



NOM-mineral interaction: Significance for speciation of cations and anions

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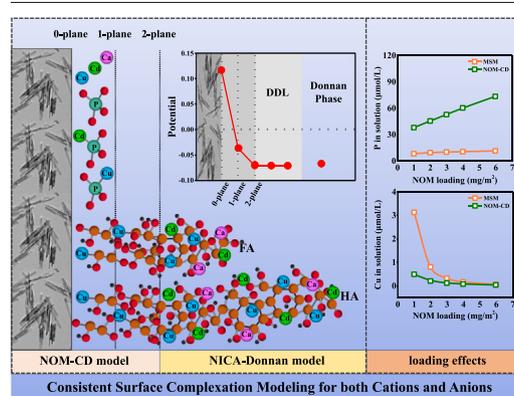
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HIGHLIGHTS

- Effect of NOM on oxyanion adsorption to minerals increases with NOM loading.
- NOM-mineral interaction has little effect on cation binding at a high NOM loading.
- At a high NOM loading, most of NOM is not influenced by the underlying minerals.
- NOM-CD based consistent model can simulate adsorption of both anions and cations.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, the nano-scale spatial distribution of natural organic matter (NOM) on the surface of iron (hydr)oxides and its relevance to oxyanion (PO_4^{3-}) and metal cation (Cd^{2+} and Cu^{2+}) adsorption to the assemblage of oxide (goethite) and NOM (humic acids (HA) or fulvic acids (FA)) was investigated with experiments and advanced surface complexation modeling. Both the linear additive Multi-Surface model (MSM) and the more sophisticated Natural Organic Matter-Charge Distribution (NOM-CD) model were used. The MSM model ignores the effects of NOM-mineral interaction on ion adsorption, whereas the NOM-CD model considers this effect. The results showed that with the increase of NOM loading on oxides, deviation between the MSM and NOM-CD model became bigger for PO_4^{3-} , but smaller for Cd^{2+} and Cu^{2+} . Oxyanions bind mainly to oxides and therefore the competitive effect of NOM cannot be neglected, which explains the large difference between these two models for PO_4^{3-} . On the contrary, at a relatively high NOM loading, a large fraction of NOM extends further away from the surface of oxides. Thus for metal cations that bind mainly to NOM, the influence of NOM-mineral interaction on their adsorption is small and the results of the MSM and NOM-CD model are similar. In top soils, the NOM loading on oxides is often high, therefore the linear additive MSM is applicable for metal cation speciation calculations as reported in many literatures. An approach based on the NOM-CD model was proposed, which can not only calculate the macroscopic solid-solution distribution of both cations and anions, but can also provide information regarding their microscopic surface speciation.

1. Introduction

Natural organic matter (NOM) and metal (hydr)oxides are important components in soil, sediments and water, which participate in many environmental processes. NOM adsorbs strongly to metal (hydr)oxides via

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chemical, electrical and hydrophobic interactions (Gu et al., 1994; Antelo et al., 2007; Xie et al., 2020). The attachment of NOM to minerals plays an important role in protecting NOM against degradation (Mikutta et al., 2006; Kramer and Chadwick, 2018). Further, the interaction between NOM and oxide minerals changes their surface properties and affects ion adsorption to both particles, influencing the mobility and bioavailability of nutrients and pollutants in the environment. A good understanding and prediction of chemical speciation of nutrients and pollutants is important for environmental management and engineering.

Surface complexation model (SCM) is a vital tool to quantify ion adsorption, which forms an essential part in geochemical modeling programs (e.g. W_{HAM} , P_{HREEQC} , M_{INTEQ} and $O_{RCHESRA}$) (Dudal and Gérard, 2004; Lützenkirchen et al., 2015). The Non-Ideal Competitive Adsorption-Donnan (NICA-Donnan) model and the Charge Distribution and Multi-Site Complexation (CD-MUSIC) model are advanced SCMs developed to describe ion adsorption to NOM and metal (hydr)oxides, respectively (Kinniburgh et al., 1996; Hiemstra and Van Riemsdijk, 1996). For natural samples containing different kinds of reactive surfaces, a relatively simple treatment is the linear additivity approach, i.e. the Multi-Surface model (MSM) (Weng et al., 2001), which assumes that ion adsorption properties of each type of surface are not affected by the presence of other surfaces. Previous studies have shown that MSM could well predict the adsorption of a range of metal cations to minerals or soils (Weng et al., 2008; Duffner et al., 2014; Rennert et al., 2017; Zhang et al., 2018), but failed to describe oxyanions adsorption in natural samples. It is unclear why the negligence of NOM-mineral interaction has different consequences in modeling cations and anion speciation.

To describe anion adsorption, SCMs incorporating NOM-mineral interaction are needed. One such model is the Natural Organic Matter-Charge Distribution (NOM-CD) model (Hiemstra et al., 2013), which is an extension of the CD-MUSIC model and uses a virtual organic molecule containing two carboxylic groups to represent NOM adsorbed to minerals. The NOM-CD model has been successfully used to describe the adsorption of phosphate and arsenate to mixtures of NOM and minerals (Hiemstra et al., 2013; Deng et al., 2019). However, so far the NOM-CD model has rarely been applied to describe cation adsorption in complex samples (Otero-Fariña et al., 2017). A consistent modeling approach, which can simultaneously predict the adsorption and speciation of both cations and anions, is lacking.

To better understand the effect of NOM-mineral interaction on processes such as ion adsorption, colloidal mobility and organic carbon sequestration, a clear picture regarding both the properties and spatial distribution of adsorbed NOM is required. However, given the submicrometer spatial scale and its chemical complexity, there exists limited instrumentation to probe the structure of NOM on mineral surfaces (Newcomb et al., 2017; Possinger et al., 2020; Lehmann et al., 2008). The zone model proposed by Kleber et al. (2007) pictured the organic coating on minerals as a three zone structure: i.e. a contact zone, a hydrophobic interaction zone and a kinetic outer zone. The more traditional view of the bilayer model has one layer less than the zone model, consisting of two layers of amphiphilic NOM particles (Wershaw, 1993). For ion adsorption, interaction between minerals and NOM in the contact layer is of higher relevance than NOM in outer layers. Furthermore, the NOM-mineral interaction will be the strongest in the compact part of the electrical double layer (EDL), which has a thickness of around 0.7 nm (Hiemstra and Van Riemsdijk, 2006; Mendez et al., 2020). Recently, Mendez et al. (2020) developed a core-shell model, which considers all soil NOM as accommodated in a layer (~1–3 nm) around the metal (hydr)oxide nanoparticles. The NOM layer is thicker than the compact part of the EDL. However, the significance of NOM distribution at this nanometer scale for metal cation and oxyanion adsorption and their modeling remains unclear.

The objectives of this work are: (i) to investigate the spatial distribution of mineral associated NOM and its impact on cation and anion adsorption using experimental and modeling methods; (ii) to develop a consistent modeling framework based on the NOM-CD approach that can

simultaneously predict metal cation and oxyanion speciation in the presence of NOM and oxides; (iii) to gain insight into the nanoscale spatial distribution of NOM on mineral surface via modeling ion adsorption.

2. Material and methods

2.1. Goethite and NOM preparation

Goethite was synthesized according to Hiemstra and Van Riemsdijk (1999). The same material has been used previously (Deng et al., 2018). The specific surface area (SSA) of this goethite is 89 m²/g and the point of zero charge (PZC) is pH 9.2, determined with BET-N₂ adsorption isotherms and acid-base titration, respectively. Stock solution of goethite was prepared by appropriate dilution with ultrapure water and the suspension was purged with clean N₂ gas to remove CO₂. The content of goethite in the stock suspension was determined by measuring the weight of subsamples of the suspension before and after being dried at 85 °C.

Humic acid (HA) and fulvic acid (FA) were extracted from the top soil of a Udic Cambisols in a forest of Ziwojing Mountain in Gansu province, northwest China, following a protocol of Zomer and Comans (2007). The HA and FA materials have been used in a previous work and their properties can be found therein (Deng et al., 2019). The stock solutions of HA and FA were prepared by dissolving the freeze-dried material with a small amount of 0.1 M NaOH, and then the solutions were diluted with ultrapure water to a concentration of 2 g/L and 1 g/L, respectively. These HA and FA materials were used to represent reactive NOM in the adsorption experiment below.

2.2. Adsorption experiment

To study the effect of NOM-mineral interaction on cation and anion adsorption, three batch adsorption experiments were carried out using HA and FA to represent NOM and goethite to represent metal (hydr)oxides: (i) Single ion (PO₄³⁻, Cd²⁺ or Cu²⁺ separately) adsorption envelopes to goethite over pH 4–8. (ii) Simultaneous adsorption of multiple ions (PO₄³⁻, Cd²⁺ and Cu²⁺) to goethite in the absence and presence of HA (300 mg/L) or FA (100 mg/L) over pH 4–8. (iii) Effects of concentration of HA (150, 300 and 450 mg/L) or FA (50, 100 and 200 mg/L) on PO₄³⁻, Cd²⁺ and Cu²⁺ adsorption to goethite at pH 5.2. To make the solution chemistry closer to the natural environment, all the adsorption experiments were performed in a 2.3 mmol/L Ca(NO₃)₂ background. The stock solutions (Ca(NO₃)₂, NaH₂PO₄, Cd(NO₃)₂, Cu(NO₃)₂) were added into 50 mL gas-tight polyethylene centrifuge tubes under N₂ atmosphere. Stock solution of Ca(NO₃)₂ was added after 1.5 h pre-equilibration of the suspension containing other components to prevent precipitation of calcium phosphate (Rietra et al., 2001; Deng et al., 2018). The pH of the prepared suspensions was adjusted with 0.1 mol/L HNO₃ and NaOH to desired values. The total volume of each suspension was 20 mL. The final concentration of goethite, PO₄³⁻, Cd²⁺ and Cu²⁺ was 1.13 g/L, 275 μmol/L, 1.08 μmol/L and 77 μmol/L, respectively. The suspensions were shaken on a horizontal shaker at 25 ± 1 °C for 7 days.

At the HA and FA loading chosen, the DOC concentration remaining in solution after adsorption to goethite is in the range of 5.6–25.2 mg/L C for the HA treatments and 8.7–25.9 mg/L C for the FA treatments (see below), in line with DOC concentrations commonly found in a soil solution. The resulted soluble PO₄³⁻ concentration is between 0.12 and 2.1 mg/L P, within the range of fertilized agricultural soils. If we take 1% as metal (hydr)oxide content in soil, the loading of Cu²⁺ and Cd²⁺ added is equivalent to 43 mg/kg soil, and 1.1 mg/kg soil respectively, in accordance with the Type II soil for Cu (50–100 mg/kg, suitable for agriculture) and close to Type III soil for Cd (1.0 mg/kg, for forest soil, soil with high metal content background or soil close to mining area, without significant impact on plants) according to the Chinese soil standards.

The suspension pH was checked and readjusted if necessary during the first 5 days. At the end of the shaking, the final pH of the suspension was measured with a pH meter. Then the suspensions were centrifuged

at 10400g for 30 min and filtered through 0.22 μm filters. The concentrations of P, Cd, Cu and Ca in the filtrate were measured with ICP-OES (PerkinElmer, USA) and the concentration of dissolved organic carbon (DOC) was determined with a TOC analyser (Analytik Jena, Germany).

2.3. Modeling

2.3.1. Multi-surface model

The Multi-Surface Model (MSM) calculates PO_4^{3-} , Cd^{2+} and Cu^{2+} adsorption to the mixture of NOM and oxides in two steps. (1), the amounts of ions adsorbed to oxides and to NOM (both NOM adsorbed (NOM_{ads}) and NOM in solution (NOM_{sol})) were calculated with the CD-MUSIC (Hiemstra and Van Riemsdijk, 1996) and NICA-Donnan model (Kinniburgh et al., 1996), respectively. (2), the amounts of ions adsorbed to oxides and NOM_{ads} were summed to derive the total amount adsorbed to the solid phases. The linear additivity nature of the MSM assumes that the ion adsorption properties of oxides or NOM in the ternary systems (oxides-NOM-ions) are the same as in the single sorbate binary systems (oxides-ions, NOM-ions).

In the CD-MUSIC model, the intrinsic proton affinities of the singly ($\equiv\text{FeOH}^{-0.5}$) and triply ($\equiv\text{Fe}_3\text{O}^{-0.5}$) coordinated surface groups of goethite were assumed to be equal to the value of the PZC. The Extended Stern model was used for the compact part of the electric double layer (EDL), which has two Stern layers and two outer electrostatic planes (1-plane and 2-plane). Indifferent electrolyte ions (Na^+ , NO_3^-) can form ion pairs with both singly and triply coordinate surface sites. For PO_4^{3-} , one monodentate ($\equiv\text{FeOPO}_2\text{OH}$) and one bidentate ($\equiv\text{Fe}_2\text{O}_2\text{PO}_2$) surface species with the singly coordinated surface groups were considered. Two bidentate ($\equiv(\text{FeOH})_2\text{Cd}$, $\equiv(\text{FeOH})_2\text{CdOH}$) Cd^{2+} surface species and four bidentate ($\equiv(\text{FeOH})_2\text{Cu}$, $\equiv(\text{FeOH})_2\text{CuOH}$, $\equiv(\text{FeOH})_2\text{Cu}_2(\text{OH})_2$, $\equiv(\text{FeOH})_2\text{Cu}_2(\text{OH})_3$) Cu^{2+} surface species were included. The surface species formed and the corresponding model parameters were adopted from literatures (Hiemstra and Van Riemsdijk, 2006; Stachowicz et al., 2008; Weng et al., 2008; Deng et al., 2018) unless otherwise mentioned (Table S1).

In the NICA-Donnan model, two types of reactive surface groups were considered: i.e. the carboxylic and phenolic type of surface groups, each with a continuous distribution of proton and ion adsorption affinity. The bimodal NICA equation was used to calculate specific ion binding to NOM, while the Donnan approach was used to describe the electrostatic interaction. Cations adsorb to NOM through specific interactions with the available binding sites and by non-specific (electrostatic) interactions due to any residual charge. The generic model parameters for HA and FA were adopted in the calculation (Milne et al., 2001; Milne et al., 2003), except the site density of carboxylic groups which are specific for the HA and FA under study (Deng et al., 2019) (Table S2).

2.3.2. NOM-CD model

The NOM-CD model is an extension of the CD-MUSIC model. The model includes a virtual component, i.e. HNOM, which is equivalent to two carboxylic groups, to represent NOM adsorbed in the Stern layer at the surface of oxides (Hiemstra et al., 2013). The surface species of HNOM and model parameters were adopted from literatures (Hiemstra et al., 2013; Deng et al., 2019) (Table S1). The model parameters for ion adsorption to goethite were kept the same as in the CD-MUSIC model (Table S1). The NOM-CD model calculation was done in three steps. (1), The total amount of the virtual component HNOM was derived by optimization using the solid-solution distribution of PO_4^{3-} measured in the experiment. (2), The NOM was divided into three categories: (i) HNOM, i.e. NOM in the Stern layer on the surface of oxides, (ii) NOM_{DDL} , adsorbed NOM extending out of the Stern layer into the diffuse double layer ($\text{NOM}_{\text{DDL}} = \text{NOM}_{\text{ads}} - \text{HNOM}$, considering the density of carboxylic groups), and (iii) NOM_{sol} , NOM in solution. The NOM-CD model was used to calculate ion adsorption to the oxides in the presence of HNOM. It was assumed that ion binding properties of NOM_{DDL} is not influenced by the underlying oxides and are

the same as NOM_{sol} . The NICA-Donnan model was used to calculate ion adsorption to NOM_{sol} free from the influence of oxides, which includes NOM_{DDL} and NOM_{sol} . (3), Ion adsorbed to the solid phase (oxides + NOM_{ads}) was calculated as the sum of those adsorbed to oxides (with HNOM) and to NOM_{DDL} .

2.3.3. Model calculations

The total concentrations of the components added (as determined in the control samples) and the final pH measured were used as model input. The model calculations were carried out using the software ECOSAT (Keizer and Van Riemsdijk, 1998). Optimization of model parameters, including the parameters for the ternary complexes of goethite-P-Cd, goethite-P-Cu, goethite-Cu-NOM and the total amount of HNOM, was conducted using ECOSAT coupled with the software FIT (Kinniburgh and Tang, 1993).

3. Results and discussion

3.1. Parameterization of the CD-MUSIC model

Before analyzing the results in the presence of NOM, the CD-MUSIC model was applied to calculate adsorption of ions (PO_4^{3-} , Cd^{2+} , Cu^{2+}) to goethite in the absence of NOM measured in the adsorption experiments. The model parameters were optimized when necessary (including affinity constants for goethite-Cd, goethite-Cu, goethite-P-Cd, and goethite-P-Cu, see below).

3.1.1. PO_4^{3-}

The CD-MUSIC model parameters for PO_4^{3-} adsorption to goethite were kept the same as in the literatures (Stachowicz et al., 2008; Deng et al., 2018). Though these parameters were derived based on the adsorption of single ion (only PO_4^{3-}) in a 1:1 electrolyte background (e.g. NaCl, NaNO_3), the model can well describe PO_4^{3-} adsorption in this study under a $\text{Ca}(\text{NO}_3)_2$ background and also with the presence of Cd^{2+} and Cu^{2+} (Fig. 1a, b). In a 1:1 electrolyte background, adsorption of PO_4^{3-} to goethite was found to decrease with the increase of pH (Rahnamaie et al., 2007), as shown with the CD-MUSIC model simulation (Fig. S1a, dash line). However, under a $\text{Ca}(\text{NO}_3)_2$ background, the adsorption of PO_4^{3-} increased with increasing pH until a broad sorption maximum (minimum for PO_4^{3-} in solution) was observed around pH 6–7 (Fig. 1a, b). The change in the pH dependence observed in the present study can be attributed to the electrostatic synergy between PO_4^{3-} and Ca^{2+} , which enhanced PO_4^{3-} adsorption on metal (hydr)oxides especially at relatively high pH. Similar results have been reported in the literatures (Antelo et al., 2015; Atouei et al., 2016; Deng et al., 2018). Only a very small difference in PO_4^{3-} adsorption was observed between the treatments with and without Cd^{2+} and Cu^{2+} , due to the much lower concentration of Cd^{2+} and Cu^{2+} compared to that of Ca^{2+} and PO_4^{3-} .

3.1.2. Cd^{2+} and Cu^{2+}

Using model parameters adopted from literatures (Ponthieu et al., 2006; Weng et al., 2008), the CD-MUSIC model underestimated Cd^{2+} adsorption in the single ion Cd system and overestimated Cu^{2+} adsorption in the single ion Cu system (results not shown). Therefore, the affinity constants ($\log K$) of the two Cd^{2+} surface species and the bidentate Cu^{2+} surface species (Table S1) were optimized based on experimental data in the Cd system (Fig. 1c, d) and Cu system (Fig. 1e, f), respectively. Comparing the model calculations for Cd^{2+} and Cu^{2+} adsorption in a Ca^{2+} background to that in a Na^+ background, there is a very small effect of Ca^{2+} (Fig. S1b, c). Therefore, the deviation of the model prediction using the parameters from Ponthieu et al. (2006) and Weng et al. (2008) may not be caused by the influence of Ca^{2+} , but rather by the deviation of the goethite materials (e.g. surface roughness, crystal face contribution, etc) (Han and Katz, 2019; Villalobos et al., 2003).

The presence of PO_4^{3-} in the multiple ion PCdCu system increased adsorption of both Cd^{2+} and Cu^{2+} (Fig. 1c-f). Though the adsorption in the

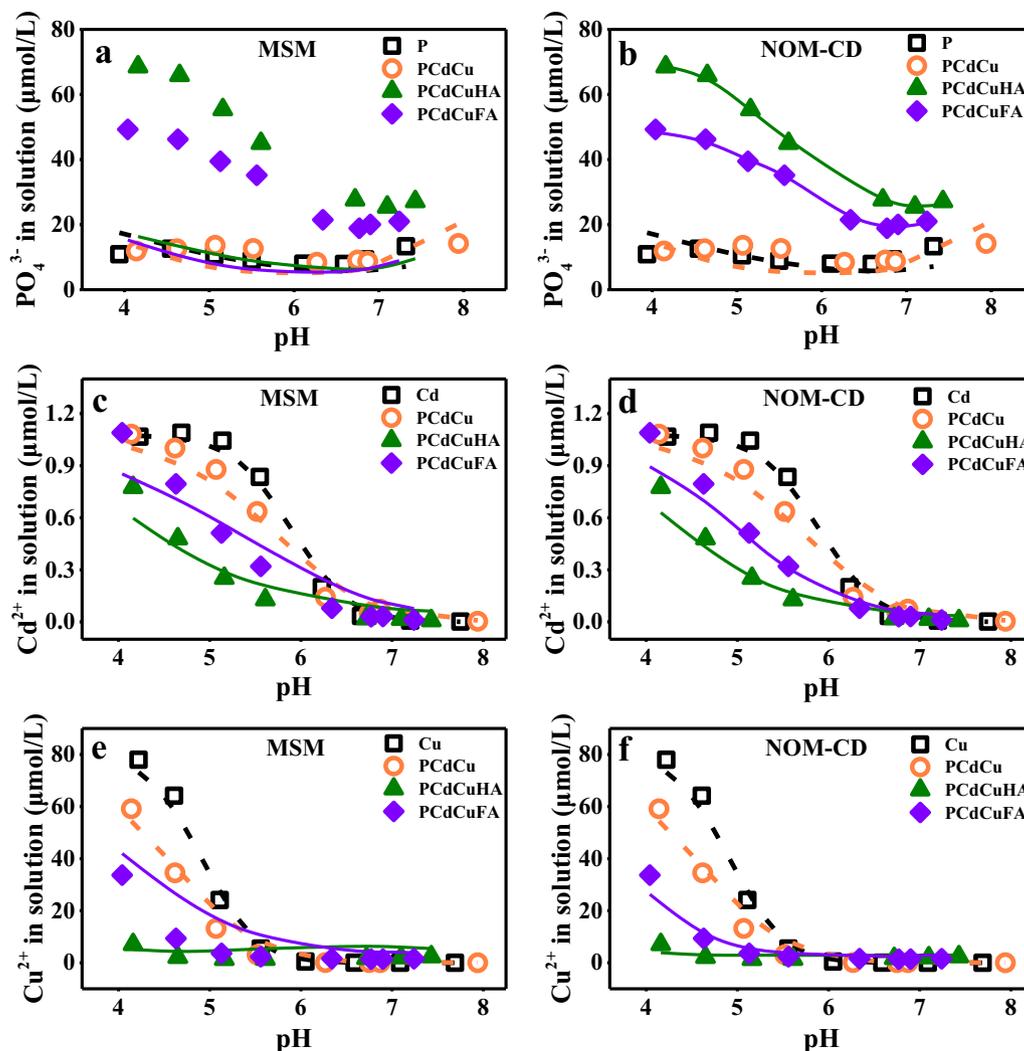


Fig. 1. Adsorption envelopes of PO_4^{3-} (275 $\mu\text{mol/L}$), Cd^{2+} (1.08 $\mu\text{mol/L}$) and Cu^{2+} (77 $\mu\text{mol/L}$) onto goethite (1.13 g/L) in the absence and presence of 300 mg/L HA or 100 mg/L FA. Background: 2.3 mmol/L $\text{Ca}(\text{NO}_3)_2$. Symbols are experimental data, dash lines are CD-MUSIC model and solid lines are Multi-Surface model (a, c, e) and NOM-CD model (b, d, f) calculations.

single ion Cd system and Cu system can be well explained after the adjustment of the $\log K$ values of the surface species (Fig. 1c-f), the Cd^{2+} and Cu^{2+} adsorption in the PCdCu system was still seriously underestimated (Fig. S2, dash line), indicating that additional surface species might exist. Previous spectroscopic observations showed that Cd^{2+} and Cu^{2+} can form P-bridged and Cd- or Cu-bridged ternary complexes at the surface of iron oxides at respectively low and high pH (Elzinga and Kretzschmar, 2013; Tiberghien et al., 2013; Liu et al., 2021). For our PCdCu systems, one P-bridged ternary complex is enough to explain the data (Fig. 1c-f). For this ternary complex, we assumed that the monodentate surface species of PO_4^{3-} ($=\text{FeOPO}_2\text{OH}^{-1.5}$) formed ternary complex with Cd^{2+} ($=\text{FeOPO}_2\text{OCd}^{-0.5}$) and Cu^{2+} ($=\text{FeOPO}_2\text{OCu}^{-0.5}$) after releasing one H^+ , and the charge distribution of PO_4^{3-} remained the same as in $=\text{FeOPO}_2\text{OH}^{-1.5}$, whereas the charge due to the exchange of Cd^{2+} or Cu^{2+} with H^+ was located at the 1- and 2-plane (Table S1). According to the model simulation, the presence of PO_4^{3-} enhanced the adsorption of Cd^{2+} and Cu^{2+} , which was caused by the electrostatic synergy between Cd^{2+} , Cu^{2+} and PO_4^{3-} , and formation of goethite-P-Cd and goethite-P-Cu ternary complexes. The contribution of different surface species to Cd^{2+} and Cu^{2+} adsorbed is given in Fig. S3, which shows that the contribution of goethite-P-Cd increases with the increase of pH and dominates at about $\text{pH} > 5.3$ (Fig. S3a). However, the contribution of goethite-P-Cu dominates at a relatively low pH range (about

$\text{pH} < 7$), whereas the $=(\text{FeOH})_2\text{Cu}_2(\text{OH})_3^0$ contributes more to Cu^{2+} adsorption at $\text{pH} > 7$ (Fig. S3b).

3.2. Multi-surface modeling

In the presence of HA or FA, the solid phase contains goethite as well as HA or FA adsorbed to goethite (goethite + NOM_{ads}). As described in the Modeling section, the MSM assumes that there is no effect of the interaction between goethite and NOM on ion adsorption, and the total amount of ions bound to the solid phase equals to the sum of bound to goethite and to HA or FA adsorbed (goethite + NOM_{ads}).

3.2.1. PO_4^{3-}

Both HA and FA decreased PO_4^{3-} adsorption (increased PO_4^{3-} in solution) (Figs. 1a, 2a). The results show that the adsorption of PO_4^{3-} to the solid phase was over-estimated (soluble PO_4^{3-} was under-estimated) using the linear additivity approach, especially at low pH range. Previous studies revealed that HA and FA bind strongly to metal (hydr)oxides and compete with oxyanions in their adsorption (Fu et al., 2013; Amini et al., 2020). The gap between the model prediction and data became bigger with the increase of HA or FA concentration (Fig. 2a). Apparently, for an oxyanion such as phosphate, the MSM cannot explain its adsorption to the assemblage of NOM and oxides.

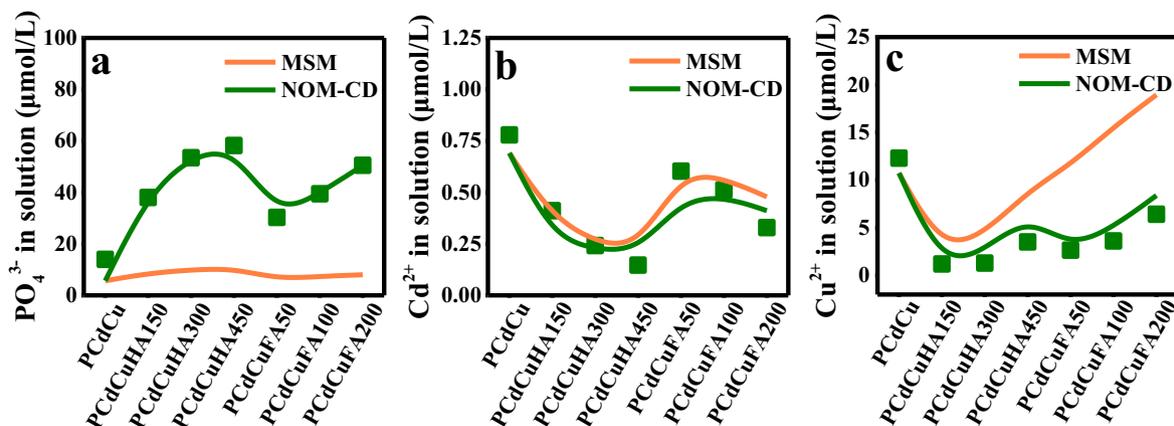


Fig. 2. Effects of HA (150, 300 and 450 mg/L) or FA (50, 100 and 200 mg/L) on the adsorption of PO_4^{3-} (275 $\mu\text{mol/L}$) (a), Cd^{2+} (1.08 $\mu\text{mol/L}$) (b) and Cu^{2+} (77 $\mu\text{mol/L}$) (c) onto goethite at pH 5.2. Background: 2.3 mmol/L $\text{Ca}(\text{NO}_3)_2$. Symbols are experimental data, lines are Multi-Surface model and NOM-CD model calculations.

3.2.2. Cd^{2+} and Cu^{2+}

Addition of HA or FA enhanced Cd^{2+} and Cu^{2+} adsorption to the solid phase at $\text{pH} < 6.3$ (Cd^{2+}) and $\text{pH} < 5.5$ (Cu^{2+}), whereas at higher pH decreased the adsorption slightly (up to 3%) (Fig. 1c-f). Generally, the amount of Cd^{2+} bound to the solid phase was reasonably predicted by the MSM (Figs. 1c, 2b). The same was true for Cu^{2+} in the presence of HA (Figs. 1e, 2c). However, the MSM underpredicted Cu^{2+} adsorption in the presence of FA, especially at $\text{pH} < 6$ (Figs. 1e, 2c). At pH 5.2, NOM at all the doses increased Cd^{2+} (Fig. 2b) and Cu^{2+} (Fig. 2c) adsorption to the solid phase compared to that without NOM. However, the total amount of Cd^{2+} adsorbed to the solid phase increased with the increase of HA or FA concentration, whereas Cu^{2+} bound to the solid phase decreased (Fig. 2b, c). This difference in the effect of NOM concentration on the adsorption of Cd^{2+} and Cu^{2+} was predicted correctly by the MSM. The stronger adsorption of Cu^{2+} to NOM remaining in solution in comparison to Cd^{2+} explains the difference between Cd^{2+} and Cu^{2+} in their reaction to the change of NOM concentration.

The MSM calculation showed that most of Cd^{2+} was bound to NOM in the solid phase at $\text{pH} < 6.5$ in the presence of HA or at $\text{pH} < 5.3$ in the case of FA, and bound mainly to goethite at higher pH (Fig. S4a, c). For Cu^{2+} , the model predicted that most of Cu^{2+} was bound to HA in the solid phase regardless of pH (Fig. S4b). However, FA in the solid phase dominated Cu^{2+} adsorption at $\text{pH} < 4.6$ only, whereas goethite was the dominant adsorbent at higher pH (Fig. S4d). At low pH, the adsorbed amounts of HA and FA were higher than at high pH, which explains the differences in their contribution to Cd^{2+} and Cu^{2+} adsorption at different pH. In addition, the pH dependency of Cd^{2+} and Cu^{2+} adsorption is stronger for goethite than for HA or FA. Compared to HA, the contribution of adsorbed FA to Cd^{2+} and Cu^{2+} adsorption is less, largely due to a lower amount of FA added and adsorbed. At pH 5.2, the contribution of Cd^{2+} and Cu^{2+} bound to NOM in the solid phase relative to that of goethite increases with the increase of NOM concentration (Fig. S4e, f).

3.3. NOM-CD modeling

In addition to the MSM, the NOM-CD model was also used to describe PO_4^{3-} , Cd^{2+} and Cu^{2+} adsorption to the solid phase in the presence of NOM measured in the adsorption experiments of this study. Differing from the MSM, the NOM-CD model considers the effect of NOM-mineral interaction on ion adsorption.

3.3.1. HNOM

The amount of HNOM in the Stern layer on the surface of oxides was an adjustable parameter in the NOM-CD modeling (Hiemstra et al., 2013), which was fitted based on PO_4^{3-} adsorption data in the current study. The

fitted amount of HNOM was compared to the amount of adsorbed NOM (NOM_{ads}) by calculating the ratio of the carboxylic groups in HNOM and NOM_{ads} ($\text{HNOM}/\text{NOM}_{\text{ads}}$). Each HNOM contains two carboxylic groups, and the site densities of carboxylic group on HA and FA were determined previously (Deng et al., 2019). Thus derived $\text{HNOM}/\text{NOM}_{\text{ads}}$ ratio ranged from 13% to 21% for HA (300 mg/L) and 37% to 47% for FA (100 mg/L). A higher $\text{HNOM}/\text{NOM}_{\text{ads}}$ ratio was found for FA than that for HA, which can be attributed to the smaller size of FA and less FA adsorbed. A good correlation between HNOM and NOM_{ads} was found in the current study, as shown in Fig. 3a. In the study of Deng et al. (2019), the HNOM and NOM_{ads} showed a linear relationship at a relatively low NOM_{ads} , whereas over the whole range of NOM loading (NOM_{ads} , the amount of NOM adsorbed per m^2 goethite), a logarithm relationship described the results better (Fig. S5a, b). For our data, there are small differences between the performance of the linear and logarithm relationship (Fig. S5c). For simplicity, a linear relationship was used. The $\text{HNOM}/\text{NOM}_{\text{ads}}$ ratios found in this study were compared to those reported in the study of Deng et al. (2019) (Fig. 3b). In the study of Deng et al. (2019), the electrolyte background was NaCl rather than $\text{Ca}(\text{NO}_3)_2$ as in the current study. The presence of Ca^{2+} in the present study has increased the adsorption of PO_4^{3-} , HA and FA. For both studies, the $\text{HNOM}/\text{NOM}_{\text{ads}}$ ratio decreased with the increase of NOM loading (NOM_{ads}) (Fig. 3b). The $\text{HNOM}/\text{NOM}_{\text{ads}}$ ratio for FA at the same loading (NOM_{ads}) is somewhat lower in the current study compared to those in Deng et al. (2019), and the increase of PO_4^{3-} adsorbed compared to that of Deng et al. (2019) may have expelled HA and FA further away from the goethite surface due to site, space and electrostatic competition.

3.3.2. PO_4^{3-}

The NOM-CD model well described PO_4^{3-} adsorption to the solid phase using fitted amount of HNOM (Figs. 1b, 2a). The modeling showed that the presence of NOM increased the contribution of the monodentate surface species ($\text{FeOPO}_2\text{OH}^{1.5}$) to PO_4^{3-} adsorption, while decreased the contribution of bidentate surface species ($\text{Fe}_2\text{O}_2\text{PO}_2^{2-}$), regardless of pH and NOM concentration (Fig. S6). The contributions of goethite-P-Cd and goethite-P-Cu ternary complex to PO_4^{3-} adsorption were less than that of goethite-P binary complexes (Fig. S6).

3.3.3. Cd^{2+} and Cu^{2+}

In the NOM-CD model, Cd^{2+} and Cu^{2+} adsorbed to the solid phase consist those adsorbed to goethite (with HNOM) and to HA and FA in the diffuse double layer (HA_{DDL} and FA_{DDL}). Using HNOM fitted with PO_4^{3-} data, the adsorption of Cd^{2+} to the solid phase was reasonably described with the NOM-CD model (Figs. 1d, 2b). Compared to the MSM calculations, the contribution of NOM_{DDL} to Cd^{2+} adsorption decreased due to the

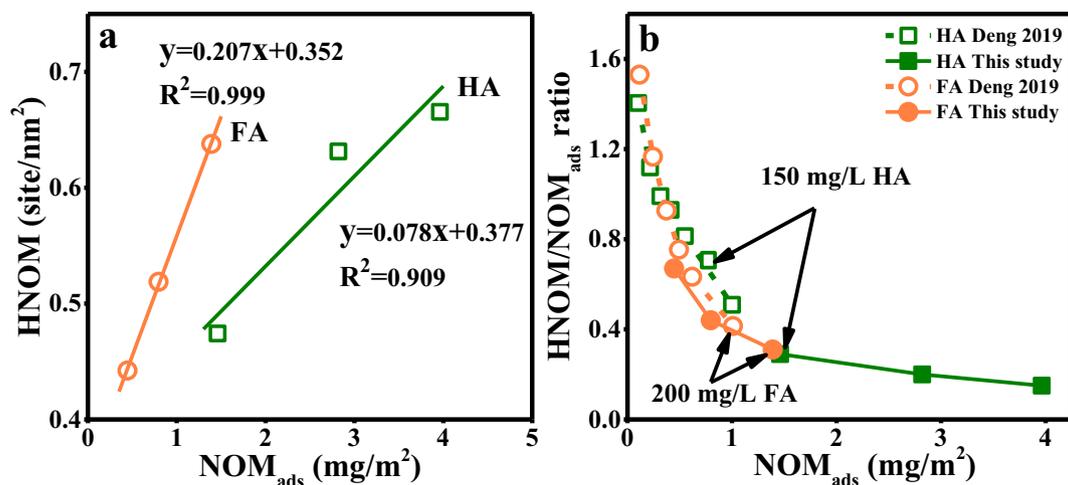


Fig. 3. Correlation between the amounts of NOM_{ads} and HNOM value derived in modeling the data of current study (a). Relation between the amounts of NOM_{ads} and $\text{HNOM}/\text{NOM}_{\text{ads}}$ ratio derived from the NOM-CD modeling of experimental data of current study and compared to those of Deng et al. (2019). The arrows indicate the data points with the same total amount of HA (150 mg/L) and FA (200 mg/L) added in this study and in the study of Deng et al. (2019), showing that more HA and FA were adsorbed in the experiment of this study (b).

following reasons: (i) part of NOM_{ads} was treated in the NOM-CD model as HNOM; (ii) the presence of HNOM promoted metal ion adsorption to goethite due to electrostatic effects. The modeling results showed that in the presence of HA (300 mg/L), most of Cd^{2+} was bound to HA_{DDL} at $\text{pH} < 5.5$ and to goethite at $\text{pH} > 5.5$, whereas in the presence of FA (100 mg/L), most of Cd^{2+} was bound to goethite at $\text{pH} > 4.3$ (Fig. S4a, c). At $\text{pH} 5.2$, goethite contributed more than HA_{DDL} to Cd^{2+} adsorption at 150 mg/L HA addition, whereas at 300 and 450 mg/L HA addition, HA_{DDL} contributed more than goethite. However, FA_{DDL} contributed less to Cd^{2+} adsorption than goethite at all the three FA concentrations (50, 100, 200 mg/L), due to the lower amount of FA added, less adsorption and higher $\text{HNOM}/\text{NOM}_{\text{ads}}$ ratio (Fig. S4e). These results were to a large extent consistent with those of the MSM.

Compared to Cd^{2+} , there is a larger deviation for Cu^{2+} between the prediction of the NOM-CD model and the experimental data, especially in the presence of FA. The model under-estimated Cu^{2+} adsorption. To explain the data, a goethite-Cu-NOM ternary complex was introduced. Previous spectroscopic observations have shown that Cu^{2+} can form Cu-bridged and NOM-bridged ternary complexes with NOM at the surface of iron oxides (Alcacio et al., 2001; Flögeac et al., 2004; Boudesocque et al., 2007; Flögeac et al., 2007). In a study of Cu^{2+} adsorption to the mixture of goethite and FA, both Cu-bridged and NOM-bridged ternary complexes were considered (Weng et al., 2008), which showed that the Cu-bridged ternary complex was dominant, while the NOM-bridged ternary complex was not important. Thus, only the Cu-bridged ternary complex (goethite-Cu-NOM) was considered in the present study. For this ternary complex, we assumed that the bidentate surface species of Cu^{2+} ($\equiv(\text{FeOH})_2\text{Cu}^{+1}$) formed ternary complex with HNOM ($\equiv(\text{FeOH})_2\text{CuNOM}^{-1}$) and the charge distribution of Cu^{2+} remained the same as in $\equiv(\text{FeOH})_2\text{Cu}^{+1}$, whereas the change of charge due to complexation of HNOM and release of H^+ was located at the 1-plane and 2-plane (Table S1). The modeling results showed that in the presence of HA (300 mg/L) most of Cu^{2+} was bound to HA_{DDL} at $\text{pH} < 5.2$ and at higher pH most of Cu^{2+} was bound as goethite-Cu-HA ternary complex, whereas Cu^{2+} bound only to goethite surface (goethite-Cu) was negligible at all pH (Fig. S4b). In the presence of FA, the goethite-Cu-FA ternary complex dominated at all pH , followed with goethite-Cu and Cu^{2+} bound to FA_{DDL} (Fig. S4d). At $\text{pH} 5.2$, goethite-Cu-HA species dominated at 150 mg/L HA addition, whereas Cu^{2+} bound to HA_{DDL} dominated at 450 mg/L HA addition (Fig. S4f). However, for FA, the goethite-Cu-FA ternary complex was the dominant adsorbed Cu^{2+} species in the solid phase at all the three FA concentrations (50, 100, 200 mg/L) (Fig. S4f).

3.4. Justification of multi-surface model for cation adsorption

As discovered in previous studies and showed in the modeling of our results, description of oxyanion adsorption needs to consider competition with NOM (Hiemstra et al., 2013; Otero-Fariña et al., 2017; Deng et al., 2019). However, the MSM can in many cases reasonably describe metal cation adsorption to mixtures of NOM and minerals or soils assuming linear additivity (Duffner et al., 2014; Rennert et al., 2017; Zhang et al., 2018). To understand why the MSM can often describe metal cation adsorption, we compared the results of the MSM and NOM-CD model for Cd^{2+} and Cu^{2+} in a soil dataset of Weng et al. (2001). In the calculation, pH , the reactively adsorbed Cd^{2+} and Cu^{2+} contents, the total surface area of iron (hydr)oxides and the amount of reactive NOM were taken from Weng et al. (2001). In both the MSM and NOM-CD models, the reactive NOM was treated as HA. In the NOM-CD modeling of this soil dataset, the amount of HNOM was derived from the correlations shown in Fig. 3a with an upper limit of $0.69 \text{ HNOM}/\text{nm}^2$. This upper limit was derived from the maximum amount of NOM that can be accommodated in the Stern layer ($0.73 \text{ mg}/\text{m}^2$) (Deng et al., 2019) using a carboxylic group density of $3.15 \text{ mol}/\text{kg}$ based on the generic NICA-Donnan model parameters for HA (Milne et al., 2003). The remaining reactive soil NOM was considered as HA free from the influence of minerals (HA_{DDL}). The calculations showed that there was a close to 1:1 relationship between the free Cd^{2+} and Cu^{2+} activities measured in 2 mM $\text{Ca}(\text{NO}_3)_2$ soil solution predicted by the MSM and NOM-CD model (Fig. 4). According to the MSM, almost all Cd^{2+} (99–100%) and Cu^{2+} (99–100%) were bound to soil NOM (NOM_{DDL}) (Fig. 4), whereas according to the NOM-CD model, most of Cd^{2+} (86–99%) and Cu^{2+} (56–95%) were bound to NOM_{DDL} , and 5–44% of adsorbed Cu^{2+} was present in the form of goethite-Cu-NOM ternary complex.

For both the experiment of current study with HA and for the soil samples of Weng et al. (2001), the results of the MSM and NOM-CD model for Cd^{2+} and Cu^{2+} adsorption were rather comparable. For both datasets, a large fraction of adsorbed NOM (79–87%, on average 83% in the current study; 73–89%, on average 84% in the soil dataset of Weng et al. (2001)) was located outside the Stern layer as NOM_{DDL} in the NOM-CD modeling. Thus, the effects of the interaction between oxides and NOM on cation adsorption were small.

3.5. Different significance of NOM-mineral interaction for cations and anions

To further illustrate the effect of NOM loading (NOM_{ads}), a simulation of PO_4^{3-} , Cd^{2+} and Cu^{2+} adsorption to the mixture of goethite and NOM with

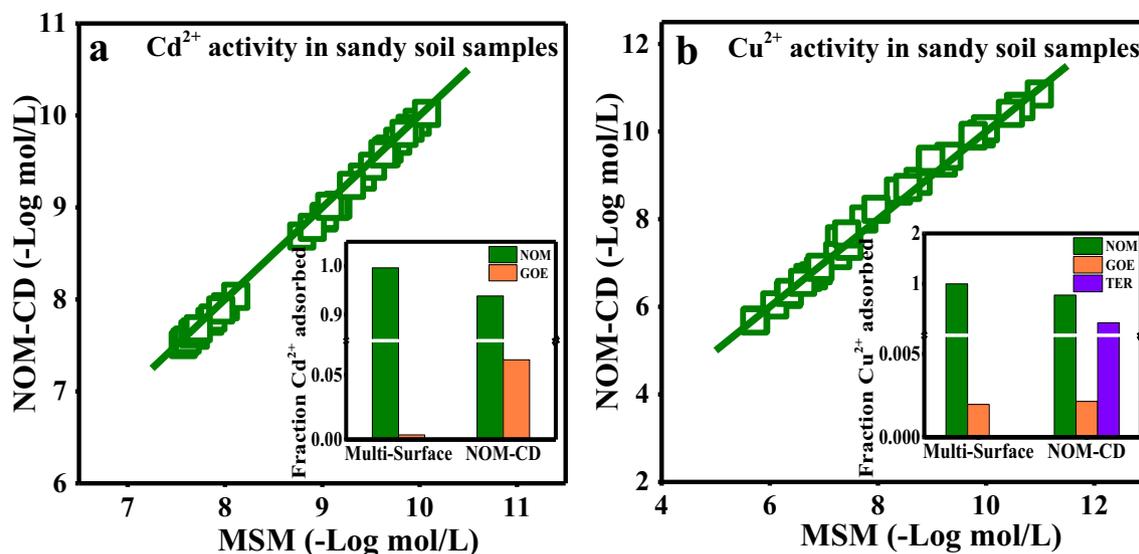


Fig. 4. Comparison of free Cd²⁺ (a) and Cu²⁺ (b) activity and speciation of adsorbed Cd²⁺ and Cu²⁺ predicted with the Multi-Surface model and NOM-CD model in the sandy soil samples of Weng et al. (2001). NOM: adsorbed to HA or FA in the solid phase; GOE: adsorbed to goethite; TER: Cu²⁺ in the form of goethite-Cu-NOM.

the MSM and NOM-CD model under different HA or FA loadings was carried out. In this calculation, the fraction of HA and FA in the Stern layer as HNOM was based on the correlations given in Fig. 3a and a maximum of 0.73 mg/m² was set as the upper limit. The results showed that with the increase of NOM_{ads}, the deviation between the MSM and NOM-CD model increased for PO₄³⁻ (Fig. 5a), but decreased for Cd²⁺ and Cu²⁺ (Fig. 5b, c). For Cd²⁺ in the presence of HA and FA and for Cu²⁺ in the presence of HA, the difference between the two models was small, and this difference almost disappeared at a NOM loading of about 4 mg/m². However, for Cu²⁺ in the presence of FA, the difference between the two models was large and this difference became insignificant only until a FA loading around 6 mg/m². Such a high loading for FA on metal (hydr)oxides is not very likely. In the experiment of current study, the NOM_{ads} was in the range of 0.5–1.4 mg/m² for FA and 1.5–4.0 mg/m² for HA. In the dataset of Weng et al. (2001), the NOM_{ads} ranged from 2.1–6.6 mg/m², among which most (>80%) was above 4.0 mg/m².

The above analysis illustrates that at a relatively high NOM loading, a small fraction of NOM is located in the Stern layer, while most of NOM extends somewhat further from the surface of oxides. In this case, the influence of the interaction with the minerals on cation adsorption to NOM is small. In addition, the effects of the NOM-mineral interaction on cation adsorption can cancel each other to a large extent. Therefore, although the microscopic speciation calculated with these two models is somewhat different, the macroscopic solid-solution distribution of the metal ions

calculated is comparable. In modeling arsenate and copper adsorption using the NOM-CD model, Otero-Fariña et al. (2017) assumed that all adsorbed NOM was present in the Stern layer. The NOM-CD modeling approach developed in the current study considers NOM present both in the Stern layer and outside, which is closer to the physical reality.

4. Conclusion

In this study, with experiments and modeling we shown that the NOM-mineral interaction is of different significance to the adsorption of metal cations (e.g. Cd²⁺ and Cu²⁺) and oxyanions (e.g. PO₄³⁻). For metal cations, adsorption to NOM is mostly dominant, whereas for oxyanions, metal (hydr)oxides are important adsorbents. At a high NOM loading on oxide minerals, a large fraction of the adsorbed NOM extends further away from the mineral surface. The influence of the NOM-mineral interaction on metal cation adsorption to NOM is therefore small, but the competition effect of NOM on oxyanion adsorption to oxides cannot be neglected. For these reasons, the linear additive Multi-Surface model can give reasonable predictions of metal cation adsorption in e.g. top soil samples, but it fails to accurately calculate oxyanion distribution. The NOM-CD model approach developed in the current study offers a consistent modeling framework that can be applied to predict distribution and speciation of both cationic and anionic nutrients and pollutants in the environment. The results also shown that surface complexation modeling is not only a powerful tool to

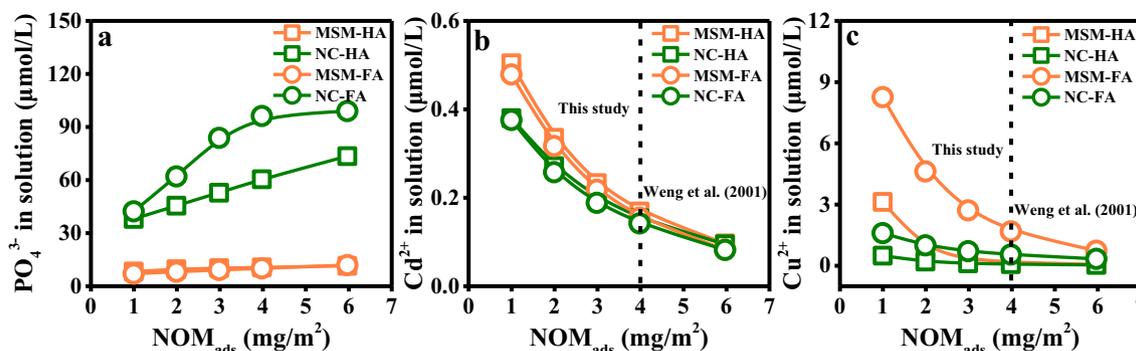


Fig. 5. Comparison between the Multi-Surface model (MSM) and the NOM-CD model (NC) simulation on PO₄³⁻ (275 μmol/L), Cd²⁺ (1.08 μmol/L), Cu²⁺ (77 μmol/L) adsorption to the mixture of goethite-HA and goethite-FA under different NOM loadings at pH 5.2. Background: 2.3 mmol/L Ca(NO₃)₂. The vertical dashed line in b and c indicates the range of NOM_{ads} in the current study and in the dataset of Weng et al. (2001).

study ion adsorption, it can also reveal the nano-scale spatial distribution of NOM on mineral surface using ions as probes.

CRedit authorship contribution statement

Junbo Li: Conceptualization, Methodology, Formal analysis, Investigation, Writing-Original Draft, Visualization. **Liping Weng:** Conceptualization, Methodology, Formal analysis, Writing-Review & Editing, Supervision, Funding acquisition. **Yingxuan Deng:** Resources, Formal analysis. **Jie Ma:** Investigation, Funding acquisition. **Yali Chen:** Writing-Review & Editing. **Yongtao Li:** Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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