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

Article

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1 **Metal removal from soil leachates using DTPA-functionalised maghemite**

2 **nanoparticles, a potential soil washing technology**

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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

2

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., 2015l 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   <u>DTPA-functionalised maghemite nanoparticles</u>

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

4

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
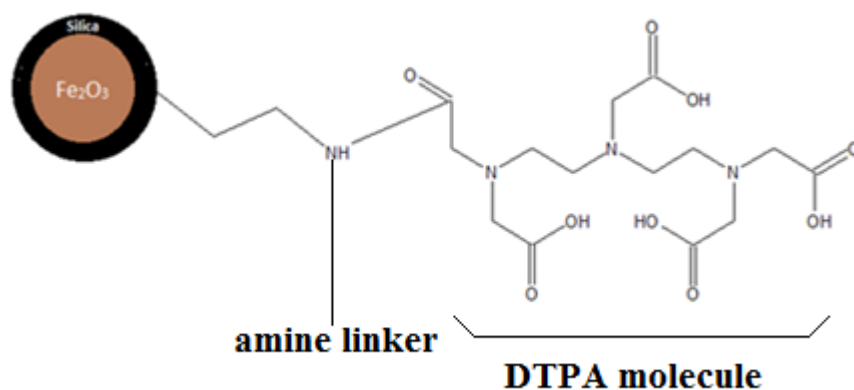
111   et al (2017).

112

113

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

115   nanoparticle.

116

117   <u>Extraction tests</u>

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 $NaNO_3$, 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 ºC). 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 H_2O. 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 x 10^{-3} mg L^{-1},

185   3.1 %), Ca (1.3 x 10^{-3} mg L^{-1}, 2.6%), Cd (8.9 x 10^{-5} mg L^{-1}, 2.9 %), Co (1.6 x 10^{-3} mg L^{-1},

186   4.2%), Cr (3.2 x 10^{-4} mg L^{-1}, 3.9%), Cu (1.3 x 10^{-3} mg L^{-1}, 2.6 %), Fe (2.1 x 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 Control	Ca NP	Cd Control	Cd NP	Co Control	Co NP	Cu Control	Cu NP	Mg Control	Mg 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

Table 2. Percentage extraction efficiencies of Ca, Cd, Co, Cu, Mg, Pb and Zn from aqueous

solution by nanoparticles at pH 2 to 8. Values are mean ± standard deviation, n = 3. Pb and

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

Table 3. Metal partition coefficients (K_d / L kg^{-1}) for Cd, Co, Cu, Pb, Zn, Ca and Mg extraction

by nanoparticles between pH 2 and 8. Values are mean ± standard deviation (n = 3). Pb and

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

Of the potentially toxic metals, extraction efficiency of Cd, Co and Cu is in the same range as

that of Pb and Zn in our previous experiments (Hughes et al., 2017) and as reported for a

range of functionalised nanoparticles (e.g. Afsar et al., 2014; Liu et al., 2008; Liu et al., 2009;

Koehler et al., 2009; Zhang et al., 2011; the review of Lofrano et al., 2016; Table S1 in the

Supplementary Information). In depth comparison of extraction efficiencies found here and in

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_ds of ≥ 500 L kg^{-1} are considered acceptable

236　and > 5000 mg/L very good (Fryxell et al., 2005). Thus the K_ds 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_ds. 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 pH ≤ 6 ion exchange with

244　protons on the protonated functional groups of the DTPA and for pH ≥ 7 electrostatic

245　adsorption to deprotonated functional groups of the DTPA is also likely to occur. The

246　differences in efficiencies and K_ds 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 (μmol L^{-1}) of metals in control (cont) and nanoparticle (NP)-treated soil leachate. Values are mean ± 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	*0.241 ± 0.075*	*415 ± 10.8*	*8.46 ± 0.380*	0.167 ± 0.00348	0.151 ± 0.116	*9.01 ± 0.997*	*145 ± 22.2*	*82.4 ± 11.1*	*7.89 ± 2.11*	*579 ± 22.8*
	NP	*BDL*	*376 ± 15.7*	*6.48 ± 0.271*	0.142 ± 0.0145	0.00900 ± 0.00417	*1.19 ± 0.213*	*1.70 ±2.30*	*119 ± 3.05*	*BDL*	*473 ± 19.9*
Barn	cont	BDL	*118 ± 2.25*	*0.00226 ± 0.000111*	BDL	0.0615 ± 0.0271	0.0197 ± 0.00143	16.4 ± 2.06	47.1 ± 0.415	*0.686 ± 0.183*	0.701 ± 0.204
	NP	BDL	*130 ± 5.39*	*BDL*	BDL	0.0621 ± 0.0137	0.0241 ± 0.00388	17.3 ± 1.91	104 ± 8.08	*0.143 ± 0.0826*	0.270 ± 0.213
Cwm	cont	BDL	14.7 ± 4.65	0.0150 ± 0.0000489	0.0293 ± 0.00361	0.0210 ± 0.0193	0.132 ± 0.0470	*10.2 ± 0.554*	*31.4 ± 2.54*	1.53 ± 0.618	11.3 ± 0.704
	NP	BDL	10.2 ± 2.39	BDL	BDL	0.00822 ± 0.00359	0.0663 ± 0.00695	*7.42 ± 1.00*	*78.5 ± 2.62*	0.075 ± 0.000503	2.07 ± 1.45
DGC	cont	*2.27 ± 0.101*	107 ± 11.9	BDL	0.0755 ± 0.00810	BDL	*11.7 ± 1.73*	16.2 ± 2.17	*15.9 ± 1.20*	BDL	1.44 ± 0.508
	NP	*1.129 ± 0.0449*	111 ± 1.42	BDL	0.0633 ± 0.00713	BDL	*0.247 ± 0.146*	16.5 ± 0.304	*66.1 ± 2.54*	BDL	0.626 ± 0.285
Graig	cont	BDL	16.2 ± 0.683	*0.157 ± 0.00535*	0.109 ± 0.0183	0.00676 ± 0.00105	*0.383 ± 0.00204*	12.4 ± 0.656	*28.3 ± 12.0*	41.4 ± 0.591	75.9 ± 1.83
	NP	BDL	18.0 ± 0.909	*0.0946 ± 0.0107*	0.0904 ± 0.00569	0.00635 ± 0.000342	*0.0787 ± 0.0236*	11.4 ± 0.293	*71.3 ± 3.15*	0.228 ± 0.145	51.0 ± 7.39
Red	cont	BDL	636 ± 47.5	BDL	BDL	BDL	0.0384 ± 0.00696	14.9 ± 0.842	*90.4 ± 3.25*	BDL	*0.459 ± 0.212*
	NP	BDL	681 ± 47.4	BDL	BDL	0.0330 ±	0.0325 ± 0.0112	18.8 ± 2.75	*35.4 ± 1.96*	BDL	*0.0404 ± 0.00485*
Rook	cont	*0.0764 ± 0.0124*	308 ± 26.4	*0.0181 ± 0.000750*	0.166 ± 0.0701	0.0600 ± 0.0476	0.0429 ± 0.0293	53.4 ± 2.72	*38.5 ± 2.54*	3.38 ± 1.46	*8.59 ± 0.966*
	NP	*0.0400 ± 0.00467*	301 ± 3.37	*BDL*	0.126 ± 0.0141	0.0200 ± 0.00547	0.024 ± 0.0118	49.6 ± 0.820	*85.7 ± 5.68*	0.952 ± 0.0782	*1.50 ± 0.532*
Scun	cont	0.181 ± 0.157	549 ± 403	0.00671 ± 0.00519	0.119 ± 0.0259	0.214 ± 0.250	0.135 ± 0.187	72.1 ± 34.3	140 ± 72.2	BDL	0.718 ± 0.525
	NP	0.230 ± 0.0552	335 ± 35.8	0.00792 ± 0.00413	0.150 ± 0.0470	0.278 ± 0.0890	0.0255 ± 0.00346	73.5 ± 11.9	129 ± 12.2	BDL	0.600 ± 0.101
Ship	cont	0.546 ± 0.0948	337 ± 3.71	0.787 ± 0.0366	0.119 ± 0.0555	0.0407 ± 0.0212	0.0314 ± 0.00786	144 ± 4.93	*61.9 ± 9.30*	0.839 ± 0.284	*177 ± 3.71*
	NP	0.400 ± 0.0501	343 ± 9.01	0.521 ± 0.0247	0.210 ± 0.0595	0.0126 ± 0.00593	0.0357 ± 0.00168	146 ± 3.83	*111 ± 3.34*	0.263 ± 0.288	*148 ± 5.95*
Wis	cont	*0.0666 ± 0.00387*	417 ± 14.3	0.00435 ± 0.00125	0.166 ± 0.0266	0.0181 ± 0.00358	*1.05 ± 0.0368*	51.9 ± 1.31	*35.6 ± 2.18*	*0.145 ± 0.0187*	2.04 ± 0.0316
	NP	*0.0409 ± 0.00306*	424 ± 2.57	0.00292 ± 0.00195	0.137 ± 0.0279	0.00839 ± 0.00388	*0.828 ± 0.0336*	50.6 ± 1.21	*101 ± 3.33*	*BDL*	1.24 ± 0.517
Detection Limit		0.0174	0.0324	0.0008	0.0272	0.0062	0.0205	0.0066	0.04	0.0579	0.013

353

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 $\pm$ 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

17

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., 979; 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 ± 0	23 ± 3.2	87 ± 2.4	97 ± 4.8	18 ± 3.4
Barn	-	62 ± 4.8	-	79 ± 12	-
Cwm	-	-	-	95 ± 0.033	82 ± 13
DGC	37 ± 16	-	97 ± 0.70	-	-
Graig	-	40 ± 6.8	79 ± 6.1	99 ± 0.35	33 ± 9.7
Red	-	-	-	-	91 ± 1.1
Rook	48 ± 6.1	91 ± 8.1	-	-	83 ± 6.2
Scun	-	-	-	-	-
Ship	-	-	-	-	16 ± 3.4
Wis	39 ± 4.6	-	21 ± 3.2	60 ± 0	39 ± 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 L kg^{-1} and many are > 5000 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$_3$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 ± 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±0.00^a	308±55.1$^{a<lo<hi}$	6750±1500$^{ab>lo=hi}$	93500±72200$^{ab=lo=hi}$	227±50.5$^{ab<lo<hi}$
Barn		1670±313$^{ab<lo=hi}$		4950±3086$^{ab=lo=hi}$	
Cwm				19400±137$^{ab=lo=hi}$	6680±5230$^{ab=lo=hi}$
DGC	1010±81.7^b		57100±27700$^{a=lo>hi}$		
Graig		674±202$^{ab<lo<hi}$	4140±1390$^{ab=lo=hi}$	233000±128000$^{a=lo=hi}$	511±236$^{ab<lo<hi}$
Red					10500±1470$^{a>hi=lo}$
Rook	927±230^{bc}	16090±10090$^{b=lo=hi}$			5420±2870$^{ab=lo=hi}$
Scun					
Ship					198±47.3$^{b<lo<hi}$
Wis	633±118^c		264±51.7$^{b<lo<hi}$	1500±0$^{b=lo=hi}$	852±778$^{ab<lo<hi}$

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467

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