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# Modeling metal ion-humic substances complexation in highly saline conditions

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25 **Highlights:**

- 26 • Model VII and NICA-Donnan are tested at high ionic strength ( $I$ ) using the SIT.
- 27 • For  $I > 1$  m, Model VII is applicable as a non-electrostatic model.
- 28 • No modification is needed for NICA-Donnan.
- 29 • Both models predict the effect of  $I$  on proton- and metal ion-humate (M-HA) binding.
- 30 • SIT parameters for simpler M-HA binding models vary with pH and metal loading.

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31 **Abstract.** Because highly saline groundwaters are found at potential repository sites for nuclear  
32 waste, geochemical models should predict the speciation of relevant radionuclides in brines,  
33 including their complexation with substances such as humic acids (HA). In this study, available  
34 experimental radionuclide-HA complexation data in high 1:1 background electrolyte solutions  
35 ( $0.01 < m_{\text{NaCl}/\text{NO}_3/\text{ClO}_4} < 4$  molal,  $m$ ) are reviewed. Discrepancies in the amplitude of ionic  
36 strength effects on radionuclide-HA complexation are observed, which might depend on the  
37 nature of the interacting radionuclide or on the origin of HA. However, significant differences in  
38 the experimental conditions and calculations applied to determine conditional metal ion-HA  
39 complexation constants hamper direct comparison between these datasets. To clarify whether  
40 metal ion-HA binding in saline solutions can be described, two sophisticated humic-ion binding  
41 models (Model VII and NICA-Donnan) are presently used. This is the first time that Model VII  
42 and NICA-Donnan are applied to predict metal ion-HA binding at high ionic strength ( $I > 1$  m).  
43 The advantage of these models, compared to more simple ones (e.g., the polyelectrolyte or the  
44 charge neutralization models), is that both electrostatic and chemical contributions to the overall  
45 metal ion-HA binding are explicitly taken into account. Model VII and NICA-Donnan are shown  
46 to produce very similar results. Trends in conditional metal ion-HA binding constants and in the  
47 maximum metal ion uptake by HA (e.g., the loading capacity) with  $I$  agree with experiments. The  
48 present data evaluation suggests that most of the apparent discrepancies between various  
49 experimental datasets arise from differences in the experimental conditions. Both Model VII and  
50 NICA-Donnan predict that the specific ion interaction theory (SIT) parameters for metal ion-HA  
51 systems, which are required for high ionic strength with more simple models, vary with pH and  
52 metal loading. Overall, Model VII and NICA-Donnan are able to account for various mechanisms  
53 involved in metal ion-HA complexation, including the metal loading effects and cation

54 competition, and might be helpful predictive tools for performance safety assessment up to highly  
55 saline conditions.

56 **Keywords:** humic, radionuclide, complexation, brine, saline, Model VII, NICA-Donnan, specific  
57 ion interaction theory.

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58

## 1. Introduction

59 Humic substances (HS) such as humic (HA) and fulvic (FA) acids are ubiquitous in  
60 natural waters and form complexes with dissolved metal ions. They play a crucial role for metal  
61 ion mobility and bioavailability in the environment. HS exhibit extreme complexity. The major  
62 HS cation-binding groups are the carboxylic and phenolic groups (Ritchie and Perdue, 2003), but  
63 less abundant softer Lewis bases (e.g., N- and S-containing groups) also contribute to cation-HS  
64 complexation (Tipping, 1998; Hesterberg et al., 2001). HS are macro-ions and electrostatic  
65 effects are relevant for their complexation properties. Moreover, several HS groups may bind a  
66 single cation, which either leads to a chelation effect (Martell and Hancock, 1996) or to the  
67 formation of a cation bridge between different organic molecules (e.g., Kunhi Mouvenchery et al.,  
68 2012). Hence, metal ions can form a large variety of complexes with HS, leading to apparent  
69 complexation constants that depend on pH, ionic strength and metal ion/HS concentration ratio  
70 (i.e., the metal loading) including the presence of competing cations like Ca and Mg. Substantial  
71 efforts have been made to determine thermodynamic metal ion-HS complexation constants and to  
72 develop predictive models for environmentally relevant conditions (e.g., Kim and Czerwinski,  
73 1996; Benedetti et al., 1995; Tipping, 1998; Milne et al., 2001; 2003; Sasaki et al., 2008).  
74 Because of the complexity of HS, very different approaches have been proposed to describe the  
75 reaction between HS and metal ions.

76 The resulting metal ion-HS complexation models were developed for, and mainly applied  
77 to describe metal ion speciation under freshwater conditions, but were shown to be applicable for  
78 the more saline conditions that occur in estuaries and seawaters (e.g., Hiemstra and van  
79 Riemsdijk, 2006; Turner et al., 2008; Stockdale et al., 2011). Nonetheless, few studies have  
80 investigated metal ion-HS interactions under highly saline conditions, such as ionic strength ( $I$ )  
81 exceeding that of seawater (i.e.,  $I > 0.7 m$ ). The latter conditions are relevant with regard to the

82 safety of nuclear waste disposal in rock salt formations or in specific clay formations. For  
83 example, deep waters in the Jurassic and lower Cretaceous clay rock formations in Northern  
84 Germany may contain salt concentrations as high as about 4 M (Mühlenberg et al., 1997).  
85 Sedimentary rocks currently investigated in Canada are in contact with brine solutions up to 6.5  
86 M (Fritz and Frapé, 1982). Although high ionic strength commonly leads to the coagulation of  
87 HS, this process has been shown to be incomplete in many cases and non-negligible amounts of  
88 dissolved HS were reported to persist (Wall and Choppin, 2003), which can react with dissolved  
89 metal ions.

90 Most of the radionuclide-HS complexation studies in saline solutions focused on HA.  
91 Because few data for FA exist, only HA binding properties at high ionic strength are discussed  
92 herein. Generally, at constant pH, the apparent radionuclide-HA complexation constants in  
93 monovalent background electrolyte solutions (e.g., NaCl or NaClO<sub>4</sub>) decrease with increasing  
94 ionic strength from very dilute aqueous solutions up to 1 molal (mol kg<sup>-1</sup>, hereafter denoted *m*).  
95 However, different binding behaviors are observed for *I* > 1 *m*. Specifically, UO<sub>2</sub><sup>2+</sup>- and Pu<sup>4+</sup>-HA  
96 complexation constants increase with increasing ionic strength (Labonne-Wall et al., 1999; Szabò  
97 et al., 2010), whereas Co<sup>2+</sup>-HA complexation does not vary substantially, and Ni<sup>2+</sup>-HA  
98 complexation slightly decreases (Kurk and Choppin, 2000) with increasing ionic strength.  
99 Although data from Czerwinski et al. (1996) and Wall et al. (2002) consistently show increasing  
100 Am<sup>3+</sup>/Cm<sup>3+</sup>-HA binding with increasing *I*, Czerwinski et al. (1996) observed minor variation in  
101 complexation constant values with *I*. This led them to propose an average value (with standard  
102 variation of ± 0.14 log units) for the entire range of *I* investigated, which contrasts with Wall et al.  
103 (2002) where much larger variations were reported (about 3 log units). Furthermore, for 1 ≤ *I* ≤  
104 3.5 *m*, the maximum amount of radionuclide that is experimentally found to bind to HA (e.g., the  
105 so called loading capacity in the charge neutralization model) was shown to decrease with

106 increasing  $I$  for trivalent actinides (Czerwinski et al., 1996), whereas it remained constant in the  
107 case of Pu(IV) (Szabò et al., 2010). All these discrepancies might be indicative of conformational  
108 changes in saline solutions, which would depend on the nature of the interacting radionuclide as  
109 well as on the origin of HA. However, significant differences exist in the experimental conditions  
110 and calculations applied to determine conditional metal ion-HA complexation constants between  
111 these different studies, which complicates data comparison. Some studies were conducted in non-  
112 complexing background electrolyte solutions ( $\text{NaClO}_4$ ; Czerwinski et al., 1996; Szabò et al.,  
113 2010). High  $[\text{Cl}^-]$  is environmentally relevant (as opposed to high  $[\text{ClO}_4^-]$ ), but metal ions can  
114 bind  $\text{Cl}^-$ , which may affect the determination of radionuclide-HA complexation constants.  
115 Complexation data for  $\text{UO}_2^{2+}$ - and  $\text{Am}^{3+}$ -HA binding from Labonne-Wall et al. (1999) and Wall  
116 et al. (2002) were obtained in acetate buffers under ambient (air) atmosphere. Like many ligands,  
117 acetate and carbonate form aqueous complexes with  $\text{UO}_2^{2+}$  and  $\text{Am}^{3+}$  and can compete with HA.  
118 Experiments were conducted at different radionuclide-to-HA concentration ratios, which might  
119 also affect HA charge and conformation. Finally, pH measurement is non-trivial in saline  
120 solutions. More specifically, “constant pH values” can refer to constant proton activity ( $\text{pH} = -$   
121  $\log a_{\text{H}^+}$ ; Szabò et al., 2010), proton molality ( $\text{pH}_m = -\log m_{\text{H}^+}$ ; Czerwinski et al., 1996;  
122 Labonne-Wall et al., 1999; Wall et al., 2002), or constant experimental values, as read on the pH-  
123 meter ( $\text{pH}_{\text{exp}}$ ; Kurk and Choppin, 2000; where the  $\text{pH}_{\text{exp}}\text{-pH}_m$  relationship is provided). Deviation  
124 between pH,  $\text{pH}_m$  and  $\text{pH}_{\text{exp}}$  as affected by  $I$  may also hamper comparison between different  
125 datasets.

126 Available radionuclide-HA complexation data have been analyzed using relatively simple  
127 models such as the Polyelectrolyte Model (PM; Torres and Choppin, 1984) or the Charge  
128 Neutralization Model (CNM; Kim and Czerwinski, 1996). These models can be conveniently  
129 included in the speciation codes used for performance safety assessment. Within these models,

130 binding parameters may vary with pH and  $I$ . High salt levels require an appropriate treatment of  
131 activity coefficients for aqueous species in geochemical models, such as application of specific  
132 ion interaction theory (SIT; Ciavatta, 1980). Metal-HA complexation constants can also be  
133 extrapolated to  $I = 0$  using SIT, when considering HA as a solute. However, due to HA  
134 complexity, SIT parameters are no more than adjustable parameters and their values have no  
135 clear physical significance according to the original authors (Czerwinski et al., 1996; Szabò et al.,  
136 2010). Given the differences in the experimental conditions between previous radionuclide-HA  
137 complexation studies and the different calculations applied for the determination of metal-HA  
138 complexation constants (e.g., with the CNM or the PM), it is difficult to evaluate how SIT  
139 parameters would evolve with changing metal ion concentrations and physico-chemical  
140 conditions.

141 More sophisticated models exist, such as the humic ion binding Model VII (Tipping et al.,  
142 2011), or its previous versions (Models V/VI: Tipping and Hurley, 1992; Tipping, 1998), and the  
143 NICA-Donnan model (Kinniburgh et al., 1996; Koopal et al., 2005). The description of HA  
144 properties relies on several assumptions, and the various models include a more or less detailed  
145 description of metal ion-HA interaction. In particular, the electrostatic and chemical contributions  
146 to the overall metal ion-HA binding are separated in the models. This is a major advantage for  
147 understanding metal ion-HA binding in saline solutions, because ionic strength is expected to  
148 more strongly affect electrostatic than chemical binding properties of HA. Unfortunately, as  
149 pointed out by Tipping (1998), the electrostatic approach included in Models V/VI/VII is  
150 unlikely to be applicable for  $I > 1$  m. In contrast, NICA-Donnan equations seem to be applicable  
151 in highly saline conditions (up to 2 M), as shown for HA proton titration data (Benedetti et al.,  
152 1996), but, to our knowledge, it has never been tested for metal ion-HA complexation data.

153 In the following, we evaluate the applicability of Model VII and the NICA-Donnan model  
 154 for saline aqueous solutions, focusing on the concomitant electrostatic approaches. The following  
 155 analysis involves close inspection of the model equations in conjunction with comparisons of  
 156 simulated and experimental HA proton titration and radionuclide complexation data. The  
 157 mechanisms responsible for the effect of ionic strength on cation-HA complexation are also  
 158 discussed within the context of the assumptions inherent to Model VII and NICA-Donnan.  
 159 Finally, the impact of the physico-chemical conditions on the experimental determination of SIT  
 160 parameters for more simple cation-HA models is discussed.

161

## 162 2. Theoretical background

### 163 2.1. Aqueous speciation calculations and codes

164 Ionic strength ( $I$ ) affects the activity of dissolved ions in solution, which must be  
 165 accounted for, for instance, when extrapolating formation constants to hypothetical infinite  
 166 dilution condition (i.e., for  $I = 0$  m). In the present study, activity coefficients ( $\gamma$ ) are calculated  
 167 according to the specific ion interaction theory (SIT; Ciavatta, 1980). SIT is generally considered  
 168 valid for ionic strengths up to 3 - 4 m. At 25 °C, activity coefficients for an aqueous species  $i$  with  
 169 a charge  $z_i$  are calculated as follows:

$$\log \gamma_i = -z_i^2 \frac{0.509 \times \sqrt{I}}{1 + 1.5\sqrt{I}} + \sum_k \varepsilon(i, k) \times m_k = -z_i^2 D + \sum_k \varepsilon(i, k) \times m_k \quad (1)$$

170 where  $D$  is the Debye-Hückel term used in SIT,  $m_k$  is the molality of the aqueous species  $k$  (mol  
 171  $\text{kg}^{-1}$ ), and  $\varepsilon(i, k)$  is the specific ion interaction coefficient between species  $i$  and  $k$  ( $\text{kg mol}^{-1}$ ).

172 In the present study, we use PHREEQC (version 2; Parkhurst and Appelo, 1999) to model  
 173 cation-HA binding with Model VII. The NICA-Donnan model is not implemented in PHREEQC  
 174 yet, which will require future modification of PHREEQC code. Therefore, Visual MINTEQ

175 (version 3.0; Gustafsson, 2012) is used to model cation-HA binding with NICA-Donnan. The SIT  
176 database provided with each code is used (which corresponds to ThermoChimie v.7.b in  
177 PHREEQC). Unless mentioned in this study, the same thermodynamic constants and SIT  
178 parameters were selected throughout. The metastability of  $\text{ClO}_4^-$ , sometimes used as background  
179 anion, is avoided in the models by defining perchlorate as a master species. The Pitzer approach  
180 (Pitzer, 1991) can be applied to calculate activity coefficients for aqueous ions in even more  
181 concentrated media than appropriate for SIT, which would be more relevant for brine solutions.  
182 However, in the present study, the SIT was chosen: (i) for the sake of simplicity, as it is  
183 approximately equivalent to a simplified Pitzer model (Grenthe et al., 1993); (ii) because most of  
184 the thermodynamic data are taken from the NEA database (Guillaumont et al., 2003), which  
185 recommends the use of SIT; and (iii) because Pitzer equations are implemented in PHREEQC but  
186 not in Visual MINTEQ, the NICA-Donnan model cannot be tested yet in combination with the  
187 Pitzer model.

188 Experimental pH measurements ( $\text{pH}_{\text{exp}}$ ) are affected by the background electrolyte  
189 concentration under saline conditions (e.g., Altmaier et al., 2003), and appropriate calibrations  
190 are necessary to relate empirical  $\text{pH}_{\text{exp}}$  to the molality of the proton ( $\text{pH}_m = -\log m_{\text{H}^+}$ ). The  
191 deviation between  $\text{pH}_{\text{exp}}$  and  $\text{pH}_m$  increases with increasing ionic strength such that  $\text{pH}_{\text{exp}} < \text{pH}_m$   
192 for concentrated electrolytes. The pH ( $= -\log a_{\text{H}^+}$ ), which is a master variable and hence required  
193 by speciation codes, can be determined from  $\text{pH}_m$  and calculated  $\gamma_{\text{H}^+}$  values. In this study, SIT is  
194 used to calculate pH.

195

196

197 **2.2. Determination of empirical metal ion-HA complexation constants**

198 Empirical models consider that the metal ion binds to one generic HA site. Non-specific  
199 metal ion-HA interactions are not considered explicitly. The general complexation reaction of a  
200 cation M with HA can be written as follows:



201 and the corresponding conditional stability constant is

$${}^{HA}\beta = \frac{[MHA]}{[M]_f[HA]_f} \quad (3)$$

202 Various approaches can be found in the literature to determine  ${}^{HA}\beta$  values. Therefore, it is not  
203 possible to directly compare  ${}^{HA}\beta$  values reported in separate M-HA complexation studies unless  
204 the same calculations were made or appropriate corrections are applied. The differences arise  
205 from the various possibilities for defining  $[M]_f$  or  $[HA]_f$  in eq. 3. For example,  $[M]_f$  may refer to  
206 (i) the total dissolved metal ion concentration at equilibrium (noted  $[M]_{\text{tot},f}$  in the following),  
207 which includes complexes of M with any ligand except HA (e.g.  $\text{OH}^-$ ,  $\text{Cl}^-$ ,  $\text{CO}_3^{2-}$  or acetate when  
208 used as a pH buffer) or (ii) the “free” aquo-ion only,  $[M^{z+}]_f$ . In the remainder of the text, M-HA  
209 complexation constants referring to the total dissolved metal ion concentration and to the aquo-  
210 ion will be denoted  ${}^{HA}\beta(\text{M})$  and  ${}^{HA}\beta(\text{M}^{z+})$ , respectively.  $[M^{z+}]_f$  can be calculated by dividing the  
211  $[M]_{\text{tot},f}$  value by the side reaction coefficient ( $\alpha_M$ ; Ringböm, 1963):

$$\alpha_M = 1 + \sum_h \frac{{}^*\beta_h}{m_{H^+}^h} + \sum_l \beta_l \times m_L^l. \quad (4)$$

212 Here,  ${}^*\beta_h$  are the hydrolysis constants, L is a ligand,  $\beta_l$  are the formation constants for  $\text{M}(\text{L})_l$   
213 complexes and  $m_{H^+}$  and  $m_L$  refer to the molalities of  $\text{H}^+$  and L. In eq. 4,  ${}^*\beta_h$  and  $\beta_l$  are  
214 conditional constants, valid at a given ionic strength. Possible ternary complexes (i.e., involving a

215 metal ion and two different ligands) or polynuclear species are not included in eq. 4 for the sake  
 216 of simplicity in the present text, but they must be taken into account in the calculations.

217 The definition of  $[HA]_f$  (eq. 3) also depends on the humic-ion binding model considered.  
 218 In the present study, the notation of Marquardt and Kim (1998) is used for the different  ${}^{\text{HA}}\beta$   
 219 (namely,  ${}^{\text{HA}}K$ ,  ${}^{\text{HA}}\beta_{\text{LC}}$  or  ${}^{\text{HA}}\beta_{\alpha}$ , as defined below). HA site density, commonly corresponding to the  
 220 proton exchange capacity of HA (PEC, in eq  $\text{g}(\text{HA})^{-1}$ ), can be taken into account to determine the  
 221 total HA site concentration ( $[HA]_{\text{tot}}$ , in eq  $\text{kg}(\text{H}_2\text{O})^{-1}$ ). The corresponding M-HA complexation  
 222 constant, denoted  ${}^{\text{HA}}K$ , can be calculated considering that:

$$[HA]_f = [HA]_{\text{tot}} - [MHA] \quad (5)$$

223 where  ${}^{\text{HA}}K$  varies with pH, ionic strength, metal loading, etc.

224 Competition between the metal ion and  $\text{H}^+$  can be included via the degree of  
 225 deprotonation ( $\alpha_{\text{HA}}$ ) in order to suppress the dependence of the M-HA complexation constant on  
 226 pH:

$$[HA]_f = [HA]_{\text{tot}} \times \alpha_{\text{HA}} - [MHA]. \quad (6)$$

227 The concomitant complexation constant is noted  ${}^{\text{HA}}\beta_{\alpha}$  and refers to the Polyelectrolyte Model  
 228 (PM; Torres and Choppin, 1984). The degree of deprotonation,  $\alpha_{\text{HA}}$ , is experimentally  
 229 determined by proton titration and depends on both pH and ionic strength.

230 Another approach is to consider the effective amount of binding sites at a given pH and  $I$ .  
 231 Here, the aim is to suppress the dependence of the M-HA complexation constant on both pH and  
 232 HA site saturation at high metal loading. In a Pu(IV)-HA study, Szabó et al. (2010) determined  
 233 the maximum complexing capacity ( $B_{\text{max}}$ , in  $\text{mol g}^{-1}$ ) of HA immobilized on silica gel (19.9 mg  
 234 HA  $\text{g}^{-1}$ ), associated with a complexation constant denoted  ${}^{\text{HA}}\beta(\text{Pu}^{4+})$ :

$$[HA]_f = B_{\text{max}} - [PuHA] \quad (7)$$

235 where  $B_{\max}$  and  ${}^{\text{HA}}\beta(\text{Pu}^{4+})$  are determined by analyzing  $\text{SiO}_2$ -HA-Pu binding isotherms with a  
 236 Langmuir-type equation.

237 The effective amount of binding considered in the Charge Neutralization Model (CNM;  
 238 Kim and Czerwinski, 1996) is the “loading capacity” (LC, generally in  $\text{mol g}^{-1}$ ). For this model, it  
 239 is assumed that the total amount of HA sites that is available to neutralize the metal depends on  
 240 the metal charge ( $z$ ). In the CNM, the free HA site concentration is defined as:

$$[HA]_f = [HA]_{tot} \times LC/z - [MHA]. \quad (8)$$

241 The corresponding M-HA complexation constant is noted  ${}^{\text{HA}}\beta_{\text{LC}}$ .

242

### 243 **2.3. Humic-ion binding models NICA-Donnan and Model VII**

#### 244 *2.3.1. Chemical part of the models*

245 NICA-Donnan and Model VII have been described in several publications (e.g., Koopal et  
 246 al., 2005; Tipping et al. 2011). Because the effect of the ionic strength is taken into account  
 247 through the electrostatic part of these models, the chemical part is only briefly discussed here.  
 248 Cation-HA complexation (including  $\text{H}^+$ ) in NICA-Donnan and Model VII follows identical  
 249 reaction equations (eq. 2). Additional equations are used to account for HA heterogeneity. NICA-  
 250 Donnan describes HA heterogeneity by a continuous affinity distribution for the interaction  
 251 between a cation and HA, whereas Model VII considers a large number of binding sites with  
 252 different but discrete affinities for the cation. The chemical cation-HA binding parts of these  
 253 models aim at describing the overall cation-HA complexation (e.g., expressed as a  $\log {}^{\text{HA}}K$  value)  
 254 as a function of pH, cation to HA concentration ratio (or “metal loading”), and take into account  
 255 cation competition with a limited number of parameters. The latter parameters are “intrinsic”  
 256 because they do not vary with the physico-chemical conditions. However, parameters usually  
 257 vary with the type of HA, including origin or composition. Generic parameters for a wide range

258 of metal ions and HAs were determined for NICA-Donnan (Milne et al., 2001; 2003) and Model  
259 VII (Tipping et al., 2011) by fitting experimental datasets. These generic parameters capture  
260 “average” HA behavior, and will be used as such in this study. Consequently, the present work  
261 does not aim at discussing the capability of the generic parameters to precisely simulate a given  
262 dataset (i.e., no parameter optimization is made). Rather the capability of NICA-Donnan and  
263 Model VII to predict variations in apparent cation-HA binding constants with the ionic strength  
264 will be discussed (e.g., trends in  $\log^{HA}K$  versus  $I$ ).

265 It is important to note that, in NICA-Donnan and Model VII,  $\text{Na}^+$  is not considered to  
266 bind specifically to HA unlike  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$ , which complex with HA in solution. Therefore, for  
267 high 1:1 Na-containing background electrolyte solution (e.g.  $\text{NaCl}/\text{NO}_3/\text{ClO}_4$ ),  $\text{Na}^+$  is considered  
268 to control the ionic strength and to affect other metal ion complexation by HA only via  
269 electrostatic effects.

270

### 271 2.3.2. Electrostatic models

272 HAs are large and negatively charged polyelectrolytes. This leads to an accumulation of  
273 cations in the vicinity of HA binding sites. Electrostatic models aim at converting the dissolved  
274 cation concentration in the bulk solution ( $[C]_i$ ) to a local dissolved cation concentration ( $[C]_{loc,i}$ )  
275 that occurs adjacent to the HA site. To accomplish this, the electrostatic potential of HA particles  
276 ( $\Psi$ , in V) is computed using a Boltzmann factor:

$$277 [C]_{loc,i} = [C]_i \times \exp(-z_i F \Psi / RT) \quad (9)$$

278 Here,  $z_i$  is the charge of the cation,  $T$  is absolute temperature,  $F$  is the Faraday constant and  $R$  is  
279 the gas constant.

280 Within the NICA-Donnan framework, HAs are considered as permeable spheres.  
281 Counter-ions are accumulated in a Donnan phase. The electrostatic potential ( $\Psi_D$ ) is constant

282 inside the Donnan volume and equals zero outside (i.e., in the bulk solution). The Donnan  
 283 volume ( $V_D$ , in  $L \text{ kg(HA)}^{-1}$ ) is calculated as follows:

$$284 \quad \log V_D = b(1 - \log I) - 1 \quad (10)$$

285 The parameter  $b$  is adjusted by fitting acid-base titration experiments at varying  $I$  and depends on  
 286 the type of HA (origin, composition, etc). In the Donnan volume, the negative charge of HA ( $Q$ )  
 287 is neutralized by counterions:

$$288 \quad \frac{Q}{V_D} + \sum_i z_i ([C]_{D,i} - [C]_i) = 0 \quad (11)$$

289 where  $C_{D,i}$  and  $C_i$  refer to the concentration of the ion  $i$  with a charge  $z_i$  in the Donnan phase and  
 290 in the bulk solution, respectively. The activity of the ion in the Donnan phase is required for  
 291 calculation of the specific binding.

292 Within the Model VII framework, HA molecules are considered as impermeable spheres.  
 293 Since the conceptualization of HA particles and the numerical treatment of the electrostatic  
 294 effects resemble a surface complexation model (e.g., see the present implementation of Model  
 295 VII in PHREEQC in the following section), we will denote the electrostatic potential  $\Psi_0$ ,  
 296 similarly to the surface potential of minerals. The electrostatic correction is an empirical equation  
 297 that mimics the Boltzmann factor:

$$298 \quad \exp(-F\Psi_0/(RT)) = \exp(-2PQ \log(I)) \quad (12)$$

299 where  $I$  is the ionic strength ( $\text{mol L}^{-1}$ ),  $P$  is an adjustable parameter (generally  $-400 < P < -100$  for  
 300 HA) and  $Q$  is the net humic acid charge ( $\text{eq g}^{-1}$ ). In  $\text{NaCl/NO}_3/\text{ClO}_4$  background electrolytes, the  
 301 molality and molarity scales do not significantly differ for  $I \leq 1 \text{ M}$  (or  $m$ ). The molality scale is  
 302 used to extrapolate the model to high  $I$ . A Donnan model is also used in the original version of  
 303 Model VII, but it only accounts for counter-ion accumulation (i.e., to calculate the amount of ion  
 304 bound to HA in a non-specific manner) and has no effect on electrostatics, in contrast to the  
 305 NICA-Donnan model. Because in Model VII, HA is considered to be an impermeable sphere of

306 radius  $r$ , the Donnan volume is a layer at the surface of the sphere, with a thickness equal to the  
307 Debye length ( $\kappa^{-1} = (3.29 \times 10^9 \times I^{1/2})^{-1}$ ; in meters,  $I$  in mol L<sup>-1</sup> and at 25°C). With the molar mass  
308 and the radius of HA (15000 g mol<sup>-1</sup>; 1.72 nm) inherent to Model VII, the surface area of HA  
309 ( $A_{\text{HA}}$ ) equals 1500 m<sup>2</sup> g<sup>-1</sup>. Hence, the Donnan volume in Model VII equals  $A_{\text{HA}} \times \kappa^{-1}$  (in m<sup>3</sup> g<sup>-1</sup>).  
310 Unfortunately, the “-donnan” keyword cannot be used with SIT and Pitzer options in PHREEQC.  
311 It can only be used with other databases, which do not involve SIT or Pitzer models (e.g. which  
312 use Davies or Debye-Hückel equations to calculate activity coefficients). However, during  
313 preliminary tests, we found very little effect of these calculations on the overall cation-HA  
314 binding (see Fig. S2), especially at high  $I$  where the Donnan volume drastically shrinks.  
315 Therefore, this option is not used in the present study, that is, counter-ion accumulation is  
316 neglected.

317

### 318 2.3.3. Implementation of Model VII in PHREEQC

319 The complete Model VII chemical reaction database, described in Tipping et al. (2011),  
320 was previously included in PHREEQC by Marsac et al. (2014) and is used in this study. In the  
321 supporting information, a file that can be used to modify Model VII chemical reaction database  
322 (e.g., to include other cations or to change binding parameters) and an example of PHREEC input  
323 file are given.

324 Previous studies, where Models V, VI or VII were coupled with PHREEQC, attempted to  
325 convert this empirical electrostatic humic ion-binding model into the diffuse layer model (DLM)  
326 formalism (Appelo and Postma, 2005; Liu et al., 2008; Marsac et al., 2011, 2014; Catrouillet et  
327 al., 2014). Such a conversion requires the calculation of a surface area ( $A_{\text{HA}}$ ) that depends on the  
328 ionic strength. Similar computations have been performed for polyelectrolytes such as  
329 polyacrylic acid (Lützenkirchen et al., 2011). Such approaches result in physically unreasonable

330 surface areas (above  $10^4 \text{ m}^2 \text{ g}^{-1}$ ) (Appelo and Postma, 2005; Liu et al., 2008; Lützenkirchen et al.,  
331 2011; Marsac et al., 2011, 2014; Catrouillet et al., 2014). Hence, we suggest the use of the  
332 constant capacitance model (CCM) might be a better choice (Catrouillet et al., 2015). For the  
333 CCM, the capacitance ( $C_1$ , in  $\text{F m}^{-2}$ ) evolves with  $\log I$  in the case of minerals (Lützenkirchen,  
334 1999), and a  $\log I$ -term is also found in the empirical electrostatic model in Model VII (eq. 12).  
335 Specifically, the CCM employs a linear relationship between the charge density at the surface ( $\sigma_0$ ,  
336 in  $\text{C m}^{-2}$ ) and the surface potential ( $\Psi_0$ , in V):

$$337 \quad \sigma_0 = C_1 \times \Psi_0. \quad (13)$$

338 Combination of equations 12 and 13 gives:

$$339 \quad C_1 = F^2 \times (2RTPA_{HA} \log(I))^{-1}. \quad (14)$$

340 Therefore, using the CCM leads to an expression for  $C_1$  that does not depend on the pH. Given  
341 the surface area of HA in Model VII ( $A_{HA} = 1500 \text{ m}^2 \text{ g}^{-1}$ ), the range of  $C_1$  values found for  $I < 1$   
342  $m$  corresponds to that commonly reported for minerals ( $0.5 < C_1 < 10 \text{ F m}^{-2}$ ; Lützenkirchen,  
343 1999). Although the CCM is not implemented in PHREEQC, it can be used by applying  
344 appropriate corrections to the three plane model (TPM) in PHREEQC. Details are given in  
345 supporting information.

346

347

### 3. Results and Discussion

#### 348 3.1. Proton titration in saline solutions

349 Although proton titrations of HA are rarely carried out for  $I > 1 m$ , a number of critical  
350 studies do exist. Kurk and Choppin (2000) and Laszak and Choppin (2001) performed proton  
351 titrations of HA at  $I = 0.1, 0.3, 1, 3$  and  $5 m$  (NaCl), and calculated apparent dissociation  
352 constants ( $\text{pK}_a$ ) for HA considering two acidic groups. They found that  $\text{pK}_a$  variation was  
353 insignificant ( $\pm 0.1$ ) within this range of ionic strengths. Marinsky et al. (1982) reported similar

354 observations for ionic strength between 0.2 and 2 M NaNO<sub>3</sub>. Furthermore, the charging curves  
 355 for HA versus the p*H*<sub>m</sub> reported by Maes et al. (1992) exhibited only slight differences between 1  
 356 and 3 M NaClO<sub>4</sub>. Van Dijk (1959) observed a shift in the titration curves to lower “p*H*” for *I*  
 357 increasing from 0.02 to 2 M NaCl but mentioned no p*H*-correction. This effect is qualitatively  
 358 consistent with the increased deviation between p*H*<sub>exp</sub>-p*H*<sub>m</sub> with increasing *I* (p*H*<sub>exp</sub> < p*H*<sub>m</sub>) that is  
 359 commonly observed (e.g., Kurk and Choppin, 2000; Altmaier et al., 2003). The surface of  
 360 biological cells, such as the seaweed *Ulva lattuca*, can be considered as a polyelectrolyte, and the  
 361 cation sorption properties onto *U. lattuca* can be treated with the models applied to HA (e.g.  
 362 Turner et al., 2008). Surface acid-base properties of such biosorbents show very little influence of  
 363 *I* above 1 *m* (e.g. Rey-Castro et al., 2003; Schijf and Ebling, 2010).

364 The apparent p*K*<sub>a</sub> of one HA site at a given ionic strength (p*K*<sub>a</sub>(*I*)), which is obtained  
 365 experimentally, can be written as follows:

$$pK_a(I) = -\log \frac{[H^+][HA^-]}{[HHA]} = pK_a(I = 0) + \log(\gamma_{H^+}) - F\Psi/(RT\ln(10)) \quad (15)$$

366 According to eq. 15, the observed small dependence of conditional HA proton dissociation  
 367 constants on *I* for highly saline conditions (*I* > 1 *m*) might occur (i) due to small dependencies of  
 368 both  $\Psi$  and  $\gamma_{H^+}$  on *I* or (ii) compensation of the effects of *I* on  $\Psi$  and  $\gamma_{H^+}$ . Figure 1a compares the  
 369 effect of *I* on  $\Psi_0$  (for Model VII) and  $\Psi_D$  (for NICA-Donnan) at constant proton activity (p*H* =  
 370 5.5). As stated by Tipping (1998), Model VI is unlikely to find application at ionic strengths  
 371 higher than *I* = 1 *m*, because of the electrostatic model (the same is true for Model VII). When the  
 372 electrostatic term is translated to the CCM formalism (e.g., to be used in PHREEQC; eq. 14), and  
 373 for the case when *I* increases to 1 *m*, *C*<sub>1</sub> tends to infinity and the model becomes essentially non-  
 374 electrostatic ( $\Psi_0 = 0$ ). When *I* > 1 *m*, *C*<sub>1</sub> is negative, which is physically unrealistic,

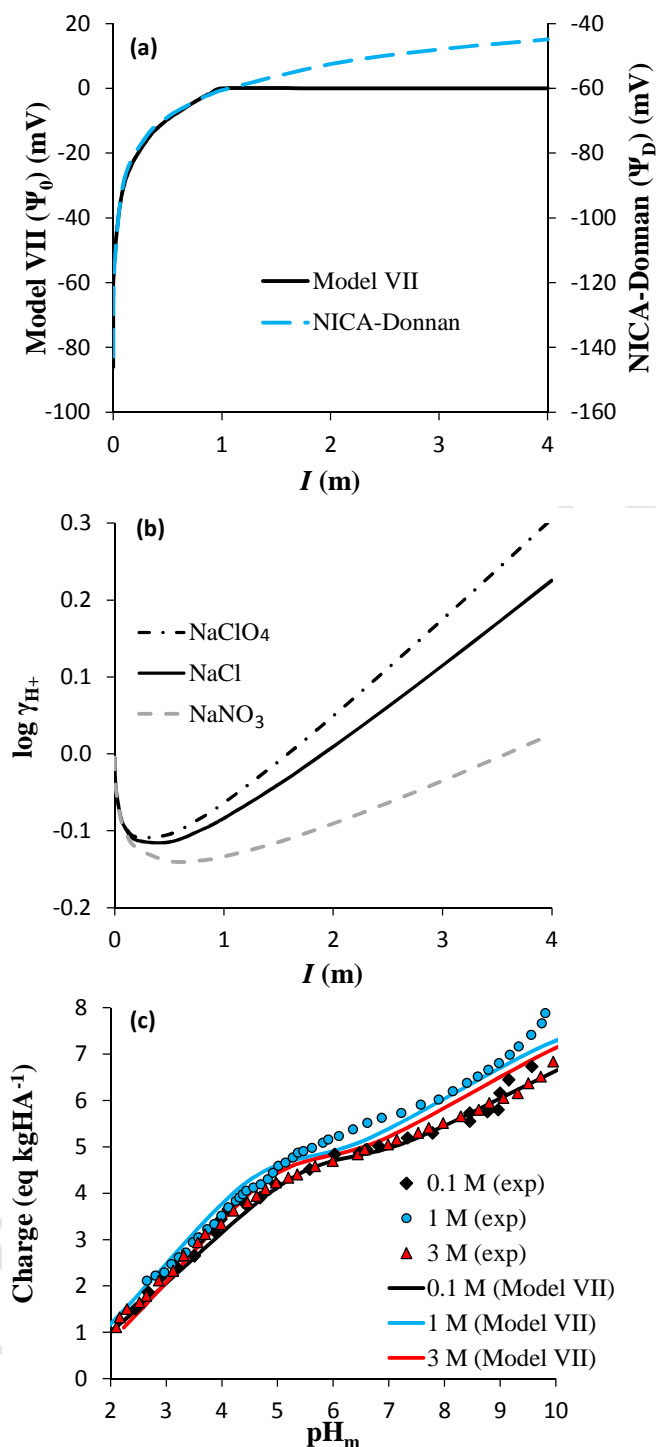
375 demonstrating that Model VII cannot be used with PHREEQC when  $I > 1\ m$  (except by  
376 suppressing the electrostatic term), consistent with the conclusion of Tipping (1998).

377 Benedetti et al. (1996) previously demonstrated the capability of NICA-Donnan to  
378 simulate HA charging curves versus pH in highly saline conditions (up to 2 M). In this case  $\Psi_D$   
379 increases with  $I$  and only small variation in  $\Psi_D$  can be seen for  $I > 1\ m$  (Fig. 1a). The NICA-  
380 Donnan model's inherent electrostatic contribution in cation-HA binding is approximately  
381 constant ( $-60\ mV \leq \Psi_D \leq -40\ mV$ ) for  $I > 1\ m$ , and only a small dependence of apparent  $pK_a$   
382 values (i.e., corrected for the activity coefficient effect) on  $\Psi_D$  is predicted. This is because the  
383 Donnan volume is small for  $I > 1\ m$  and only slightly shrinks when  $I$  further increases.  
384 Interestingly, the amplitude of the variation in  $\Psi$  is similar for both models when using the  
385 generic parameters:  $\Psi_D \approx \Psi_0 - 60\ mV$  for  $I < 1\ m$  and  $pH = 5.5$ , as highlighted in Figure 1a.  
386 Therefore, by suppressing the electrostatics in Model VII for  $I \geq 1\ m$ , we produce a comparable  
387 effect of  $I$  on cation-HA binding constants as in NICA-Donnan. This leads to a simplification of  
388 Model VII equations compared to lower  $I$ .

389 Figure 1b shows the change of  $\log \gamma_{H^+}$  versus  $I$  between 0.1 and 4  $m$  for different  
390 background electrolyte solutions (i.e.,  $NaNO_3$ ,  $NaCl$ , and  $NaClO_4$ ) computed according to the  
391 SIT equation, where  $\varepsilon(H^+, NO_3^-) = 0.07 \pm 0.07$  for  $NaNO_3$ ,  $\varepsilon(H^+, Cl^-) = 0.12 \pm 0.01$  for  $NaCl$ , and  
392  $\varepsilon(H^+, ClO_4^-) = 0.14 \pm 0.03$  for  $NaClO_4$  electrolytes. The maximum variation in  $\log(\gamma_{H^+})$  between  
393 1 and 4  $m$ , as calculated with SIT, is approximately 0.16 in  $NaNO_3$ , 0.31 in  $NaCl$  and 0.37 in  
394  $NaClO_4$ , corresponding to a small dependence of the predicted apparent  $pK_a$  values on  $\log(\gamma_{H^+})$ .  
395 The slight variation in both  $\Psi$  and  $\gamma_{H^+}$  for  $1 < I < 4\ m$  is consistent with the experimental  
396 observations showing little dependence of apparent  $pK_a$  with  $I$  under highly saline conditions  
397 (Marinsky et al., 1982; Maes et al., 1992; Kurk and Choppin, 2000). Note that the value of  $\gamma_{H^+}$   
398 has no direct impact on NICA-Donnan results, because concentrations are involved in the

399 equations, and cannot compensate the effects of  $I$  on  $\Psi_D$ . Therefore, a slight decrease in  $\text{pK}_a(I)$   
400 values is predicted with the NICA-Donnan Model when  $I$  increases.

401 To illustrate how PHREEQC-Model VII reproduces acid-base titration data for  $I > 1$  m,  
402 Figure 1c shows HA charge versus  $\text{pH}_m$  in 0.1, 1 and 3 M (0.1, 1.051, 3.503 m)  $\text{NaClO}_4$   
403 determined by Maes et al. (1992), together with results from Model VII. Experimental data of  
404 Marinsky et al. (1982) (in  $\text{NaNO}_3$ ) and Laszak and Choppin (2001) (in  $\text{NaCl}$ ) with Model VII  
405 simulations are shown in Figure S4. For a better illustration, slight adjustment of site densities  
406 and  $\text{pK}_a$  values was made (see table S1), in order to better reproduce experimental data for  $I = 0.1$   
407 M, and predictions are made for higher  $I$ . HA charge increases between  $I = 0.1$  and 1 M, which is  
408 well predicted. Between  $I = 1$  and 3 M, experimental HA charge decreases, as also predicted by  
409 Model VII. This charge decrease is actually related to the use of a  $\text{pH}_m$ -scale: with a  $\text{pH}$ -scale  
410 (see Fig. S3), Model VII simulations for  $I = 1$  and 3 M cannot be differentiated (due to the  
411 suppression of the electrostatic term), and the difference between the two experimental curves is  
412 smaller. Beside small discrepancies between experimental and model results, it can be concluded  
413 that Model VII does a relatively good job in predicting HA charging curves in saline conditions.



414

415 **Figure 1.** (a) Surface potential ( $\Psi_0$ ) and Donnan potential ( $\Psi_D$ ) calculated for Model VII and  
 416 NICA-Donnan, respectively, for  $\text{pH} (= -\log a_{H^+}) = 5.5$  versus the ionic strength. The y-axis for  
 417  $\Psi_D$  is shifted by 60 mV compared with the one of  $\Psi_0$  to highlight their similar evolution with  $I$ .  
 418 (b) Activity coefficient of the proton ( $\log \gamma_{H^+}$ ) versus  $I$  in NaCl, NaClO<sub>4</sub> and NaNO<sub>3</sub> solutions,

419 calculated with SIT. (c) HA charge versus  $\text{pH}_m$  in 0.1 M (black curve), 1 M (blue curve), and 3  
 420 M (red curve) [0.1, 1.051, 3.503 m, respectively]  $\text{NaClO}_4$ . Points are experimental results of  
 421 Maes et al. (1992) and lines are results from Model VII. (For interpretation to references to color,  
 422 the reader is referred to the web version of this article.)

423

### 424 3.2. Anticipated effects of high ionic strengths on metal ion-HA binding

425 As for the proton, apparent metal ion complexation constants with one HA site at a given  
 426 ionic strength ( $\log K(I)$ ; data that can be obtained experimentally) can be calculated as follows:

$$\begin{aligned} \log {}^{\text{HA}}\beta(I) &= \log \frac{[M^{\text{HA}z_i-x}]}{[M^{\text{HA}z_i+}][\text{HA}^{x-}]} \\ &= \log {}^{\text{HA}}\beta(I=0) + \log(\gamma_{M^{\text{HA}z_i+}}) - z_i F\Psi / (RT \ln(10)) \end{aligned} \quad (16)$$

427 The term  $z_i F\Psi / (RT \ln(10))$  leads to substantial  $\log {}^{\text{HA}}\beta(I)$  variations for  $I < 1$  m. The amplitude  
 428 of  $\log {}^{\text{HA}}\beta(I)$  variations should increase with increasing metal ion charge  $z_i$ . It should also vary  
 429 with  $\Psi$ , and hence with the HA charge,  $Q$ . Therefore, we can expect that larger  $\log {}^{\text{HA}}\beta(I)$   
 430 variations would be observed at high pH and low metal loading compared to low pH and high  
 431 metal loading. These three anticipated effects are purely related to HA physico-chemical behavior,  
 432 which are predicted by Model VII and NICA-Donnan equations and parameters.

433 Other effects can be anticipated, which are not related to HA behavior but to physico-  
 434 chemical phenomena in solution. As for the proton,  $\gamma_{M^{\text{HA}z_i+}}$  varies with the ionic strength and the  
 435 nature of background electrolytes (eq.1), which would directly affect  $\log {}^{\text{HA}}\beta(I)$  in eq.16. In the  
 436 presence of complexing ligands other than HA (e.g.,  $\text{OH}^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{Cl}^-$ , acetate, etc), conditional  
 437 metal-ligand complexation constants will also evolve with ionic strength, which would affect  
 438  $\alpha_M$  (eq.4). Therefore, we can expect that (i) the presence of ligands will affect trends in  $\log {}^{\text{HA}}\beta$   
 439 versus  $I$  whatever the mathematical expression used for  $\log {}^{\text{HA}}\beta$  (see section 2.2) is, and (ii) M-  
 440 HA complexation constants referring to the total dissolved metal ion concentration ( ${}^{\text{HA}}\beta(M)$ ) and

441 to the aquo-ion ( ${}^{\text{HA}}\beta(\text{M}^{\text{z}+})$ ) might diverge when varying  $I$ . For instance, if all conditional metal-  
442 ligand complexation constants increase with increasing  $I$ ,  ${}^{\text{HA}}\beta(\text{M})$  will decrease, whereas  
443  ${}^{\text{HA}}\beta(\text{M}^{\text{z}+})$  will increase because  $\alpha_{\text{M}}$  increases with increasing  $I$ . Prediction of ionic strength effects  
444 on  $\gamma_{\text{M}^{\text{z}+}}$  and metal-ligand complexation constants pertain to the thermodynamic database used for  
445 aqueous solution (thermodynamic constants and SIT parameters). Therefore, in the presence of  
446 ligands other than HA, it is more difficult to test the applicability of Model VII and NICA-  
447 Donnan in saline solutions because ionic strength effects on metal-ligand complexation must be  
448 discussed in parallel. In particular, experiments conducted in NaCl solutions are affected by M-Cl  
449 complexation, which increases with increasing  $[\text{Cl}^-]$ , and consequently, the conditional M-Cl  
450 complexation constants also evolve with  $I$ . For this reason, metal ion-HA binding data measured  
451 in  $\text{NaClO}_4$  are initially discussed below (i.e., section 3.3), followed by data collected in NaCl  
452 background electrolyte solutions (section 3.4).

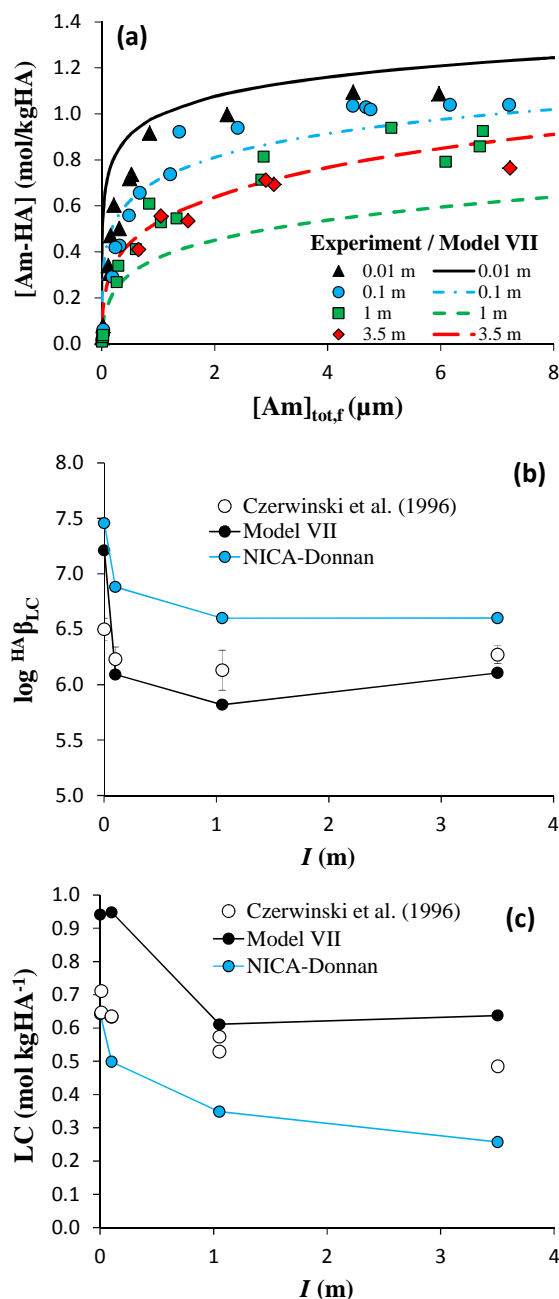
453

### 454 3.3. Cation-HA complexation in $\text{NaClO}_4$ solutions

455 **Am(III)/Cm(III).** Czerwinski et al. (1996) investigated  $\text{Am}^{3+}$  and  $\text{Cm}^{3+}$  complexation  
456 with HA at  $\text{pH}_{\text{m}} = 6$  and in various  $I$  ( $\text{NaClO}_4$  electrolyte solution). Because (i) most of the data  
457 are available for  $\text{Am}^{3+}$  and (ii)  $\text{Am}^{3+}$  and  $\text{Cm}^{3+}$  are generally considered as chemical analogues,  
458 they will not be distinguished and we will only refer to  $\text{Am}^{3+}$  for both datasets in this section. The  
459 authors interpreted the data according to the CNM. Only those datasets that allow the  
460 determination of the  $LC$  (i.e., for  $I = 0.01, 0.1, 1.05$  and  $3.5$   $m$ ) and that are within the  
461 applicability of SIT ( $I < 4$   $m$ ) are considered in the present study. The original authors provided  
462 the complete raw dataset, which are not reproduced herein. The data are plotted in the form of a  
463 binding isotherm,  $[\text{AmHA}]$  (in  $\text{mol kg}_{\text{HA}}^{-1}$ ) versus  $[\text{Am}]_{\text{tot,f}}$  (in  $\mu\text{m}$ ), for each  $I$  on Figure 2a. Note  
464 that the experimental data for  $[\text{Am}]_{\text{tot,f}} > 8$   $\mu\text{m}$ , which are only available for  $0.1$  and  $3.5$   $m$ , are not

465 shown for clarity. In addition, the two separate series of experiments in  $I = 0.01, 0.1$  and  $1\text{ m}$   
466 cannot be visually distinguished on Figure 2a. All the isotherms exhibit a plateau at  $\sim 1\text{ mol kg}_{\text{HA}}^{-1}$   
467 <sup>1</sup>. However, a linear decrease of the  $LC$  was observed with  $\sqrt{I}$ . For  $I < 1\text{ m}$ ,  $\log^{\text{HA}}\beta_{\text{LC}}$  was shown  
468 to decrease, whereas it increased for  $I > 1\text{ m}$ , although in all cases the maximum variation in  $\log$   
469  $\beta_{\text{LC}}$  is relatively small. Accordingly, the original authors reported an average value of  $\log$   
470  $\beta_{\text{LC}} = 6.24 \pm 0.14$ . Below, we test the capabilities of Model VII and NICA-Donnan to predict  
471 the effect of the ionic strength on  $\log^{\text{HA}}\beta_{\text{LC}}$  and  $LC$  for data from Czerwinski et al. (1996). To do  
472 so, simulations are made with Model VII and NICA-Donnan under the same conditions as those  
473 studied by Czerwinski et al. (1996). The model results are then treated using the equations of the  
474 CNM.

475 The results of the simulations with Model VII are shown on Figure 2a, where the  
476 measured and simulated Am-HA binding isotherms for various  $I$  are compared. Some  
477 discrepancies (either underestimation or overestimation of the model) are observed, which we  
478 attribute to the use of generic Model VII parameters and will not be further discussed. As  
479 observed experimentally, Model VII predicts decreasing Am-HA complexation with increasing  $I$   
480 from  $0.01$  to  $1\text{ m}$ . However, unlike the experimental results, Am-HA complexation is predicted to  
481 increase as ionic strength increases from  $1\text{ m}$  to  $3.5\text{ m NaClO}_4$ . Because Model VII is used as a  
482 non-electrostatic model ( $\Psi_0 = 0$ ) for  $I \geq 1\text{ m}$ , the discrepancy between the experimental data and  
483 the model results can best be explained by changes in the activity coefficient of  $\text{Am}^{3+}$ , which  
484 increases between  $1$  and  $3.5\text{ m NaClO}_4$  according to SIT ( $\varepsilon(\text{Am}^{3+}, \text{ClO}_4^-) = 0.49\text{ kg mol}^{-1}$ ;  
485 Guillaumont et al., 2003), as anticipated in eq.1 and eq.16.



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**Figure 2.** (a) Experimental Am-HA binding isotherms of Czerwinski et al. (1996) for  $\text{pH}_m = 6$  and  $m_{\text{NaClO}_4} = 0.01, 0.1, 1$  and  $3.5$  m (symbols) compared with simulations using Model VII (lines). Experimental (b)  $\log^{\text{HA}} \beta_{\text{LC}}$  and (c) loading capacity ( $LC$ ) values for Am compared with Model VII and NICA-Donnan predictions versus  $I$  ( $\text{NaClO}_4$ ) in the experimental conditions of Czerwinski et al. (1996). Experimental error bars are generally smaller than the symbols.

494 Although Model VII accounts for HA heterogeneity, over a limited range of  $[Am]_{tot}$ , the  
495 model Am-HA isotherm can be approximated by a Langmuir-type isotherm. With this  
496 approximation, simulations of Am-HA binding with Model VII are treated according to the CNM  
497 equations (given in detail in Czerwinski et al., 1996) to determine  $^{HA}\beta_{LC}$  and  $LC$ . The results are  
498 plotted, respectively, on Figure 2b and 2c. Within the CNM formalism, Model VII consistently  
499 predicts a decrease of both  $LC$  and  $^{HA}\beta_{LC}$  with increasing  $I$  from 0.01 and 1  $m$ . The increasing  
500 activity of  $Am^{3+}$  between 1 and 3.5  $m$   $NaClO_4$  leads to an apparent increase of both  $LC$  and  $^{HA}\beta_{LC}$ .  
501 Overall, the effect of  $I$  predicted by Model VII is consistent with the experimental observations  
502 although the variations in  $LC$  and  $^{HA}\beta_{LC}$  values are larger, as already pointed out. The same  
503 exercise with NICA-Donnan yields  $LC$  and  $^{HA}\beta_{LC}$  that are also shown in Fig. 2b,c. Although  $LC$   
504 and  $^{HA}\beta_{LC}$  values obtained with NICA-Donnan are lower and higher than the experimental values,  
505 respectively, the effect of  $I$  is generally well predicted. Unlike Model VII, NICA-Donnan predicts  
506 decreasing Am-HA complexation between 1 and 3.5  $m$   $NaClO_4$  because the change in  $\gamma_{Am^{3+}}$   
507 cannot compensate for the increase in  $\Psi_D$  with increasing  $I$ , according to NICA-Donnan  
508 equations (i.e. based on  $Am^{3+}$  concentrations).

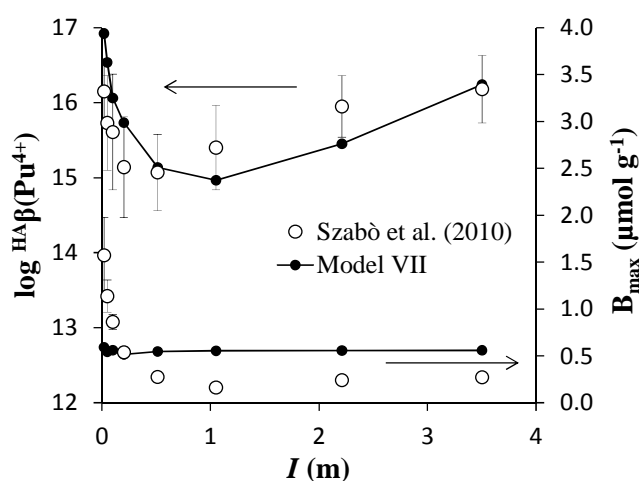
509 **Pu(IV).** A further example that can be analyzed in the present context is the study by  
510 Szabò et al. (2010) on Pu(IV) complexation to a HA grafted silica gel ( $HA = 20 \text{ mg g}^{-1}$ ) at  $pH = 4$   
511 and  $0.02 < I < 3.5 \text{ m}$  ( $NaClO_4$ ). To our knowledge, no Pu(IV)-HA binding parameters are  
512 available for NICA-Donnan, and hence, only Model VII can be discussed. The Pu(IV)-HA  
513 binding parameters for Model VII are taken from Marsac et al. (2014). Preliminary calculations  
514 showed that the formation of polynuclear Pu(IV) species in the presence of HA (Marsac et al.,  
515 2014) is not expected for the experimental conditions studied by Szabò et al. (2010). Marsac et al.  
516 (2014) used a DLM to account for electrostatic effects when coupling PHREEQC and Model VII,

517 but the surface area of HA was adjusted to obtain results similar to the original version of Model  
518 VII. Here, the same results are obtained when using the CCM to account for electrostatic effects.  
519 A modeling approach similar to that used for Am is applied to Pu (Fig. 3). Simulations were  
520 performed with Model VII for conditions comparable to those studied by Szabò et al. (2010). The  
521 simulated Pu-HA binding isotherms for each ionic strength are treated according to the equations  
522 given in the latter study to determine the maximal binding capacity of the HA grafted silica gel  
523 for Pu ( $B_{\max}$ ) and  $\log^{HA}\beta(\text{Pu}^{4+})$ . The calculations include the side reaction coefficient for Pu(IV)  
524 (i.e., eq. 4), and the Pu(IV) hydrolysis constants and SIT parameters employed by Szabò et al.  
525 (2010), which were originally obtained from Guillaumont et al. (2003). It is important to note that  
526 Pu(IV) exhibits strong hydrolysis and that, at pH = 4,  $\alpha_{Pu}$  varies with  $I$  because of ionic strength  
527 effects on conditional Pu(IV) hydrolysis constants.

528 Simulations with Model VII are compared to the experimental results of Szabò et al.  
529 (2010) in Figure 3. The experimental  $B_{\max}$  decreases with increasing  $I$  up to  $I = 0.5\text{ m}$  and  
530 thereafter remains nearly constant up to  $I = 3.5\text{ m}$ . Model VII predicts little variation in  $B_{\max}$  with  
531 ionic strength (i.e., predicted  $B_{\max}$  ranges between  $0.52\text{-}0.59\ \mu\text{mol g}^{-1}$ ), in contrast to variation of  
532 the experimental results ( $0.16\text{-}1.57\ \mu\text{mol g}^{-1}$ ), and to the modeled  $\text{LC}_{\text{Am(III)}}$  variations. Differences  
533 between modeling results for  $\text{Am}^{3+}$  and  $\text{Pu}^{4+}$  likely arise either from the different metal loadings  
534 investigated ( $[\text{Am(III)-HA}] \leq 1$  and  $[\text{Pu(IV)-HA}] \leq 3 \times 10^{-2}\ \text{mol kgHA}^{-1}$ ), which has an impact on  
535 HA charge, because  $\text{Pu}^{4+}$  and  $\text{Am}^{3+}$  show different hydrolysis behavior, or because HA grafted  
536 silica gel behaves differently than dissolved HA. Presently, we cannot explain the discrepancies  
537 between experimental and model results for  $\text{Pu}^{4+}$ . Nevertheless, the predicted variation in  $B_{\max}$   
538 falls within the experimental range reported by Szabò et al. (2010) so that the impact on the  
539 prediction of overall  $\text{Pu}^{4+}$ -HA binding is limited. Experimental and simulated  $\log^{HA}\beta(\text{Pu}^{4+})$   
540 values are also shown in Figure 3. Generally good agreement is found between the experimental

541 and predicted  $\log^{\text{HA}}\beta(\text{Pu}^{4+})$  values (Fig. 3), i.e., a decrease up to  $I = 1\text{ m}$  followed by an increase  
 542 up to  $3.5\text{ m}$ . The differences are about  $\pm 0.5$  log units for the stability constant. For  $\Psi_0 = 0$  (i.e., for  
 543  $I > 1\text{ m}$ ), the increase in  $\log^{\text{HA}}\beta(\text{Pu}^{4+})$  between  $I = 1$  and  $3.5\text{ m}$  is due to  $\alpha_{\text{Pu}}$ , which increases by  
 544  $0.84$  log units over this range of  $I$  at  $\text{pH} = 4$ . Indeed, according to the SIT model,  $[\text{Pu}^{4+}]$  decreases  
 545 with increasing  $I$  because of the formation of its hydrolysis products (i.e. the  $\sum_h \frac{\beta_h}{m_{\text{H}^+}^h}$  term  
 546 increases in eq. 4). This phenomenon is not observed with  $\text{Am}^{3+}$  because its hydrolysis can be  
 547 neglected at  $\text{pH} = 6$  and  $0 < I < 4\text{ m}$ .

548



549  
 550 **Figure 3.** Experimental binding capacity ( $B_{\text{max}}$ ) and  $\log^{\text{HA}}\beta(\text{Pu}^{4+})$  values of Szabò et al. (2010)  
 551 versus  $I$  ( $\text{NaClO}_4$ ) compared with Model VII predictions. Arrows refer to the y-axis  
 552 corresponding to the data. Experimental error bars for  $B_{\text{max}}$  are generally smaller than the  
 553 symbols.

554

555

### 556 3.4. Cation-HA complexation in NaCl solutions

557 In a number of laboratory studies, Choppin and co-workers (Labonne-Wall et al., 1999;  
558 Kurk and Choppin, 2000; Laszak and Choppin, 2001; Wall et al., 2002) investigated  $U^{VI}O_2^{2+}$ ,  
559  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Ca^{2+}$  and  $Am^{3+}$  complexation with HA in  $m_{NaCl}$  solutions by solvent extraction  
560 methods in ambient (air) atmosphere. A summary of the experimental conditions is given in  
561 Table 1. Only data within the applicability of SIT ( $I < 4 m$ ) are considered in the present study.  
562 Although  $Cl^-$  is clearly a more relevant background anion than  $ClO_4^-$  in the environment, the  
563 interpretation of M-HA complexation data obtained for high  $m_{NaCl}$  are more difficult because,  
564 unlike  $ClO_4^-$ ,  $Cl^-$  is a complexing anion, albeit, a weak one. In addition, the Am- and U(VI)-HA  
565 experiments were carried out in the presence of 0.01 M acetate buffer. Acetate is known to bind  
566 to metal ions and must therefore be taken into account in the calculations (Labonne-Wall et al.,  
567 1999; Wall et al., 2002). Finally, unlike the other cations, for  $pH_m \approx 5$  under ambient (air)  
568 atmosphere,  $UO_2^{2+}$  hydrolysis and complexation by carbonate anions cannot be neglected  
569 (Langmuir, 1978; Labonne-Wall et al., 1999). Therefore, M-HA complexation datasets obtained  
570 for high  $m_{NaCl}$  are less suitable for testing the applicability of NICA-Donnan and Model VII than  
571 experiments conducted in a more inert background electrolyte such as  $NaClO_4$ . Indeed, it was  
572 found that the modeling results discussed below strongly depend on the thermodynamic  
573 databases in solution and their respective capabilities to accurately handle the speciation of  $Am^{3+}$ ,  
574  $UO_2^{2+}$ ,  $Ni^{2+}$ ,  $Co^{2+}$  and  $Ca^{2+}$  in saline solutions, even in the absence of HA.

575

576

577 **Table 1.** Summary of the experimental conditions for the M-HA complexation experiments of  
 578 Wall et al. (2002) ( $\text{Am}^{3+}$ ), Labonne-Wall et al. (1999) ( $\text{UO}_2^{2+}$ ), Kurk and Choppin (2000) ( $\text{Co}^{2+}$   
 579 and  $\text{Ni}^{2+}$ ) and Laszak and Choppin (2001) ( $\text{Ca}^{2+}$ ).

	[M] (mol L <sup>-1</sup> )	[HA] (mg L <sup>-1</sup> )	$m_{\text{NaCl}}$ (m)	pH	pH buffer
$\text{Am}^{3+}$	$1 \times 10^{-9}$	1 - 10	0.1 - 6	5.1 (pH <sub>m</sub> )	10 <sup>-2</sup> M acetate
$\text{UO}_2^{2+}$	$5.24 \times 10^{-7}$	2 - 10	0.1 - 6	4.9 (pH <sub>m</sub> )	10 <sup>-2</sup> M acetate
$\text{Ni}^{2+}$	$1 \times 10^{-9}$	$2 \times 10^{-3}$ - $1.6 \times 10^{-2}$	0.3 - 5	6.0 (pH <sub>exp</sub> )	No
$\text{Co}^{2+}$	$1 \times 10^{-10}$	$1.3 \times 10^{-2}$ - $2.2 \times 10^{-1}$	0.3 - 5	6.0 (pH <sub>exp</sub> )	No
$\text{Ca}^{2+}$	$1 \times 10^{-8}$	0 - 500	0.1 - 3	4.5 - 9.5 (pH <sub>m</sub> )	No

580  
 581  
 582 The reported M-HA complexation constants pertain to the PM (Labonne-Wall et al.,  
 583 1999; Kurk and Choppin, 2000; Laszak and Choppin, 2001; Wall et al., 2002). For the studies  
 584 listed in Table 1,  $\alpha_{\text{HA}}$  values were determined for each pH and  $I$  from HA proton titrations for the  
 585 specific metal ion-HA complexation studies. Because NICA-Donnan and Model VII are able to  
 586 describe M-HA complexation as a function of the pH, it is more convenient to compare  
 587 experimental constants that have not been corrected for  $\alpha_{\text{HA}}$ . This can be easily accomplished  
 588 because all of these studies focused on low metal loadings, where [MHA] can be neglected in eq.  
 589 6 (i.e.,  $[\text{HA}]_{\text{f}} \approx [\text{HA}]_{\text{tot}} \times \alpha_{\text{HA}}$ ). Note that the carboxylic groups of HA were considered  
 590 responsible for M-HA complexation and only these groups were considered in the calculation of  
 591  $[\text{HA}]_{\text{tot}}$  (eq. 5-6) (Labonne-Wall et al., 1999; Laszak and Choppin, 2001; Wall et al., 2002).  
 592 Labonne-Wall et al. (1999) and Wall et al. (2002) reported 1:1 and 1:2  $\text{UO}_2^{2+}/\text{Am}^{3+}$ -HA  
 593 complexation constants. Because, the constants show similar variation with  $I$ , either for  $\text{UO}_2^{2+}$  or  
 594  $\text{Am}^{3+}$ , the 1:2 complexes are not discussed here and the simulations are made for the lowest [HA]  
 595 investigated experimentally (i.e., where the 1:1 complex prevails).

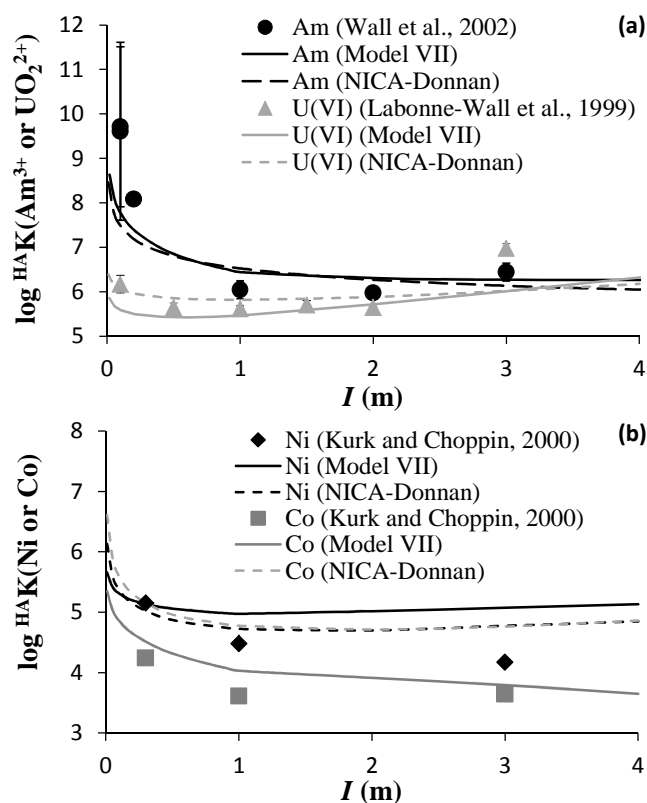
596 **Am(III).** Wall et al. (2002) investigated the effect of NaCl on Am-HA complexation for  
 597 pH<sub>m</sub> = 5.1 in 0.01 M acetate buffer. Although constants were corrected for effects of side

598 reactions, such as the formation of  $\text{Am}^{3+}$ -acetate complexes (eq. 4), Am-Cl complexation was not  
599 taken into account by the original authors. Side reaction corrections for the formation of  $\text{Am}^{3+}$ -  
600 acetate complexes employed stability constants reported by Moore et al. (1999).

601 Our simulations using Model VII and NICA-Donnan are for the lowest HA concentration  
602 ( $[\text{HA}] = 1 \text{ mg L}^{-1}$ ). Preliminary calculations showed that Am-Cl and Am-acetate complexation  
603 have no more than a minor impact on the trend in  $^{\text{HA}}\text{K}(\text{Am}^{3+})$  versus  $I$ . Experimental and  
604 simulated results (now accounting for Am-Cl complexation) are compared on Figure S5. Good  
605 prediction of  $\text{Am}^{3+}$ -HA binding is obtained by both models using generic parameters for  $I = 0.1$   
606 m, where experimental uncertainty is relatively large, whereas data for all other  $I$  are  
607 overestimated (see Fig. S5). To better compare experimental and simulated effects of  $I$  on  
608  $^{\text{HA}}\text{K}(\text{Am}^{3+})$ , model results were decreased by 1.5 log unit on Figure 4a. In fact, the adjustment of  
609 Am-HA binding parameters would produce the same results. When using the generic Am-HA  
610 binding parameters, both models produce similar results, especially for the evolution of log K  
611 with  $I$ , as would be expected from the similar variation of  $\Psi_0$  and  $\Psi_D$  with  $I$  (Fig. 1a). Although  
612 model log  $^{\text{HA}}\text{K}(\text{Am}^{3+})$  values variations with  $I$  are not as pronounced as experimental ones, the  
613 trend is consistent. Nearly constant log  $^{\text{HA}}\text{K}(\text{Am}^{3+})$  values are predicted for  $I > 1 \text{ m}$  by both  
614 approaches, which agrees relatively well with the experimental results. Unlike Model VII (where  
615  $\Psi_0 = 0$  for  $I > 1 \text{ m}$ ), NICA-Donnan predicts a slight decrease of  $^{\text{HA}}\text{K}(\text{Am}^{3+})$  for  $I > 1 \text{ m}$ . This is  
616 related to the evolution of  $\Psi_D$  with  $I$ , and the fact that NICA-Donnan equations do not account for  
617  $\gamma_{\text{Am}^{3+}}$ . Overall, the deviation between both models is small, as expected (Fig. 1a), showing that,  
618 by accounting for electrostatic effects, results from Model VII and NICA-Donnan can be  
619 extrapolated to highly saline conditions, provided that the specific binding parameters are  
620 calibrated for the respective type of HA.

621 **U(VI)**. Labonne-Wall et al. (1999) investigated the effect of  $I$  on U(VI)-HA complexation  
622 for  $\text{pH}_m = 4.9$  and 0.01 M acetate.  $\text{UO}_2^{2+}$ -acetate complexation constants were taken from Moore  
623 et al. (1999) and are also presently used. We simulated the experimental data of Labonne-Wall et  
624 al. (1999) using Model VII and NICA-Donnan for the lowest HA concentration ( $[\text{HA}] = 2 \text{ mg L}^{-1}$ )  
625 and the generic U(VI)-HA binding parameters. As for Am, preliminary tests showed that  
626 inclusion or omission of  $\text{UO}_2^{2+}$ -Cl complexation did not impact the trend in  $^{\text{HA}}\text{K}(\text{UO}_2^{2+})$  versus  $I$ .  
627 Experimental and simulated results are compared on Figure 4a. The generic U(VI)-HA  
628 parameters produce accurate predictions of the  $^{\text{HA}}\text{K}(\text{UO}_2^{2+})$  measured by Labonne-Wall et al.  
629 (1999) as well as the evolution of  $^{\text{HA}}\text{K}(\text{UO}_2^{2+})$  with  $I$  up to 2  $m$ . At  $I = 3 m$ , a higher  $^{\text{HA}}\text{K}(\text{UO}_2^{2+})$   
630 value than at  $I = 2 m$  was measured, which is also predicted by Model VII. As in the case of  $\text{Pu}^{4+}$ ,  
631 where the apparent hydrolysis constants increase with  $m_{\text{NaClO}_4}$  above 1  $m$ , this increase in  
632  $^{\text{HA}}\text{K}(\text{UO}_2^{2+})$  is driven by  $\alpha_{\text{U(VI)}}$ . Similar conclusions can be made with NICA-Donnan, except a  
633 smaller re-increase in  $^{\text{HA}}\text{K}(\text{UO}_2^{2+})$  that was observed with increasing  $I$ , as seen and explained for  
634  $\text{Am}^{3+}$ . Interestingly, in agreement with the experimental data, Model VII and NICA-Donnan  
635 predict a more pronounced decrease in  $^{\text{HA}}\text{K}(\text{Am}^{3+})$  than for  $^{\text{HA}}\text{K}(\text{UO}_2^{2+})$  when  $I$  increases from 0  
636 to 1  $m$ . This feature is driven by the Boltzman factor (eq. 9), which involves the net charge of the  
637 cation (i.e. +3 versus +2, respectively) for Am(III) and U(VI).

638



639  
 640 **Figure 4.** (a) Apparent Am-HA and U(VI)-HA complexation constants (Wall et al., 2002;  
 641 Labonne-Wall et al., 1999) versus  $I$  (NaCl) for  $\text{pH}_m = 5.1$  and  $4.9$ , respectively. (b) Apparent M-  
 642 HA complexation constants ( $M = \text{Ni}^{2+}$  or  $\text{Co}^{2+}$ , Kurk and Choppin, 2000) versus  $I$  (NaCl) for  
 643  $\text{pH}_{\text{exp}} = 6$ . For both figures, lines are predictions by Model VII (full line) and NICA-Donnan  
 644 (dashed lines) using the generic parameters (but shifted down for the case of Am-HA, see text for  
 645 details). Experimental error bars are commonly smaller than the symbols.

646  
 647 **Co(II)/Ni(II).** Kurk and Choppin (2000) investigated the effect of  $I$  on Co- and Ni-HA  
 648 complexation. Unlike Am and U(VI), with data obtained for constant  $\text{pH}_m$ , Co and Ni data are  
 649 reported for constant  $\text{pH}_{\text{exp}} = 6$  by Kurk and Choppin (2000), noting that the deviation between  
 650  $\text{pH}_{\text{exp}}$  and  $\text{pH}_m$  increases with increasing  $I$ . For example, for  $\text{pH}_{\text{exp}} = 6$  and  $I = 4$  m, and with the  
 651 calibration provided by the original authors, the corresponding  $\text{pH}_m$  value is 6.95. The originally  
 652 reported constants were not corrected for side reactions. Again, our simulations using Model VII

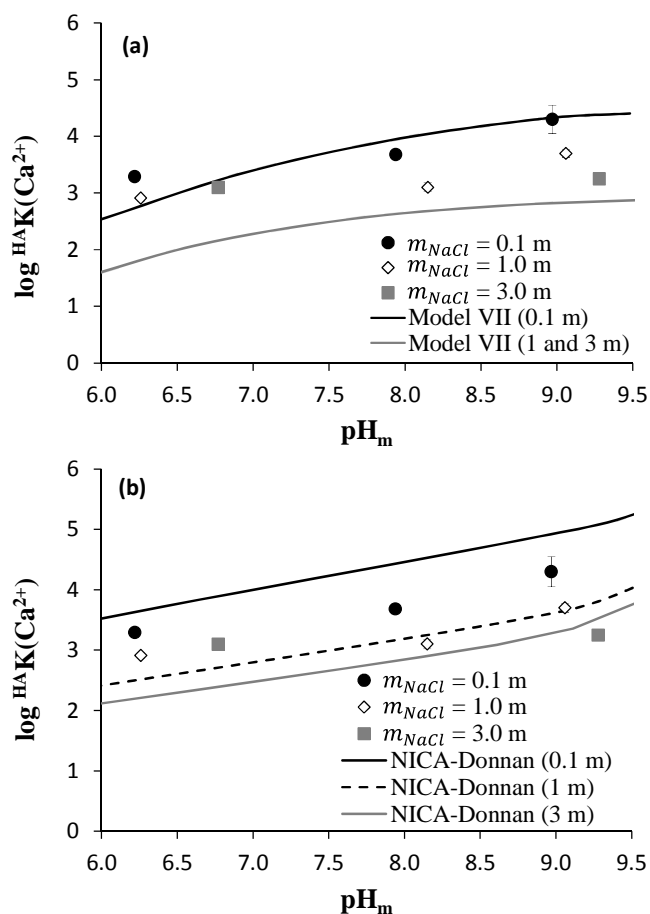
653 and NICA-Donnan were conducted using the lowest HA concentrations reported by Kurk and  
 654 Choppin (i.e.,  $[HA] = 1.3 \times 10^{-2} \text{ mg L}^{-1}$  for Co;  $[HA] = 2 \times 10^{-3} \text{ mg L}^{-1}$  for Ni).

655 Experimental and simulated results are compared on Figure 4b. With the generic Co/Ni-  
 656 HA parameters, Model VII overestimates Co/Ni-HA complexation by 1 log unit in the worst case  
 657 (i.e., for  ${}^{\text{HA}}K(\text{Ni})$  at  $I = 3 \text{ m}$ ). Model VII consistently predicts a decrease in  ${}^{\text{HA}}K$  with  $I$  increasing  
 658 from 0.3 to 1  $m$ , whereas for  $I > 1 \text{ m}$ , the predicted  ${}^{\text{HA}}K$  for Co and Ni diverge. Although  $\text{pH}_m$   
 659 increases by 0.6 units (for constant  $\text{pH}_{\text{exp}}$ ) between  $I = 1$  and 3  $m$ ,  ${}^{\text{HA}}K(\text{Ni})$  remains almost  
 660 constant, whereas  ${}^{\text{HA}}K(\text{Co})$  decreases by 0.2 log units. These variations reflect the complexation  
 661 of both of these transition metals by  $\text{Cl}^-$  in solution. In the SIT database provided with  
 662 PHREEQC, only the  $\text{NiCl}^+$  species is included, with  $\epsilon(\text{NiCl}^+; \text{Cl}^-) = 0.1$ , whereas four Co-Cl  
 663 complexes are considered (i.e., from  $\text{CoCl}^+$  to  $\text{CoCl}_4^{2-}$ ), all without SIT parameters (i.e.  $\epsilon(i;k) =$   
 664 0). In the SIT database provided with Visual MINTEQ, Co- and Ni-Cl complexation are  
 665 described similarly and NICA-Donnan predicts the same trend in  ${}^{\text{HA}}K(\text{Ni})$  and  ${}^{\text{HA}}K(\text{Co})$  versus  $I$ .  
 666 The reliability of the thermodynamic aqueous databases is beyond the scope of the present paper.  
 667 Nonetheless, despite the potential uncertainties in the databases, overall, the predicted effect of  $I$   
 668 is relatively small above 1  $m$  for both Ni and Co, in agreement with the experimental results.

669 **Ca(II).** Figure 5 shows  ${}^{\text{HA}}K(\text{Ca}^{2+})$  measured by Laszak and Choppin (2001) for  $m_{\text{NaCl}} =$   
 670 0.1, 1 and 3  $m$  at various  $\text{pH}_m$  under ambient atmosphere. The originally reported constants were  
 671 corrected for side reactions (including Ca complexation to chloride and carbonate). Simulations  
 672 are made with Model VII and NICA-Donnan for  $100 \text{ mg L}^{-1}$  HA using the generic Ca-HA  
 673 binding parameters and compared to experimental  $\log {}^{\text{HA}}K(\text{Ca}^{2+})$  versus  $\text{pH}_m$  for  $I = 0.1$  and 3  $m$   
 674 (NaCl) in Figure 5. Simulations with Model VII for  $I = 1 \text{ m}$  do not significantly differ from  $I = 3$   
 675  $m$  and consequently are not shown. Experimentally,  ${}^{\text{HA}}K(\text{Ca}^{2+})$  increases with  $\text{pH}_m$  and decreases  
 676 with increasing  $I$ , as for the other cations investigated. Both Model VII (Fig. 5a) and NICA-

677 Donnan do a relatively good job at predicting these trends, although the measured effect of  $I$  is  
678 weaker between 0.1 and 1  $m$ , and  $\log {}^{\text{HA}}\text{K}(\text{Ca}^{2+})$  are not predicted to evolve substantially for  $I$   
679 between 1 and 3  $m$  with Model VII. Interestingly, the measured effect of  $I$  appears more  
680 pronounced for  $\text{pH}_m \approx 9$  than for  $\text{pH}_m \approx 6.5$ , which is indeed predicted by both models as  
681 anticipated (eq.16). According to the models, the larger negative charge of HA ( $Q$  being  
682 proportional to  $\Psi_0$  or  $\Psi_D$ ) at high pH is responsible for the larger ionic strength dependence of  
683  ${}^{\text{HA}}\text{K}(\text{Ca}^{2+})$ .

684 To summarize, beside the deviations between experimental and simulated results that are  
685 directly related to the parameterization of  $\text{Am}^{3+}/\text{UO}_2^{2+}/\text{Co}^{2+}/\text{Ni}^{2+}/\text{Ca}^{2+}$ -HA complexation for a  
686 specific type of HA, the generally observed  $\log {}^{\text{HA}}\text{K}(\text{M}^{Z+})$  dependence with  $I$  is relatively well  
687 predicted at low metal ion concentration by simply suppressing the electrostatic term in Model  
688 VII for  $I > 1 m$ . The NICA-Donnan model shows very similar results without the need to modify  
689 the model. More experimental results are required, however, to parameterize these models at high  
690  $I$  and to test the relevance of additional corrections at high  $I$  to explain the noted discrepancies,  
691 which would make the models more complex. More specifically, complexation studies in non-  
692 complexing background electrolyte (e.g.,  $\text{NaClO}_4$ ) in the absence of pH-buffer (e.g., without  
693 acetate) and under inert atmosphere (i.e., in the absence of carbonate) are recommended.



694  
 695 **Figure 5.** Experimental apparent  $\text{Ca}^{2+}$ -HA complexation constants versus  $\text{pH}_m$  for  $I = 0.1, 1$  and  
 696  $3 \text{ m NaCl}$  (Laszak and Choppin, 2001) compared with (a) Model VII (simulated curves for  $I = 1$   
 697 and  $3 \text{ m NaCl}$  overlap) and (b) NICA-Donnan predictions. Experimental error bars are commonly  
 698 smaller than the symbols on all three figures.

699

### 700 3.5. Metal ion-HA complexation using SIT

701 To apply simple models such as the PM or the CNM to various ionic strength solutions,  
 702 they must include the activities of the aqueous species. According to equations 1 and 3, when all  
 703 physico-chemical conditions are kept constant except  $I$  ( $\text{pH}$ ,  $T$ , total metal ion concentration), the  
 704 value of  $\log \beta$  (i.e.  $\log {}^{\text{HA}}K$ ,  $\log {}^{\text{HA}}\beta_{\alpha}$ , or  $\log {}^{\text{HA}}\beta_{\text{LC}}$ ) can be extrapolated to  $I = 0$  ( $\log \beta_0$ ) using:

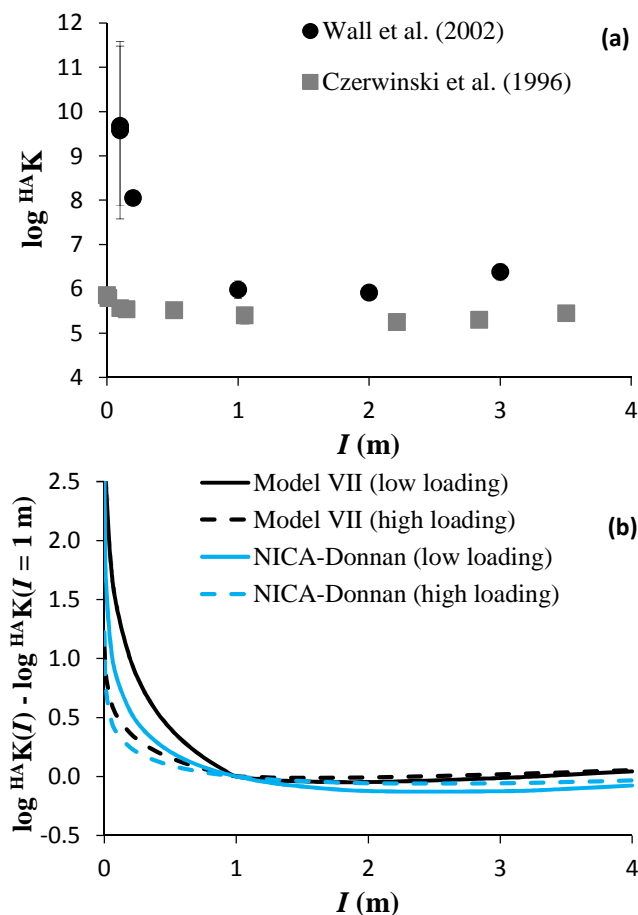
$$\log \beta = \log \beta_0 - \Delta z^2 \times D - \Delta \varepsilon \times I. \quad (17)$$

705 For 1:1 complexes between a metal ion ( $M^z$ ) and a simple ligand ( $L^y$ ),  $\Delta\varepsilon = \varepsilon(ML^{y+z},k) - \varepsilon(M^z,k) -$   
706  $\varepsilon(L^y,k)$ , and  $\Delta z^2 = (z+y)^2 - z^2 - y^2$ . Due to the complexity of HA,  $\Delta z^2$  and  $\Delta\varepsilon$  become adjustable  
707 parameters of unclear physical meaning (Czerwinski et al., 1996; Szabò et al., 2010).

708 Comparing Fig. 2b and Fig. 4a, the effect of  $I$  on Am-HA complexation appears to differ  
709 between the studies of Wall et al. (2002) and Czerwinski et al. (1996), but it is difficult to directly  
710 compare the original datasets because: (i) the thermodynamic constants refer to different models;  
711 (ii)  $\text{pH}_m$  differs by one unit; and (iii) the metal loading differs by 3 orders of magnitude. As in  
712 Figure 4a for the  $\log^{HA}K$  values reported by Wall et al. (2002),  $\log^{HA}\beta_{LC}$  values determined by  
713 Czerwinski et al. (1996) are recalculated to  $\log^{HA}K$  values using the  $LC$  values and imposing  
714 negligible  $[AmHA]$  in eq. 8. The results are shown in Figure 6a. Although Wall et al. (2002)  
715 studied Am-HA complexation at one  $\text{pH}_m$  unit lower than Czerwinski et al. (1996), their  $\log^{HA}K$   
716 values are higher. This can be attributed to the effect of the metal loading. Specifically, at low  
717 loading, Am binds to low abundance, strong HA sites, whereas, at high loading, these sites are  
718 saturated and Am mainly binds to the more abundant, weaker HA sites (e.g., see Marsac et al.,  
719 2010). The effect of  $I$  below 1  $m$  is more pronounced for the dataset of Wall et al. (2002), which  
720 would lead to different SIT parameters ( $\Delta z^2$  and  $\Delta\varepsilon$ ) in eq. 17. Therefore, it is difficult to  
721 confidently apply an ionic strength correction for cation-HA binding constants using simple  
722 metal ion-HA binding models.

723 The different ionic strength effects observed by Wall et al. (2002) and Czerwinski et al.  
724 (1996) might also arise from differences in metal loading. As pointed out by Hummel et al.  
725 (2000), ionic strength effects tend to vanish at high loadings. To illustrate this,  $\log^{HA}K$  values for  
726 Am-HA complexation are calculated using both Model VII and NICA-Donnan for  $\text{pH} = 5.5$ ,  $10^{-3}$   
727  $< I < 4 m$  (NaCl),  $1 \text{ mg L}^{-1}$  HA, and  $[Am]_{\text{tot}} = 10^{-9}$  or  $10^{-6} m$ . The results are normalized to the  $\log$

728  $^{\text{HA}}\text{K}$  value obtained for  $I = 1 \text{ m}$  (i.e.  $\log ^{\text{HA}}\text{K}(I) - \log ^{\text{HA}}\text{K}(I = 1 \text{ m})$ ) and plotted versus  $I$  in Figure  
 729 6b. Both models indeed predict a more pronounced effect of  $I$  on  $\log ^{\text{HA}}\text{K}$  at low loading.



730  
 731 **Figure 6.** (a) Experimentally observed effect of the ionic strength on Am-HA complexation at  
 732 low (Wall et al., 2002;  $\text{pH}_m = 5.1$ ; NaCl) and high metal loading (Czerwinski et al., 1996;  $\text{pH}_m =$   
 733 6;  $\text{NaClO}_4$ ). (b) Simulated effect of the ionic strength on Am-HA complexation at low ( $[\text{Am}]_{\text{tot}} =$   
 734  $10^{-9} \text{ m}$ ) and high metal loading ( $[\text{Am}]_{\text{tot}} = 10^{-6} \text{ m}$ ) with Model VII (black curves) and NICA-  
 735 Donnan (blue curves) in NaCl for a HA concentration of  $1 \text{ mg L}^{-1}$  and  $\text{pH} = 5.5$ . (For  
 736 interpretation to references to color, the reader is referred to the web version of this article.)  
 737

738 The effect of  $I$  on cation-HA complexation is commonly discussed in terms of  
 739 conformational changes, which make the physical meaning of the values of SIT parameters in the  
 740 case of humic materials questionable. Multivalent ions are known to bridge between organic

741 molecules (Kunhi Mouvenchery et al., 2012), and high concentrations of trivalent actinides lead  
742 to the aggregation of HA (Lippold et al., 2005). Hence, the different evolution of  $\log^{HA}K$  with  $I$   
743 observed by Wall et al. (2002) and Czerwinski et al. (1996) may be partially attributed to the  
744 aggregation state (or the conformation) of HA in response to different  $[Am]$  to  $[HA]$  ratios. In  
745 Model VII, conformational changes of HA in response to variations of  $I$  are not explicitly treated,  
746 except via a change in Donnan volume, which we find to have a negligible effect on M-HA  
747 complexation in saline solutions. Because the charging behavior of HA is related to its  
748 conformation, such behavior can implicitly be taken into account within the electrostatic term. In  
749 NICA-Donnan, the ionic strength directly affects the Donnan volume. However, none of these  
750 models includes effects of conformational changes of HA when  $[Am]_{tot}$  increases (e.g., in the  
751 case of NICA-Donnan,  $10^{-6}$  m of Am would not affect the Donnan volume), by contrast with the  
752 more recent Elastic Polyelectrolyte Network electrostatic model (Montenegro et al., 2014).  
753 Instead, NICA-Donnan and Model VII explain the less pronounced effect of  $I$  at increased  
754 loading via the charging behavior of HA. In the experiments of Czerwinski et al. (1996), the  
755 observed  $LC$  ranges between 50 and 70% of the PEC. The charge of HA is almost neutralized by  
756 Am at the highest  $[Am]_{tot}$  investigated, which decreases electrostatic effects and flattens the  $\log$   
757  $^{HA}K$  versus  $I$  curve. Therefore, metal loading is an important parameter not only for the  
758 determination of apparent metal ion-HA complexation constants for given pH and  $I$  conditions,  
759 but also for their extrapolation to various ionic strengths (e.g., with SIT).

760 Unlike Na, with non-specific HA interaction, Ca and Mg bind more strongly to HA, and  
761 consequently may affect the charge of HA in brines. Furthermore, other metal ions (e.g. Fe(III),  
762 Al(III), divalent transition metals) strongly bind to HA in natural conditions (Kinniburgh et al.,  
763 1999; Pinheiro et al., 2000; Tipping et al., 2002; Gustafsson et al., 2007; Marsac et al., 2012;  
764 2013). Hence, the metal loading must be defined on the basis of all cations bound to HA,

765 including  $H^+$ . Additional cation competition studies should be conducted at high  $I$  to improve and  
766 homogenize metal ion-HA binding models. As an example, in NICA-Donnan  $Ca^{2+}$  mainly  
767 interacts electrostatically with HA at high  $[Ca^{2+}]$  (Christl, 2012) whereas it chiefly binds  
768 specifically to HA in Model VII. As shown in Figure S6, Model VII predicts larger effects from  
769  $[Ca]$  on Am-HA complexation than does NICA-Donnan. For  $pH = 5$ ,  $1\text{ m NaCl}$ ,  $[Am] = 10^{-9}\text{ m}$   
770 and  $1\text{ mg L}^{-1}$  HA, between  $0$  and  $1\text{ m CaCl}_2$ , Model VII predicts a decrease of  $^{HA}K(Am)$  by  $1.5$   
771 log units against  $0.9$  using NICA-Donnan. These results highlight another source of variation and  
772 uncertainty for  $\Delta z^2$  and  $\Delta \epsilon$  at high  $[Ca]$ . Because it is also suggested that  $Ca^{2+}$ -HA interaction is  
773 purely electrostatic (van Leeuwen and Town, 2016),  $Ca^{2+}$ -metal ion competition experiments at  
774 high  $I$  are required to unravel the role of Ca on metal ion-HA complexation.

775 As shown above, the ionic strength dependence of  $^{HA}K(Ca^{2+})$  becomes more pronounced  
776 at high pH because of the higher charge of HA. It appears that  $\Delta z^2$  and  $\Delta \epsilon$ , when applied to  
777 simple models for M-HA complexation, remain conditional parameters, which depend on the pH,  
778 the ionic strength, and the composition of the solution, which in turn affects the loading of HA.  
779 Therefore, empirical determination of  $\Delta z^2$  and  $\Delta \epsilon$  for various conditions requires a large  
780 experimental dataset. Because most metal ion-HA binding data at  $I > 1\text{ m}$  were obtained at  $pH_m \leq$   
781  $6$ , data at higher pH would be necessary to further test the reliability of NICA-Donnan and Model  
782 VII.

783 More generally, the use of non-electrostatic models was recently shown to be particularly  
784 suitable for the prediction of metal ion sorption to various types of surfaces in brines, including  
785 marine microalgae (Schjif and Herbling, 2010; Zoll and Schjif, 2012), bacteria (Ams et al.,  
786 2013), illite and smectite (Schnurr et al., 2015). The present data evaluation suggests that this  
787 approach can be extended to humic substances using Model VII. Although NICA-Donnan

788 remains an electrostatic model in highly saline solution, the almost invariant Donnan potential  
789 produces similar ionic strength effects to those observed using Model VII.

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790

#### 4. Conclusions

791 The applicability of Model VII and NICA-Donnan was tested at high 1:1 background  
792 electrolyte concentration (NaCl/ClO<sub>4</sub>) in combination with SIT ( $I < 4 m$ ). The empirical  
793 electrostatic term used in Model VII is related to the constant capacitance model (CCM). A  
794 method is proposed to use the CCM in the speciation code PHREEQC, for easier and more  
795 consistent implementation of Model VII in this code. The electrostatic term used in this model  
796 tends towards zero for  $I = 1 m$ , and thus, further metal ion accumulation in the vicinity of HA  
797 molecules can be neglected. Consequently, a non-electrostatic model in combination with the  
798 binding site definition in Model VII was tested for  $I > 1 m$ . The approach simplifies the model  
799 under these high ionic strength conditions, whereas NICA-Donnan can be used without  
800 modification. Both models do a relatively good job in predicting proton dissociation for HA  
801 groups where the apparent pK<sub>a</sub> variations at high  $I$  are mainly controlled by the activity  
802 coefficient of the proton. The trend in apparent metal ion-HA complexation constants with  $I$  is  
803 consistent with experimental results for Am<sup>3+</sup>, UO<sub>2</sub><sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Ca<sup>2+</sup> and Pu<sup>4+</sup>, both at low and  
804 high metal loading. The maximum metal ion uptake by HA (e.g., the loading capacity) for  
805 various conditions is relatively well predicted. Because of the simple approaches used here and  
806 due to the limited number of datasets that are available for highly saline solutions, no attempt was  
807 made to improve the models in order to eliminate the discrepancies observed in the evolution of  
808 apparent complexation constants with  $I$ . Most of the discrepancies between experiments and  
809 predictions with Model VII or NICA-Donnan are related to the specific cation-HA binding  
810 parameters used. With appropriately calibrated specific binding parameters for a given type of  
811 HA (e.g. a given composition or origin), both models are expected to reliably predict cation-HA  
812 binding for a wide range of ionic strengths.

813           The impact of the physico-chemical conditions on the experimental determination of SIT  
814 parameters for metal ion-HA complexation was also discussed. When HA is treated as a simple  
815 dissolved ligand, the obtained SIT parameters values are difficult to interpret with regards to their  
816 specific physical meaning owing to the complexity of HA molecules. It is shown here that the  
817 experimentally investigated pH and metal loading variations have a strong impact on SIT  
818 parameters via their effect on the charge of HA. Some effects of pH and metal loading on cation-  
819 HA complexation are well known, but the present study shows that they imply additional effects  
820 related to HA charge, which must be taken into account when extrapolating constants at various  
821 ionic strengths. Unlike Na, which only interacts electrostatically with HA, Ca or Mg can bind  
822 more strongly to HA. Because, highly saline waters commonly have substantial Ca or Mg  
823 concentrations, as well as other metal ions, relatively high overall loadings are to be expected.  
824 Although Model VII and NICA-Donnan can account for both the metal loading effects and cation  
825 competition at  $I < 1$  m, additional cation competition experiments at high ionic strength are  
826 required to further validate or improve these models. Nevertheless, we suggest that both models  
827 might be used as helpful predictive tools in performance safety assessment even under highly  
828 saline conditions.

829

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- 1009

1010 **Table and figure captions:**

1011 **Table 1.** Summary of the experimental conditions for the M-HA complexation experiments of  
 1012 Wall et al. (2002) ( $\text{Am}^{3+}$ ), Labonne-Wall et al. (1999) ( $\text{UO}_2^{2+}$ ), Kurk and Choppin (2000) ( $\text{Co}^{2+}$   
 1013 and  $\text{Ni}^{2+}$ ) and Laszak and Choppin (2001) ( $\text{Ca}^{2+}$ ).

1014 **Figure 1.** a) Surface potential ( $\Psi_0$ ) and Donnan potential ( $\Psi_D$ ) calculated for Model VII and  
 1015 NICA-Donnan, respectively, for  $\text{pH} (= -\log a_{\text{H}^+}) = 5.5$  versus the ionic strength. The y-axis for  
 1016  $\Psi_D$  is shifted by 60 mV compared with the one of  $\Psi_0$  to highlight their similar evolution with  $I$ .  
 1017 (b) Activity coefficient of the proton ( $\log \gamma_{\text{H}^+}$ ) versus  $I$  in NaCl,  $\text{NaClO}_4$  and  $\text{NaNO}_3$  solutions,  
 1018 calculated with SIT. (c) HA charge versus  $\text{pH}_m$  in 0.1 M (black curve), 1 M (blue curve), and 3  
 1019 M (red curve) [0.1, 1.051, 3.503 m, respectively]  $\text{NaClO}_4$ . Points are experimental results of  
 1020 Maes et al. (1992) and lines are results from Model VII. (For interpretation to references to color,  
 1021 the reader is referred to the web version of this article.)

1022 **Figure 2.** (a) Experimental Am-HA binding isotherms of Czerwinski et al. (1996) for  $\text{pH}_m = 6$   
 1023 and  $m_{\text{NaClO}_4} = 0.01, 0.1, 1$  and 3.5 m (symbols) compared with simulations using Model VII  
 1024 (lines). Experimental (b)  $\log^{\text{HA}} \beta_{\text{LC}}$  and (c) loading capacity ( $LC$ ) values for Am compared with  
 1025 Model VII and NICA-Donnan predictions versus  $I$  ( $\text{NaClO}_4$ ) in the experimental conditions of  
 1026 Czerwinski et al. (1996). Experimental error bars are generally smaller than the symbols.

1027 **Figure 3.** Experimental binding capacity ( $B_{\text{max}}$ ) and  $\log^{\text{HA}} \beta(\text{Pu}^{4+})$  values of Szabò et al. (2010)  
 1028 versus  $I$  ( $\text{NaClO}_4$ ) compared with Model VII predictions. Arrows refer to the y-axis  
 1029 corresponding to the data. Experimental error bars for  $B_{\text{max}}$  are generally smaller than the  
 1030 symbols.

1031 **Figure 4.** (a) Apparent Am-HA and U(VI)-HA complexation constants (Wall et al., 2002;  
 1032 Labonne-Wall et al., 1999) versus  $I$  ( $\text{NaCl}$ ) for  $\text{pH}_m = 5.1$  and 4.9, respectively. (b) Apparent M-  
 1033 HA complexation constants ( $M = \text{Ni}^{2+}$  or  $\text{Co}^{2+}$ , Kurk and Choppin, 2000) versus  $I$  ( $\text{NaCl}$ ) for  
 1034  $\text{pH}_{\text{exp}} = 6$ . For both figures, lines are predictions by Model VII (full line) and NICA-Donnan  
 1035 (dashed lines) using the generic parameters (but shifted down for the case of Am-HA, see text for  
 1036 details). Experimental error bars are commonly smaller than the symbols.

1037 **Figure 5.** Experimental apparent  $\text{Ca}^{2+}$ -HA complexation constants versus  $\text{pH}_m$  for  $I = 0.1, 1$  and  
 1038  $3 \text{ m NaCl}$  (Laszak and Choppin, 2001) compared with (a) Model VII (simulated curves for  $I = 1$   
 1039 and  $3 \text{ m NaCl}$  overlap) and (b) NICA-Donnan predictions. Experimental error bars are commonly  
 1040 smaller than the symbols on all three figures.

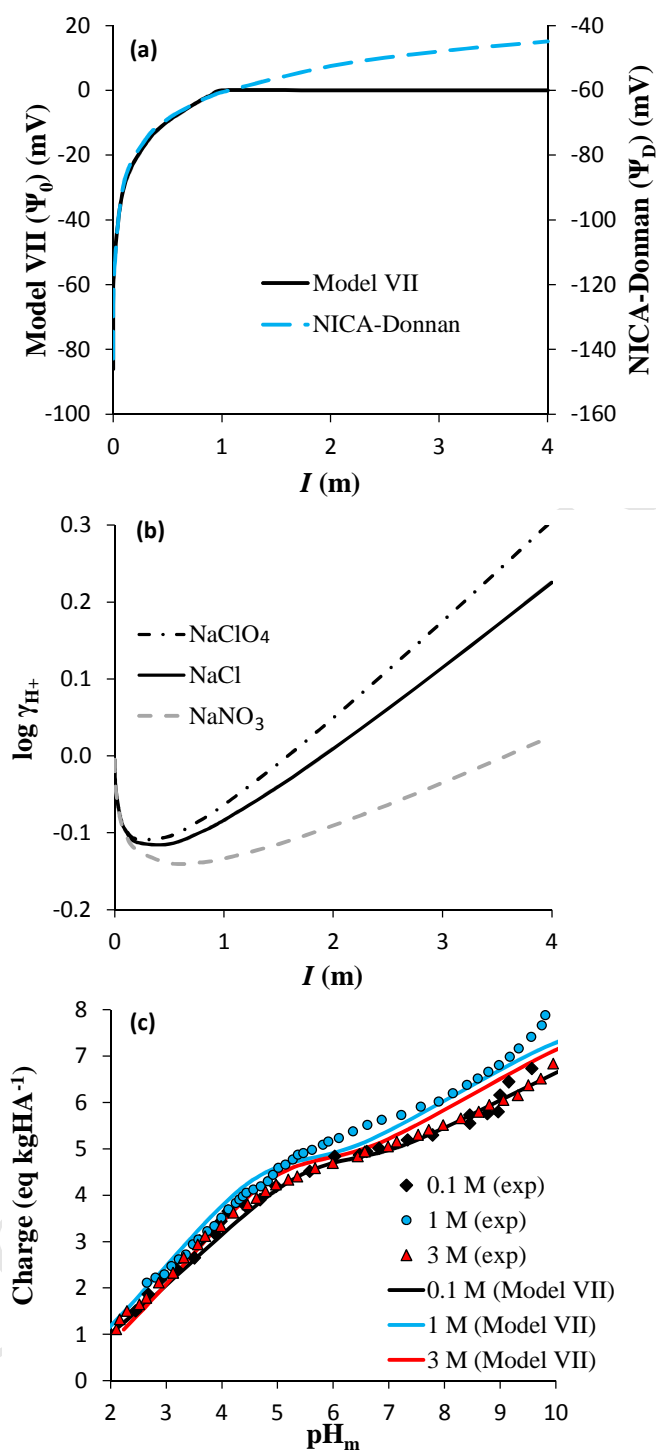
1041 **Figure 6.** (a) Experimentally observed effect of the ionic strength on Am-HA complexation at  
 1042 low (Wall et al., 2002;  $\text{pH}_m = 5.1$ ;  $\text{NaCl}$ ) and high metal loading (Czerwinski et al., 1996;  $\text{pH}_m =$   
 1043  $6$ ;  $\text{NaClO}_4$ ). (b) Simulated effect of the ionic strength on Am-HA complexation at low ( $[\text{Am}]_{\text{tot}} =$   
 1044  $10^{-9} \text{ m}$ ) and high metal loading ( $[\text{Am}]_{\text{tot}} = 10^{-6} \text{ m}$ ) with Model VII (black curves) and NICA-  
 1045 Donnan (blue curves) in  $\text{NaCl}$  for a HA concentration of  $1 \text{ mg L}^{-1}$  and  $\text{pH} = 5.5$ . (For  
 1046 interpretation to references to color, the reader is referred to the web version of this article.)

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	[M] ( $\text{mol L}^{-1}$ )	[HA] ( $\text{mg L}^{-1}$ )	$m_{\text{NaCl}}$ (m)	pH	pH buffer
$\text{Am}^{3+}$	$1 \times 10^{-9}$	1 - 10	0.1 - 6	5.1 ( $\text{pH}_m$ )	$10^{-2} \text{ M}$ acetate
$\text{UO}_2^{2+}$	$5.24 \times 10^{-7}$	2 - 10	0.1 - 6	4.9 ( $\text{pH}_m$ )	$10^{-2} \text{ M}$ acetate
$\text{Ni}^{2+}$	$1 \times 10^{-9}$	$2 \times 10^{-3} - 1.6 \times 10^{-2}$	0.3 - 5	6.0 ( $\text{pH}_{\text{exp}}$ )	No
$\text{Co}^{2+}$	$1 \times 10^{-10}$	$1.3 \times 10^{-2} - 2.2 \times 10^{-1}$	0.3 - 5	6.0 ( $\text{pH}_{\text{exp}}$ )	No
$\text{Ca}^{2+}$	$1 \times 10^{-8}$	0 - 500	0.1 - 3	4.5 - 9.5 ( $\text{pH}_m$ )	No

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**Table 1**



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Figure 1

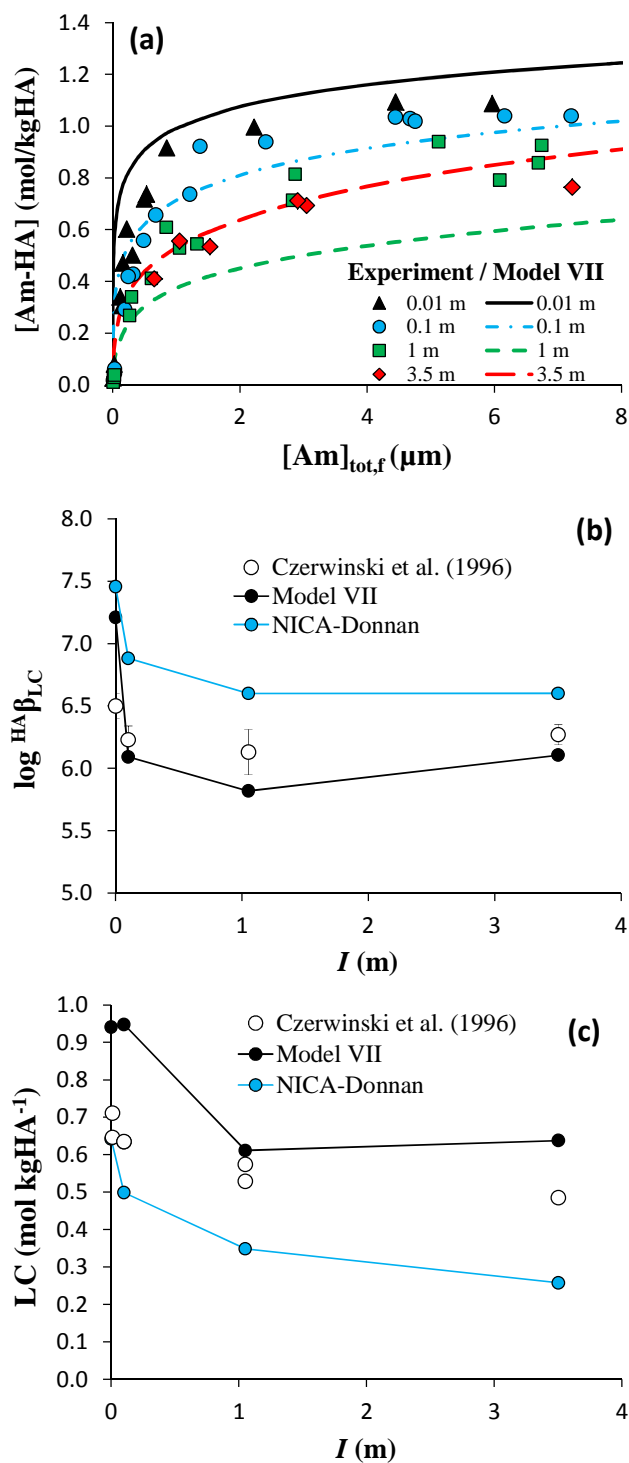
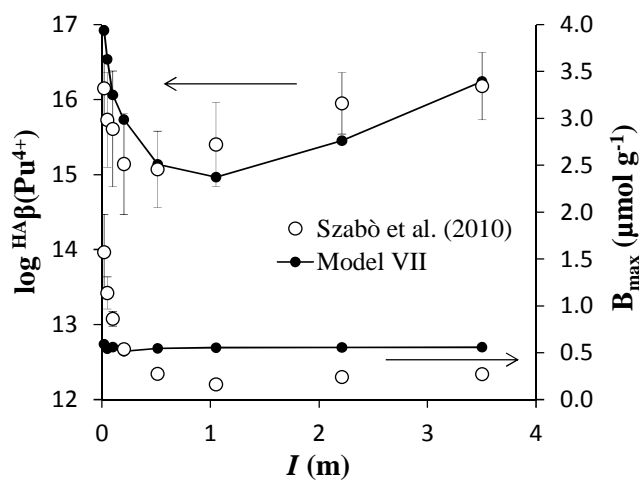


Figure 2

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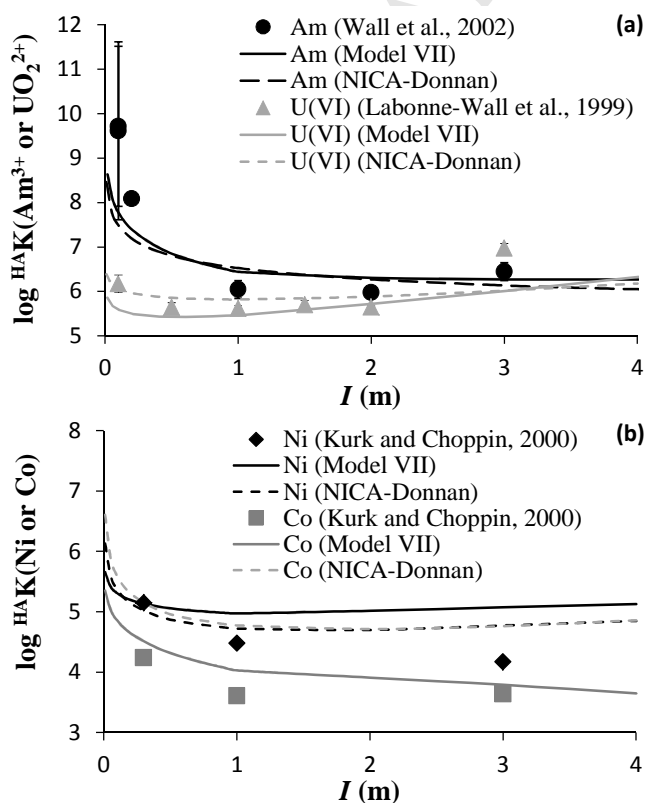


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Figure 3



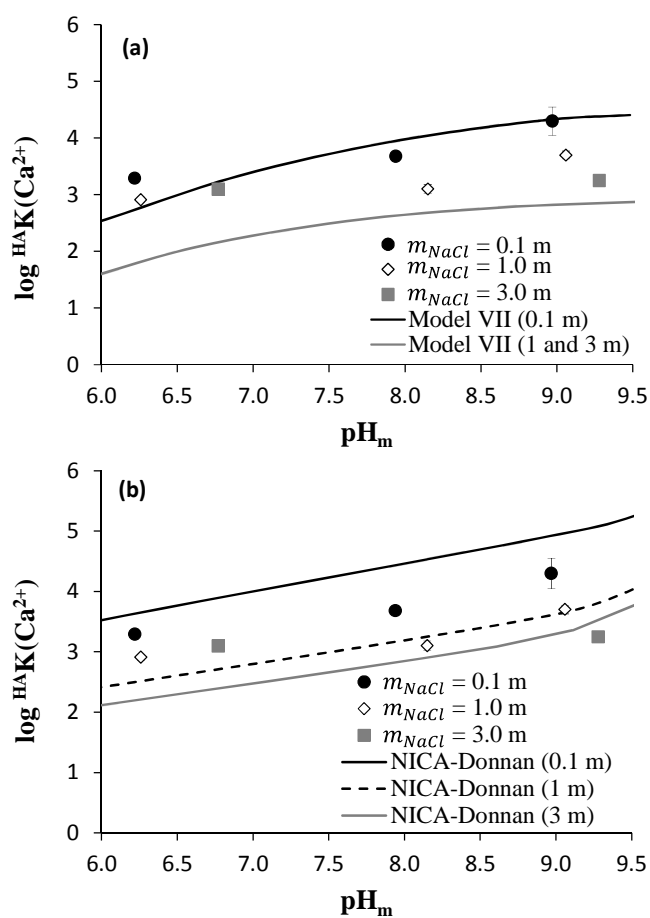
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Figure 4

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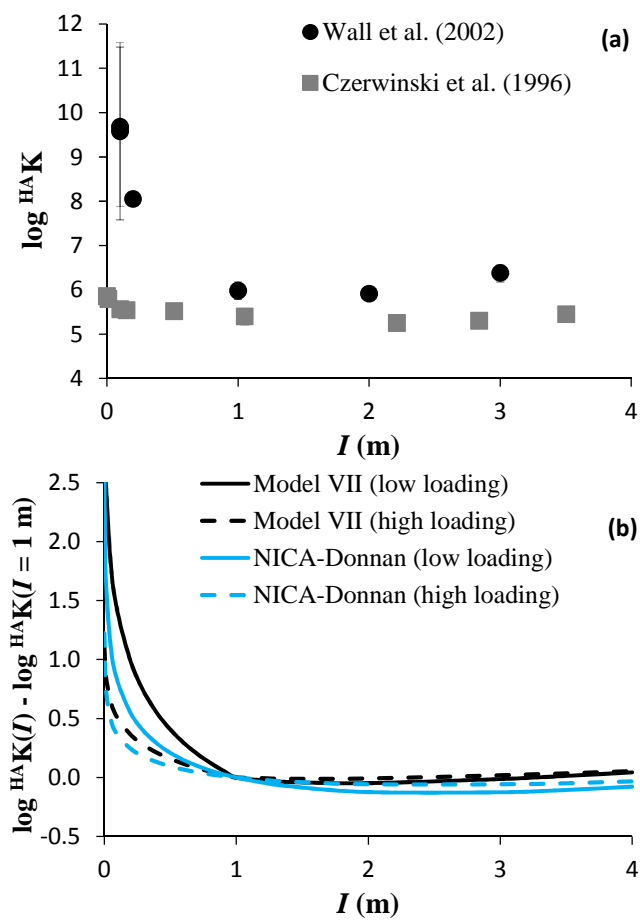
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Figure 5

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Figure 6