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Article (refereed)

1   **Estimation of Model VII humic binding constants for Pd^{2+}, Sn^{2+}, U^{4+}, NpO_2^{2+}, Pu^{4+} and**

2   **PuO_2^{2+}**

3

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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 (Pd^{2+}, Sn^{2+}, U^{4+}, NpO_2^{2+}, Pu^{4+} and PuO_2^{2+}). 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 Project[2], 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 (WHAM[4]) 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-Donnan[8]) or for complexation

66 with lactic acid (Model VI[9]) 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 Toro[7] 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 program[4]

75 with Humic Ion Binding Model VII[5]. 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 VI[9]). Experimental evidence for the association of

3

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 Rossotti[11] 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     $\log K_{ML} = \alpha \log K_{HL} + \beta$ (1)

95   where α is the slope, and β the intercept. Carbonaro and Di Toro[7] referred to these

96   parameters as the Irving–Rossotti slope and intercept, respectively. It was subsequently

97   shown[12] 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 Toro[7] 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 VII[5] (Equations 2 and 3) by plotting fitted log

106   K_{MA} for different metals (individual datasets) against α_O, the Irving–Rossotti slope.

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

108   FA log $K_{MA} = 3.81\alpha_O + 0.37$ ($r^2 = 0.80$)   (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 Equation[14] with b = 0.3; and constants with data spanning ±5°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 Sn^{2+}, U^{4+} and Pu^{4+}) were estimated from the Drago equation

120   (Equation 4) and associated parameters, as described in Martell and Hancock[12] and

121   references therein.

122     $$\log K_1 = E_A^{aq} \cdot E_B^{aq} + C_A^{aq} \cdot C_B^{aq} + D_A \cdot D_B \tag{4}$$

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 NH_3

134   (Equation 5),

135     $$\Delta LK_2 = 0.58\, K_{NH3} \tag{5}$$

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 Hancock[12] 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     $K_{NH3} = m\,(\log K_1^{IDA} - \log K_1^{ODA}) + c$ (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_{NH3} 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_{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_{MA} values

166   and much higher ΔLK_2s. 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 oxycations

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 data[17-19] 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   (~ 0.2 mol L^{-1}), PuO_2^{2+} (10^{-12} mol L^{-1}) and fulvic acid (1 mg L^{-1}) in both the absence and

188   presence of carbonate ($\Sigma[CO_3^{2-}]$; 10^{-3} 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

210   **Acknowledgements**

214

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256

257

Tables

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

* NDA/DECC[6]

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

Table 3. Linear Free Energy Relationship analysis for metal complexes of several long-lived radionuclides, including derived WHAM/Model VII log K_{MA} values for humic and fulvic acid, and strong 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_{NH3} 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

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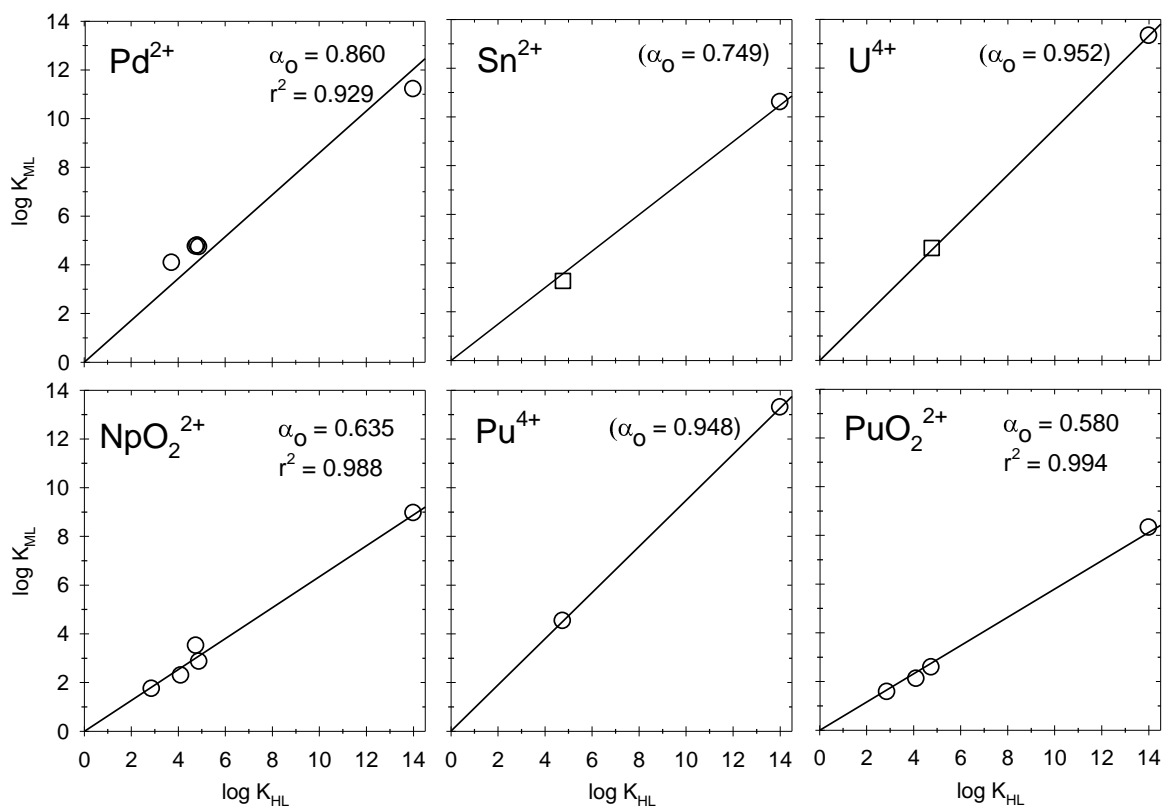
286 and fulvic acid, in both the absence (panel A) and presence (panel B) of carbonate. See text
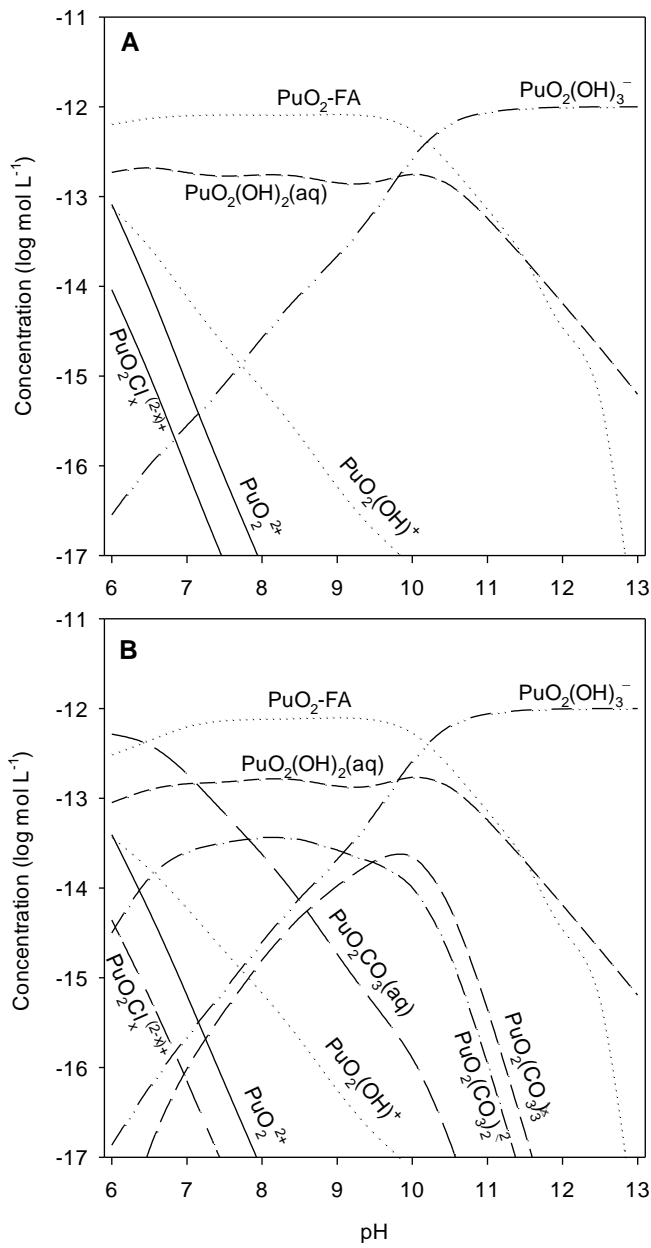
287 for discussion.

288

289 **Figures**

290 Figure 1.

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292

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293   Figure 2.

294