

1 **Uranyl binding to humic acid under conditions relevant to cementitious**  
2 **geological disposal of radioactive wastes**

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17

18 **Abstract**

19 Few studies have sought to investigate specifically the potential for dissolved organic  
20 matter (DOM) to bind (and thus potentially transport) radionuclides under the high pH  
21 regimes expected from cementitious disposal. Here, we have used equilibrium  
22 dialysis to investigate uranyl binding to humic acid over a pH range of ~10 to 13. The  
23 experimental results provide evidence that DOM can bind uranyl ions over this pH  
24 range, including in the presence of competing ions. There is a general decrease in  
25 binding with increasing pH, from ~80% of total uranyl bound at pH 9.8 to ~10% at pH  
26 12.9. Modelling of the system with WHAM/Model VII can yield representative results  
27 up to pH ~10.5.

28

29 **Introduction**

30 Strategies for disposal of intermediate level radioactive wastes (ILW) in several  
31 countries involve geological emplacement, followed by addition of a cementitious  
32 backfill. The aim is to provide a chemical barrier that retards radionuclide transport  
33 from the geological disposal facility (GDF). Aqueous phase reactions, such as  
34 dissolution, leaching and associated processes create a high pH environment within  
35 the interstitial waters of the cement (Glasser et al., 2008). These reactions induce  
36 gradual changes to the composition of the interstitial water, from typical “young”  
37 concrete leachate with a pH above 13 to more evolved leachate with a pH lower than  
38 10 (Jacques et al., 2010).

39

40 Natural dissolved organic matter (DOM) is ubiquitous in aquatic environments and is  
41 present in groundwaters with concentrations dependent upon the host rock  
42 environment and recharge source and pathway. It exerts a powerful control on  
43 chemical conditions in waters and soils, influencing the transport and retention of  
44 metals (Tipping et al., 2011). Binding of cationic metals to DOM can result in  
45 increased solubility of metal salts and transport of DOM may result in simultaneous  
46 transport of bound metals. The influence of these processes on radionuclide  
47 migration has been recognised as a significant source of uncertainty in radioactive  
48 waste management (Glaus et al., 1997).

49

50 Few studies have sought to investigate specifically the potential for DOM to bind (and  
51 thus potentially transport) radionuclides under the high pH regimes expected from  
52 cementitious disposal. Here, we have used equilibrium dialysis to investigate uranyl  
53 binding to humic acid over a pH range of ~9 to 13. We then compare the results with  
54 predictions from a widely used chemical speciation model to assess the potential for  
55 modelling to predict satisfactory results at high pH.

56

## 57 **Experimental**

### 58 *Reagents*

59 Solutions were prepared using the following reagents; NaCl and Na<sub>2</sub>CO<sub>3</sub>  
60 (TraceSelect, Fluka Analytical), CuCl<sub>2</sub>·H<sub>2</sub>O (≥99.999%; Aldrich), CaCl<sub>2</sub> (99.9%; Alfa  
61 Aesar). Humic acid was the reference material Suwanee River Humic acid (SRHA)  
62 obtained from the International Humic Substances Society. Any pH adjustments were  
63 undertaken using 1 M solutions of HCl (prepared from 34% NORMATOM grade,  
64 VWR) or NaOH (freshly prepared for each use from 99.99% purity salt; Alfa Aesar).  
65 All experiments were performed in acid washed (10% v/v HNO<sub>3</sub>) 180 ml  
66 polypropylene pots. U-238 was prepared by dissolving UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> salt into 1 M HCl  
67 and subsequent dilution to achieve a 10<sup>-7</sup> mol L<sup>-1</sup> stock. U-232, used as a tracer  
68 (stock concentration 400 Bq mL<sup>-1</sup>), was separated from active daughter nuclides with  
69 a UTEVA column (Triskem International) using a previously reported method  
70 (Horwitz et al., 1992).

71

### 72 *Instrumental analysis*

73 Measurement of pH was performed using a Mettler Toledo Seven Multi meter and a  
74 Mettler Toledo InLab Routine Pro electrode. A five point calibration was performed  
75 using the following buffers; NIST traceable pH 4, 7 and 10; pH 9 (Scientific  
76 Laboratory Supplies, UK), and pH 13 (Fluka Analytical). Calibration slopes below  
77 98% were rejected and the calibration procedure repeated until this value was  
78 achieved or exceeded. Calibration was carried out before each set of measurements.  
79 Samples for liquid scintillation counting (Wallac Quantulus 1220 ultra-low level liquid  
80 scintillation spectrometer) were prepared by addition of 1 mL of 1 M HCl to 1 mL of  
81 sample, followed by 10 mL of ScintiSafe 3 cocktail (Fisher Scientific).

82

83

84

85 *Equilibrium dialysis procedure*

86 In the dialysis experiments, the outer solution had a total volume of 150 mL, and at  
87 the start of the experiment contained the HA and uranyl. The dialysate solution was  
88 contained within pre-cleaned regenerated cellulose dialysis membrane tubing, with a  
89 molecular weight cut-off of 1000 Da (SpectraPor 7) and sealed with SpectraPor clips  
90 at both ends. The volume was 4 mL, and initially the ionic strength and pH were the  
91 same as the outer solution, but with no HA or uranyl. The procedure differs in several  
92 ways from previously described methods (e.g., Glaus et al., 1995). The relative  
93 volumes of dialysate and bulk solution differed significantly and the total  
94 concentration of HA was lower. No additional competing ligands were added as OH<sup>-</sup>  
95 performs this function at high pH. This is required for many elements at lower pH  
96 values to ensure that there are measurable fractions of radionuclides in both the  
97 dialysate and outer fractions.

98  
99 The outer solution was prepared as two discrete solutions that were added to the  
100 experiment simultaneously. These solutions contained HA or uranyl, with the pH and  
101 ionic strength adjusted to those required for the experiment. This was done in order  
102 to control the pH conditions under which the uranyl was added to the humic acid.  
103 This prevents potential kinetic effects associated with dissociation of uranyl-humic  
104 complexes if the pH of a binary mixture is changed. Where Cu, Ca or carbonate were  
105 added to experiments, these were included within the uranyl solution, and added so  
106 that the final experimental concentrations were 10<sup>-7</sup>, 10<sup>-4</sup> and 10<sup>-4</sup> mol L<sup>-1</sup>,  
107 respectively. Once the solution was added to the airtight pot containing the dialysis  
108 bag, the container was additionally sealed with laboratory film to further prevent  
109 ingress of CO<sub>2</sub>, and left to stand for 7 days. Solutions were prepared under ambient  
110 laboratory conditions but in order to exclude carbonates as much as possible during  
111 the preparation, freshly drawn MQ water was used throughout, prepared solutions  
112 were stored in air evacuated containers before use and the experiments were

113 prepared in the shortest time possible (these effects are quantitatively evaluated in  
114 the results and discussion section).

115

#### 116 *Calculation of humic bound fraction of uranyl*

117 The total uranyl in solution is represented by the sum of the inorganic ( $[UO_2']$ ) and  
118 organic fractions, with the concentration of the uranyl humic complex ( $[UO_2\text{-HA}]$ )  
119 related to the amount bound ( $UO_2\text{-HA}$ ; mol  $mg^{-1}$ ) and the humic acid concentration  
120 ( $[HA]$   $mg\ L^{-1}$ ). The concentration in the two compartments will be directly related to  
121 the measured tracer activity ( $A_{bag}$  and  $A_{bulk}$ ; Bq) and can be expressed as Equations  
122 1 and 2, assuming equal binding properties of the humic acid within and outside the  
123 dialysis membrane.

$$124 \quad A_{bag} \propto [UO_2^{2+}]_{Tot-bag} = UO_2\text{-HA} \times [HA]_{bag} + [UO_2'] \quad (1)$$

$$125 \quad A_{bulk} \propto [UO_2^{2+}]_{Tot-bulk} = UO_2\text{-HA} \times [HA]_{bulk} + [UO_2'] \quad (2)$$

126 Where  $[HA]_{bag}$  and  $[HA]_{bulk}$  represent the humic acid concentration within and outside  
127 the dialysis membrane, respectively. Considering measured tracer activity and  
128 subtracting Equation 1 from 2, yields Equation 3.

$$129 \quad A_{UO_2\text{-HA}} = (A_{bulk} - A_{bag}) / ([HA]_{bulk} - [HA]_{bag}) \quad (3)$$

130 Where  $A_{UO_2\text{-HA}}$  can be considered as the tracer activity contribution of the humic  
131 bound uranyl per  $mg\ L^{-1}$  of HA in the experiment.

132

133 In order to calculate the organic bound fraction of uranyl, it is first necessary to  
134 calculate the tracer activity of the inorganic fraction (Equation 4). Using data from  
135 either the bulk solution or the dialysate results in the same value.

$$136 \quad A_{inorganic} = A_{bulk} - A_{UO_2\text{-HA}} \times [HA]_{bulk} \quad (4)$$

137 The fraction of humic bound metal ( $f_{organic}$ ) can then be calculated from Equation 5.

$$138 \quad f_{organic} = A_{UO_2\text{-HA}} \times [HA]_{effective} / (A_{UO_2\text{-HA}} \times [HA]_{effective} + A_{inorganic}) \quad (5)$$

139 Where  $[HA]_{\text{effective}}$  is the effective mean concentration of HA when the total  
140 experimental volume is considered.

141

#### 142 *Contribution of regenerated cellulose to the UV measured [HA]*

143 Humic acid is measured using UV visible spectrophotometry, and the concentrations  
144 in this work are  $2 \text{ mg L}^{-1}$  in the outer solution and typically  $\leq 0.25 \text{ mg L}^{-1}$  in the  
145 dialysate at the end of the experiment (measurements are made on unmodified  
146 solutions at the end of the experiments). The presence of low levels of regenerated  
147 cellulose degradation products yields absorbance signals in the same range as those  
148 used for the determination of humic acid. Where high concentrations of HA are used,  
149 this contribution will be negligible, however, this is not the case at the concentrations  
150 found within the dialysate (no contribution from these degradation products is  
151 detected by UV absorbance increases to the higher volume bulk solution). In order to  
152 account for this contribution, experiments in the absence of HA determined the UV  
153 visible absorbance from degradation of regenerated cellulose. A subsection of 27  
154 experiments were selected to measure HA absorbance values within the dialysate  
155 (due to the low signals in these dilute HA solutions we used the mean absorbance  
156 over the wavelength range 360-410 nm). These data are then used to give a range of  
157 values for the HA within the dialysate ( $[HA]_{\text{bag}}$ ) which are reflected as error bars  
158 where the data are presented.

159

#### 160 *Speciation modelling*

161 The Windermere Humic Aqueous Model (WHAM; Tipping, 1994) is a widely used  
162 chemical speciation code used in geochemical and ecotoxicological research and in  
163 regulation. The sub-model dealing with natural organic matter binding has recently  
164 been updated (Model VII; Tipping et al, 2011) to include the most up to date  
165 information on humic and fulvic acid binding of protons and metal cations (40 cationic  
166 species). This also includes improved prediction of cation binding at higher pH than

167 the previous version, due to increased numbers of available data and stricter data  
168 selection criteria than previously applied. Data are now included for proton binding  
169 data up to pH ~10.5. Additional radionuclide cations have also been added to the  
170 database (Stockdale et al, 2011). The uranyl binding constant is an average based  
171 upon separate values derived from six experimental datasets on a range of humic  
172 and fulvic acid types and a reference value based on linear free energy relationships  
173 (see Tipping et al, 2011, including supporting information, for full details). It is  
174 important to highlight that the Humic Ion Binding Models are first parameterised for  
175 protons. Only then are the metal datasets fitted using the generic proton conditions  
176 (rather than for each specific humic or fulvic acid type). Thus, the aim of the model is  
177 to provide a predictive capacity for a 'generic' humic or fulvic acid in a natural system.  
178 Binding constants for specific humic or fulvic acid types, if available, can be  
179 substituted into the model calculations, depending upon the users requirements.  
180 However, there are no data available for the HA used in this work and thus, we use  
181 the model generic binding value. The model, subsequently referred to as  
182 WHAM/Model VII, is used with default values with the exception of the uranyl  
183 hydrolysis stability constants that are taken from the compilation of Duro et al (2006).  
184 Errors within the model predictions are assessed by varying the humic binding  
185 constants by  $\log \pm 0.3$  from their default values (Lofts and Tipping, 2011).

186

## 187 **Results and discussion**

### 188 *Contribution of regenerated cellulose to the UV measured [HA]*

189 The upper recommended pH limit for the dialysis membrane is 12. However, no  
190 increased absorbance (indicating degradation of the cellulose) was seen within the  
191 dialysate volume when exposed to pH 13 solutions for the same time interval as the  
192 HA experiments. Based upon the results of the UV-visible spectrophotometry study  
193 on the dialysate membrane only samples and the 27 HA dialysate and bulk solution  
194 samples, a mean concentration of dialysate HA was determined, as well as a 90%

195 confidence interval. The HA concentration within the bag had a mean of 4.2% of the  
196 bulk solution value and a range of 0% to 13.3%. To illustrate the uncertainty in the  
197 presented data, the upper and lower limits were used to obtain error ranges and  
198 these data presented as error bars. Uncertainty from the HA concentration within the  
199 dialysate typically results in ranges of bound metal that are within <10% of the mean  
200 value. No statistically significant variations in the shape of the absorbance profiles  
201 was observed for the different samples over the pH range of the experiment, nor  
202 between the bulk solution and dialysate samples.

203

#### 204 *Uranyl binding to humic acid in a binary system*

205 The majority of studies of natural organic matter binding to trace cations present  
206 results in the form of complexation constants that relate the humic bound metal to the  
207 free ion concentration of the cation and the concentration or proton exchange  
208 capacity of the organic matter. For uranyl in the circumneutral and slightly acidic  
209 range, the organic bound fraction will dominate and reporting of experimental results  
210 in terms of log complexation constants enables small variations caused by different  
211 experimental conditions (e.g., ionic strength) to be assessed quantitatively. As the pH  
212 increases, hydrolysis products of metal ions become more prevalent and  
213 consequently decrease the free ion concentration. Changes in complexation  
214 constants due to hydrolysis induced changes to the free ion concentrations may  
215 obfuscate variations caused by subtle changes in organic bound metal in high pH  
216 systems. For example, if the free ion decreases by orders of magnitude but the  
217 organic bound changes by a factor of <10, changes to the complexation constant will  
218 largely reflect the changes to the free ion concentrations. With this in mind, we report  
219 results in terms of the percentage of total metal or the concentration that is bound to  
220 the humic acid. Equations 1-5 reflect the fact that we are considering inorganic  
221 components of the system as a whole, rather than the constituent complexes as is  
222 the case in other studies (Glaus et al., 1997).



223

224 Figure 1A shows the change in relative concentrations of humic bound uranyl with  
225 pH. There is a general decrease in binding with increasing pH from ~80% of the total  
226 bound at pH 9.8 to ~10% at pH 12.9. Previous data have been obtained for uranyl  
227 binding at  $\text{pH} \leq 10$  in the presence of competing ligands (Glaus et al, 1997). However,  
228 this is the first time that it has been practically demonstrated that binding can be  
229 significant over the pH 10 to 13 range. These are the conditions that are expected  
230 during the evolution of a cementitious GDF.

231

232 Previous studies have examined uranyl complexation with HA up to pH 10 (Zeh et al,  
233 1997; Glaus et al, 1997). Zeh et al (1997) performed experiments on pH adjusted  
234 natural Gorleben groundwaters to which additional uranyl was added. They observed  
235 binding in the absence of carbonate of 5.9% at pH 8.8 and 1% at pH 10.1. Glaus et  
236 al (1997) reported results of 60 binding experiments at a range of ionic strengths,  
237 organic acid types (purified Aldrich humic acid, Laurentian soil fulvic acid and  
238 Suwannee River fulvic acid), and ratios of uranyl to humic/fulvic acid, performed in  
239 the presence of  $0.2 - 1 \times 10^{-3} \text{ mol L}^{-1} \text{ CO}_3^{2-}$ . The fraction of uranyl bound increases  
240 with the ratio of uranyl to organic acid, from  $7.5 \pm 2\%$  at  $3 \times 10^{-8} \text{ mol U mg}^{-1} \text{ HA/FA}$  to  
241  $28 \pm 11\%$  at  $1.2 \times 10^{-9} \text{ mol mg}^{-1}$ . The results from these two studies contrast  
242 somewhat with our experimental observations. These discrepancies may be the  
243 result of the presence of a cocktail of competing metals in the case of the natural  
244 Gorleben groundwater and, for the Glaus et al (1997) study, the presence of high  
245 carbonate concentrations and the comparatively higher uranyl/HA ratios than in our  
246 work. There also likely to be variations in binding strengths between humic acid  
247 types, which could be a further reason for differences between the data sets.

248

249

250

251 *Uranyl binding to humic acid in the presence of Ca or Cu*

252 Competitive reactions with other cationic metals may influence the concentration of  
253 humic bound uranyl. In order to quantify such effects, we performed experiments  
254 where either  $\text{Cu}^{2+}$  ( $10^{-7}$  mol L<sup>-1</sup>) or  $\text{Ca}^{2+}$  ( $10^{-4}$  mol L<sup>-1</sup>) were added. These metal ions  
255 were chosen due to their relative binding strengths and typical concentrations in  
256 natural waters. The concentrations of these metals will be controlled by various  
257 mineral solubility controls within a cement matrix. However, here we are studying  
258 only the competition effects in the simple aqueous system.  $\text{Cu}^{2+}$  typically binds very  
259 strongly to organic matter and is present in trace concentrations in groundwater  
260 (mean European groundwater value  $\sim 5 \times 10^{-8}$  mol L<sup>-1</sup>; Shand and Edmunds, 2008).  
261  $\text{Ca}^{2+}$  typically has weaker binding to organic matter, but is present at greater  
262 concentrations (mean European groundwater  $\sim 1.6$  mmol L<sup>-1</sup>). Competition from  
263 these metal ions in the europium-humic acid system at pH 5.5 has been assessed  
264 previously (Marang et al, 2008; 2009). Panel B in Figure 1 shows that, in the  
265 presence of either metal, uranyl is not significantly displaced from humic acid. For  
266  $\text{Cu}^{2+}$ , only a small reduction in bound uranyl is observed at pH 12 and 10. This may  
267 be attributed to an excess of humic binding sites available for both metals. However,  
268 this is unlikely to be the case for  $\text{Ca}^{2+}$ , where the results suggest that uranyl is able to  
269 compete for the available binding sites. Further work is required to test the scale of  
270 these effects over different relative metal concentrations and should also be  
271 performed on a range of HA types.

272

273 *Comparison of measured and modelled data*

274 In order to test the measurements against a comprehensive speciation model we  
275 modelled the exact experimental conditions using WHAM/Model VII (Tipping et al.,  
276 2011). Figure 1 shows the model predictions in terms of the fraction of uranyl present  
277 as humic complexes vs. pH. Figure 2 shows the data expressed in terms of the log  
278 concentration of the humic bound uranyl. Error bars for the modelled values are

279 determined by variation of the humic binding constants by a fixed value of  $\log \pm 0.3$   
280 (Lofts and Tipping, 2011). In the uranyl only system, the model gives reasonable  
281 predictions up to pH  $\sim 10.5$ . Greater deviation from measured values is then observed  
282 as the pH increases. The data, as presented in Figure 2, shows clearly that even in  
283 the case where the binding strength is varied to be higher by  $\log 0.3$  units, the model  
284 still significantly underestimates binding at pH 13. Predictions of binding to organics  
285 will also be affected by the accuracy of the data for the speciation of the inorganic  
286 complexes.

287

288 We stress the fact that the model is parameterised using proton binding data only up  
289 to the same pH value (i.e., 10.5), and that for the majority of metal ions in the  
290 database, binding data are calculated from experimental data at much lower pH  
291 values (for example four of five uranyl humic acid binding datasets contain data at pH  
292  $< 5$ , with the other dataset at pH  $\sim 5-10$  and all Cu humic binding datasets fall in the  
293 pH range 2.0 to 8.3). Moreover, as detailed in the theory section, we use the generic  
294 Model VII value for binding of the uranyl ion. Should SRHA bind stronger than the  
295 average value, this will result in experimental binding values higher than predictions.  
296 Preliminary results from the authors for neptunyl binding show SRHA binds stronger  
297 than purified Aldrich humic acid under the same aqueous conditions (Stockdale and  
298 Bryan, unpublished results). The higher complexation capacity of the SRHA could  
299 also partly explain why no competition effects are observed in the presence of  $\text{Cu}^{2+}$ .  
300 The high pH range is of interest in geodisposal environments, but the model has the  
301 majority of its applications in natural waters where such pH regimes rarely exist. The  
302 model operates on the basis that only the free ion and first hydrolysis product can  
303 bind to organic matter. Increasing competition between organic binding and  
304 hydrolysis will operate as the pH increases, and higher hydrolysis products that may  
305 bind are not captured by the model. Figure 1C shows the inorganic speciation in the  
306 modelled system of Figure 1A. This illustrates the increased hydrolysis over the

307 experimental range and the dominance of negatively charged species throughout.  
308 Previous work has determined that the apparent charge of the uranyl ion can be  
309 considered to be greater than 2+ (2.1 to 4; Perez-Bustamante, 1971; Rao and  
310 Choppin, 1984). Thus, uranyl species with an apparent positive charge may exist at a  
311 higher pH than that predicted from formation of nominally zero or negatively charged  
312 hydrolysis species and it is possible that these as well as  $\text{UO}_2^{2+}$  and  $\text{UO}_2\text{OH}^+$  are  
313 able to bind to humic substances. Experimental data of the type presented here will  
314 enable further considerations of high pH systems when fitting and testing humic  
315 binding models for high pH.

316

#### 317 *Effect of carbonate on the uranyl-humic system*

318 An important consideration in the speciation of  $\text{UO}_2^{2+}$  is the formation of carbonate  
319 complexes. Our experiments were conducted in such a way as to minimise  $\text{CO}_2$   
320 dissolution, but were not performed in  $\text{CO}_2$  free conditions. It is therefore necessary  
321 to evaluate the potential of  $\text{CO}_3^{2-}$  species to affect the humic binding results. Figure 3  
322 shows modelling results for organically complexed uranyl in the presence of varying  
323 concentrations of  $\text{CO}_3^{2-}$ . Predicted values at 0.1  $\text{mmol L}^{-1}$  are within  $\log < 0.005$  of the  
324 values where  $\text{CO}_3^{2-}$  is absent. Increasing concentrations from 1  $\text{mmol L}^{-1}$  to 3  $\text{mmol}$   
325  $\text{L}^{-1}$  results in a marked reduction in humic bound uranyl at all the pH values  
326 considered. This is consistent with the experimental procedure of Glaus et al. (1997),  
327 where concentrations in this range were used in competition equilibrium dialysis  
328 experiments for a fulvic acid uranyl system and at similar DOM : uranyl ratios. The  
329 predictions suggest that lower  $\text{CO}_3^{2-}$  concentrations (from 0.1 to 1  $\text{mmol L}^{-1}$ ) only  
330 significantly decrease the humic bound uranyl concentration at pH 10. The fact that  
331 the model underestimates uranyl binding to humic acid means that these results will  
332 be conservative as it will underestimate competition between the carbonate ligand  
333 and humic binding sites. Experiments performed at pH 10 with addition of 0.1  $\text{mmol}$

334  $L^{-1} CO_3^{2-}$  (panel B of Figure 1) demonstrate that no decrease of humic bound uranyl  
335 is observed. We therefore conclude that any  $CO_3^{2-}$  present in the experiment is  
336 insufficient to suppress humic binding. We recognise that the binding to HA of mixed  
337 uranyl-carbonate complexes could also partly explain the apparent lack of  
338 competition in this system. Such mixed complexes for europium speciation have  
339 been identified by Dierckx et al (1994).

340

### 341 **Conclusions**

342 The experimental results presented here provide evidence that within simple high pH  
343 environments dissolved organic matter can bind uranyl ions, including in the  
344 presence of competing ions. The results therefore, suggest that DOM has the  
345 potential to be important in the transport of uranium from a cementitious (alkali)  
346 geological disposal facility, despite formation of highly hydrolysed species.

347

348 Using the default Model VII uranyl binding values we can not accurately predict  
349 uranyl humic interactions for the HA used in this work at pH values above ~10.5..

350 The reason for the discrepancies may be due to a possible underestimation of the  
351 binding of more hydrolysed species, or be related to higher binding strengths for the  
352 specific HA used in this work. Further experimental work of the type presented here,  
353 and on a range of HA types, will enable further considerations of high pH  
354 environments when fitting and testing humic binding models for such pH systems.

355

### 356 **Acknowledgements**

357 We acknowledge funding from the UK Natural Environment Research Council  
358 through the BIGRAD consortium (NE/H007768/1). NDB is grateful to the UK  
359 Engineering and Physical Sciences Research Council Diamond consortium for  
360 funding (EP/F055412/1).

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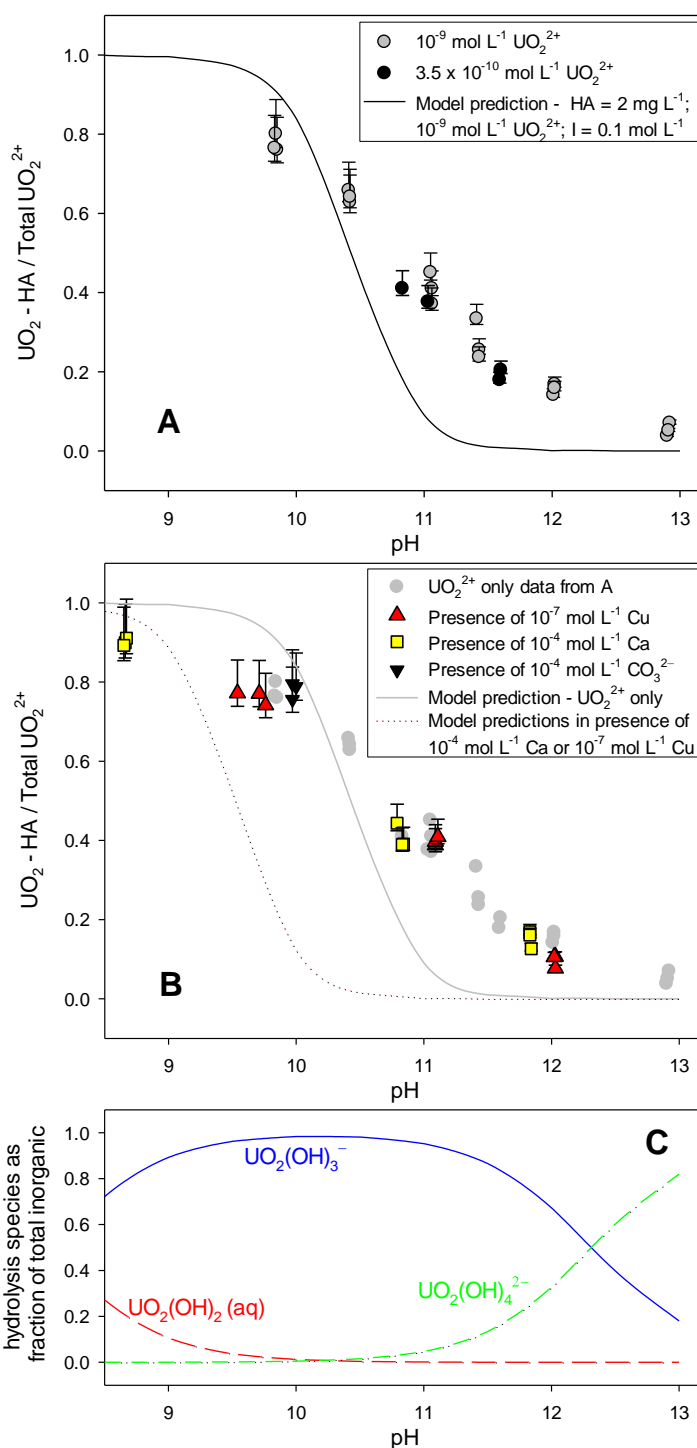
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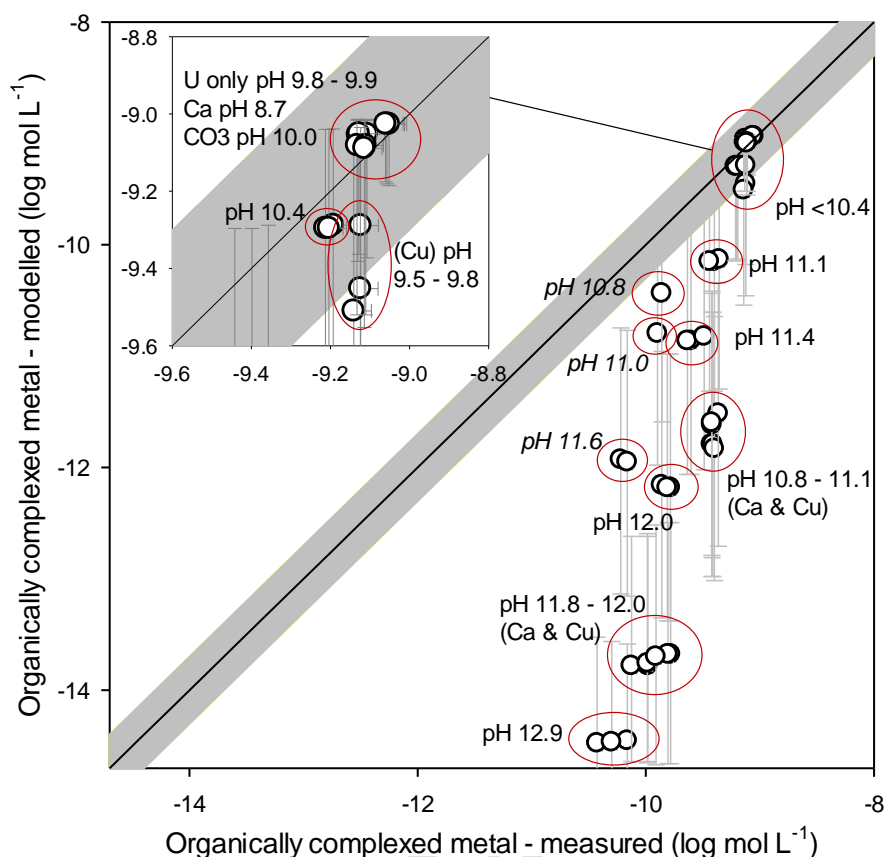
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412 Figure 1. Complexation of  $\text{UO}_2^{2+}$  with Suwannee River humic acid (SRHA). Panel A  
 413 shows the fraction of total uranyl bound to SRHA in a solution containing  $2 \text{ mg L}^{-1}$   
 414 SRHA (added electrolyte,  $0.1 \text{ mol L}^{-1} \text{ NaCl}$ ), the solid line represents the predicted  
 415 values using WHAM/Model VII. Panel B show the fraction of uranyl bound to SRHA  
 416 in the presence of competing metal ions or carbonate. Only one model prediction line  
 417 is shown for both the  $\text{Cu}^{2+}$  and  $\text{Ca}^{2+}$  systems due to very similar effects at the metal  
 418 ion concentrations considered. Panel C shows the modelled changes to the  
 419 hydrolysis in the inorganic system over the pH range considered in the experiments  
 420 and modelling.





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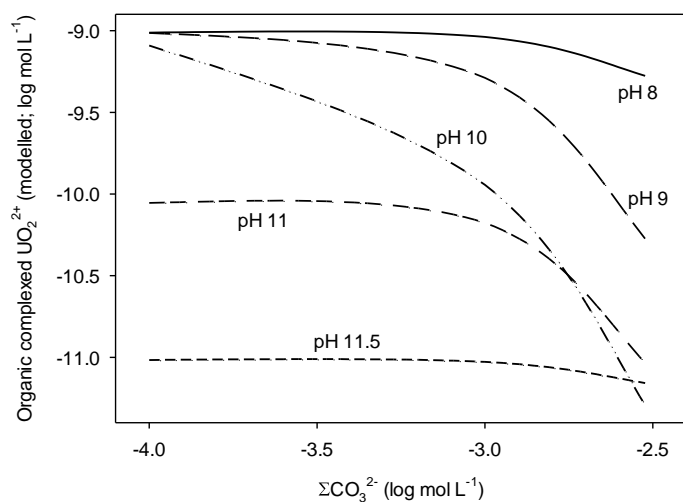
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424 Figure 2. Comparison of WHAM/Model VII calculated concentrations of organically  
 425 complexed metal and those derived from experimental data. The solid line represents  
 426 the 1:1 line and the grey area shows those points that fall within 0.3 of a log unit from  
 427 this line. Experimental conditions are defined in Figure 1. Italicised data indicate  
 428 those points in Figure 1A where a  $\text{UO}_2^{2+}$  concentration of  $3.5 \times 10^{-10} \text{ mol L}^{-1}$  was  
 429 used.

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435 Figure 3. Modelled humic complexation of uranyl in the presence of varying

436 concentrations of carbonate. Concentrations are the same as the grey circles in

437 Figure 1A. See text for discussion.

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