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1 Evaluation of the impact of organic matter composition on metal speciation in calcareous soil
2 solution: comparison of Model VI and NICA-Donnan

3

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19 **Keywords:** alkaline soil, metal speciation, modelling, dissolved organic matter

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21

22 **Abstract**

23 To assess the influence of the composition of dissolved organic matter (DOM) on metal
24 speciation, two models have been used: Model VI and NICA-Donnan. The speciation of Cu,
25 Ni, Pb and Zn in the soil solution of 36 samples characterized by alkaline pH and different
26 contamination levels has been determined. Four assumptions about DOM composition have
27 been tested: (i) 100% of humic substances (HS) are fulvic acids (FA), (ii) 100% are humic
28 acids (HA), (iii) 35% are HA and 65% FA and (iv) 84% are HA and 16% FA. The results
29 obtained with the two distinct models are of the same order of magnitude; however, few
30 differences have been highlighted regarding the description of the non-specific interactions,
31 the Zn-FA interactions and the lowest free ion concentrations. The main result of this study is
32 that the free ion concentrations calculated with the two models may differ by one order of
33 magnitude depending on whether HA and/or FA are used to represent DOM. This work
34 demonstrates the impact of the assumptions made about the DOM nature for metal speciation
35 modelling.

36

37 **1. Introduction**

38 A wide knowledge of soil geochemistry is necessary to determine the impact of anthropogenic
39 activities and resulting toxicities (Khalil et al., 2013; Khan et al., 2008). It is widely
40 recognized that the environmental impact of metals is not dependent on the total soil metal
41 content, but it is mediated through dissolved metal species (Nolan et al., 2003; Tipping et al.
42 2003). Studying the chemical speciation of metals in the soil solution is a necessary parameter
43 for evaluating metal bioavailability and thus understanding their potential environmental
44 impacts. Trace elements exist in soil solution as free metal ions or as inorganic or organic
45 complexes bound to various ligands. As in aquatic systems, free metal ion concentration is an

46 essential parameter because it can influence uptake by plants and dermal uptake by soil and
47 aquatic organisms (Ardestani et al., 2014; Oste et al., 2002). The metal speciation depends on
48 pH, metal ion concentration and ligand concentrations (Weng et al., 2002). It has been shown
49 that dissolved organic matter (DOM) can strongly bind metal ions such as Cu, Ni, Pb and Zn
50 (Kinniburgh et al., 1999; Koopal et al., 2005; Van Riemsdijk et al., 2006; Weng et al., 2002).
51 DOM is a complex mixture of many more or less reactive molecules. The reactive part of
52 DOM is dominated by humic substances (HS), comprising humic acids (HA) and fulvic acids
53 (FA) (Dudal and Gérard 2004). Numerous models have been developed to describe the
54 electrostatic and specific interactions between HS and ions. Among the most reliable and
55 well-tested models that describe ion binding to HS are Model VI and NICA-Donnan
56 (Kinniburgh et al., 1999; Tipping, 1998). Both models are recognized as providing good fit to
57 most data, but due to their different formulations, their predictions do not necessarily
58 converge (Ahmed et al., 2014; Unsworth et al., 2006). One of the key uncertainties using
59 these models is whether the HS considered in the modelling are truly representative of the soil
60 solution DOM. To describe the interactions of DOM with ions using Model VI or NICA-
61 Donnan, it is necessary to evaluate the fraction of active DOM (i.e., proportion of DOM that
62 can effectively complex with metals) and its composition (relative proportions of HA and
63 FA). In most cases, assumptions are made on these two parameters to model the ion
64 speciation, but the proportions of FA and HA in DOM, as well as their concentrations, depend
65 on the type of organic matter and can thus vary from one soil to another (Baken et al., 2011;
66 Dudal and Gérard, 2004; Groenenberg et al., 2010). However, as the DOM plays a major role
67 in the speciation of metals in soil solution, changes in its composition or its quantification can
68 strongly influence the free metal ion concentrations and can thus alter their environmental
69 impact (Amery et al., 2007; Cloutier-Hurteau et al., 2007; Groenenberg et al., 2010; Weng et
70 al., 2002). Weng et al. (2002) compared the chemical speciation of metals obtained with

71 Model VI and NICA-Donnan with a variation of DOM composition, but to our knowledge,
72 this is the only study using this approach and only focusing on acidic soils. In calcareous soils
73 the presence of carbonates and the alkaline pH strongly influence the speciation of metals and
74 then their mobility (Daldoul et al., 2015).

75 The objectives of this study were (i) to compare the metal speciation results in soil solution
76 obtained by two distinct models and (ii) to assess the impact of the DOM composition on the
77 metal speciation. After the evaluation of trace metal elements (i.e., Cu, Ni, Pb and Zn)
78 mobility in alkaline soils using partition coefficients, their speciation in the soil solution was
79 evaluated using Model VI and NICA-Donnan with various proportions of HA and FA.

80

81 **2. Materials and methods**

82 2.1. Study area

83 The study site is located in the north east of France and covers approximately 3 ha. All of the
84 studied soils are developed over calcareous substratum. Several activities have occurred on
85 the studied site, including: crop growth, landfills, wastewater spreading and scrap dealer
86 activities. All of these activities have led to soil contamination with inorganic pollutants (Cu,
87 Pb, Zn, etc.). To evaluate the impact of these activities on the soil quality, spatial modelling of
88 Cu, Ni, Pb and Zn was performed. Fifty-eight topsoil samples (5-10 cm) were collected and
89 geolocalized. Maps of the distribution of the selected trace elements were produced using
90 ordinary kriging with a cross validation using the VESPER (Minasny et al., 2005) and
91 ArcGIS software (Figure A1).

92 Based on the maps, 4 soil profiles (SPs) were sampled from the surface down to the bedrock
93 (approximately 70 cm of depth). All of the studied SPs were defined as calcisols (WRB,

94 2014) characterized by the presence of an A horizon developed over a calcareous substratum.
95 SP1 is located near the cultivated area, SP2 near the scrap dealer activities zone, SP3 in a
96 wooded part of the site and SP4 near the wastewater spreading disposal. During sampling of
97 SP2, it was noted that the first 30 cm were backfilled with many types of waste (glass, plastic,
98 metal, bricks, etc.). This uppermost soil horizon can be referred to as an anthropogenic
99 horizon overlying a natural soil profile. Below 30 cm, SP2 became similar to SP1, SP3 and
100 SP4.

101

102 2.2. Analyses of soil

103 The soils were air-dried and sieved at 2 mm for chemical analyses. Pseudo total soil metal
104 contents were determined by ICP-OES (Thermo Scientific iCAP 6000 series) following aqua
105 regia digestion of ground samples. Soil pH was determined in a mixture of 1:2.5 soil:water
106 (w/v). The CaCO₃ and organic carbon contents were determined following ISO 10693 and
107 ISO 14235, respectively (AFNOR 2009).

108

109 2.3. Analyses of soil solution

110 Different protocols are available to extract a soil solution. In this work, the soil solutions were
111 obtained by extraction with a diluted salt solution. The protocol was adapted from Sauvé et al.
112 (2000a). 200 mL of 5 mmol.L⁻¹ KNO₃ solution was added to 100 g of soil. The mixture was
113 shaken for 20 min and then centrifuged at 3500 rpm for 10 min. The solutions were then
114 passed through 0.45 µm cellulosic membranes.

115 The soil solutions were analysed for pH, dissolved organic carbon (DOC) and inorganic
116 carbon using a TOC analyser (OI Analytical 1010 TOC analyser), anions by ionic
117 chromatography (DIONEX, ICS-2000) and metals after acidification by ICP-OES.

118

119 2.4. Partition coefficient

120 Metal mobility can be evaluated using a simple partition coefficient (K_d , expressed in $L.kg^{-1}$)
121 between the metal bound to soil solids (sorbed metal in $mg.kg^{-1}$) and the dissolved metal in
122 the soil solution (dissolved metal in $mg.L^{-1}$), as follows:

$$123 \quad K_d = \frac{\textit{sorbed metal}}{\textit{dissolved metal}}$$

124 The lower the K_d value, the more mobile the metal is in the soil, and vice versa.

125

126 2.5. Chemical speciation calculations

127 To perform chemical speciation calculations, the measured concentration in the soil solution
128 of Al, Ca, Cu, Fe, Mg, Ni, Pb, Zn, HCO_3^- , Cl^- and SO_4^{2-} , as well as the pH values, are used as
129 input data. Al, Ca, Fe and Mg are considered because they can bind to DOM and compete
130 with metals of interest, and the anions influence the speciation of the non-binding elements
131 (Ge et al., 2005; Ren et al., 2015). Only organic ligands are considered for the modelling
132 because they are recognized to be key parameters for metal complexes (Ren et al., 2015;
133 Tipping et al., 2003; Zhao et al., 2007). Moreover, preliminary tests demonstrated that the
134 impact of Fe oxides was negligible on the metal speciation in our soil solution. The
135 DOM/DOC ratio of all samples is taken to be equal to 2 (Weng et al., 2002). The HS fractions
136 of DOM in the soil solution could vary between 14 and 63% depending on the samples
137 (Groenenberg et al., 2010). In the speciation calculations presented here, 50% of the DOM is

138 considered to consist of HS able to complex metals (Almas et al., 2006; Pourret et al., 2015),
139 thus, the active-DOM/DOC ratio is taken as equal to unity for these samples. Four hypotheses
140 have been tested with different proportions of FA and HA to describe DOM: (i) 100% of HS
141 are FA, (ii) 100% are HA, (iii) 35% are HA, and 65% FA and (iv) 84% are HA, and 16% FA.
142 To determine the influence of the DOM nature, we chose to investigate the two extreme
143 compositions (hypotheses i and ii). Groenenberg et al. (2010) and Ren et al. (2015)
144 demonstrated in their soil solution that DOM consists mainly of FA. Thus, hypothesis (i)
145 seems to be more realistic, but it is not necessarily the one that is used in all modelling works.
146 Two intermediate assumptions have been tested to evaluate the respective part of FA and HA
147 in metal complexes: hypothesis (iii) close to the one tested by Cloutier-Hurteau et al. (2007),
148 and hypothesis (iv) corresponds to the soil organic matter composition proposed by Tipping et
149 al. (2003).

150 Two main approaches are used to describe the binding of protons and metal ions with HS:
151 Model VI (Tipping, 1998) and NICA-Donnan (Kinniburgh et al., 1999). Model VI is a
152 discrete binding site model that assumes that metal complexation by organic matter involves
153 two types of discrete sites. NICA-Donnan describes these interactions using two types of
154 binding sites, each with a continuous distribution of binding strengths. Both models use the
155 Donnan approach to describe the electrostatic effects and consider competitive binding to the
156 functional groups. The calculations were executed with the computer programs WHAM 6
157 (Tipping, 1994) and ECOSAT (Keizer and Van Riemsdijk, 1999) including Model VI and
158 NICA-Donnan, respectively. The default constant values for metal and proton humic binding
159 in each program were used (Milne et al., 2003; Tipping, 1998, 2002).

160

161 **3. Results and discussion**

162 3.1. Metal concentrations in soil and soil solution

163 SP1 located near the cultivated area presents the lowest metal concentrations, and SP2 located
164 near the scrap dealer activity zone, the highest metal concentrations. SP3 and SP4, which are
165 located in a wooded part of the site and near the wastewater spreading disposal, respectively,
166 also exhibit high metal concentrations (Table A1).

167 High CaCO_3 contents were measured all along the profiles, and the soil pH ranged between
168 7.0 and 8.4 (i.e., expected values for soil developed over calcareous substratum). Soil organic
169 carbon (SOC) contents decrease with depth and are lower in SP1 for the first 20 cm. DOC
170 concentrations present the same evolution with depth as SOC, except for SP2. The DOC
171 concentrations in SP2 are very low, between 5 and 30 cm, compared to the other SPs (Table
172 A1).

173 The concentrations of Cu, Ni, Pb and Zn strongly decrease with depth in SP2, 3 and 4. This
174 vertical distribution is in agreement with a contamination that mainly originates from
175 superficial deposition.

176 The Cu, Ni, Pb and Zn concentrations in the soil solutions are presented in Figure 1. The
177 highest concentrations of Cu, Ni and Zn in soil solution are measured in the topsoil samples
178 (0-30 cm) of SP4. Except for Pb, the concentrations measured in the solution of the topsoil of
179 SP2 are not the highest, as could have been expected based on soil concentrations. Metals
180 mobility seems different in SP2 compared to the three other SPs.

181

182 3.2. Metal mobility

183 The K_d values of Cu, Ni, Pb and Zn are of the same order of magnitude in SP1, SP3 and SP4:
184 $\text{Log}(K_d)$ values are between 2.5 and 3 for Cu and Ni, around 4.5 for Pb and between 2.9 and

185 3.5 for Zn. In SP2, the Log(K_d) values are higher in the first 30 cm than in the other SPs for
186 the four elements (4.5 for Cu, 5 for Ni, 6 for Pb and 4.5 for Zn; Figure A2). These results
187 indicate that (i) Cu, Ni, Pb and Zn present the same behaviour in SP1, SP3 and SP4 and (ii)
188 for the first 30 cm, their mobility in SP2 is systematically far lower than that in the other SPs.
189 The calculated K_d values (Table 1) are of the same order of magnitude as those reported by
190 Sauvé et al. (2000b) and Luo et al. (2006). The observed order of metal mobility is consistent
191 with previous studies: Cu>Ni>Zn>>Pb, with Pb always being the least mobile element. For a
192 given element, K_d values can greatly vary depending on the soil properties or the nature of the
193 contamination (Sauvé et al. 2000b). The observations of SP2 suggest that the properties of the
194 upper part of this SP have been modified, likely by anthropogenic activities. During sampling,
195 it was noted that the first 30 cm of SP2 has been backfilled with a significant amount of
196 wastes. At the surface of SP2, an important soil contamination occurs that seems to be linked
197 to scrap dealer activities. The mobility of this fraction of metal brought to the soil is relatively
198 low.

199 Solid-solution partition was a first approach to evaluate metal mobility in soil and potential
200 leaching losses. However, partition coefficients are not sufficient to estimate metal
201 bioavailability, and to predict their potential environmental impacts, knowledge of their
202 chemical speciation is necessary. Different approaches are used to evaluate this speciation in
203 the soil like chemical extractions (Malandrino et al. 2011; Ferreyroa et al. 2014) or in the soil
204 solution like Donnan membrane technique (DMT, Temminghoff et al., 2000; Cancès et al.
205 2003; Weng et al. 2002). However free ion concentrations predicted by speciation modelling
206 is often preferred as it is easier to determine. Indeed, speciation modelling only requires total
207 metal concentrations and basic physico-chemical properties.

208

209

210 3.3. Metal speciation in the soil solution

211 Two models with different assumptions were used to evaluate the reliability of speciation
212 results in the soil solution. The discussion will focus on two fractions of metal in the soil
213 solution: the metal associated to DOM and the free metal ion. These two fractions represent
214 between 70% and 100% of the 4 metal concentrations in the soil solutions (100% for Cu and
215 Pb, Table 2). The remaining fraction for Ni and Zn mainly consist of carbonate species
216 (ZnHCO_3^+ and NiHCO_3^+). These results are consistent with the high content of CaCO_3 in the
217 soil and the alkaline pH (Courdouan et al., 2008; Unsworth et al., 2006).

218 3.3.1. Me-DOM interactions

219 Figure 2 and Table 2 present the calculated concentrations of metal bound to DOM (expressed
220 in logarithm and percentage, respectively) using the two approaches (NICA-Donnan and
221 Model VI) and considering the first two assumptions: active DOM assimilated to (i) FA or (ii)
222 HA.

223 The mean fraction of metal associated with DOM ranged between 8.2% and 100% of the bulk
224 dissolved concentration depending on the element and the samples (Table 2). The
225 complexation with DOM is found to be more important for Cu and Pb (almost 100%) than for
226 Ni and Zn, as observed in other studies (Weng et al., 2002; Ren et al., 2015).

227 The results of the two models are identical for Cu and Pb. As observed by Unsworth et al.
228 (2006) and Weng et al. (2002), Model VI slightly under-estimates the Ni fraction associated
229 with DOM, and contrary to the observations of Weng et al. (2002), it over-estimates the Zn
230 fraction associated with DOM compared to NICA-Donnan. The agreement between the

231 concentrations calculated with NICA-Donnan and Model VI is within one order of magnitude
232 for the four elements.

233 The impact of the component used to simulate DOM (assumption i or ii) on the metal
234 speciation is significant and depends on the element considered. For Cu and Pb, the variations
235 are negligible, and a good agreement is observed between the two models regardless of the
236 composition of DOM. Cu and Pb present high affinity for humic substances thereby leading to
237 between 80% and 100% of metal bound to DOM irrespective of the DOM nature. The
238 proportions of Ni and Zn associated with DOM are higher when HA are considered, as
239 already observed by Weng et al. (2002) and Unsworth et al. (2006). These results are in
240 agreement with the work of Groenenberg et al. (2010), who found that the impact of the DOM
241 composition on metal speciation is most important for metals with a relatively low affinity for
242 DOM.

243 A significant impact of DOM composition on model agreement is observed for Zn.
244 Considering only FA (Table 2, Figure 2a), Model VI predicts largely more Zn associated with
245 DOM than NICA-Donnan. When only HA are considered (Table 2, Figure 2b), concentrations
246 of Zn associated with DOM are in better agreement for both models, even if Model VI always
247 predicts slightly more Zn associated with DOM. This difference could be linked to the affinity
248 constant values. In Model VI, the affinity constants of Zn for FA and HA are of the same
249 order of magnitude (Tipping, 2002), while in NICA-Donnan, the affinity constants optimized
250 by Milne et al. (2003) for Zn are higher for HA than for FA. Moreover, the affinity constants
251 of Zn used in NICA-Donnan and in Model VI are optimized on a limited set of data compared
252 to the other studied elements (Milne et al., 2003; Tipping, 2002).

253 The two models distinguish between electrostatic and specific interactions of metal with
254 DOM. For Cu and Pb, mainly specific interactions are involved in complexation, and

255 electrostatic interactions are negligible. The electrostatic interactions are more important for
256 Zn and Ni and can represent up to 80% of the Zn-DOM interactions. The contribution of non-
257 specific binding is greater for weakly bound metal (Tipping, 2002), which is the case for Zn
258 and Ni compared to Cu and Pb.

259 Regardless of the composition of DOM, NICA-Donnan always predicts more Zn and Ni
260 electrostatically associated with DOM than Model VI (Figure 3). When only HA are taken
261 into account, the proportions of Zn and Ni associated with DOM are higher and the
262 electrostatic interactions are lower, with the specific interactions being dominant for both
263 models. In this case, the predictions of the two models are closer for Ni. Both models adopt
264 the Donnan volume concept, but they differ slightly in its implementation. The Donnan
265 volume in the NICA-Donnan model is smaller and less variable than in Model VI, which
266 results in greater attraction of divalent ions to neutralize the fixed charge on the humic
267 molecule (Tipping, 2002). This difference could also explain the divergence between the
268 results of NICA-Donnan and Model VI.

269 The two other assumptions (iii: active DOM assimilated to 35% HA and 65% FA; iv: active
270 DOM assimilated to 84% HA and 16% FA) were tested, and the results are presented in
271 Figure 4.

272 The results obtained with assumptions (iii) and (iv) are in agreement with the previous results
273 and are an intermediate between a calculation considering only FA and a calculation
274 considering only HA (Figure 4). These results could be directly derived from the results
275 obtained with assumptions (i) and (ii) using simple linear equations:

$$276 \text{ Me-DOM (35\% HA and 65\% FA) = Me-DOM (100\%HA)*0.35+Me-DOM (100\%FA)*0.65} \quad \text{eq. 1}$$

$$277 \text{ Me-DOM (84\% HA and 16\% FA) = Me-DOM (100\%HA)*0.84+Me-DOM (100\%FA)*0.16} \quad \text{eq. 2}$$

278 The concentrations calculated with equations 1 and 2 are compared to the concentrations
279 obtained with assumptions (iii) and (iv) (Figure A3). Because the impact of the nature of
280 DOM is negligible on Cu and Pb, only the results for Ni and Zn are discussed.

281 The concentrations of Ni and Zn associated with DOM calculated with equations 1 and 2 are
282 similar to those predicted with the models. The same results are obtained considering
283 assumption (iv) (results not shown). These results are consistent because the two organic
284 components (HA and FA) are considered for modelling as two independent components.

285 When DOM is assimilated to a mixture of HA and FA, it is interesting to study how Cu, Ni,
286 Pb and Zn are distributed among the two organic components. Figure 5 presents the
287 proportions of metal associated with HA predicted by NICA-Donnan compared to the
288 proportions predicted by Model VI. It appears that the two models provide similar results. The
289 four studied elements present different behaviours. With assumption (iii) (Figure 5a), Pb is
290 principally associated with FA, Ni and Cu are approximately equally distributed among the
291 two components, and Zn is principally associated with HA. NICA-Donnan predicts slightly
292 more Cu, Ni and Zn associated with HA than Model VI. With assumption (iv) (Figure 5b), the
293 four elements are principally associated with HA. However, a difference is still observable
294 between Pb and the 3 other elements. The association of Pb with FA represents between 10%
295 and 40% of the Pb associated to DOM, while it represents less than 10% for the other metals.

296 The two models predict close concentrations of metal associated with DOM using FA, HA or
297 a mixture of them, with an exception for Zn associated with FA. The fraction of metal
298 associated electrostatically with DOM is slightly higher with NICA-Donnan. When a mixture
299 of HA and FA is used to mimic DOM, NICA-Donnan predicts slightly more Cu, Ni and Zn
300 associated with HA than Model VI. Both models are therefore coherent. By contrast, the
301 consideration of DOM composition, when modelling metal speciation, has a significant

302 impact on model results and thus on the prediction reliability of the metal proportions
303 associated with organic matter.

304

305 3.3.2. Free metal concentrations

306 The comparison of free metal concentrations calculated with both models following two
307 distinct assumptions, (i) and (ii), is presented in Figure 6 and Table 2.

308 The mean fraction of free metal ions ranged between 0.03% and 78% of the total dissolved
309 concentration, depending on the element and the samples (Table 2). The two models predict
310 free ion concentrations of the same order of magnitude, except for the lower concentrations
311 for which the differences are significant. When the DOM is assimilated to FA, both models
312 predict the same range of Zn, Ni and Cu free ion concentrations, although Cu²⁺ concentrations
313 of few samples are far from the y=x line. The Pb²⁺ concentrations predicted by Model VI are
314 slightly higher than those predicted by NICA-Donnan (Figure 6). Similar results have been
315 observed by Weng et al. (2002). This difference could be explained by an uncertainty in the
316 Pb generic parameters used to describe Pb-DOM interactions with NICA-Donnan (Ren et al.,
317 2015). Xiong et al. (2013) proposed new parameters to describe these interactions that
318 improved the Pb binding to FA predictions compared with experimental results (Ren et al.,
319 2015). These new parameters have been tested in our study, but the Pb²⁺ concentrations
320 calculated with NICA-Donnan were largely higher (2 order of magnitude) than the Pb²⁺
321 concentrations calculated with Model VI. The use of the generic parameters defined by Milne
322 et al. (2003) provided closer results to those obtained with Model VI.

323 When the DOM is assimilated to HA, the two models predict fewer free ions in solution,
324 which is in agreement with more associations with DOM. The results of the two models are
325 comparable for Ni²⁺ concentrations. The differences between the two models are more

326 marked for Cu^{2+} , Pb^{2+} and Zn^{2+} and exceed one order of magnitude for a few samples. For
327 these elements, the concentrations calculated by NICA-Donnan are generally slightly higher
328 than those calculated by Model VI.

329 Pb and Cu are principally associated with DOM. Their free ion concentrations are very low in
330 the studied samples, which leads to a great difference between the two models. In the same
331 context, several studies (Ahmed et al., 2014; Ren et al., 2015; Unsworth et al., 2006) have
332 concluded that the concentrations of free ions, when they represent a very small fraction of
333 total dissolved concentrations, may be underestimated by several orders of magnitude by the
334 models compared with analytical techniques. Ren et al. (2015) explained this discrepancy by
335 the assumptions on the DOM nature made for the modelling.

336 The concentrations of free ions calculated by the two models with assumptions (iii) and (iv)
337 on the DOM composition are not presented. These concentrations can be estimated with
338 simple linear equations using the free ion concentrations predicted, considering assumptions
339 (i) and (ii) as evidence for the concentrations of metal associated with DOM.

340 To assess the impact of the assumptions made on the DOM nature, the ratio between the free
341 metal ion concentrations calculated with active DOM assimilated to (i) FA and (ii) HA is
342 calculated for each sample. The mean ratios are presented in Table 3.

343 The impact of the DOM nature on metal speciation is different depending on the elements.
344 The concentrations of free metal can be from 1.2 to 11 times more important if FA are
345 considered rather than HA. As observed before, the impact is more marked for Cu, Pb and Zn.
346 The impact of the DOM nature seems to be more important on the Model VI predictions.
347 Inverse tendency was observed by Weng et al. (2002). In our alkaline soil samples, Cu and Pb
348 are mainly associated with DOM. The free ion concentrations are still very low, regardless of
349 the assumption of DOM composition, which is not the case in acidic soils. Indeed, in acidic

350 conditions, the free ion concentrations are higher, and the impact of the DOM composition on
351 speciation modelling could thus be more important for the consequences on environmental
352 impact prediction. These results demonstrate the importance of the assumptions made about
353 DOM composition for speciation modelling.

354

355 **4. Conclusion**

356 The aims of this study were to evaluate the mobility of Cu, Ni, Pb and Zn in alkaline
357 contaminated soils, to compare the metal speciation results obtained by two different models
358 and to assess the impact of the composition of the DOM on metal speciation predictions. This
359 study was carried out on 36 soil samples defined as calcisols (pH range between 7.0 and 8.4)
360 and that have different contamination levels. The K_d values indicated a relatively low
361 mobility of the four metals, especially on the most contaminated soil samples. Moreover the
362 soil solution speciation study has evidenced that the free metal concentrations are very low in
363 field conditions (alkaline pH and high DOM content). The environmental risks presented by
364 the studied site are currently limited. However, as being controlled by the field conditions,
365 metal mobility and environmental impact of the site could be substantially increased if any
366 changes of these conditions occur.

367 The modelling results obtained showed that the two tested models (NICA-Donnan and Model
368 VI) provided comparable speciation results, even if some differences have been highlighted in
369 this work, including the description of the electrostatic interactions, the Zn-FA interactions
370 and the very low predicted free ions concentrations. A comparison with experimental
371 speciation results would have been helpful to allow a validation of the modelling. The main
372 result of this work shows the impact of the composition of the DOM on the modelling results,
373 especially the free ion concentrations, which could vary from one order of magnitude

374 depending on whether HA or FA is used to represent DOM. A way to avoid this uncertainty is
375 to characterize the DOM by measuring the respective proportions of HA and FA. Different
376 techniques are available to approach the DOM composition, but they are not always easily
377 operable (McDonald et al., 2004; Mueller et al., 2012; Van Zomeren and Comans, 2007). It is
378 thus essential to be aware of the impact of the assumptions made on the nature of the DOM
379 for the modelling regardless of the model used.

380

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384

385

386 References

387 Afnor (2009) *Qualité des sols – Pédologie*, Association Française de Normalisation, Paris.

388 Almas A.R., Lombnaes P., Sogn T.A., Mulder J., 2006. Speciation of Cd and Zn in
389 contaminated soils assessed by DGT-DIFS, and WHAM/Model VI in relation to uptake by
390 spinach and ryegrass. *Chemosphere*, 62, 1647-1655.

391 Ahmed I.A.M., Hamilton-Taylor J., Bieroza M., Zhang H., Davison W., 2014. Improving and
392 testing geochemical speciation predictions of metal ions in natural waters. *Water Research*,
393 67, 276-291.

394 Amery F., Degryse F., Degeling W., Smolders E., and Merckx R., 2007. The copper-
395 mobilizing-potential of dissolved organic matter in soils varies 10-fold depending on soil
396 incubation and extraction procedures. *Environmental Science and Technology* 41, 2277-2281.

397 Ardestani M.M., van Straalen N.M., van Gestel C.A.M., 2014. The relationship between
398 metal toxicity and biotic ligand binding affinities in aquatic and soil organisms: A review.
399 *Environmental Pollution*, 195, 133-147.

400 Baken S., Degryse F., Verheyen L., Merckx R., Smolders E., 2011. Metal complexation
401 properties of freshwater dissolved organic matter are explained by its aromaticity and by
402 anthropogenic ligands. *Environmental Science and Technology*, 45, 2584-2590.

403 Cancès B., Ponthieu M., Castrec-Rouelle M., Aubry E. Benedetti, M.F., 2003. Metal ions
404 speciation in a soil and its solution: experimental data and model results. *Geoderma*, 113, 341-
405 355.

406 Cloutier-Hurteau B., Sauvé S., Courchesne F., 2007. Comparing WHAM 6 and MINEQL+4.5
407 for the chemical speciation of Cu^{2+} in the rhizosphere of forest soils. *Environmental Science*
408 *and Technology*, 41, 8104-8110.

409 Courdouan A., Christl I., Rabung T., Wersin P., Kretzschmar R., 2008. Proton and trivalent
410 metal cation binding by dissolved organic matter in the Opalinus Clay and the Callovo-
411 Oxfordian formation. *Environmental Science and Technology*, 42, 5985-5991.

412 Daldoul G., Souissi R., Souissi F, Jemmali N., Chakroun H.K., 2015. Assessment and
413 mobility of heavy metals in carbonated soils contaminated by old mine tailings in North
414 Tunisia. *Journal of African Earth Sciences*, 110, 150-159.

415 Dudal Y., Gérard F., 2004. Accounting for natural organic matter in aqueous chemical
416 equilibrium models : a review of the theories and applications. *Earth-Science Reviews*, 66,
417 199-216.

418 Ferreyroa G.V., Montenegro A.C., Tudino M.B., Lavado R.S. and Molina F.V., 2014. Time
419 evolution of Pb(II) speciation in Pampa soil fractions. *Chemical Speciation & Bioavailability*,
420 26, 210-218.

421 Ge Y., MacDonald D., Sauvé S., Hendershot W., 2005. Modeling of Cd and Pb speciation in
422 soil solutions by WinHumicV and NICA-Donnan model. *Environmental Modelling and*
423 *Software*, 20, 353-359.

424 Groenenberg J.E., Koopmans G.F., Comans R.N.J., 2010. Uncertainty analysis of the
425 Nonideal Competitive Adsorption-Donnan Model: Effects of dissolved organic matter
426 variability on predicted metal speciation in soil solution. *Environmental Science and*
427 *Technology*, 44, 1340-1346.

428 Keizer M.G., van Riemsdijk W.H., 1999. ECOSAT: Equilibrium Calculation of Speciation
429 and Transport, User Manual, Version 4.7. Wageningen Agricultural University, The
430 Netherlands.

431 Khalil A., Hanich L., Bannari A., Zouhri L., Pourret O., Hakkou R., 2013. Assessment of soil
432 contamination around an abandoned mine in a semi-arid environment using geochemistry and
433 geostatistics: Pre-work of geochemical process modeling with numerical models. *Journal of*
434 *Geochemical Exploration*, 125, 117-129.

435 Khan S., Cao Q., Zheng Y.M., Huang Y.Z. and Zhu Y.G., 2008. Health risks of heavy metals
436 in contaminated soils and food crops irrigated with wastewater in Beijing, China.
437 *Environmental Pollution*, 152, 686-692.

438 Kinniburgh D.G., Van Riemsdijk W.H., Koopal L.K., Borkovec M., Benedetti M.F., and
439 Avena M.J., 1999. Ion binding to natural organic matter : competition, heterogeneity,
440 stoichiometry and thermodynamic consistency. *Colloids and Surfaces A-Physicochemical and*
441 *Engineering Aspects*, 151, 147-166.

442 Koopal L.K., Saito T., Pinheiro J.P., van Riemsdijk W.H., 2005. Ion binding to natural
443 organic matter: General considerations and the NICA-Donnan model. *Colloids and Surfaces*
444 *A: Physicochemical and Engineering Aspects*, 265, 40-54.

445 Luo X.S., Zhou D.M., Liu X.H., Wang Y.J., 2006. Solid/solution partitioning and speciation
446 of heavy metals in the contaminated agricultural soils around a copper mine in eastern
447 Nanjing city, China. *Journal of Hazardous Materials*, A131, 19-27.

448 Malandrino M., Abollino O., Buoso S., Giacomino A., La Gioia C., Mentasti E., 2011.
449 Accumulation of heavy metals from contaminated soil to plants and evaluation of soil
450 remediation by vermiculite. *Chemosphere*, 82, 169-178.

451 McDonald S., Bishop G., Prenzler P.D., Robards K., 2004. Analytical chemistry of freshwater
452 humic substances. *Analytica Chimica Acta*, 527, 105-124.

453 Milne C.J., Kinniburgh D.G., van Riemsdijk W.H., Tipping E., 2003. Generic NICA-Donnan
454 model parameters for metal ion binding by humic substances. *Environmental Science and*
455 *Technology*, 37, 958-971.

456 Minasny B., Mc Bratney A.B., Whelan B.M., 2005. VESPER version 1.62. Australian Centre
457 for Precision Agriculture, McMillan Building A05, The University of Sydney, NSW 2006.

458 Mueller K.K., Lofts S., Fortin C., Campbell P.G.C., 2012. Trace metal speciation predictions
459 in natural aquatic systems: incorporation of dissolved organic matter (DOM) spectroscopic
460 quality. *Environmental Chemistry*, 9, 356-368.

461 Nolan A.L., McLaughlin J., Mason S.D., 2003. Chemical speciation of Zn, Cd, Cu and Pb in
462 pore waters of agricultural and contaminated soils using donnan dialysis. *Environmental*
463 *science and technology*, 37, 90-98.

464 Oste L.A., Temminghoff E.J.M., Lexmond T.M., Van Riemsdijk W.H., 2002. Measuring and
465 Modeling Zinc and Cadmium Binding by Humic Acid. *Analytical Chemistry*, 74, 856-862.

466 Pourret O., Lange B., Houben D., Collinet G., Shutcha M. and Faucon M-P., 2015. Modeling
467 of cobalt and copper speciation in metalliferous soils from Katanga (Democratic Republic of
468 Congo). *Journal of Geochemical Exploration*, 149, 87-96.

469 Ren Z.L., Tella M., Bravin M.N., Comans R.N.J., Dai J., Garier J.M., Sivry T., Doelsch E.,
470 Straathof A., Benedetti M.F., 2015. Effect of dissolved organic matter composition on metal
471 speciation in soil solutions. *Chemical Geology*, 398, 61-69.

472 Sauvé S., Norvell W.A., McBride M., and Hendershot W., 2000a. Speciation and
473 Complexation of Cadmium in Extracted Soil Solutions. *Environmental Science and*
474 *Technology*, 23, 291-296.

475 Sauvé S., Hendershot W., Allen H.A., 2000b. Solid-solution partitioning of metals in
476 contaminated soils: dependence on pH, total metal burden, and organic matter. *Environmental*
477 *Science and Technology*, 34, 1125-1131.

478 Temminghoff E.J.M., Plette A.C.C., Van Eck R., Van Riemsdijk W.H. (2000). Determination
479 of the chemical speciation of trace metals in aqueous systems by the Wageningen Donnan
480 Membrane Technique. *Analytica Chimica Acta* 417 (2), 149-157.

481 Tipping E., 1994. WHAM – A chemical equilibrium model and computer code for waters,
482 sediments, and soils incorporating a discrete site/electrostatic model of ion-binding by humic
483 substances. *Computers & Geosciences*, 20, 973-1023.

484 Tipping E., 1998. Humic Ion-Binding Model VI: an improved description of the interactions
485 of protons and metal ions with humic substances. *Aquatic Geochemistry*, 4, 3-48.

486 Tipping, E., 2002. Cation binding by humic substances. University Press, Cambridge, 434 pp.

487 Tipping E., Rieuwerts J., Pan G., Ashmore M.R., Lofts S., Hill M.T.R., Farago M.E.,
488 Thornton I., 2003. The solid-solution partitioning of heavy metals (Cu, Zn, Cd, Pb) in upland
489 soils of England and Wales. *Environmental Pollution*, 125, 213-225.

490 Unsworth E.R., Warnken K.W., Zhang H., Davison W., Black F., Buffle J., Cao J., Cleven R.,
491 Galceran J., Gunkel P., Kalis E., Kistler D., Van Leeuwen H.P., Martin M., Noël S., Nur Y.,
492 Odzak N., Puy J., Van Riemsdijk W., Sigg L., Temminghoff E., Tercier-Waeber M-L.,
493 Toepperwien S., Town R. M., Weng L., Xue H., 2006. Model Predictions of Metal Speciation
494 in Freshwaters Compared to Measurements by In Situ Techniques. *Environmental Science
495 and Technology*, 40, 1942-1949.

496 Van Riemsdijk W.H., Koopal L.K., Kinniburgh D.G., Benedetti M.F., Weng L., 2006.
497 Modling the interactions between humics, ions, and mineral surfaces. *Environmental Science
498 and Technology*, 40, 7473-7480.

499 Van Zomeren A., Comans R.N.J., 2007. Measurement of humic and fulvic acid
500 concentrations and dissolution properties by a rapid batch procedure. *Environmental Science
501 and Technology*, 41, 6755-6761.

502 Weng L., Temminghoff E.J.M., Lofts S., Tipping E., Van Riemsdijk W.H., 2002.
503 Complexation with dissolved organic matter and solubility control of heavy metals in a sandy
504 soil. *Environmental Science and Technology*, 36, 4804-4810.

505 World reference base for soil resources 2014, World Soil Resources Reports 106, FAO

506 Zhao L.Y.L., Schulin R., Weng L., Nowack B., 2007. Coupled mobilization of dissolved
507 organic matter and metals (Cu and Zn) in soil columns. *Geochimica et Cosmochimica Acta*,
508 71, 3407-3418.

509 Xiong J., Koopal L.K., Tan W., Fang L., Wang M., Zhao W., Liu F., Zhang J., Weng L.,
510 2013. Lead Binding to Soil Fulvic and Humic Acids: NICA-Donnan Modeling and XAFS
511 Spectroscopy. *Environmental Science and Technology*, 47, 11634-11642.

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1 Evaluation of the impact of organic matter composition on metal speciation in calcareous soil
2 solution: comparison of Model VI and NICA-Donnan

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5 **Table captions**

6 Table 1. Partition coefficients (K_d ; 10^4L.kg^{-1}) for the four studied elements: arithmetic mean,
7 corresponding standard deviation (SD), median, minimum and maximum values and
8 $\log K_d$ (median), $n=36$.

9 Table 2. Mean percentage and standard deviation ($n=36$) of free ion metal and metal
10 associated with DOM calculated with NICA-Donnan and Model VI. Active DOM is
11 assimilated to FA (i) or to HA (ii).

12 Table 3. Mean ratio between the free ion concentration with active DOM assimilated to FA
13 and to HA and standard deviation calculated with NICA-Donnan and Model VI ($n=36$).

14

15

16 Table 1. Partition coefficients (K_d ; 10^4L.kg^{-1}) for the four studied elements: arithmetic mean,
 17 corresponding standard deviation (SD), median, minimum and maximum values and
 18 $\log K_d$ (median), $n=36$.

| Element | Mean | SD | Median | Min | Max | Log K_d (median) |
|---------|-------|-------|--------|------|-------|--------------------|
| Cu | 0.76 | 2.14 | 0.07 | 0.02 | 27.52 | 2.81 |
| Ni | 1.16 | 2.13 | 0.07 | 0.03 | 41.84 | 2.82 |
| Pb | 14.94 | 38.34 | 2.95 | 1.13 | 537.9 | 4.47 |
| Zn | 0.73 | 1.18 | 0.30 | 0.07 | 26.42 | 3.47 |

19

20 Table 2. Mean percentage and standard deviation ($n=36$) of free ion metal and metal
 21 associated with DOM calculated with NICA-Donnan and Model VI. Active DOM is
 22 assimilated to FA (i) or to HA (ii).

| | | | Cu | Ni | Pb | Zn |
|-----------------|-----------------|--------------------|---------------|---------------|---------------|---------------|
| NICA- Donnan | (i) 100% FA | % Me^{2+} | 0.18 +/- 0.21 | 59.5 +/- 13.3 | 0.04 +/- 0.03 | 77.9 +/- 6.3 |
| | | % Me-DOM | 99.8 +/- 0.2 | 40.4 +/- 13.3 | 100 +/- 0.04 | 8.2 +/- 4.8 |
| | (ii) 100% HA | % Me^{2+} | 0.03 +/- 0.04 | 33.3 +/- 12.9 | 0.08 +/- 0.08 | 30.9 +/- 16.9 |
| | | % Me-DOM | 100 +/- 0.1 | 66.6 +/- 12.9 | 99.9 +/- 0.1 | 63.7 +/- 19.4 |
| Model VI | (i) 100% FA | % Me^{2+} | 0.12 +/- 0.16 | 48.7 +/- 11.5 | 0.10 +/- 0.12 | 44.9 +/- 11.1 |
| | | % Me-DOM | 98.6 +/- 2.9 | 21.3 +/- 10.4 | 99.4 +/- 1.3 | 41.0 +/- 15.0 |
| | (ii) 100% HA | % Me^{2+} | 0.04 +/- 0.08 | 41.2 +/- 13.9 | 0.06 +/- 0.13 | 11.2 +/- 9.8 |
| | | % Me-DOM | 99.6 +/- 1.5 | 33.7 +/- 17.0 | 99.6 +/- 1.4 | 85.4 +/- 12.6 |

23

24 Table 3. Mean ratio between the free ion concentration with active DOM assimilated to FA
 25 and to HA and standard deviation calculated with NICA-Donnan and Model VI ($n=36$).

| | NICA-Donnan | Model VI |
|----|--|--|
| | $[\text{Me}^{2+}]_{100\% \text{ FA}} / [\text{Me}^{2+}]_{100\% \text{ HA}}$ Mean +/- standard deviation | $[\text{Me}^{2+}]_{100\% \text{ FA}} / [\text{Me}^{2+}]_{100\% \text{ HA}}$ Mean +/- standard deviation |
| Cu | 5.64 ± 0.77 | 11.16 ± 7.55 |
| Ni | 1.94 ± 0.41 | 1.23 ± 0.20 |
| Pb | 0.47 ± 0.80 | 7.12 ± 9.84 |
| Zn | 3.33 ± 2.03 | 6.53 ± 4.25 |

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27

1 Evaluation of the impact of organic matter composition on metal speciation in calcareous soil
2 solution: comparison of Model VI and NICA-Donnan

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7 **Figure captions**

8 Figure 1. Cu, Ni, Pb and Zn concentrations in the extracted soil solutions: \diamond SP1; + SP2; \bullet
9 SP3; \blacktriangle SP4.

10 Figure 2. Comparison of metal bound to DOM concentrations (\square Cu, Δ Ni, \times Pb, \circ Zn)
11 calculated with NICA-Donnan and Model VI expressed as logarithm: active DOM is
12 assimilated to FA (a) or HA (b). The solid line is the $y=x$ line, and the dotted lines indicate +/-
13 one order of magnitude.

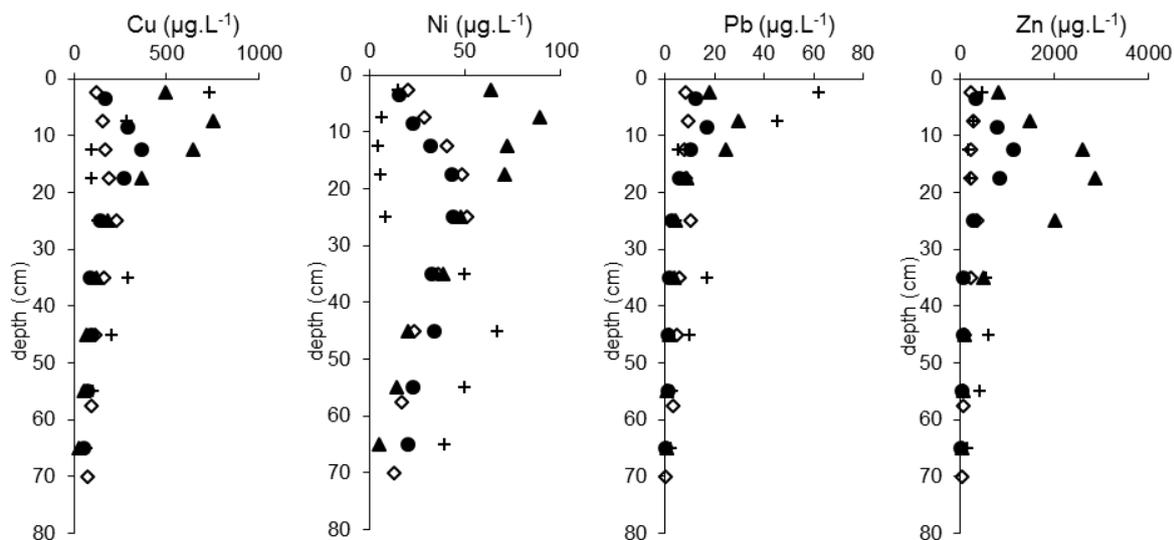
14 Figure 3. Comparison of the concentrations of metal bound to DOM via electrostatic
15 interactions (Δ Ni, \circ Zn) calculated with NICA-Donnan and Model VI expressed as
16 logarithm: active DOM assimilated to FA (a) or HA (b). The solid line is the $y=x$ line, and the
17 dotted lines indicate +/- one order of magnitude.

18 Figure 4. Comparison of metal bound to DOM concentrations, (\square : Cu, Δ : Ni, \times : Pb, \circ : Zn)
19 calculated with NICA-Donnan and Model VI expressed in logarithm: active DOM assimilated
20 to 35% HA and 65% FA (a) or to 84% HA and 16% FA (b). The solid line is the $y=x$ line, and
21 dotted lines indicate +/- one order of magnitude.

22 Figure 5. Comparison of the percentage of the metal associated with HA (\square Cu, Δ Ni, \times Pb,
23 \circ Zn) with respect to the total metal associated with DOM with NICA-Donnan and Model
24 VI: active DOM is assimilated to (iii) 35% HA and 65% FA (a), and (iv) 84% HA and 16%
25 FA (b). The solid line is the $y=x$ line, and the dotted line represents 20% deviation from the
26 $y=x$ line.

27 Figure 6. Comparison of free metal ion concentrations (\square Cu, Δ Ni, \times Pb, \circ Zn,) calculated
28 with NICA-Donnan and Model VI expressed in logarithm. Active DOM is assimilated to FA
29 (a) or HA (b). The solid line is the $y=x$ line, and the dotted lines indicate \pm one order of
30 magnitude.

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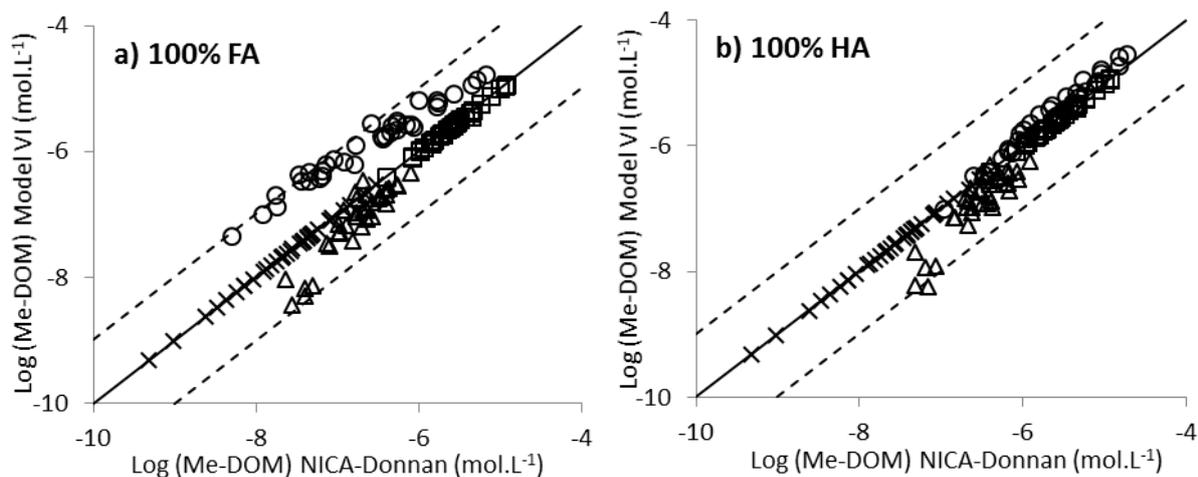
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33 Figure1. Cu, Ni, Pb and Zn concentrations in the extracted soil solutions: \diamond SP1; + SP2; \bullet

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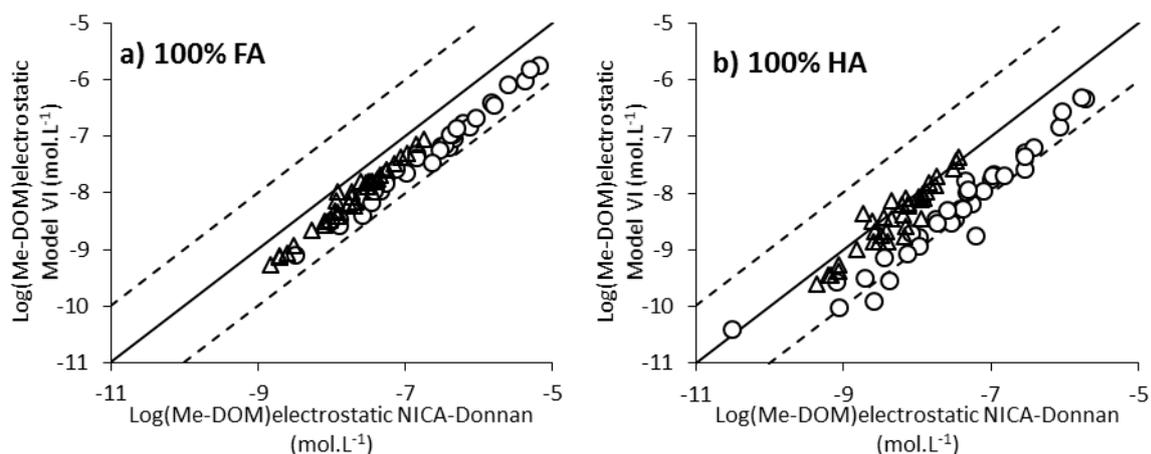
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38 Figure 2. Comparison of metal bound to DOM concentrations (\square Cu, Δ Ni, \times Pb, \circ Zn)

39 calculated with NICA-Donnan and Model VI expressed as logarithm: active DOM is

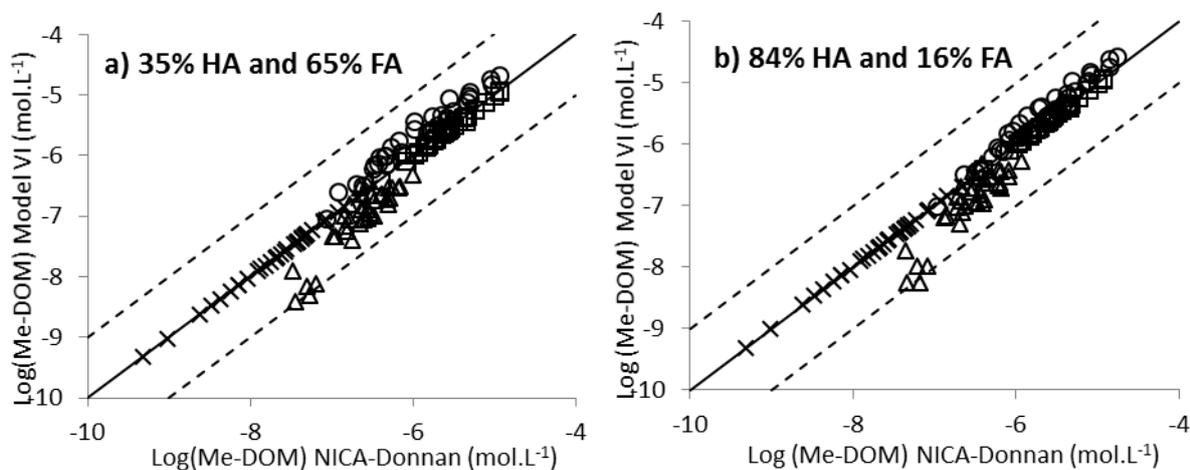
40 assimilated to FA (a) or HA (b). The solid line is the $y=x$ line, and the dotted lines indicate +/-

41 one order of magnitude.

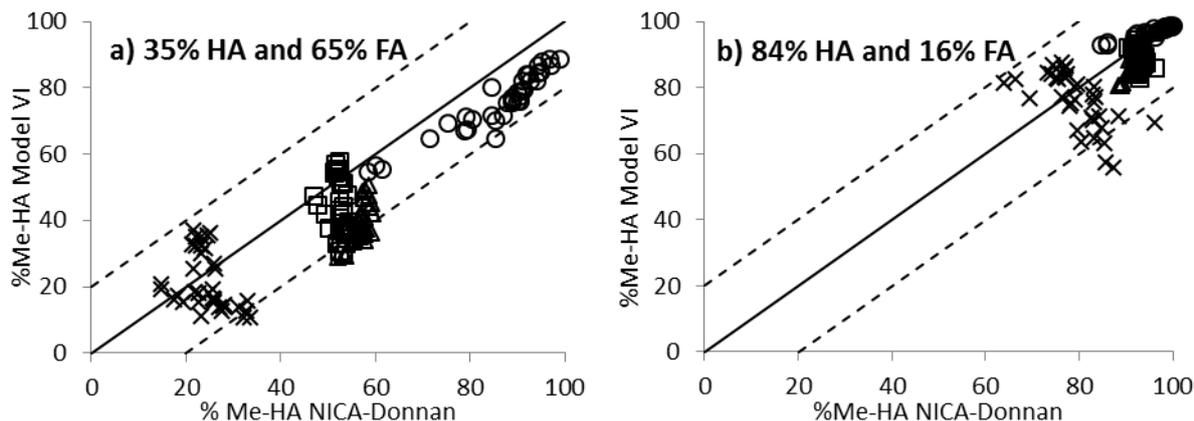


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 45 logarithm: active DOM assimilated to FA (a) or HA (b). The solid line is the $y=x$ line, and the
 46 dotted lines indicate +/- one order of magnitude.

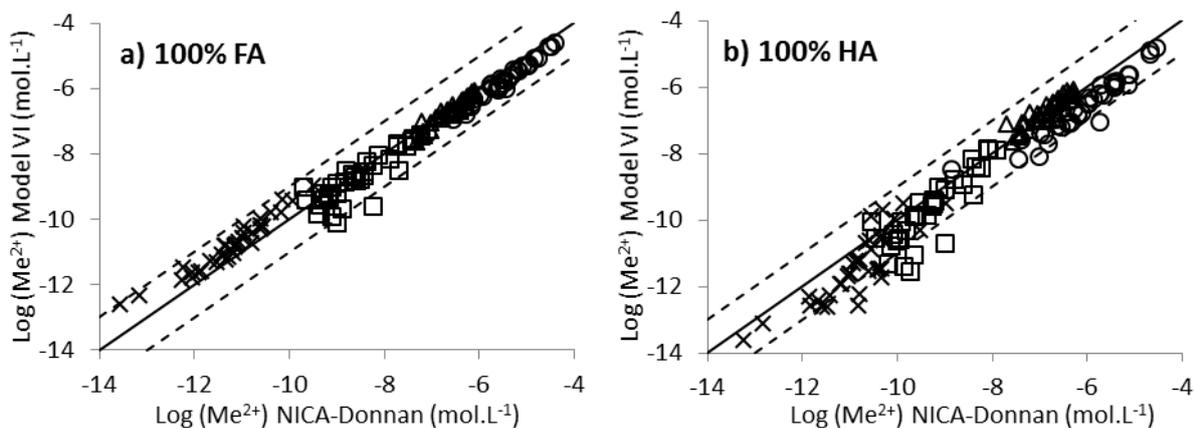
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 55 \circ Zn) with respect to the total metal associated with DOM with NICA-Donnan and Model
 56 VI: active DOM is assimilated to (iii) 35% HA and 65% FA (a), and (iv) 84% HA and 16%
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60
 61 Figure 6. Comparison of free metal ion concentrations (\square Cu, Δ Ni, \times Pb, \circ Zn,) calculated
 62 with NICA-Donnan and Model VI expressed in logarithm. Active DOM is assimilated to FA
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 64 magnitude.