



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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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⁻¹ ; 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⁻¹), 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

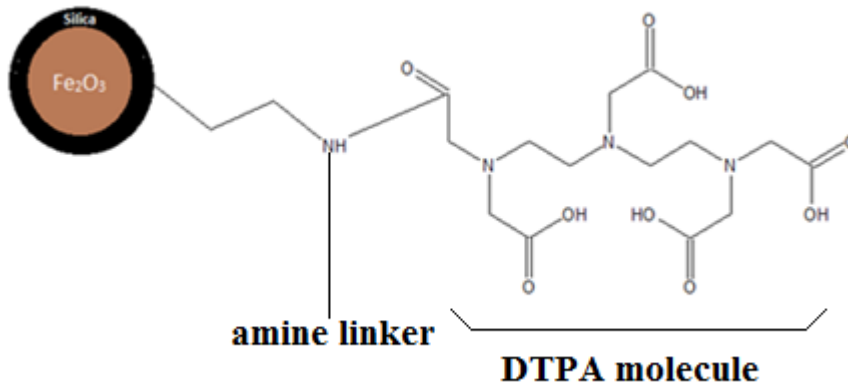
98 **Methods**

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 Fe^{2+} and Fe^{3+} ions present in FeCl_2 and 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 ± 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 NaNO₃, 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⁻¹ 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⁻¹ (Ca), 0.01 mg L⁻¹ (Cd), 0.007 mg L⁻¹ (Cu), 0.009 mg L⁻¹ (Co), 0.001 mg L⁻¹ (Fe),
148 0.001 mg L⁻¹ (Mg), 0.008 mg L⁻¹ (Pb) and 0.01 mg L⁻¹ (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 19th 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 18th and 19th 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 H₂O. 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 (1.3×10^{-3} mg L⁻¹,
185 3.1 %), Ca (1.3×10^{-3} mg L⁻¹, 2.6%), Cd (8.9×10^{-5} mg L⁻¹, 2.9 %), Co (1.6×10^{-3} mg L⁻¹,
186 4.2%), Cr (3.2×10^{-4} mg L⁻¹, 3.9%), Cu (1.3×10^{-3} mg L⁻¹, 2.6 %), Fe (2.1×10^{-3} mg L⁻¹, 4.5

187 %), Mg (1.6×10^{-4} mg L⁻¹, 2.5%), Na (9.2×10^{-4} mg L⁻¹, 3.1 %), Ni (3.3×10^{-3} mg L⁻¹, 2.7%), P
188 (3.3×10^{-2} mg L⁻¹, 2.7 %), Pb (1.2×10^{-2} mg L⁻¹, 3.3 %), Zn (8.5×10^{-4} mg L⁻¹, 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 1.31×10^{-4} mg L⁻¹ and the precision value for the 12 samples measured in
192 duplicate was ± 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⁻¹) and the concentration of metal in solution at
208 equilibrium (mmol L⁻¹) for the extractions and are presented in Table 3.

209

210 Table 1. Concentrations (mmol L⁻¹) 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 \pm 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 \pm 0.54	31 \pm 14	62 \pm 3.3	65 \pm 5.3	66 \pm 1.9	74 \pm 2.1	75 \pm 3.0
Cd	62 \pm 3.7	89 \pm 0.57	92 \pm 2.0	91 \pm 2.8	91 \pm 3.1	92 \pm 1.4	92 \pm 0.13
Co	81 \pm 7.5	90 \pm 1.2	90 \pm 0.53	88 \pm 1.2	89 \pm 0.66	87 \pm 0.23	87 \pm 0.40
Cu	86 \pm 0.17	90 \pm 0.10	82 \pm 1.5	79 \pm 0.18	82 \pm 0.060	75 \pm 1.8	79 \pm 3.2
Mg	1.0 \pm 1.5	16 \pm 7.4	17 \pm 6.3	18 \pm 7.6	18 \pm 3.8	14 \pm 3.5	2.7 \pm 2.0
Pb	91 \pm 2.8	97 \pm 0.32	94 \pm 0.78	95 \pm 0.92	94 \pm 1.6	62 \pm 9.4	71 \pm 8.1
Zn	76 \pm 10	92 \pm 2.6	92 \pm 1.8	91 \pm 1.4	91 \pm 1.7	91 \pm 0.53	88 \pm 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 \pm 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 \pm 250	5140 \pm 3190	6270 \pm 88.1	10800 \pm 4400	4050 \pm 2850	37.3 \pm 5.80	10.4 \pm 15.9
3	7780 \pm 441	8750 \pm 1070	8580 \pm 91.2	32800 \pm 3440	12000 \pm 3560	486 \pm 329	200 \pm 112
4	12100 \pm 2950	8630 \pm 483	4700 \pm 494	17300 \pm 2780	12000 \pm 2660	1650 \pm 222	212 \pm 95.6
5	11000 \pm 3290	7570 \pm 836	3810 \pm 40.9	18900 \pm 3760	10000 \pm 1720	1990 \pm 425	228 \pm 120
6	11100 \pm 3570	7870 \pm 520	4670 \pm 19.4	16000 \pm 4240	10900 \pm 2440	1960 \pm 171	220 \pm 57.5
7	11400 \pm 1950	6820 \pm 141	3060 \pm 281	1760 \pm 747	10100 \pm 636	2880 \pm 324	160 \pm 47.8
8	12300 \pm 234	6800 \pm 242	3890 \pm 706	2670 \pm 1140	7560 \pm 189	3120 \pm 499	28.4 \pm 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 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⁻¹;
285 Mg = 0.1-28.6 g kg⁻¹) (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⁻¹ and 21 mg L⁻¹ 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⁺ 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	<i>0.241 \pm 0.075</i>	<i>415 \pm 10.8</i>	<i>8.46 \pm 0.380</i>	0.167 \pm 0.00348	0.151 \pm 0.116	<i>9.01 \pm 0.997</i>	<i>145 \pm 22.2</i>	<i>82.4 \pm 11.1</i>	<i>7.89 \pm 2.11</i>	<i>579 \pm 22.8</i>
	NP	<i>BDL</i>	<i>376 \pm 15.7</i>	<i>6.48 \pm 0.271</i>	0.142 \pm 0.0145	0.00900 \pm 0.00417	<i>1.19 \pm 0.213</i>	<i>1.70 \pm 2.30</i>	<i>119 \pm 3.05</i>	<i>BDL</i>	<i>473 \pm 19.9</i>
Barn	cont	BDL	<i>118 \pm 2.25</i>	<i>0.00226 \pm 0.000111</i>	BDL	0.0615 \pm 0.0271	0.0197 \pm 0.00143	16.4 \pm 2.06	47.1 \pm 0.415	<i>0.686 \pm 0.183</i>	0.701 \pm 0.204
	NP	BDL	<i>130 \pm 5.39</i>	<i>BDL</i>	BDL	0.0621 \pm 0.0137	0.0241 \pm 0.00388	17.3 \pm 1.91	104 \pm 8.08	<i>0.143 \pm 0.0826</i>	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	<i>10.2 \pm 0.554</i>	<i>31.4 \pm 2.54</i>	<i>1.53 \pm 0.618</i>	<i>11.3 \pm 0.704</i>
	NP	BDL	10.2 \pm 2.39	BDL	BDL	0.00822 \pm 0.00359	0.0663 \pm 0.00695	<i>7.42 \pm 1.00</i>	<i>78.5 \pm 2.62</i>	<i>0.075 \pm 0.000503</i>	<i>2.07 \pm 1.45</i>
DGC	cont	<i>2.27 \pm 0.101</i>	107 \pm 11.9	BDL	0.0755 \pm 0.00810	BDL	<i>11.7 \pm 1.73</i>	16.2 \pm 2.17	<i>15.9 \pm 1.20</i>	BDL	1.44 \pm 0.508
	NP	<i>1.129 \pm 0.0449</i>	111 \pm 1.42	BDL	0.0633 \pm 0.00713	BDL	<i>0.247 \pm 0.146</i>	16.5 \pm 0.304	<i>66.1 \pm 2.54</i>	BDL	0.626 \pm 0.285
Graig	cont	BDL	16.2 \pm 0.683	<i>0.157 \pm 0.00535</i>	0.109 \pm 0.0183	0.00676 \pm 0.00105	<i>0.383 \pm 0.00204</i>	12.4 \pm 0.656	<i>28.3 \pm 12.0</i>	<i>41.4 \pm 0.591</i>	<i>75.9 \pm 1.83</i>
	NP	BDL	18.0 \pm 0.909	<i>0.0946 \pm 0.0107</i>	0.0904 \pm 0.00569	0.00635 \pm 0.000342	<i>0.0787 \pm 0.0236</i>	11.4 \pm 0.293	<i>71.3 \pm 3.15</i>	<i>0.228 \pm 0.145</i>	<i>51.0 \pm 7.39</i>
Red	cont	BDL	636 \pm 47.5	BDL	BDL	BDL	0.0384 \pm 0.00696	14.9 \pm 0.842	<i>90.4 \pm 3.25</i>	BDL	<i>0.459 \pm 0.212</i>
	NP	BDL	681 \pm 47.4	BDL	BDL	0.0330 \pm	0.0325 \pm 0.0112	18.8 \pm 2.75	<i>35.4 \pm 1.96</i>	BDL	<i>0.0404 \pm 0.00485</i>
Rook	cont	<i>0.0764 \pm 0.0124</i>	308 \pm 26.4	<i>0.0181 \pm 0.000750</i>	0.166 \pm 0.0701	0.0600 \pm 0.0476	0.0429 \pm 0.0293	53.4 \pm 2.72	<i>38.5 \pm 2.54</i>	3.38 \pm 1.46	<i>8.59 \pm 0.966</i>
	NP	<i>0.0400 \pm 0.00467</i>	301 \pm 3.37	<i>BDL</i>	0.126 \pm 0.0141	0.0200 \pm 0.00547	0.024 \pm 0.0118	49.6 \pm 0.820	<i>85.7 \pm 5.68</i>	0.952 \pm 0.0782	<i>1.50 \pm 0.532</i>
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	<i>61.9 \pm 9.30</i>	0.839 \pm 0.284	<i>177 \pm 3.71</i>
	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	<i>111 \pm 3.34</i>	0.263 \pm 0.288	<i>148 \pm 5.95</i>
Wis	cont	<i>0.0666 \pm 0.00387</i>	417 \pm 14.3	0.00435 \pm 0.00125	0.166 \pm 0.0266	0.0181 \pm 0.00358	<i>1.05 \pm 0.0368</i>	51.9 \pm 1.31	<i>35.6 \pm 2.18</i>	<i>0.145 \pm 0.0187</i>	2.04 \pm 0.0316
	NP	<i>0.0409 \pm 0.00306</i>	424 \pm 2.57	0.00292 \pm 0.00195	0.137 \pm 0.0279	0.00839 \pm 0.00388	<i>0.828 \pm 0.0336</i>	50.6 \pm 1.21	<i>101 \pm 3.33</i>	<i>BDL</i>	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⁻¹ 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 ¹
	NP	6.78 ± 0.09	23.6 ± 24.5 ²
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 ¹ individual values were 48.8, 9.7 and 7.9 mg L⁻¹. The initial value is likely to be an error which would give a mean composition
 358 of 8.8 ± 1.3 mg L⁻¹

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

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⁻¹ 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_3 , CH_3COOH , 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 ($K_d / L \text{ kg}^{-1}$) 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). ^{<lo/hi} indicates significantly lower and ^{>lo/hi} 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, ^{=lo/hi} 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 ^a	308 \pm 55.1 ^{a<lo<hi}	6750 \pm 1500 ^{ab>lo=hi}	93500 \pm 72200 ^{ab=lo=hi}	227 \pm 50.5 ^{ab<lo<hi}
Barn		1670 \pm 313 ^{ab<lo<hi}		4950 \pm 3086 ^{ab=lo=hi}	
Cwm				19400 \pm 137 ^{ab=lo=hi}	6680 \pm 5230 ^{ab=lo=hi}
DGC	1010 \pm 81.7 ^b		57100 \pm 27700 ^{a=lo>hi}		
Graig		674 \pm 202 ^{ab<lo<hi}	4140 \pm 1390 ^{ab=lo=hi}	233000 \pm 128000 ^{a=lo=hi}	511 \pm 236 ^{ab<lo<hi}
Red					10500 \pm 1470 ^{a>hi=lo}
Rook	927 \pm 230 ^{bc}	16090 \pm 10090 ^{b=lo=hi}			5420 \pm 2870 ^{ab=lo=hi}
Scun					
Ship					198 \pm 47.3 ^{b<lo<hi}
Wis	633 \pm 118 ^c		264 \pm 51.7 ^{b<lo<hi}	1500 \pm 0 ^{b=lo=hi}	852 \pm 778 ^{ab<lo<hi}

466

467

468

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476

477 **References**

- 478 Afsar, A., Harwood, L.M., Hudson, M.J., Hodson, M.E., Shaw, E.J. (2014) Meocuproine-
479 functionalised silica-coated magnetic nanoparticles for extraction of copper (II) from
480 aqueous solution. *Chemical Communications* 50 7477-7490.
- 481 Alexander, P.D., Alloway, B.J., Dourado, A.M. (2006) Genotypic variations in the
482 accumulation of Cd, Cu, Pb and Zn exhibited by six commonly grown vegetables.
483 *Environmental Pollution*, 144, 736-745.
- 484 Alizadeh, B., Delnavaz, M., Shakeri, A. (2018) removal of Cd(II) and phenol using novel
485 cross-linked magnetic ETA/chitosan/TiO₂ nanocomposite. *Carbohydrate Polymers* 181
486 675-683.
- 487 Alloway, B.J. (1990) Cadmium. In: *Heavy metals in soils*. 1st Ed. Blackie Academic and
488 Professional: London pp 100 – 124.
- 489 Anderegg, G., Nageli, P., Muller, F., Schawarenbach, G. (1959) Komplexe .30.
490 Diathylentriamin-pentaessigsäure (DTPA). *Helvetica Chimica Acta* 42 827-836.
- 491 Bao, S., Tang, L., Li, K, Ning, P., Peng, J., Guo, H., Zhu, T., Liu, Y. (2016) Highly selective
492 removal of Zn(II) ion from hot-dip galvanizing pickling waste with amino-functionalized
493 Fe₃O₄@SiO₂ magnetic nano-adsorbent. *Journal of Colloid and Interface Science* 462
494 235–242.

495 Bell, P.F., James, B.R. and Chaney, R.L. (1991) Heavy metal extractability in long-term
496 sewage-sludge and metal salt-amended soils. *Journal of Environmental Quality* 20
497 481-486.

498 Carvallaro, N. and McBride, M.B. (1984) Zinc and copper sorption and fixation by an acid soil
499 clay: effect of selective dissolutions. *Soil Science Society of America Journal* 48 1050-
500 1054.

501 Chen, D., Shen, W., Wu, S., Chen, C., Luo, X., Guo, L. (2016) Ion exchange induced
502 removal of Pb(II) by MOF-derived magnetic inorganic sorbents, *Nanoscale* 8 7172–
503 7179.

504 Chen, Z. Geng, Z. Zhang, Z., Ren, L., Tao, T., Yang, R., Guo, Z. (2014) Synthesis of
505 magnetic Fe₃O₄@C nanoparticles modified with SO₃H and COOH groups for fast
506 removal of Pb²⁺, Hg²⁺, and Cd²⁺ ions, *Eur. J. Inorg. Chem.* 2014 3172–3177.

507 Chung, J. Chun, J. Woo, J., Lee, S.H., Lee, Y.J., Hong, S.W. (2012) Sorption of Pb(II) and
508 Cu(II) onto multi-amine grafted mesoporous silica embedded with nano-magnetite:
509 effects of steric factors, *J. Hazard. Mater.* 239–240 183–191.

510 Crane, R.B., Scott, T.B. (2012) Nanoscale zero-valent iron: future prospects for an emerging
511 water treatment technology, *J. Hazard. Mater.* 211 112–125.

512 Dennis, I. (2005) The impact of historical metal mining on the river Swale catchment, North
513 Yorkshire, UK. PhD Thesis. University of Aberystwyth.

514 Dines H.G., 1956. The metalliferous mining region of south-west England. HMSO, London

515 Dixit, S. and Hering, J.G. (2003) Comparison of arsenic (V) and arsenic (III) sorption onto iron
516 oxide minerals: implications for arsenic mobility. *Environ. Sci. Technol.* 37 4182-4189.

517 Dojino, 2017. Dojino Molecular Technologies, Inc.
518 [https://www.dojindo.com/Images/Product%20Photo/Chelate_Table_of_Stability_Const](https://www.dojindo.com/Images/Product%20Photo/Chelate_Table_of_Stability_Constants.pdf)
519 [ants.pdf](https://www.dojindo.com/Images/Product%20Photo/Chelate_Table_of_Stability_Constants.pdf). Accessed 8th May 2017.

520 Figueira, P., Lopes, C.B., Daniel-da-Silva, A.L., Pereira, E., Duarte, A.C., Trindade, T. (2011)
521 removal of mercury (II) by dithiocarbamate surface functionalized magnetic particles:
522 Application to synthetic and natural spiked waters. *Water Research* 45 5773-5784.

523 Finzgar, N., Lestan, D. (2008) The two-phase leaching of Pb, Zn and Cd contaminated soil
524 using EDTA and electrochemical treatment of the washing solution. *Chemosphere* 73
525 1484-1491.

526 Fryxell, G.E., Lin, Y., Fiskum, S., Birnbaum, J.C., Wu, H., Kemner, K., Kelly, S. (2005)
527 Actinide sequestration using self-assembled monolayers on mesoporous supports.
528 *Environmental Science and Technology* 39 1324-1331.

529 Fu, F.L., Dionysiou, D.D., Liu, H. (2014) The use of zero-valent iron for groundwater
530 remediation and wastewater treatment: a review. *Journal of Hazardous Materials* 267
531 194–205.

532 Gill, R. and Ramsey, M.H. (1997) What a geochemical analysis means. In: Gill, R. (ed.)
533 *Modern Analytical Geochemistry: An Introduction to Quantitative Chemical Analysis*
534 *Techniques for Earth, Environment and Materials Scientists (Longman Geochemistry*
535 *Series)*. Pp 1 – 11.

536 Hang, F., Lan, J., hao, Z., Yang, Y., Tan, R., Song, W. (2012) Removal of heavy metal ions
537 from aqueous solution using Fe₃O₄-SiO₂-poly(1, 2-diaminobenzene) core-shell sub-
538 micron particles. *Journal Colloid and Interface Science* 387 205-212.

539 Huang, Y., Wu, H., Shao, T., Zhao, X., Peng, H., Gong, Y., Wan, H. (2018) Enhanced
540 copper adsorption by DTPA-chitosan/alginate composite beads: mechanism and
541 application in simulated electroplating wastewater. *Chemical Engineering Journal* 339
542 322-333.

543 Hughes, S.J.S, 1981. *The Cwmystwyth Mines: British mining no. 17. Monograph of the*
544 *Northern Mine Research Society.*

545 Hughes, D.L., 2015. Remediation of metal contaminated soils and waters with engineered
546 nanoparticles. University of Reading, unpublished thesis.

547 Hughes, D.L., Asfar, A., Harwood, L.M., Jiang, T., Laventine, D.M., Shaw, L.J., Hodson,
548 M.E. (2017) Adsorption of Pb and Zn from binary metal solutions an in the presence of
549 dissolved organic carbon by DTPA-functionalised, silica-coated magnetic nanoparticles.
550 *Chemosphere* 183 519-527.

551 Kaur, M., Zhang, H., Martin, L., Todd, T., Qiang, Y. (2013) Conjugates of magnetic
552 nanoparticle-actinide specific chelator for radioactive waste separation. *Environmental*
553 *Science and Technology* 47 11942-11959

554 Kiekens, L., (1995) Zinc. In: Alloway B.J., (ed.) *Heavy Metals in Soils: 2nd edition*. Blackie
555 Academic, London.

556 Kim, H.J., Leitch, M., Naknakom, B., Tilton, R.D., Lowry, G.V. (2017) Effect of emplaced
557 nZVI mass and groundwater velocity on PCE dechlorination and hydrogen evolution in
558 water-saturated sand. *Journal Hazardous Materials* 322 136–144.

559 Koehler, F.M., Rossier, M., Waelle, M., Athanassiou, E.K., Limbach, L.K., Grass, R.N.,
560 Günther, D., Stark, W.J. (2009) Magnetic EDTA: coupling heav metal chelators to
561 metal nanomagnets for rapid removal of cadmium, lead and copper from contaminated
562 water. *Chemical Communications* 4862-4864.

563 Lofrano, G., Carotenuto, M., Libralato, G., Domingos, R.F., Markus, A., Dini, L., Gautam,
564 R.K., Baldantoni, D., Rossi, M., Sharma, S.K., Chattopadhyaya, M.C., Giugni, M.,
565 Meric, S. (2016) Polymer functionalised nanocomposites for metals removal from
566 water and wasterwater: an overview. *Water Research* 92 22-37.

567 Lei, M., Zhang, Y., Khan, S., Qin, P., Liao, B., (2010). Pollution, fractionation and mobility of
568 Pb, Cd, Cu and Zn in garden and paddy soils from a Pb/Zn mining area.
569 *Environmental Monitoring and Assessment* 168 215-222.

570 Lestan, D., Luo, C.-L., Li, X.-D., 2008. The use of chelating agents in the remediation of
571 metal-contaminated soils: A review. *Environmental Pollution* 153 3-13.

572 Li, X.-Q., Elliott, D.W., Zhang, W.-X. (2006) Zero-valent iron nanoparticles for abatement of
573 environmental pollutants: Materials and engineering aspects. *Critical Reviews in Solid*
574 *State and Materials Science* 31 111-122.

575 Liu, X., Hu, Q., Fang, Z., Zhang, X., Zhang, B. (2009) Magnetic chitosan nanocomposites: A
576 useful recyclable tool for heavy metal ion removal. *Langmuir* 25, 3 – 8.

577 Liu, J.-F., Zhao, Z.-S., Jiang, G.-B. (2008) Coating Fe₃O₄ magnetic nanoparticles with humic
578 acid for high efficient removal of heavy metals in water. *Environmental Science and*
579 *Technology* 42 6949-6954.

580 Lo, I.M., Zhang, W.H., 2005. Study on the optimal conditions for the recovery of EDTA from
581 soil washing effluents. *Journal of Environmental Engineering* 131 1507-1513.

582 Ma, J., Zhou, G., Chu, L., Liu, Y., Liu, C., Luo, S., Wei. Y. (2017) Efficient removal of heavy
583 metal ions with an EDTA functionalised chitosan/polyacrylamide double network
584 hydrogel. *Sustainable Chemical Engineering* 5 843-851.

585 McBride, M.B. (1994) *Environmental Chemistry in soils*. Oxford University Press, Oxford.

586 Nahmani, J., Hodson, M.E., Black, S., 2007. Effects of metals on life cycle parameters of the
587 earthworm *Eisenia fetida* exposed to field-contaminated, metal-polluted soils.
588 *Environmental Pollution* 149 44-58.

589 Oughton, D., Koin, P., Bleyl, S., Filip, J., Skácelová, P., Klaas, N., von der Kammer, F.,
590 Gondikas, A. (2017) Development and application of analytical methods for monitoring
591 nanoparticles in reemdaton: *NanoRem 5*. CL:AIRE, London, UK, pp 6.

592 Palumbo-Roe, B., Cave, M. R., Klinck, B.A., Wragg, J., Taylor, H., O'Donnell, K.E., Shaw,
593 R.A., 2005. Bioaccessibility of arsenic in soils developed over Jurassic ironstones in
594 eastern England. *Environmental Geochemistry and Health*, 27 121-130.

595 Palumbo-Roe, B., Wragg, J., Cave, M., Wagner, D. (2013) Effect of weathering product
596 assemblages on Pb bioaccessibility in mine waste: implications for risk management.
597 Environmental Science and Pollution Research 20 7699-7710.

598 Pan, S., Li, J., Wan, G., Liu, C., Fan, W., Wang, L. (2016) Nanosized yolk–shell Fe₃O₄@Zr
599 (OH)_x spheres for efficient removal of Pb(II) from aqueous solution. J. Hazardous
600 Materials 309 1–9.

601 Papassiopi, N., Tambouris, S., Kontopoulos, A. (1999) Removal of Heavy Metals from
602 Calcareous Contaminated Soils by EDTA Leaching. Water, Air, and Soil Pollution 109
603 1-15.

604 Partey, F., Norman, D., Ndur, S. and Nartey, R. (2008) Arsenic sorption onto laterite iron
605 concretions: temperature effect. J. Colloid. Interface Sci. 321 493-500.

606 Pocięcha, M., Lestan, D., 2009. EDTA leaching of Cu contaminated soil using
607 electrochemical treatment of the washing solution. Journal of Hazardous Materials,
608 165, 533-539.

609 Richardson, P.H.G., 1991. Mines of the Dartmoor and Tamar Valley After 1913. Devon
610 Books, Tiverton.

611 Sahuquillo, A., Lopez-Sanchez, J.F., Rubio, R., Rauret, G., Thomas, R.P., Davidson, C.M.,
612 Ure, A.M. (1999) Use of a certified reference material for extractable trace metals to
613 assess sources of uncertainty in the BCR three stage sequential extraction procedure.
614 Analytica Chimica Acta 382 317-327.

615 Seguin, V., Gagnon, C., Courchesne, F. (2004) Changes in water extractable metals, pH
616 and organic carbon concentrations at the soil-root interface of forested soils. Plant and
617 Soil 260 1-17.

618 Shan, C., Ma, Z., Tong, M. (2015) Efficient removal of free and nitrilotriacetic acid complexed
619 Cd(II) from water by poly(1-vinylimidazole)-grafted Fe₃O₄@SiO₂ magnetic
620 nanoparticles. Journal of Hazardous Materials 299 479–485.

621 Siegel, F.R., 2002. Environmental geochemistry of potentially toxic metals. Springer-Verlag,
622 Berlin.

623 Sizmur, T., Watts, M.J., Brown, G.D., Palumbo-Roe, B., Hodson, M. E., 2011. Impact of gut
624 passage and mucus secretion by the earthworm *Lumbricus terrestris* on mobility and
625 speciation of arsenic in contaminated soil. *Journal of Hazardous Materials* 197 169-
626 175.

627 Varanasi, P., Fullana, A., Sidhu, S. (2007) Remediation of PCB contaminated soils using
628 iron nano-particles. *Chemosphere* 66 1031-1038.

629 Venkateswarlu, S., Yoon, M., 2015. Core–Shell Ferromagnetic Nanorod Based on Amine
630 Polymer Composite (Fe₃O₄@DAPF) for Fast Removal of Pb(II) from Aqueous
631 Solutions. *ACS Applied Materials & Interfaces*, 7, 25362-25372. Walsh, J.N. (1997)
632 Inductively coupled plasma-atomic emission spectrometry (ICP-AES). In: Gill, R. (ed.)
633 *Modern Analytical Geochemistry: An Introduction to Quantitative Chemical Analysis*
634 *Techniques for Earth, Environment and Materials Scientists (Longman Geochemistry*
635 *Series)*. Pp 41-66.

636 Wang, X.S., Zhu, L., Lu, H.J. (2011) Surface chemical properties and adsorption of Cu (II) on
637 nanoscale magnetite in aqueous solution. *Desalination* 276 154–160.

638 Wang, Y., Shi, L., Gao, L., Wei, Q., Cui, L., Hu, L., Yan, L., Du, B. (2015) The removal
639 of lead ions from aqueous solution by using magnetic hydroxypropyl chitosan/oxidized
640 multiwalled carbon nanotubes composites, *Journal Colloid Interface Science* 451 7–
641 14.

642 Weng, C.-H. (2004) Modeling Pb(II) adsorption onto sandy loam soil. *Journal Colloid and*
643 *Interface Science* 272 262-270.

644 Yang, J.-K., Lee, S.-M., Davis, A. P., 2006. Effect of background electrolytes and pH on the
645 adsorption of Cu (II) /EDTA onto TiO₂. *Journal of Colloid and Interface Science*, 295,
646 14-20.

647 Yang, T, Hodson, ME (In press) Investigating the potential of synthetic humic-like acid to
648 remove metal ions from contaminated water. *Science of the Total Environment*

649 Yen, C.-H., Lin, H.-L., Chuung, J.-S., Yeh, H.-D. (2017) Adsorption of precious metals in
650 water by dendrimer modified magnetic nanoparticles. *Journal Hazardous Materials* 322
651 215-222.

652 Yuan, C., Mingtong, C., Feng, L., Wang, J., Peng, Y. (2016) Efficient removal of Cu(II) using
653 amino-functionalised superparamagnetic nanoparticles prepared via SI-ATRP. *J*
654 *Applied Polymer Science* 42859.

655 Zeng, G., Pang, Y., Zeng, Z., Tang, L., Zhang, Y., Liu, Y., Zhang, J. , Lei, X., Li, Z., Xiong,
656 Y., Xie, G. (2012) Removal and recovery of Zn²⁺ and Pb²⁺ by imine-functionalized
657 magnetic nanoparticles with tunable selectivity. *Langmuir* 28 468–473.

658 Zhang, X., Lin, Y. -M., Chen, Z. -I. (2009) 2,4,6-Trinitrotoluene reduction kinetics in aqueous
659 solution using nanoscale zero-valent iron. *J. Hazardous Materials* 165 923–927.

660 Zhang, F., Zhu, Z., Dong, Z., Cui, Z., Wang, H., Hu, W., Zhao, P., Wang, P., Wei, S., Li, R.,
661 Ma, J. (2011) Magnetically recoverable facile nanomaterials: Synthesis,
662 characterisation and application in remediation of heavy metals. *Microchemical Journal*
663 98 328-333.

664 Zhang, H.J., McDowell, R.G., Martin, L.R., Qiang, Y. (2016) Selective Extraction of Heavy
665 and Light Lanthanides from Aqueous Solution by Advanced Magnetic Nanosorbents.
666 *ACS Applied Materials and Interfaces* 8 9523-9531.

667 Zhang, Y., Chu, C., Li, T., Xu, S., Liu, L., Ju, M., 2017. A water quality management strategy for
668 regionally protected water through health risk assessment and spatial distribution of heavy
669 metal pollution in 3 marine reserves. *Science of The Total Environment*, 599-600, 721-731.

670 Zhao, F.P., Repo, E., Sillanpaa, M., Meng, Y., Yin, D.L., Tang, W.Z. (2015) Green Synthesis
671 of Magnetic EDTA- and/or DTPA-Cross-Linked Chitosan Adsorbents for Highly

672 Efficient Removal of Metals. Industrial and Engineering Chemistry Research 54 1271-
673 1281.
674