65 A crucial aspect of the electrokinetic system is the pH, which can range between 2 to 10 that can affect
66 contaminant solubility and charge. This is mainly due to electrolysis reactions of water at the
67 electrodes, which alkalify the soil adjacent to the cathode and acidify the soil adjacent to the anode
68 (Jensen et al., 2007). Another dominant process in the electrokinetic system in soil is electro-osmotic
69 flow, where water is transported towards the cathode (Acar and Alshawabkeh, 1993), which is
70 particularly efficient in low permeability clay soils (Reddy and Saichek., 2003). Soil constituents,
71 especially clay particles and organic carbon, have dominantly negatively charged surfaces under
72 natural pH (Sposito et al., 1999). The charge neutrality in the soil is therefore maintained by cationic
73 solution ions, such as H^+ , Mg^{2+} , and Ca^{2+} (Sposito, 1998). Because of the relatively higher abundance of
74 cationic solution ions, the dominant ion electromigration vector is towards the cathode, and the higher
75 ion concentration induces an osmotic gradient towards the cathode. Thus, anionic compounds, such
76 as many PFASs, may be influenced by both electromigration and electro-osmosis, with opposing
77 transport vectors, which could be a promising *in-situ* remediation technique for PFAS-contaminated
78 soil and groundwater.

79 The aim of this study was to assess, for the first time, the effect of the electrokinetic remediation
80 process on PFASs ($n = 23$) in natural soil contaminated with PFAS-containing AFFFs. The specific
81 objectives of the study were to, i) assess the transport vectors of various PFASs in the electrokinetic
82 system, and ii) determine the distribution of individual PFASs in all phases of the electrokinetic system.

83 2. Material and Methods

84 2.1 Analytical standards

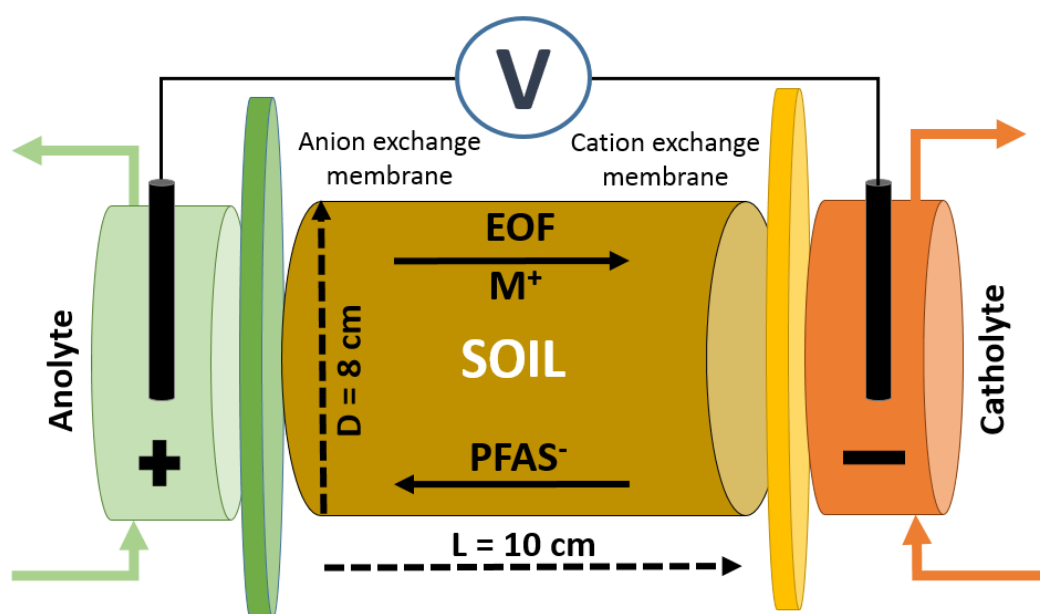
85 The targeted PFASs were: C₃-C₁₁ PFCAs (PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA,
86 PFDoDA), C₄, C₆, and C₈ PFSAs (PFBS, PFHxS, PFOS), 6:2 and 8:2 fluorotelomer sulfonic acids (FTSAs)
87 and following C₈ perfluorooctane sulfonamides (FOSAs) (FOSA, MeFOSA, EtFOSA), C₈ perfluorooctane
88 sulfonamide ethanols (FOSEs) (MeFOSE, EtFOSE), and C₈ perfluorooctane sulfonamidoacetic acids
89 (FOSAAAs) (FOSAA, MeFOSAA, EtFOSAA). In addition, 16 isotopically labeled internal standards (ISs)
90 were included (¹³C₄-PFBA, ¹³C₂-PFHxA, ¹³C₄-PFOA, ¹³C₅-PFNA, ¹³C₂-PFDA, ¹³C₂-PFUnDA, ¹³C₂-PFDoDA,
91 ¹⁸O₂-PFHxS, ¹³C₄-PFOS, ¹³C₈-FOSA, D₃-MeFOSA, D₅-EtFOSA, D₇-MeFOSE, D₉-EtFOSE, D₃-MeFOSAA, and
92 D₅-EtFOSAA). Abbreviation, supplier, and purity of the native PFASs and ISs are listed in Table S2 in SI.

93 2.2 Sampling and soil characterization

94 In July 2015, composite soil samples were collected using a stainless steel shovel from a depth of 0.10-
95 0.30 m at a fire-fighter training site known to be contaminated with PFASs (Gobelius et al., 2017) and
96 located at Stockholm Arlanda Airport, Sweden (59°39'43.00477"N, 17°56'11.08658"E). The samples
97 were stored in airtight polypropylene (PP) bags at 4 °C before the experiments started. The soil texture
98 at sampling consisted of 7% sand, 34% silt, and 59% clay, the soil pH was 6.0 (liquid solid ration (L/S)
99 of 10, 691 pH Meter, Metrohm, Switzerland), and the electrical conductivity was 23 μS cm⁻¹ (L/S of 10,
100 PW 9527, Labasco Hanna instruments, USA). Grain size distribution was estimated by wet sieving
101 (Swedish standardized methodology (SS027123)). The organic carbon content, measured using loss of
102 ignition at 550 °C for 24 h, was 3.3%. Water content was estimated by weight after freeze-drying (7
103 days) the soil samples. Concentrations of the major soil elements and heavy metals (Al, Ca, Fe, K, Mg,
104 Mn, Na, V, Cr, Cu, Ni, Pb, Zn) were measured by inductively coupled plasma-optical emission
105 spectroscopy (ICP-OES) (*n* = 3) according to Danish Standard (DS259), and are shown in Table S3 in SI.
106 The soil elements and heavy metals only measured before the experiment as initial variables and were
107 not assessed after the electrokinetic experiments.

108 2.3 Experimental set-up

109 Two electrokinetic experiments were performed, using a three-compartment cell with two different
110 current densities (0.19 and 0.38 mA cm^{-2}) (Fig. 1) (similar to e.g. Hansen et al., 1999). The middle
111 compartment comprised a hollow cylindrical Plexiglas container (diameter = 8 cm , length = 10 cm) and
112 was filled with homogenized PFAS-contaminated soil (0.95 kg wet weight (ww) and 1.2 kg ww,
113 respectively) wetted with deionized water to approximately field capacity (22% water content). The
114 electrodes and two electrolyte compartments were attached to the middle soil compartment using
115 silica gel and exterior metal clamps.



116

117 **Figure 1.** Conceptual schematic of the experimental set-up of the electrodialytic system, including the processes of electro-
118 osmotic flow (EOF), electromigration of cationic soil counter-ions (M^+), and electromigration of anionic PFASs.

119

120 The described electrokinetic system set-up is often referred as electrodialytic remediation, where
121 intrusion of electrode products (H^+ , OH^-) into the soil is regulated by ion exchange membranes to
122 control the pH (Ottosen et al., 2000). A selective anion exchange membrane (SUEZ, art. No.
123 AR204SZRA, MKIII, France), was placed between soil and anolyte to prevent hydrogen ions (H^+)
124 generated at the anode from entering the soil, while a selective cation exchange membrane (Ionics,
125 art. no. CR67HMP, MKIII, France) was placed between the soil and catholyte to prevent hydroxide ions

126 (OH⁻) generated at the cathode from entering the soil. Each of the electrolytes, consisting of 350 mL
127 sodium nitrate (NaNO₃, 0.01 M, VWR, ≥99.5% purity) in Millipore water, was continuously pumped in
128 a closed system to the anode or cathode, using a peristaltic pump (~30 mL min⁻¹). A constant direct
129 current (DC) of 10 mA or 20 mA from a power supply (Hewlett Packard E3612A) was applied to the soil
130 for 21 days, placing the electrodes in the respective electrolyte. Voltage, pH and conductivity (the latter
131 two in the electrolyte) were measured daily (Tables S4 and S5 in SI) and, if the pH was below 1 or above
132 3, the electrolyte was adjusted with an appropriate amount of nitric acid (HNO₃, 7 M, VWR, AnalaR
133 NORMAPUR grade) or hydrochloric acid (HCl, 35%, VWR, TECHNICAL grade), respectively (Tables S4
134 and S5 in SI). The electrodes used were platinum-coated titanium rod electrodes. After the treatment,
135 the electrolytes, ion exchange membranes, and soil (10-11 slices of 0.9-1.0 cm thickness perpendicular
136 to the electric field) were stored in darkness at 4°C in separate sealed polypropylene (PP) bags until
137 analysis. The soil from the 0.19 mA cm⁻² experiment was analyzed for eight PFASs (PFBA, PFHpA, PFHxA,
138 PFOA, PFBS, PFHxS, PFOS, and FOSA), while the soil from the 0.38 mA cm⁻² experiment was analyzed
139 for all 23 PFASs in all soil samples, due to an extension of the analytical method. In addition,
140 membranes and electrolytes from the 0.38 mA cm⁻² experiment were analyzed for all 23 PFASs. The
141 aqueous phase PFASs were measured (*n* = 2) in the electrolytes before and after the experiment, with
142 sampling in both the anolyte and catholyte in the latter case. To compensate for the initial PFAS
143 contamination in the electrolytes (Table S6 in SI), the PFAS concentrations at the beginning of the
144 experiment were subtracted from the end concentrations. Soil samples were characterized for pH,
145 particle size distribution, conductivity, moisture content, carbon content, and organic carbon content.
146 Statistical analysis (ANOVA) was performed using Matlab with a significance level (α) of 0.05 applied
147 to identify significant PFAS concentration changes in the soil column after treatment. When PFAS
148 concentrations were under the method detection limit (MDL), a value of MDL/2 was used for statistical
149 analysis.

150 2.4 PFAS analysis

151 The electrolyte solution (500 μL) was transferred into a PP Eppendorf tube, and 400 μL methanol and
152 100 μL of an IS mixture (concentration (c) = 10 ng mL^{-1}) were added. The mixture was then vortexed
153 for 10 min and filtered (Sartorius, recycled cellulose, 0.45 μm) into a 1.5 mL auto-injector brown glass
154 vial. The solid samples (i.e., ion exchange membranes and soil) were analyzed using solid-liquid
155 extraction as described elsewhere (Ahrens et al., 2009). In brief, 3.0 g of freeze-dried (7 days) solid
156 sample were homogenized using a ceramic mortar, spiked with 100 μL of an IS mixture (c = 10 ng mL^{-1})
157 and extracted with solid-liquid extraction using methanol (LiChrosolv, Merck, Germany). The extract
158 was concentrated under a nitrogen gas stream to 500 μL , and then centrifuged for 10 min at 3000 rpm.
159 The 500 μL extract was fortified with 500 μL Millipore water in an Eppendorf tube, and 1000 μL of 1 M
160 sodium hydroxide (NaOH, in Millipore water) were added to the extract, which was then vortexed for
161 15 minutes, centrifuged at 15000 rpm for 15 min, and filtered through 0.45 μm recycled cellulose
162 syringe filters (Sartorius, Germany) into 1.5 mL auto-injector brown glass vials (Eppendorf, Germany).
163 The instrumental analysis was performed with an ultra-high performance liquid chromatograph
164 coupled to tandem mass spectroscopy (UHPLC-MS/MS) (Quantiva TSQ; Thermo Fisher, MA, USA). The
165 injection volume was 10 μL separated on a C18 column (1.7 μm , 50 mm, Waters). The eluents were
166 methanol and water with 5mM ammonium acetate, and the eluent gradient was set to 12 min. The
167 isotope dilution method was employed for quantification, using an eight-point calibration curve
168 ranging between 0.01 and 100 ng mL^{-1} . The data were evaluated using TraceFinder™ software (Thermo
169 Fisher, MA, USA).

170 2.5 Quality control and quality assurance

171 The PFAS concentrations in the blanks ($n = 3$) for the solid samples ranged from not detected to 0.57
172 $\mu\text{g kg}^{-1}$ dry weight (PFBA) and those in the blanks for the aqueous samples ($n = 2$) ranged from not
173 detected to 0.18 ng mL^{-1} (EtFOSAA) (Tables S7 and S8 in SI). The MDLs for PFASs were calculated using
174 average blank concentration ($n = 3$) plus three times standard deviation and, if no PFAS was detected
175 in the blanks, the lowest calibration point was used. The average MDL for all PFASs was 0.21 $\mu\text{g kg}^{-1} \pm$

176 0.36 $\mu\text{g kg}^{-1}$ for the solid samples and $0.07 \pm 0.14 \text{ ng mL}^{-1}$ (excluding MeFOSE and EtFOSE, which were
 177 not detected in the solid or aqueous samples) for the aqueous phase (Tables S7 and S8 in SI). The
 178 method recovery was calculated on the losses of IS during sample preparation and matrix effects, and
 179 was compared against the calibration curve. On average, the recovery was $84\% \pm 22\%$ for individual
 180 PFASs in the aqueous phase and $104\% \pm 34\%$ for individual PFASs in the solid samples (Table S9 in SI).
 181 The average regression coefficient (R^2) of the calibration curves was >0.99 in all cases. Measurement
 182 (replicate) error for the triplicate soil extractions ($n = 10$) was on average $45\% \pm 26\%$ for the individual
 183 PFASs, due to the low concentrations for some PFASs, while it was lower for the PFASs found at higher
 184 concentrations (e.g., 15%, 11%, and 28% for PFHxS, PFOS, and PFOA respectively) (Table S10 in SI).
 185 Although the replicate error was high for some PFASs, the large number of samplings per experiment
 186 (30 soil samples per experiment) was considered sufficient to allow significant trends ($p < 0.05$) to be
 187 identified. Experimental mass balance recovery (MBR) was calculated for each individual PFAS as:

$$188 \quad MBR[\%] = \frac{\sum_{i=1}^{i=10} w_{i,soil} c_{i,soil} + c_{catholyte} v_{catholyte} + c_{anolyte} v_{anolyte} + M_{-membrane} + M_{+membrane}}{\sum_{i=1}^{i=10} c_{0,soil} w_{0,soil}} \quad (1)$$

189 where w is the soil mass, i is the sample slice from the experiment, c is the individual PFAS
 190 concentration, v is the end volume of the electrolytes, and M is the absolute mass on the membranes
 191 (Table S11 in SI).

192

193 3. Results and discussion

194 3.1 Performance parameters of the electrodialytic experiment

195 The initial soil characteristics, concentrations of major elements, and PFAS concentrations are
 196 presented in Table 1. The soil from the fire-fighter training site at Stockholm Arlanda Airport can be
 197 characterized as a clay (Fig. S1 in SI), with a relatively low carbon content of $3.3\% \pm 0.12\%$, conductivity
 198 of $23 \mu\text{S cm}^{-2}$ and relatively low buffering capacity of $2.2\% \pm 1.2\% \text{ CaCO}_3$. To keep the current constant,
 199 an average voltage of $8.5 \text{ V} \pm 3.0 \text{ V}$ and $20 \text{ V} \pm 3.3 \text{ V}$ was needed for the 0.19 mA cm^{-2} and 0.38 mA cm^{-2}
 200 2 experiments, respectively (Tables S4 and S5 in SI). The soil variables measured in the 0.38 A cm^{-2}

201 experiment (Table 1) were similar to those determined in previous electro-dialytic experiments (Jensen
202 et al., 2007). After 21 days of the experiment, the pH did not drastically change throughout the soil
203 column. However, although the pH was controlled with the anion exchange membrane at the anode,
204 at 2-3 cm distance from the anode the pH decreased to below pH 3.0, whereas the remaining soil had
205 pH of around 4 (Fig. 2A). The latter was 2 pH units below the initial pH, a change that can have large
206 importance since organic pollutants ion state is determined by the pH where e.g. FOSA included in this
207 study has a reported pK_a value of 6.2-6.5 (Rayne and Forest, 2009), and hence it is not ionized under
208 the current experimental condition. Previous studies have reported a similar finding and have
209 attributed it to water splitting at the membrane or leakage of the small hydrogen ions (1 Da) through
210 the membrane (Hansen et al., 1999; Ottosen et al., 2000). Electrical conductivity was, as expected,
211 inversely correlated with pH and was 220-630 $\mu\text{S cm}^{-1}$ at the anode (0-3 cm) and 28-65 $\mu\text{S cm}^{-1}$ with
212 increasing distance from the anode (4-10 cm) (Fig. 2B, Fig. S2 in SI). The water content was higher at
213 the cathode (23%) and gradually decreased towards the anode (21%) (Fig. 2C). The catholyte volume
214 increased from 350 to 590 mL after 21 days, whereas the anolyte volume decreased from 350 to 190
215 mL in the same period. This net water transport towards the cathode indicates electro-osmotic flow
216 towards the cathode. The soil organic carbon content, an important soil component, showed a
217 transport vector towards the anode, which is opposite to the transport along the water flow (Fig. 2D).
218 This can be explained by the fact that soil organic carbon is dominantly negatively charged under
219 environmental pH because of dissociation of phenol and carboxylic groups (Kinniburgh et al., 1999),
220 and hence can be affected by electromigration.

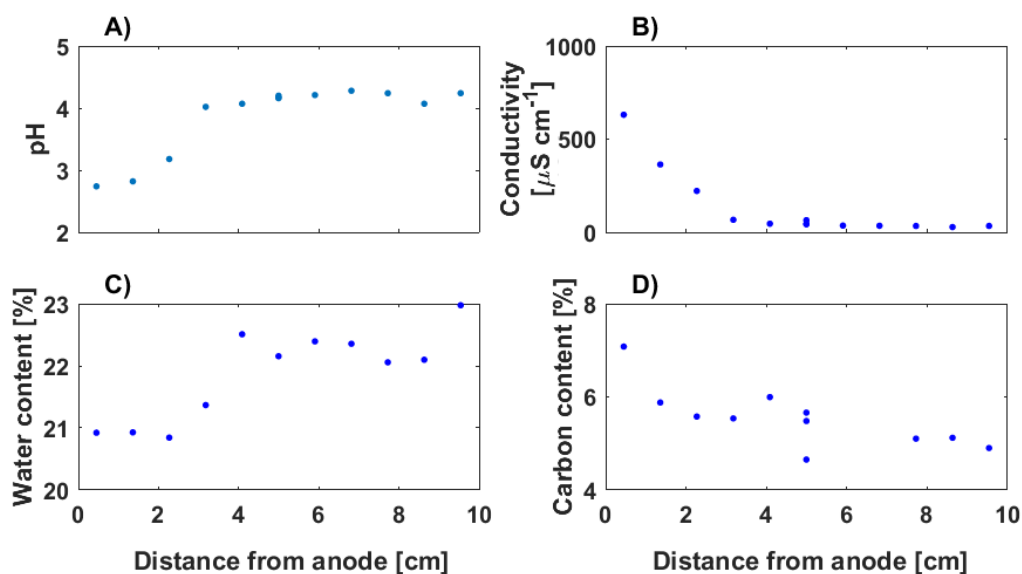
221

222 **Table 1.** Soil characteristics ($n = 3$), soil elements [mg kg^{-1}] ($n = 3$), and individual PFAS concentrations [$\mu\text{g kg}^{-1}$] in the soil
 223 samples at the beginning of the experiment ($n = 2$)^a.

| Soil characteristics | | Initial soil metal composition [mg kg^{-1}] | Initial PFCA and PFSA concentrations [$\mu\text{g kg}^{-1}$] | Initial FTSA, FOSA, FOSE, FOSAA concentrations [$\mu\text{g kg}^{-1}$] |
|--|-----|--|--|--|
| Sand [%] | 7 | Fe 37000 | PFBA 1.1 | 6:2 FTSA 0.45 |
| Silt [%] | 34 | Al 25000 | PFPeA 2.6 | 8:2 FTSA <0.085 |
| Clay [%] | 59 | Mg 6100 | PFHxA 1.3 | FOSA 0.64 |
| Organic carbon [%] | 3.3 | K 4200 | PFHpA 0.99 | MeFOSA <0.0017 |
| Water content [%] | 22 | Ca 3500 | PFOA 1.0 | EtFOSA 0.21 |
| CaCO ₃ [%] | 2.2 | Mn 390 | PFNA <0.33 | MeFOSE <0.17 |
| Conductivity [$\mu\text{S cm}^{-1}$] | 23 | P 270 | PFDA 0.11 | EtFOSE <0.83 |
| pH | 6.0 | Na 300 | PFUnDA 0.068 | FOSAA <0.070 |
| | | Pb 88 | PFDODA 0.054 | MeFOSAA 0.0175 |
| | | PFBS 0.34 | EtFOSAA 0.21 | |
| | | PFHxS 3.4 | | |
| | | PFOS 28 | | |
| | | PFDS 0.025 | | |

224 ^aValues below the respective method detection limit (MDL) are indicated with “<”.

225



226

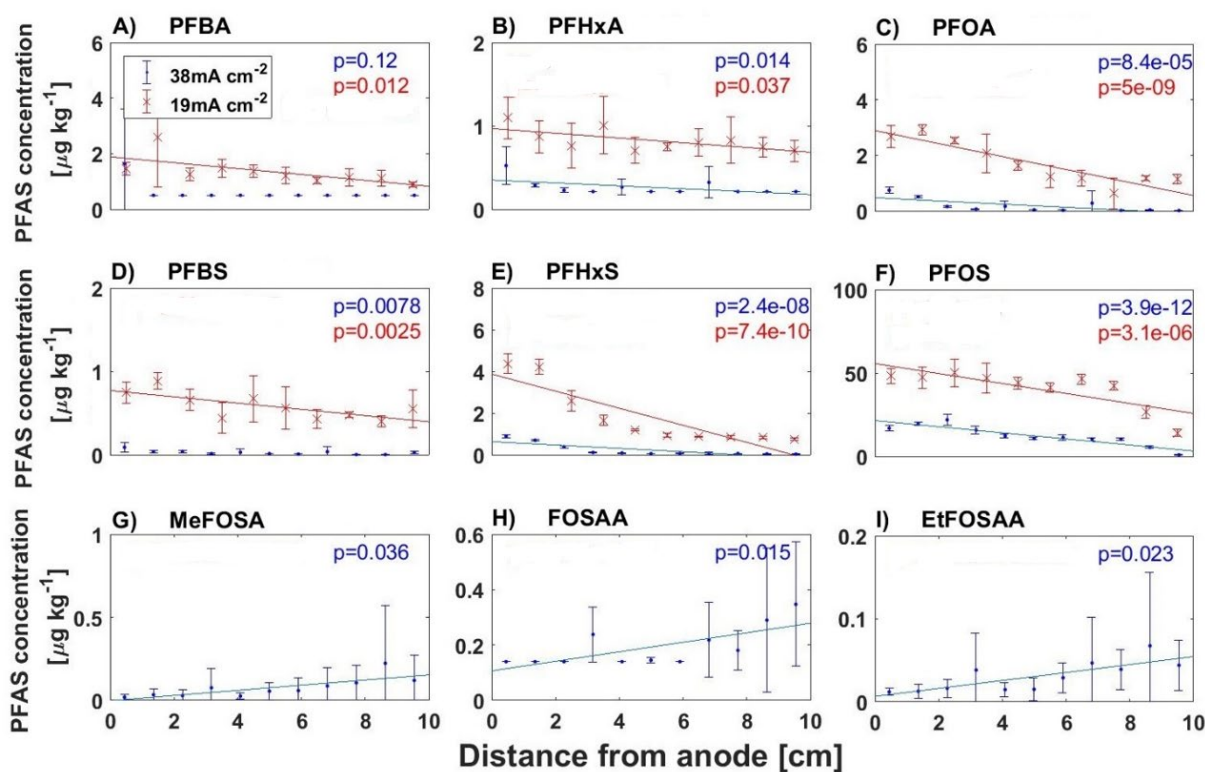
227 **Figure 2.** Electrochemical remediation performance in the soil in the 0.38 mA cm^{-2} experiment, shown as changes in A) pH, B)
 228 conductivity [$\mu\text{S cm}^{-1}$], C) water content [%], and D) organic carbon content [%] after 21 days.

229 3.2 Electromigration of PFASs

230 In the untreated soil, 16 of the 23 individual PFASs were detected (all except PFNA, MeFOSA, EtFOSA,
231 MeFOSE, EtFOSE, FOSAA, and 8:2 FTSA) (Table 1, Table S5 in SI). However, after the 21-day experiment
232 with 0.38 mA cm^{-2} , MeFOSA, FOSAA, and 8:2 FTSA were detected at low concentrations, while EtFOSE
233 was not detected, which can be explained by low concentration levels, close to the MDL (Figs. S3-S5 in
234 SI). The majority of negatively charged PFASs were observed to be significantly transported towards
235 the anode ($p < 0.05$, ANOVA), although the net transport vector of electro-osmotic flow was towards
236 the cathode (Figs. 2 and 3). A significant trend was found for PFBA, PFPeA, PFHxA, PFOA, PFBS, PFHxS,
237 and PFOS using 0.19 mA cm^{-2} ($p < 0.05$, ANOVA), and for PFHpA, PFHxA, PFOA, PFHxS, PFOS, and 8:2
238 FTSA using 0.38 mA cm^{-2} ($p < 0.05$, ANOVA) (Fig. 3). PFOS is mainly removed from close to the cathode
239 and this can be explained by PFAS having 1-2 orders of magnitude higher concentration than the
240 other PFASs. These results indicate that the dominant treatment mechanism is electrokinetic
241 transport, which is in agreement with findings in previous studies on anionic organic compounds in
242 electro-dialytic systems, where the negatively charged methyl orange and the pesticides 2,4-D and
243 chlorosulfuron also were transported towards the anode (Souza et al., 2017; Yusni and Tanaka, 2015).
244 The other PFASs (i.e., PFHpA, PFDA, PFUnDA, PFDoDA, PFDS, and 6:2 FTSA), which were predominantly
245 charged under the experimental pH conditions, did not show a significant gradient over the soil column
246 in the 0.38 mA cm^{-2} experiment (Figs. S3 and S4 in SI). These PFASs were detected close to their MDL
247 and were predominantly longer-chain PFASs. Previous studies have been shown that longer-chain
248 PFASs adsorb much more strongly to soil, sediments and soil organic matter than short-chain PFASs
249 (Higgins and Luthy, 2006; Ahrens et al., 2010; Campos Pereira et al., 2018), and strong sorption could
250 explain the immobility of the longer-chain PFASs in the present study. Noteworthy was that PFHpA,
251 with physicochemical similarities to PFHxA and PFOA, accumulated at the cathode (S3 in the SI),
252 however, the trend was not significant ($p < 0.05$).

253 In contrast to the electromigration of the charged PFASs, the predominantly neutral PFASs (i.e.,
254 MeFOSA, FOSAA, and EtFOSAA) showed significant transport towards the cathode. The functional

255 group of MeFOSA has been reported to be neutral at the experimental pH (Rayne and Forest, 2009),
 256 however to the best of the author's knowledge, the pK_a of FOSAA, and EtFOSAA has not been
 257 determined in the scientific literature. The transport of the predominantly neutral PFASs can be
 258 possibly explained by the electro-osmotic flow. Similarly, previous studies have reported trends
 259 towards the cathode for neutral organic contaminants, e.g., petroleum hydrocarbons (Lee et al., 2016),
 260 trichloroethylene (Chung and Lee, 2007), 2,4,6-trichlorophenol (Ruiz et al., 2014) and
 261 perchloroethylene (Gholami et al., 2014), and have attributed these to extraction from soil due to
 262 electro-osmotic flow. Hence, electro-remediation of soil can be applied for both charged and neutral
 263 PFASs, which can be retrieved at opposing electrodes.



264
 265 **Figure 3.** Spatial concentration distributions and corresponding significant (ANNOVA, Matlab) linear regression lines for the
 266 PFCAs (A-C), PFSAs (D-F), MeFOSA (G), and FOSAAs (H-I) measured in the soil parallel to the electric field applying 0.19 mA
 267 cm^{-2} (red) and 0.38 mA cm^{-2} (blue). For concentrations below the method detection limit (MDL), a value of MDL/2 was used.
 268 Error bars are the standard deviation of triplicates.

269 Comparing the impact of the two different current densities revealed that the lower current of 0.19
 270 mA cm^{-2} resulted in consistently steeper gradients for some shorter-chain PFASs (i.e., PFBA, PFOA,
 271 PFBS, and PFHxS) towards the cathode than the higher current of 0.38 mA cm^{-2} . This indicates that

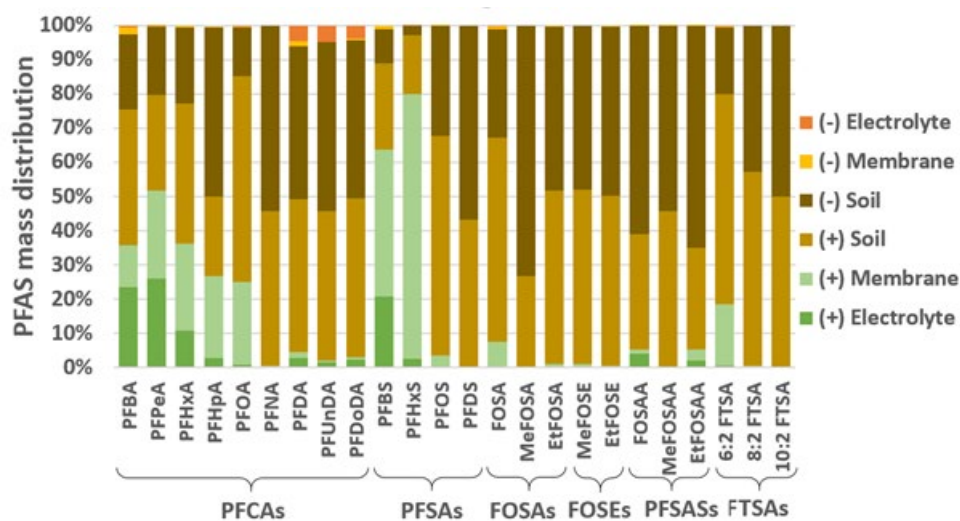
272 higher current does not necessarily result in better PFAS transport, which makes the remediation
273 technique more cost-efficient. However, the concentrations of most PFASs in soil were lower in the
274 0.38 mA cm⁻² experiment than in the 0.19 mA cm⁻² experiment, which indicates higher accumulation
275 of PFASs in the membrane or in the electrolyte when using higher currents. In future studies, more
276 mass balance comparisons using varying currents are needed to confirm and optimize these findings
277 in order to reach a cost efficient remediation for the field scale.

278 3.3 Mass balance distribution of PFASs in the electrodialytic system

279 The mass balance of PFASs in the electrodialytic system in the 0.38 mA cm⁻² experiment was
280 heterogeneous (Fig. 4). In general, there was a difference between the short-chain and long-chain
281 PFASs. The shorter-chain PFASs were to a large extent distributed either in the anolyte (2-26% of PFBA,
282 PFPeA, PFHxA, PFBS, and PFHxS mass distribution) or on the anion exchange membrane (12-78% of
283 PFBA, PFPeA, PFHxA, PFBS, and PFHxS mass distribution). This means that substantial amounts of the
284 short-chain PFASs were removed from the soil. On the other hand, the longer-chain PFASs (i.e., PFOS
285 and PFOA) were transported towards the anode (Fig. 3), but did not pass over the cation exchange
286 membrane (<LOQ-1.0 % of PFOS and PFOA mass distribution) into the electrolyte. The perfluorocarbon
287 chain length is strongly linearly correlated to physiochemical properties such as molecular weight,
288 octanol water partitioning coefficient ($\log K_{ow}$) (Rostvall et al., 2018), hence these results could be
289 transferred to other organic micropollutants.

290 For PFASs which are concentrated in the aqueous phase of the electrolyte, conventional remediation
291 methods can potentially be applied for removal or destruction (Arias et al., 2015). At the cathode, only
292 a few PFASs were accumulated (i.e., MeFOSA, FOSAA, EtFOSAA) (Fig. 3). However, the mass balance
293 calculations comparing the total mass of PFASs before and after the experiment (Equation 1) showed
294 a low average recovery of 53 ± 46 % (excluding MeFOSA as an outlier, Table S8 in SI). This high mass
295 balance recovery can be explained by some individual PFAS concentrations lying close to MDL and by
296 measurement uncertainty due to the high composition of ions, which can cause matrix effects. In
297 general, the shorter-chained PFCAs (PFBA, PFPeA, PFHxA and PFHpA) and PFSAAs (PFBS and PFHxS) had

298 lower mass balance recovery (on average 26 % and 20 %, respectively) than the longer-chained PFCAs
 299 (PFOA, PFDA, PFUnDA and PFDoDA) and PFSAs (PFOS and PFDS) (on average 59 % and 70 %, respectively),
 300 which remained in the soil to a higher extent (Fig. 4). The short chain PFASs were small
 301 enough to transferred through the anion exchange membrane into the electrolyte, and a possible
 302 source of losses of the short-chain PFASs was that they could have been subjected to degradation on
 303 the anode, as shown in previous studies using electrode degradation (Carter and Farrell, 2008). Electro-
 304 Fenton degradation mechanism of PFAS on electrode surface has been attributed to stepwise
 305 decarboxylation reducing the perfluorocarbon chain by one CF_2 moiety, forming a shorter chained
 306 PFAS, until fully mineralized (Liu et al., 2015). The PFAS losses in the electrochemical system via
 307 possible degradation needs to be validated in the future, but it is noteworthy that such mechanism
 308 could be beneficial for using electrokinetic remediation of contaminated soil because of the benefits
 309 of combining both PFAS soil extraction and degradation.



310
 311 **Figure 4.** Mass distribution of individual PFASs between the electrolytes, ion exchange membranes, and soil (see Fig. 1) after
 312 21 days of applying a current of 0.38 mA cm^{-2} . The soil is represented by slices of 5 cm closest to the cathode ((-) Soil) and
 313 slices of 5 cm closest to the anode ((+) Soil).

314 Overall, this study showed that electrokinetic system supports a promising removal mechanism for the
 315 PFAS group and the results showed that electrochemical remediation of soil can be applied for anionic
 316 short chained, anionic long chained and neutral PFASs, however the latter two with greater difficulties.
 317 The techniques efficiency on multiple PFASs, chain lengths and functional groups, is crucial for the

318 techniques environmental relevance because the vast number of PFAS homologues with over 4700 on
319 the global market (Boston et al., 2019), and variety of anionic, cationic, zwitterionic and neutral PFAS
320 found in e.g. AFFFs (Baduel et al., 2015; Barzen-Hanson et al., 2017; Munoz et al., 2018; Zhi and Liu,
321 2018).

322 Ultimately, the results indicate that the technique for PFAS removal can be mature for *in-situ* pilot-
323 scale trial since field-scale electrokinetic remediation methods of soil and groundwater already have
324 been developed for field-scale with success on other contaminants e.g. arsenic, copper, lead and
325 chromium (Kim et al., 2011, 2012; Jeon et al., 2015) and herbicides (López-Vizcaíno et al., 2017). For
326 the future environmental remediation relevance, the authors are raising the following future research
327 challenges: (i) determining if PFASs can be removed sufficiently with longer remediation times, (ii)
328 validation and analysis on more varieties of PFASs found in contaminated soils (e.g. by total oxidizable
329 precursor assays (Houtz and Sedlak, 2012) or total organic fluorine (Yeung et al., 2013)) (iii)
330 determining how long a remediation would take to reach sufficient levels and estimating the
331 associated energy costs, and (iv) if the system can be designed without or with another anion exchange
332 membrane so that the larger PFASs (e.g. PFOS) can be transferred to the electrolyte phase, which in
333 the field scale is advantageous since the electrolyte phase can be pumped out from the ground and
334 further treated in the aqueous phase (Arias et al., 2015).

335

336 Supporting Information

337 Supporting Information is available free of charge on the...

338 Figures S1-S5 and Tables S1-S11 are available.

339

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342

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