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**Assessment of co-contaminant effects on uranium and thorium
speciation in freshwater using geochemical modelling**

Stephen LOFTS^a, Laureline FEVRIER^b, Nele HOREMANS^c, Rodolphe GILBIN^b, Christophe BRUGGEMAN^c, Hildegard VANDENHOVE^c

^a NERC Centre for Ecology and Hydrology, Lancaster Environment Centre, Bailrigg, Lancaster, LA1 4AP, U.K.. stlo@ceh.ac.uk

^b IRSN, DEI/SECRE/LRE-Bât 186, B.P.3, Cadarache Center, F-13115 Saint-Paul-lez-Durance cedex, France. laureline.fevrier@irsn.fr, rodolphe.gilbin@irsn.fr

^c Belgian Nuclear Research Centre SCK•CEN, BE-2400 Mol, Belgium. nhoreman@sckcen.be, cbruggeman@sckcen.be, hvandenhove@sckcen.be

Corresponding author: S. Lofts

22 **Abstract**

23 Speciation modelling of uranium (as uranyl) and thorium, in four freshwaters impacted by
24 mining activities, was used to evaluate (i) the influence of the co-contaminants present on the
25 predicted speciation, and (ii) the influence of using nine different model/database combinations
26 on the predictions. Generally, co-contaminants were found to have no significant effects on
27 speciation, with the exception of Fe(III) in one system, where formation of hydrous ferric oxide
28 and adsorption of uranyl to its surface impacted the predicted speciation. Model and database
29 choice on the other hand clearly influenced speciation prediction. Complexes with dissolved
30 organic matter, which could be simulated by three of the nine model/database combinations,
31 were predicted to be important in a slightly acidic, soft water. Model prediction of uranyl and
32 thorium speciation needs to take account of database comprehensiveness and cohesiveness,
33 including the capability of the model and database to simulate interactions with dissolved
34 organic matter. Measurement of speciation in natural waters is needed to provide data that may
35 be used to assess and improve model capabilities and to better constrain the type of predictive
36 modelling work presented here.

37 **Keywords**

38 Uranium; Thorium; speciation; modelling; contaminants

39 **Abbreviations**

40 HFO: hydrous ferric oxide

41 HAIO: hydrous aluminium oxide

42 BLM: biotic ligand model

43 DOC: dissolved organic carbon

44 DOM: dissolved organic matter

45

46 1. Introduction

47 Ecological risk assessment of contaminants focuses largely on exposure to contaminants
48 singly, yet in the natural environment exposure to multiple contaminants is the norm. This is
49 likely to be the case both for radioactive and non-radioactive contaminants. Understanding and
50 quantifying the effects of exposure to multiple contaminants (both radionuclides and non-
51 radioactive substances) is clearly important for improving risk assessment and is an active
52 research area, yet prediction of the effects of multiple contaminants is as yet poorly developed.
53 Understanding of multiple contaminant impacts needs to incorporate factors known to
54 influence the impacts of single contaminants. An extensive body of research exists
55 demonstrating that total or dissolved concentrations of metallic contaminants in surface waters
56 are not generally predictive of toxic effects on biota, and that the extent of the metal toxicity is
57 modified by other factors such as pH and the concentrations of dissolved major ions and
58 organic matter (Franklin et al., 2000; Meyer, 2002; Markich, 2013; Trenfield et al., 2011a).
59 This is generally accepted to be the result of chemical speciation differences in the exposure
60 medium, coupled with competitive uptake effects, as exemplified by the Biotic Ligand Model
61 (BLM) for metals (Paquin et al., 2002). In the conceptual framework used by the BLM,
62 competition for the potentially toxic metal between the organism and solution ligands, such as
63 CO_3^{2-} or dissolved organic matter (DOM), and competition among the metal and major ions
64 for binding to the solution ligands, controls organismal uptake of the metal, and thus the toxic
65 effects. The conceptual framework of the BLM has recently been extended to consider metal
66 mixtures (e.g. Farley et al., 2014; Jho et al., 2011), where metal competition effects, both on
67 solution speciation and on uptake by the organism, are taken into account.

68 Since many radionuclides encountered in the environment are metallic in nature, bioavailability
69 models such as the BLM are in principle applicable to them. In developing such a model, there
70 is a need firstly to assess the prediction of radionuclide speciation under realistic environmental
71 conditions. Furthermore, since conditions entail exposure of organisms to multiple
72 contaminants, there is a need to assess whether and how the presence of such co-contaminants
73 influences radionuclide speciation. This study evaluates the influence of co-contaminants on
74 the modelled speciation of uranium and thorium in surface waters by applying a set of
75 speciation model frameworks to a collection of real-life examples of surface waters impacted
76 by uranium and thorium contamination. This study places the similarities and differences
77 among the predictions of speciation in the context of the different model frameworks and
78 databases of thermodynamic parameters (binding constants) used. The latter is particularly

79 pertinent for radionuclides, given the historic effort into producing internally consistent
80 databases of binding constants for use in thermodynamic models (e.g. Grenthe et al., 2004) and
81 the number of different databases that consequently exist.

82 We have chosen uranium and thorium as the radioelements of interest given the potential for
83 their release to the environment during mining, milling and processing operations, nuclear fuel
84 production, power station discharges and waste storage/processing, alongside a range of
85 potential co-contaminants (e.g. chromium, nickel, zinc) and other radionuclides (e.g. Garnier-
86 Laplace et al., 2009; Herlory et al., 2013; Vanhoudt et al., 2012). The equilibrium speciation
87 of uranium, including redox transformations and binding to environmentally-relevant colloidal
88 and mineral phases (e.g. humic substances, iron(III) oxyhydroxides), has been extensively
89 studied (e.g. Amme, 2002; Maher et al., 2013; O'Loughlin et al., 2011; Vitorge and Capdevila,
90 2003) and can be readily computed using geochemical speciation models (Denison and
91 Garnier-Laplace, 2005; Vercouter et al., 2015). Equilibrium constants for uranium
92 complexation with important freshwater ligands (e.g. CO_3^{2-} , organic matter) have been
93 compiled into a number of databases for use with specific speciation models. Thorium
94 speciation in freshwaters has also been studied (e.g. Moulin et al., 1992). We originally
95 intended to include radium and polonium also. However, initial screening of the model
96 databases showed that none contained any data on radium or polonium complex formation,
97 thus speciation of these elements could not be simulated. We will thus focus in the results on
98 the uranium and thorium modelling, but will also tackle the situation with respect to modelling
99 radium and polonium speciation in the Discussion section.

100 It is now recognized that uranium speciation determines directly the bioavailability of uranium
101 to living organisms. Although no clear consensus exists about the bioavailability of the
102 different inorganic or organic uranium complexes, dissolved organic matter, water hardness
103 and pH have been shown to modulate uranyl toxicity to various organisms due to their effect
104 on speciation (Denison, 2004; Fortin et al., 2004, 2007; Lavoie et al., 2014; Markich, 2013;
105 Trenfield et al., 2011a, 2011b; Zeman et al. 2008). The relationship between thorium speciation
106 and bioavailability is less well studied though there is evidence of chemical effects on
107 bioavailability from soil studies (e.g. Hegazy et al., 2013).

108 We have performed comparative uranium and thorium speciation calculations using seven
109 different combinations of speciation model and binding constant database. Predictions of
110 uranium speciation have been made in four real-life freshwaters impacted by discharges of
111 uranium and other contaminants. By comparing speciation predictions in the presence and

112 absence of other contaminants, we assess the potential for such contaminants to impact the
113 speciation of uranium in freshwaters. We assess the comparative predictions of the different
114 speciation models and databases, and make recommendations for future consolidation and
115 updating of databases.

116 **2. Materials and methods**

117 *2.1. Geochemical speciation models*

118 In this study we apply a number of speciation models to predict uranium and thorium speciation
119 in freshwaters, to assess the role of co-contaminants on the speciation. In doing so, we make a
120 number of key assumptions. Firstly, all uranium is assumed to be present as uranyl, U(VI).
121 Secondly, we allow the modelling of uranyl and thorium binding to dissolved organic matter
122 (DOM), if the geochemical speciation model can simulate this. Thirdly, if the model has the
123 capacity to simulate the formation of colloidal hydrous ferric oxide (HFO) and the
124 complexation of uranyl and thorium to its surface, this will also be taken into account.
125 Dissolved organic matter and HFO are widely known to complex uranyl (e.g. Saito et al., 2004;
126 Waite et al., 1994) and thorium (e.g. Nash and Choppin, 1980; Rojo et al., 2009)

127 Many geochemical speciation models are currently available, with differing capabilities. All
128 models share the ability to compute the equilibrium speciation of a solution containing ions
129 and simple ligands, without consideration of the oxidation–reduction state of the system.
130 Additionally many models can simulate oxidation–reduction and precipitation–dissolution
131 equilibria, and some advanced models couple equilibrium, reaction kinetics and transport
132 modelling. Furthermore, some models can also simulate the reactions of ions with DOM and
133 mineral surfaces such as HFO.

134 We have used five models in this work: the Windermere Humic Aqueous Model (WHAM7),
135 Visual MINTEQ, CHESS, the Geochemist’s Workbench, and PHREEQC.

136 *2.2. Windermere Humic Aqueous Model (WHAM7)*

137 The WHAM7 system is a speciation model that includes Humic Ion–Binding Model VII
138 (Tipping et al., 2011), a discrete site/electrostatic model of cation binding to humic substances,
139 which may be used to simulate ion interactions with DOM. Currently the model is
140 parameterised for the binding of 46 cations (considering different oxidation states of the same
141 element to represent different cations), including uranyl. WHAM7 also includes a surface
142 complexation model (Lofts and Tipping, 1998) parameterised for oxides of iron(III),

143 aluminium, manganese and silicon, as well as a conventional submodel for speciation in the
144 solution phase. Oxidation–reduction equilibria are not simulated. Precipitation of hydrous
145 aluminium and iron(III) (hydr)oxides (HAIO and HFO) may be simulated. In all calculations,
146 iron(III) was allowed to precipitate as HFO if its solubility product was exceeded. The
147 solubility expression given by Lofts and Tipping (2011),

$$148 \quad a_{\text{Fe}^{3+}} \cdot a_{\text{H}^{+}}^{-2.49} \geq 10^{-0.52},$$

149 was used to check for HFO precipitation. Precipitated HFO may be allowed to have a
150 chemically active surface that binds ions.

151 WHAM scenario simulations were done with two variants of the solution database:

- 152 i. The default database (simulations denoted WHAM–d). This database was originally
153 compiled by Tipping (1994) and updated for WHAM7 to allow simulation of the
154 formation of the uranyl complexes $\text{UO}_2(\text{CO}_3)_3^{4-}$, $\text{UO}_2(\text{SO}_4)_2^{2-}$, $\text{UO}_2(\text{SO}_4)_3^{4-}$,
155 $\text{UO}_2\text{HPO}_4^0$, $\text{UO}_2\text{H}_2\text{PO}_4^+$, $\text{UO}_2\text{H}_3\text{PO}_4^{2+}$, UO_2Cl^+ , UO_2Cl_2^0 , UO_2F^+ , UO_2F_2^0 , UO_2F_3^- and
156 $\text{UO}_2\text{F}_4^{2-}$, and the thorium complexes $\text{Th}(\text{CO}_3)_5^{6-}$, $\text{Th}(\text{OH})_2(\text{CO}_3)_3^{4-}$, $\text{Th}(\text{OH})_3\text{CO}_3^-$,
157 ThSO_4^{2+} , $\text{Th}(\text{SO}_4)_2^0$ and $\text{Th}(\text{SO}_4)_3^{2-}$. Precipitated HFO was assumed to have a
158 chemically active surface capable of binding protons and cations, including uranyl
159 (UO_2^{2+} and UO_2OH^+) and thorium (Th^{4+} and ThOH^{3+}). Constants for the binding of
160 uranyl and thorium to HFO were calculated using the linear free energy relationship of
161 Lofts and Tipping (1998) (see Supplementary Information for details).
- 162 ii. A modified database allowing formation of the uranyl alkaline earth metal–carbonate
163 complexes $\text{MgUO}_2(\text{CO}_3)_3^{2-}$, $\text{CaUO}_2(\text{CO}_3)_3^{2-}$, $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0$, $\text{SrUO}_2(\text{CO}_3)_3^{2-}$,
164 $\text{BaUO}_2(\text{CO}_3)_3^{2-}$, and $\text{Ba}_2\text{UO}_2(\text{CO}_3)_3^0$, and the hydroxy–carbonate complexes
165 $(\text{UO}_2)_2(\text{OH})_3\text{CO}_3^-$, $(\text{UO}_2)_3(\text{OH})_3\text{CO}_3^+$ and $(\text{UO}_2)_{11}(\text{OH})_{12}(\text{CO}_3)_6^{2-}$. (simulations
166 denoted WHAM–m). Binding constants for the alkaline earth metal–carbonate
167 complexes were calculated from the results of Dong and Brooks (2006), using log K
168 values for the $\text{UO}_2(\text{CO}_3)_3^{4-}$ complex corrected to the experimental ionic strength using
169 the extended Debye–Hückel equation. Updated binding constants for uranyl and
170 thorium binding to HFO were derived by an evaluation of literature data; details of the
171 data, fitting and parameters derived are given in the Supplementary Information.

172 2.3. *Visual MINTEQ (VMIN) and the NICA–Donnan model*

173 Visual MINTEQ is a development of the MINTEQA2 model (Hydrogeologic Inc. and Allison
174 Geoscience Consultants Inc., 1999). The model combines codes for aqueous speciation,

175 oxidation–reduction equilibria, and mineral equilibria. It includes the NICA–Donnan model
176 (Benedetti et al., 1995) for simulating the complexation of protons and metals to humic
177 substances and the generalised two–layer model (GTLM) for the binding of metals to HFO
178 (Dzombak and Morel, 1990). The NICA–Donnan implementation in Visual MINTEQ is
179 parameterised for the binding of 23 metal species including uranyl. The GTLM binding
180 constant database as supplied with the model does not contain constants for the binding of
181 uranyl to HFO, therefore we added the binding constants derived by Mahoney et al. (2009) to
182 the database.

183 Version 3.0 of Visual MINTEQ and the default inorganic speciation database were used for
184 computations. The database is based on the original MINTEQA2 model database, with binding
185 constants updated with values from the NIST thermodynamic database, version 7.0 (Smith et
186 al., 2003), where possible. Simulations are denoted VMIN–d.

187 2.4. *Chemical equilibrium of species and surfaces (CHESS)*

188 CHESS (Van der Lee, 1998) combines aqueous speciation, oxidation–reduction equilibria and
189 mineral equilibria. The model has the capability to simulate ion exchange and surface
190 complexation on minerals and colloids. CHESS simulations were done using two solution
191 databases: the default chess.tdb database (simulations denoted CHESS–ch) and the
192 ctdpv3_Dong database (simulations denoted CHESS–ct). The default database is derived from
193 the original database for the EQ3/6 speciation model. It contains parameters for ion binding to
194 HFO using the GTLM. It also contains a small number of parameters for ion binding to humic
195 acid; however these do not include parameters for uranyl. The ctdpv3_Dong database is based
196 on a database released in 2004 in the framework of the *Common Thermodynamic Database*
197 *Project* (van der Lee and Lomenech, 2004), which merged a review of uranyl thermodynamic
198 data performed by Denison (2004) and the default Chess database, augmented with binding
199 constants for the complexes $\text{MgUO}_2(\text{CO}_3)_3^{2-}$, $\text{CaUO}_2(\text{CO}_3)_3^{2-}$, $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0$, $\text{SrUO}_2(\text{CO}_3)_3^{2-}$
200 and $\text{Sr}_2\text{UO}_2(\text{CO}_3)_3^0$ (Dong and Brooks, 2006; Geipel et al., 2008).

201 2.5. *Geochemist's Workbench (GWB)*

202 The GWB (Bethke and Yeakel, 2012) can simulate solution, oxidation–reduction and
203 precipitation equilibria. It can also simulate ion binding to mineral surfaces, including ion
204 exchangers (clays). Three databases for ion binding to HFO using the GTLM are available;
205 however, none contain binding parameters for uranyl. The model does not have a submodel for
206 ion–binding to humic substances.

207 GWB simulations were done using two solution databases: the Thermo.com.v8.r6+ database
208 (simulations denoted GWB-c) and the Thermo.Minteq database (simulations denoted GWB-
209 m). The Thermo.com.v8.r6+ database is derived from the Lawrence Livermore National
210 Laboratory ‘combined’ database, version 8 release 6. The Thermo.Minteq database is the
211 database used by version 2.40 of Visual MINTEQ.

212 2.6. *PHREEQC*

213 PHREEQC can simulate solution, oxidation–reduction and precipitation equilibria, ion
214 exchange reactions and adsorption on mineral surfaces. Simulations were done using two
215 databases: the llnl.dat database (simulations denoted PHREEQC–l) and the minteq.dat database
216 (PHREEQC–m). Both databases contain parameters for the binding of ions to HFO using the
217 GTLM, however neither database contains binding constants for uranyl or thorium. The model
218 does not have a submodel for ion–binding to humic substances, although it is possible to
219 include the Humic Ion-Binding Model in the code (Liu *et al.*, 2008; Marsac *et al.*, 2011). The
220 minteq.dat database has no binding constants for thorium, therefore this combination could not
221 be used to assess thorium speciation.

222 3. **Model predictions of uranyl and thorium speciation**

223 We firstly describe the freshwater scenarios used for comparative simulations. Water
224 characteristics are presented in Tables 1 and 2.

225 3.1.1. *Ritord*

226 The Ritord basin is situated in the Limousin region of France and contains several closed
227 uranium mines. Chemically treated mine waters are discharged to surface water at two
228 locations within the catchment. For this scenario we chose a single water sample, taken on 18th
229 June 2009, downstream of the uppermost mine water discharge (Herlory *et al.*, 2013). The
230 chemical treatment of the mine water comprises addition of barium chloride to precipitate
231 radium, aluminium sulphate to co–precipitate iron and uranium, and a flocculating agent to
232 minimise suspended solids. The system is slightly acidic, with moderate hardness, although
233 this is elevated compared to an upstream unimpacted site, as a result of the mine water
234 discharge. The DOC, sulphate and aluminium concentrations are also elevated. The mine
235 discharge also increases the dissolved barium and uranium concentrations. The dissolved iron
236 concentration is reduced downstream of the discharge, possibly due to formation and

237 aggregation or settling out of HFO. No measurements of thorium were available for this
238 scenario.

239 3.1.2. *Beaverlodge Lake*

240 The location of the scenario is close to Uranium City in northern Saskatchewan, Canada. Past
241 uranium mining operations have caused contamination of a number of local surface waters
242 (lakes and streams). The scenario location is at the outflow of Greer Lake, upstream of its
243 inflow into Beaverlodge Lake, the largest water body in the area. We used mean water
244 chemistry data for the period July 1st 2003 to June 30th 2004, with the exception of DOC, for
245 which a single monitored value from 2011 was used since no corresponding data were available
246 for the earlier time period (KHS Environmental Management Group Ltd., 2004; Cameco Corp.,
247 2011). Each determinant was the mean of between two and 11 individual samples.

248 The water was alkaline with moderate hardness. Mean water temperature was 1°C. Based on
249 the water composition (Table 2) barium is the main co-contaminant of non-radionuclide origin
250 in the system. The dissolved organic carbon concentration was 14 mg C dm⁻³.

251 3.1.3. *Tajikistan*

252 The chemical compositions of the waters were taken from data published by Skipperud et al.
253 (2013). Two samples from around the Taboshar uranium mine were selected as scenarios. The
254 first is a water-filled opencast mine hole (sample name Pit Lake) at the mine. The second is a
255 sample from a stream draining from the mine tailings dump, named the 'Yellow Mountain'
256 (sample name Yellow Mountain).

257 Both waters were alkaline. Hardness, calculated from measurements of dissolved magnesium
258 and calcium, was very high (463 and 507 mg CaCO₃ dm⁻³ respectively). Alkalinity was not
259 measured, but simulations using WHAM7, assuming the measured ionic charge deficit in the
260 waters to be due to carbonates, predicted carbonate alkalinities of 207 and 257 mg CaCO₃ dm⁻³
261 respectively.

262 Concentrations of U in the samples were the highest in the scenarios, being 2000 µg dm⁻³ and
263 1100 µg dm⁻³ for Pit Lake and Yellow Mountain respectively. Concentrations of arsenic,
264 nickel, chromium, molybdenum, selenium, manganese, thorium and zinc were also measured.

265 3.2. *Scenario simulations*

266 In order to provide a reasonable comparison among models, including those capable and not
267 capable of simulating natural organic matter, we firstly computed the speciation of each

268 scenario without including organic matter. We then ran a second set of simulations using
269 WHAM7 and Visual MINTEQ, including natural organic matter and allowing the formation
270 of colloidal HFO and ion binding to its surface. In both cases, simulations were run both with
271 and without the following co-contaminants:

272 Ritord: aluminium, iron(III), barium.

273 Beaverlodge: iron(III), nickel, copper, zinc, barium, lead.

274 Pit Lake and Tajikistan: manganese, iron(III), nickel, zinc, lead.

275 4. Results

276 4.1. Scope of model/database combinations for uranyl speciation

277 Table S1 in the Supplementary Information shows the binding constants for the inorganic
278 uranyl solution species (complexes) in each model/database combination. The databases for
279 CHESS–ch, GWB–c and PHREEQC–l are identical not only for the uranyl complexes which
280 may be formed, but also have the same thermodynamic constants for their formation; thus
281 speciation predictions using these model/database combinations should be similar if not
282 identical. The GWB–m database is very similar to the VMIN–d database, being an older
283 version of the same database, however VMIN–d does not have binding constants for the
284 hydroxy–carbonate complexes $(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-$ and $(\text{UO}_2)_3\text{CO}_3(\text{OH})_3^+$, which GWB–m
285 does. The binding constants for the alkaline earth metal–uranyl–carbonate complexes
286 $\text{CaUO}_2(\text{CO}_3)_3^{2-}$ and $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0$ also differ between the two databases.

287 With the exception of PHREEQC–m, all the model/database combinations simulate formation
288 of the monomeric hydrolysis products $\text{UO}_2(\text{OH})_n^{(2-n)}$ ($n = 1, 2, 3$ or 4), the simple carbonate
289 complexes $\text{UO}_2(\text{CO}_3)_n^{(2-2n)}$ ($n = 1, 2$ or 3), the sulphate complexes $\text{UO}_2(\text{SO}_4)_n^{(2-2n)}$ ($n = 1$ or 2),
290 the phosphate complexes $\text{UO}_2\text{H}_n\text{PO}_4^{(n-1)}$ ($n = 0, 1, 2$ or 3) and the halide complexes $\text{UO}_2\text{H}_n^{(2-n)}$
291 (H is Cl^- or F^- , $n = 1$ or 2 for Cl^- and $n = 1, 2, 3$ or 4 for F^-). The PHREEQC–m database is
292 generally sparser with respect to the range of complexes simulated compared to the other
293 databases; of the monomeric hydrolysis products, it simulates only UO_2OH^+ , and does not
294 simulate formation of UO_2SO_4^0 , UO_2PO_4^- or UO_2Cl_2^0 .

295 An appreciable number of other uranyl species are included in a relatively small number of the
296 databases. This is particularly notable in the cases of the hydroxy–carbonate species –
297 $(\text{UO}_2)_2(\text{OH})_3\text{CO}_3^-$, $(\text{UO}_2)_3(\text{OH})_3\text{CO}_3^+$, $(\text{UO}_2)_3(\text{OH})_5\text{CO}_2^+$ and $(\text{UO}_2)_{11}(\text{CO}_3)_6(\text{OH})_{12}^{2-}$, the
298 alkaline earth metal–carbonate complexes $\text{CaUO}_2(\text{CO}_3)_3^{2-}$, $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0$ and

299 $\text{MgUO}_2(\text{CO}_3)_3^{2-}$, the phosphate species $\text{UO}_2(\text{H}_2\text{PO}_4)_2^0$, $\text{UO}_2(\text{H}_2\text{PO}_4)_3^-$, $\text{UO}_2(\text{H}_2\text{PO}_4)(\text{H}_3\text{PO}_4)^+$
300 and $\text{UO}_2(\text{H}_2\text{PO}_4)_2^0$ the sulphate species $(\text{UO}_2)_2(\text{OH})_2(\text{SO}_4)_2^{2-}$, $(\text{UO}_2)_3(\text{OH})_4(\text{SO}_4)_4^{6-}$ and
301 $(\text{UO}_2)_4(\text{OH})_7(\text{SO}_4)_4^{7-}$ and the silicate complex $\text{UO}_2\text{H}_3\text{SiO}_4^+$.

302 4.2. Impacts of co-contaminants in scenarios

303 Removing co-contaminants from model runs generally had negligible influence on the
304 predicted uranyl and thorium speciation. An exception was for the WHAM scenarios, where
305 removal of iron(III) from consideration was predicted to produce a shift in speciation from
306 uranyl adsorbed to colloidal HFO to uranyl complexed to other ligands. This is illustrated in
307 Figure 1, which shows predicted speciation for the Ritord scenario, using WHAM–m, under
308 conditions where (i) precipitated HFO has a chemically active surface, (ii) precipitated HFO
309 does not have a chemically active surface, (iii) iron(III) is absent. When HFO has a chemically
310 active surface, a small but non-negligible proportion (~9%) of the uranyl is predicted to be
311 adsorbed to HFO, with the major proportion (~85%) predicted to be bound to DOM and small
312 amounts present in free and hydrolysed forms (~2%) and carbonate complexes (~3%). If HFO
313 does not have a chemically active surface, binding to DOM is predicted to be higher (~93%)
314 with the amounts predicted to be free and hydrolysed (~3%) and as carbonate complexes (~4%)
315 slightly higher. If Fe(III) is absent then the prediction is for virtually all uranyl (>99%) to be
316 bound to DOM. Predicted free uranyl concentrations under these assumptions were 1.9×10^{-10}
317 mol dm^{-3} , $2.1 \times 10^{-10} \text{ mol dm}^{-3}$ and $1.9 \times 10^{-11} \text{ mol dm}^{-3}$ respectively.

318 4.3. Scope of model/database combinations for thorium speciation

319 Table S1 in the Supplementary Information shows the binding constants for the inorganic
320 thorium solution species (complexes) in each model/database combination. The WHAM
321 database, which is identical in both the WHAM–d and WHAM–m situations, allows formation
322 of the monomeric thorium hydrolysis products $\text{Th}(\text{OH})_n^{(4-n)+}$ ($n = 1-4$), the carbonate
323 complexes ThCO_3^{2+} and $\text{Th}(\text{CO}_3)_5^{6-}$, the hydroxy-carbonate complexes $\text{Th}(\text{OH})_2(\text{CO}_3)_3^{4-}$ and
324 $\text{Th}(\text{OH})_3\text{CO}_3^-$, the sulphate complexes $\text{Th}(\text{SO}_4)_n^{(4-2n)+}$ ($n = 1$ to 3) and the halide complexes ThCl^{3+} ,
325 ThF^{3+} and ThF_2^{2+} . As with uranyl, the databases for CHESS–ch, GWB–c and PHREEQC–l are
326 identical in respect of the thorium complexes that may form and their binding constants. The
327 databases all allow formation of the monomeric thorium hydrolysis products $\text{Th}(\text{OH})_n^{(4-n)+}$
328 ($n = 1-4$), three polymeric hydrolysis products $\text{Th}_m(\text{OH})_n^{(4m-n)+}$ with $m = 2$ and $n = 2$, $m = 4$ and
329 $n = 8$, $m = 6$ and $n = 15$. They also allow formation of a range of complexes with Cl^- , F^- , SO_4^{2-}
330 and PO_4^{3-} (see Table S1 for details). However, they have no binding constants for carbonate or
331 hydroxy-carbonate complex formation. VMIN–d and GWB–m also have similar databases,

332 albeit simulating formation of different complexes. Of the hydrolysis products, they simulate
333 only ThOH^{3+} , $\text{Th}(\text{OH})_2^{2+}$ and $\text{Th}_2(\text{OH})_2^{6+}$, and of the carbonate and hydroxy-carbonate
334 complexes only $\text{Th}(\text{CO}_3)_5^{6-}$ and $\text{Th}(\text{OH})_3\text{CO}_3^-$. They also simulate ThCl^{3+} , ThF^{3+} , ThF_2^{2+} ,
335 ThF_3^+ , ThF_4^0 and ThNO_3^{3+} , but have no constants for complexes with PO_4^{3-} . CHESS-ct
336 simulates a similar range of complexes to CHESS-ch, also including $\text{Th}(\text{CO}_3)_5^{6-}$ and
337 $\text{Th}(\text{OH})_3\text{CO}_3^-$ but excluding any complexes with PO_4^{3-} except for the hydroxy-phosphate
338 complex $\text{Th}(\text{OH})_4\text{PO}_4^{3-}$, which is not found in any of the other databases. PHREEQC-m does
339 not simulate any thorium complexes and so is not considered.

340 4.4. Predicted occurrence of major uranyl species

341 Default predictions for all scenarios in the absence of natural organic matter are shown in
342 Figure 2.

343 In the Ritord scenario, WHAM-d and WHAM-m predicted that hydrolysis products and
344 complexes containing carbonate would dominate when DOM/HFO were absent, comprising
345 ~96% and ~97% of the uranyl respectively. Minor contributions from phosphate complexes
346 (~2%) were predicted. WHAM-m, which allowed the formation of mixed hydroxy-carbonate
347 complexes, predicted ~24% of uranyl to be present in this form. VMIN-d, which does not
348 allow formation of hydroxy-carbonate complexes, also predicted that hydrolysis products
349 (~20%) and carbonate complexes (~65%) would dominate, with a contribution from the silicate
350 complex $\text{UO}_2\text{H}_3\text{SiO}_4^+$ (~14%). Predictions using CHESS-ch, GWB-c and PHREEQC-l were
351 similar, as expected. Free and hydrolysed forms were predicted to dominate (~85%) with
352 contributions from carbonate (~10–15%) and hydroxy-carbonate species (~1–3%). The
353 CHESS-ct simulation predicted a much smaller contribution from free and hydrolysed species
354 (~19%), with larger contributions from carbonate (~41%) and hydroxy-carbonate complexes
355 (~39%). Inspection of the model outputs indicated that this was due to the standard log K for
356 the $\text{UO}_2(\text{OH})_2^0$ species being 1.44 greater in CHESS-ch, thus favouring formation of
357 $\text{UO}_2(\text{OH})_2^0$ in CHESS-ch at the expense of UO_2CO_3^0 and $(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-$. Similar
358 dominance of free and hydrolysed species was predicted by GWB-c and PHREEQC-l, as
359 expected given that their databases are identical to that of CHESS-ch.

360 Similar differences were seen when comparing the simulations done using the Geochemist's
361 Workbench. In the GWB-c simulation, free and hydrolysed species were predicted to dominate
362 (~84%) with carbonate complexes also present (~15%). In the GWB-m simulation, carbonate
363 complexes were predicted to dominate (~75%), with contributions from free and hydrolysed
364 species (~12%), hydroxy-carbonate complexes (~6%) and the silicate complex $\text{UO}_2\text{H}_3\text{SiO}_4^+$

365 (~8%). The PHREEQC-1 simulation predicted a dominance of free and hydrolysed species
366 (~96%) with carbonate complexes (~3%) making up most of the remainder, while in the
367 PHREEQC-m simulation the speciation was predicted to be made up largely of near equal
368 contributions from carbonate complexes (~35%), free and hydrolysed species (~33%) and
369 $\text{UO}_2\text{H}_3\text{SiO}_4^+$ (~29%).

370 In contrast to the Ritord results, the predicted speciation for the Beaverlodge scenario was
371 consistently dominated by carbonate-containing complexes, regardless of the model or
372 database used. Important differences among the predictions were still seen, particularly in
373 respect to the predicted importance of the alkaline earth-uranyl-carbonate complexes. Where
374 the database employed contained such ternary complexes, these were predicted to be dominant
375 (~84% for WHAM-m, ~92% for Visual MINTEQ, ~97% for CHES-ct, ~95% for GWB-m).
376 In the remaining simulations carbonate complexes were predicted to dominate (~97-99%) with
377 small amounts (~1-2%) present in the free ion and hydrolysed forms.

378 The simulations for Pit Lake also predicted dominance of alkaline earth-uranyl-carbonate
379 complexes. In the four model/database combinations where they could form (WHAM-m,
380 VMIN-d, CHES-ct and GWB-m), they were predicted to make up at least 97% of the uranyl.
381 In the CHES-ch, GWB-c and PHREEQC-1 scenarios, uranyl was predicted to be largely
382 present as carbonate complexes split between free and hydrolysed forms (~14%), binary
383 carbonate species (~43-44%) and mixed hydroxyl-carbonate species (~43%). Carbonate
384 species were predicted to dominate in the WHAM-m and PHREEQC-m scenarios (~99-
385 100%).

386 The Yellow Mountain scenario presented a more varied set of predictions than either
387 Beaverlodge or Pit Lake. The WHAM-d scenario predicted dominance by carbonate
388 complexes (>99%), while the WHAM-m scenario predicted that alkaline earth-carbonate
389 complexes would dominate (~98%) with a minor contribution of carbonate complexes (~2%).
390 VMIN-d predicted a dominance of alkaline earth-carbonates (~95%) with small contributions
391 from carbonate complexes (~4%) and the free ion and hydrolysis products (~1%). The CHES-
392 ch and PHREEQC-1 scenarios gave similar predictions, with the dominant species being free
393 and hydrolysed forms (~39%) and hydroxy-carbonate species (~54-55%) with a small (~6%)
394 contribution from carbonates. The CHES-ct and GWB-m scenarios also predicted similar
395 speciation, dominated by alkaline earth-carbonates (~76-81%) with contributions from
396 hydroxy-carbonates (~15-17%) and carbonates (~3-6%). The PHREEQC-m scenario
397 predicted carbonates (~64%) and free and hydrolysed forms (~36%) to dominate. The GWB-

398 c scenario predicted the free ion and hydrolysis products to dominate (~96%) with a small
399 contribution from hydroxy-carbonate complexes (~3%).

400 For the Ritord scenario, predictions including DOM and colloidal HFO (Figure 3) presented a
401 contrasts compared to those predictions obtained in the absence of DOM and HFO. WHAM-
402 d predicted that uranyl bound to precipitated HFO was the dominant form (~58%), followed
403 by uranyl bound to DOM (~40%), with small (<2% each) contributions from free and
404 hydrolysed forms and carbonate complexes. In the WHAM-m scenario, predicted binding of
405 uranyl to HFO was much reduced (~9%) while binding to DOM was predicted to be higher
406 (~85%), with a small increase in the amounts predicted as the free ion and hydrolysed species,
407 and as carbonate complexes. Addition of alkaline earth metal-carbonate and mixed hydroxy-
408 carbonate complexes had a negligible effect on the predicted speciation. VMIN-d predicted
409 that uranyl was almost entirely bound to organic matter, with minor contributions from free
410 and hydrolysed forms, carbonate and silicate complexes. No adsorption to HFO was predicted,
411 since strong complexation of Fe(III) by organic matter was predicted to prevent precipitation
412 of HFO. In contrast, inclusion of DOM and colloidal HFO in the modelling of the remaining
413 scenarios had only minor effects on the speciation. The Beaverlodge WHAM-d and WHAM-
414 m predictions were similar to those made in the absence of DOM/HFO, with organic and HFO-
415 bound species predicted to be <1%. VMIN-d predicted ~2% organically-complexed uranyl in
416 Beaverlodge. Complexation to DOM and HFO in Pit Lake was negligible in all model/database
417 combinations. In Yellow Mountain, VMIN-d predicted ~1% complexation to DOM, otherwise
418 there were negligible differences compared to the predictions without DOM/HFO.

419 4.5. *Predicted occurrence of major thorium species*

420 As with uranyl, the predicted occurrence of thorium species across the different model/database
421 combinations, in the absence of DOM and HFO, was variable. A notable pattern across the
422 scenarios was the dominance of two specific complexes, $\text{Th}(\text{OH})_4^0$ and $\text{Th}(\text{OH})_3\text{CO}_3^-$. An
423 important component of the variability of the predicted speciation was determined by whether
424 the database used contained binding constants for these complexes. In Beaverlodge, WHAM-
425 d/WHAM-m predicted that $\text{Th}(\text{OH})_4^0$ dominated (~79%) with a major contribution from
426 $\text{Th}(\text{OH})_3\text{CO}_3^-$ (~21%). In the VMIN-d and GWB-m model/database combinations, for which
427 the binding constant for $\text{Th}(\text{OH})_4^0$ was absent, $\text{Th}(\text{OH})_3\text{CO}_3^-$ completely dominated speciation
428 (~100%). Conversely, CHESS-ch, GWB-c and PHREEQC-l, for which the binding constant
429 for $\text{Th}(\text{OH})_3\text{CO}_3^-$ was absent, predicted ~100% $\text{Th}(\text{OH})_4^0$. CHESS-ct, which has binding
430 constants for both $\text{Th}(\text{OH})_4^0$ and $\text{Th}(\text{OH})_3\text{CO}_3^-$, predicted complete dominance of $\text{Th}(\text{OH})_4^0$.

431 Patterns of prediction for VMIN–d, GWB–m, CHESS–ch, GWB–c and PHREEQC–l in the Pit
432 Lake and Yellow Mountain scenarios were similar to their predictions in the Beaverlodge
433 scenario. WHAM–d and WHAM–m predicted dominance of $\text{Th}(\text{OH})_4^0$ and $\text{Th}(\text{OH})_3\text{CO}_3^-$ in
434 Pit Lake and Yellow Mountain, with differing degrees of importance (~23% and ~77% in Pit
435 Lake, ~52% and ~48% in Yellow Mountain). CHESS–ct predicted thorium to be largely
436 present as $\text{Th}(\text{OH})_4^0$ (~99% in Pit Lake and ~95% in Yellow Mountain) with the remainder
437 being $\text{Th}(\text{OH})_4^0$.

438 When including DOM/HFO in the WHAM–d, WHAM–m and VMIN–d predictions,
439 contrasting patterns were found. WHAM predicted that DOM–bound thorium was a minor
440 component in all the scenarios (~2% in Beaverlodge and <1% in both Pit Lake and Yellow
441 Mountain). In contrast, VMIN–d consistently predicted complete dominance (~100%) of
442 DOM–complexed thorium in all three scenarios. The contribution of HFO–bound thorium was
443 consistently negligible in all predictions.

444 5. Discussion

445 Dissolved uranyl and thorium speciation is somewhat complex in comparison with other
446 metallic cations due to the possibility of forming a relatively large number of hydrolysis
447 products (including small polymeric species) and complexes with inorganic ligands,
448 particularly carbonate, at environmentally relevant concentrations. This is coupled with the
449 possibility of forming mixed complexes containing either another metal centre (alkali metal–
450 carbonate complexes, in the case of uranyl) or two ligand types (e.g. hydroxy–carbonate
451 complexes).

452 In general the effects of co-contaminants on predicted uranyl and thorium speciation were
453 negligible. The exception is the WHAM7 simulation for Ritord where Fe is considered as a
454 co-contaminant. Here, inclusion of Fe (as Fe(III)) in the simulation inputs results in the
455 prediction of precipitation of HFO and adsorption of uranyl to the HFO surface. Simulation
456 preventing adsorption to HFO predicts speciation to be dominated by DOM complexes, with a
457 higher predicted UO_2^{2+} activity due to the lower ligand concentration. Simulation with Fe(III)
458 absent, on the other hand, predicts the greatest extent of complexation (almost entirely to
459 DOM) and the lowest UO_2^{2+} activity, due to the removal of Fe(III) as a competing ion for
460 uranyl binding to DOM. A predicted difference in the free uranyl activity of approximately one
461 order of magnitude was seen between the scenarios where Fe(III) was present and absent.
462 However, since freshwaters are frequently oversaturated with respect to HFO (e.g. Lofts and

463 Tipping, 2008) and Fe(III) is thus under solid phase control, the competitive effect of Fe^{3+} ions
464 on complexation of cations is ubiquitous whether Fe(III) is present as a co-contaminant or not.
465 It is possible that uranyl binding to HFO may be important in pyritic acid mine drainage
466 systems, where oxidation of high concentrations of Fe(II) produced by pyrite dissolution can
467 produce elevated concentrations of HFO which may exert a significant control on metal
468 speciation and transport (e.g. Balistrieri et al., 2007).

469 The effect of Fe(III) was negligible in the other scenarios, due to its relatively low
470 concentrations (Table 2) and the higher hardness and/or pH, which increased uranyl-carbonate
471 association. This limited the formation of HFO and thus of uranyl-HFO adsorbed complexes.
472 Formation of uranyl adsorbed to HFO did not exceed ~1% of total uranyl in the other scenarios.

473 The considerable variations in predicted speciation for each scenario across the different
474 model/database combinations illustrate how differences among the databases clearly influence
475 the computed speciation. Complexation of uranyl to DOM is predicted to be of importance in
476 scenarios where the DOM:carbonate ratio is sufficiently high to allow DOM to effectively
477 compete with carbonate for uranyl, such as in the Ritord scenario. In the Beaverlodge scenario,
478 almost complete formation of simple carbonate complexes is predicted if formation of alkaline
479 earth-carbonate complexes is not allowed, whereas alkaline earth-carbonate complexes
480 dominate if they can form. A similar pattern is seen in the Pit Lake and Yellow Mountain
481 scenarios: if neither alkaline earth-carbonate complexes nor hydroxy-carbonate complexes
482 may form, simple carbonates are predicted to dominate; if hydroxy-carbonate complexes may
483 form, but not alkaline earth-carbonate complexes, then hydroxy-carbonate complexes are
484 important, but if alkaline earth-carbonate complexes can form then they dominate. The patterns
485 observed in the thorium predictions are simpler and dominated by $\text{Th}(\text{OH})_4^0$ and $\text{Th}(\text{OH})_3\text{CO}_3^-$
486 ; for specific model/database combinations, the predicted speciation is highly dependent on
487 whether either or both of these complexes are allowed to form. Simulations involving
488 DOM/HFO showed contrasting predicted binding behaviour of thorium between WHAM and
489 Visual MINTEQ, with the latter predicting that DOM complexes completely dominated
490 thorium speciation, while the former predicted them to be of minor importance. Further work
491 is clearly needed to better quantify the actual importance of DOM for uranyl and thorium
492 complexation in surface waters, to provide data against which to further assess and improve
493 the models and to constrain their predictions. Coupled with this, there needs to be a raising of
494 awareness among users of geochemical speciation modelling, regarding the importance of
495 assessing database coverage and completeness prior to performing computations.

496 As noted in the introduction, a further intention of this study was to model radium and polonium
497 alongside uranium and thorium, but this was not possible due to a general lack of binding
498 constants in the model databases. This is a notable data gap given the importance of radium as
499 a decay product of uranium and thorium. Some work on estimating Ra^{2+} binding constants
500 exists; Langmuir and Riese (1985) estimated binding constants and enthalpies for some simple
501 Ra^{2+} complexes (RaOH^+ , RaCO_3^0 , RaCl^+ , RaSO_4^0) by extrapolation from the relationship
502 between the corresponding binding constants for other Group II metals (Ca, Sr, Ba) and the
503 effective ionic radius of the cation. However, such estimated constants for solution complexes
504 are not generally incorporated into speciation modelling databases. While no literature studies
505 on the binding of radium to humic substances could be identified, in this case the estimation of
506 binding constants is possible in principle (e.g. Tipping et al., 2011). In order to incorporate
507 radium complex formation into speciation model databases, experimental research is required
508 on the solution complexation of radium, and ideally also on its interactions with humic
509 substances.

510 **6. Conclusions**

- 511 • Well-characterised field waters, with minor extrapolation where required, were used to
512 compare geochemical model predictions of dissolved uranyl (in four scenarios) and
513 thorium speciation (in three scenarios) and to investigate the influence of co-
514 contaminants on the predicted forms of uranyl and thorium.
- 515 • Removal of co-contaminants from simulations generally had negligible effects on the
516 predicted speciation, with the exception of the Ritord scenario where simulation using
517 WHAM7 in the absence of iron prevented formation of uranyl adsorbed to HFO. This
518 suggests iron could have a significant influence on uranyl speciation in waters receiving
519 iron-rich inputs such as acid mine drainage.
- 520 • Speciation predictions were dependent on model capabilities and the coverage of
521 inorganic and organic complexes in the database used.
- 522 • Organic complexation, where it could be simulated, was predicted to be important for
523 uranyl in a slightly acidic water of relatively high DOM concentration. Binding of
524 thorium to DOM was predicted to dominate speciation in circumneutral waters when
525 modelled using Visual MINTEQ, however predictions of the same waters using
526 WHAM7 predicted only a minor role for DOM in binding thorium.

- 527 • Thorium speciation was predicted to be controlled by a small number of specific
528 complexes. Variations in predicted speciation were strongly dependent on the
529 presence/absence of these complexes from the database used.
- 530 • In circumneutral waters, formation of carbonate complexes, including hydroxy-
531 carbonates and alkaline earth metal-carbonates, was predicted to dominate the uranyl
532 speciation.
- 533 • Differences in the range of carbonate complexes considered in the model databases had
534 an important influence on uranyl speciation predictions in circumneutral waters, where
535 inorganic complexes were predicted to dominate. Alkaline earth metal-carbonate and
536 hydroxy-carbonate complexes were predicted to be important species in such waters,
537 when they were included in simulations. Where they were absent, simple carbonate
538 species were generally predicted to be important.
- 539 • Complexation constants for radium and polonium were entirely absent from all the
540 databases and so no assessment of speciation was possible. There is a need for
541 experimental determination of radium and polonium complexation constants in order
542 to properly incorporate these elements into geochemical speciation models.
- 543 • Model users need to be aware of the differences among model databases before
544 applying models, in particular the status with respect to updates and the incorporation
545 of the most up to date binding constants.

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698 processes of the freshwater cladoceran *Daphnia magna*. *Aquatic Toxicology* 86(3): 370–378.

699

700 Table 1. Major ion concentrations in scenario waters. nm = not measured.

	pH	DOC	Na	Mg	Al	K	Ca	Determinant								F	Si
		mg dm ⁻³	mg dm ⁻³	mg dm ⁻³	mg dm ⁻³	mg dm ⁻³	mg dm ⁻³	NH ₄	Cl	NO ₃	SO ₄	HCO ₃	Alk				
								mg dm ⁻³	mg dm ⁻³	mg dm ⁻³	mg dm ⁻³	mg C dm ⁻³ ^a	mg CaCO ₃ dm ⁻³	mg dm ⁻³	mg dm ⁻³		
Ritord	6.38	9.57	6.2	3.1	0.205	2.7	17.4	0.22	14.4	1.7	48	1.97	nm	nm	12.17		
Beaverlodge ^b	8.05 ^b	14.0 ^c	54.7 ^b	5.2 ^b	nm	1.5 ^b	25.2 ^b	nm	6.64 ^b	nm	50.6 ^b	169.7 ^b	nm	nm	nm		
Pit Lake	8.0	2.23	111	36	nm	3.6	126	nm	14	0.15	471	nm	207 ^e	0.37	nm		
Yellow Mountain	7.4	0.78	89	28	nm	3.3	157	nm	14	5	399	nm	258 ^e	0.45	nm		

701 ^a mg inorganic carbon dm⁻³.

702 ^b *n* = 11.

703 ^c *n* = 1.

704 ^d mg inorganic C dm⁻³.

705 ^e Estimated using WHAM7, assuming ionic charge difference to be due to carbonate species.

706

707 Table 2. Trace metal, metalloid, uranium and thorium concentrations in scenario waters. nm = not measured.

	Determinand											
	As	Cu	Mn	Fe	Ni	Zn	Se	Mo	Ba	Pb	U	Th
	$\mu\text{g dm}^{-3}$	$\mu\text{g dm}^{-3}$	$\mu\text{g dm}^{-3}$	$\mu\text{g dm}^{-3}$	$\mu\text{g dm}^{-3}$	$\mu\text{g dm}^{-3}$	$\mu\text{g dm}^{-3}$	$\mu\text{g dm}^{-3}$	$\mu\text{g dm}^{-3}$	$\mu\text{g dm}^{-3}$	$\mu\text{g dm}^{-3}$	pg dm^{-3}
Ritord	nm	nm	307	721	nm	nm	nm	nm	241	nm	35	nm
Beaverlodge	1.8 ^a	1 ^b	nm	65 ^b	1 ^b	5 ^b	4.8 ^c	nm	0.56 ^d	3 ^b	483.6	0.079
Pit Lake	25	nm	13	18	3.8	(65) ^e	nm	34	nm	0.37	2000	4989
Yellow Mountain	31	nm	1	13	4.8	(65) ^e	nm	15	nm	0.3	1100	499

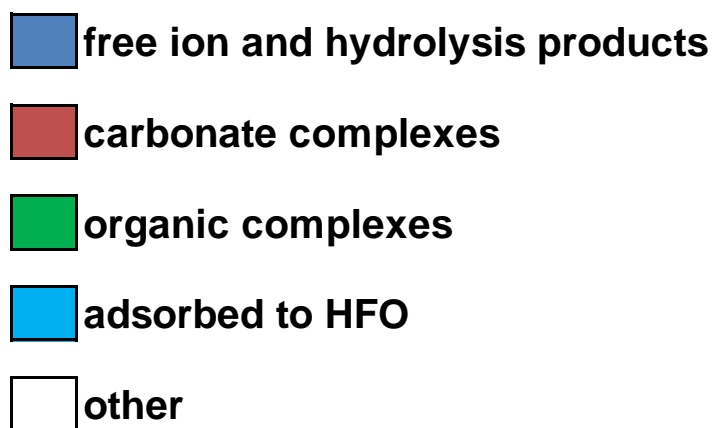
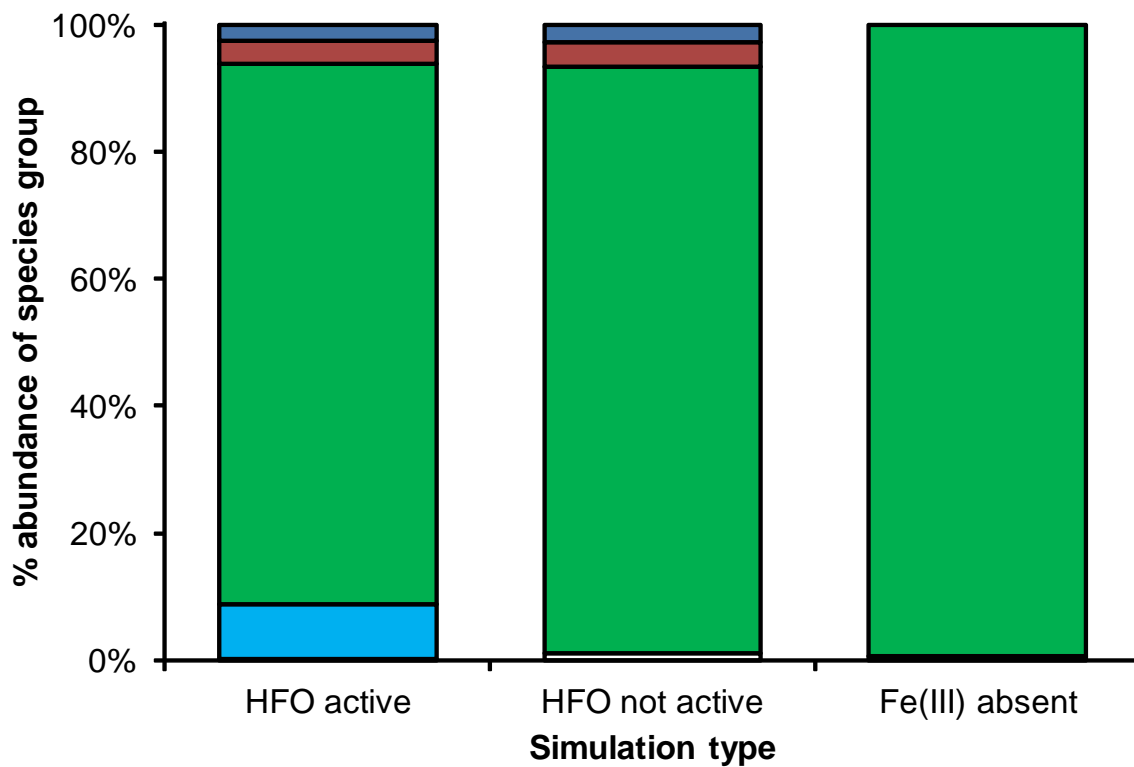
708 ^a $n = 2$.

709 ^b $n = 4$.

710 ^c $n = 7$.

711 ^d $n = 9$.

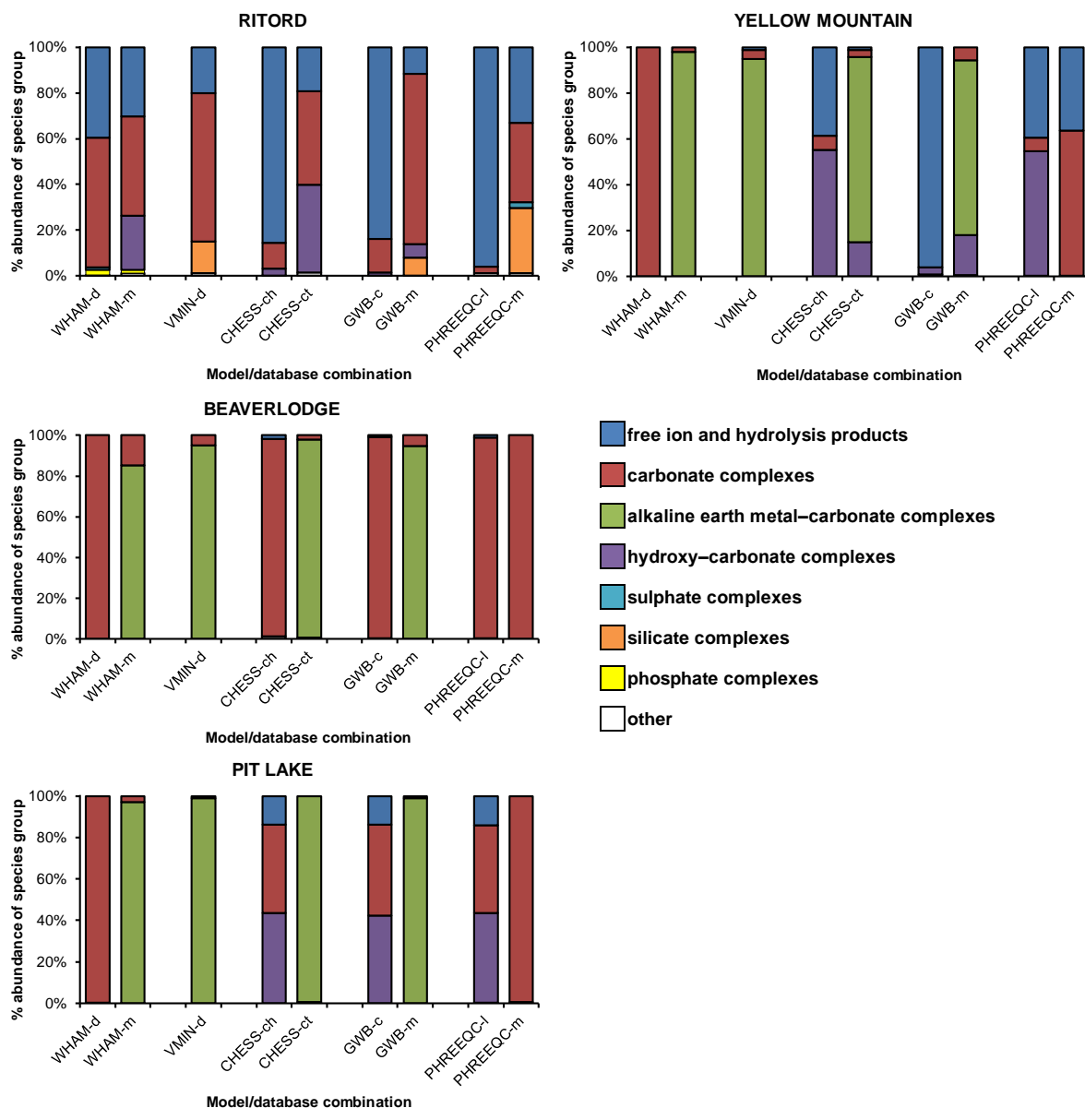
712 ^e Estimated at $10^{-6} \text{ mol dm}^{-3}$.



713

714

Figure 1.



715

716

Figure 2.

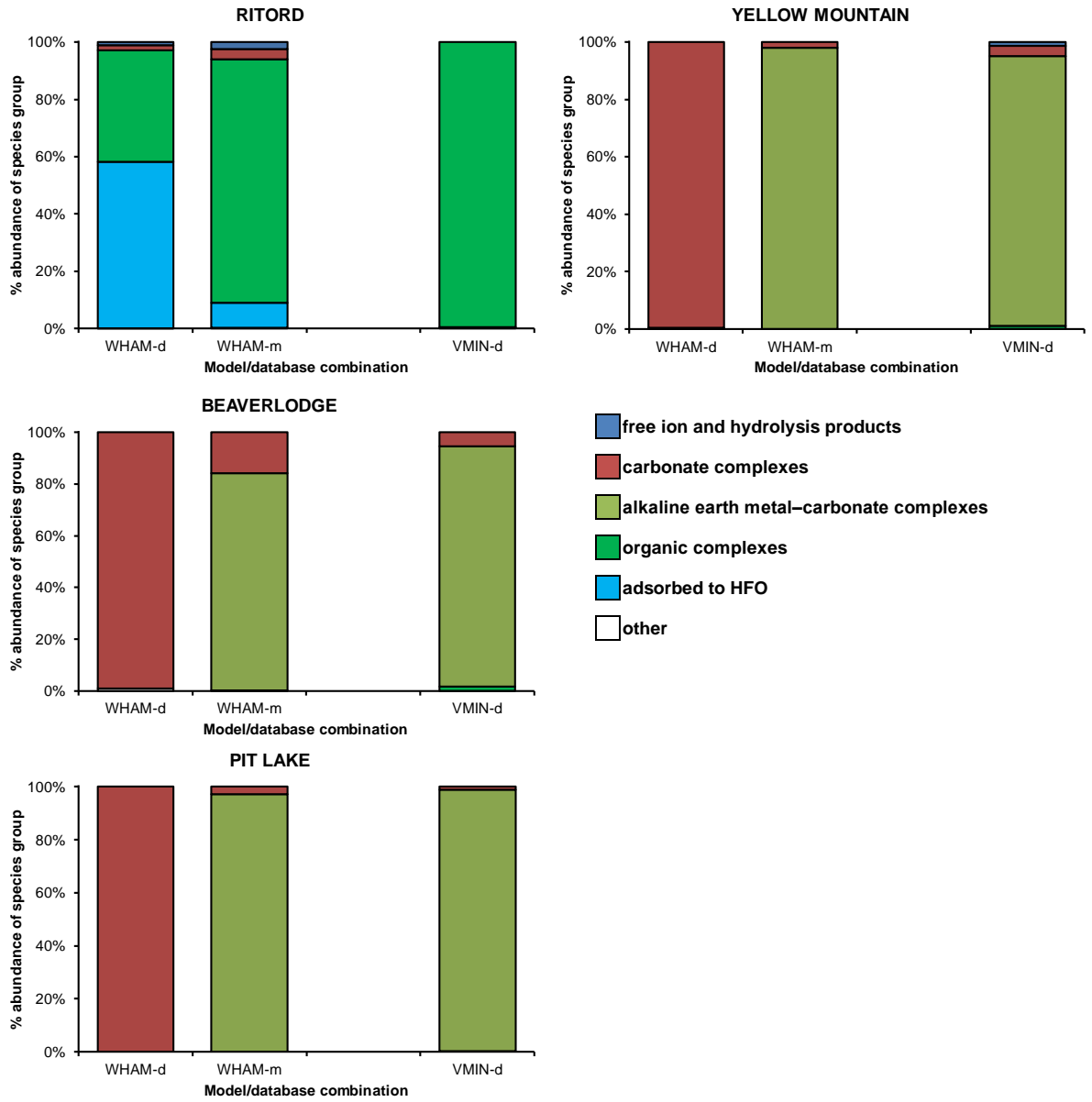
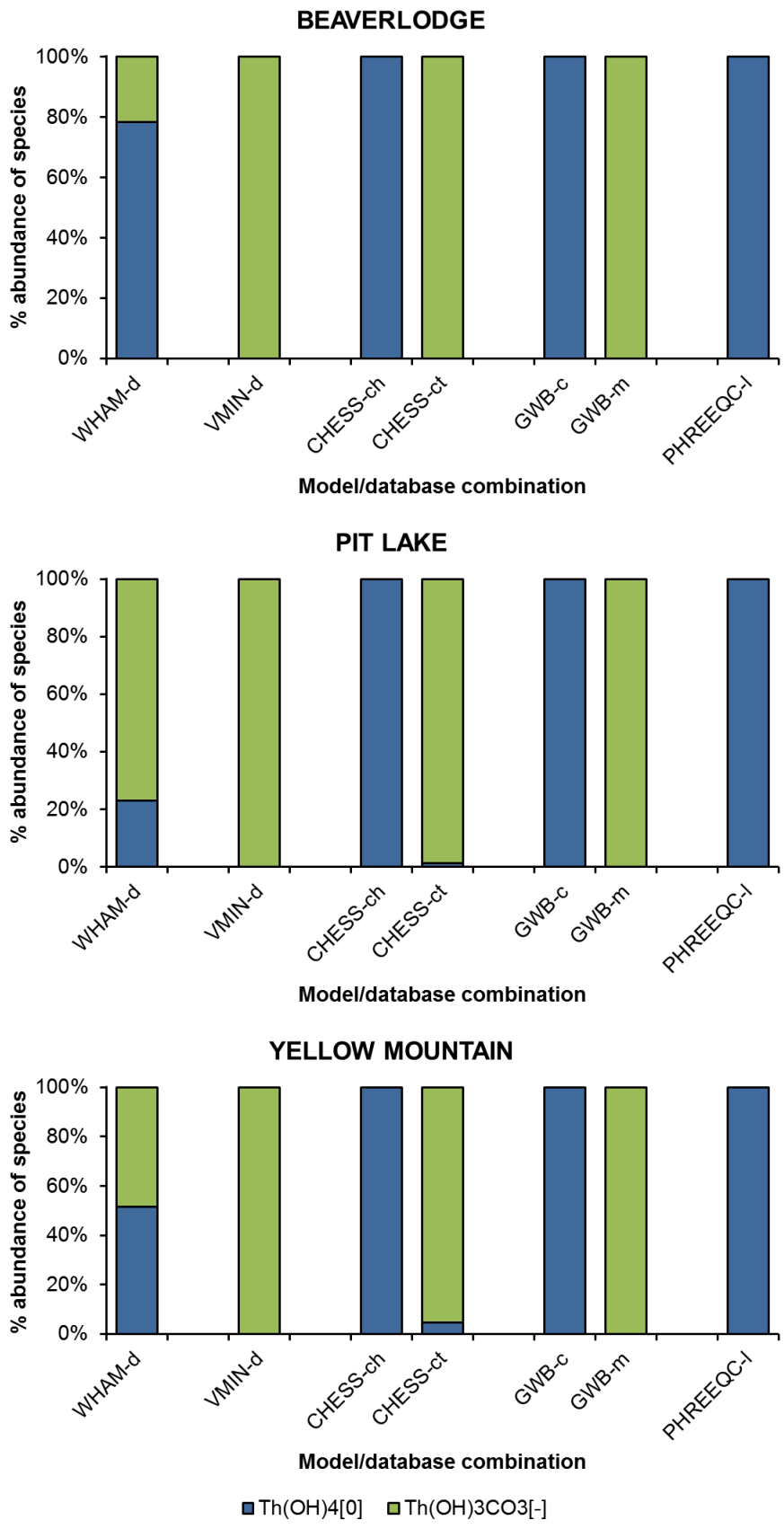


Figure 3.



720

721

Figure 4.

722 **Figure captions**

723 Figure 1. Predictions of speciation in the Ritord scenario using WHAM–m, under three
724 assumptions: Fe(III) present and able to form HFO with a chemically active surface; Fe(III)
725 present but not allowed to form HFO; Fe(III) not present.

726 Figure 2. Predicted distribution of uranyl among groups of complexes for each model/database
727 combination, in the absence of natural organic matter and colloidal HFO. Charts show the
728 distribution of uranyl among defined groups of species: the free ion and its hydrolysis products,
729 carbonate complexes, alkaline earth metal–carbonate complexes, hydroxy–carbonate
730 complexes, sulphate complexes, silicate complexes and phosphate complexes. Species groups
731 whose occurrence represent <1% of the uranyl in a given calculation are shown under ‘Other’.
732 Mixed hydroxy–carbonate complexes can form only in the CHESS–ch, CHESS–ct, GWB–c
733 and GWM–m simulations. Silicate complexation can only be simulated where Si
734 measurements were made (Ritord scenario) and in the VMIN–d, GWB–m and PHREEQC–m
735 simulations.

736 Figure 3. Predicted distribution of uranyl among groups of complexes for the model/database
737 combinations WHAM–d, WHAM–m and VMIN–d, in the presence of natural organic matter
738 and allowing colloidal HFO to form.

739 Figure 4. Predicted distribution of thorium among complexes for each model/database
740 combination, in the absence of natural organic matter and colloidal HFO. Only the dominant
741 species $\text{Th}(\text{OH})_4^0$ and $\text{Th}(\text{OH})_3\text{CO}_3^-$ are shown. The complex $\text{Th}(\text{OH})_4^0$ can form in the
742 WHAM–d, CHESS–ch, CHESS–ct, GWB–c and PHREEQC–l simulations. The complex
743 $\text{Th}(\text{OH})_3\text{CO}_3^-$ can form in the WHAM–d, VMIN–d, CHESS–ct and GWB–m simulations.

1 **Supplementary Information**

2 **Assessment of co-contaminant effects on uranium and thorium**
3 **speciation in freshwater using geochemical modelling**

4

5 Stephen LOFTS^a, Laureline FEVRIER^b, Nele HOREMANS^c, Rodolphe GILBIN^b, Christophe
6 BRUGGEMAN^c, Hildegarde VANDENHOVE^c

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8 ^a NERC Centre for Ecology and Hydrology, Lancaster Environment Centre, Bailrigg, Lancaster,
9 LA1 4AP, U.K.. stlo@ceh.ac.uk

10 ^b IRSN, DEI/SECRE/LRE-Bât 186, B.P.3, Cadarache Center, F-13115 Saint-Paul-lez-Durance
11 cedex, France. laureline.fevrier@irsn.fr, rodolphe.gilbin@irsn.fr

12 ^c Belgian Nuclear Research Centre SCK•CEN, BE-2400 Mol, Belgium. nhoreman@sckcen.be,
13 cbruggeman@sckcen.be, hvandenhove@sckcen.be

14 Corresponding author: S. Lofts

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16

1. Summary of binding complexes

Table S1. Thermodynamic data^{a,b,c,d} for solution complexes of uranyl and thorium simulated by each model/database combination. Reaction enthalpies for the CHES–ch/GWB–c and CHES–ct databases are computed by interpolation of point log *K* values for 0°C and 25°C using the Van't Hoff equation. Underlining denotes where the value in the database is the same as that in the NEA-TDB compilation (Guillaumont et al., 2003).

Model/database combination	WHAM-d ^{a,b}		WHAM-m ^{a,b}		VMIN-d, GWB-m		CHES–ch ^{c,d} , GWB–c ^{c,d}		CHES–ct ^{c,d}		PHREEQC–l ^{c,d}		PHREEQC–m ^b	
Database name	default		modified		v3.0, thermo.minteq		chess.tdb, thermo.com.v8.r6+		ctdpv3_Dong.tdb		llnl		minteq	
Complex	log <i>K</i> , 25°C	Δ <i>H</i> , kJ/mol	log <i>K</i> , 25°C	Δ <i>H</i> , kJ/mol	log <i>K</i> , 25°C	Δ <i>H</i> , kJ/mol	log <i>K</i> , 25°C	Δ <i>H</i> , kJ/mol	log <i>K</i> , 25°C	Δ <i>H</i> , kJ/mol	log <i>K</i> , 25°C	Δ <i>H</i> , kJ/mol	log <i>K</i> , 25°C	Δ <i>H</i> , kJ/mol
UO ₂ OH ⁺	-5.2	44.94	-5.2	44.94	<u>-5.25</u>	^e	-5.2073	43.7	-5.36	42.8	-5.2073	41.2	-5.09	
UO ₂ (OH) ₂ ⁰	-11.9		-11.9		<u>-12.15</u>		-10.3146		-11.75		-10.3146			
UO ₂ (OH) ₃ ⁻	-21		-21		<u>-20.25</u>		-19.2218		-19.6		-19.2218			
UO ₂ (OH) ₄ ²⁻	-32.4	156.3	-32.4	156.3	<u>-32.4</u>		-33.0291		-34.23		-33.0291			
(UO ₂) ₂ OH ³⁺					<u>-2.7</u>		-2.7072		<u>-2.7</u>		-2.7072			
(UO ₂) ₂ (OH) ₂ ²⁺	-5.6	40.1	-5.6	40.1	<u>-5.62</u>	48.9	-5.6346	39.8	-5.7		-5.6346	37.6	-5.645	
(UO ₂) ₃ (OH) ₄ ²⁺					<u>-11.9</u>		-11.929		<u>-11.9</u>		-11.929			
(UO ₂) ₃ (OH) ₅ ⁺	-15.7	100.4	-15.7	100.4	<u>-15.55</u>	123	-15.5862	102.0	-15.59		-15.5862	97.1	-15.593	104.9
(UO ₂) ₃ (OH) ₇ ⁻					<u>-32.2</u>		-31.0508		-30.18		-31.0508			
(UO ₂) ₃ (OH) ₈ ²⁻									-37.65					
(UO ₂) ₃ (OH) ₁₀ ²⁻									-62.4					
(UO ₂) ₄ (OH) ₇ ⁺					<u>-21.9</u>		-21.9508		<u>-21.9</u>		-21.9508			
UO ₂ CO ₃ ⁰	9.4	4.6	9.4	4.6	<u>9.94</u>	5.0	9.6654	-0.4	<u>9.68</u>	1.5	9.6654	5.0	10.071	3.5
UO ₂ (CO ₃) ₂ ²⁻	16.4	14.6	16.4	14.6	<u>16.61</u>	18.5	16.9109	9.8	<u>16.95</u>	11.1	16.9109	18.5	17.008	14.6
UO ₂ (CO ₃) ₃ ⁴⁻	21.6	-38.9	21.6	-38.9	<u>21.84</u>	-39.2	21.5562	-50.5	<u>21.61</u>	-49.9	21.5562	-39.2	21.384	-36.7
(UO ₂) ₃ (CO ₃) ₆ ⁶⁻					<u>54</u>	-62.7	53.9127	-92.2	<u>54.01</u>	-84.4	53.9127	-62.7		
Ca ₂ UO ₂ (CO ₃) ₃ ⁰			29.82		30.7				30.7					

Table S1. (contd.)

Model/database combination	WHAM-d ^{a,b}		WHAM-m ^{a,b}		VMIN-d, GWB-m		CHESS-ch ^{c,d} , GWB-c ^{c,d}		CHESS-ct ^{c,d}		PHREEQC-l ^{c,d}		PHREEQC-m ^b	
Database name	default		modified		v3.0		chess.tdb, thermo.com.v8.r6+		ctdvp3_Dong.tdb		llnl		minteq	
Complex	log <i>K</i> , 25°C	Δ <i>H</i> , kJ/mol	log <i>K</i> , 25°C	Δ <i>H</i> , kJ/mol	log <i>K</i> , 25°C	Δ <i>H</i> , kJ/mol	log <i>K</i> , 25°C	Δ <i>H</i> , kJ/mol	log <i>K</i> , 25°C	Δ <i>H</i> , kJ/mol	log <i>K</i> , 25°C	Δ <i>H</i> , kJ/mol	log <i>K</i> , 25°C	Δ <i>H</i> , kJ/mol
CaUO ₂ (CO ₃) ₃ ²⁻			26.37		27.18				27.18					
MgUO ₂ (CO ₃) ₃ ²⁻			25.3						25.8					
(UO ₂) ₂ CO ₃ (OH) ₃ ⁻			<u>-0.851</u>				-0.8941		-0.85		-0.8941			
(UO ₂) ₃ O(OH) ₂ (HCO ₃) ⁺			<u>0.609</u>				0.6159		0.66		0.6159			
(UO ₂) ₃ (OH) ₅ CO ₂ ⁺							0.7094				0.7094			
(UO ₂) ₁₁ (CO ₃) ₆ (OH) ₁₂ ²⁻			<u>36.2381</u>				<u>36.2381</u>				<u>36.2381</u>			
UO ₂ NO ₃ ⁺					<u>0.3</u>	<u>-12</u>	0.2805		0.3		0.2805			
UO ₂ SO ₄ ⁰	3		3		<u>3.15</u>	<u>19.5</u>	3.0703	16.5	3.15	19.2	3.0703	19.8	2.709	21.3
UO ₂ (SO ₄) ₂ ²⁻	<u>4.14</u>		<u>4.14</u>		<u>4.14</u>	<u>35.1</u>	3.9806	28.5	4.14	34.7	3.9806	35.6	4.183	25.5
UO ₂ (SO ₄) ₃ ⁴⁺	<u>3.02</u>		<u>3.02</u>						2.62					
(UO ₂) ₂ (OH) ₂ (SO ₄) ₂ ²⁻									-0.69					
(UO ₂) ₃ (OH) ₄ (SO ₄) ₄ ⁶⁻									-6					
(UO ₂) ₄ (OH) ₇ (SO ₄) ₄ ⁷⁻									-19.01					
UO ₂ PO ₄ ⁻	<u>13.23</u>		<u>13.23</u>		<u>13.23</u>		14.4016		<u>13.21</u>		14.4016			
UO ₂ HPO ₄ ⁰	<u>19.615</u>		<u>19.615</u>		<u>19.615</u>		20.7616		19.62		20.7616		20.814	-8.8
UO ₂ H ₂ PO ₄ ⁺	<u>20.693</u>		<u>20.693</u>		<u>20.693</u>		23.9937		22.75		23.9937		22.643	-15.5
UO ₂ H ₃ PO ₄ ²⁺	<u>22.481</u>		<u>22.481</u>		<u>22.481</u>		23.6337		<u>22.43</u>		23.6337			
UO ₂ (HPO ₄) ₂ ²⁻													42.988	-47.693

Table S1. (contd.)

Model/database combination	WHAM-d ^{a,b}		WHAM-m ^{a,b}		VMIN-d, GWB-m		CHESS-ch ^{c,d} , GWB-c ^{c,d}		CHESS-ct ^{c,d}		PHREEQC-l ^{c,d}		PHREEQC-m ^b	
Database name	default		modified		v3.0, thermo.minteq		chess.tdb, thermo.com.v8.r6+		ctdpv3_Dong.tdb		llnl		minteq	
Complex	log <i>K</i> , 25°C	Δ <i>H</i> , kJ/mol	log <i>K</i> , 25°C	Δ <i>H</i> , kJ/mol	log <i>K</i> , 25°C	Δ <i>H</i> , kJ/mol	log <i>K</i> , 25°C	Δ <i>H</i> , kJ/mol	log <i>K</i> , 25°C	Δ <i>H</i> , kJ/mol	log <i>K</i> , 25°C	Δ <i>H</i> , kJ/mol	log <i>K</i> , 25°C	Δ <i>H</i> , kJ/mol
UO ₂ (H ₂ PO ₄) ₃ ⁻													66.245	-119.7
UO ₂ (H ₂ PO ₄)(H ₃ PO ₄) ⁺							47.3973		44.99		47.3973			
UO ₂ (H ₂ PO ₄) ₂ ⁰							46.3873		44.84		46.3873		44.7	-69.0
UO ₂ H ₃ SiO ₄ ⁺					<u>-1.9111</u>								-2.4	
UO ₂ Cl ⁺	<u>0.17</u>	8	<u>0.17</u>	8	<u>0.17</u>	8	0.1572	5.9	<u>0.17</u>	8	0.1572	8.0	0.22	5.2
UO ₂ Cl ₂ ⁰	<u>-1.1</u>	15	<u>-1.1</u>	15	<u>-1.1</u>	15	-1.1253	13.7	<u>-1.1</u>	15	-1.1253	15.0		
UO ₂ F ⁺	<u>5.16</u>	1.7	<u>5.16</u>	1.7	<u>5.16</u>	1.7	5.0502	-0.3	5.09	1.9	5.0502	1.7	5.105	-1.9
UO ₂ F ₂ ⁰	<u>8.83</u>	2.1	<u>8.83</u>	2.1	<u>8.83</u>	2.1	8.5403	-1.7	8.62	1.9	8.5403	2.1	8.92	-3.8
UO ₂ F ₃ ⁻	<u>10.9</u>	2.51	<u>10.9</u>	2.51	<u>10.9</u>	2.35	10.7806	-0.6	10.9	2.5	10.7806	2.3	11.364	-3.6
UO ₂ F ₄ ²⁻	<u>11.84</u>	0.3	<u>11.84</u>	0.3	<u>11.84</u>	0.29	11.5407	-4.8	11.7	0	11.5407	0.28	12.607	-4.6

Table S1. contd.

Model/database combination	WHAM-d ^{a,b} , WHAM-m ^{a,b}		VMIN-d, GWB-m		CHESS-ch ^{c,d} , GWB-c ^{c,d}		CHESS-ct ^{c,d}		PHREEQC-l ^{c,d}	
Database name	default, modified		v3.0, thermo.minteq		chess.tdb, thermo.com.v8.r6+		ctdvp3_Dong.tdb		llnl	
Complex	log <i>K</i> , 25°C	Δ H, kJ/mol	log <i>K</i> , 25°C	Δ H, kJ/mol	log <i>K</i> , 25°C	Δ H, kJ/mol	log <i>K</i> , 25°C	Δ H, kJ/mol	log <i>K</i> , 25°C	Δ H, kJ/mol
ThOH ³⁺	-2.34	20.74	-3.197	22.81	-3.8871	25.53	-3.80	24.84		
Th(OH) ₂ ²⁺	-6.36	39.43	-6.894	57.62	-7.1068	59.73	-7.02	59.03	-7.1068	58.668
Th(OH) ₃ ⁺	-11.7	59.69			-11.8623		-11.77			
Th(OH) ₄ ⁰	-15.9	88.06			-16.0315	100.77	-15.94	106.23		
Th ₂ (OH) ₂ ⁶⁺			-6.094	61.62	-6.4618	65.92	-6.26	64.54		
Th ₄ (OH) ₈ ⁸⁺					-21.7568	253.15	-21.41	250.38		
Th ₆ (OH) ₁₅ ⁹⁺					-37.7027	472.53	-37.18	468.38		
ThCO ₃ ²⁺	11.03									
Th(CO ₃) ₅ ⁶⁻	31		32.3				32.33			
Th(OH) ₂ (CO ₃) ₃ ⁴⁻	30.8									
Th(OH) ₃ CO ₃ ⁻	40.1		-0.5				41.47			
ThSO ₄ ²⁺	<u>6.17</u>	20.92			5.3143	11.67	5.40	10.97		
Th(SO ₄) ₂ ⁰	<u>9.69</u>	40.38			9.617	25.11	9.71	30.57		
Th(SO ₄) ₃ ²⁻	<u>10.748</u>				10.4014		10.49			
Th(SO ₄) ₄ ⁴⁻					8.4003		8.49			
ThCl ³⁺	1.18		1.38		0.9536	-2.02	1.04	-2.71		
ThCl ₂ ²⁺					0.6758		0.76			
ThCl ₃ ⁺					1.4975		1.59			
ThCl ₄ ⁰					1.0731		1.16			
ThF ³⁺	8.44		8.65	1	7.8725	-6.73	7.96	-7.43		
ThF ₂ ²⁺	15.06		15.26	4.1	14.0884	-11.57	14.18	-12.27		
ThF ₃ ⁺			20.2	7.9	18.7357	-17.52	18.82	-18.21		
ThF ₄ ⁰			23.2		22.1515	-22.86	22.24	-17.42		

Table S1. contd.

Model/database combination	WHAM-d ^{a,b} , WHAM-m ^{a,b}		VMIN-d, GWB-m		CHESS-ch ^{c,d} , GWB-c ^{c,d}		CHESS-ct ^{c,d}		PHREEQC-l ^{c,d}	
Database name	default, modified		v3.0, thermo.minteq		chess.tdb, thermo.com.v8.r6+		ctdpv3_Dong.tdb		llnl	
Complex	log <i>K</i> , 25°C	Δ <i>H</i> , kJ/mol	log <i>K</i> , 25°C	Δ <i>H</i> , kJ/mol	log <i>K</i> , 25°C	Δ <i>H</i> , kJ/mol	log <i>K</i> , 25°C	Δ <i>H</i> , kJ/mol	log <i>K</i> , 25°C	Δ <i>H</i> , kJ/mol
ThNO ₃ ³⁺			1.75							
Th(HPO ₄) ₂ ⁰					47.3375	-56.36			47.3375	-43.0576
Th(HPO ₄) ₃ ²⁻					68.1548				68.1548	
ThH ₂ PO ₄ ³⁺					24.0279					
ThH ₃ PO ₄ ⁴⁺					23.4415					
ThHPO ₄ ²⁺					23.0017					
Th(OH) ₄ PO ₄ ³⁻							-27.22			
Th(H ₂ PO ₄) ₂ ²⁺					57.8506				47.8506	

^a Uranyl hydrolysis product formation data have been converted to refer to the generic reaction schema $n\text{UO}_2^{2+} + m\text{H}_2\text{O} \Leftrightarrow (\text{UO}_2)_m(\text{OH})_n^{2n-m}$. Conversion used the log *K*, 25°C and Δ*H* values in the same database.

^b Reaction enthalpy data have been converted from kcal/mol to kJ/mol using a factor of 1 kcal = 4.184 kJ.

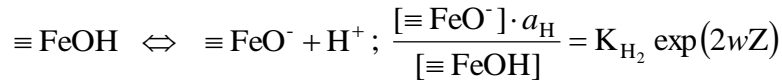
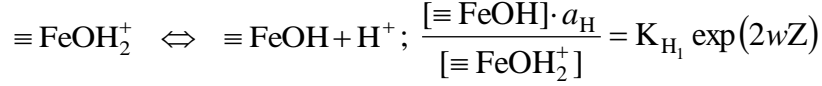
^c Uranyl carbonate and uranyl hydroxy-carbonate complex formation data have been converted to refer to CO₃²⁻, not HCO₃²⁻, as the reacting ligand. Conversion was done using the parameters for the reaction $\text{HCO}_3^- \Leftrightarrow \text{H}^+ + \text{CO}_3^{2-}$ present in the same database.

^d Data for formation of phosphate complexes converted to refer to PO₄³⁻, not HPO₄³⁻, as the reacting ligand. Conversion was done using the parameters for the reaction $\text{HPO}_4^{2-} \Leftrightarrow \text{H}^+ + \text{PO}_4^{3-}$ present in the same database.

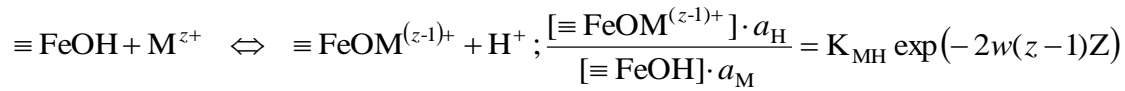
^e Value in database (0.9 kJ/mol) deemed incorrect so not used.

2. Modelling the binding of uranyl and thorium to hydrous ferric oxide in WHAM7

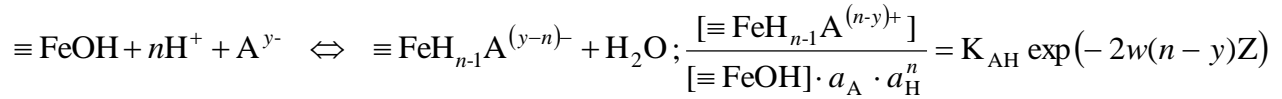
The model used for ion binding to HFO is that of Lofts and Tipping (1998), and unless otherwise stated, all model parameters used in this study are taken from that study. Proton binding to hydrous ferric oxide is considered using a two- K model:



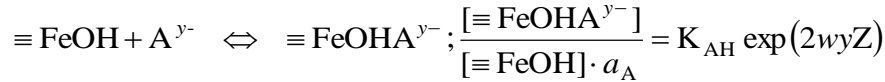
Binding of other cations is simulated by monodentate metal-proton exchange:



and binding of anions by monodentate ligand exchange:



or

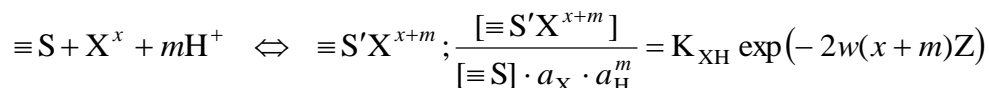


The K terms are intrinsic equilibrium constants, which describe the binding strength to an uncharged surface. The exponential terms quantify the electrostatic component of the binding strength, with the term Z being the surface charge of the oxide (eq g^{-1}) and w being an electrostatic term where

$$w = \frac{P_{\text{A}} \cdot \log_{10} I}{\text{SSA}}$$

the term I being the bulk solution ionic strength (mol dm^{-3}), SSA is the oxide surface area in $\text{m}^2 \text{g}^{-1}$ and P_{A} is a fitted electrostatic parameter.

The equilibrium expression for cation or anion binding can be generalised to:



where m is the proton stoichiometry of the reaction, which can take both positive and negative values ($m = -1$ for cations, $m \geq 0$ for anions), X is the binding ion, $\equiv S$ represents the neutral $\equiv FeOH$ surface species and $\equiv S'$ represents either $\equiv FeO$, $\equiv Fe$ or $\equiv FeOH$, depending upon the stoichiometry of proton interaction.

Heterogeneity of binding site strengths for cations is represented by having three surface binding site types, denoted 0, 1 and 2, with binding constants given by

$$pK_{MH,y} = pK_{MH} + y \cdot \Delta pK_{MH}$$

where $y = 0$ for 90.1% of the binding sites, $y = 1$ for 9.0% of the sites and $y = 2$ for 0.9% of the sites. The term ΔpK_{MH} is a heterogeneity term. In the work of Lofts and Tipping (1998), where only cation binding was considered, a values of -2 for ΔpK_{MH} was adopted for all cation binding to HFO. This provides a range of binding site affinities, with the less-abundant sites having higher affinities. Anion binding strength is assumed the same for all the site types, i.e. there is no heterogeneity of binding strength.

The surface reactions give rise to a charge on the oxide surface. Counterions may bind electrostatically by diffuse accumulation adjacent to the surface, in response to this charge. Counterion concentrations are calculated using the expression

$$\frac{c_D(i)}{c_S(i)} = K_{sel}(i)R^{|z(i)|}$$

where $c_S(i)$ and $c_D(i)$ are the concentrations of counterion i in the diffuse layer and bulk solution, respectively, $K_{sel}(i)$ is a selectivity coefficient for i and $z(i)$ is the charge on i . The parameter R is a ratio term which is optimised such that the charge due to counterion accumulation balances the surface charge. In this work, as in Lofts and Tipping (1998), all $K_{sel}(i)$ values were set to unity, i.e. counterion accumulation was a function of ionic charge only.

Optimisation of binding constants for CO_3^{2-} and uranyl species

Initial fitting suggested an important role for carbonate as a competing ion at high pH. Possible effects of carbonate are:

1. Competition as a solution ion for uranyl with HFO;
2. Ternary binding of uranyl-carbonate complexes;
3. Competitive binding of carbonate and uranyl to the HFO surface.

The first possibility is automatically accounted for by including carbonate in the speciation calculations, while the second may be accounted for by allowing uranyl-carbonate complexes to

adsorb to HFO. Accounting for the third possibility requires parameterisation of the model for carbonate binding to HFO in the absence of uranyl; thus we first parameterised the model for carbonate binding and fixed the derived parameters in the uranyl fitting efforts.

General considerations

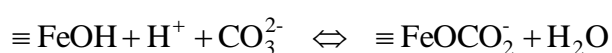
All model parameters apart from the CO_3^{2-} and uranyl binding constants were taken from Lofts and Tipping (1998) (Table S2).

Table S2. Basic physicochemical parameters for the HFO surface complexation model. All values are from Lofts and Tipping (1998).

Parameter	Units	Value
Bulk density	kg m^{-3}	3.57×10^6
pK_{H1}	–	6.26
pK_{H2}	–	9.66
Site density	mol m^{-2}	8.33×10^{-6}
SSA	$\text{m}^2 \text{g}^{-1}$	600
P_A	–	-1.46×10^6
$\Delta\text{pK}_{\text{MH}}$	–	-2

Optimisation of CO_3^{2-} binding

Parameters for carbonate binding to HFO were obtained by fitting to the data of Zachara et al. (1987), which comprised two pH adsorption edges with HFO concentrations of 0.78 and 7.8 g dm^{-3} respectively and total carbonate concentration fixed to $4.6 \times 10^{-6} \text{ mol dm}^{-3}$. The model fits are shown in Figure 1. A single surface reaction was used:



Binding site heterogeneity was not invoked for anion binding, following Dzombak and Morel (1990), so $\Delta\text{pK}_{\text{XH}}$ was set to zero. An optimised pK_{AH} of -11.85 was computed. Addition of further binding reactions did not improve the fit. The model fit is shown in Figure S1.

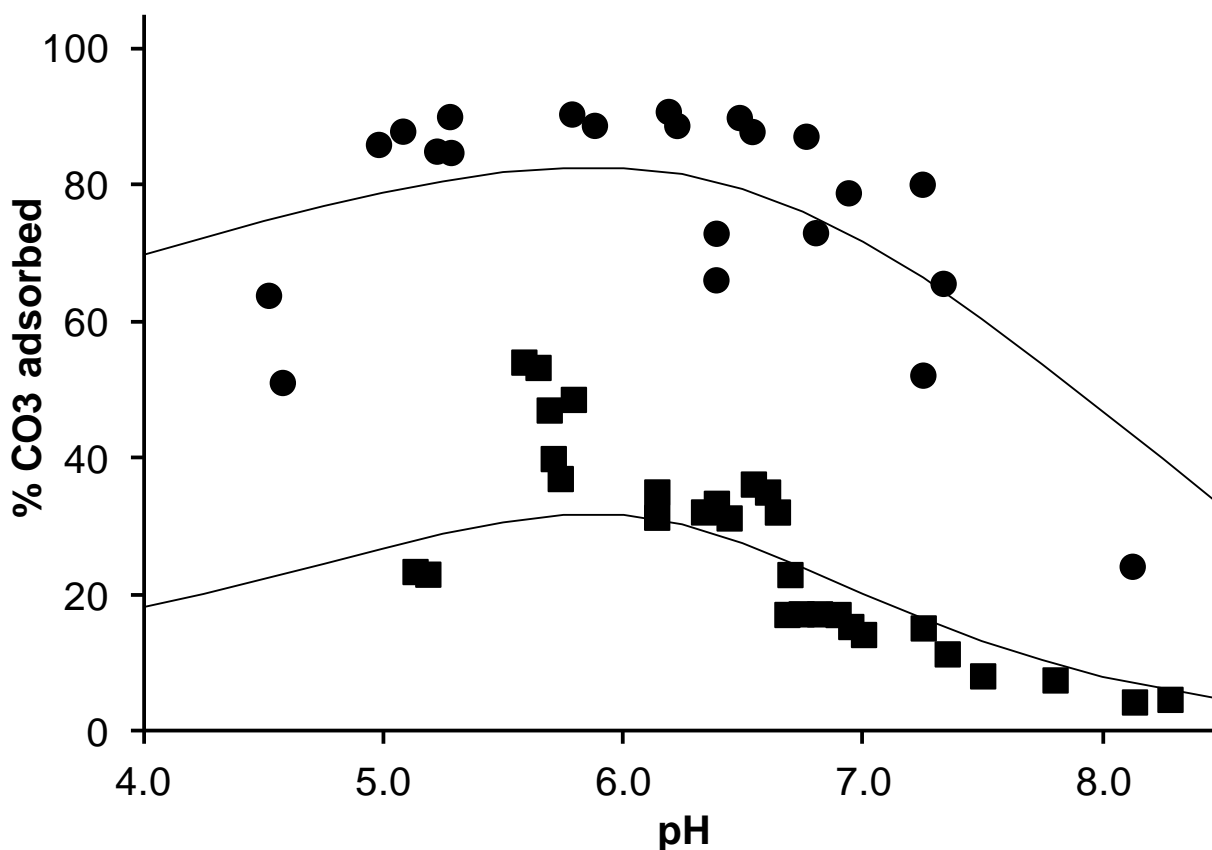


Figure S1. Model fits to the carbonate–HFO binding data of Zachara et al. (1987). Ionic strength = 0.1 mol dm^{-3} , total $\text{CO}_3 = 4.6 \times 10^{-6} \text{ mol dm}^{-3}$. HFO = 0.78 g dm^{-3} (circles), 7.8 g dm^{-3} (squares).

Optimisation of uranyl binding

Existing literature datasets on uranyl binding to HFO were collated from the literature (Table S3). A single parameter fit was made to all datasets. Where only % UO_2 adsorption data were available, rather than direct measurements of dissolved uranyl, points representing less than 20% or greater than 80% adsorption were removed, to avoid errors in deriving dissolved uranyl concentrations. The total number of data points found was 289, of which 165 points were suitable for fitting.

Fitting was done by minimising the sum of squares error in the log dissolved uranyl concentrations. Following Lofts and Tipping (1998), we initially postulated that the binding species comprised the uranyl free ion (UO_2^{2+}) and its first hydrolysis product (UO_2OH^+). Initial fitting suggested a need to include additional carbonate binding species, e.g. UO_2CO_3^0 , as has been done by other authors (e.g. Waite et al., 1994, Mahoney et al., 2009). This produced an optimised set of binding reactions and constants:





The RMSE in log dissolved uranyl was 0.34.

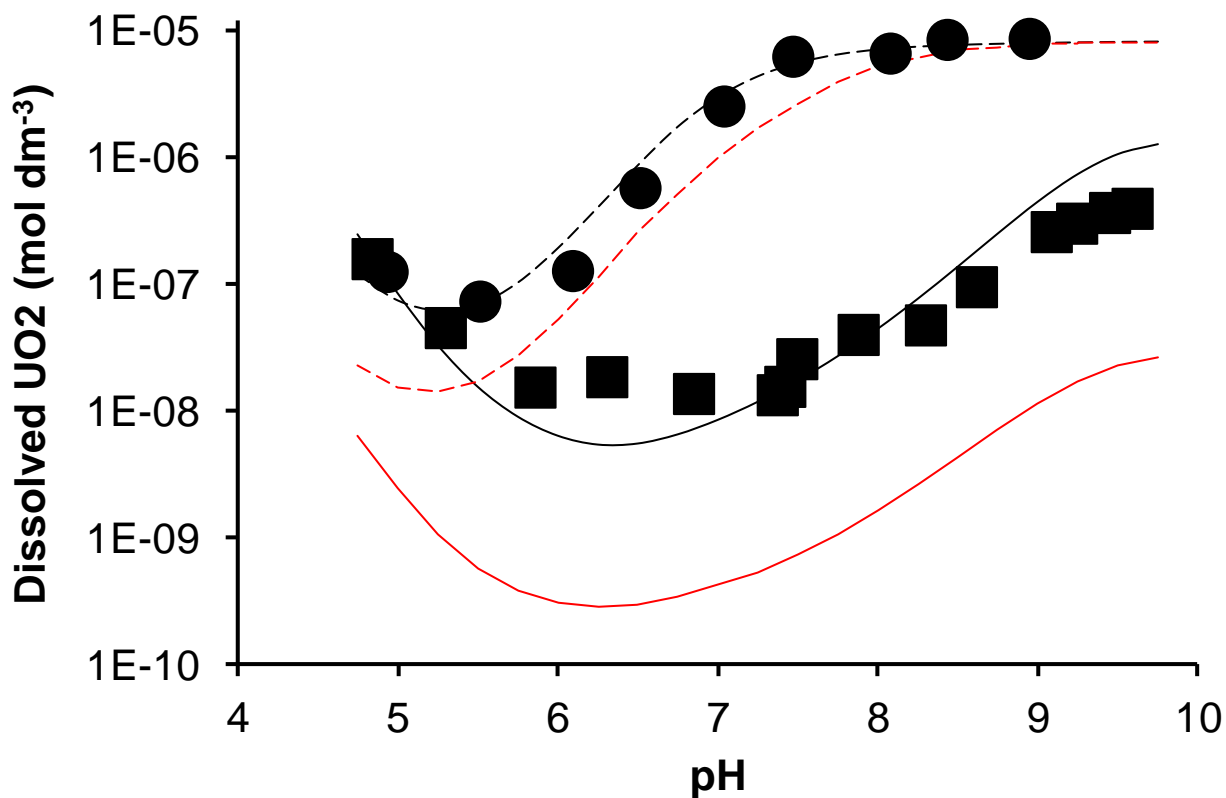


Figure S2 and Figure S3 show example model predictions, including data points not used for fitting, and for comparison predictions of uranyl binding to HFO predicted using the binding constants estimated by the linear free energy relationship of Lofts and Tipping (1998), as used in the WHAM-d predictions.

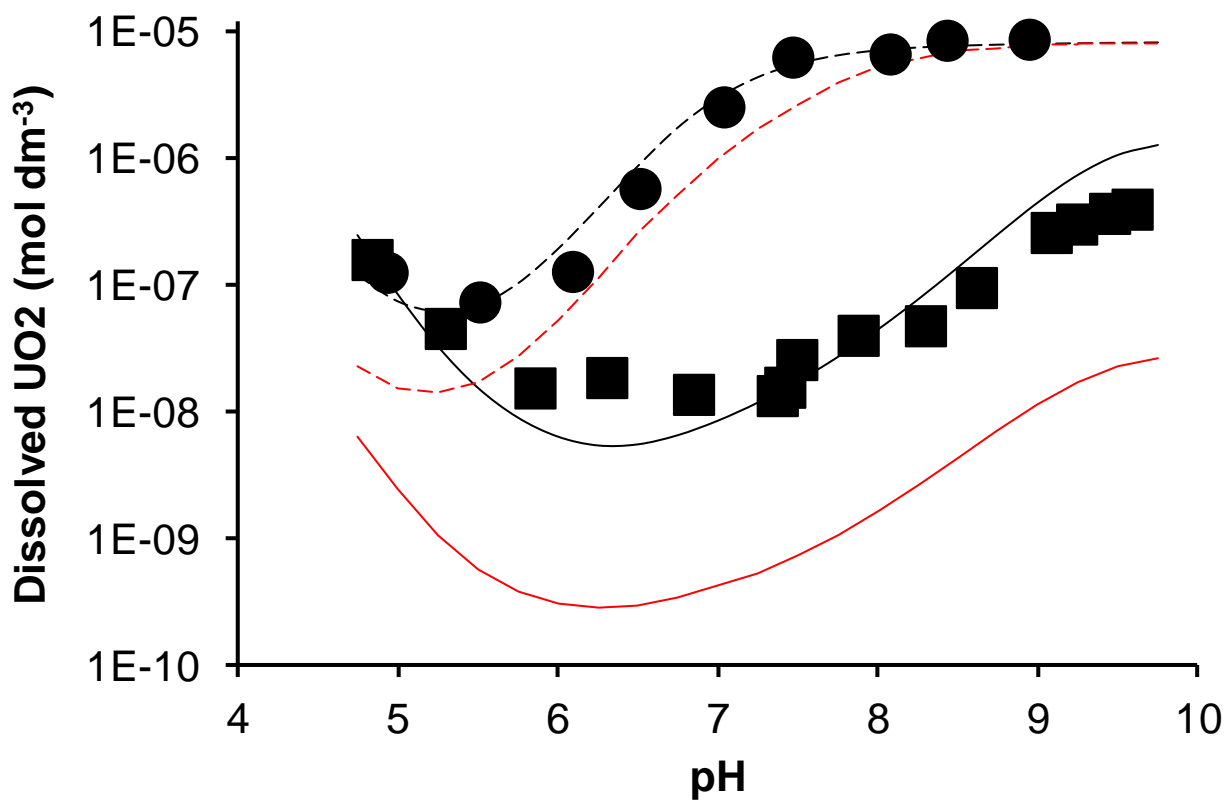


Figure S2. Model fit to datasets FeUO₂-3a (squares, solid lines) and FeUO₂-3b (circles, dashed lines). Points are the observed variation in dissolved uranyl with pH (see Table S3 for experimental conditions). The black line is the universal model fit. The red lines are predictions obtained using binding constants estimated from the linear free energy relationship of Lofts and Tipping (1998).

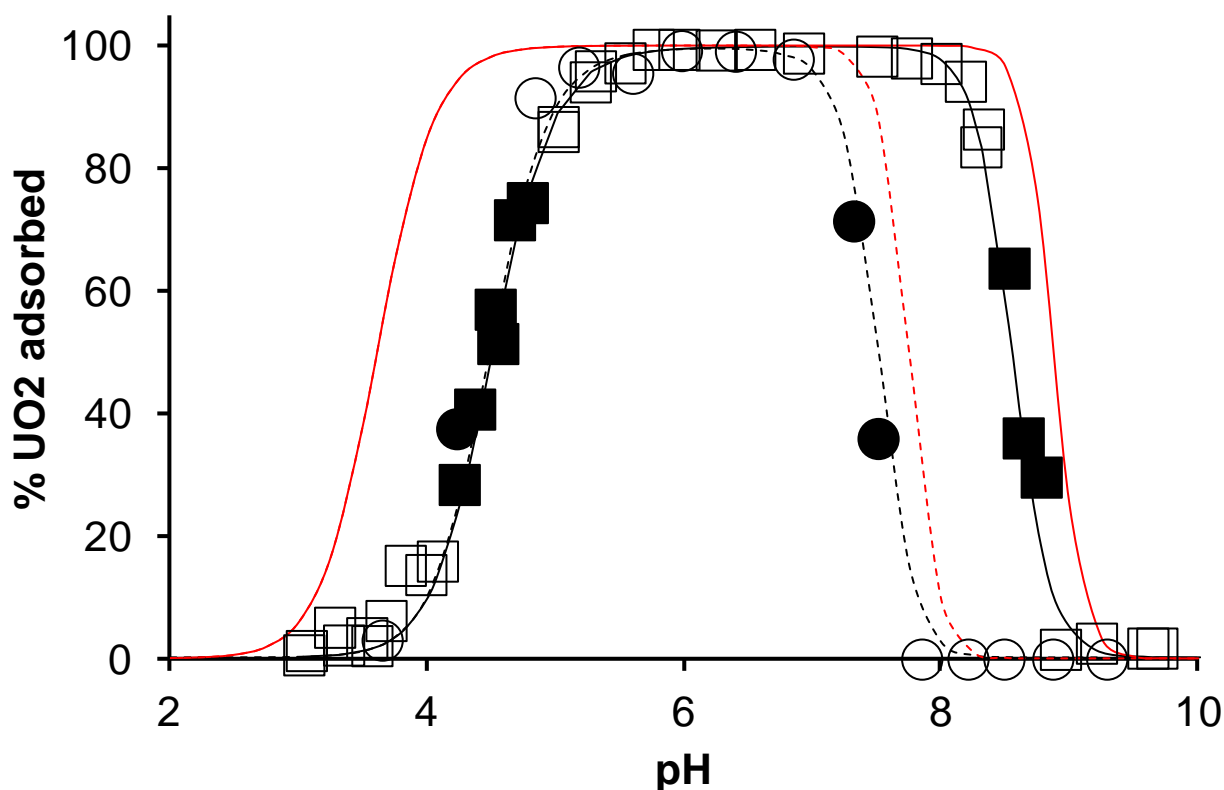


Figure S3. Model fit to datasets FeUO₂-2g (squares, solid lines) and FeUO₂-2j (circles, dashed lines). See Table S1 for experimental conditions. Closed symbols are those data points used in the universal fitting, open symbols are data points not used in fitting. Black lines are model predictions using the universally-fitted binding constants, red lines are predictions using the binding constants derived from the linear free energy relationship of Lofts and Tipping (1998).

Optimisation of thorium binding

Thorium binding was optimised using the data of Rojo et al. (2009), who presented three pH adsorption envelopes for Th on HFO in the pH range 1.5–4.5. Three concentrations of thorium – 0.95 μM, 1.1 μM and 1.7 μM – were used, and an HFO concentrations HFO of 10 g dm⁻³. The background electrolyte was NaClO₄ and the ionic strength was 0.01M when the thorium concentration was 0.95 μM or 1.7 μM, and 0.1M when the thorium concentration was 1.1 μM. The experiments were done open to the atmosphere, A total of 14 points were suitable for fitting.

Prediction of Th⁴⁺/ThOH³⁺ binding was underestimated using the default pK_{MH} value of -2.3 computed by Lofts and Tipping (1998). Optimisation, keeping the pK_{MH} value for both Th⁴⁺ and ThOH³⁺ equal, produced a value of -5.12. The data are presented in Figure S5, along with default and optimised model lines.

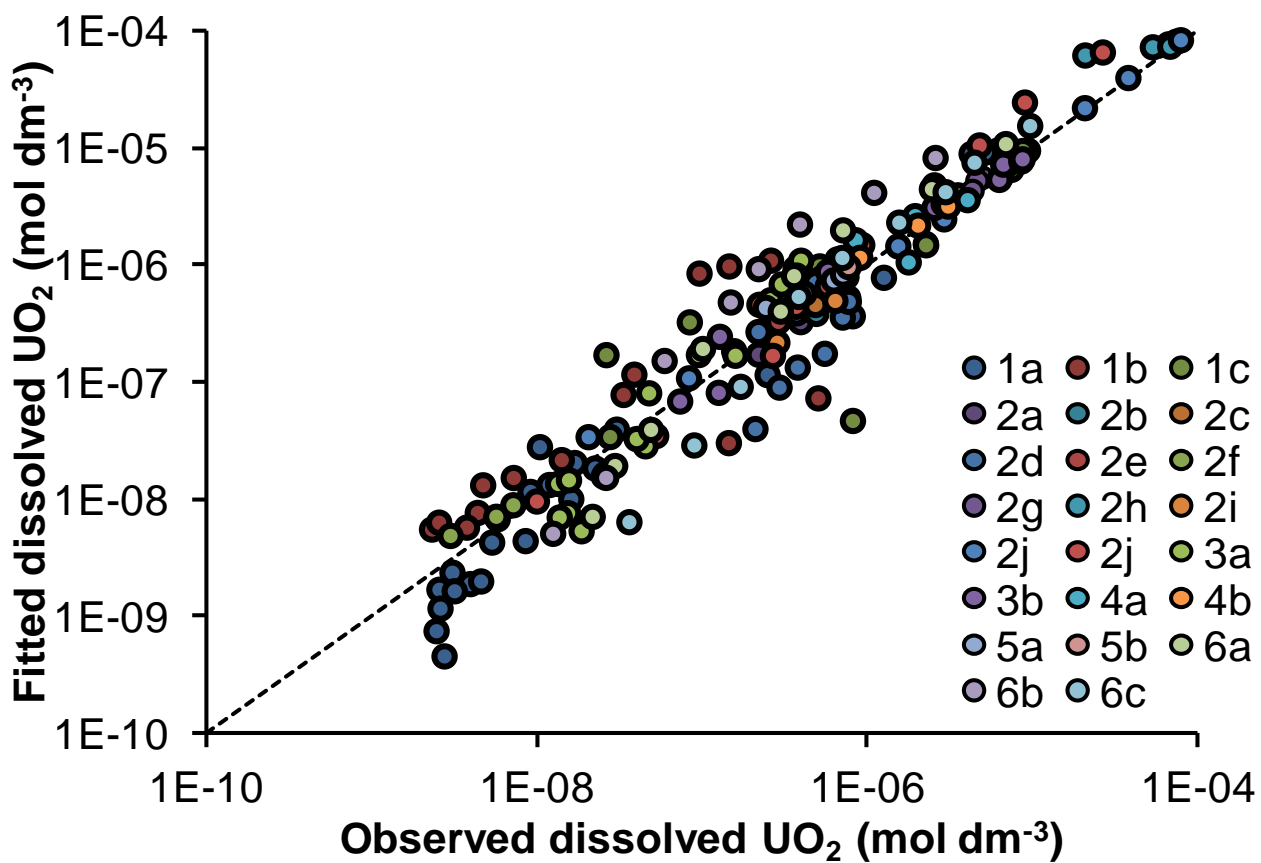


Figure S4. Modelled dissolved UO_2 calculated by fitting, plotted against observed dissolved UO_2 for all data points ($n = 169$) used in fitting HFO binding constants.

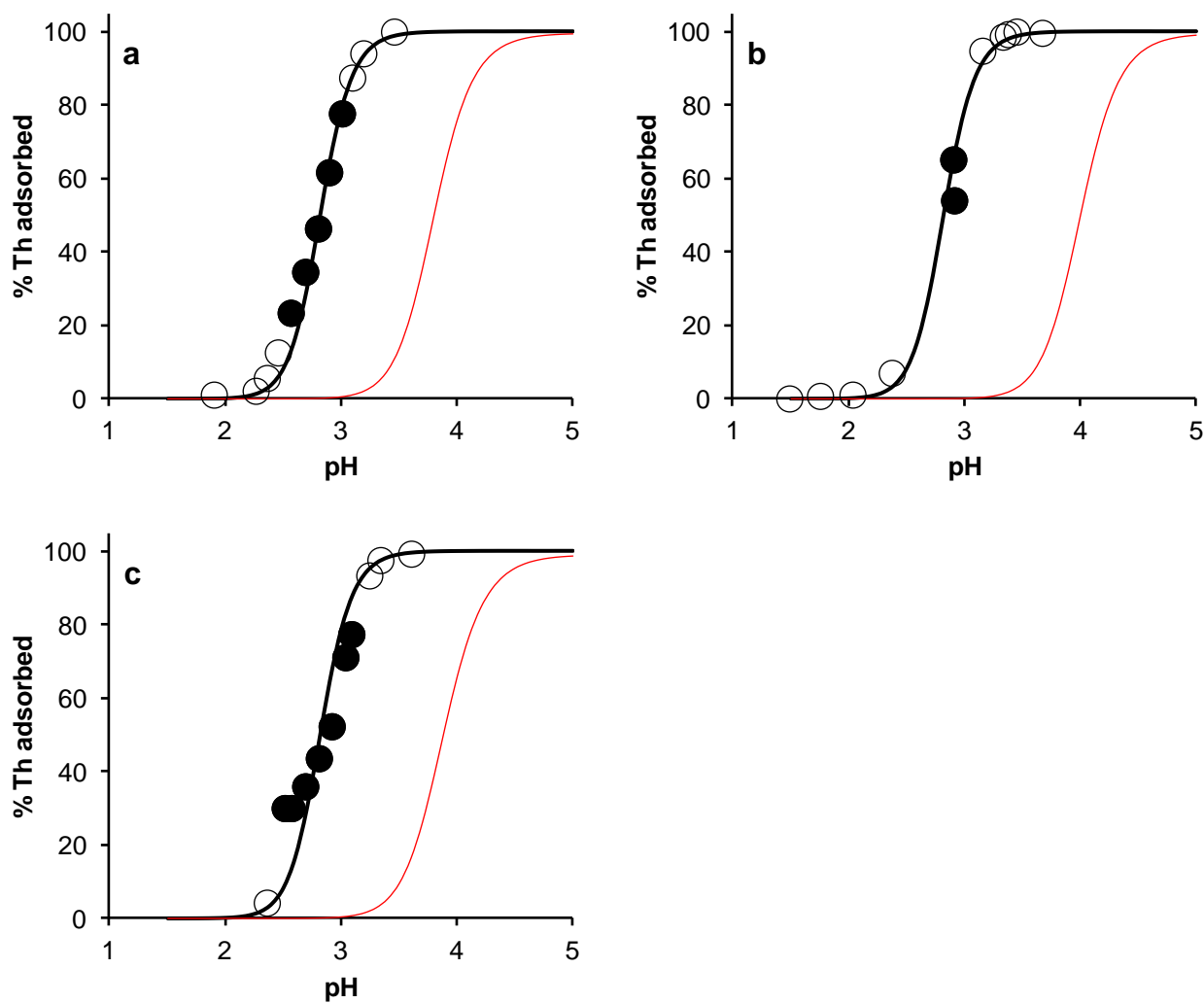


Figure S5. Model descriptions of the pH adsorption envelopes of Rojo et al. (2009), using default constants (red lines) and fitted constants (black lines). Solid points are those used in fitting, open points were not used in fitting. a: 0.95 μM Th, $I = 0.01\text{M}$ NaClO_4 ; b: 1.1 μM Th, $I = 0.1\text{M}$ NaClO_4 ; c: 1.7 μM Th, $I = 0.01\text{M}$ NaClO_4 . The concentration of HFO was 10 g dm^{-3} throughout.

Table S3. Datasets used for fitting of UO₂ binding to HFO.

Reference	Experiment type	<i>n</i> total	<i>n</i> used for fitting	Total UO ₂ mol dm ⁻³	Total HFO g dm ⁻³	Ionic strength mol dm ⁻³	pH	Carbonate system	Reference
FeUO ₂ -1a	Adsorption edge	28	28	10 ⁻⁵	1	0.1	3.3–9.6	T _{CO3} = 0	Hsi & Langmuir 1985
FeUO ₂ -1b	Adsorption edge	15	15	10 ⁻⁵	1	0.1	5.0–9.8	T _{CO3} = 10 ⁻³ mol dm ⁻³	Hsi & Langmuir 1985
FeUO ₂ -1c	Adsorption edge	12	12	10 ⁻⁵	1	0.1	3.2–9.7	T _{CO3} = 10 ⁻² mol dm ⁻³	Hsi & Langmuir 1985
FeUO ₂ -2a	Adsorption edge	7	4	10 ⁻⁶	0.09	0.004	3.6–5.2	pCO ₂ = 10 ^{-3.5} atm	Waite et al. 1994; Payne, 1999
FeUO ₂ -2b	Adsorption edge	18	6	10 ⁻⁶	0.09	0.02	3.5–9.2	pCO ₂ = 10 ^{-3.5} atm	Waite et al. 1994; Payne, 1999
FeUO ₂ -2c	Adsorption edge	40	9	10 ⁻⁶	0.09	0.1	3.5–9.7	pCO ₂ = 10 ^{-3.5} atm	Waite et al. 1994; Payne, 1999
FeUO ₂ -2d	Adsorption edge	18	9	10 ⁻⁶	0.09	0.5	3.6–9.1	pCO ₂ = 10 ^{-3.5} atm	Waite et al. 1994; Payne, 1999
FeUO ₂ -2e	Adsorption edge	20	4	10 ⁻⁶	1.8	0.1	3.6–9.3	pCO ₂ = 10 ^{-3.5} atm	Waite et al. 1994; Payne, 1999
FeUO ₂ -2f	Adsorption edge	5	3	10 ⁻⁸	0.09	0.1	4.0–5.1	pCO ₂ = 10 ^{-3.5} atm	Waite et al. 1994; Payne, 1999
FeUO ₂ -2g	Adsorption edge	18	6	10 ⁻⁵	0.09	0.1	3.9–6.7	pCO ₂ = 10 ^{-3.5} atm	Waite et al. 1994; Payne, 1999
FeUO ₂ -2h	Adsorption edge	17	5	10 ⁻⁴	0.09	0.1	3.9–8.7	pCO ₂ = 10 ^{-3.5} atm	Waite et al. 1994; Payne, 1999
FeUO ₂ -2i	Adsorption edge	15	3	10 ⁻⁶	0.09	0.1	3.6–9.3	pCO ₂ = 10 ⁻² atm	Waite et al. 1994; Payne, 1999
FeUO ₂ -2j	pH isotherm	11	11	10 ^{-7.02} –10 ^{-3.53}	0.09	0.02	4.5	pCO ₂ = 10 ^{-3.5} atm	Payne, 1999
FeUO ₂ -2k	pH isotherm	13	13	10 ^{-6.52} –10 ^{-3.02}	0.09	0.02	5.25	pCO ₂ = 10 ^{-3.5} atm	Payne, 1999
FeUO ₂ -3a	Adsorption edge	15	15	10 ⁻⁵	1	0.1	4.8–9.6	T _{CO3} = 10 ⁻³ mol dm ⁻³	Morrison et al. 1995
FeUO ₂ -3b	Adsorption edge	9	9	10 ^{-5.08}	0.52	0.1	4.9–9.0	T _{CO3} = 0.0195 mol dm ⁻³	Morrison et al. 1995
FeUO ₂ -4a	Adsorption edge	16	5	10 ^{-5.38}	0.128	0.1	3.4–9.6	T _{CO3} = 10 ⁻² mol dm ⁻³	Wazne et al. 2003
FeUO ₂ -4b	Adsorption edge	17	3	10 ^{-5.38}	0.128	0.1	3.0–9.9	T _{CO3} = 10 ⁻⁵ mol dm ⁻³	Wazne et al. 2003
FeUO ₂ -5a	Adsorption edge	9	4	10 ⁻⁶	0.009	0.0109	6.9–8.5	pCO ₂ = 10 ^{-3.37} atm	Fox et al. 2006
FeUO ₂ -5b	Adsorption edge	7	2	10 ⁻⁶	0.9	0.005	6.5–8.2	pCO ₂ = 10 ^{-1.7} atm	Fox et al. 2006
FeUO ₂ -6a	pH isotherm	9	9	10 ^{-6.80} –10 ^{-4.84}	0.009	0.001	5.9	pCO ₂ = 10 ^{-3.5} atm	Jang et al. 2007
FeUO ₂ -6b	pH isotherm	8	8	10 ^{-6.55} –10 ^{-4.95}	0.009	0.001	6.8	pCO ₂ = 10 ^{-3.5} atm	Jang et al. 2007
FeUO ₂ -6c	pH isotherm	9	9	10 ^{-6.75} –10 ^{-4.76}	0.009	0.001	7.8	pCO ₂ = 10 ^{-3.5} atm	Jang et al. 2007

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