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**Published in:**  
Chemical Geology

**DOI:**  
[10.1016/j.chemgeo.2013.08.030](https://doi.org/10.1016/j.chemgeo.2013.08.030)

**Publication date:**  
2013

**Link:**  
[Link to publication in PEARL](#)

**Citation for published version (APA):**  
Eagling, J., Worsfold, P. J., Blake, W. H., & Keith-Roach, M. J. (2013). Influence of sediment redox conditions on uranium mobilisation during saline intrusion. *Chemical Geology*, 357(0), 158-163. <https://doi.org/10.1016/j.chemgeo.2013.08.030>

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1 **Influence of sediment redox conditions on uranium mobilisation during saline intrusion**

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13 publication. A definitive version was subsequently published in Chemical Geology, [VOL  
14 357, (DATE 24 October 2013)] DOI 10.1016/j.chemgeo.2013.08.030

15

16 Abstract (word count 212)

17 In the UK, several coastal nuclear sites have been identified as vulnerable to future sea level  
18 rise. Legacy contamination at these sites has accumulated in sub-surface sediments at risk of  
19 future seawater inundation and intrusion. Porewater salinization, changes in pH and the influx  
20 of oxygen into sediments may impact the stability of sediment associated uranium (U). In this  
21 study, saturated column experiments were performed to compare the mobilisation of U from  
22 oxic and reduced sediments into seawater under environmentally relevant flow conditions.  
23 Uranium release profiles were independent of the initial geochemistry of the sediments.  
24 Uranium release from the sediments was kinetically controlled, showing relatively slow

25 desorption kinetics, with release initially limited by the impact of the sediments on the pH of  
26 the seawater. Significant U release only occurred when the pH was sufficiently high for the  
27 formation of U-carbonate complexes ( $\text{pH}_{\text{oxic}} 6.3$ ;  $\text{pH}_{\text{reduced}} 7.5$ ). Uranium was more strongly  
28 bound to the reduced sediments and after 400 pore volumes of seawater flow, release was  
29 more extensive from the initially oxic (46%) compared with initially nitrate reducing (27%)  
30 and iron reducing (18%) sediments. The products of iron cycling appeared to act as a buffer  
31 limiting U mobilisation, but the on-going dissolution of the Fe-phases suggests that they did  
32 not form a permanent protective layer.

### 33 **Highlights**

- 34 • Seawater intrusion promotes U mobilisation from oxic and reduced sediments
- 35 • Initially reducing conditions result in stronger binding of U to the sediment
- 36 • Mobilisation was pH dependent and kinetically controlled
- 37 • Fe(III) phases formed during Fe(II) oxidation retard U release temporarily

38

39 **Keywords:** *Uranium; porewater salinization; desorption; transport; oxic and reduced*  
40 *sediments; oxidation*

### 41 **1. Introduction**

42 Radioactive waste is generated throughout the nuclear cycle and accidental discharges, and  
43 70 years of nuclear activities have resulted in a significant legacy of contaminated soil and  
44 sediment at nuclear facilities worldwide (McKenzie and Armstrong-Pope, 2010; Reistad et al.,  
45 2008; Zachara et al., 2013). Due to their need for cooling water several nuclear facilities  
46 (example.g. in the UK, USA and Japan) are located in low lying coastal areas and this close

47 proximity to the shoreline raises questions regarding their future safety with respect to  
48 projected climate change and rising sea levels.

49 Much of the contamination at nuclear sites has accumulated in the sub-surface sediments  
50 (McKenzie and Armstrong-Pope, 2010; McKinley et al., 2006) and these will be at risk of  
51 seawater inundation and intrusion. Uranium is a long lived radionuclide ( $^{238}\text{U}$   $t_{1/2} = 4.5 \times 10^9$   
52 years) and is both a persistent and widespread contaminant found at uranium mining and mill  
53 tailings sites, nuclear facilities and waste disposal sites worldwide (McKinley et al., 2006;  
54 Riley and Zachara, 1992). All of the U isotopes are alpha emitters, chemotoxic and radiotoxic  
55 and any remobilisation of U from sediments may lead to human dietary exposure through the  
56 consumption of contaminated food (Belles et al., 2013).

57 Localised areas of reduced sediments are found in sub-surface environments at legacy nuclear  
58 sites. The redox conditions in sub-surface sediments are variable; therefore uranium is found  
59 in both the reduced U(IV) and oxidised U(VI) forms (Sharp et al., 2011; Zhou and Gu, 2005).  
60 Uranium(VI) sorbs to a variety of minerals and related phases including clays (Rodriguez et  
61 al., 2008; Whicker et al., 2007), iron (oxy)hydroxides (Duquene et al., 2008; Gómez et al.,  
62 2006; Martinez et al., 1995; Sherman et al., 2008) and aluminium and silica oxides  
63 (Sylwester et al., 2000). Uranium(VI) can also co-precipitate with iron oxy-hydroxides and  
64 calcium carbonates (Duff et al., 2002; Reeder et al., 2000) and so its behaviour, at least in  
65 some situations, can be influenced by the cycling of other elements in the system.

66 Uranium(IV) species form under reducing conditions, and have a higher affinity for surface  
67 binding sites and a lower solubility than U(VI) species (Langmuir, 1978). The product of  
68 U(VI) reduction is often uraninite ( $\text{UO}_2$ ) (Campbell et al., 2011; Ginder-Vogel et al., 2006).  
69 Additionally, U(VI) that is sorbed to sediments surfaces can be reduced to sorbed U(IV)  
70 phases (Begg et al., 2011; Gu et al., 2005).

71 Uranium(VI) mobilisation can be promoted by the formation of U(VI) carbonate complexes,  
72 such as  $\text{UO}_2(\text{CO}_3)_2^{2-}$  or  $\text{UO}_2(\text{CO}_3)_3^{4-}$ , when the pH is  $>6$  (Choy et al., 2006; Zhou and Gu,  
73 2005). Thermodynamic data suggests that carbonate does not complex U(IV) or promote  $\text{UO}_2$   
74 dissolution under reducing conditions (Guillaumont et al., 2003). However, the production of  
75  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$  during microbial respiration has been shown to promote the formation of  
76 stable uranyl carbonate complexes under reducing conditions (Wan et al., 2008).

77 Since sediments can interact with seawater and lower its pH until the sediment's reactive  
78 phases are exhausted, column experiments have been shown to be more appropriate than  
79 batch experiments for investigating the impact of seawater inundation on U mobilisation from  
80 oxic Dounreay sediments (Eagling et al., 2013). In these column experiments, pH changes  
81 were monitored as a function of flow volume and U mobilisation, which began when the pH  
82 reached 6.9 due to the formation of U-carbonate complexes. As the pH increased further,  
83 mobilisation of U was slow and the elution profile was consistent with kinetically slow  
84 release processes.

85 As well as inducing pore water salinization and altering the porewater pH, seawater intrusion  
86 introduces oxygen into reduced sediments, allowing the re-oxidation of sediment associated  
87 U(IV). Uranium re-oxidation has been observed in batch experiments at circumneutral pH  
88 where U(IV) was rapidly oxidised to U(VI), followed by mobilisation (Law et al., 2011), and  
89 this can be accelerated by bicarbonate complexation (Ulrich et al., 2008). However, sediment  
90 re-oxidation may not always lead to the mobilisation of U(VI); e.g. Zhong *et al.*, (2005)  
91 found that during re-oxidation U mobilisation from Fe-rich Oak Ridge sediments was limited  
92 by sorption of U(VI) to the secondary Fe(III) minerals formed. Additionally, Fe(II) sorbed to  
93 the outer surface of sediments may re-oxidise to form an Fe(III) oxide veneer that acts as a  
94 diffusional barrier, protecting against U(IV) re-oxidation (Zhong et al., 2005).

95 Relatively few studies have investigated the mobilisation of U(VI)/(IV) from sediments under  
96 more environmentally relevant flow conditions (Abdelouas et al., 1999; Komlos et al., 2008a;  
97 Komlos et al., 2008b; Moon et al., 2007; Moon et al., 2009). Re-oxidation studies have  
98 shown that secondary products formed during Fe reduction did not protect U(IV) from  
99 oxidation and mobilisation under flow conditions (Komlos et al., 2008b; Moon et al., 2007).  
100 A similar effect resulting from the low solubility of Fe re-oxidation products has been  
101 observed during Tc remobilisation from Fe rich sediments, with flow conditions promoting  
102 more Tc mobilisation compared with batch systems (Eagling et al. 2012). However, iron  
103 sulphide precipitates formed under more extensively reducing conditions have been reported  
104 to act as a buffer, preventing U oxidation and/or release under flow conditions (Abdelouas et  
105 al., 1999; Moon et al., 2009). Mackinawite was particularly effective and provided long term  
106 protection when formed in sufficient quantities (Abdelouas et al., 1999). Uranium oxidation  
107 and/or release from geochemically reducing sediments into seawater has not, however, been  
108 investigated.

109 The aim of this study was to investigate how the initial geochemical conditions of an Fe-rich  
110 sediment affect the mobilisation of U during seawater intrusion. Iron-rich sediments with  
111 similar properties to the Sellafield, UK site were contaminated with U and either stored open  
112 for six months in the dark, or sealed and stored in the dark for different lengths of time to  
113 allow the natural microbial communities to change the geochemical redox conditions to  
114 nitrate-reducing and then iron-reducing. The sediments were then used in column  
115 experiments simulating seawater intrusion to investigate U cycling and release processes in  
116 sub-surface environments under environmentally relevant flow through conditions.

## 117 **2. METHODS**

118 **2.1. Sediment and water.** Sandy, iron rich sediments with a similar mineralogical  
119 composition (quartz, silicates and feldspars) and geochemical characteristics to the  
120 Quaternary alluvial flood plain deposits that underlie the Sellafield site (Cumbria, UK), as  
121 previously characterised by Law et al. (2010), were sampled from Crediton UK (Lat:  
122  $50^{\circ}.8091'N$  ; Long:  $03^{\circ}.6815'W$ ), homogenised and sieved (<2 mm) in a field-moist state.  
123 Seawater was collected from the L4 coastal monitoring station in the Western English  
124 Channel to avoid estuarine influence (see [www.westernchannelobservatory.org.uk](http://www.westernchannelobservatory.org.uk) ) and  
125 filtered (0.4  $\mu\text{m}$  Nuclepore<sup>TM</sup> track edge membrane, Whatman). Characterisation of the  
126 sediments is detailed elsewhere (Eagling et al., 2012). A synthetic groundwater solution (pH  
127 = 7.2) representative of the Sellafield region (Wilkins et al., 2007) was prepared by  
128 dissolving salts in Milli-Q water (the constituents are shown in SI Table 1).

129 **2.2. Contamination of oxic sediments with U.** Sieved sediment (< 2 mm) was amended  
130 with simulated groundwater containing  $U \approx 25 \mu\text{M}$  ( $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) at a 1(g):1(mL)  
131 sediment to solution ratio. After a 7 day sorption period, the supernatant was separated from  
132 the sediment by centrifugation (10 min at 7500 g). Moist sediments were transferred to a  
133 container and stored in the dark at 21 °C for a 6 month ageing period. Periodically the  
134 container was opened to allow entry of air and ensure that the sediments did not become  
135 reducing.

136 **2.3. Contamination of anoxic sediments with U.** The U-amended synthetic groundwater  
137 was added to sieved sediment to give a 1(g):1(mL) sediment:solution ratio and incubated  
138 anaerobically in 250 mL serum bottles in the dark at 21 °C. The natural microbial consortium  
139 reduced the sediments over time without the addition of amendments. At pre-selected time  
140 intervals the serum bottles were transferred to an anaerobic chamber (COY Laboratory  
141 Products Inc., MI; 95%  $\text{N}_2$ , 5%  $\text{H}_2$ ,  $\text{O}_2 < 50 \text{ ppm}$ ) and the slurries transferred into centrifuge  
142 vessels. The Eh and pH of the slurries were measured using hand held electrodes. Sediments

143 were separated from the porewater by centrifugation and then the U concentration in the  
144 supernatant was determined by ICP-MS (Thermo X Series 2, Thermo Scientific). Redox  
145 indicators ( $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ ) were determined by ion chromatography (Dionex DX-500). Acid  
146 (0.5 M HCl) extractable Fe(II) was determined spectrophotometrically ( $\lambda_{\text{max}} = 562 \text{ nm}$ ) using  
147 ferrozine (Lovely and Phillips, 1986; Stookey, 1970). The incubations were targeted to obtain  
148 nitrate-reducing and iron-reducing conditions.

149 **2.4. Column experiments.** Column experiments were used to simulate the intrusion of  
150 seawater into the sediment in order to investigate the release of U from contaminated  
151 sediments. Each contaminated sediment (i.e. oxic, nitrate reducing and iron reducing) was  
152 packed into a separate polyetheretherketone (PEEK) self-pack column (50 mm x 10 mm;  
153 Applied Biosciences) according to Eagling et al. (2012). In order to avoid re-oxidation,  
154 reduced sediments were packed into the columns within the anaerobic chamber. The columns  
155 were then removed from the anaerobic chamber and oxic seawater was pumped through at a  
156 constant flow rate of  $1.2 \text{ mL h}^{-1}$  using an HPLC pump. The eluate was collected in fractions  
157 using a fraction collector at 1.2-3.6 mL intervals. Pre-weighed vessels were placed after every  
158 10 sample vials to check the flow rate (uncertainties associated with the flow rate were  $< 5\%$ ).  
159 Experiments involving oxic sediment were shorter (400 pore volumes) than those with  
160 initially nitrate-reducing and iron-reducing sediments (1000 pore volumes). Flow was  
161 stopped for 2 weeks after approximately 765 pore volumes to investigate whether the U in the  
162 eluate was in equilibrium with sorbed uranium in the nitrate- and iron-reducing sediment  
163 columns (Qafoku et al., 2005; Yin et al., 2011). At the end of each experiment, the column  
164 porosity was characterised using a conservative  $\text{Br}^-$  tracer injected as a pulse onto the column.  
165 At the end of each experiment, the column porosity was characterised using a conservative  
166  $\text{Br}^-$  tracer injected as a pulse onto the column. There was only minor variation in  $\text{Br}^-$   
167 breakthrough (SI Figure S1), which indicates that there was only minor variability in column



168 packing and hence in the column porosity. The linear column flow velocities were  $268 \text{ m y}^{-1}$   
169 (oxic aged),  $235 \text{ m y}^{-1}$  (nitrate-reducing) and  $262 \text{ m y}^{-1}$  (iron-reducing). These flow velocities  
170 are within the range of flow velocities observed in sandy aquifers under natural  
171 hydrogeological conditions (Mackay et al., 1985). The pH and Eh of the eluate were  
172 measured as soon as practically possible after elution and the concentrations of U, Fe and Br  
173 were determined by ICP-MS with collision cell technology to eliminate  $^{40}\text{Ar}^{16}\text{O}$  interference  
174 on the  $^{56}\text{Fe}$  signal. Standards were matrix matched (10 % seawater) and  $^{115}\text{In}$  and  $^{209}\text{Bi}$  were  
175 used as internal standards to account for instrumental drift. Independent standard checks were  
176 used to ensure both quality control and consistency between runs. All results were blank  
177 corrected to account for U and Fe naturally present in seawater. The limits of detection for Fe  
178 and U were  $3.0 \text{ nM}$  and  $0.09 \text{ nM}$  respectively.

### 179 **3. RESULTS AND DISCUSSION**

180 **3.1. Sediment characterisation.** Sediment from the same location has been described  
181 previously (Eagling et al. 2012) and characterisation data are shown in SI Tables 2 and 3. The  
182 sediment mineralogy was dominated by quartz but also contained silicates, feldspars and  
183 hematite, with a high proportion of sand (61 %) and silt (36 %) and a low clay content (3 %).  
184 The sediments were iron rich ( $420 \pm 6 \text{ mmol Fe kg}^{-1}$ ), had a surface area of  $6.57 \text{ m}^2 \text{ g}^{-1}$ , a  
185 cation exchange capacity of the  $9.3 \pm 1 \text{ cmol kg}^{-1}$  and a pH of  $3.9 \pm 0.3$  (measured in Milli-Q  
186 water using a 1:1 sediment: solution ratio). The total organic carbon content of the sediment  
187 was 2% w/w.

188 **3.2. U immobilisation under oxic conditions.** Uranium sorbed rapidly to the oxic sediments,  
189 with  $96 \pm 2 \%$  of the uranium sorbed after the 7 day period. There was no significant change  
190 in the percentage of U sorbed during the subsequent 6 month ageing period and, because

191 conditions remained oxic throughout this time, U was expected to be associated with the  
192 sediments as U(VI).

193 **3.3. U immobilisation during reduction.** The conditions in the sealed serum bottles became  
194 increasingly reducing over time (Table 1). After 30 days, pore water nitrate concentrations  
195 had decreased significantly, indicating that nitrate reduction had been the dominant  
196 respiration process. The pH of the sediment had increased, which is consistent with the  
197 generation of  $\text{CO}_3^{2-}$  during nitrate reduction (Law et al., 2010). In these sediments,  $99 \pm 0.5 \%$   
198 of U(VI) had been removed from solution. In general U(VI) reduction does not occur  
199 alongside nitrate reduction (Finneran et al., 2002), and it is likely that U remained in the  
200 oxidised form, i.e. as U(VI).

201 After a 120 day reduction period, the nitrate concentration was below the limit of  
202 detection. Iron reduction had started by this time, as indicated by ingrowth of 0.5 M HCl  
203 extractable Fe(II) ( $16 \pm 1 \text{ mmol kg}^{-1}$ ). Porewater  $\text{SO}_4^{2-}$  concentrations increased over the 120  
204 day reduction period, evidence that sulfate reduction had not occurred in the sediments. In  
205 these sediments  $98 \pm 1 \%$  of the U had become associated with the sediments. Abiotic or  
206 microbial reduction of U(VI) to U(IV) is generally observed in sediments alongside Fe(III)  
207 reduction (Begg et al., 2011; Finneran et al., 2002; Gu et al., 2005; Senko et al., 2002).  
208 However, in our experiments, there was no significant change in the percentage of U sorbed  
209 to the sediments as conditions changed from nitrate- to iron-reducing, which suggests that the  
210 oxidation state of U did not change. Calculations performed with the Hydra hydrochemical  
211 database with MEDUSA software (Puigdomenech, 2004) also predicted that U(VI) species  
212 would dominate. Therefore it is likely that U remained as U(VI) throughout the experiments.  
213 Begg et al. (2011) used sequential extractions to show that U(IV) sorbed to reduced iron rich  
214 sediments was bound more strongly than U(VI) sorbed to oxic sediments. Sequential  
215 extraction data from our experiments however showed no significant change in the

216 fractionation of U in the three sediments (SI Figure 2), providing further evidence that there  
217 was no change in the oxidation state of U in the systems reported here.

218

### 219 **3.4. Changing geochemical conditions within the column during seawater intrusion.**

220 The pH of the eluent from all three columns was initially low (3.4-5.9), and increased  
221 with flow volume, reaching the pH of the inflowing seawater (7.8) after 33-160 pore volumes.  
222 The nitrate-reducing and iron-reducing sediments showed a similar pH elution profile, but  
223 with a slower increase in the oxic sediment column due to the lower initial pH (Table 1). The  
224 pH of the outflow was comparable with that of the other two columns after  $\approx$  160 pore  
225 volumes of seawater had been eluted. The pH then remained relatively constant (7.2 - 8.0)  
226 over the remainder of each experiment. A similar rapid reduction in pH has been observed  
227 previously in column experiments (Eagling et al., 2012). The low initial pH of the eluents in  
228 all cases is probably due to the high ionic strength of seawater displacing protons sorbed to  
229 the sediments, hence decreasing the pH (Wong et al., 2010), coupled with the high sediment  
230 to solution ratios at the start of the column experiments. The 2 week stop-start event applied  
231 to the initially nitrate-reducing and iron-reducing columns had no effect on the pH.

232 The Eh of the outflow from the oxic columns remained relatively constant (370 - 440  
233 mV). In contrast, the Eh of the nitrate-reducing and iron-reducing columns increased rapidly,  
234 suggesting that the sediments were re-oxidised as seawater flowed through the column. It is  
235 interesting to note that despite re-oxidation, the Eh remained lower in the oxic column  
236 throughout the experiment and the redox conditions in the initially oxic and initially anoxic  
237 columns were not the same at any point. The initially Fe-reducing sediments re-oxidised  
238 more quickly than the nitrate-reducing sediments, and the Eh remained relatively constant  
239 throughout the experiment. The stop-start event had no effect on the Eh of the initially iron

240 reducing sediments. In contrast, the Eh of the nitrate-reducing column was variable, which  
241 may be due to flow path modifications and channeling resulting from oxidative mineral  
242 dissolution and precipitation (Eagling et al., 2012; Moon et al., 2009). The Eh decreased in  
243 the initially nitrate-reducing sediments when the flow was stopped but the reason for this is  
244 unclear.

245         In the first 10 pore volumes eluted from the column there was a pulse of Fe (3.3  $\mu\text{M}$ )  
246 mobilised from the oxic column, suggesting that a limited pool of labile or exchangeable Fe  
247 was readily desorbed (Figure 1). Release of Fe from the initially iron-reducing sediments was  
248 also immediate and significant (188  $\mu\text{M}$ ) and was due to Fe(II) in the pore waters. After the  
249 initial release, Fe leached steadily from the oxic and iron-reducing sediments over the course  
250 of the experiment. In contrast, the onset of flow did not result in the initial mobilisation of Fe  
251 from the nitrate-reducing sediments. In these columns Fe release was variable and increased  
252 between 20 and 120 pore volumes but did not correlate with changes in Eh or pH, supporting  
253 the flow path modification hypothesis. After the 2 week stop-start flow event Fe was  
254 mobilised from both the nitrate-reducing and iron-reducing sediments within the first pore  
255 volume when flow was resumed. The concentration of Fe released rapidly decreased to pre-  
256 stop/start flow concentrations, suggesting that this pool of labile Fe was limited.

257

### 258 **3.5. Uranium cycling during inundation and intrusion**

259         In the first 10 pore volumes, there was a pulse release of U from the oxic sediments  
260 which was not seen from the initially reduced sediments (both nitrate-reducing and iron-  
261 reducing). This suggests that a limited (0.3 %) but rapidly exchangeable fraction of U(VI)  
262 was sorbed to the surface of the oxic sediments. The U pulse was concurrent with the low pH  
263 and Fe pulse release observed. After this, in the early period (< 40 pore volumes) in every

264 column profile, no measurable U was mobilised from the sediments. The eluent pH was also  
265 low throughout this period (< 6.3), suggesting that the increased ionic strength of the pore  
266 waters alone had a limited effect on U mobilisation. Uranium release was only observed after  
267 the pH of the eluted seawater increased above 6.3. This is consistent with the desorption of  
268 surface associated U(VI) promoted by the formation of soluble U(VI) species such as  
269  $\text{UO}_2(\text{CO}_3)_2^{2-}$  and  $\text{UO}_2(\text{CO}_3)_3^{4-}$  (Dong et al., 2005; Duff et al., 2002; Fox et al., 2006; Zhong  
270 et al., 2005). Uranyl carbonate complexes are less likely to be sorbed to sediment surfaces  
271 and therefore will increase U mobility in sub-surface environments (Wazne et al., 2003).  
272 Uranium was mobilised after fewer pore volumes of seawater had flowed through the initially  
273 nitrate-reducing (38 pore volumes) and iron-reducing (22 pore volumes) sediments compared  
274 with the oxic sediments (46 pore volumes). However, U was released at a lower pH from the  
275 oxic sediments (pH 6.3) compared with the initially reduced sediments (pH ~7.5).

276         After the onset of mobilisation, U release was most rapid from the oxic sediments and  
277 maximum concentrations of U were eluted after fewer pore volumes of seawater had flowed  
278 through the column (85 pore volumes) compared with the initially anoxic sediments (nitrate-  
279 reducing 140 pore volumes; iron-reducing 150 pore volumes). Additionally, higher  
280 concentrations of U were mobilised from the oxic sediments ( $U_{\text{max}}$  220 nM) compared with  
281 the anoxic sediments (nitrate-reducing 115 nM; iron-reducing 72 nM). These observations,  
282 together with the higher pH associated with the onset of U mobilisation from the anoxic  
283 sediments suggest that the U was more strongly bound to the anoxic sediments. This is  
284 consistent with the physico-chemical changes that take place in the sediments during  
285 reduction and/or during re-oxidation in seawater. Despite the differences in the maximum  
286 concentration released, a similar fraction of the U ( $\approx 6\%$ ) initially associated with the  
287 sediments was released between time zero and the time at which maximum concentrations of  
288 U were observed. This shows that although U was mobilised at different rates and was

289 associated with different binding sites in the three sediments, a similar fraction of U was  
290 readily mobilised from each sediment during this period.

291 After the peak U release (85-150 pore volumes), there was a slower on-going release,  
292 producing a tail in all of the elution profiles (Figure 1a). This tailing is indicative of  
293 kinetically controlled release, which involves U release from a range of binding sites with  
294 different desorption kinetics and/or a re-distribution between slow and fast reactive sites  
295 (Handley-Sidhu et al., 2009; Liu et al., 2008; Qafoku et al., 2005). The differences in the  
296 shape of the release profiles during the tailing section (Figure 2) suggests that more than one  
297 release process was occurring. The majority of the U mobilised (83-90 %) was released  
298 during the tail section (i.e. after the peak in U concentration was observed). Therefore  
299 relatively slow desorption kinetics dominated the mobilisation of U from all of the sediments.

300 Flow was stopped for 2 weeks in the initially nitrate-reducing and iron-reducing  
301 columns. During this period U was mobilised from the nitrate- reducing and iron-reducing  
302 sediments (Figure 1a), which provides further evidence that U release was kinetically  
303 controlled. The highest concentrations of U were mobilised in the first pore volume after flow  
304 resumed; U concentrations then decreased rapidly and only a small fraction of the U  
305 originally associated with the sediments was released from the nitrate-reducing (1.4 %) and  
306 iron-reducing (0.9 %) sediments respectively. Uranium mobilisation correlated with Fe  
307 release in the first 10 pore volumes when flow was resumed ( $r = 0.875$  (nitrate-reducing),  
308  $0.970$  (iron-reducing);  $p=0.000$ ,  $n=12$ ); evidence that Fe phases play a role in controlling U  
309 mobility, with desorption/dissolution of Fe phases promoting U release. The association and  
310 cycling of U with Fe (oxy)hydroxides has also been observed in marine sediments (Barnes  
311 and Cochran, 1993; Morford et al., 2007).

312           After 400 pore volumes of seawater had flowed through each column, more U had  
313 been released from the oxic sediments (46 % of the total U initially associated with the  
314 sediments) compared with the nitrate-reducing sediments (27 %) and iron-reducing sediments  
315 (18 %). Release from the reduced sediments occurred throughout the experiment and in total  
316 53 % was released from nitrate-reducing sediments and 38 % from initially iron-reducing  
317 sediments ( $\approx 1000$  pore volumes). The lower U release from the iron-reducing sediment is  
318 consistent with the hypothesis that low solubility Fe(III) phases form during the re-oxidation  
319 of Fe(II) and these phases provide effective surfaces for U sorption and/or a physical barrier  
320 preventing U mobilisation. The stop-start events showed that kinetically slow Fe mobilisation  
321 correlated with U mobilisation, supporting this hypothesis. Although slow, the release of both  
322 U and Fe continued throughout the experiment, which suggests that U mobilisation was only  
323 retarded, rather than prevented by these phases. Similar results have been reported in  
324 freshwater sediments (Moon et al., 2009; Zhong et al., 2005) where Fe(II) containing  
325 minerals did not permanently protect U from mobilisation.

326           The results from the oxic sediment columns show similarities with those obtained in a  
327 similar experiment conducted using sediment from the nuclear site at Dounreay (Scotland)  
328 (Eagling et al., 2013). These two sediments have several common characteristics; they are  
329 both iron rich, acidic, sandy loams with a low clay content and similar cation exchange  
330 capacities (SI Tables S2 and S3). Uranium was mobilised at a similar pH from the two  
331 sediments (this study pH 6.3; Dounreay pH 6.9), and both peak profiles showed long tailing  
332 sections (Figure 2). There were differences in the elution volume before U began to be  
333 released (85 pore volumes in this study compared with 160 pore volumes for Dounreay  
334 sediment), however a similar fraction ( $\approx 47$  %) of sorbed U was mobilised from each  
335 sediment over 400 pore volumes, with the majority of the U mobilised during the tail section.  
336 The fact that these two sediments show similar U remobilisation behavior supports the view

337 that these trends can be extrapolated to predict the impact of future sea level rise on other  
338 legacy nuclear sites with similar geochemical conditions.

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### 340 **3.6. Conclusions and Environmental Implications**

341 Seawater intrusion into U-contaminated sediments causes U mobilisation by introducing  
342 oxygen into reduced sediments and increasing the pH of the sediment pore waters. However,  
343 U release from the sediment was kinetically controlled, showing relatively slow desorption  
344 kinetics. The profiles differed according to the initial geochemical conditions and there was  
345 evidence that Fe-phases play an important role in retarding U release. However, the on-going  
346 dissolution of the Fe-phases suggests that they do not form a permanent protective layer.  
347 Despite the differences in the initial geochemistry of the sediments prior to pore water  
348 salinization and quantitative differences in U release, the general trends in the U release  
349 profiles were broadly similar. The oxic column data showed excellent agreement with results  
350 from similar column experiments using Dounreay sediments. This suggests that, regardless of  
351 the geochemical redox conditions, U(VI) release is; (a) dependent on pH, (b) kinetically slow,  
352 and (c) on-going from iron rich, sandy loam sediments with a low clay content.

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### 354 **Acknowledgments**

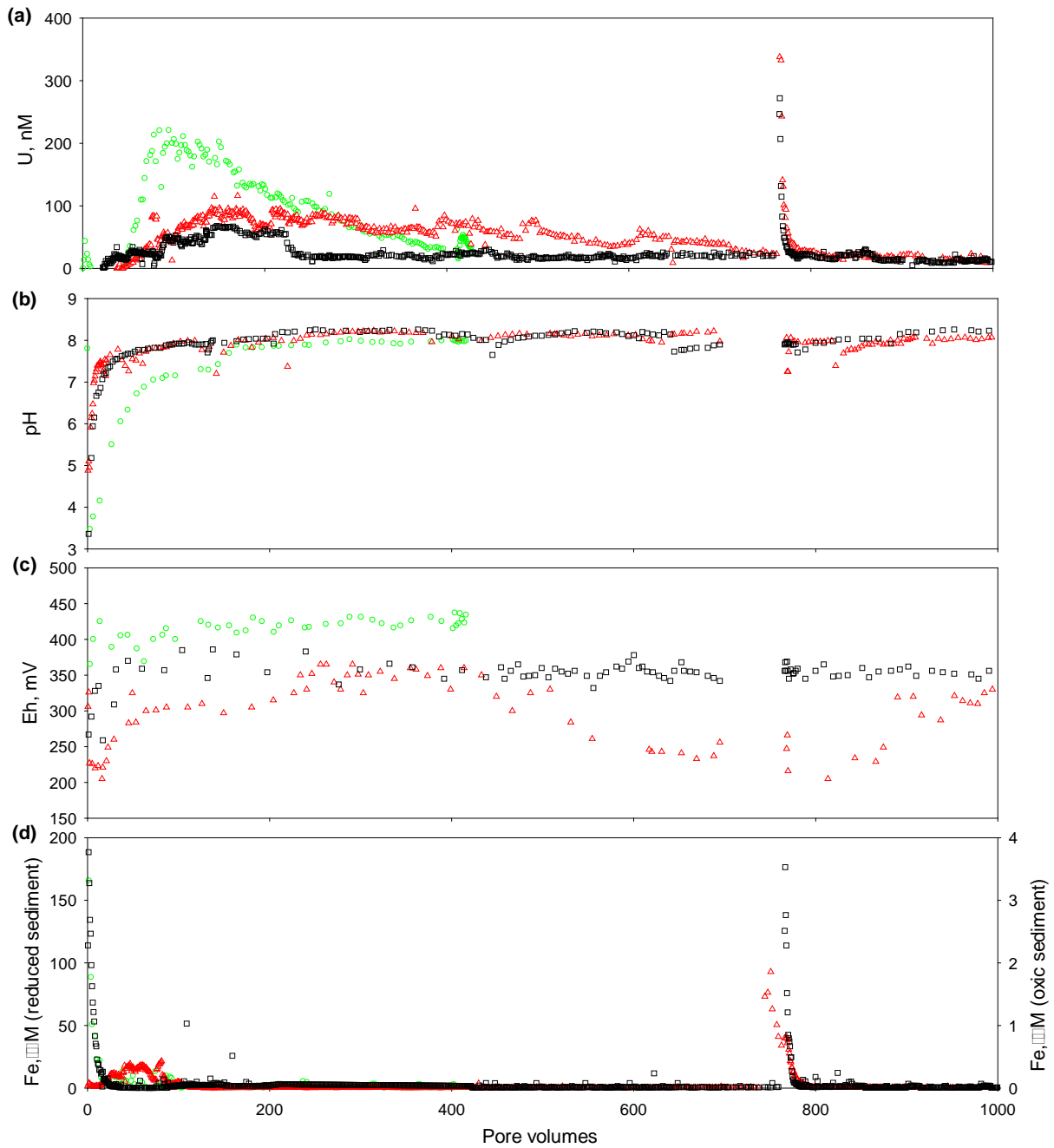
355 This research was funded by the Natural Environment Research Council (grant  
356 NE/C506799/1: Studentship NE/H527116/1). We would like to thank Dr Andrew Fisher for  
357 technical advice and Prof. Geoff Millward for constructive comments.

### 358 **Appendix A. Supplementary data**



359 Supplementary data to this article can be found online at

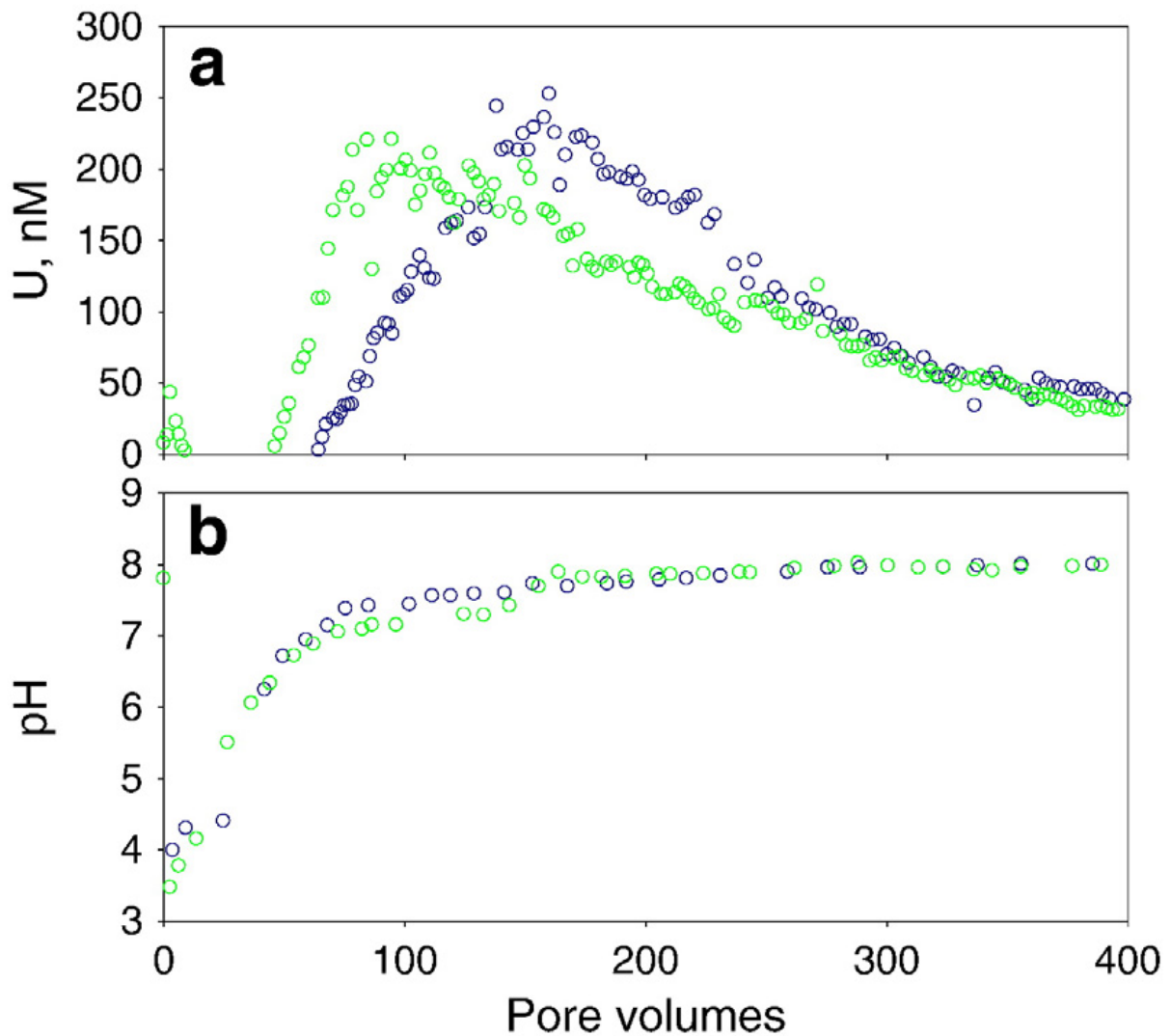
360 <http://dx.doi.org/10.1016/j.chemgeo.2013.08.030>.



364 Figure 1. Concentration of (a) uranium and (d) iron mobilised from sediments with  
365 corresponding changes in (b) pH and (c) Eh in the eluate during saturated flow through  
366 column experiments. Columns were packed with; ( $\circ$ ) oxic sediments that had been aged for 6  
367 months; ( $\Delta$ ) nitrate-reducing sediments and ( $\square$ ) iron-reducing sediments. Seawater was used

368 as the mobile phase. All values were above the limit of detection for the respective techniques  
369 throughout the run. Figure 1(d) shows Fe mobilised from columns packed with reduced  
370 sediments (nitrate-reducing and iron-reducing) on the primary axis and Fe mobilised from  
371 columns packed with oxic sediments (aged 6 months) on the secondary axis.

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373

374 Fig. 2. Concentration of (a) uranium from sediments with corresponding changes in (b) pH in  
 375 the eluate during saturated flow through column experiments. Columns were packed with ( )  
 376 oxic sediments (this study) and ( ) oxic Dounreay sediments that had been aged for 6 months;  
 377 using seawater as the mobile phase. All values were above the limit of detection throughout  
 378 the run for the respective techniques used. (For interpretation of the references to colour in  
 379 this figure legend, the reader is referred to the web version of this article.)

380

381 Table 1. Conditions in the sediments and porewaters prior to use immobilisation experiments.  
 382 Data show means  $\pm$  1 standard deviation (n = 10). LOD is the limit of detection — shown in  
 383 brackets.

384		Oxic (aged)	Nitrate reducing	Extensively iron reducing
385	Time	6 months	30 days	120 days
386	Eh, mV	469 $\pm$ 30	170 $\pm$ 1	15 $\pm$ 5
387	pH	3.9 $\pm$ 0.3	6.4 $\pm$ 0.6	7.0 $\pm$ 0.5
388	% U associated with sediments			
389		96 $\pm$ 2	99 $\pm$ 1	98 $\pm$ 1
390	NO <sub>3</sub> <sup>-</sup> , $\mu$ M	4800 $\pm$ 300	4.4 $\pm$ 0.6	<LOD (2.5)
391	Acid extractable Fe(II), nmol kg <sup>-1</sup>			
392		<LOD(0.55)	<LOD (0.55)	16 $\pm$ 1.0
393	SO <sub>4</sub> <sup>2-</sup> , $\mu$ M	3.8 $\pm$ 0.7	4.2 $\pm$ 0.9	4.8 $\pm$ 0.1

394 Appendix A **Supplementary Information**

395

396 **Influence of initial sediment redox conditions on U mobilisation during saline intrusion**

397 *Jane Eagling,<sup>1,2\*</sup> Paul J. Worsfold,<sup>1</sup> William H. Blake,<sup>2</sup> and Miranda J. Keith-Roach<sup>1,2,3</sup>*

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403 Telephone +44(0)1752584568

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413 Table S1: Constituents of synthetic groundwater (Wilkins et al., 2007).

<i>Salt</i>	<i>Concentration,</i> <i>g L<sup>-1</sup></i>
<i>KCl</i>	<i>0.0066</i>
<i>MgSO<sub>4</sub>·7H<sub>2</sub>O</i>	<i>0.0976</i>
<i>MgCl<sub>2</sub>·6H<sub>2</sub>O</i>	<i>0.0810</i>
<i>CaCO<sub>3</sub></i>	<i>0.1672</i>
<i>Na<sub>2</sub>SiO<sub>3</sub></i>	<i>0.0829</i>
<i>NaNO<sub>3</sub></i>	<i>0.0275</i>
<i>NaCl</i>	<i>0.0094</i>
<i>NaHCO<sub>3</sub></i>	<i>0.2424</i>

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422 Table S2. Sediment characteristics

<b>Composition</b>	<b>Crediton</b>	<b>Dounreay</b>
Sand (%)	61	52
Silt(%)	36	43
Clay (%)	3	5
Specific surface area (m <sup>2</sup> g <sup>-1</sup> )	6.57	5.92
Cation exchange capacity (CEC)	(9.3 ± 1 mEq/100 g)	12 ± 1 mEq/100 g
total organic carbon (% by mass)	2.0	4.0
pH	3.9 ± 0.3	4.4 ± 0.2

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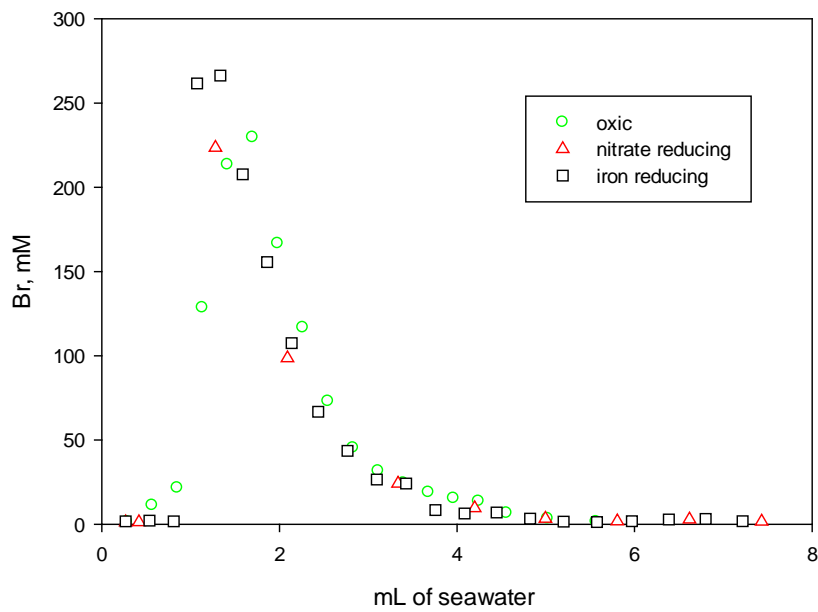


432 Table S3. Major elemental composition of the sediments determined using inductively  
433 coupled plasma mass spectrometry (ICP-MS) following aqua regia digestion. Means shown  
434 (n=3)  $\pm$  1 standard deviation.

	<b>Crediton, mmol kg<sup>-1</sup></b>	<b>Dounreay, mmol kg<sup>-1</sup></b>
<b>Al</b>	670 $\pm$ 20	300 $\pm$ 9
<b>Ca</b>	38 $\pm$ 1	33 $\pm$ 3
<b>Fe</b>	420 $\pm$ 6	280 $\pm$ 8
<b>Mg</b>	120 $\pm$ 4	140 $\pm$ 4
<b>Mn</b>	16 $\pm$ 0.1	5.0 $\pm$ 0.3
<b>Si</b>	25 $\pm$ 2	25 $\pm$ 1
<b>Sr</b>	0.15 $\pm$ 0.01	0.10 $\pm$ 0.01

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438 Figure SI 1. Characterisation of column experiments using a conservative Br<sup>-</sup> tracer. Columns  
439 were packed with (○) oxic sediments that had been aged for 6 months; (Δ) nitrate-reducing  
440 and (□) iron-reducing sediments, with seawater as the mobile phase.

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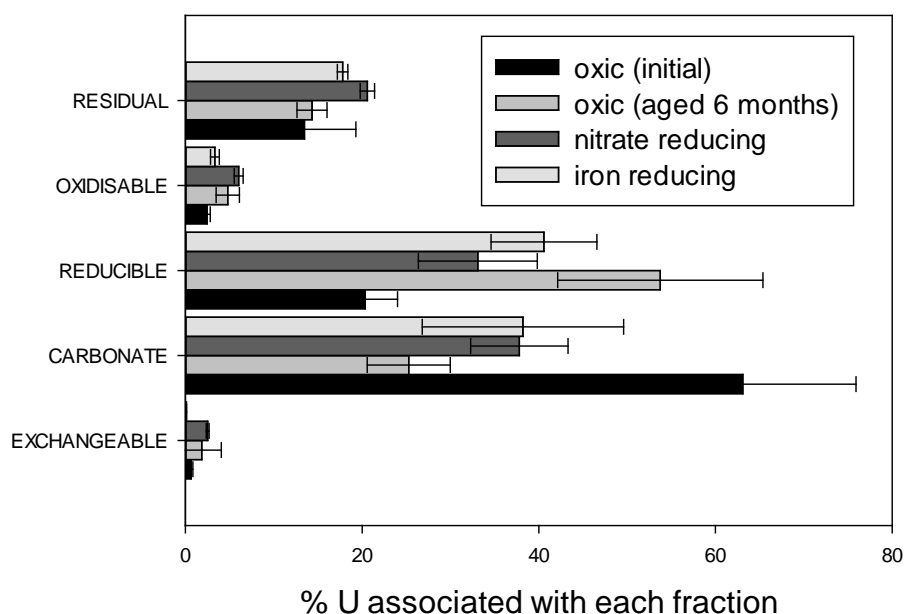
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448 **Figure SI 2.** Sequential extraction data for U extracted from initially oxic sediment  
 449 (immediately after the sorption experiments), sediment aged for 6 months, nitrate-reducing  
 450 and iron-reducing sediments. Each bar represents the mean of three separate extractions  $\pm$  1  
 451 standard deviation. Sequential extractions were carried out using a modified 5 step Tessier  
 452 sequential extraction procedure suitable for use in anaerobic environments (Keith-Roach et  
 453 al., 2003; Tessier et al., 1979). Oxic ( 6month aged) and reduced (nitrate-reducing and iron-  
 454 reducing) sediments were progressively leached to determine (1) the exchangeable fraction (1  
 455 M MgCl<sub>2</sub>/ pH 7 /1 h), (2) carbonate fraction (1 M sodium acetate/ pH 5/ 5 h), (3) reducible  
 456 fraction (0.1 M ammonium oxalate/ pH 2/ 16 h), (4) oxidisable fraction (H<sub>2</sub>O<sub>2</sub>/ followed by 1  
 457 M ammonium acetate/ 6% HNO<sub>3</sub>/ 16 h) and (5) the residual fraction (aqua regia/ 2 h). In  
 458 order to maintain anaerobic conditions, approximately 1.00 g of reduced sediment was  
 459 accurately weighed into each centrifuge tube within the anaerobic chamber. To prevent  
 460 oxidation of samples, all manipulations during steps 1-3 (i.e. those prior to the oxidising  
 461 leach) were also carried out in the anaerobic chamber. Leachate solutions for these steps were

462 degassed with N<sub>2</sub> and the centrifuge tubes were sealed with parafilm and double bagged  
463 during shaking and centrifugation to prevent entry of air.

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