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1 **Estimation of Model VII humic binding constants for Pd²⁺, Sn²⁺, U⁴⁺, NpO₂²⁺, Pu⁴⁺ and**
2 **PuO₂²⁺**

3

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14

15 **Environmental impact statement**

16 Understanding of the interactions between radionuclide cations and humic substances is
17 important in the performance assessment of radioactive waste geological disposal options.

18 Ultimately, any potential transport associated with humic substances (humic and fulvic acids)
19 will be directly related to the capacity to bind a given radionuclide cation. Here we present
20 the determination of several fulvic and humic acid binding constants for the chemical
21 speciation model WHAM/Model VII. Modelling can be used to predict how partitioning may
22 occur under a range of differing conditions and can help inform priorities for laboratory and
23 field studies.

24

25 **Summary**

26 Using previously established procedures that utilise linear free energy relationships, we
27 estimated binding constants for the Windermere Humic Aqueous Model VII (WHAM/Model
28 VII) for several radionuclide cations (Pd²⁺, Sn²⁺, U⁴⁺, NpO₂²⁺, Pu⁴⁺ and PuO₂²⁺). This extends

29 the number of cations that can be calculated with the model above the 40 included in the
30 original Model VII work. When combined with equilibrium constants for inorganic species this
31 allows the calculation of equilibrium distributions of chemical species under a wide range of
32 conditions.

33

34 **Introduction**

35 Thermodynamic data are important for the modelling of potential chemical processes in both
36 engineered parts of nuclear waste repository systems (the 'near-field') and in ground water
37 and surface water systems that may affect transport to the biosphere (the 'far-field').¹

38 Significant efforts have been made in the collation of and assessment of thermodynamic
39 data for the solubility and inorganic speciation of radionuclides, in particular the Nuclear
40 Energy Agency's Thermodynamic Data Base Project², which is now in its third decade.
41 Whilst data for simple organic ligands have been collated, there has largely been an
42 absence of the assessment of binding data for natural organic matter (humic and fulvic
43 acids). There remains a large uncertainty associated with the importance of colloidal species
44 for repository safety cases.³ Overestimation of the effect of humic substances could lead to a
45 safety case that necessitates over-engineering of a repository. In order to make more
46 reliable safety predictions we need to improve confidence in model predictions, and this is
47 not achieved by simply over-estimating effects. Furthermore, overestimates that may be
48 conservative for near-field transport may have the opposite influence when considering
49 bioavailability and toxicology issues that may affect the far-field.

50

51 The Windermere Humic Aqueous Model (WHAM⁴) is a widely used chemical speciation
52 code used in geochemical and ecotoxicological research and in regulation. The sub-model
53 dealing with natural organic matter binding has recently been updated (WHAM/Model VII)⁵ to
54 include the most up to date information on humic and fulvic acid binding of protons and
55 metal cations (40 cationic species). This also includes improved prediction of cation binding
56 at higher pH due to increased numbers of available data and stricter data selection criteria

57 than previously applied. Table 1 identifies those radionuclides present in significant
58 quantities in the UK waste inventory and with half-lives longer than 10^5 years, which may be
59 relevant to radiological performance assessments for long-term geological disposal.
60 WHAM/Model VII includes humic and fulvic acid binding data for some of these
61 radionuclides such as Be^{2+} , Ca^{2+} , Th^{4+} and UO_2^{2+} . In this work we have used previously
62 described methods,⁷ involving linear free energy relationships, to estimate WHAM/Model VII
63 binding constants, for the following radionuclide cations, Pd^{2+} , Sn^{2+} , U^{4+} , NpO_2^{2+} , Pu^{4+} and
64 PuO_2^{2+} . Previous models used relationships between organic binding parameters and the
65 equilibrium constants for the first hydrolysis product (NICA-Donnan⁸) or for complexation
66 with lactic acid (Model VI⁹) in the calculation/estimation of humic and fulvic binding
67 constants. However, because of differences between models (i.e. NICA-Donnan, Models V,
68 VI and VII), the binding parameters need to be calculated for each individual model.
69 Furthermore, because the approach of Carbonaro and Di Toro⁷ involves the use of a range
70 of simple ligands rather than a single ligand, this should give an improvement over using
71 single values and ligands.

72

73 **Theory/methods**

74 The Windermere Humic Aqueous Model combines the WHAM inorganic speciation program⁴
75 with Humic Ion Binding Model VII⁵. The model is described in more detail in Tipping et al.⁵
76 The combination of the organic and inorganic codes is referred to here as WHAM/Model VII.
77 The model uses a structured formulation of discrete, chemically-plausible, humic binding
78 sites for protons, in order to allow the creation of regular arrays of bidentate and tridentate
79 binding sites for metals. Metal ion binding at the type A (carboxylic acid type groups) and B
80 (weaker acids, such as phenolic acids) sites is described with average intrinsic equilibrium
81 constants (K_{MA} and K_{MB} , which are interrelated). High values of K_{MA} mean that the metal ion
82 is strongly bound at the high abundance “weak” sites. A low density of strong binding sites
83 are defined and are postulated to be associated with nitrogen groups (represented by ΔLK_2)
84 in the model (first proposed in Model VI⁹). Experimental evidence for the association of

85 cations with strong binding nitrogen sites has been reviewed by Tipping.¹⁰ High values of
86 ΔLK_2 mean that the metal ion favours the low abundance “strong” sites. If ΔLK_2 is small, the
87 strong sites are not favoured, and binding is predominantly due to binding at oxygen
88 containing sites.

89

90 *Estimating binding constants for oxygen containing sites*

91 Irving and Rossotti¹¹ observed that the linear free energy relationship (LFER) between
92 thermodynamic constants for metal-ligand ($\log K_{ML}$) and proton-ligand ($\log K_{HL}$) complexation
93 reactions could be defined by Equation 1:

$$94 \log K_{ML} = \alpha \log K_{HL} + \beta \quad (1)$$

95 where α is the slope, and β the intercept. Carbonaro and Di Toro⁷ referred to these
96 parameters as the Irving–Rossotti slope and intercept, respectively. It was subsequently
97 shown¹² that in some cases plots of $\log K_{ML}$ versus $\log K_{HL}$ for complexes with monodentate
98 ligands containing negatively-charged oxygen donor atoms (carboxylic acids, substituted-
99 phenols, and hydroxide ion) are linear with an intercept nearly equal to zero ($\beta \approx 0$).
100 Consequently, the magnitude of the formation constant for metal–ligand complexation
101 increases linearly with the basicity of the negatively-charged oxygen donor. The magnitude
102 of α_O indicates the relative preference of metal binding to negatively-charged oxygen donor
103 atoms.⁸ Carbonaro and Di Toro⁷ showed that α_O gave good correlations to the $\log K_{MA}$
104 binding parameters for humic acid (HA) and fulvic acid (FA) in WHAM V. These relationships
105 were recalculated by Tipping for WHAM/Model VII⁵ (Equations 2 and 3) by plotting fitted \log
106 K_{MA} for different metals (individual datasets) against α_O , the Irving–Rossotti slope.

$$107 \text{HA } \log K_{MA} = 3.51\alpha_O + 0.75 \quad (r^2 = 0.68) \quad (2)$$

$$108 \text{FA } \log K_{MA} = 3.81\alpha_O + 0.37 \quad (r^2 = 0.80) \quad (3)$$

109

110 In order to extend the WHAM database for long-lived radionuclide cations, we have compiled
111 data to enable the calculation of α_O and thus, the $\log K_{MA}$ values for several radionuclide

112 cations. Data selection was consistent with the work of Carbonaro and Di Toro,⁷ i.e., the
 113 selected ligands were the same; thermodynamic constants were taken from the NIST Critical
 114 Database,¹³ where proton-ligand (K_{HL}) and metal-ligand (K_{ML}) complexation reactions are
 115 described according to $K_{HL} = \{HL\}/(\{H^+\}\{L^-\})$ and $K_{ML} = \{ML^{z-1}\}/(\{M^{z+}\}\{L^-\})$; data up to ionic
 116 strengths of 1 mol L⁻¹ were used; values were corrected to an ionic strength of $I = 0.0$ mol L⁻¹
 117 using the Davies Equation¹⁴ with $b = 0.3$; and constants with data spanning $\pm 5^\circ\text{C}$ from 25°C
 118 were used without temperature corrections. In addition to the NIST data, values for metal ion
 119 bonding to ethanoic acid (for Sn²⁺, U⁴⁺ and Pu⁴⁺) were estimated from the Drago equation
 120 (Equation 4) and associated parameters, as described in Martell and Hancock¹² and
 121 references therein.

$$122 \quad \log K_1 = E_A^{\text{aq}} \cdot E_B^{\text{aq}} + C_A^{\text{aq}} \cdot C_B^{\text{aq}} + D_A \cdot D_B \quad (4)$$

123 The parameters are defined as the tendency of a Lewis acid A or Lewis base B to undergo
 124 either electrostatic (E_A^{aq} and E_B^{aq}) or covalent (C_A^{aq} and C_B^{aq}) bonding. The parameters D_A
 125 and D_B correct for steric hindrance to solvation of the Lewis acid or base on complex
 126 formation, however, these terms have zero values for the ligands considered in this present
 127 work. Table 2 lists those values for species referred to in this work. The predictions are
 128 closely correlated with estimates, with an r squared of 0.85, based on data for 29 different
 129 metal complexes with ethanoate (figure shown in the supporting information).

130

131 *Constants for strong binding sites*

132 The value for the affinity of cations to strong binding sites (ΔLK_2) is defined in WHAM/Model
 133 VII using a direct relationship with the equilibrium constant for complex formation with NH₃
 134 (Equation 5),

$$135 \quad \Delta LK_2 = 0.58 K_{\text{NH}_3} \quad (5)$$

136 Thus, only a single value is required for each cation (this approach is based on data fitting
 137 and the philosophy is explained in the previous work of Tipping.^{9,10}). These data are directly
 138 available from the NIST database for Pd, however, estimation is required in the cases of

139 Sn^{2+} , U^{4+} , NpO_2^{2+} , Pu^{4+} , and PuO_2^{2+} . Martell and Hancock¹² established that there is a LFER
140 for NH_3 complexation compared to pairs of ligands where one ligand has a saturated
141 nitrogen donor and the other has a saturated oxygen (Equation 6; where m is the slope, and
142 c the intercept).

$$143 \quad K_{\text{NH}_3} = m (\log K_1^{\text{IDA}} - \log K_1^{\text{ODA}}) + c \quad (6)$$

144 Thus estimation of NH_3 constants can be obtained for elements where complexation
145 constant data are available for both oxydiacetic acid (ODA) and iminodiacetic acid (IDA).
146 This procedure was used to determine constants for NpO_2^{2+} and PuO_2^{2+} (see supporting
147 information for a figure showing the relationship). Values for other cations were calculated
148 using Equation 4 and the variables cited in Martell and Hancock.¹²

149

150 **Results and discussion**

151 Figure 1 shows the Irving-Rossotti slopes for Pd^{2+} , Sn^{2+} , U^{4+} , NpO_2^{2+} , Pu^{4+} and PuO_2^{2+} . The r
152 squared values and binding constants calculated from α_0 are shown in Table 3. Data in
153 parentheses are those obtained from only a two point plot. Other species, such as Zr^{4+} , Sn^{4+} ,
154 Np^{4+} , Np^{3+} and Pu^{3+} were included in the data search, but were absent or did not fulfil the
155 data selection criteria. Monovalent cations (e.g., Cs^+ , NpO_2^+ and PuO_2^+) were not included
156 as the model only considers metal species that have appreciably greater affinities for humic
157 functional groups. Monovalent cations are assumed to bind only non-specifically as
158 counterions.^{4,15} Values for the strong binding parameters and the source of the K_{NH_3} constant
159 are shown in Table 3. The variables calculated for Equation 6 were $m = 0.660$ and $c = -$
160 0.058 , with an r squared of 0.934 (see supporting information for the figure used to derive
161 these values).

162

163 It may be expected that similar actinide species may have analogous binding parameters.
164 Model VII $\log K_{\text{MA}}$ values for Th^{4+} are 3.58 and 3.34 for humic and fulvic acid respectively,
165 and ΔLK_2 has a value of 0.23 . Values for U^{4+} and Pu^{4+} (Table 3) show higher $\log K_{\text{MA}}$ values

166 and much higher ΔLK_2 s. However, the ΔLK_2 disparities are predictable when the differences
167 in variables for Equation 4 are considered (Table 2). Th^{4+} has a greater electrostatic
168 contribution (E_A) and lower covalent contribution (C_A) than U^{4+} and Pu^{4+} (which have similar
169 values). As the electrostatic term for ammonia complexation is negative, the result is a lower
170 strong binding constant for Th^{4+} . Thus, whereas U^{4+} and Pu^{4+} may be considered analogous,
171 the data suggests that Th^{4+} should be considered in isolation. Model VII $\log K_{MA}$ values for
172 UO_2^{2+} are 2.61 and 2.38 for humic and fulvic acid respectively, and ΔLK_2 has a value of 1.16.
173 Whilst the values derived here for NpO_2^{2+} and PuO_2^{2+} are slightly higher than those for
174 UO_2^{2+} , they are within the predicted margin of error for binding constants included in the
175 uncertainty analysis within Model VII (± 0.3).¹⁶ This suggests that these divalent oxyocations
176 may be analogous in their binding behaviour. It is worth noting here that WHAM/Model VII
177 includes options to perform uncertainty analysis using the Monte Carlo statistical method.¹⁶

178

179 To model aqueous speciation fully in WHAM, a comprehensive dataset of important
180 inorganic equilibrium constants is required. To achieve this, we have compiled these data
181 using a pragmatic procedure extracting the latest available data¹⁷⁻¹⁹ for each radionuclide
182 cation. These data are tabulated in the supporting information including a brief outline of the
183 procedure used for their compilation.

184

185 *Modelling example*

186 Figure 2 shows the results of speciation calculations for a simple solution containing NaCl
187 ($\sim 0.2 \text{ mol L}^{-1}$), PuO_2^{2+} ($10^{-12} \text{ mol L}^{-1}$) and fulvic acid (1 mg L^{-1}) in both the absence and
188 presence of carbonate ($\Sigma[\text{CO}_3^{2-}]$; $10^{-3} \text{ mol L}^{-1}$). Predictions show that in the absence of
189 carbonates, binding to fulvic acid dominates up to a pH of ~ 10 , when the tri-hydroxyl species
190 becomes dominant. In the presence of carbonates, fulvic acid still dominates but the di-
191 carbonate complex is also present at a significant concentration. Above pH 10, the tri-

192 hydroxyl species becomes dominant over the carbonate and organic species. This illustrates
193 the capacity of the model to yield useful predictions under many different conditions.

194

195 **Conclusions**

196 Using previously established procedures we have estimated WHAM/Model VII binding
197 constants for Pd^{2+} , Sn^{2+} , U^{4+} , NpO_2^{2+} , Pu^{4+} and PuO_2^{2+} . When combined with constants for
198 inorganic species this allows the calculation of equilibrium distributions of chemical species
199 under a wide range of conditions. This has vastly improved the applicability of the WHAM
200 speciation model for radioactive isotope speciation and thus makes the model applicable to
201 radiological performance assessment calculations. Whilst efforts should be made to enable
202 determination of K_{MA} values from laboratory data, estimates based on sound chemical
203 principles provide a useful starting point to predicting behaviour of these cations in aqueous
204 solutions in the presence of humic substances and there is a pressing need to perform such
205 estimations. Models such as WHAM/Model VII allow comparison of different datasets for the
206 same cation using a consistent framework. Furthermore, these simple procedures allow
207 easy recalculation of constants should further data become available for these or other
208 radionuclide cations.

209

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214

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256
257

258 **Tables**

259 Table 1. Radionuclides with both half-lives greater than 10^5 years and with
 260 more than 0.1 TBq of activity in UK quantified waste streams. Half-lives,
 261 activity and equivalent quantities in terms of mass and molar quantity are
 262 shown.

Nuclide	Half life (My)	Activity (TBq) reported in 2010 UK inventory*	Equivalent as:	
			Kg	Moles (10^3)
^{10}Be	1.60×10^0	4.10×10^{-1}	0.50	0.050
^{36}Cl	3.02×10^{-1}	1.13×10^1	9.32	0.259
^{41}Ca	1.03×10^{-1}	3.72×10^0	1.19	0.029
^{93}Zr	1.53×10^0	7.30×10^2	7882	84.8
^{99}Tc	2.13×10^{-1}	2.98×10^3	4768	48.2
^{107}Pd	6.50×10^0	2.96×10^1	1562	14.6
^{126}Sn	1.00×10^{-1}	2.25×10^2	215	1.71
^{129}I	1.57×10^1	6.80×10^{-1}	104.5	0.810
^{135}Cs	2.30×10^0	1.97×10^2	4637	34.3
^{232}Th	1.41×10^4	2.30×10^{-1}	57093	246
^{233}U	1.59×10^{-1}	1.60×10^0	4.50	0.019
^{234}U	2.46×10^{-1}	1.71×10^1	74.5	0.319
^{235}U	7.04×10^2	5.51×10^{-1}	6917	29.4
^{236}U	2.34×10^1	1.51×10^0	631	2.67
^{238}U	4.47×10^3	1.70×10^1	1.37×10^6	5776
^{237}Np	2.14×10^0	9.80×10^1	3772	15.9
^{242}Pu	3.74×10^{-1}	6.41×10^0	44.0	0.182

263 * NDA/DECC⁶

264

265

266 Table 2. Drago equation parameters for those
 267 Lewis acids and bases referred to in this work
 268 (from reference 12). D_A and D_B values are not
 269 shown as the value for the two Lewis bases is
 270 zero.

	E_A or E_B	C_A or C_B
Lewis acid		
Sn^{2+}	5.65	0.700
Th^{4+}	8.44	0.771
U^{4+}	7.55	0.968
Pu^{4+}	7.90	0.950
Lewis base		
CH_3OO^-	0.00	4.760
NH_3	-1.08	12.34

271

272

273 Table 3. Linear Free Energy Relationship analysis for metal complexes of several long-lived
 274 radionuclides, including derived WHAM/Model VII $\log K_{MA}$ values for humic and fulvic acid, and strong
 275 binding constants plus the source of the NH_3 stability constant data.

Metal / species	n	Irving–Rossotti slope, α_O	r^2	HA $\log K_{MA}$	FA $\log K_{MA}$	ΔLK_2	Source of K_{NH_3} data
Pd^{2+}	4	0.860	0.929	3.77	3.65	5.57	NIST database
Sn^{2+}	2	(0.749)	-	3.38	3.22	1.47	Equation 4
U^{4+}	2	(0.952)	-	4.09	4.00	2.20	Equation 4
NpO_2^{2+}	5	0.635	0.988	2.98	2.79	1.33	Equation 6
Pu^{4+}	2	(0.948)	-	4.08	3.98	1.85	Equation 4
PuO_2^{2+}	4	0.580	0.994	2.79	2.58	1.32	Equation 6

276

277 **Figure captions**

278 Figure 1. Plots of $\log K_{ML}$ for metal complex formation versus the corresponding ligand \log

279 K_{HL} for a series of monodentate ligands containing negatively-charged oxygen donor atoms.

280 Solid lines represent results from linear regression with intercepts forced through zero.

281 Irving–Rossotti slopes for negatively-charged oxygen donor atoms, α_o , and the r squared,

282 are indicated on each plot. Circles represent data from the NIST database,¹³ squares

283 represent data for ethanoic acid calculated using the Drago equation (Equation 4; Table 2).

284

285 Figure 2. Example speciation calculations for a simple aqueous solution containing PuO_2^{2+}

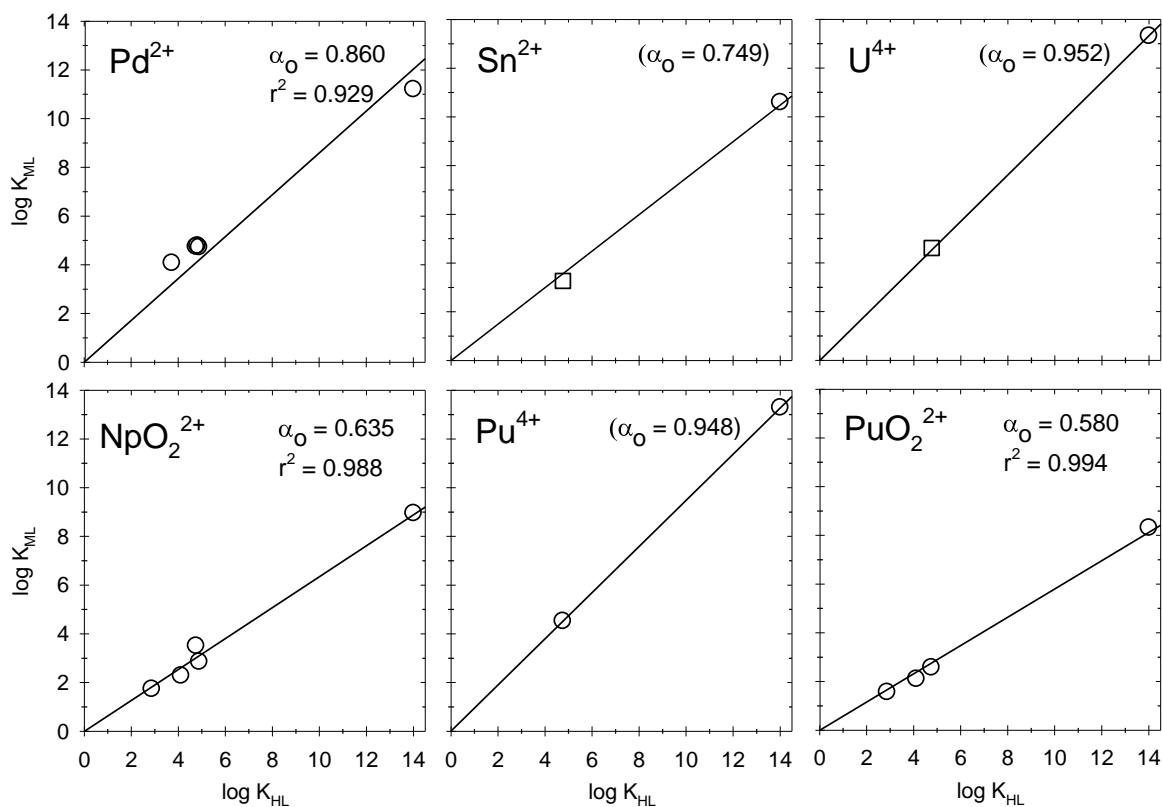
286 and fulvic acid, in both the absence (panel A) and presence (panel B) of carbonate. See text

287 for discussion.

288

289 **Figures**

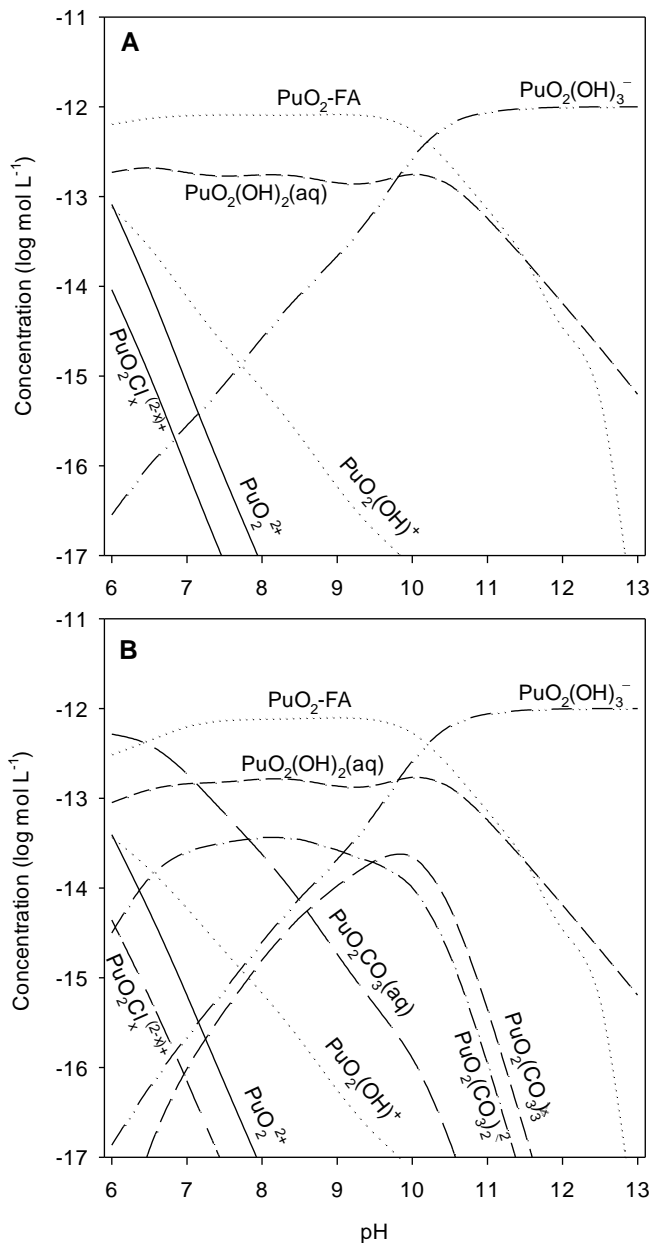
290 Figure 1.



291

292

293 Figure 2.



294