

# *Metal removal from soil leachates using DTPA-functionalised maghemite nanoparticles, a potential soil washing technology*

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1 **Metal removal from soil leachates using DTPA-functionalised maghemite**  
2 **nanoparticles, a potential soil washing technology**

3

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6

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13

14 **Abstract**

15 There is significant current interest in the application of magnetic (magnetite or maghemite)  
16 nanoparticles functionalised with chelating agents for the environmental remediation of metal  
17 contaminated waters and solutions. Whilst there is a body of knowledge about the potential  
18 remediation efficacy of such engineered nanoparticles from studies involving synthetic  
19 solutions of single metals, there is relatively little data involving mixed-metal solutions and  
20 virtually no studies about nanoparticle performance in chemically complex environmental  
21 solutions representing those to which a scaled-up nanoremediation process might eventually  
22 be applied. Therefore, we investigated the ability of diethylenetriaminepentaacetic acid  
23 (DTPA)-functionalised, silica-coated maghemite nanoparticles to extract potentially toxic (Cd,  
24 Co, Cu) and “non-toxic” (Ca, Mg) metals from solution (initial [metal] = 10 mg L<sup>-1</sup> ; pH range:  
25 2-8) and to extract a wider range of elements (As, Ca, Cd, Co, Cr, Cu, Mg, Na, Pb, Zn) from  
26 leachate obtained from 10 different contaminated soils with variable initial pH, (semi-)metal

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27 and dissolved organic carbon (DOC) concentrations. The functionalised nanoparticles could  
28 extract the potentially toxic metals with high efficiency (in general >70 %) from single metal  
29 solutions and with efficiencies that were either unaffected or reduced from the soil leachates.  
30  $K_d$  values remained high (> 500 L kg<sup>-1</sup>), even for the soil leachate extractions. Our findings  
31 show that DOC and relatively high concentrations of non-toxic elements do not necessarily  
32 reduce the efficiency of metal contaminant removal by DTPA-functionalised magnetic  
33 nanoparticles and thus demonstrate the potential of this process when applied to chemically  
34 complex soil-derived contaminated solutions.

35

36 **Keywords:** metals; soil; DTPA; adsorption; remediation; nanoparticles

37

## 38 **Introduction**

39 The contamination of soils with toxic metals can potentially lead to significant health effects  
40 in humans, flora and fauna (Siegel, 2002). This occurs if a pathway of exposure to toxic  
41 metals is established. Toxic metals are present in many different phases in the soil including  
42 being bound to organic matter, iron or manganese hydroxides and being incorporated within  
43 the structure of mineral grains (Sahuquillo et al. 1999; Lei et al. 2010). However the most  
44 important fraction with regards to potential risk is the water soluble fraction as the metals  
45 within this fraction are both mobile and bioavailable (Seguin et al. 2004). This means they  
46 can be taken up by organisms and leach into rivers, lakes and groundwater thereby  
47 providing a pathway for plant, animal and human exposure. When metal contamination of  
48 soils poses a risk to the surrounding ecosystem and human health, remediation schemes  
49 are often instigated. Soil washing is an established technology used for removing toxic  
50 metals from soils, and aminocarboxylate chelating agents such as DTPA and EDTA are  
51 often used to enhance metal removal (Lestan et al., 2008). Whilst using chelating agents  
52 improves the effectiveness of metal removal, the techniques currently used for removing the  
53 chelating agents from solution after use, such as membrane separation, electrochemical  
54 treatment or precipitation via the addition of ferric chloride or calcium hydroxide can often

55 add to remediation costs as they require inputs of energy or chemical reagents (Lo and  
56 Zhang, 2005; Finzgar and Lestan, 2008; Pochieca and Lestan, 2009).

57

58 The nanoparticle revolution has impacted on many areas of modern life. In the field of  
59 remediation perhaps most practical applications of nanotechnology have focussed on the  
60 use of zero valent iron as a treatment of organic contaminants in ground water (e.g. Li et al,  
61 2006; Varanasi et al., 2007; Kim et al., 2017; Zhang et al., 2009; Crane and Scott, 2012; Fu  
62 et al., 2014). However, a challenge with the use of zero valent iron is the concern regarding  
63 the environmental fate of nanoparticles post injection into aquifers (Oughton et al., 2017).

64 Another promising application of nanotechnology in the field of remediation focusses on the  
65 use of magnetic nanoparticles as there is the potential for recovery of the nanoparticles  
66 using magnets following deployment. Many studies have now investigated the use of  
67 magnetic nanoparticles, typically magnetite or maghemite, which are then functionalised with  
68 chelating agents to enable the particles to adsorb metal contaminants in a highly efficient  
69 way. The majority of these studies have currently been conducted in the laboratory using  
70 ideal solutions of single (Liu et al., 2009; Wang et al., 2011; Zhang et al., 2011; Figueira et  
71 al., 2011; Koehler et al., 2009; Afsar et al., 2014; Yen et al., 2017; Chung et al., 2012; Wang  
72 et al., 2015| Chen et al., 2014; Chen et al., 2016; Pan et al., 2016) or far less frequently,  
73 multiple (Zhang et al., 2011; Liu et al., 2008; Zeng et al., 2012; Hughes et al., 2017; Shan et  
74 al., 2015) potentially toxic metals. To increase levels of realism some studies have  
75 considered the impact of dissolved organic matter (DOM) on the efficiencies of metal  
76 removal by such nanoparticles, either through additions of organic acids to metal solutions  
77 (Zhang et al., 2012; Hughes et al., 2017) through the use of metal-amended natural waters  
78 (Figueira et al., 2011; Liu et al., 2008) or, rarely, the use of actual metal contaminated  
79 environmental solutions (Bao et al., 2016).

80

81 In our previous study we described a synthetic method for preparing DTPA-functionalised  
82 maghemite nanoparticles and tested the efficiency of the nanoparticles for Pb and Zn  
83 removal from solution for both single and binary metal solutions and in the presence and  
84 absence of fulvic acid as a model form of DOM. Metal-bearing solutions arising from soil  
85 washing will contain a wider range of metals (both contaminant and non-contaminant) and a  
86 more diverse range of forms of DOM. Therefore, the aims of the current study were to  
87 consider the effectiveness of our nanoparticles for 1) adsorption of a wider range of metals  
88 (Ca, Cd, Co, Cu and Mg) from solution and 2) extraction of metals from leachate obtained  
89 from metal contaminated soils. Our study is novel in the following respects. Firstly, it uses  
90 DTPA functionalised nanoparticles; despite the established chelating capacity of DTPA there  
91 are hardly any reports of the synthesis and use of DTPA-functionalised magnetic  
92 nanoparticles (Koehler et al., 2009; Zhao et al., 2015; Zhang et al., 2016; Hughes et al.,  
93 2017 to date that we are aware of). Secondly, and from the perspective of assessing the  
94 practical applications of this emerging technology more importantly, it uses soil leachate  
95 from metal contaminated soils resulting in mixed metal solutions with relatively high DOM  
96 contents and the presence of “non-toxic” metals such as Ca and Mg.

97

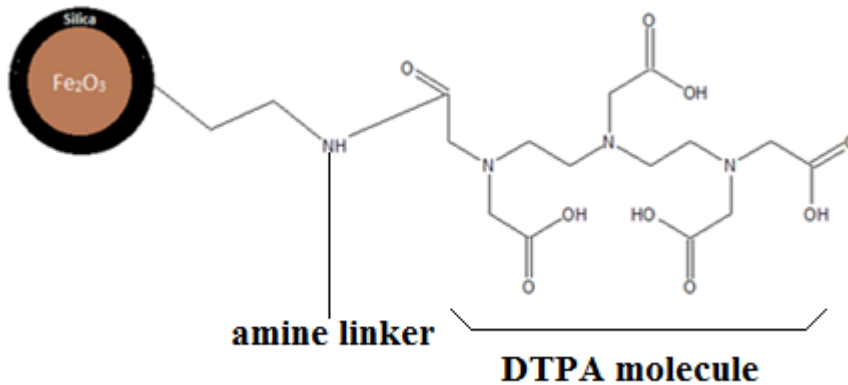
## 98 **Methods**

### 99 DTPA-functionalised maghemite nanoparticles

100 DTPA-functionalised maghemite nanoparticles were synthesised as previously described  
101 (Hughes et al., 2017). In brief, the maghemite nanoparticles were synthesised by the  
102 reaction of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions present in  $\text{FeCl}_2$  and  $\text{FeCl}_3$  solutions in a 1:2 molar ratio in the  
103 presence of 2 M NaOH as a base. The nanoparticles were given a silica coating by reacting  
104 them in tetraethyl orthosilicate (TEOS) and an amine linker added to the surface via reaction  
105 with 3-aminopropyltriethoxysilane (APTES). The nanoparticles were washed in  
106 dimethylformamide (DMF) and the diethylenetriaminepentaacetic acid (DTPA) added to the  
107 amine linker by reaction with triethylamine (TEA) and DTPA dianhydride to give the final  
108 composite nanoparticle (Fig. 1). Finally the nanoparticles were washed four times in

109 methanol and stored in deionised water. The average diameter of the resulting particles was  
110  $47 \pm 6.9$  nm (according to TEM). Full details of particle characterization are given in Hughes  
111 et al (2017).

112



113

114 Fig. 1. Theoretical structure of the silica coated DTPA-functionalised maghemite  
115 nanoparticle.

116

### 117 Extraction tests

118 The extraction tests (for both single metal solutions and soil leachates) followed the same

119 basic protocol detailed in Hughes et al (2017). 2 mL of an aqueous suspension of DTPA-

120 functionalised nanoparticles (10 mg in total) were added to 8 mL of either a test solution

121 containing a background electrolyte of 0.1M  $\text{NaNO}_3$ , to maintain a constant ionic strength in

122 the extraction solutions (Yang et al. 2006) or a soil leachate. For fixed pH experiments the

123 pH of the suspensions were adjusted by dropwise addition of 0.01M HCl and 0.1M NaOH.

124 pH was measured using a Jenway 3310 pH meter with a Fisherbrand FB68793 glass

125 electrode. The pH meter was calibrated using pH 4 and pH 7 buffers. Calibration was

126 conducted at the start of analysis and after every 10 samples. Following addition of the

127 nanoparticles, each solution was shaken for 18 hours on an end-over-end shaker at constant

128 temperature (20 °C). The nanoparticles were then removed from solution using a

129 neodymium permanent magnet and the solution analysed for the metal(s) of interest by

130 either a Perkin Elmer 100B Atomic absorption spectrometer (AAS) or a Perkin Elmer

131 OPTIMA 3000 inductively coupled plasma optimal emission spectrometer (ICP-OES). In the  
132 single metal experiments, to check for nanoparticle stability and / or remnant nanoparticles in  
133 suspension, Fe in solution was also analysed by AAS or ICP-OES. In all cases Fe was  
134 below detection in solution indicating that the nanoparticles were stable and removal of at  
135 least 99.99% of the added nanoparticles (Hughes et al, 2017). Nanoparticle free controls  
136 were also run. All experiments were performed in triplicate. Metal extraction efficiency was  
137 calculated as the difference in concentration between the test and a control solution  
138 expressed as a percentage of the control solution concentration. Partition coefficients ( $K_d$ )  
139 were calculated as the ratio of metal concentration on the nanoparticles to the metal  
140 concentration remaining in solution.

141

#### 142 *Single metal solutions*

143 In the first set of experiments, solutions containing 10 mg L<sup>-1</sup> of either Ca, Cd, Co, Cu or Mg  
144 were used (though note that results are expressed in terms of moles to allow comparison  
145 between elements). The metals were introduced as nitrate salts and the pH was adjusted to  
146 pH 2, 3, 4, 5, 6, 7 and 8. Metal concentrations were analysed by AAS. Detection limits were  
147 0.02 mg L<sup>-1</sup> (Ca), 0.01 mg L<sup>-1</sup> (Cd), 0.007 mg L<sup>-1</sup> (Cu), 0.009 mg L<sup>-1</sup> (Co), 0.001 mg L<sup>-1</sup> (Fe),  
148 0.001 mg L<sup>-1</sup> (Mg), 0.008 mg L<sup>-1</sup> (Pb) and 0.01 mg L<sup>-1</sup> (Zn), whilst precision was 3.16% (Ca),  
149 4.62% (Cd), 2.99% (Cu), 3.71% (Co), 2.66% (Fe), 3.40% (Mg), 3.52% (Pb) and 3.08% (Zn).  
150 Accuracy was 98% (Ca), 97% (Cd), 98% (Cu), 95% (Co) and 96% (Mg).

151

#### 152 *Soil leachates*

153 For a second set of experiments, soils were collected from metal contaminated sites:  
154 Avonmouth (ST 532 803) a former Pb/Zn smelter, which was operational until 2003  
155 (Nahmani et al. 2007); Barney Beck (SD 992 998), an episodically flooded pasture located  
156 near a small tributary of the River Swale in North Yorkshire, an area that was extensively  
157 mined for Pb from the Roman era up until the late 19<sup>th</sup> Century when the mine was  
158 abandoned (Dennis, 2005); Cwmystwyth (SN 804 747) a former Pb/Zn mine site located in



159 Ceredigion, central Wales that was mined from the beginning of the Roman era to 1950  
160 (Hughes, 1981); Devon Great Consols (DGC) (SX 728 964) an abandoned Cu and As mine  
161 which operated between 1844 and 1930 (Richardson, 1991); Graig Goch (SN 802 741) an  
162 abandoned Pb mine located in Ceredigion, central Wales and a part of the central Wales  
163 orefield (Palumbo-Roe, 2013); Redruth (SW 724 397) the former Tresavean Cu and Sn mine  
164 site, which ceased operating in 1928 (Dines, 1956); Rookhope (NY 894 441) a former Pb  
165 and fluorspar mine (Sizmur et al. 2011); Scunthorpe (SE 893 108) the site of the  
166 Buckingham allotments which have elevated soil As concentrations due to the underlying  
167 geology of the area which consists of arsenic rich Jurassic ironstone (Palumbo-Roe et al.  
168 2005); Shipham (ST 448 573) a former Zn mining site, active in the 18<sup>th</sup> and 19<sup>th</sup> centuries in  
169 Somerset (Kiekens, 1995); and, Wisley (TQ 065 592) an uncontaminated sandy loam soil  
170 that was spiked with lead nitrate, copper sulphate and zinc sulphate in 2005 (Alexander et al.  
171 2006). These soils were used to generate leachates that were in turn used to investigate the  
172 ability of the DTPA-functionalised nanoparticles to remove metals from mixed-metal  
173 solutions that also contained natural dissolved organic matter. This allowed an assessment  
174 of the potential use of the nanoparticles as a component of soil washing remedial treatments  
175 or to remediate metal-contaminated water courses. The soil leachates were prepared by  
176 adding 2.5 g of soil (air dried, 2mm sieved) to 50 mL of ultrapure H<sub>2</sub>O. This ratio was based  
177 on the 1:20 to 1:40 range of optimal ratios for extraction of metals from soil washing  
178 solutions using EDTA (Papassiopi et al., 1999). The suspension was shaken on an end over  
179 end shaker for 24 hours then centrifuged for 20 minutes at 3500 rpm. The supernatant was  
180 decanted off, producing the final soil leachate. The pH of the leachate was measured and  
181 then 10 mg of nanoparticles in 2mL of ultrapure water were added to 8 mL of leachate. After  
182 removal of the nanoparticles, solutions were syringe filtered using 0.45µm cellulose nitrate  
183 filters before being analysed for a range of metals by ICP-OES (As, Ca, Cd, Co, Cr, Cu, Fe,  
184 Mg, Na, Ni, P, Pb, Zn). Detection limits and precision were as follows: As ( $1.3 \times 10^{-3}$  mg L<sup>-1</sup>,  
185 3.1 %), Ca ( $1.3 \times 10^{-3}$  mg L<sup>-1</sup>, 2.6%), Cd ( $8.9 \times 10^{-5}$  mg L<sup>-1</sup>, 2.9 %), Co ( $1.6 \times 10^{-3}$  mg L<sup>-1</sup>,  
186 4.2%), Cr ( $3.2 \times 10^{-4}$  mg L<sup>-1</sup>, 3.9%), Cu ( $1.3 \times 10^{-3}$  mg L<sup>-1</sup>, 2.6 %), Fe ( $2.1 \times 10^{-3}$  mg L<sup>-1</sup>, 4.5

187 %), Mg ( $1.6 \times 10^{-4}$  mg L<sup>-1</sup>, 2.5%), Na ( $9.2 \times 10^{-4}$  mg L<sup>-1</sup>, 3.1 %), Ni ( $3.3 \times 10^{-3}$  mg L<sup>-1</sup>, 2.7%), P  
188 ( $3.3 \times 10^{-2}$  mg L<sup>-1</sup>, 2.7 %), Pb ( $1.2 \times 10^{-2}$  mg L<sup>-1</sup>, 3.3 %), Zn ( $8.5 \times 10^{-4}$  mg L<sup>-1</sup>, 3.6 %).

189 Dissolved organic carbon (DOC) was measured using a Shimadzu TOC-L total carbon  
190 analyser equipped with a non-dispersive infra-red (NDIR) detector. The detection limit for the  
191 DOC was  $1.31 \times 10^{-4}$  mg L<sup>-1</sup> and the precision value for the 12 samples measured in  
192 duplicate was  $\pm 2.4$  %.

193

#### 194 *Statistical analysis*

195 Data were analysed using SigmaPlot 12 for Windows.

196

## 197 **Results and Discussion**

198

### 199 **Single metal studies**

200 Metal concentrations in the control and nanoparticle-treated mono-metallic solutions are  
201 presented in Table 1 and calculated extraction efficiencies in Table 2. The decrease in  
202 control solution concentrations with increasing pH for Cu and, to a lesser extent Cd and Co,  
203 indicate that some precipitation occurred at higher pH values for these metals. However,  
204 differences in concentration between the control and nanoparticle-treated solution  
205 concentrations at a given pH are indicative of adsorption as the metal removal process.  $K_d$   
206 values were calculated as the ratio of the concentration of metal on the nanoparticles at  
207 equilibrium concentrations (mmol kg<sup>-1</sup>) and the concentration of metal in solution at  
208 equilibrium (mmol L<sup>-1</sup>) for the extractions and are presented in Table 3.

209

210 Table 1. Concentrations (mmol L<sup>-1</sup>) of metals in solution in control and nanoparticle treated solutions. Values are mean ± standard deviations (n  
 211 = 3).

pH	Ca		Cd		Co		Cu		Mg	
	Control	NP	Control	NP	Control	NP	Control	NP	Control	NP
2	0.232 ± 0.004	0.223 ± 0.001	0.086 ± 0.001	0.032 ± 0.003	0.173 ± 0.002	0.033 ± 0.013	0.163 ± 0.002	0.022 ± 0.00	0.406 ± 0.002	0.402 ± 0.006
3	0.233 ± 0.003	0.161 ± 0.032	0.085 ± 0.001	0.010 ± 0.000	0.171 ± 0.002	0.018 ± 0.002	0.158 ± 0.001	0.017 ± 0.000	0.416 ± 0.004	0.348 ± 0.031
4	0.237 ± 0.003	0.090 ± 0.008	0.080 ± 0.000	0.006 ± 0.002	0.168 ± 0.001	0.017 ± 0.001	0.150 ± 0.007	0.026 ± 0.002	0.407 ± 0.004	0.337 ± 0.026
5	0.227 ± 0.001	0.079 ± 0.012	0.065 ± 0.001	0.006 ± 0.002	0.169 ± 0.001	0.020 ± 0.002	0.154 ± 0.003	0.032 ± 0.000	0.410 ± 0.002	0.336 ± 0.031
6	0.236 ± 0.001	0.080 ± 0.004	0.077 ± 0.000	0.007 ± 0.002	0.168 ± 0.001	0.019 ± 0.001	0.150 ± 0.002	0.026 ± 0.000	0.413 ± 0.005	0.339 ± 0.016
7	0.228 ± 0.002	0.059 ± 0.005	0.077 ± 0.003	0.006 ± 0.001	0.152 ± 0.001	0.019 ± 0.000	0.067 ± 0.004	0.017 ± 0.001	0.410 ± 0.002	0.354 ± 0.014
8	0.231 ± 0.000	0.057 ± 0.007	0.079 ± 0.000	0.006 ± 0.000	0.152 ± 0.003	0.020 ± 0.000	0.058 ± 0.011	0.012 ± 0.002	0.402 ± 0.016	0.391 ± 0.008

212

213

214

215 Table 2. Percentage extraction efficiencies of Ca, Cd, Co, Cu, Mg, Pb and Zn from aqueous  
216 solution by nanoparticles at pH 2 to 8. Values are mean ± standard deviation, n = 3. Pb and  
217 Zn data from Hughes et al. (2017).

pH Metal	2	3	4	5	6	7	8
Ca	3.6 ± 0.54	31 ± 14	62 ± 3.3	65 ± 5.3	66 ± 1.9	74 ± 2.1	75 ± 3.0
Cd	62 ± 3.7	89 ± 0.57	92 ± 2.0	91 ± 2.8	91 ± 3.1	92 ± 1.4	92 ± 0.13
Co	81 ± 7.5	90 ± 1.2	90 ± 0.53	88 ± 1.2	89 ± 0.66	87 ± 0.23	87 ± 0.40
Cu	86 ± 0.17	90 ± 0.10	82 ± 1.5	79 ± 0.18	82 ± 0.060	75 ± 1.8	79 ± 3.2
Mg	1.0 ± 1.5	16 ± 7.4	17 ± 6.3	18 ± 7.6	18 ± 3.8	14 ± 3.5	2.7 ± 2.0
Pb	91 ± 2.8	97 ± 0.32	94 ± 0.78	95 ± 0.92	94 ± 1.6	62 ± 9.4	71 ± 8.1
Zn	76 ± 10	92 ± 2.6	92 ± 1.8	91 ± 1.4	91 ± 1.7	91 ± 0.53	88 ± 0.26

218

219 Table 3. Metal partition coefficients ( $K_d / L\ kg^{-1}$ ) for Cd, Co, Cu, Pb, Zn, Ca and Mg extraction  
220 by nanoparticles between pH 2 and 8. Values are mean ± standard deviation (n = 3). Pb and  
221 Zn values taken from Hughes et al (2017).

pH	Cd	Co	Cu	Pb	Zn	Ca	Mg
2	1680±250	5140±3190	6270±88.1	10800±4400	4050±2850	37.3±5.80	10.4±15.9
3	7780±441	8750±1070	8580±91.2	32800±3440	12000±3560	486±329	200±112
4	12100±2950	8630±483	4700±494	17300±2780	12000±2660	1650±222	212±95.6
5	11000±3290	7570±836	3810±40.9	18900±3760	10000±1720	1990±425	228±120
6	11100±3570	7870±520	4670±19.4	16000±4240	10900±2440	1960±171	220±57.5
7	11400±1950	6820±141	3060±281	1760±747	10100±636	2880±324	160±47.8
8	12300±234	6800±242	3890±706	2670±1140	7560±189	3120±499	28.4±21.7

222

223 Of the potentially toxic metals, extraction efficiency of Cd, Co and Cu is in the same range as  
224 that of Pb and Zn in our previous experiments (Hughes et al., 2017) and as reported for a  
225 range of functionalised nanoparticles (e.g. Afsar et al., 2014; Liu et al., 2008; Liu et al., 2009;  
226 Koehler et al., 2009; Zhang et al., 2011; the review of Lofrano et al., 2016; Table S1 in the  
227 Supplementary Information). In depth comparison of extraction efficiencies found here and in  
228 other studies is compromised by differences in initial solution composition and solid/liquid

229 ratios. Two way Analysis of Variance (ANOVA) indicates that significant ( $p \leq 0.01$ )  
230 differences are present between metals and between pH for both extraction efficiencies and  
231  $K_d$  values and that there are significant interaction terms between the two. Extraction  
232 efficiency is greater for Cd, Co, Cu, Pb and Zn than it is for Ca and Mg at all pH levels  
233 except at pH 7 and 8 when extraction efficiency of Ca increases; relative to the other “toxic”  
234 metals Cd shows reduced extraction efficiency at pH 2 and Cu at pHs 4 – 6. Pb extraction  
235 efficiency decreases at pH 7 and 8. In general  $K_d$ s of  $\geq 500 \text{ L kg}^{-1}$  are considered acceptable  
236 and  $> 5000 \text{ mg/L}$  very good (Fryxell et al., 2005). Thus the  $K_d$ s determined for our  
237 nanoparticles across a range of potentially toxic metals are suggestive of them being a  
238 useful adsorbent. Ca and Mg always have the lowest  $K_d$ s. Similar results are reported in  
239 other studies using functionalised nanoparticles.

240

241 The iso-electric point of the nanoparticles is 6.74 (Hughes et al., 2017). Thus whilst our  
242 previous data suggest that adsorption of the metals is most likely dominated by chelation  
243 with the nitrogen atoms in the DTPA (Hughes et al., 2017) for  $\text{pH} \leq 6$  ion exchange with  
244 protons on the protonated functional groups of the DTPA and for  $\text{pH} \geq 7$  electrostatic  
245 adsorption to deprotonated functional groups of the DTPA is also likely to occur. The  
246 differences in efficiencies and  $K_d$ s between the different metals are due in part to the metal-  
247 DTPA complexation stability constants for the potentially toxic metals tested being higher  
248 than those for Ca and Mg (e.g. Lindsay et al., 1979; Dojino, 2017; Liu et al., 2008). However,  
249 in addition, as initial concentrations in solutions for the single metal tests were equal for all  
250 metals on a  $\text{mg L}^{-1}$  basis the different atomic masses of the elements result in differing molar  
251 concentrations which may also have an impact. For example, both Ca and Mg have lower  
252 atomic masses than the toxic metals and therefore their molar concentrations are higher.  
253 Adsorption sites on the nanoparticles are potentially closer to saturation in the Ca and Mg  
254 extraction tests which may reduce extraction efficiency.

255 The reduced extraction efficiency of Cd at pH 2 compared to Cu and Pb (Hughes et al.,  
256 2017) is consistent with previous studies using EDTA-functionalised nanoparticles (Koehler  
257 et al., 2009; Zhang et al., 2011) and is due to the lowering of the pH-dependent complex  
258 formation constant (Anderegg et al., 1959). Reduced extraction efficiency of Cu relative to  
259 Cd and Pb at similar concentrations to those used in our experiment has been previously  
260 observed at pH 6 (Koehler et al., 2009) and pH 5 (Zhang et al. 2011) and attributed to the  
261 lower molar concentration of Cd and Pb solutions relative to Cu for solutions of the same  
262 concentration by mass leading to increased saturation levels of adsorption sites for the Cu.  
263 The high extraction efficiency and  $K_d$  values for Pb at pH 2 – 6 are consistent with a number  
264 of other studies using a variety of functionalised nanoparticles (Koehler et al., 2009; Zhang  
265 et al., 2011; Liu et al, 2009; Liu et al., 2008) and are related to high stability constants and  
266 the low molar concentration of Pb in the test solution relative to the other metals. We have  
267 discussed the reduced extraction efficiency and  $K_d$  values of Pb at pH 7 and 8 previously  
268 (Hughes et al., 2017); it is consistent with previous studies on a variety of functionalised  
269 nanoparticles and is attributed to changes in speciation at these pH values (Hughes et al.,  
270 2017; Wang et al., 2015; Weng, 2004; Liu et al., 2009).

271

272 Similar to other studies on a variety of chelating agent functionalised magnetic nanoparticles  
273 (e.g. Chen et al., 2016; Liu et al., 2008; Liu et al., 2009; Shi et al., 2016; Zhang et al., 2012,  
274 Zhang et al., 2011; Table S1 in Supporting Information) our single metal extraction  
275 experiments show that our functionalised nanoparticles can extract a range of contaminant  
276 metals. This is to be expected as the chelating agents used to functionalise the  
277 nanoparticles are not specific for a single metal. This is encouraging for use of functionalised  
278 nanoparticles in real world situations where mixed metal contamination is more likely than  
279 single metal contamination. However, although previous studies have shown the capacity of  
280 functionalised nanoparticles to maintain high extraction efficiencies in mixed metal solutions  
281 often containing high concentrations of nontoxic elements such as Ca and Mg (e.g. Hughes

282 et al., 2017; Liu et al., 2008; Shan et al., 2015; Zhang et al., 2012) extraction efficiency can  
283 be reduced relative to single metal solutions (e.g. Hughes et al., 2017; Liu et al., 2008;  
284 Zhang et al., 2011). Ca and Mg often occur at high concentrations in soils (Ca =1-200 g kg<sup>-1</sup>;  
285 Mg = 0.1-28.6 g kg<sup>-1</sup>) (Bolan et al. 2004) and solutions and leachates from soil could  
286 therefore contain higher concentrations of such elements than concentrations considered in  
287 experiments to date. Similarly although previous studies have shown high levels of metal  
288 extraction in the presence of DOC (Hughes et al., 2017; Liu et al., 2008; Shan et al., 2015;  
289 Zhang et al. 2012) our previous experiments (Hughes et al., 2017) also showed significant  
290 reductions in extraction efficiency at concentrations of 2.1 mg L<sup>-1</sup> and 21 mg L<sup>-1</sup> DOC. Metal-  
291 rich extracts obtained by leaching soils with water may contain higher concentrations of DOC  
292 than this which could potentially have an impact on the extraction efficiency of toxic metals  
293 from such soils. Therefore to investigate further the potential use of our DTPA-functionalised  
294 nanoparticles for removal of metal from the aqueous leachates of contaminated soils, we  
295 determined extraction efficiencies using leachates from soils containing a mixture of  
296 inorganic contaminants and variable, native concentrations of DOC.

297

### 298 **Soil extractions**

299 The chemistry of the soil leachates in control and nanoparticle-present treatments is  
300 presented in Tables 4 and 5. All the leachates were filtered to 0.45 µm prior to use.  
301 Operationally we have assumed that this filtration step results in the production of a pure  
302 solution and that differences between control and nanoparticle-present treatments are  
303 therefore due to interactions between ions in solution and the added nanoparticles. We did  
304 not analyse our filtered solutions for the presence of colloids but these may be present and  
305 have an impact on our results. However, from a practical perspective the aim of our  
306 investigation was to determine whether our nanoparticles were effective at removing metals  
307 from leachates obtained from metal contaminated soils regardless of whether colloidal  
308 particles play a role or not. The leachates contain relatively low concentrations of metals

309 despite samples being taken from former mine sites with soils that have high total metal  
310 concentrations reported in the literature; this reflects the speciation of the metals in the soils  
311 and highlights the important difference between concentrations of “total” metals compared to  
312 other fractions such as “bioavailable”, “bioaccessible” and “mobile”. The Scunthorpe soil is a  
313 good example of this. Palumbo-Roe et al (2005) report elevated As concentrations in soils  
314 taken from this sample locality but also that the majority of this As is not bio-accessible.  
315 Further the pH of the leachate (c. neutral) lies in the range where As sorption to Fe oxides is  
316 high which reduces the likelihood of As passing into solution (Dixit and Hering, 2003; Partey  
317 et al. 2008). However, in this study we are not concerned with the issue of bioavailability of  
318 metals in soils. Rather, the contaminated soils were used to generate leachates containing  
319 metals which could be used to determine the ability of the DTPA-functionalised nanoparticles  
320 to remove metals from mixed metal solutions that also contained dissolved organic matter.  
321 This allowed us to assess the potential use of the nanoparticles as a stage in soil washing  
322 remedial treatments and / or for remediating metal-contaminated natural waters.

323

324 The total concentration of “non toxic” elements (Ca, Mg, Na) in the control leachate was  
325 significantly greater ( $p \leq 0.05$ , Kruskal-Wallis analysis of variance on ranks) than that of the  
326 total concentration of potentially toxic elements (As, Cd, Co, Cr, Cu, Pb, Zn). Despite this the  
327 nanoparticles removed significantly more toxic than non-toxic (either Ca+Mg or Ca+Mg+Na)  
328 elements from solution ( $p \leq 0.05$ , Kruskal-Wallis analysis of variance on ranks). Out of the  
329 10 soils studied, where there are significant differences ( $p \leq 0.05$ ; t-tests) between the  
330 concentrations in the nanoparticle-present and control treatments (As – 4 soils, Cd – 4 soils,  
331 Cu – 4 soils, Pb – 5 soils, Zn – 6 soils), the nanoparticle-present treatments contain lower  
332 concentrations of potentially toxic metals than the controls. Cd, Cu, Pb and Zn would be  
333 present as cations under the solution conditions whereas As would be present as an  
334 oxyanion. As with the single element extractions, adsorption of the cations is most likely  
335 dominated by chelation but will also involve, depending on pH, ion exchange or electrostatic



336 adsorption whilst adsorption of the As is most likely due to non-specific adsorption between  
337 the As oxyanion and the protonated nanoparticle surface.

338

339 With respect to the effect of the nanoparticle treatment on concentrations of the major, non-  
340 toxic elements, Na usually has significantly higher concentrations in the nanoparticle-present  
341 treatments (7 out of 8 soils) whereas Mg was lower in the nanoparticle-present leachates for  
342 two soils (Avonmouth and Cwmystwyth) and Ca showed no consistent trend in the two soils  
343 (Avonmouth and Barney Beck) where there were significant differences. The production of  
344 the nanoparticles involves precipitation of Fe oxide in 2 M NaOH. Despite subsequent  
345 washing stages, the most obvious explanation for the increase in Na in solution on addition  
346 of the nanoparticles to the leachates is that residual Na<sup>+</sup> is still present associated with the  
347 nanoparticles.

348 Table 4. Mean concentrations ( $\mu\text{mol L}^{-1}$ ) of metals in control (cont) and nanoparticle (NP)-treated soil leachate. Values are mean  $\pm$  standard  
 349 deviations (n = 3). BDL indicates concentration below detection limit. ***Bold italics indicate a significant difference ( $p \leq 0.05$ ; t-test) between***  
 350 ***control and nanoparticle present solution element concentrations.*** For statistical analysis of solutions where concentrations were below  
 351 detection limits, concentrations were fixed at the detection limit. Avon = Avonmouth, Barn = Barney Beck, Cwm = Cwmystwyth, DGC = Devon  
 352 Great Consols, Graig= Graig Goch, Red – Red Ruth, Rook = Rookhope, Scun = Scunthorpe, Ship = Shipham, Wis = Wisley.

Soil	Treatment	As	Ca	Cd	Co	Cr	Cu	Mg	Na	Pb	Zn
Avon	cont	<b><i>0.241 <math>\pm</math> 0.075</i></b>	<b><i>415 <math>\pm</math> 10.8</i></b>	<b><i>8.46 <math>\pm</math> 0.380</i></b>	0.167 $\pm$ 0.00348	0.151 $\pm$ 0.116	<b><i>9.01 <math>\pm</math> 0.997</i></b>	<b><i>145 <math>\pm</math> 22.2</i></b>	<b><i>82.4 <math>\pm</math> 11.1</i></b>	<b><i>7.89 <math>\pm</math> 2.11</i></b>	<b><i>579 <math>\pm</math> 22.8</i></b>
	NP	<b><i>BDL</i></b>	<b><i>376 <math>\pm</math> 15.7</i></b>	<b><i>6.48 <math>\pm</math> 0.271</i></b>	0.142 $\pm$ 0.0145	0.00900 $\pm$ 0.00417	<b><i>1.19 <math>\pm</math> 0.213</i></b>	<b><i>1.70 <math>\pm</math> 2.30</i></b>	<b><i>119 <math>\pm</math> 3.05</i></b>	<b><i>BDL</i></b>	<b><i>473 <math>\pm</math> 19.9</i></b>
Barn	cont	BDL	<b><i>118 <math>\pm</math> 2.25</i></b>	<b><i>0.00226 <math>\pm</math> 0.000111</i></b>	BDL	0.0615 $\pm$ 0.0271	0.0197 $\pm$ 0.00143	16.4 $\pm$ 2.06	47.1 $\pm$ 0.415	<b><i>0.686 <math>\pm</math> 0.183</i></b>	0.701 $\pm$ 0.204
	NP	BDL	<b><i>130 <math>\pm</math> 5.39</i></b>	<b><i>BDL</i></b>	BDL	0.0621 $\pm$ 0.0137	0.0241 $\pm$ 0.00388	17.3 $\pm$ 1.91	104 $\pm$ 8.08	<b><i>0.143 <math>\pm</math> 0.0826</i></b>	0.270 $\pm$ 0.213
Cwm	cont	BDL	14.7 $\pm$ 4.65	0.0150 $\pm$ 0.0000489	0.0293 $\pm$ 0.00361	0.0210 $\pm$ 0.0193	0.132 $\pm$ 0.0470	<b><i>10.2 <math>\pm</math> 0.554</i></b>	<b><i>31.4 <math>\pm</math> 2.54</i></b>	<b><i>1.53 <math>\pm</math> 0.618</i></b>	<b><i>11.3 <math>\pm</math> 0.704</i></b>
	NP	BDL	10.2 $\pm$ 2.39	BDL	BDL	0.00822 $\pm$ 0.00359	0.0663 $\pm$ 0.00695	<b><i>7.42 <math>\pm</math> 1.00</i></b>	<b><i>78.5 <math>\pm</math> 2.62</i></b>	<b><i>0.075 <math>\pm</math> 0.000503</i></b>	<b><i>2.07 <math>\pm</math> 1.45</i></b>
DGC	cont	<b><i>2.27 <math>\pm</math> 0.101</i></b>	107 $\pm$ 11.9	BDL	0.0755 $\pm$ 0.00810	BDL	<b><i>11.7 <math>\pm</math> 1.73</i></b>	16.2 $\pm$ 2.17	<b><i>15.9 <math>\pm</math> 1.20</i></b>	BDL	1.44 $\pm$ 0.508
	NP	<b><i>1.129 <math>\pm</math> 0.0449</i></b>	111 $\pm$ 1.42	BDL	0.0633 $\pm$ 0.00713	BDL	<b><i>0.247 <math>\pm</math> 0.146</i></b>	16.5 $\pm$ 0.304	<b><i>66.1 <math>\pm</math> 2.54</i></b>	BDL	0.626 $\pm$ 0.285
Graig	cont	BDL	16.2 $\pm$ 0.683	<b><i>0.157 <math>\pm</math> 0.00535</i></b>	0.109 $\pm$ 0.0183	0.00676 $\pm$ 0.00105	<b><i>0.383 <math>\pm</math> 0.00204</i></b>	12.4 $\pm$ 0.656	<b><i>28.3 <math>\pm</math> 12.0</i></b>	<b><i>41.4 <math>\pm</math> 0.591</i></b>	<b><i>75.9 <math>\pm</math> 1.83</i></b>
	NP	BDL	18.0 $\pm$ 0.909	<b><i>0.0946 <math>\pm</math> 0.0107</i></b>	0.0904 $\pm$ 0.00569	0.00635 $\pm$ 0.000342	<b><i>0.0787 <math>\pm</math> 0.0236</i></b>	11.4 $\pm$ 0.293	<b><i>71.3 <math>\pm</math> 3.15</i></b>	<b><i>0.228 <math>\pm</math> 0.145</i></b>	<b><i>51.0 <math>\pm</math> 7.39</i></b>
Red	cont	BDL	636 $\pm$ 47.5	BDL	BDL	BDL	0.0384 $\pm$ 0.00696	14.9 $\pm$ 0.842	<b><i>90.4 <math>\pm</math> 3.25</i></b>	BDL	<b><i>0.459 <math>\pm</math> 0.212</i></b>
	NP	BDL	681 $\pm$ 47.4	BDL	BDL	0.0330 $\pm$	0.0325 $\pm$ 0.0112	18.8 $\pm$ 2.75	<b><i>35.4 <math>\pm</math> 1.96</i></b>	BDL	<b><i>0.0404 <math>\pm</math> 0.00485</i></b>
Rook	cont	<b><i>0.0764 <math>\pm</math> 0.0124</i></b>	308 $\pm$ 26.4	<b><i>0.0181 <math>\pm</math> 0.000750</i></b>	0.166 $\pm$ 0.0701	0.0600 $\pm$ 0.0476	0.0429 $\pm$ 0.0293	53.4 $\pm$ 2.72	<b><i>38.5 <math>\pm</math> 2.54</i></b>	3.38 $\pm$ 1.46	<b><i>8.59 <math>\pm</math> 0.966</i></b>
	NP	<b><i>0.0400 <math>\pm</math> 0.00467</i></b>	301 $\pm$ 3.37	<b><i>BDL</i></b>	0.126 $\pm$ 0.0141	0.0200 $\pm$ 0.00547	0.024 $\pm$ 0.0118	49.6 $\pm$ 0.820	<b><i>85.7 <math>\pm</math> 5.68</i></b>	0.952 $\pm$ 0.0782	<b><i>1.50 <math>\pm</math> 0.532</i></b>
Scun	cont	0.181 $\pm$ 0.157	549 $\pm$ 403	0.00671 $\pm$ 0.00519	0.119 $\pm$ 0.0259	0.214 $\pm$ 0.250	0.135 $\pm$ 0.187	72.1 $\pm$ 34.3	140 $\pm$ 72.2	BDL	0.718 $\pm$ 0.525
	NP	0.230 $\pm$ 0.0552	335 $\pm$ 35.8	0.00792 $\pm$ 0.00413	0.150 $\pm$ 0.0470	0.278 $\pm$ 0.0890	0.0255 $\pm$ 0.00346	73.5 $\pm$ 11.9	129 $\pm$ 12.2	BDL	0.600 $\pm$ 0.101
Ship	cont	0.546 $\pm$ 0.0948	337 $\pm$ 3.71	0.787 $\pm$ 0.0366	0.119 $\pm$ 0.0555	0.0407 $\pm$ 0.0212	0.0314 $\pm$ 0.00786	144 $\pm$ 4.93	<b><i>61.9 <math>\pm</math> 9.30</i></b>	0.839 $\pm$ 0.284	<b><i>177 <math>\pm</math> 3.71</i></b>
	NP	0.400 $\pm$ 0.0501	343 $\pm$ 9.01	0.521 $\pm$ 0.0247	0.210 $\pm$ 0.0595	0.0126 $\pm$ 0.00593	0.0357 $\pm$ 0.00168	146 $\pm$ 3.83	<b><i>111 <math>\pm</math> 3.34</i></b>	0.263 $\pm$ 0.288	<b><i>148 <math>\pm</math> 5.95</i></b>
Wis	cont	<b><i>0.0666 <math>\pm</math> 0.00387</i></b>	417 $\pm$ 14.3	0.00435 $\pm$ 0.00125	0.166 $\pm$ 0.0266	0.0181 $\pm$ 0.00358	<b><i>1.05 <math>\pm</math> 0.0368</i></b>	51.9 $\pm$ 1.31	<b><i>35.6 <math>\pm</math> 2.18</i></b>	<b><i>0.145 <math>\pm</math> 0.0187</i></b>	2.04 $\pm$ 0.0316
	NP	<b><i>0.0409 <math>\pm</math> 0.00306</i></b>	424 $\pm$ 2.57	0.00292 $\pm$ 0.00195	0.137 $\pm$ 0.0279	0.00839 $\pm$ 0.00388	<b><i>0.828 <math>\pm</math> 0.0336</i></b>	50.6 $\pm$ 1.21	<b><i>101 <math>\pm</math> 3.33</i></b>	<b><i>BDL</i></b>	1.24 $\pm$ 0.517
Detection Limit		0.0174	0.0324	0.0008	0.0272	0.0062	0.0205	0.0066	0.04	0.0579	0.013

354 Table 5. Leachate pH and dissolved organic carbon content / mg L<sup>-1</sup> in control (cont) and  
 355 nanoparticle (NP)-treated soil leachate. Soil names are as specified in the legend for Table  
 356 4. Values are means ± standard deviation (n = 3).

Soil	Treatment	pH	Dissolved organic carbon
Avon	cont	5.32 ± 0.20	9.16 ± 1.73
	NP	5.17 ± 0.07	10.0 ± 0.375
Barn	cont	6.94 ± 0.40	22.1 ± 23.1 <sup>1</sup>
	NP	6.78 ± 0.09	23.6 ± 24.5 <sup>2</sup>
Cwm	cont	5.44 ± 0.05	15.5 ± 0.633
	NP	5.43 ± 0.13	18.7 ± 0.522
DGC	cont	4.48 ± 0.12	1.85 ± 0.233
	NP	4.38 ± 0.05	2.66 ± 0.206
Graig	cont	4.41 ± 0.32	9.69 ± 0.600
	NP	4.44 ± 0.18	10.8 ± 0.510
Red	cont	7.70 ± 0.21	11.2 ± 0.576
	NP	7.51 ± 0.29	15.6 ± 2.25
Rook	cont	6.30 ± 0.11	10.7 ± 0.924
	NP	5.90 ± 0.06	11.5 ± 0.454
Scun	cont	7.74 ± 0.38	7.11 ± 3.63
	NP	7.71 ± 0.31	7.56 ± 2.09
Ship	cont	5.79 ± 0.06	30.9 ± 2.42
	NP	5.53 ± 0.12	30.9 ± 5.13
Wis	cont	6.98 ± 0.33	19.2 ± 6.14
	NP	6.52 ± 0.23	20.9 ± 6.17

357 <sup>1</sup> individual values were 48.8, 9.7 and 7.9 mg L<sup>-1</sup>. The initial value is likely to be an error which would give a mean composition  
 358 of 8.8 ± 1.3 mg L<sup>-1</sup>

359 <sup>2</sup> individual values were 51.9, 10.4 and 8.6 mg L<sup>-1</sup>. The initial value is likely to be an error which would give a mean composition  
 360 of 9.5 ± 1.3 mg L<sup>-1</sup>

361

362 The lower concentrations of Mg in the nanoparticle-present treatments seems most likely to  
 363 be due to adsorption of Mg, despite the relatively low Mg-DTPA complexation stability  
 364 constants (e.g. Lindsay et al., 1979; Dojino, 2017; Liu et al., 2008) and adsorption efficiencies  
 365 measured in our single metal experiments.

366  
 367 Extraction efficiencies (Table 6) were calculated for the metals that showed significant  
 368 reductions in concentration between the controls and the nanoparticle treatments.

369  
 370 Table 6. Percentage extraction efficiencies from soil solutions by nanoparticles where  
 371 nanoparticles cause a significant decrease in solution concentration. Values are mean  $\pm$   
 372 standard deviations (n = 3). Soil names are as specified in the legend for Table 4.

373

Metal Soil	As	Cd	Cu	Pb	Zn
Avon	93 $\pm$ 0	23 $\pm$ 3.2	87 $\pm$ 2.4	97 $\pm$ 4.8	18 $\pm$ 3.4
Barn	-	62 $\pm$ 4.8	-	79 $\pm$ 12	-
Cwm	-	-	-	95 $\pm$ 0.033	82 $\pm$ 13
DGC	37 $\pm$ 16	-	97 $\pm$ 0.70	-	-
Graig	-	40 $\pm$ 6.8	79 $\pm$ 6.1	99 $\pm$ 0.35	33 $\pm$ 9.7
Red	-	-	-	-	91 $\pm$ 1.1
Rook	48 $\pm$ 6.1	91 $\pm$ 8.1	-	-	83 $\pm$ 6.2
Scun	-	-	-	-	-
Ship	-	-	-	-	16 $\pm$ 3.4
Wis	39 $\pm$ 4.6	-	21 $\pm$ 3.2	60 $\pm$ 0	39 $\pm$ 25

374

375 Extraction efficiencies are variable between soils (no significant differences for As, ANOVA  
 376 on Ranks; significant differences for Cd and Cu between all soils, ANOVA and Holm-Sidak  
 377 multiple comparisons; between Graig Goch and Wisley for Pb and between Redruth and  
 378 Shipham for Zn, ANOVA on ranks and Tukey test multiple comparisons) and are similar or  
 379 lower to those obtained from the single metal solutions (Table 2). These results are  
 380 consistent with previous findings in which extraction efficiencies of metals from mixtures are  
 381 high and either unaffected or reduced by the presence of multiple metals, presumably due to  
 382 competition for adsorption sites and preferential adsorption (Zhang et al., 2012; Liu et al.,  
 383 2008; Zhang et al., 2011, Hughes et al., 2017; Shan et al., 2015) with precise trends

384 depending on a range of variables including the metal concentration, pH and nanoparticle  
385 concentration. Additionally there will be competition for metal binding between the adsorption  
386 sites on the nanoparticles and complexation sites on the dissolved organic matter present in  
387 solution. In our study Zn extraction efficiencies in particular appear to be depressed  
388 compared to the typical range (70 – 90%) found in single metal extraction experiments which  
389 is consistent with our previous findings from mixed Pb-Zn solutions (Hughes et al., 2017). Pb  
390 extraction efficiencies remain high except for from the Wisley soil which has a relatively high  
391 pH. Reduced Pb extraction at high pH is consistent with our previous findings on the effect of  
392 pH on Pb extraction (Hughes et al., 2017). Considering individual replicates rather than  
393 mean values the DOC content of the control leachate was in the range 2 – 49 mg L<sup>-1</sup> with no  
394 significant differences (two-way ANOVA,  $p \geq 0.05$ ) between the DOC content of the control  
395 and treated leachates. The maximum DOC values are higher than those in previous studies  
396 (e.g. Zhang et al., 2012; Liu et al., 2008; Shan et al., 2015; Hughes et al., 2017) where  
397 extraction efficiencies have been found to remain high but have been reduced by the  
398 presence of the DOC. Thus our results indicate that even in the presence of dissolved  
399 organic matter, the nanoparticles could be used to remove metals from solution. There were  
400 insufficient data to perform meaningful multiple regression analysis to determine any  
401 controlling variables for extraction efficiency. Correlation analysis between the extraction  
402 efficiency of individual metals and the pH, DOC, individual metal concentration and total  
403 metal concentration in controls for As, Cd, Cu, Pb and Zn only gave a significant correlation  
404 for % Pb extraction and pH ( $r = -0.89$ ,  $p \leq 0.05$ ).

405

406  $K_d$  values were calculated for metals that showed a significant decrease in concentration  
407 between the controls and nanoparticle treatments (Table 7). The  $K_d$  for specific metals  
408 largely show no significant differences between soils. The  $K_d$  values for individual elements  
409 determined from the soil samples were usually either significantly lower (16 out of 40 values)  
410 or had no significant difference (21 out of 40 values) compared to the  $K_d$  values obtained on  
411 single metal solutions at similar pH values. The lower  $K_d$  values relative to those obtained

412 from single metal solutions are consistent with the reduced extraction efficiencies observed  
413 and again, reflect competition for adsorption sites and competition between adsorption on  
414 the nanoparticles and complexation with the dissolved organic matter. Despite the  
415 reductions in  $K_d$  values, they are still typically  $> 500 \text{ L kg}^{-1}$  and many are  $> 5000 \text{ L kg}^{-1}$   
416 indicating the potential for the nanoparticles to be used as adsorbents (Fryxell et al., 2005).  
417 As with the extraction efficiency data, there were insufficient data to carry out multiple linear  
418 regression to determine controlling variables on the  $K_d$  values. There were no correlations  
419 between the  $K_d$  for a particular metal and the pH, DOC, individual metal concentration and  
420 total metal concentration in the controls. The reduction in  $K_d$  values compared to single-  
421 metal solutions and the lack of extraction of some elements from the leachates despite the  
422 presence of those elements in solution indicates the importance for more studies such as  
423 this one in which real, rather than synthetic, metal-bearing solutions are used to test the  
424 potential of novel sorbents for remediation.

425

426 Due to the significant variation between the different soil leachates used in our study in  
427 terms of pH, metal concentration, DOC and also the variations between this study and  
428 others in the literature (again pH, metal concentration, DOC but also the nature of the  
429 chelating agent added to the magnetic nanoparticles), together with the paucity of multi-  
430 element studies using real solutions in the literature it is difficult to make comparisons that  
431 are other than rather general as above. However, this study further demonstrates the  
432 potential for chelating agent functionalised magnetic nanoparticles to remove a range of  
433 metal contaminants from contaminated solutions and indicates that dissolved organic carbon  
434 and relatively high concentrations of non-toxic elements should not necessarily reduce the  
435 efficiency of the process.

436

437 Although not considered in our study, an important consideration in the viability of  
438 adsorbents for metal removal is their potential for reuse. There are various studies in the  
439 literature where solutions including HCl, HNO<sub>3</sub>, CH<sub>3</sub>COOH, NaOH, EDTA and water are

440 used to desorb metals from sorbents including those that present DTPA, EDTA and other  
441 chelating agents at their surface (e.g. Huang et al., 2018; Alizadeh et al., 2018; Ma et al.,  
442 2017; Yuan et al., 2016; Zhao et al., 2015; Liu et al., 2009; Zhang et al., 2011; Yang and  
443 Hodson, In press; Kaur et al., 2013; Venkateswarlu and Yoon, 2015, Zhang et al. 2016 (and  
444 references therein)and thus we are confident that reuse of the DTPA functionalised magnetic  
445 nanoparticles should be possible. Whilst that should be confirmed in laboratory studies,  
446 more important requirements for future studies are further investigations using “real” rather  
447 than synthetic test solutions and also the large scale application of this potential remediation  
448 technology. Larger scale trials would address issues concerned with potential mixing of  
449 nanoparticles in larger volumes of solution and also removal efficiencies of the nanoparticles  
450 when, depending on the design of reactor vessels, the nanoparticles may be further from the  
451 magnets required to collect the nanoparticles.

452

453

454 Table 7. Metal partition coefficients ( $K_d / L\ kg^{-1}$ ) for As, Cd, Cu, Pb and Zn extraction by  
 455 nanoparticles from different soil leachates. Values are means  $\pm$  standard error ( $n = 3$ ).  
 456 Where solution concentrations were below detection limits these were set at the detection  
 457 limits for the purposes of calculation. For each element, values with an alphabetic  
 458 superscript in common are not significantly different ( $p \geq 0.05$ ) between soils as assessed by  
 459 analysis of variance (ANOVA) and Holm Sidak pair wise comparisons (As) or ANOVA on  
 460 ranks and Tukey tests (Cd, Cu, Pb, Zn). <sup><lo/hi</sup> indicates significantly lower and <sup>>lo/hi</sup> significantly  
 461 higher values than the  $K_d$  determined on a single metal solution at the nearest pH below (lo)  
 462 or above (hi) that of the soil experiment, <sup>=lo/hi</sup> indicates no significant difference (Analysis of  
 463 variance and Holm-Sidak pair wise comparisons except for Avon and DGC Cu and Avon,  
 464 Barn, Graig and Wis Pb which were analysed by ANOVA on ranks and Tukey tests). Soil  
 465 names are as specified in the legend for Table 4.

Soil	As	Cd	Cu	Pb	Zn
Avon	12900 $\pm$ 0.00 <sup>a</sup>	308 $\pm$ 55.1 <sup>a&lt;lo&lt;hi</sup>	6750 $\pm$ 1500 <sup>ab&gt;lo=hi</sup>	93500 $\pm$ 72200 <sup>ab=lo=hi</sup>	227 $\pm$ 50.5 <sup>ab&lt;lo&lt;hi</sup>
Barn		1670 $\pm$ 313 <sup>ab&lt;lo&lt;hi</sup>		4950 $\pm$ 3086 <sup>ab=lo=hi</sup>	
Cwm				19400 $\pm$ 137 <sup>ab=lo=hi</sup>	6680 $\pm$ 5230 <sup>ab=lo=hi</sup>
DGC	1010 $\pm$ 81.7 <sup>b</sup>		57100 $\pm$ 27700 <sup>a=lo&gt;hi</sup>		
Graig		674 $\pm$ 202 <sup>ab&lt;lo&lt;hi</sup>	4140 $\pm$ 1390 <sup>ab=lo=hi</sup>	233000 $\pm$ 128000 <sup>a=lo=hi</sup>	511 $\pm$ 236 <sup>ab&lt;lo&lt;hi</sup>
Red					10500 $\pm$ 1470 <sup>a&gt;hi=lo</sup>
Rook	927 $\pm$ 230 <sup>bc</sup>	16090 $\pm$ 10090 <sup>b=lo=hi</sup>			5420 $\pm$ 2870 <sup>ab=lo=hi</sup>
Scun					
Ship					198 $\pm$ 47.3 <sup>b&lt;lo&lt;hi</sup>
Wis	633 $\pm$ 118 <sup>c</sup>		264 $\pm$ 51.7 <sup>b&lt;lo&lt;hi</sup>	1500 $\pm$ 0 <sup>b=lo=hi</sup>	852 $\pm$ 778 <sup>ab&lt;lo&lt;hi</sup>

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