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4   **Humic Ion-Binding Model VII: a revised parameterisation of cation-**

5   **binding by humic substances**

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28 **Environmental context**

29 Natural organic matter exerts a powerful control on chemical conditions in waters and soils,

30 affecting pH and influencing the biological availability, transport and retention of metals. To

31 quantify the reactions, we collated a wealth of laboratory data covering 40 metals and acid-

32 base reactions, and used them to parameterise the latest in a series of Humic Ion-Binding

33 Models. Model VII is now available to interpret field data, and contribute to the prediction of

34 environmental chemistry.

35

36   **Abstract**

37   Humic Ion-Binding Model VII aims to predict the competitive reactions of protons and metals

38   with natural organic matter in soils and waters, based on laboratory results with isolated

39   humic and fulvic acids (HA and FA). Model VII is simpler in its postulated multidentate metal

40   binding sites than the previous Model VI. Three model parameters were eliminated by using

41   a formal relationship between monodentate binding to strong- and weak-acid oxygen-containing

42   ligands, and removing factors that provide ranges of ligand binding strengths. Thus Model VII

43   uses a single adjustable parameter, the equilibrium constant for monodentate binding to strong-

44   acid (carboxylate) groups (K_{MA}), for each metallic cation. Proton-binding parameters, and mean

45   values of log K_{MA} were derived by fitting 248 published datasets (28 for protons, 220 for

46   cationic metals). Default values of log K_{MA} for FA were obtained by combining the fitted values

47   for FA, results for HA, and the relationship for different metals between log K_{MA} and equilibrium

48   constants for simple oxygen-containing ligands. The equivalent approach was used for HA.

49   The parameterised model improves on Model VI by incorporating more metals (40), providing

50   better descriptions of metal binding at higher pH, and through more internally-consistent

51   parameter values.

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54   **Introduction**

55   The Windermere Humic Aqueous Model (WHAM)[1,2] incorporating Humic Ion-Binding Model

56   V[3] or VI[4] permits the calculation of equilibrium chemical speciation for waters and soils in

57   which natural organic matter plays a significant role. The ion-binding models are based on

58   conventional chemical reactions involving O-containing weak acids, with empirical estimation

59   of the influence of soft ligand atoms (N, S) and electrostatic corrections, and are

60   parameterised from laboratory studies with isolated humic and fulvic acids. The NICA

61   model[5] is similarly parameterised and provides an alternative picture based on continuous

62   binding-site distributions. Tipping[2] identified both the Humic Ion-Binding Models and NICA

63   as comprehensive models, meaning that they deal with competitive interactions involving all

64   cations (including H^+), and take account of ionic strength effects and metal-proton exchange

65   ratios. They seek to represent cation-binding by the complex mixtures that comprise natural

66   organic matter as efficiently as possible, with the minimum number of parameters, in order to

67   be useful in addressing chemical processes in the environment. A different approach to

68   these parameterised models, but also potentially comprehensive, is the "forward modelling"

69   developed by Cabaniss[6] in which binding is calculated *a priori* from the known or assumed

70   distributed chemistry of humic substances.

71   WHAM has been applied in a variety of research and regulatory areas. Examples include

72   the acidification of soils[7-14] and surface waters[15], trace metal behaviour in soils[16-22], surface

73   waters[23-31] and groundwaters[32], lake sediment diagenesis[33,34], rare earth geochemistry[35-

74   37], iron and manganese geochemistry[38-41], radionclide geochemistry[42-45], organic matter

75   solubility in soils[46,47], catchment modelling[48,49], interactions of metals with biota[50,51],

76   ecotoxicology[52-59] and Critical Loads[60-62]. Given this evident utility, it is worthwhile to

77   continue to improve the humic ion-binding model and incorporate new data into its

78   parameterisation. Here we report on activities undertaken towards these goals, namely

79   modification of assumptions about multidentate binding, the fitting of new data, and the

80   introduction of a procedure to obtain more internally-consistent parameters.

81   Changes in binding site formulation were prompted by experience in applying Model VI to

82   new data for the binding of lanthanides, Co and UO_2 by humic and fulvic acids[63,64]. It

83   became apparent that too strong a pH dependence was predicted by the model at higher pH

84   values, which could be attributed to assumed multidentate sites involving more than one

85   weak-acid ligand (e.g. phenolic oxygen). Therefore we modified the formulation of the array

86   of assumed binding sites, to create Humic Ion-Binding Model VII.

87   Humic Ion-Binding Model VI is parameterised with data for the interactions of cationic metals

88   with isolated humic substances that were available in the late 1990s. Since then, the number

89   of data sets suitable for parameterisation has approximately doubled, with new results
90   notably available for protons, Al, Sc, Cr, Co, Ni, Cu, Zn, Y, Ag, Cd, Hg, MeHg, Pb, UO_2 and
91   the lanthanides.   All available data sets were fitted with Model VII to obtain binding
92   parameters.

93   In past work[2,4] linear free energy relationships (LFERs) were derived to relate model
94   parameters for metal binding to conventional equilibrium constants for simple ligands, and
95   the LFERs were used in some cases to estimate parameters in cases where measured data
96   were not available.   We extended this approach, making use of the study of Carbonaro &
97   DiToro[65] who showed how the Irving-Rossotti[66] approach could be brought to bear to
98   regularise equilibrium constants.

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102 **Modelling**

103 *WHAM*

104 The original version of WHAM was simply a combination of a humic ion-binding model (see
105 below) with an inorganic speciation model[1]. The latter deals with reactions among the
106 inorganic master species (protons, metal cations, hydroxyl ion, carbonate and phosphate
107 species, sulphate, fluoride, chloride). Ionic strength effects on the inorganic reactions are
108 taken into account using the extended Debye-Hückel equation. Temperature effects on
109 reactions between inorganic species are taken into account using published or estimated
110 enthalpy data; in the absence of experimental information, reactions involving humic
111 substances are assumed to be independent of temperature. A given speciation problem is
112 solved by finding the activities of all the master species at equilibrium, using a combination of
113 algorithms. Inputs to the model are the total concentrations of reactants, as would be
114 obtained by chemical analysis. The model can work with a specified pH, or calculate the pH
115 if the necessary input data are available. The software package currently associated with the
116 model is WHAM6.0 (http://windermere.ceh.ac.uk/Aquatic_Processes/wham/). It includes the
117 Humic Ion-Binding Model VI and the inorganic model, together with further sub-models for
118 the binding of cations to the oxides of Al, Si, Mn and Fe, and to a simple cation-exchanger.

119 *Humic Ion-Binding Model VI*

120 Humic Ion-Binding Model VI is the most important component of WHAM, describing the
121 interactions of protons and metals with natural organic matter. The model was described in
122 detail by Tipping[4]. It uses a structured formulation of discrete, chemically-plausible, binding
123 sites for protons, in order to allow the creation of regular arrays of bidentate and tridentate
124 binding sites for metals.

125 Proton dissociation is represented by postulating 8 groups with different acid strengths, the
126 reactions being characterised by intrinsic equilibrium constants, the negative logarithms of
127 which are denoted by pK_1 - pK_8. The four most strongly-acid groups (groups 1-4) are referred
128 to as type A groups, and consist mainly of carboxylic acid groups, while the remaining 4 groups
129 (type B) represent weaker acids, such as phenolic acids. The 8 pK_i values are expressed in
130 terms of 4 constants; pK_A and pK_B are the average pK values of the two types of group, and
131 ΔpK_A and ΔpK_B are measures of the spread of the individual pK_i values around the means.
132 Each type A group is assigned an abundance of $n_A/4$ mol g^{-1} humic matter, and each type B
133 group an abundance of $n_A/8$ mol g^{-1}. Thus, within a type, each group is present in equal
134 amounts, and there are half as many type B groups as type A groups. The imposed regularity
135 of the groups facilitates the formulation of bidentate and tridentate sites for metals (Table 1).

136   Metal binding at the type A and B sites is described with average intrinsic equilibrium
137   constants (K_{MA}, K_{MB}) and associated "spread factors" ΔLK_{A1} and ΔLK_{B1}. Thus K_{MA} is the
138   average equilibrium constant for the binding of a metal to a type A (carboxylate) group. The
139   occurrence of bidentate and tridentate sites at the surface of the humic acid or fulvic acid
140   molecule is calculated probabilistically. Additional binding site heterogeneity is generated by
141   a parameter, ΔLK_2, that characterises the tendency of the metal to interact with "softer" ligand
142   atoms such as N and S. Thus, 9% of the bidentate sites have the logarithms of their binding
143   constants increased by ΔLK_2, while 0.9% have increases of $2\Delta LK_2$. For the tridentate sites, the
144   respective increases are $1.5\Delta LK_2$ and $3\Delta LK_2$. In the standard model, all metal cations (e.g.
145   Al^{3+}, Cu^{2+}, Hg^{2+}) and their first hydrolysis products ($AlOH^{2+}$, $CuOH^+$, $HgOH^+$) compete with
146   each other, and with protons, for binding. The combination of multi-denticity and the
147   increased binding strength of some sites, due to ΔLK_2, generates many binding sites with a
148   wide range of affinities. The most abundant (monodentate) sites are the weakest binders,
149   while the least abundant (tridentate sites enhanced by $3\Delta LK_2$) are the strongest.

150   The intrinsic equilibrium constants are modified by empirical electrostatic terms, incorporating
151   the electrostatic parameter P, that take into account the attractive or repulsive interactions
152   between ions and the charged macromolecule. A Donnan sub-model is used to compute
153   counterion accumulation in the diffuse zone around the molecule; each counterion can be
154   assigned a selectivity coefficient (K_{sel}), so that accumulation can be made to depend on more
155   than just the counterion charge; for example, Ca^{2+} can be favoured over Mg^{2+}. The selectivity
156   coefficients are only used in soil applications where exchanges of major cations on solid-phase
157   organic matter are important.

158   The maximum number of parameters that can be optimised to describe metal binding is six
159   (K_{MA}, K_{MB}, ΔLK_{A1}, ΔLK_{B1}, ΔLK_2, K_{sel}). In practice however, this number can be substantially
160   reduced. Thus, Tipping[4] described the setting of a single universal value for ΔLK_{A1} and ΔLK_{B1},
161   and the estimation of ΔLK_2 by correlation with the logarithm of the equilibrium constant for
162   complex formation with NH_3 (log K_{NH3}) according to the equation;

$$\Delta LK_2 = 0.58 \log K_{NH3} \tag{1}$$

164   For dilute systems, as in laboratory experiments, K_{sel} can be set to unity. Finally, K_{MA} and K_{MB}
165   are strongly correlated. Therefore, the fitting of a new data set can be achieved by adjusting
166   only K_{MA}, which was the approach taken in the present work. High values of K_{MA} mean that the
167   metal is strongly bound at the high-abundance "weak" sites. High values of ΔLK_2 mean that
168   the metal is favoured by the low-abundance "strong" sites, associated, according to the model,
169   with N or S atoms. If ΔLK_2 is small, the strong sites are not favoured, and binding is
170   predominantly due to binding at oxygen-containing sites.

171   During the course of developing Model VII from Model VI, we discovered a coding error in

172   Model VI which means that the parameters ΔLK_{A1} and ΔLK_{B1} were not used as originally

173   intended, and this means that Model VI was actually different from that described by

174   Tipping[4]. This error, which is described in full in the Accessory Material, did not invalidate

175   Model VI as used with code written by ourselves, since fitting and model applications were

176   performed consistently. As reported below, ΔLK_{A1} and ΔLK_{B1} are entirely absent from Model

177   VII.

178   *Humic Ion-Binding Model VII*

179   Model VII is identical to VI with respect to its formulation of total monodentate binding sites,

180   proton binding constants and electrostatic effects. It differs from Model VI with respect to

181   metal cation binding, in that the arrangement of multidentate sites has been modified, and

182   some parameters eliminated.

183   In Model VI there can be four parameters that describe monodentate metal binding, namely

184   log K_{MA}, log K_{MB}, ΔLK_{A1} and ΔLK_{B1}. Tipping[2] noted that the relationship between log K_{MB} and

185   log K_{MA}, i.e. mean equilibrium constants for binding to weaker and stronger acid sites, was

186   roughly as expected on the basis of data for simple ligands, i.e. binding of a given metal (also

187   the proton) to weak-acid groups such as phenolic OH groups is consistently stronger then to

188   carboxylate groups. The work of Carbonaro & Di Toro[65] showed this much more generally,

189   and demonstrated that relative binding strengths of a given metal to different oxygen-

190   containing ligands are interrelated. Therefore we defined log K_{MB} formally by the equation;

$$\log K_{MB} = \log K_{MA} \times (pK_B / pK_A) \qquad (2)$$

192   In other words, the relative binding strengths for a given metal are the same as those for the

193   proton. We attempted to apply this idea also to the spread factors ΔLK_{A1} and ΔLK_{B1}, i.e. to

194   predict them from $\Delta pK_{H,A}$ and $\Delta pK_{H,B}$. However, when fitting the data for metal binding, we

195   found that the spread factors could be entirely eliminated, i.e. it was preferable to fix log K_{MA}

196   at the same value for each of the four type A sites, and log K_{MB} at the same value for each of

197   the four type B sites.

198   Multi-dentate sites are formed in the model by combining mono-dentate (proton-binding)

199   sites, but the choice of combinations has been found to be important. When fitting new data

200   for Co, lanthanides and UO_2 with Model VI, we found overestimation of the pH dependence

201   of binding at pH > 7. Examination of model outputs revealed that this was due to the

202   assumed presence in humic matter of binding sites containing 2 or 3 weak-acid (type B)

203   groups. Therefore multidentate sites containing more than one type B group are omitted

204   from Model VII.

205 *Data sets*

206 The number of data sets available to calibrate Model VII was approximately twice as many

207 as for Model VI. For protons, we used 15 data sets for HA (4313 data points in all) and 13

208 for FA (4334 data); several of the sets previously used for Model VI were abandoned

209 because they were incomplete. A total of 107 data sets were available to quantify the

210 binding of 36 different cationic metals by HA (4420 data) and 108 data sets for the binding of

211 34 different metals by FA (4004 data). The grand total of data points was 17,116. Most of

212 the previous metal data sets used by Tipping[4] were retained, and augmented with additional

213 data sets obtained from the collation of Milne and colleagues[67,68], and by searching the

214 literature. The data sources are summarised in the Accessory Material.

215 *Data fitting*

216 The model was coded in BASIC, and the Nelder-Mead polytope method used for function

217 minimisation and parameter estimation. Since the previous fitting of proton binding data, a

218 significant number of new studies have been published. The availability of these extra data

219 made it possible to apply stronger acceptability criteria, with the objective of selecting data

220 best suited to provide robust estimates of the proton binding parameters. The criteria were

221 (a) the pH range of the data set had to extend above pH 10, in order to obtain good

222 estimates of the weak acid site binding parameters $pK_{H,B}$ and $\Delta pK_{H,B}$, and (b) each data set

223 had to refer to several ionic strengths, so that a value of the ionic strength dependency

224 parameter P could be calculated for each data set. Fitting involved the optimisation of six

225 parameters, namely the strong acid site density (n_A), the average strong and weak acid

226 binding site pK values ($pK_{H,A}$ and $pK_{H,B}$), the factors giving the spread of pK values around

227 the averages ($\Delta pK_{H,A}$ and $\Delta pK_{H,B}$), and the electrostatic factor P. We found that when fitting

228 individual data sets, adjustment of all the parameters simultaneously produced values that

229 were sometimes physically unreasonable. Therefore we adopted a two stage fitting process.

230 Firstly, $\Delta pK_{H,A}$ and $\Delta pK_{H,B}$ were fixed at the values derived by Tipping[4], and all the data sets

231 were fitted individually to obtain values of the remaining four parameters, and an overall

232 goodness-of-fit parameter (sum of all squared deviations in HA or FA charge, Z), calculated

233 from all the data sets. Then the spread factors were adjusted and the process repeated

234 iteratively to minimise the goodness-of-fit parameter.

235 Metal binding data were fitted by optimising log K_{MA}, using the default parameters obtained

236 from proton-binding data, and with ΔLK_2 obtained from equation (1). In the great majority of

237 cases, optimisation was done by minimising squared errors in log v, where v is the moles of

238 metal bound per gram of humic matter. In a few cases, the effects of metal binding on

239 measured pH were modelled, and optimisation performed by minimising squared errors in

240 pH. To establish the new arrangement of multidentate sites, we forced a uniform

241 representation of the monodentate sites, while keeping the system as simple as possible. All

242 data sets were fitted with a number of trial multidentate arrangements and universal values of

243 ΔLK_{A1} and ΔLK_{B1} (i.e. the same values for all data sets). The best arrangement of sites (Table

244 1) requires 50 different binding sites rather than the 80 sites of Model VI. Overall fitting was

245 no worse if ΔLK_{A1} and ΔLK_{B1} were both set to zero, enabling these parameters to be

246 eliminated. Thus, for dilute systems, Model VII has only two formal parameters for each

247 cationic metal, namely log K_{MA} and ΔLK_2, as opposed to the potential five in Model VI

248 (although this number could be reduced to three in practice).

249

250 **Results**

251 Default parameter values for proton binding and ionic strength dependence were calculated

252 as the means of the values obtained from each individual data set. New and previous

253 parameter values are compared in Table 2, while Figure 1 compares calculated humic and

254 fulvic net charge as a function of pH for the two parameter sets.

255 Mean values of log K_{MA} for the different metals are shown in the fourth and fifth columns of

256 Table 3. The average root-mean-squared deviation in log ν was 0.21 for HA and 0.23 for FA,

257 and overall the fits with Model VII were marginally better than those with Model VI. Figure 2

258 shows how Model VII performs better than Model VI for lanthanum.

259 We applied the approach and findings of Carbonaro & Di Toro[65] to analyse the Model VII

260 results, by plotting log K_{MA} against α_O, the slope of the equation of Irving & Rossotti[66] for

261 ligands with oxygen donor atoms. Results for HA and FA (Figure 3) show reasonable

262 correlations between log K_{MA} and α_O, indicating that HA and FA behave approximately as

263 expected from simpler ligands with respect to binding at the major oxygen-containing ligand

264 sites. A plot of log $K_{MA,HA}$ against log $K_{MA,FA}$ (Figure 4) falls close to the expected line, which

265 has a slope of 1.11 on the basis of the pK_A values for HA and FA, which are 4.1 and 3.7

266 respectively. Thus log $K_{MA,HA}$ for each metal is expected to be greater than $K_{MA,FA}$ by a factor

267 of 1.11. The mean ratio (log $K_{MA,HA}$ / log $K_{MA,FA}$) for the 33 metals with constants for both HA

268 and FA was 1.09, supporting this expectation.

269 We used these results to improve estimates of log K_{MA}, and thereby reduce the possibility of

270 excessive outliers. To derive the default constant for the binding of a given metal to FA we

271 applied the equation;

272 $\log K_{MA,FA,def} = \{n_{FA}\log K_{MA,FA,mean} + (n_{HA}\log K_{MA,HA,mean}/1.11) + (3.81\alpha_O+0.37)\} / (n_{FA}+n_{HA}+1)$ (3)

273 where n_{FA} and n_{HA} are the numbers of datasets for FA and HA yielding estimates of the

274 parameter log K_{MA}, and log $K_{MA,FA,mean}$ and log $K_{MA,HA,mean}$ are the mean values obtained from

275 fitting. Thus, we first weight the mean log K_{MA} value for FA. Second we weight the results

276 for HA, taking into account that the average log K_{MA} for HA is 1.11 times the value for FA

277 (Figure 4). Then we add a prediction of log K_{MA} using the equation from Figure 3. Finally the

278 overall weighted mean is taken. For HA, the same approach leads to

279 $\log K_{MA,HA,def} = \{n_{HA}\log K_{MA,HA,mean} + 1.11 n_{FA}\log K_{MA,FA,mean} + (3.51\alpha_O+0.74)\} / (n_{HA}+n_{FA}+1)$ (4)

280 Consequently the default parameters are more internally consistent. In a number of cases

281 there is no available value of α_O, while for three cations (Be^{2+}, Fe^{2+} and Ba^{2+}) there is a value

282 of α_O but there are no data for humic substances. The equations can still be applied under

283   either circumstance, but omitting the missing values. The seventh and eighth columns of

284   Table 3 show the derived default log K_{MA} values for 40 metallic cations.

285   *Comparisons of outputs from Models VI and VII*

286   Differences between the models with respect to multidentate binding site arrangements and

287   proton binding parameters generally lead to somewhat larger values of log K_{MA}, especially for

288   HA (Table 4). Differences will also have arisen from the use of additional data, and the new

289   procedure for deriving default constants. The best-defined values of log K_{MA} are those of Cu,

290   for which log K_{MA} for Model VII exceeds the Model VI value by 0.4 for HA but only 0.1 for FA;

291   these differences can be used as references to compare metals between models (Table 4).

292   Thus, for HA the differences in log K_{MA} between Models VII and VI are largest for Cr(III), Mn,

293   Fe(III), Ba, Eu and Th, while for FA, those for Cr(III), FeIII, Ba and Th are relatively large.

294   Only for Ca binding by FA is the difference in log K_{MA} appreciably smaller than that for Cu.

295   Further comparisons can be made from calculated binding isotherms, examples of which are

296   presented in Figure 5. For both HA and FA, Model VII predicts weaker binding of Al at high

297   pH, because of the removal of binding sites containing two or three type B (weak acid)

298   groups. A similar effect is seen for Eu, except that Model VII predicts stronger binding at low

299   pH, but weaker at pH 8; Am and Cm also behaved like this. There is little change in the

300   prediction of copper binding by either HA or FA. Zinc binding hardly differs between the

301   models for HA, while Model VII predicts slightly stronger binding for FA, due to the new

302   procedure for estimating default values of log K_{MA}.

303   The new Model VII parameterisation leads to changes in predicted competition effects. Due

304   to the complexity of competition reactions, and the large number of potential combinations of

305   metals, generalised analysis of the results is not possible. However, some illustrative

306   examples are given in Figure 6 of the effects on Cu and Zn binding of Mg, Al and Ca, three

307   important competitors in typical soils and waters. The predictions of the two models do not

308   differ very much for Al; only for Cu binding by HA is there a noticeable change, with weaker

309   competition leading to lower concentrations of Cu^{2+}. In the case of HA, competition by both

310   Mg and Ca for both Cu and Zn is calculated to be considerably stronger when Model VII is

311   applied, reflecting higher log K_{MA} values for the alkaline earths. For FA, competition by Mg

312   and Ca is weaker towards Zn, but stronger towards Cu.

313

314

315 **Discussion**

316 Because Models VI and VII are identical with respect to the six parameters (n_A, P, pK_A, pK_B,

317 ΔpK_A and ΔpK_B) that together describe total binding site density, electrostatic effects and

318 proton binding affinity, the new parameter values (Table 2) reflect the use of new more

319 extensive data on proton dissociation from humic substances, especially for HA. The main

320 differences are that, in comparison with Model VI, the Model VII HA and FA have slightly

321 higher site densities, the FA type A groups are weaker acids, the HA type B groups are

322 stronger acids, and the HA electrostatic factor is smaller. These led to the differences in

323 calculated proton dissociation as a function of pH shown in Figure 1.

324 With regard to metal binding, Model VII is appreciably simpler than Model VI, having fewer

325 combinations of monodentate sites to make multidendate sites (Table 1), a formalised

326 relationship between log K_{MA} and log K_{MB} (equation 2), and with the spread factors (ΔLK_{A1}

327 and ΔLK_{B1}) set to zero. There is an apparent inconsistency in that the model requires the

328 equilibrium constants for metal-binding not to vary within the type A and B groups, but to

329 differ between the type A and B groups. Full application of the model of Carbonaro & Di

330 Toro[65] would mean that ΔLK_{A1} and ΔLK_{B1} were non-zero, proportional to ΔpK_A and ΔpK_B

331 respectively. However, we obtained appreciably better fits if such parallelism was not

332 invoked. Inspection of the Carbonaro-Di Toro plots of log K_{ML} vs log log K_{HL} shows that in

333 several cases there is a lower local slope in the range of carboxylate groups (3 < log K_{HL} < 5)

334 indicating less relative variation in the log K_{ML} values than in log K_{HL}, and so setting ΔLK_{A1} to

335 zero is perhaps defensible. There are insufficient data to judge this for higher log K_{ML}, log

336 K_{HL}, and $\Delta LK_{A2.}$ The values of log K_{MA} can be considered chemically reasonable in that they

337 are similar to equilibrium constants for the equivalent reaction of metallic cations with simple

338 carboxylate ligands such as lactic acid, as demonstrated for Model VI[4]. But it is perhaps

339 worth re-emphasising that log K_{MA} values *per se* do not describe binding to humic

340 substances; rather, they predict binding to weak-acid groups (via equation 2), and are the

341 basis for the appreciably greater constants that apply to multidentate sites, which can be

342 further increased due to soft-ligand effects (equation 1).

343 Default Model VI parameters for different metallic cations were derived simply by taking the

344 averages of the calibrated values of log K_{MA}, a procedure which implies that samples of

345 humic substances used in laboratory experiments have been taken from a range of different

346 materials in the field, so that the average log K_{MA} is the best overall estimate, and the range

347 of possible values can be characterised by the standard deviation of the log K_{MA} values. This

348 is satisfactory when a reasonable number of different data sets can be analysed, but may

349 produce an unrepresentative log K_{MA} if data for the metal in question come from only one or

350   two data sets. The new method of establishing default constants presented here (equations

351   3 and 4) makes greater use of relationships among the different metals, and between HA

352   and FA, and draws directly upon relationships between WHAM parameters and equilibrium

353   constants for well-defined ligands via the Irving-Rossotti slope α_O. This both improves the

354   reliability of the parameters and makes the parameter set more internally consistent.   In

355   addition, the approach means that log K_{MA} can be estimated from constants for a wider range

356   of simpler ligands.

357   In 19 cases for HA and 13 for FA there are at least two data sets per metal, and these can be

358   used to compute standard deviations in log K_{MA}. These range from 0.04 to 1.19, with means

359   of 0.33 and 0.32 for HA and FA respectively. The standard deviations reflect differences in

360   several factors, including the source of the humic substances, experimental methods and

361   experimental conditions. The standard deviations for Cu are relatively low, 0.24 for HA and

362   0.21 for FA, and given that techniques for quantifying Cu binding are better than those for

363   other metals, they probably reflect mostly humic variability. A standard deviation of 0.3 in log

364   K_{MA} might reasonably be adopted as a standard when applying the model to estimate

365   uncertainty in field predictions.

366   Although Model VII represents an improvement on Model VI, its predictions do not differ

367   greatly (Figures 5 and 6). Therefore calculations that have already been run using Model VI

368   are unlikely to be invalidated by the new model, except perhaps for metal binding at alkaline

369   pH. There is probably merit in running both models, and also the NICA model[5] for new

370   problems, since any differences may provide insights or highlight uncertainty. It should also

371   be borne in mind that "higher" models (such as the CHUM catchment model[48,49], Critical

372   Limit Functions[62,70] and WHAM-F_{TOX}[59]) that use predicted speciation, will have parameter

373   values specific to the chosen Humic Ion Binding Model.

374   In summary, this work has produced a simpler Humic Ion-Binding Model, based on a

375   considerably larger data set, with greater internal consistency, and parameterised for protons

376   and 40 metallic cations. This should improve our ability to predict chemical speciation

377   involving natural organic matter in field situations.

378

379   **Acknowledgements**

388

389   **References**

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391

392   Table 1. Combinations of monodentate sites making bidentate and tridentate binding sites in

393   Models VI and VII, expressed in terms of n_A the number of the most strongly-acid groups.

394   Sites 1 to 4 are type A, present in equal amounts. Sites 5 to 8 are type B, and they total half

395   of the type A sites. The factor f_{prB} specifies the fraction of the sites that are close enough to

396   form bidentate sites, and f_{prT} does the same for tridentate sites. The values of f_{prB} and f_{prT} are

397   0.42 and 0.03 respectively for FA and 0.50 and 0.065 for HA. For each site combination

398   there are three binding strengths governed by the parameter ΔLK_2, their fractional

399   abundances being 0.901, 0.09 and 0.009, so the model has three times as many

400   multidentate sites as those shown here, 72 in Model VI and 42 in Model VII.

401

Model VI		Model VII	
sites	abundance	sites	abundance
Bidentate sites			
1-2	$f_{prB} \times n_A / 6$	1-2	$f_{prB} \times n_A / 8$
3-4	$f_{prB} \times n_A / 6$	3-4	$f_{prB} \times n_A / 8$
1-5	$f_{prB} \times n_A / 12$	1-5	$f_{prB} \times n_A / 8$
2-6	$f_{prB} \times n_A / 12$	2-6	$f_{prB} \times n_A / 8$
3-7	$f_{prB} \times n_A / 12$	3-7	$f_{prB} \times n_A / 8$
4-8	$f_{prB} \times n_A / 12$	4-8	$f_{prB} \times n_A / 8$
5-6	$f_{prB} \times n_A / 24$		
7-8	$f_{prB} \times n_A / 24$		
Tridentate sites			
1-2-3	$f_{prT} \times n_A / 27$	1-2-5	$f_{prT} \times n_A / 16$
1-2-4	$f_{prT} \times n_A / 27$	1-2-6	$f_{prT} \times n_A / 16$
1-3-4	$f_{prT} \times n_A / 27$	1-2-7	$f_{prT} \times n_A / 16$
2-3-4	$f_{prT} \times n_A / 27$	1-2-8	$f_{prT} \times n_A / 16$
5-6-7	$f_{prT} \times n_A / 216$	3-4-5	$f_{prT} \times n_A / 16$
5-6-8	$f_{prT} \times n_A / 216$	3-4-6	$f_{prT} \times n_A / 16$
5-7-8	$f_{prT} \times n_A / 216$	3-4-7	$f_{prT} \times n_A / 16$
6-7-8	$f_{prT} \times n_A / 216$	3-4-8	$f_{prT} \times n_A / 16$
1-2-5	$f_{prT} \times n_A / 18$		
3-4-6	$f_{prT} \times n_A / 18$		
1-3-7	$f_{prT} \times n_A / 18$		
2-4-8	$f_{prT} \times n_A / 18$		
1-5-6	$f_{prT} \times n_A / 36$		
2-7-8	$f_{prT} \times n_A / 36$		
3-5-7	$f_{prT} \times n_A / 36$		
4-6-8	$f_{prT} \times n_A / 36$		

402

403   Table 2. Default proton binding parameters for humic and fulvic acid.

Parameter	HA		FA	
	Model VI	Model VII	Model VI	Model VII
n_A*	3.3	3.4	4.8	5.2
pK_A	4.1	4.1	3.2	3.7
pK_B	8.8	8.3	9.4	9.6
ΔpK_A	2.1	2.6	3.3	3.1
ΔpK_B	3.6	3.1	4.9	4.4
P	-330	-196	-115	-119

404   * mmol $(gHS)^{-1}$

405

406   Table 3. Default cationic metal parameters for Model VII. Values of log $K_{MA,HA,mean}$ and log

407    $K_{MA,FA,mean}$ are averages from data-fitting (n_{HA} and n_{FA} are the numbers of data sets), while log

408    $K_{MA,HA,def}$ and log $K_{MA,FA,def}$ are default values derived with equations (3) and (4), which involve

409   the Irving-Rosotti parameter α_O. Values of ΔLK_2 were derived with equation (1) using the

410   compilation of log K_{NH3} values by Martell & Hancock[69].

metal	n_{HA}	n_{FA}	log $K_{MA,HA,mean}$	log $K_{MA,FA,mean}$	α_O	log $K_{MA,HA,def}$	log $K_{MA,FA,def}$	ΔLK_2
Be	0	0	-	-	0.433	2.27	2.02	0.99
Mg	1	2	0.98	1.01	0.176	1.14	0.99	0.13
Al	4	4	2.67	2.69	0.607	2.82	2.57	0.46
Ca	8	11	1.19	1.17	0.194	1.26	1.13	0.00
Sc	1	0	3.61	-	-	3.61	3.28	0.39
VO	0	1	-	2.51	-	2.76	2.51	1.74
Cr	1	0	2.52	-	0.818	3.07	2.89	1.97
Mn	2	1	2.21	1.67	0.255	1.98	1.76	0.58
Fe(II)	0	0	-	-	0.287	1.76	1.46	0.81
Fe(III)	2	1	3.19	3.03	0.861	3.37	3.12	2.20
Co	2	8	1.51	1.32	0.306	1.50	1.35	1.22
Ni	2	5	1.6	1.41	0.301	1.60	1.43	1.57
Cu	13	16	2.54	2.07	0.466	2.38	2.16	2.34
Zn	2	4	1.87	1.71	0.304	1.87	1.68	1.28
Sr	1	1	1.49	1.01	0.171	1.32	1.13	0.00
Y	1	1	2.84	2.93	-	3.03	2.76	0.22
Ag	4	1	1.50	1.14	0.177	1.44	1.27	1.91
Cd	10	6	1.61	1.58	0.306	1.67	1.51	1.48
Ba	0	0	-	-	0.158	1.30	0.97	0.00
La	1	1	2.64	2.74	0.414	2.62	2.36	0.11
Ce	1	1	2.68	2.7	0.451	2.66	2.41	0.13
Pr	1	1	2.69	2.74	-	2.85	2.59	0.16
Nd	1	1	2.68	2.71	-	2.83	2.57	0.18
Sm	1	1	2.76	2.81	-	2.93	2.66	0.20
Eu	5	10	2.97	2.61	0.530	2.89	2.62	0.29
Gd	1	1	2.77	2.84	-	2.95	2.68	0.24
Tb	1	1	2.86	2.92	-	3.04	2.76	0.26
Dy	2	1	3.19	2.93	-	3.20	2.91	0.28
Ho	1	1	2.95	2.96	-	3.10	2.82	0.30
Er	1	1	3.03	3.09	-	3.21	2.92	0.32
Tm	1	1	3.09	3.07	-	3.23	2.94	0.35
Yb	1	1	3.12	3.05	-	3.24	2.94	0.37
Lu	1	1	3.17	3.1	-	3.29	2.99	0.39
Hg	3	5	4.1	3.4	0.796	3.84	3.51	5.10
MeHg	4	1	0.53	0.39	-	0.51	0.46	3.60
Pb	9	10	2.39	2.14	0.442	2.37	2.15	0.93
Th	2	0	3.41	-	0.902	3.58	3.34	0.23
UO2	4	4	2.64	2.28	0.621	2.61	2.38	1.16
Am	7	3	2.95	2.74	0.543	2.94	2.68	1.57
Cm	3	1	2.58	1.91	0.537	2.50	2.27	1.57

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412 Table 4. Comparison of default log K_{MA} values for Models VI and VII. Values in bold indicate

413 that the difference between the models is more than 0.2 log units greater or less than the

414 difference for Cu.

	Model VI		Model VII	
	HA	FA	HA	FA
Mg	0.7	1.1	1.1	1.0
Al	2.6	2.5	2.8	2.6
Ca	0.7	1.3	1.3	**1.1**
VO	2.5	2.4	2.8	2.5
CrIII	2.2	2.2	**3.1**	**2.9**
Mn	0.6	1.7	**2.0**	1.8
FeII	1.3	1.6	1.8	1.5
FeIII	2.4	2.6	**3.4**	**3.1**
Co	1.1	1.4	1.5	1.4
Ni	1.1	1.4	1.6	1.4
Cu	2.0	2.1	2.4	2.2
Zn	1.5	1.6	1.9	1.7
Sr	1.1	1.2	1.3	1.1
Cd	1.3	1.6	1.7	1.5
Ba	-0.2	0.6	**1.3**	**1.0**
Eu	2.1	2.4	**2.9**	2.6
Dy	2.9	2.5	3.2	**2.9**
Hg	3.5	3.5	3.8	3.5
Pb	2.0	2.2	2.4	2.2
Th	2.8	2.7	**3.6**	**3.3**
UO_2	2.2	2.1	2.6	2.4
Am	2.5	2.6	2.9	2.7
Cm	2.2	2.0	2.5	2.3

415

Figure captions

416

417   Figure 1   Proton dissociation calculated with Model VI and VII default parameters; Z is the
418   charge per g of HA or FA. The upper of each pair of plots refers to an ionic
419   strength of 0.1 M, the lower to 0.001M.

420   Figure 2   Experimental data of Sonke (2006) for the binding of La(III) by humic acid (open
421   circles) and fulvic acid (closed circles), expressed as $K_{app} = \nu / [La^{3+}]$, where ν is
422   the amount of bound metal in mol g^{-1}. The lines are fits with Models VI (dashed
423   lines) and VII (full lines).

424   Figure 3   Fitted log K_{MA} for different metals (individual data sets) plotted against α_O, the
425   Irving-Rossotti slope.

426   Figure 4   Fitted log K_{MA} for HA (average value for each metal) plotted against the
427   corresponding value for FA. The line has the expected slope of 1.11 (see
428   Results). The triangles show data for lanthanides.

429   Figure 5   Metal binding isotherms calculated with the default parameters of Models VI and
430   VII. Nu (ν) is moles bound per gram FA. Open symbols Model VI, closed
431   symbols Model VII. Circles pH 4, squares pH 6, triangles pH 8.

432   Figure 6   Competition by Mg, Al and Ca for Cu and Zn binding by HA and FA; comparison of
433   results with default parameters for Models VI (broken lines) and VII (full lines). The
434   calculations refer to pH 5 for Al and pH 7 for Mg and Ca, and an ionic strength of
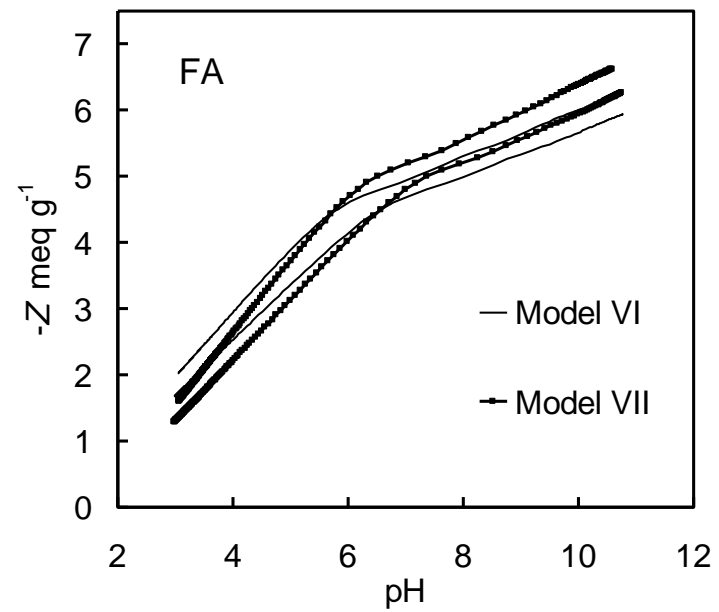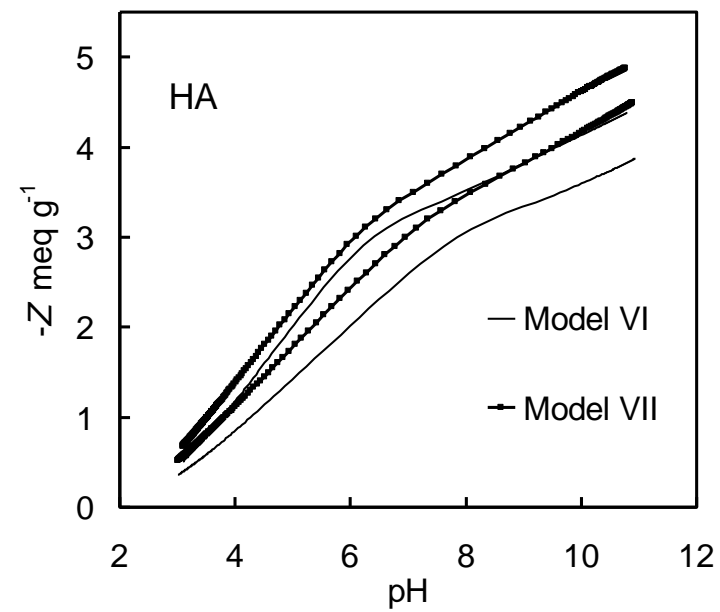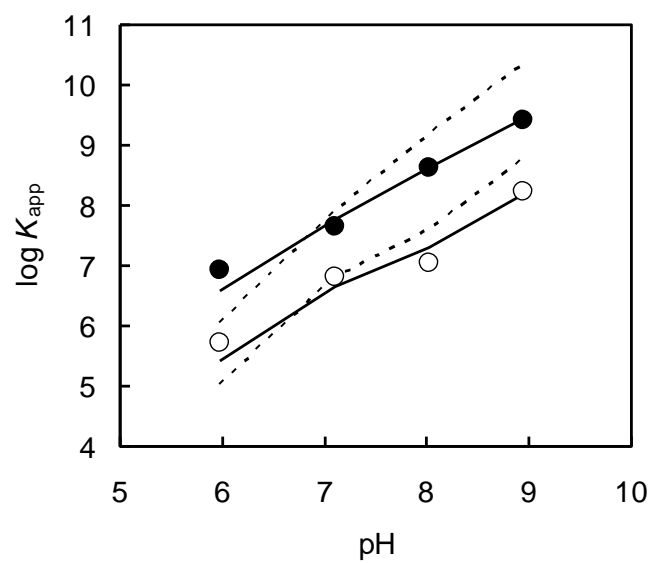435   0.01 M.

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450   Figure 1

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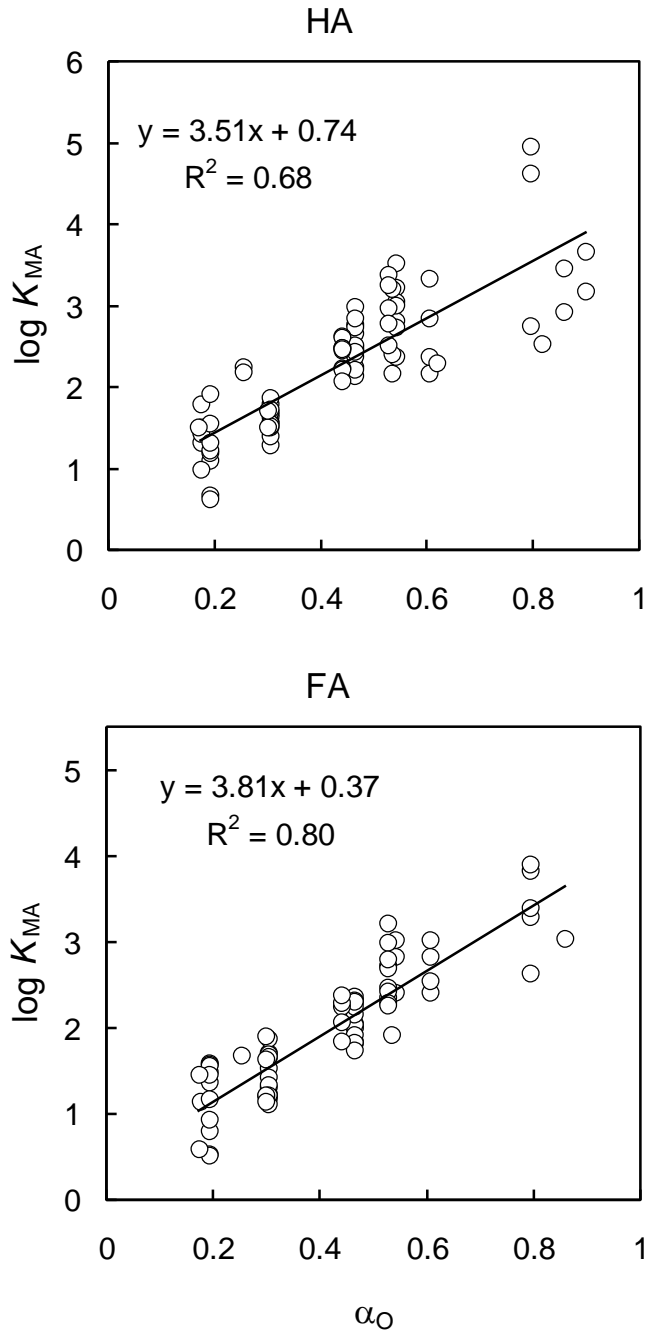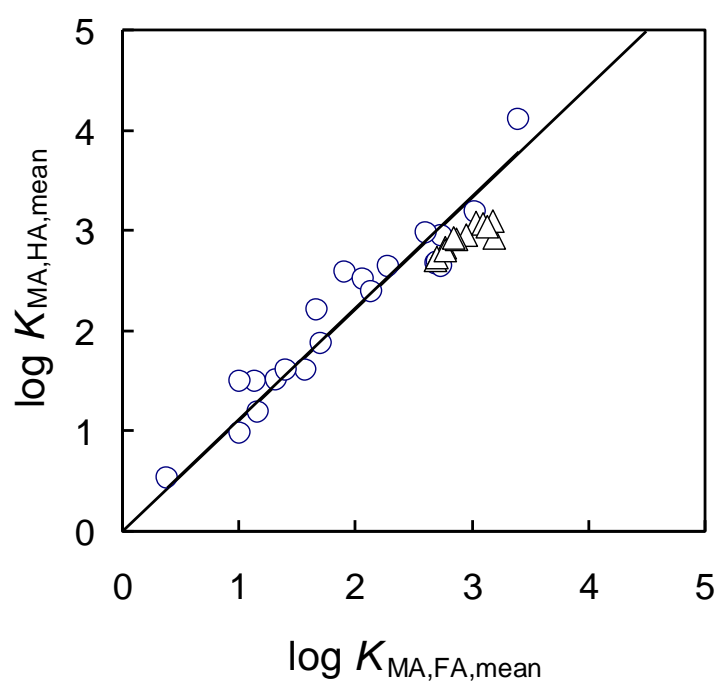453   Figure 2

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Figure 3

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483 Figure 4

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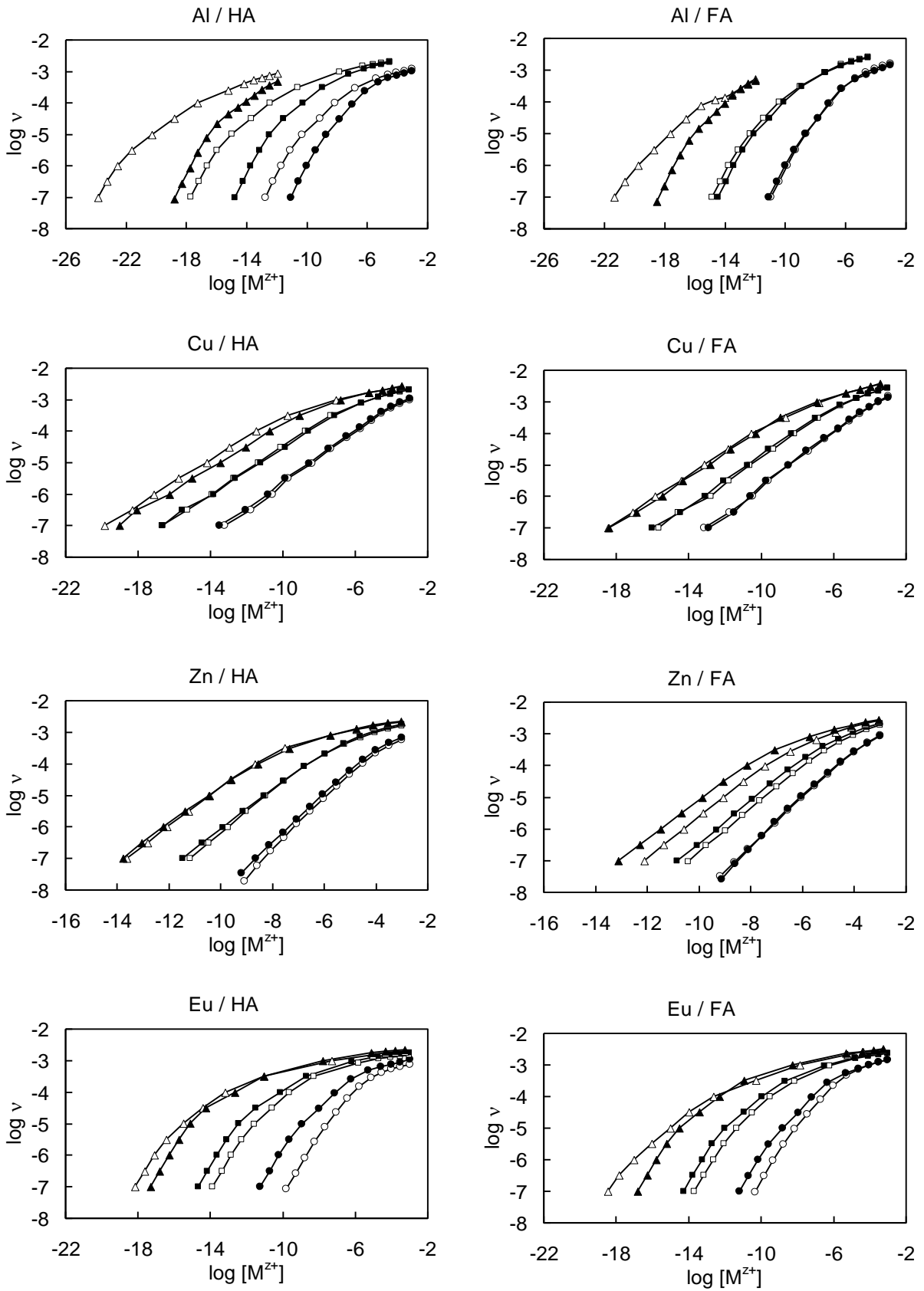507

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513　Figure 5

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537 Figure 6

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