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

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Abstract

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

1. Introduction

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

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

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

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

2. Materials and methods

2.1. Study area

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

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

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

2.2. Analyses of soil

The soils were air-dried and sieved at 2 mm for chemical analyses. Pseudo total soil metal contents were determined by ICP-OES (Thermo Scientific iCAP 6000 series) following aqua regia digestion of ground samples. Soil pH was determined in a mixture of 1:2.5 soil:water (w/v). The CaCO_3 and organic carbon contents were determined following ISO 10693 and ISO 14235, respectively (AFNOR 2009).

2.3. Analyses of soil solution

Different protocols are available to extract a soil solution. In this work, the soil solutions were obtained by extraction with a diluted salt solution. The protocol was adapted from Sauvé et al. (2000a). 200 mL of 5 mmol.L⁻¹ KNO_3 solution was added to 100 g of soil. The mixture was shaken for 20 min and then centrifuged at 3500 rpm for 10 min. The solutions were then passed through 0.45 μm cellulosic membranes.

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

2.4. Partition coefficient

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

$$K_d = \frac{\text{sorbed metal}}{\text{dissolved metal}}$$

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

2.5. Chemical speciation calculations

To perform chemical speciation calculations, the measured concentration in the soil solution 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 input data. Al, Ca, Fe and Mg are considered because they can bind to DOM and compete with metals of interest, and the anions influence the speciation of the non-binding elements (Ge et al., 2005; Ren et al., 2015). Only organic ligands are considered for the modelling because they are recognized to be key parameters for metal complexes (Ren et al., 2015; Tipping et al., 2003; Zhao et al., 2007). Moreover, preliminary tests demonstrated that the impact of Fe oxides was negligible on the metal speciation in our soil solution. The DOM/DOC ratio of all samples is taken to be equal to 2 (Weng et al., 2002). The HS fractions of DOM in the soil solution could vary between 14 and 63% depending on the samples (Groenenberg et al., 2010). In the speciation calculations presented here, 50% of the DOM is

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

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

3. Results and discussion

3.1. Metal concentrations in soil and soil solution

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

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

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

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

3.2. Metal mobility

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

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

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

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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

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

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

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

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

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

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

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

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

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

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

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

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

3.3.2. Free metal concentrations

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

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

When the DOM is assimilated to HA, the two models predict fewer free ions in solution, which is in agreement with more associations with DOM. The results of the two models are comparable for Ni^{2+} 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

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

4. Conclusion

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

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

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

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

Table captions

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

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

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

Table 1. Partition coefficients (K_d ; 10^4L.kg^{-1}) for the four studied elements: arithmetic mean, corresponding standard deviation (SD), median, minimum and maximum values and 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

Table 2. Mean percentage and standard deviation (n=36) of free ion metal and metal associated with DOM calculated with NICA-Donnan and Model VI. Active DOM is 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

Table 3. Mean ratio between the free ion concentration with active DOM assimilated to FA 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

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

Figure captions

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

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

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

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