Geochemical Multisurface Modeling of Reactive Zinc Speciation in Compost as Influenced by Extraction Conditions

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ABSTRACT: Knowledge on organic matter (OM) concentration and composition is of major importance for predicting Zn speciation and bioavailability in soils, especially for low-Zn soils. However, comprehensive knowledge on the effect of soil-like organic amendments such as compost on metal speciation is limited. For the first time, multisurface modeling is applied on compost to study the effect of solid and dissolved OM composition on the speciation of reactive Zn as influenced by conditions applied in frequently used extractions to estimate Zn bioavailability. First, compost OM composition was determined by fractionation in operationally defined humic, fulvic, and hydrophilic acid pools under various extraction conditions, and subsequently, Zn speciation was modeled using the generic non-ideal competitive adsorption-Donnan (NICA-Donnan) model in addition to adsorption to hydrous ferric oxide (HFO) and clay. The results show a strong effect of extraction conditions on OM concentration and composition and related dissolved Zn speciation. Model predictions show that Zn in solution is mainly bound to dissolved humic acids. Analysis of deviations between measured and modeled Zn concentrations reveal specific limitations of the current generic model parameters, particularly with regard to Zn binding to OM at low concentrations and Ca-Zn competition, that is, typical conditions that occur in low-Zn soils.

INTRODUCTION

Multisurface models are important in predicting and understanding metal behavior in soils. These models assume the soil solid phase to consist of independent reactive surfaces such as clay minerals, iron oxides, and organic matter and can be used to predict metal speciation over the reactive surfaces and solution species under equilibrium conditions. Previously, these models have successfully been applied to predict metal speciation in contaminated soils and recently in metal deficient soils also, in particular for zinc (Zn). Since more than 30% of the soils worldwide contain suboptimal levels of plant available Zn, improving our understanding of the mechanisms that control soil Zn speciation in such low-Zn soils is of major importance to optimize management practices. A multisurface modeling study has recently shown that the organic matter (OM) plays a key role in controlling Zn speciation in these soils. In addition, several studies have shown that complexation of Zn with organic ligands in soil solution can increase plant uptake of Zn significantly. Especially at high pH levels and low Zn concentrations, which are typical characteristics of low-Zn soils, Zn complexation by the dissolved organic matter (DOM) is important and generally assumed to be controlled by the humic and fulvic acid fractions (HA and FA). This observation suggests that in a practical agricultural setting, organic amendments can be an effective means to improve Zn availability to crops when such amendments can supply adequate DOM to solubilize native soil Zn. Especially, compost deserves attention as a broadly available organic soil amendment. The capacity of these amendments to increase Zn concentrations in soil solution is highly influenced by the solid/liquid partitioning of the organic matter (OM) and DOM composition, particularly the contribution of the HA and FA fractions.

To determine OM concentrations and composition, chemical extractions are a commonly used approach. Due to the complex and highly dynamic nature of OM in heterogeneous materials such as soil and compost, the sample preparation and extraction method will have a large influence on recovered DOM concentration and composition and the related complexation of metals, including Zn. When OM is used as a model input variable, these compositional differences subsequently influence model output, that is, predicted Zn speciation and bioavailability. Drying of soil samples is an often applied technique to store samples over time, although recovered DOM concentration and composition have generally been observed to change substantially compared to the fresh samples.
and Zn were determined with 0.43 M HNO₃ extraction with a 1:10 solid/solution ratio. Despite these studies, comprehensive knowledge on the effect of sample pretreatment and extraction conditions on DOM composition and related metal speciation and bioavailability is limited for soils and particularly for soil-like organic amendments such as compost.

This study focuses on modeling of reactive Zn speciation in compost as affected by the solid/liquid partitioning of OM and its individual fractions, in particular HA and FA. These humic substances have been shown to be functional proxies for the metal binding properties of natural OM, despite the current debate on their actual existence. For the first time, multisurface modeling is applied to compost to obtain a quantitative, mechanistic understanding of Zn speciation as affected by OM composition. The effects of drying, type of extractant and equilibration time on OM composition and Zn speciation are studied in particular. Modeled Zn speciation is related to compost characteristics, and observed deviations between predicted and measured dissolved Zn concentrations are evaluated in the light of uncertainties in model parameters.

**MATERIALS AND METHODS**

**Collection of Composts.** Four composts with low reactive Zn contents derived from a broad range of plant/wood-based input materials were selected for this study. Two composts were obtained from the Van Iersel composting facility, Biezenmortel, The Netherlands: a three-month-old compost of 100% forest litter (FL) and a three-month-old green waste compost (GWC), comprised of 55% shredded wood, 25% grass litter, and 20% leaf litter. The third compost (wood chips, WC) was obtained from the Orgapower/Van Berkel Groep composting facility, Wintelre, The Netherlands. This compost, from a mixture of both coniferous and deciduous wood chips, had been composted for 2 years. All composts were taken from a minimum depth of 30 cm below the surface of the compost heap, and samples from several points in one heap were combined and homogenized to a mixed sample of 10−15 kg. All fresh composts were collected at the same day and stored moist in closed plastic bags in the dark at 4 °C until use. The fourth compost was a reference material (MARSEP 235), used in the MARSEP (Manure and Refuse Sample Exchange Program) program of WEPAL (Wageningen Evaluating Programs for Analytical Laboratories, Wageningen, the Netherlands). MARSEP 235 (MAR; certificate of analysis available from WEPAL upon request) is a compost that originated from De Ceuster Meststoffen (DCM) N.V., Grobbendonk, Belgium, which was previously dried at 40 °C and milled to pass a 0.5 mm sieve. The analyses of the composts as described above were all performed within a few weeks to limit changes in OM properties over time.

**Preprocessing and Characterization of Composts.** The FL, GWC, and WC composts were sieved moist over a plastic 2 mm sieve to homogenize the samples. The moisture content of all composts was determined by drying for 48 h at 105 °C. The total OM content was determined by the loss on ignition from 105 to 550 °C. Reactive concentrations of Cu and Zn were determined with 0.43 M HNO₃ extraction with a 1:10 solid/solution ratio based on the compost dry weight (4 h of equilibration). Ammonium-oxalate extractable Al, Fe, and Mn were determined according to Schwertmann. The clay content (<2 μm) was determined by laser diffraction. Volume percentages of clay were converted to a mass fraction by assuming a clay particle density of 2.6 g cm⁻³, and fresh compost density was assumed to be equal to dry compost density. All these characteristics were determined for both moist and dried composts. Total elemental concentrations of the four composts dried at 40 °C were determined by X-ray fluorescence spectroscopy (XRF).

**Extraction Conditions To Measure Total Dissolved Zn and Organic Carbon (DOC).** To determine dissolved Zn and total DOC concentrations of the composts, the following default extraction conditions were used: equilibration of fresh compost for 2 h with 0.001 M CaCl₂ with a 1:10 solid/solution ratio based on the compost dry weight. Samples were equilibrated by horizontal shaking with 180 bpm at 20 °C. A 0.001 M CaCl₂ concentration was chosen as the default extraction for this study since strong coagulation of HA has been shown to occur around 0.01 M Ca²⁺. MAR was only extracted with 0.001 M CaCl₂.

To investigate the effect of extraction conditions on the compost OM concentration and composition and associated Zn speciation, three extraction conditions were altered for the GWC, WC, and FL composts. Either the moisture content (original) moist material, a material dried for 48 h at room temperature under forced air ventilation or a material dried for 48 h at 40 °C under forced air ventilation), extractant (ultrapure water (UPW), 0.001 M CaCl₂ or 0.01 M CaCl₂), or equilibration time (2 or 168 h) was modified from the default extraction conditions, while the other conditions were kept at the default setting. Given the high OM content and binding capacity of the composts, an equilibration time of 168 h was chosen to better approximate equilibrium. The bottles were wrapped in aluminum foil to prevent photodegradation of OM. For MARSEP, which was dry as received, a comparison was made between the dry material and material brought to a 50% water content and incubated in the dark for 8 days at 20 °C.

After equilibration of the samples, a subsample was taken for pH determination and the rest of the solutions were centrifuged at 3000 rpm for 10 min (Beckman Coulter Allegra X-12R). Subsequently, the supernatants were centrifuged at 10,000 rpm for 10 min by ultracentrifugation (Thermo Scientific Sorvall RC6+) to facilitate filtration over 0.45 μm membrane filters. From the filtered samples, subsamples were taken for determination of Al, Ca, Fe, Mg, P, and S concentrations by inductively coupled plasma-atomic emission spectroscopy (ICP-AES; Varian Vista Pro or Thermo Scientific iCAP6500) and Cd, Cu, Mn, and Zn concentrations were determined by high-resolution inductively coupled plasma-mass spectrometry (HR-ICP-MS; Thermo Scientific Element 2). Total DOC concentrations were calculated from the difference between total carbon (TC) and inorganic carbon concentrations (IC) in the extracts as determined by a segmented flow analyzer (SFA-TOC; SKALAR San+) and converted to a mass fraction (%). The remainder of the filtered solutions was used for fractionation of DOC.

**DOC Fractionation.** After extraction of the total DOC, the DOC solutions were fractionated in four operationally defined fractions: humic acids (HA), fulvic acids (FA), hydrophilics (Hy), and hydrophobic neutrals (HON). FA was desorbed with 0.1 M KOH from the DAX-8 resin in two subsequent
steps of 1 h as preliminary experiments showed that FA desorption was >95% after two steps.

**Fractionation of NaOH-Extractable Organic Carbon (OC).** Besides determination of dissolved HA, FA, Hy, and HON concentrations, NaOH-extractable OC fractions were determined by acid/base fractionation, Al and Fe determined by ammonium oxalate extraction, the clay content by laser diffraction, reactive Cu and Zn by 0.43 M HNO₃ extraction, and total Cu and Zn by XRF. The clay content was determined on volume basis. Numbers are an estimation based on estimated clay and compost densities. Numbers between brackets are clay percentages v/v.

**Results and Discussion**

**Compost Characteristics.** Chemical characteristics of the composts for default extraction conditions are shown in Table 1 and include pH, OM content, metal contents, and the most important reactive surfaces with regard to Zn speciation. The four composts show a large variation in the OM content, reactive surface content, and Zn loading. For all composts, NaOH-extractable OC was dominated by HA, covering between 61% of the total for WC and 82% for GWC. Reactive Zn concentrations of the composts were low to medium compared to Zn concentrations in green waste composts measured across Europe (141–470 mg kg⁻¹ dw). Reactive Cu contents were comparable among the composts except for WC, which had a distinctly lower Cu concentration (1.0 mg kg⁻¹ dw). Table 1 shows that FL and GWC on the one hand and MAR and WC on the other hand shared similar characteristics. FL and GWC have similar and relatively high pH values and oxalate extractable Al and Fe concentrations, and lower total OM contents and NaOH-extractable OC levels compared to MAR and WC. MAR had a distinctly lower pH and reactive Zn content and relatively high HA, Hy, and related total OC concentrations compared to the other composts. The reactive surfaces of WC were almost fully determined by NaOH-extractable OC. Clay particles in the

| compost | pH | OM | NaOH-extractable OC | reactive metals | total metals |
|---------|----|----|---------------------|----------------|-------------|
|         |    | (g kg⁻¹ dw) | | | |
| FL      | 7.67 | 349 | HA 14.4 | 2.6 | 2.1 | 0.9 | 20.0 | 0.49 | 1.44 | 71 | 1.1% | 6.7 | 95.0 | 27.6 | 249 |
| GWC     | 7.32 | 251 | HA 21.5 | 2.1 | 2.1 | 0.6 | 26.2 | 0.56 | 2.56 | 84 | 1.6% | 6.5 | 90.6 | 35 | 196 |
| MAR     | 5.22 | 899 | HA 48.6 | 8.2 | 14.1 | 2.2 | 73.1 | 0.29 | 0.49 | 53 | 0.8% | 5.0 | 25.4 | 17.9 | 50 |
| WC      | 6.50 | 883 | HA 27.3 | 5.5 | 10.9 | 1.1 | 44.8 | 0.12 | 0.32 | 12 | 0.1% | 1.0 | 166.6 | 17.3 | 470 |

pH was determined in 0.001 M CaCl₂, OM by loss on ignition, NaOH-extractable OC fractions were determined by acid/base fractionation, Al and Fe determined by ammonium oxalate extraction, the clay content by laser diffraction, reactive Cu and Zn by 0.43 M HNO₃ extraction, and total Cu and Zn by XRF.

**Table 1. Compost Characteristics under Default Extraction Conditions**

| compost | pH | OM | NaOH-extractable OC | reactive metals | total metals |
|---------|----|----|---------------------|----------------|-------------|
|         |    | (g kg⁻¹ dw) | | | |
| GC      | 7.67 | 349 | HA 14.4 | 2.6 | 2.1 | 0.9 | 20.0 | 0.49 | 1.44 | 71 | 1.1% | 6.7 | 95.0 | 27.6 | 249 |
| GWC     | 7.32 | 251 | HA 21.5 | 2.1 | 2.1 | 0.6 | 26.2 | 0.56 | 2.56 | 84 | 1.6% | 6.5 | 90.6 | 35 | 196 |
| MAR     | 5.22 | 899 | HA 48.6 | 8.2 | 14.1 | 2.2 | 73.1 | 0.29 | 0.49 | 53 | 0.8% | 5.0 | 25.4 | 17.9 | 50 |
| WC      | 6.50 | 883 | HA 27.3 | 5.5 | 10.9 | 1.1 | 44.8 | 0.12 | 0.32 | 12 | 0.1% | 1.0 | 166.6 | 17.3 | 470 |

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composts were likely associated with plant materials in the feedstock. Compared to organic waste materials such as biosolids, total Zn, Cu, P, and Fe concentrations of the composts were low. XRF shows that the composts contain an additional fraction of nonexchangeable Zn (Table S4). Based on the nearly quantitative recovery of reactive Zn by the HNO₃ extraction, we assume that this nonextractable amount does not contribute to the Zn partitioning with the solution.

Compost OC Concentration and Composition in Relation to Extraction Conditions. Effect of Extractant. Results of the DOC fractionation of the four composts for the different extraction conditions are shown in Figure 1. Measurement data are listed in Table S5. For all composts, reactive OM was predominantly located in the solid phase; at most, 11% of NaOH-extractable OC was extracted as DOC (for WC-UPW, Figure 1a). DOC concentrations of MAR and WC were higher than those of FL and GWC in accordance with the higher total OM and NaOH-extractable OC contents (Table 1). Extraction at increasing Ca²⁺ concentrations showed a distinct decrease in recovered DOC concentrations for all composts, caused by particularly decreased HA, and to a lesser extent FA and Hy concentrations (Figure 1a). Similar trends have been shown for soils in that lower recovered HA concentrations were observed and attributed to coagulation of HA by Ca²⁺ ions and subsequent flocculation. Especially DOC extraction with a 0.01 M CaCl₂ solution resulted for all composts in a pronounced decrease of HA concentration compared to extraction with UPW or 0.001 M CaCl₂. This finding is in good agreement with previous work using purified forest floor HA in which strong HA coagulation was observed starting from a background Ca concentration of approximately 10⁻⁷ M. Despite its relatively high NaOH-extractable HA content, a low dissolved HA concentration was observed for MAR, which can be partly explained by the low pH of this compost (5.22) and the relatively slow dissolution kinetics of HA as described below.

Effect of Equilibration Time. Increasing the equilibration time of the composts from 2 to 168 h resulted in increased solubilization of OC (Figure 1b). The increase in DOC concentrations can predominantly be attributed to an increased HA concentration in solution, irrespective of compost origin and composition. The observed slower dissolution of HA versus FA may be related to the lower diffusivity of HA in relation to the larger size of its molecular associations. MAR displays the largest increase in HA concentration in solution: from 1.7 to 14.8% of DOC after 1 week of equilibration. The slow solubilization but strong increase between 2 and 168 h of the HA fraction of MAR is consistent with the relatively low pH of the sample together with its high NaOH-extractable HA content.

Effect of Drying. Drying the composts at increasing temperatures resulted in increased DOC concentrations for all composts (Figure 1c). This increase was related to increased concentrations of the Hy fraction, which is generally assumed to be caused by microbial cell lysis upon drying. However, next to increased Hy concentrations, FA concentrations also increased in both absolute and relative terms in all dried composts. This effect could either point to the presence of microbial components in the FA fraction or competitive sorption of hydrophilic and fulvic acids on aluminum and iron (hydr)oxides in the composts. Although this assumption could not be validated, this interpretation is supported by increased FA concentrations for FL and GWC, which contained the highest amount of reactive mineral surfaces. For the MAR compost, the total DOC concentration of the incubated sample dropped by 35% and absolute FA and Hy concentrations by 37 and 43%, respectively, relative to the immediately extracted sample. The incubation of this originally dry standard sample has likely favored microbial decom-

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Figure 1. DOC composition of composts under different extraction conditions, expressed as the percentage of NaOH-extractable OC. Figures show variation in (a) extraction solution, (b) equilibration time, and (c) drying. NaOH-extractable OC concentrations are presented in Table 1 for fresh composts; data on dried composts can be found in the Supporting Information (Table S5). Numbers above the bars are absolute total DOC concentrations in g C kg⁻¹ dw. Default extraction conditions are marked with an asterisk (*).
position, resulting in a preferential decomposition of the Hy fraction.40

Multisurface Modeling. The above described generic multisurface model is used to relate reactive Zn speciation to OM speciation and other characteristics of the individual compost samples as affected by the different extraction conditions. Modeling is thus used to analyze the major underlying processes that control Zn speciation in compost. The accuracy of the predicted dissolved Zn concentrations is very similar to that found for soils.5

Effect of Extractant. Model predictions of Zn speciation in both solution and solid phase under the different extraction conditions are shown in Figure 2. Except for WC, >95% of the total reactive Zn is bound to the solid phase, irrespective of

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Figure 2. Zn speciation of the composts under the different extraction conditions, that is, variation in (a) extraction solution, (b) equilibration time, and (c) drying. Left column displays speciation in solution; right column displays speciation in the solid phase. Due to large differences in Zn concentrations, the Zn concentration of WC is shown at the secondary y-axis for clarity. Default extraction conditions are marked with an asterisk (*).
high-a FL and GWC, the increase in dissolved Zn is higher than that MAR and WC composts (respectively 6.8 Ca concentrations after 168 h of equilibration compared to the composts experienced a relatively large increase in dissolved CaCl₂ extract remains relatively large compared to the FL and the HA-rich WC, the fraction HA in solution in the 0.01 M suggesting strong competition of Ca²⁺ with Zn²⁺ for binding to HA and FA decreased as a result of increased Ca ²⁺ concentration of WC remained virtually unchanged (Figure 1a). For FL and GWC in contrast to an increase for WC and MAR. Both the WC and MAR samples contained a high DHA concentration, and particularly, MAR showed a large increase after 1 week of equilibration (Figure 1b). For these composts, the increase in DHA is larger than the increase in dissolved Zn, resulting in increased Zn-DHA complexation especially to (phenolic) high-a (Tables S6). For FL and GWC, the increase in dissolved Zn is higher than that of DHA, resulting in a predicted decrease in Zn binding to high-affinity sites of DHA. In addition, the FL and GWC composts experienced a relatively large increase in dissolved Ca concentrations after 168 h of equilibration compared to the MAR and WC composts (respectively 6.8× and 6.6× increase compared to 1.5× for MAR and 4.9× for WC, Figure S1), consistent with a decrease in pH (except for MAR). This increased Ca competition contributes to the relatively strong predicted increase of free Zn in solution.

Effect of Equilibration Time. Extending equilibration times to 1 week resulted in a marked increase in Zn concentrations in solution for all composts (Figure 2b) in parallel with strongly increased DHA concentrations after 168 h equilibration (Figure 1b). For all composts, Zn electrostatically bound to HA and FA decreased as a result of increased Ca²⁺ concentrations (see further below) and the related decreased Donnan volume. Careful examination of Figure 2b shows a decrease in the relative importance of Zn-DHA complexes for FL and GWC in contrast to an increase for WC and MAR. Both the WC and MAR samples contained a high DHA concentration, and particularly, MAR showed a large increase after 1 week of equilibration (Figure 1b). For these composts, the increase in DHA is larger than the increase in dissolved Zn, resulting in increased Zn-DHA complexation especially to (phenolic) high-affinity binding sites of DHA. For FL and GWC, the increase in dissolved Zn is higher than that of DHA, resulting in a predicted decrease in Zn binding to high-affinity sites of DHA. In addition, the FL and GWC composts experienced a relatively large increase in dissolved Ca concentrations after 168 h of equilibration compared to the MAR and WC composts (respectively 6.8× and 6.6× increase compared to 1.5× for MAR and 4.9× for WC, Figure S1), consistent with a decrease in pH (except for MAR). This increased Ca competition contributes to the relatively strong predicted increase of free Zn in solution.

Effect of Drying. Total predicted dissolved Zn concentrations are following fluctuations in measured DHA concentrations. For FL and GWC, the DHA concentration reduced about 2-fold upon drying, whereas the DHA concentration of WC remained virtually unchanged (Figure 1c). For FL and GWC, the contribution of Zn-DFA to total dissolved Zn doubled (from 6.3 to 12.2% and 4.7 to 11.2%, respectively, between moist and 40 °C dried) at the expense of Zn-DHA complexation (Figure 2c). For WC, a small increase in DFA is reflected in slightly increased total dissolved Zn concentrations. However, conclusions on the relative importance of Zn-FA complexation should be drawn with caution since the generic NICA-Donnan parameters for Zn-FA complexation are derived based on a very few data, with relatively high uncertainty margins.27

Model Performance and Limitations. The multisurface model consistently overestimated Zn concentrations in solution for the FL, GWC, and WC samples (Figure 3).

This overprediction suggests limitations in the current parameters for Zn binding to HA and/or FA resulting in a too weak binding as HA and FA dominate Zn binding and are predominantly present in the solid phase (Table 1). Inaccuracies in Zn binding to HFO would have been the major cause for the overestimation, the prediction for samples without HFO (i.e., WC and MAR) would have been much better, which is not the case. In contrast to the data shown here, Duffner et al.7 found a good agreement between measured and predicted Zn²⁺ concentrations for low-Zn soils. This observation can most likely be explained by a strong overestimation of SHA concentrations in their study. The estimated reactive HA concentrations in that study were 4 to 19 times higher than we have recently measured directly in four of their low-Zn soils (Klinkert et al., unpublished results). Duffner et al.7 similarly overestimated DHA concentrations, but given the low DOC concentrations in their soils, the net result of their approach is a predicted stronger Zn binding to the solid phase at low Zn²⁺ concentrations.

Concerning the samples where total Zn in solution was overpredicted compared to measured concentrations, especially the composts extracted with 0.01 M CaCl₂ should be noted (Figure 3). To study possible effects of Ca-Zn competition, we have also analyzed the Ca speciation in the same way as we have done for Zn (cf. Figure 2 and Figure S1). Figure S1 shows that the Ca speciation in the solid phase resembles that of Zn and is dominated by binding to SHA, while the Ca in solution is for a greater proportion bound to DFA than Zn. As shown in Tables S6 and S7, Ca-Zn competition occurs predominantly in the Donnan volume and to a greater extent for FA than for HA. We also note that this electrostatic competition between Cu²⁺ and Ca²⁺ is negligible (Tables S7 and S8), while the model prediction of Cu in solution is much more accurate (Figure S2 and Table S9). As the current generic parameters imply a much greater relative importance of electrostatic binding for Zn than for Cu, Zn is much more susceptible to competitive electrostatic binding of divalent Ca²⁺ and thus to inaccuracies in the description of the electrostatic binding component. These observations suggest that the accuracy of the model predictions may be related to the electrostatic binding component of Zn to FA. This interpretation is consistent with the suggestion of Hiemstra et al.31 (2006) that the Donnan volume of FA has been overestimated in the NICA-Donnan model, resulting in an
overestimation of the electrostatic binding component and consequently the magnitude of the Ca-Zn competition on FA. As most of the FA is located in the solid phase, the net effect is an overestimation of Zn in solution. These findings thus indicate that the description of the electrostatic binding of cations by HA and especially FA needs further research.

In contrast to FL, GWC, and WC, Zn concentrations in solution were underestimated for MAR (Figure 3). This compost differs from the other three in that an even larger fraction of the HA is located in the solid phase, while a relatively large fraction of FA is present in solution (Table S5). As a result, overestimation of Ca-Zn competition on FA leads to an underestimation of Zn in solution. Moreover, MAR contained a high concentration of reactive OC and low concentration of reactive Zn (Table 1). As a result of this low Zn loading of the reactive OC, Zn is likely to be more prominently associated with high-affinity binding sites, both within and between carboxylic and phenolic site groups. The predicted distribution of Zn over the carboxylic and phenolic binding sites of HA and FA did not show any relevant difference between the MAR and the other composts and thus cannot explain the underprediction of MAR in contrast to the overprediction of Zn in solution for the other composts (Table S6). However, the underprediction of Zn in solution for the MAR sample may also be related to the proportionally much higher association of Zn with high-affinity sites within the carboxylic and phenolic groups as a result of its much lower loading compared to the other composts. In the data used by Milne et al. (2003) for derivation of the generic Zn parameters of the NICA-Donnan model, an increasing overprediction of Zn-HA complexation toward low Zn loadings has been shown to occur especially around pH 6, which is, around the pH of the MAR sample (Table 1). In that study, the lowest Zn loadings measured were 1.3 \times 10^{-2} \text{ mole Zn kg}^{-1} \text{ HA for pH 6}, which is still relatively high compared to the Zn loading of MAR (3.9 \times 10^{-3} \text{ mole Zn kg}^{-1} \text{ HA}). This observation suggests that overestimation of Zn-HA complexation at such a low Zn loading may even be more pronounced for MAR and may thus contribute to the observed underestimation of Zn in solution for that compost (Figure 3). Figure S2 and Table S9 suggest that these limitations are not associated with the NICA-Donnan model as such nor the input variables since Cu in solution is adequately predicted for all compost samples including MAR.

Finally, we note that the primary purpose of this paper was to base modeling predictions on generic parameters for identifiable OM in addition to HFO and clay. Thus, we have used a frequently applied multisurface model setup for soil systems in which binding to OM is assumed to be controlled only by the HA and FA fractions. Consequently, possible complexation of Zn with hydrophilic organic acids was not considered. As the composition of the Hy fraction is unknown and variation of Hy properties between the different composts is likely to exist, metal complexation by Hy can currently only be predicted based on assumptions. Since the Hy fraction is an important part of DOM and even of solid OM (representing 7–25% of SOC, Table S5), specific research on the nature and reactivity of Hy in soils and organic amendments may further improve the accuracy of multisurface model predictions. The same may hold for SOM that is not extracted with the current fractionation protocols for humic substances as well as for other than currently considered inorganic Zn species in the solid phase (e.g., by surface spectroscopic analysis).

Predicting Zn speciation by multisurface modeling has revealed the same underlying mechanisms in composts as in soils and that optimization of Zn binding parameters of the NICA-Donnan model is needed. Modeling showed that especially at low Zn concentrations, Zn solubility is controlled by HA. Deviations between measured and predicted dissolved Zn concentrations are likely associated with limitations in the description of Ca-Zn competition, particularly in their electrostatic binding to FA, as well as in the concentration-dependent binding affinity of Zn. These findings are especially relevant for application of multisurface modeling to predict Zn speciation in low-Zn soils as these soils often contain high levels of CaCO₃ and low dissolved Zn concentrations.

Improving model descriptions with regard to these features will widen the applicability of multisurface models in predicting Zn speciation and further our knowledge on mechanistic relationships between OM characteristics and Zn speciation.

## ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.9b04104.

NICA parameters for Fe³⁺ binding to FA; model input ORCHESTRA; explanation of treatment codes; total elemental concentrations of the composts; OC composition of the composts for all extraction conditions; Zn, Cu, and Ca distribution over specific and electrostatic binding sites of HA and FA; Ca speciation under the different extraction conditions; measured versus predicted dissolved Cu; RMSE for Cu and Zn concentrations (PDF)

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### Notes

The authors declare no competing financial interest.

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