

# Heavy Metal Sorption on Clay Minerals Affected by the Siderophore Desferrioxamine B

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Siderophores are released by microorganisms to ensure their iron nutrition through the dissolution of iron(III) oxides. These compounds can also chelate divalent heavy metal ions and may therefore affect heavy metal sorption and mobility in soils. Using model systems, we studied the influence of the hydroxamate siderophore desferrioxamine B (DFOB) on the adsorption of Cu, Zn, and Cd on Na-montmorillonite and kaolinite. In the absence of heavy metals, DFOB was adsorbed onto montmorillonite much stronger than onto kaolinite. In montmorillonite suspensions, heavy metal sorption was enhanced by DFOB due to electrostatic interactions. Only at high pH values, a mobilizing effect of DFOB was observed for Zn and Cd. In kaolinite suspensions, DFOB drastically diminished heavy metal sorption. Surface complexation modeling revealed that the different effects of DFOB on the metal sorption by kaolinite and montmorillonite can be explained by the large difference in their permanent negative surface charge responsible for the attraction of the positively charged metal DFOB complexes. The effect of DFOB on the adsorption of heavy metal ions on montmorillonite and kaolinite decreased in the sequence Cu > Zn > Cd in accordance with complex stability constants.

## Introduction

Mobility and toxicity of heavy metals in soil are governed by various parameters including pH and the content of clay minerals and organic matter. Complex formation with naturally occurring or synthetic complexing agents may enhance metal mobility. For this reason, adding organic ligands as mobilizing agents has been proposed as a means to increase heavy metal availability and plant uptake in soil remediation by phytoextraction using metal accumulating plants. In some studies, synthetic ligands such as EDTA were used (1). Chelating agents that occur naturally in the rhizosphere as exudates of plants and microorganisms are of particular interest because they are biodegradable and in general nontoxic to soil biota. In addition, leaching of contaminants can be kept to a minimum since mobilization would occur in the immediate surroundings of the roots of metal accumulating plants. Chelation may also help to increase the phytoavailability of essential trace elements under conditions of deficiency. Zn deficiency for example is probably the most important heavy metal micronutrient problem in crop growth (2).

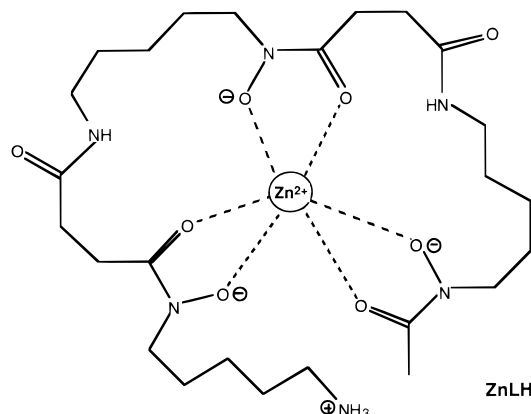


FIGURE 1. Complexation of Zn by the siderophore DFOB.  $L^{3-}$  represents DFOB deprotonated at the three hydroxamate moieties. The hydroxamate groups offer binding sites for metal cations. Thus complex formation depends on the protonation state of these groups. The neutral species ZnLH is dominant at pH > 8.

Siderophores are natural complexing agents, which occur especially in the rhizosphere (3, 4). They are exuded by the majority of soil microorganisms under iron deficiency to enhance Fe(III) availability and uptake (5). In soils, a wide range of siderophore-to-metal ratios is found. For a bacterial microniche, Hersman et al. (6) estimated siderophore concentrations in soil solutions to range from tens of micromoles to a few millimoles per liter. The stability constants for 1:1 Fe(III)–siderophore complexes are typically around  $10^{30}$ . Siderophores form stable complexes also with divalent heavy metal cations but exhibit lower stability constants than with Fe(III). Nevertheless, heavy metals influence siderophore production, and *vice versa* siderophores influence heavy metal toxicity (7–9). Chemical structures were analyzed (10, 11), and complex stability constants for Fe(III) and other metal complexes are known for a number of siderophores (12–14). The mechanisms of iron acquisition by siderophores have been the subject of many studies (15), and the relevance of microbial siderophores for plant nutrition has also been discussed (16, 17). Brainard et al. (18) showed that siderophores are extremely effective in solubilizing actinides. Nevertheless, there is a lack of detailed information concerning the influence of siderophores on heavy metal mobility in soils.

In this work, a model system for a soil was used. It consisted of the siderophore desferrioxamine B (DFOB, Figure 1), the heavy metals Cu(II), Zn(II), or Cd(II), and the clay minerals montmorillonite or kaolinite. DFOB represents the group of hydroxamate siderophores, which are found in soils (3). Montmorillonite was chosen to represent a 2:1 layer clay mineral carrying a high permanent negative charge. Kaolinite, a 1:1 layer type with only poor isomorphous substitution, is nearly uncharged. To understand the chemical nature of the binding mechanisms, experiments with varying metal concentrations, pH, and ionic strengths were carried out.

## Experimental Section

**Reagents.** Na-montmorillonite (SWy-2, Crook County, Wyoming, U.S.A.) and kaolinite (KGa-2, Warren County, Georgia, U.S.A.) were obtained from the Clay Minerals Society, Columbia, MO. Both clay minerals were fractionated to obtain the particle fraction  $\leq 2 \mu\text{m}$  for montmorillonite and  $\leq 1 \mu\text{m}$  for kaolinite. The clay minerals were washed three times with 1 M NaCl and with NANOpure water as many times

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until the suspension was free of chloride ( $\text{AgNO}_3$  test). The concentrations of clay mineral stock suspensions were 12.5 and 25.0 g/L Na-montmorillonite and 21.4 g/L kaolinite. In the sorption experiments, the concentration of montmorillonite and kaolinite was generally 1 g/L, and in some exceptions 0.5 or 2 g/L were used. Aqueous solutions of  $\text{ZnCl}_2$  (p.a., Merck) or  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , and  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (all p.a., Fluka) were used. Exact concentrations of these stock solutions were determined by flame atomic absorption spectrometry (F-AAS) and also by differential pulse anodic stripping voltammetry (DPASV). Standard solutions of the respective metal salt (Merck) were used for calibration. DFOB was obtained as mesylate salt from Ciba-Geigy and used without further treatment. Stock solutions of DFOB were prepared at concentrations of 20 mM and 200  $\mu\text{M}$ . As background electrolytes  $\text{NaClO}_4 \cdot \text{H}_2\text{O}$  (p.a., Fluka) or  $\text{Ca}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (Alfa) were used. Chromeazurole S and 2-[N-morpholino]ethanesulfonic acid (MES) monohydrate, purchased from Fluka and Sigma, respectively, were used for the quantitative determination of DFOB. All solutions were made with NANOpure water.

**Adsorption of Metals Influenced by pH.** Sorption of Cu, Zn, and Cd, both in the absence and presence of DFOB on Na-montmorillonite and kaolinite, was determined in batch experiments. Small amounts of the clay mineral stock suspensions were added to 10 mL of 0.1 M  $\text{NaClO}_4$  in 10 mL polypropylene tubes to obtain a solid concentration of 1 g/L. Subsequently, DFOB and heavy metal stock solutions were added under stirring with a magnetic stirrer resulting in total heavy metal concentrations of approximately  $10^{-6}$ ,  $10^{-5}$ , or  $10^{-4}$  M and a siderophore concentration of about  $3 \cdot 10^{-4}$  M. The pH value was adjusted by adding small volumes of diluted NaOH or  $\text{HClO}_4$  solutions and monitored by a pH electrode (InLab 423, Mettler Toledo) connected to a pH meter (Metrohm 691). The pH varied from about 4 to 10. Sample tubes were closed with polyethylene caps and then shaken on an over-head shaker for 2 h. According to previous kinetic studies (19) and other experimental evidence (20) this was longer than sufficient to reach sorption equilibrium. After another pH measurement, samples were centrifuged (Heraeus Sepatech, 5000 rpm, 15 min), filtered (0.45  $\mu\text{m}$ , cellulose acetate), and acidified. Dissolved heavy metal concentrations were determined using F-AAS. Three acidified samples without solids were prepared in each case to obtain the exact total concentrations of heavy metals. Experiments were carried out at 22 °C without exclusion of  $\text{CO}_2$ . This was chosen since precipitation of carbonates is only expected for Cd in absence of DFOB (21). The addition of sufficient DFOB prevents formation of metal-carbonate complexes or solid carbonates. According to our model calculations, the formation of solid  $\text{CdCO}_3$  is of minor importance in the Cd concentration range used in this work. Batch experiments with solid-free samples showed that measurable metal adsorption on tube walls, filter paper, or precipitation only occurred in absence of DFOB and at high pH, i.e., for Cu, Zn, and Cd above pH 6.5, pH 7.0, and pH 8.5, respectively (data not shown). For instance, at pH 8.0, 75% of total Cu and 40% of total Zn were lost from the solution. The addition of DFOB kept the heavy metals in solution over the entire pH range studied.

**Sorption of DFOB Influenced by pH.** Sorption studies with DFOB in absence of heavy metals were conducted likewise but without acidification of the samples after centrifugation. The total DFOB concentration was about  $3 \cdot 10^{-4}$  M. Reference samples without solids but with the same concentrations of DFOB were prepared to account for losses due to decomposition or adsorption onto the surfaces of tubes and filters. Samples with and without solids that did not contain DFOB were prepared for different pH values to account for the influence of the background solution on the

TABLE 1. Surface Site Concentrations (in mmol/g) and Other Parameters of the Montmorillonite and Kaolinite Used in This Study

	Na-montmorillonite	kaolinite
$\equiv\text{S}^\circ\text{OH}$	0.0025 <sup>a</sup>	
$\equiv\text{S}^w\text{OH}$	0.2 <sup>a</sup>	
$\equiv\text{SOH}$		0.036 <sup>b</sup>
$\equiv\text{X}^-$	0.86 <sup>a</sup>	(0.02–0.1) <sup>b,c</sup>
EDL model	diffuse layer	none <sup>b</sup>
surface area	34 m <sup>2</sup> /g	24 m <sup>2</sup> /g

<sup>a</sup> Reference 26. <sup>b</sup> Reference 25. <sup>c</sup> Not used for modeling.

determination of DFOB. After centrifugation, all samples were diluted with NANOpure water to obtain DFOB concentrations below 100  $\mu\text{M}$ . Dissolved concentrations of DFOB were determined with the Cu-Chromeazurole S method (22) using a Varian Cary 1E UV/visible spectrophotometer. For calibration, a series of standard solutions containing 0–100  $\mu\text{M}$  DFOB in NANOpurewater was used.

**In Situ Determination of Metal Sorption Isotherms and Influence of Ionic Media and Strength.** Isotherms for Zn and Cd sorption on Na-montmorillonite and kaolinite in aqueous suspensions with 0.1 M  $\text{NaClO}_4$  as background electrolyte were determined for total heavy metal concentrations between  $10^{-8}$  and  $10^{-4}$  M. The concentration of DFOB was 0 or  $3 \cdot 10^{-4}$  M. The samples were purged with argon. Isotherms were determined for different pH values, which were adjusted by adding small volumes of diluted NaOH or  $\text{HClO}_4$  solutions and monitored using a pH electrode (Metrohm 6.0204.100 connected to a Metrohm 713 pH meter). No buffers were used. Total dissolved concentrations of Zn and Cd species including the metal–DFOB complexes were determined directly in suspension with voltammetry. The experimental setup and details on the voltammetric methods are described elsewhere (19). The purchased montmorillonite contained 0.9  $\mu\text{mol/g}$  Zn as determined by acidic extraction. This background concentration was taken into account in computing sorption isotherms.

Zn sorption isotherms for Na-montmorillonite in the presence of DFOB were also determined in 0.01 M  $\text{NaClO}_4$  and in 0.1 and 0.01 M  $\text{Ca}(\text{ClO}_4)_2$  at pH 6.9 as described above.

**Modeling.** The chemical speciation of metals and DFOB was calculated for aqueous solutions ( $I = 0.1$  M) with stability constants given by refs 12 and 13 using the program ChemEQL (23). The log  $K$  values of the surface species were fitted using the program FITEQL4 (24). For kaolinite one type of surface hydroxyl groups ( $\equiv\text{SOH}$ ) was assumed with no electrostatic corrections according to (25). Two types of surface hydroxyl groups ( $\equiv\text{S}^\circ\text{OH}$  with high affinity and  $\equiv\text{S}^w\text{OH}$  with low affinity) were chosen for Na-montmorillonite as considered in refs 21 and 26. Cation exchange sites ( $\equiv\text{X}^-$ ) were also taken into account for montmorillonite. The parameters of two minerals used in modeling are shown in Table 1. The main difference between the two minerals is the much higher cation exchange capacity of the montmorillonite (870 mequiv/kg (26)) compared to the kaolinite (between 20 and 100 mequiv/kg (27)).

## Results and Discussion

**Sorption of DFOB.** DFOB showed a strong affinity to montmorillonite but only a weak affinity to kaolinite (Figure 2). Two-thirds of the total initial DFOB concentration of 298  $\mu\text{M}$  were sorbed to montmorillonite in the acidic pH range, resulting in a concentration of about 200  $\mu\text{mol/g}$ . Above pH 7, DFOB sorption decreased to very low levels. The shape of the adsorption edge can be modeled assuming adsorption

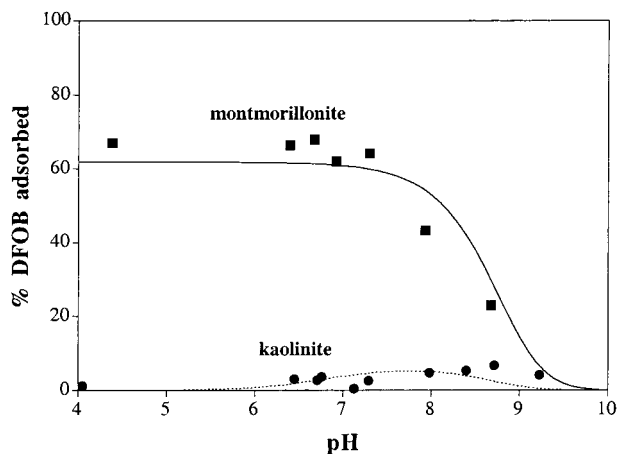


FIGURE 2. Sorption of DFOB on Na-montmorillonite and kaolinite in absence of heavy metals. The lines are the model fits calculated with the constants from Table 2. Conditions: 298  $\mu\text{M}$  DFOB, 0.95 g/L montmorillonite, 1 g/L kaolinite, 0.1 M  $\text{NaClO}_4$ .

of  $\text{LH}_4^+$  onto the permanently charged sites and formation of a neutral surface complex.



As consequence of the disappearance of the positive charge of DFOB above pH 7, sorption of DFOB decreased.

Sorption of DFOB onto kaolinite on the other hand was very weak at low pH and increased slightly with increasing pH. However, only a small fraction of the initial 298  $\mu\text{M}$  DFOB was adsorbed (1–5%) which results in a large error in the determination of the adsorbed amount of DFOB. As no adsorption of metals onto the permanently charged sites was found, we also did not consider adsorption of  $\text{LH}_4^+$  to these sites. Adsorption of DFOB increases above pH 7, where the concentration of the variably charged sites  $\equiv\text{SO}^-$  begins to increase ( $\text{p}K_{a2}$ : 7.2). For adsorption of DFOB on kaolinite, we therefore postulate a surface complex  $\equiv\text{SO}^-\text{LH}_4^+$ .



The same reaction is also possible in the DFOB-montmorillonite system but was not included in the model. The weak adsorption onto the variably charged sites is occluded by the strong adsorption onto the permanently charged sites.

**Sorption of Metals in the Absence of DFOB.** Sorption of Cu, Zn, and Cd was studied as a function of pH and as a function of added metal at constant pH. A small fraction of the metals was bound to montmorillonite at low pH (Figure 3), whereas in the presence of kaolinite no significant metal ion sorption occurred at low pH (Figure 4). Increasing the pH, the sorption edges were reached for Cu, Zn, and Cd in this sequence. Sorption edges for kaolinite were observed at lower pH than for montmorillonite. The shape of the sorption curves for montmorillonite and kaolinite were in good agreement with results from Lothenbach et al. (21) and Spark et al. (28), respectively, who observed the same pH sequence of the sorption edges as in our experiments.

The sorption behavior on montmorillonite can be explained by a combination of cation exchange at low pH and specific binding due to surface complexation at higher pH. The increase in metal adsorption on montmorillonite with increasing pH is modeled using the  $\equiv\text{S}^-\text{OMe}^+$  and  $\equiv\text{S}^-\text{OMeOH}$  surface complexes. The adsorption constants of the high affinity sites of montmorillonite ( $\equiv\text{S}^-\text{OH}$ ) were determined from adsorption isotherms at constant pH (for Cd and Zn) (see section labeled **Sorption Isotherms**). The constants for the weak affinity sites were determined from

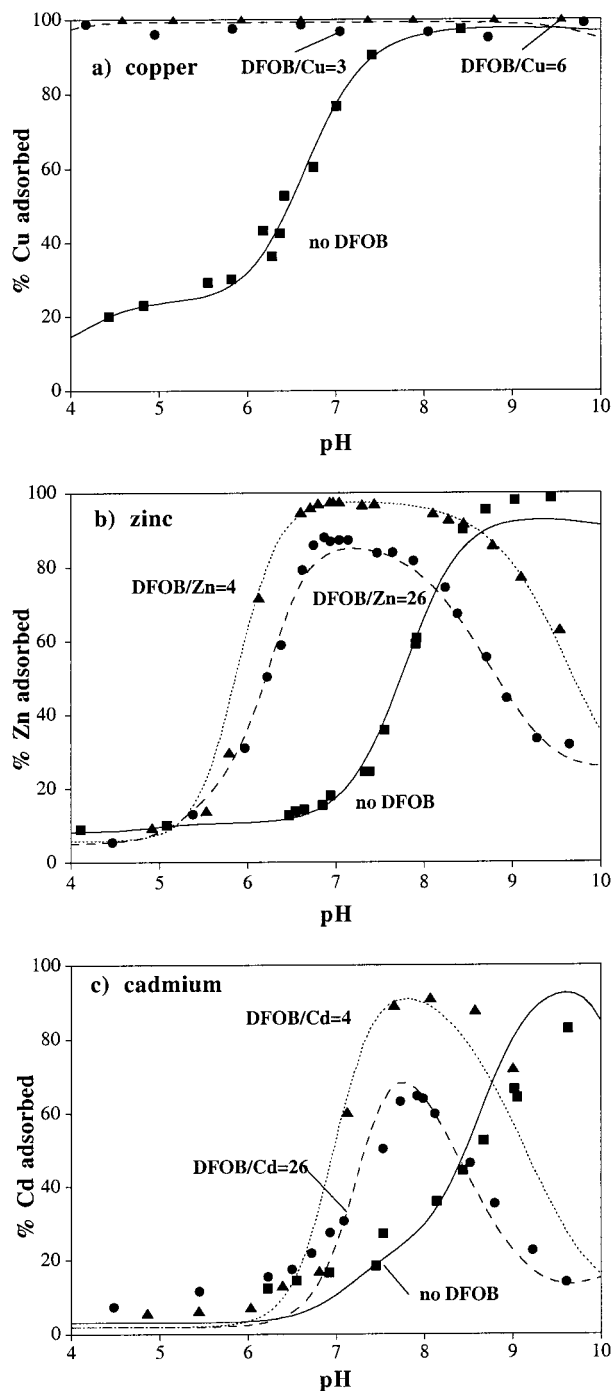


FIGURE 3. Sorption of Cu, Zn, and Cd as a function of pH in the absence and presence of DFOB on montmorillonite. Solid lines represent modeled sorption curves in the absence of DFOB, dotted curves in the presence of DFOB at two DFOB/metal ratios (with the constants from Table 2). Conditions: (a) ■ 84.5  $\mu\text{M}$  Cu, ● 283  $\mu\text{M}$  DFOB, 84.52  $\mu\text{M}$  Cu, ▲ 47.2  $\mu\text{M}$  Cu, 284  $\mu\text{M}$  DFOB, 0.94 g/L montmorillonite; (b) ■ 87.5  $\mu\text{M}$  Zn, ● 301  $\mu\text{M}$  DFOB, 10.84  $\mu\text{M}$  Zn, ▲ 289  $\mu\text{M}$  DFOB, 82  $\mu\text{M}$  Zn, 0.94 g/L montmorillonite; and (c) ■ 11.5  $\mu\text{M}$  Cd, ● 290  $\mu\text{M}$  DFOB, 11.2  $\mu\text{M}$  Cd, ▲ 282  $\mu\text{M}$  DFOB, 72.75  $\mu\text{M}$  Cd, 0.94 g/L montmorillonite. All experiments were conducted in 0.1 M  $\text{NaClO}_4$ .

the sorption experiments under varying pH. The cation exchange constant for Cd was determined from the adsorption isotherm at pH 7.2, for Cu and Zn from the pH edges. The lines in Figure 3 are the model fits with the constants reported in Table 2.

Cation exchange in the presence of kaolinite was insignificant probably due to the compensation of the permanent

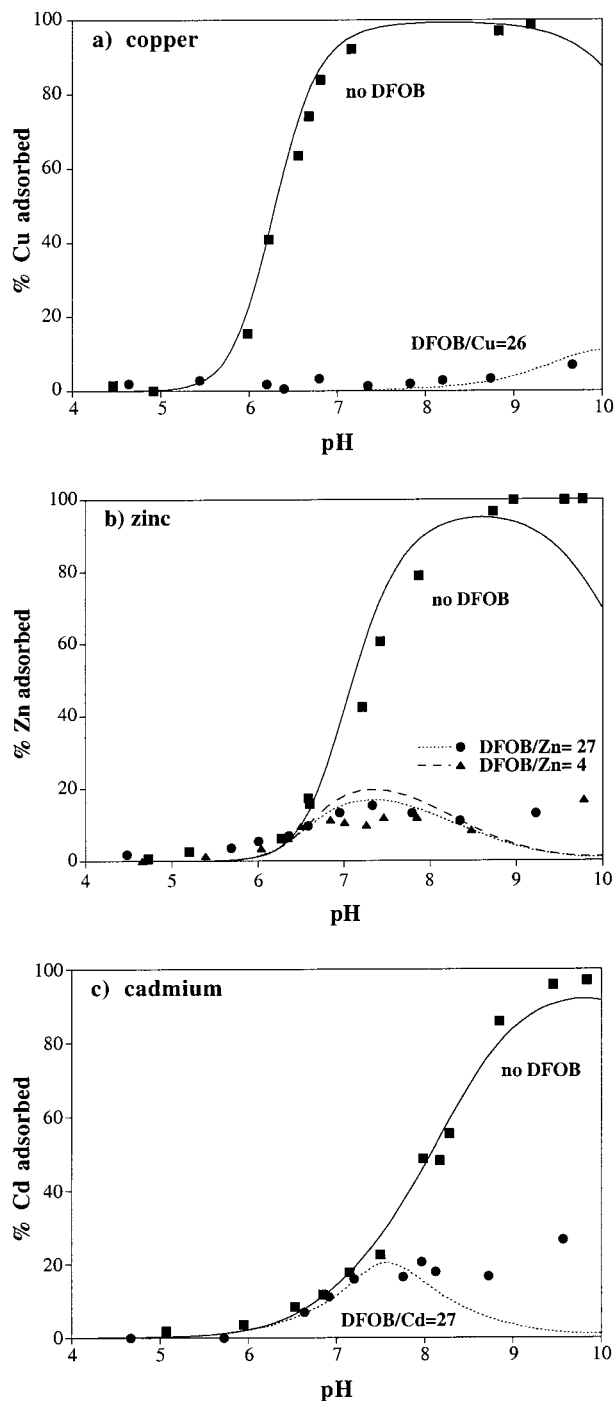


FIGURE 4. Sorption of Cu, Zn, and Cd as a function of pH in the presence and absence of DFOB on kaolinite. Solid lines represent modeled sorption curves in the absence of DFOB, dotted curves in the presence of DFOB for Zn at two DFOB/metal ratios (with the constants from Table 2). Conditions: (a) ■ 10.3  $\mu\text{M}$  Cu, ● 289  $\mu\text{M}$  DFOB, 11.51  $\mu\text{M}$  Cu, 1.0 g/L kaolinite; (b) ■ 10.9  $\mu\text{M}$  Zn, ● 298  $\mu\text{M}$  DFOB, 11.08  $\mu\text{M}$  Zn, ▲ 160  $\mu\text{M}$  DFOB, 41.99  $\mu\text{M}$  Zn, 1.0 g/L kaolinite; and (c) ■ 11.1  $\mu\text{M}$  Cd, ● 296  $\mu\text{M}$  DFOB, 10.8  $\mu\text{M}$  Cd, 0.99 g/L kaolinite. All experiments were conducted in 0.1 M  $\text{NaClO}_4$ .

negatively charged sites by  $\text{Na}^+$  ions from the background electrolyte. Therefore, only adsorption onto the variably charged sites was considered. Cu and Zn adsorption could be explained by formation of  $\equiv\text{SOMeOH}$  alone, while additionally  $\equiv\text{SOCd}^+$  was needed for the modeling of the Cd data. The lines in Figure 3 represent model calculations with the constants reported in Table 2.

TABLE 2. Conditional Stability Constants and Surface Site Concentrations Used for Modeling Sorption of Metals and DFOB to Na-Montmorillonite and Kaolinite<sup>a</sup>

#### Na-montmorillonite

$\equiv\text{S}^{\circ}\text{OH} + \text{H}^{+} \leftrightarrow \equiv\text{S}^{\circ}\text{OH}_2^{+}$	4.6 <sup>b</sup>			
$\equiv\text{S}^{\circ}\text{OH} \leftrightarrow \equiv\text{S}^{\circ}\text{O}^{-} + \text{H}^{+}$	-7.9 <sup>b</sup>			
$\equiv\text{S}^{\text{w}}\text{OH} + \text{H}^{+} \leftrightarrow \equiv\text{S}^{\text{w}}\text{OH}_2^{+}$	4.6 <sup>b</sup>			
$\equiv\text{S}^{\text{w}}\text{OH} \leftrightarrow \equiv\text{S}^{\text{w}}\text{O}^{-} + \text{H}^{+}$	-7.9 <sup>b</sup>			
$\equiv\text{X}^{-} + \text{L}^{3-} + 4\text{H}^{+} \leftrightarrow \equiv\text{X}^{-}\text{LH}_4^{+}$	41.2			
		Cu	Zn	Cd
$\equiv\text{S}^{\circ}\text{OH} + \text{Me}^{2+} \leftrightarrow \equiv\text{S}^{\circ}\text{OMe}^{+} + \text{H}^{+}$	2.1	-1.4	-2.7	
$\equiv\text{S}^{\text{w}}\text{OH} + \text{Me}^{2+} \leftrightarrow \equiv\text{S}^{\text{w}}\text{OMe}^{+} + \text{H}^{+}$	-2.9	-4.7	-6.5	
$\equiv\text{S}^{\text{w}}\text{OH} + \text{Me}^{2+} \leftrightarrow \equiv\text{S}^{\text{w}}\text{OMeOH} + 2\text{H}^{+}$	-10.2	-11.8	-14.4	
$2\equiv\text{X}^{-} + \text{Me}^{2+} \leftrightarrow (\equiv\text{X})_2\text{Me}$	5.2	5.1	4.7	
$\equiv\text{X}^{-} + \text{Me}^{2+} + \text{L}^{3-} - 2\text{H}^{+} \leftrightarrow \equiv\text{X}^{-}\text{MeLH}_2^{+}$	38.8	32.3;	30.3;	
		33.1 <sup>c</sup>	31.0 <sup>c</sup>	

#### kaolinite

$\equiv\text{SOH} + \text{H}^+ \rightleftharpoons \equiv\text{SOH}_2^+$	3.5 <sup>d</sup>		
$\equiv\text{SOH} \rightleftharpoons \equiv\text{SO}^- + \text{H}^+$	-7.2 <sup>d</sup>		
$\equiv\text{SOH} + \text{L}^{3-} + 3\text{H}^+ \rightleftharpoons \equiv\text{SO}^-\text{LH}_4^+$	34.2		
	Cu	Zn	Cd
$\equiv\text{SOH} + \text{Me}^{2+} \rightleftharpoons \equiv\text{SOMe}^+ + \text{H}^+$	<i>e</i>	<i>e</i>	-3.2
$\equiv\text{SOH} + \text{Me}^{2+} \rightleftharpoons \equiv\text{SOMeOH} + 2\text{H}^+$	-8.0	-9.4	-10.9
$\equiv\text{SOH} + \text{Me}^{2+} + \text{L}^{3-} + \text{H}^+ \rightleftharpoons \equiv\text{SO}^-\text{MeLH}_2^+$	29.5	25.4	23.6

#### dissolved species

$\text{L}^{3-} + \text{H}^+ \leftrightarrow \text{LH}^{2-}$				10.9 <sup>f</sup>	
$\text{L}^{3-} + 2\text{H}^+ \leftrightarrow \text{LH}_2^-$				20.4 <sup>f</sup>	
$\text{L}^{3-} + 3\text{H}^+ \leftrightarrow \text{LH}_3$				29.4 <sup>f</sup>	
$\text{L}^{3-} + 4\text{H}^+ \leftrightarrow \text{LH}_4^+$				37.8 <sup>f</sup>	
			Cu	Zn	Cd
$\text{Me}^{2+} + \text{H}_2\text{O} \leftrightarrow \text{MeOH} + \text{H}^+$	-7.1 <sup>g</sup>	-8.6 <sup>g</sup>	-9.7 <sup>g</sup>		
$\text{Me}^{2+} + \text{L}^{3-} + \text{H}^+ \leftrightarrow \text{MeLH}$	24.4 <sup>c</sup>	20.4 <sup>c</sup>	18.8 <sup>d</sup>		
$\text{Me}^{2+} + \text{L}^{3-} + 2\text{H}^+ \leftrightarrow \text{MeLH}_2^+$	33.4 <sup>c</sup>	28.3 <sup>c</sup>	26.0 <sup>d</sup>		
$\text{Me}^{2+} + \text{L}^{3-} + 3\text{H}^+ \leftrightarrow \text{MeLH}_3^{2+}$	37.1 <sup>c</sup>	33.7 <sup>c</sup>	32.7 <sup>c</sup>		

<sup>a</sup> Stability constants were determined with FITEQL (24) if not marked differently. <sup>b</sup> Reference 26. <sup>c</sup> For ZnDFOB and CdDFOB two log *K* values for the DFOB/metal ratio of 4 and 28 were found. <sup>d</sup> Reference 25. <sup>e</sup> Not significant. <sup>f</sup>  $\equiv\text{SOH}$ : surface hydroxyl groups ( $\equiv\text{S}^{\circ}\text{OH}$ : high affinity sites,  $\equiv\text{S}^{\text{w}}\text{OH}$ : low affinity sites),  $\equiv\text{X}^-$ : permanent negatively charged sites. <sup>f</sup> Reference 12. <sup>g</sup> Reference 37. <sup>h</sup> Reference 13.

**Sorption of Metals in the Presence of DFOB: 1. Montmorillonite.** Also shown in Figure 3 are the effects of DFOB on the sorption of Cu, Zn, and Cd on Na-montmorillonite. DFOB strongly influenced metal sorption, but effects differed considerably between the metals. An almost complete removal of Cu from solution in the presence of DFOB is observed over the pH range from 4 to 10. For Zn and Cd, sorption edges were shifted to lower pH values, maximum sorption was reached at about pH 7 for Zn and pH 8 for Cd, and a mobilization effect was observed at high pH values. Heavy metal-DFOB complex formation depends on the protonation state of the hydroxamate groups and is favored at high pH values. Stability constants of the metal-DFOB complexes are reported to decrease in the sequence  $\text{Cu} > \text{Zn} > \text{Cd}$  (12, 13). The effect of DFOB on metal adsorption followed the same sequence.

The ratio of DFOB to metal used in the pH sorption studies was either 3–4 or 26–28. In general, the shape of the sorption curves was the same for both ratios, but sorption of Zn and Cd was more pronounced at the lower ligand-to-metal ratio (which corresponds to a higher metal concentration at the same DFOB concentration).

Electrostatic interactions are also the reason for enhanced heavy metal sorption on montmorillonite in the presence of



DFOB. As described in detail by Stadler and Schindler (29), positively charged complexes may be removed from solution by cation exchange. In the case of Zn and Cd, enhanced sorption due to complex formation with DFOB is limited to pH values above 5 because no complexes are formed under acidic conditions. Maximum sorption of Zn and Cd was observed at pH 7 and 8, respectively. The positively charged metal–DFOB complexes are the dominant species in this pH range. At pH above 8 or 9, sorption of Zn and Cd to montmorillonite decreased due to the formation of neutral metal–DFOB complexes, which are the dominant species above pH 7.4 and pH 8.0 for Zn and Cd, respectively. Cu–DFOB complexes are much stronger than those with Zn and Cd. The positive charge is lost by the Cu–DFOB complex only above pH 9, i.e., at higher pH in comparison to Zn and Cd. Therefore, sorption of Cu showed no decrease up to pH 10. Even at high suspension pH values, positively charged  $\text{CuLH}_2^+$  complexes dominate metal speciation.

The adsorption of the metals in the presence of DFOB was perfectly modeled assuming that the neutral DFOB–metal surface complex is formed.



The observed pH dependence with the maximum for Zn at pH 7 and for Cd at pH 8 is predicted by this model. For CuDFOB, the fitted value of  $\log K$  is the smallest possible value with which we obtained good description of the data. The complete removal of Cu from solution did not allow for determining the  $\log K$  value more accurately.

Figure 5a shows the distribution of the surface species for the ratio DFOB/Zn = 26. The observed adsorption of Zn is modeled as a combination of the adsorption of uncomplexed Zn onto the variably and permanently charged sites and of  $\text{ZnLH}_2^+$  onto the permanently charged sites. Adsorption of uncomplexed Zn is dominated by the high-affinity sites, i.e., the surface complex  $\equiv\text{S}^-\text{OZn}^+$ . Only at pH higher than 9.5, adsorption of Zn onto the weak affinity sites was found to play a role.

#### Sorption of Metals in the Presence of DFOB: 2. Kaolinite.

In kaolinite suspensions, DFOB hindered the adsorption of Cu, Zn, and Cd almost completely over the pH range from 4 to 10 (Figure 4). Only at pH values above 6, some adsorption of the metals was observed in the presence of DFOB mainly for Zn and Cd. The sorption of Zn was almost the same for the two DFOB/Zn ratios.

As no adsorption of metals or DFOB onto the permanently charged sites of kaolinite was observed, the adsorption of metals onto kaolinite in the presence of DFOB has to be explained by adsorption of metal–DFOB complexes onto the variably charged sites. We assumed that the following surface reaction takes place



This surface complex is able to explain the increase in metal adsorption up to pH about 8. At higher pH, this surface species becomes less important because of the decrease in the concentration of dissolved  $\text{MeLH}_2^+$ . The adsorption of metals in this pH range could be explained by the formation of the surface species  $\equiv\text{SO}^-\text{MeLH}$ . The dissolved species  $\text{MeLH}$  carries a terminal positively charged amino group, which can interact with deprotonated negatively charged surface hydroxyl groups. Another possibility is that at pH above 9, adsorption of uncomplexed metals is stronger than predicted. Because at pH above 9, 100% adsorption was achieved in the experiments at varying pH, little information about the strength of the surface complexes could be inferred from these data. Underestimation of the surface complexes of uncomplexed metals may therefore be possible. However,

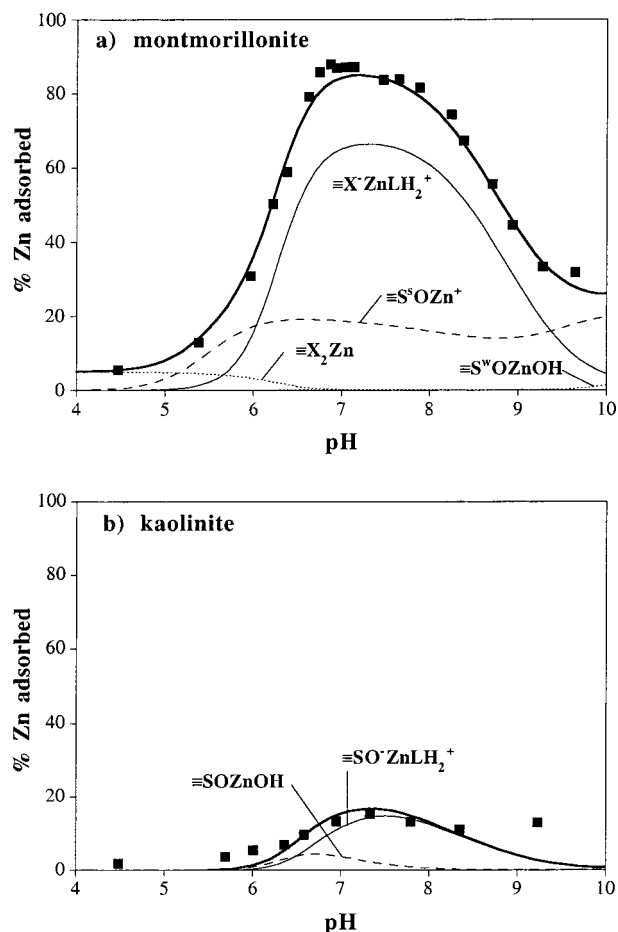


FIGURE 5. Speciation of the Zn-surface complexes for montmorillonite (a) and kaolinite (b) in the presence of DFOB. Conditions the same as in Figure 3b (DFOB/Zn = 4) and Figure 4b (DFOB/Zn = 4).

there are only very few data points of metal adsorption in the presence of DFOB at pH above 9, which is why we have not attempted to model the adsorption in this pH region.

Figure 5b shows that the surface complex with uncomplexed Zn can exist around pH 6.5 to some extent, while at higher pH, adsorption of complexed Zn takes place.

**Sorption Isotherms.** Figure 6 shows the isotherms for Zn and Cd sorption on Na-montmorillonite in the absence and presence of DFOB. In contrast to isotherms in absence of DFOB, isotherms for Zn in the presence of DFOB exhibited two distinct regions characterized by different slopes. At low Zn concentrations, DFOB diminished Zn sorption. At higher Zn concentrations, DFOB enhanced sorption strongly as indicated by a steep increase of the isotherm. DFOB enhanced Cd sorption over the entire ranges of metal concentrations. The promotive effect was more pronounced at higher Cd concentrations.

The fact that the adsorption of Zn and Cd increased with increasing metal concentration in the presence of DFOB is also reflected in the fitting of the pH edges shown in Figure 3. For the two DFOB/metal ratios, different  $\log K$  values have been obtained. The value at  $82 \mu\text{M}$  Zn was considerably higher than at  $11 \mu\text{M}$  Zn (33.1 compared to 32.3). The same applies for Cd, where at the high concentration a  $\log K$  value of 31.0 was found, in comparison to 30.3 at the low concentration. The lines in Figure 6 have been calculated with the lower of the two values. With these  $\log K$  values, Zn and Cd adsorption is predicted accurately for the total metal concentrations used in the adsorption experiments under varying pH. However, it is largely overestimated at lower metal concen-

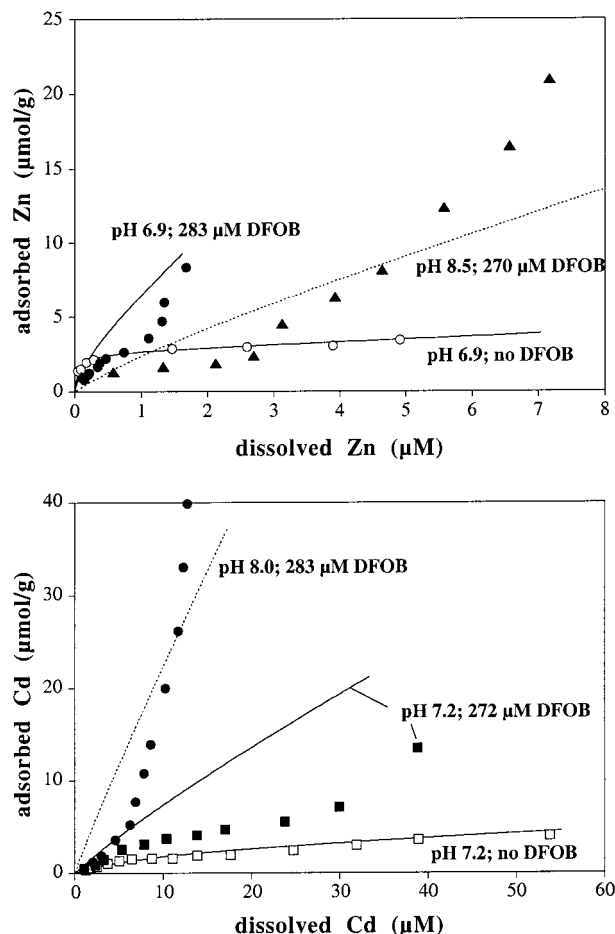


FIGURE 6. Sorption isotherms for Zn and Cd on Na-montmorillonite in absence (open symbols) and presence (closed symbols) of DFOB at different pH values. The lines are the model calculations with the constants derived from the pH edges (Figure 3). Conditions: (a)  $\circ$  pH 6.9, no DFOB,  $\bullet$  pH 6.9; 283  $\mu\text{M}$  DFOB, 1.04 g/L montmorillonite,  $\blacktriangle$  pH 8.5; 270  $\mu\text{M}$  DFOB, 0.98 g/L montmorillonite and (b)  $\square$  pH 7.2, no DFOB,  $\blacksquare$  pH 7.2; 272  $\mu\text{M}$  DFOB, 1.0 g/L montmorillonite,  $\bullet$  pH 8.0; 283  $\mu\text{M}$  DFOB, 1.05 g/L montmorillonite. All experiments were conducted in 0.1 M  $\text{NaClO}_4$ .

trations and underestimated at higher concentrations. The adsorption of Cd at pH 7.2 was overestimated by the model in the whole concentration range.

In all experiments with DFOB a large excess of uncomplexed DFOB was present which results in a surface concentration of DFOB of about 200  $\mu\text{mol/g}$ . At pH 8.5, a plateau for Zn of 2  $\mu\text{mol/g}$  was observed at a dissolved Zn concentration of 1  $\mu\text{M}$ . The amount of adsorbed Zn remained more or less constant until 3  $\mu\text{M}$  dissolved Zn was reached. Then a steep increase in adsorbed Zn was observed. Such a behavior could be explained by surface precipitation of a  $\text{ZnDFOB}$  phase or by a surfactant-type interaction of dissolved  $\text{ZnDFOB}$  with adsorbed  $\text{ZnDFOB}$ , where adsorption is facilitated once a monolayer is formed. In the DFOB–Zn system however, there is already a DFOB surface concentration that is about 50 times higher than the Zn surface concentration. Therefore, interaction of dissolved  $\text{ZnDFOB}$  with  $\equiv\text{X}-\text{ZnLH}_2^+$  rather than with  $\equiv\text{X}-\text{LH}_4^+$  would be required to explain the observed behavior. Further spectroscopic studies could give more insights into the responsible processes.

**Influence of Ionic Strength.** Sorption isotherms at different  $\text{NaClO}_4$  concentrations showed that adsorption was stronger at lower ionic strength (Figure 7). With calcium as the background cation, adsorption was stronger at higher

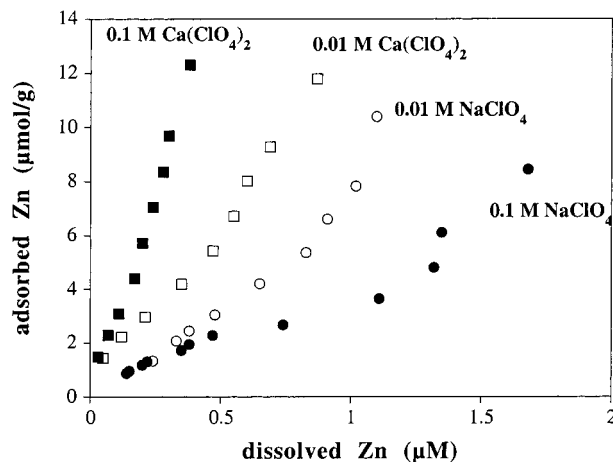


FIGURE 7. Influence of ionic strength and electrolyte composition on Zn sorption on Na-montmorillonite in the presence of DFOB. DFOB concentration = 302  $\mu\text{M}$ , except in the case of 0.1 M  $\text{NaClO}_4$ ; 283  $\mu\text{M}$ . Sorption isotherms were determined in  $\text{Ca}(\text{ClO}_4)_2$  (squares) and  $\text{NaClO}_4$  (circles) for  $I = 0.1$  M (filled symbols) and 0.01 (open symbols).

Ca concentration. Nevertheless, the promotive effect of Ca was not expected as Ca is reported to be very effective in hindering Zn and Cd sorption in soils (30). Even at low concentrations, a significantly higher Zn sorption was observed with the Ca than with the Na background electrolyte. Flocculation and/or DFOB complex formation with the divalent cation, which are both favored in the divalent electrolyte, may block surface sites and change the solution composition. However, the stability constant for the  $\text{CaLH}$  complex is much lower than that for the  $\text{ZnLH}$  complex ( $10^{13.5}$  in comparison to  $10^{20.4}$ ). According to chemical speciation calculations, formation of  $\text{CaLH}$  is not expected to any significant degree below pH 8. A positive effect of Ca on ligand adsorption has been observed so far for phosphate (31), humic acids (32, 33), and phosphonic acids (34). The results of our study show that this effect can be relevant also for metal–ligand complexes. For a better understanding of this phenomenon, more studies with different electrolyte concentrations and compositions at different pH values are required.

**Environmental Implications.** Our results show that the hydroxamate siderophore DFOB can drastically affect heavy metal adsorption on clay minerals. Soil minerals are often negatively charged and similar effects as observed for montmorillonite are expected, meaning that a mobilizing effect should only occur for Zn and Cd in soils with high pH values. In the rhizosphere, where pH values are in general lower than in the bulk soil, DFOB is expected to increase metal sorption to negatively charged soil minerals and thus may diminish heavy metal toxicity to plants. Nevertheless, the increased metal sorption does not necessarily lead to reduced bioavailability of these elements because the chelates were bound electrostatically and thus are assumed to be exchangeable. In soils with high contents of kaolinite, DFOB may enhance dissolved concentrations of metal ions.

As DFOB is mainly an Fe(III) chelator the presence of Fe(III) will probably weaken the influence of DFOB on heavy metal sorption. However, solubility of Fe(III) oxides in soils is low. The dissolved concentration of  $\text{Fe}^{3+}$  in equilibrium with  $\text{Fe}(\text{OH})_3$  at pH 7 is lower than  $10^{-18}$  M. Typical dissolved concentrations of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  are about  $10^{-11}$  and  $10^{-8}$  M, respectively (35). Heavy metal cations, which are sorbed to soil particles, may be more accessible for chelation than Fe. In this case, the kinetic behavior is decisive, and thermodynamic constants cannot describe the process correctly. In a following paper we will focus on studies conducted in the

presence of Fe(III) (36). Further studies with other siderophores, other minerals, and real soil samples are required to draw conclusions about the transferability to field situations.

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