Influence of humic substances on the sorption of heavy metal cations on mineral surfaces

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Influence of Humic Substances on the Sorption of Heavy Metal Cations on Mineral Surfaces

A dissertation submitted to the
SWISS FEDERAL INSTITUTE OF TECHNOLOGY ZÜRICH
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DOCTOR OF NATURAL SCIENCES

presented by

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2000
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Chapter 5 was published, apart from minor modifications, as
Iso Christl and Ruben Kretzschmar
Competitive sorption of copper and lead at the oxide-water interface:
Implications for surface site density

The publication of Chapters 3, 4, and 6 in peer reviewed journals is planned.
SUMMARY

In soil and aquatic environments, mineral surfaces are coated with natural organic matter such as humic substances to a large extent. Adsorbed humic substances strongly alter the physical and chemical properties of mineral particles. In this thesis, the influence of adsorbed humic substances such as humic and fulvic acid on metal cation sorption to mineral surfaces is investigated. Colloidal hematite is used as a representative of a mineral sorbent. The main objectives of this study are (1) to extensively characterize the soil humic and fulvic acids used, (2) to measure proton, Cu(II), and Pb(II) binding to humic and fulvic acids as well as to colloidal hematite, (3) to accurately describe proton, Cu(II), and Pb(II) binding to organic and inorganic sorbent materials with models using model parameters which are in good agreement to characterization results, and (4) to measure metal cation binding to an organic matter-mineral complex and to compare experimental results with predictions based on an additive approach assuming that adsorbed humic substances simply contribute additional binding sites to the solid phase.

Humic substances such as humic and fulvic acid are very heterogeneous in terms of physical and chemical properties. Understanding the heterogeneity of humic substances is a prerequisite for understanding cation binding to humic substances. To elucidate the heterogeneity of humic substances, the soil humic acid isolated is further separated into four fractions of different molecular size using a hollow fiber ultrafiltration technique. Fulvic acid, humic acid and humic acid size fractions are characterized by a variety of techniques (elemental analysis, size exclusion chromatography, UV-VIS, CP-MAS $^{13}$C-NMR, FT-IR, and fluorescence spectroscopy). The characterization results shown in Chapter 2 clearly demonstrate that fulvic and humic acid are chemically different. For the humic acid size fractions, it is shown that the chemical composition varies with the size of the fractions.
Differences of humic substances in their chemical composition result in a different proton binding behavior. In Chapter 3, it is demonstrated that differences in proton binding behavior correspond very well to differences in chemical composition. Results from Cu(II) and Pb(II) binding experiments shown in Chapter 4 suggest that metal cation binding is not strongly affected by chemical differences of humic substances even though metal humate complexes may be different for different cations. The results of this study indicate that Pb(II) is bound by humic substances mainly in monodentate complexes. For Cu(II) binding, the stoichiometry of proton Cu(II) exchange reactions indicates that Cu(II) is bound in monodentate and bidentate complexes.

The NICA-Donnan model is used to describe proton and metal binding to humic substances. Results of modeling proton and metal binding data presented in Chapter 3 and 4, respectively, demonstrate the great flexibility of the NICA-Donnan model to excellently describe cation binding data. A good description of the entire data set including proton, Cu(II), and Pb(II) binding data with physically and chemically reasonable model parameters is only achieved when some model parameters are related to characterization results and when, in addition, proton, Cu(II), and Pb(II) data are fitted simultaneously.

Data of proton, Cu(II), and Pb(II) sorption to colloidal hematite are modeled with two surface complexation models, the triple layer model and a 2-pK basic Stern model with ion-pair formation. As shown in Chapter 5, excellent fits are obtained for proton, Cu(II), and Pb(II) sorption data regardless of the hematite surface site density chosen as model parameter. However, the accuracy of predictions of competitive metal sorption strongly depends on the surface site density chosen for model calibrations. This result suggests that the surface site density is a key parameter if surface complexation models are exposed to complex, multi-component environments.

The influence of organic coatings on heavy metal sorption to mineral surfaces is investigated in a Cu(II)-fulvic acid-hematite system. The results presented in Chapter 6 indicate that at acidic pH conditions, metal cation sorption to the solid phase strongly increases in the presence of fulvic acid. At neutral and basic pH conditions, the presence of fulvic acid resulted in a slight decrease of metal sorption to the solid phase due to the formation of soluble metal fulvic acid complexes. This result suggests that the presence
of surface-bound humic substances strongly decreases the mobility of heavy metal cations in acidic soils.

Finally, experimental data of the Cu(II)-fulvic acid-hematite system are compared with model predictions using a simple additive approach. In this approach, the amount of Cu(II) sorbed to the solid phase is calculated as the sum of Cu(II) sorbed to the mineral surface itself and the amount of Cu(II) bound by the percentage of fulvic acid adsorbed to the mineral surface. The model predictions mimic the pH and ionic strength dependence of Cu(II) binding to the fulvic acid-hematite complex fairly well. Between pH 4 and 6, Cu(II) sorption is slightly underestimated by the additive approach. Incorporation of electrostatic interactions between adsorbed organic polyelectrolyte and mineral surface as well as fractionation of polydisperse polyelectrolytes upon adsorption of natural organic polyelectrolytes to mineral surfaces may improve model predictions.
ZUSAMMENFASSUNG


Huminstoffe wie Humin- und Fulvosäuren sind hinsichtlich ihrer physikalischen und chemischen Eigenschaften sehr heterogen. Das Verstehen dieser Heterogenität ist eine Voraussetzung dafür, die Kationenbindung an Huminstoffen zu verstehen. Zur Aufklärung der Heterogenität von Huminstoffen wird die aus einem Boden isolierte Huminsäure in vier verschiedene Molekülgrößenfraktionen mittels einer sogenannten Hohl-Faser-Ultrafiltrationstechnik aufgetrennt. Fulvosäure, Huminsäure und Huminsäure-Größenfraktionen werden mit einer Vielzahl von verschiedenen Techniken charakterisiert (Elementaranalyse, Gel-Chromatographie, UV-VIS, CP-MAS $^{13}$C-NMR, FT-IR und


Die Daten der Protonen-, Kupfer-, und Bleisorption an kolloidalem Hämatit werden mit zwei Oberflächenkomplexierungsmodellen, dem Triple-Layer-Modell und einem 2-pK Basic-Stern-Modell mit Ionenpaar-Bildung modelliert. Wie in Kapitel 5 gezeigt wird, werden hervorragende Beschreibungen der Protonen-, Kupfer-, sowie der Bleisorptionssdaten erhalten, unabhängig davon, welche Dichte an Oberflächenbindungspätze für Hämatit als Modellparameter gewählt wird. Die Genauigkeit der Vorhersagen von kom-
petitiver Metallsorption hängt dagegen erheblich von der gewählten Oberflächenbindungsplatzdichte ab. Dieses Ergebnis weist darauf hin, dass die Oberflächenbindungsplatzdichte ein Schlüsselparameter für die Anwendung von Oberflächenkomplexierungsmodellen in komplexen Umweltsystemen ist.


CHAPTER 1
INTRODUCTION

The fate of trace metals in our environment is a major concern in environmental sciences. Most metals can be toxic to living organisms. The toxicity largely depends on the metal speciation and the total metal concentration, since these determine the concentration of the toxic species (Stumm and Morgan, 1996). For most metals, the free aquo-ion is the most bioavailable and thus potentially toxic species (Robertson, 1996). In natural systems such as soils, the metal speciation is largely controlled by sorption reactions at the water-solid interface (Stumm, 1992). For metal cations as well as oxyanions, iron oxide phases and clay minerals are the most important inorganic sorbents in soils. In addition, organic soil compounds such as humic and fulvic acid can contribute to the total sorption capacity of soils to a large extent (Sparks, 1995).

In natural soil and aquatic systems, mineral surfaces are often coated with natural organic matter such as humic substances (Sposito, 1984). Humic substances are anionic polyelectrolytes which are very heterogeneous in terms of physical and chemical properties. Humic substances are able to strongly bind to mineral surfaces. Hereby, the most important binding mechanism is the specific adsorption by ligand exchange with protonated surface hydroxyl groups (Murphy and Zachara, 1995). Even though mineral surfaces are often coated by humic substances to a large extent in natural systems, the effect of organic mineral coatings on the sorption behavior of contaminants such as heavy metal cations is still poorly understood (Harter and Naidu, 1995; Murphy and Zachara, 1995).

Since the binding sites of mineral surfaces, which exhibit a high affinity for heavy metal cations, are supposed to be involved in specific adsorption of humic substances such as humic and fulvic acid, the metal sorption to mineral surfaces may be largely con-
trolled by adsorbed humic substances in natural environments (Davis and Leckie, 1978; Davis, 1984). Studies on the influence of humic substances on metal sorption to mineral surfaces conducted with different metals and sorbent materials led to variable and sometimes controversial results (Dalang et al., 1984; Laxen, 1985; Xu et al., 1989; Zachara et al., 1994; Robertson, 1996; Vermeer et al., 1999). By providing additional binding sites for metal complexation, adsorbed humic substances may increase metal binding to the solid phase. However, adsorbed humic substances may partially occupy sorption sites which are able to bind metals, too. This would lead to a decrease to metal sorption to the mineral surface itself. Furthermore, the presence of dissolved humic substances can decrease metal sorption to the solid phase by forming soluble metal complexes (Harter and Naidu, 1995; Murphy and Zachara, 1995). Considering the metal sorption behavior of humic substances and mineral surfaces as well as the sorption humic substances to mineral surfaces, greatest effects of humic substances on metal cation binding to the solid phase is expected at acidic pH conditions. At low pH, humic substances strongly sorb to mineral surfaces, whereas metal cations are not strongly bound by mineral surfaces under acidic conditions (Benjamin and Leckie, 1981; Schindler et al., 1987).

A precise quantification of the effect of humic substances on metal sorption to the solid phase is a prerequisite for an accurate prediction of the fate of metal cations in natural environments. Up to now, it has not yet been fully resolved whether adsorbed humic substances simply provide additional binding sites without blocking the mineral surface for metal complexation, according to a linear additivity model (Zachara et al., 1994), or whether the interactions of metal cations and humic substances at the mineral-water interface are more complex. It has been proposed that metal cations exhibit a higher affinity to adsorbed humic substances than to dissolved humic substances (Davis, 1984; Laxen, 1985). Robertson (1996) found that copper sorption to a goethite-humic acid system was strongly non-additive. Under certain conditions, less than 20 percent of the amount of copper calculated based on the additivity rule was bound to the solid phase. The extent of the non-additive behavior of copper binding widely differed depending on pH, ionic strength, goethite-humic acid ration, and copper loading. Vermeer et al. (1999) also reported deviations from the additivity rule for a cadmium-humic acid-
hematite system. At acidic pH conditions, the additivity approach tended to overestimate cadmium sorption to the humic acid-hematite complex. At neutral to basic pH conditions, the sorption of cadmium was underestimated. The extent of deviation from the additivity increased with increasing cadmium concentration. In contrast to these results, Zachara et al. (1994) found no specific interaction between humic acid and cobalt at the mineral-water interface for different mineral sorbent such as kaolinite, gibbsite, and goethite.

In the work presented here, the interaction of metal cations (Cu(II) and Pb(II)) and humic substances (humic and fulvic acid) at the mineral-water were investigated. Hematite as a representative of an oxide was used as mineral sorbent. Since commercial humic substances widely differ from natural humic substances in terms of physical and chemical properties (Malcolm, 1986), the humic substances used were isolated from an organic soil horizon. The humic and fulvic acid were extensively characterized to understand the heterogeneity of these organic polyelectrolytes, which may be a prerequisite to understand metal binding to humic and fulvic acid. The general approach of this study to understand the effect of humic substances on metal sorption is to investigate the metal sorption to the mineral and organic sorbent first. A 2-pK basic Stern model and the NICCA-Donnan model were extensively tested to accurately describe the metal binding behavior of the mineral and organic sorbents, respectively. In a final step, the models calibrated based on data from two component systems were used to predict metal partition in a system containing all components. For the prediction of metal sorption in the three-component system, an additive approach is tested. Results from model predictions and data measured in the three-component systems were compared and discussed in detail.
Bibliography


INTRODUCTION


CHAPTER 2
CHEMICAL HETEROGENEITY OF HUMIC SUBSTANCES: CHARACTERIZATION OF SIZE FRACTIONS OBTAINED BY HOLLOW FIBRE ULTRAFLTRATION

Abstract

To investigate the chemical heterogeneity of humic substances in relation to molecular size, fulvic and humic acids were extracted and purified from the surface horizon of a Humic Gleysol in northern Switzerland. A fractionation scheme using hollow fibre ultrafiltration cartridges was developed and used to obtain four size fractions of the humic acid with nominal molecular weight ranges > 300 kD, 100-300 kD, 30-100 kD, and 10-30 kD. The fulvic acid and all humic acid fractions were characterized by size exclusion chromatography, elemental analysis (C, H, N, S), as well as spectroscopic techniques including UV-VIS, CP-MAS $^{13}$C-NMR, FT-IR, and fluorescence spectroscopy.

Clear chemical differences between the humic acid size fractions were observed. Smaller size fractions of the soil humic acid contained more chargeable functional groups and a larger percentage of aromatic carbon than the larger size fractions. Conversely, the percentage of aliphatic carbon increased with increasing apparent molecular weight. The chemical composition of the smallest humic acid fraction differed clearly from the fulvic acid fraction, despite similar apparent molecular size and carboxyl carbon content. Small humic acids contained much more aromatic carbon and less aliphatic carbon than the ful-
vic acid fraction. Apparently, humic size fractions differ in their chemical composition, which can have important implications for their environmental behaviour.
2.1 Introduction

Humic substances constitute a large portion of the total organic carbon pool in terrestrial and aquatic environments (Schlesinger, 1991). They play an important role in global carbon cycling and in the regulation of the mobility and fate of plant nutrients and environmental contaminants (Weber, 1988; Schlesinger, 1991; Schlautman and Morgan, 1993; Murphy and Zachara, 1995). Despite intensive research on humic substances during the past decades, the chemical nature of humic and fulvic acids is not fully understood. Studies using a variety of spectroscopic techniques have led to major advances in understanding the chemical structure of humic substances (Stevenson, 1994). The elemental composition and major types of functional groups of humic and fulvic acids are well established, but the macromolecular structure and chemical heterogeneity of humic substances in relation to molecular size distribution is still subject of controversial discussion (Clapp and Hayes, 1999). The classical view of humic substances states that they are macromolecular, negatively charged, branched polyelectrolytes with mainly carboxylic and phenolic type acidic functional groups (Swift, 1989). Some researchers have recently proposed an alternative model of humic acids, stating that they are self-associates of small, uniform humic acid molecules which are held together by weak hydrophobic forces (Piccolo et al., 1996; Conte and Piccolo, 1999; Piccolo et al., 1999). Evidence for this view stems primarily from size exclusion chromatography (SEC), in which addition of low-molecular weight organic acids leads to drastic decreases in the apparent molecular size (Piccolo et al., 1996; Piccolo et al., 1999). However, the interpretation of such experiments has been questioned because addition of organic acids in SEC may cause experimental artifacts (Perminova, 1999).

A better understanding of the macromolecular structure, molecular size distribution, and chemical heterogeneity in relation to molecular size is a prerequisite for the further development of geochemical models involving humic and fulvic acids. In general, low molecular weight, hydrophilic humic fractions are expected to be more mobile in soils and groundwater than the high molecular weight, hydrophobic humic fractions (Davis and Gloor, 1981). Only few studies are available on the chemical heterogeneity of humic
acids in relation to molecular size distribution (Silva et al., 1981; Summers et al., 1987; Swift et al., 1992; Lakshman et al., 1993; Lobartini et al., 1997; Tombácz, 1999). The results of these studies are somewhat contradictory; however, most studies suggest that the chemical composition varies with the size of the humic molecules. Differences in the chemical composition between size fractions may have a strong influence on the environmental behaviour of humic substances (Silva et al., 1981).

The influence of chemical differences between humic acid size fractions or humic substances from different origins on the binding of protons, metal cations, and organic chemicals has not been studied in great detail. Thus, a reliable database of model parameters describing proton and metal binding to humic and fulvic acids is lacking, making geochemical modeling in the presence of humic substances difficult. Humic substances are often considered to be too heterogeneous for compiling a generalized database for geochemical modeling.

The objective of this study were (i) to develop a new scheme for molecular size fractionation of humic acids using hollow fibre ultrafiltration, and (ii) to characterize the fulvic acid and size fractions of the humic acid extracted from the surface horizon of a humic Gleysol. This research is part of a larger study, in which the influence of chemical differences between humic acid fractions on proton and metal binding are investigated. The results of ion binding to the humic fractions will be presented in Chapter 3 and 4.

2.2 Materials and Methods

2.2.1 Extraction and Purification of Soil Fulvic and Humic Acid

Soil material was taken from a well humified organic horizon (H) of a Humic Gleysol at Unterrickenzopfen near Langenthal, northern Switzerland. The field-moist soil was passed through a 5-mm sieve and stored at $-17^\circ$C. Fulvic and humic acids were isolated using standard extraction and purification procedures as recommended by the International Humic Substances Society (Swift, 1996). Briefly, 500 g of moist soil material was suspended in 5 l of N$_2$-purged 0.1 M NaOH, shaken for 24 hours at $25 \pm 1^\circ$C under nitrogen gas atmosphere, and centrifuged for 15 minutes at 15 000 $\times$ g. The supernatant
solution containing fulvic and humic acids was filtered through glasswool and acidified to pH 1 with HCl to flocculate the humic acids. To achieve complete separation of fulvic acid, the precipitated humic acid was resuspended in 0.1 M NaOH and flocculated with HCl twice as described above. All acidic supernatants containing fulvic acid were combined and further purified using a DAX-8 resin (Supelite DAX-8, Supelco) column technique (Thurman and Malcolm, 1981). Before use, the DAX-8 resin was cleaned by repeated Soxhlet extraction with methanol, acetonitrile, and ethanol. The purified fulvic acid was converted to the protonated form by passing it through a proton-saturated cation exchange resin (Amberlite IR-120, Fluka). The humic acid fractions were combined and treated three times with a 0.1 M HCl-0.3 M HF solution to remove mineral impurities. The ash-free humic acid was dialyzed for two weeks against deionized water containing a mixed-bed ion exchange resin (Amberlite IR-120, Fluka, and Serdolit MB 45500, Serva), followed by dialysis against deionized water for one month. For dialysis, Spectra/Por 2 membranes (Spectrum) were used. The purified fulvic and humic acids were stored as concentrated stock solutions in the dark at 3°C. Subsamples of all fractions were freeze-dried for chemical analysis.

2.2.2 Size Fractionation of Humic Acid

The isolated and purified humic acid was separated into four molecular size fractions using a cross-flow hollow fibre ultrafiltration technique. The experimental setup is illustrated in Figure 2.1. A humic acid suspension was pumped through hollow fibre filtration cartridges with nominal molecular weight cut-offs of 300, 100, 30, and 10 kD (UFP-E-3A, A/G Technology Corporation, MA) at a flow rate of 10 ml per minute. The humic acid solution containing 1 mM NaHCO₃ was adjusted to pH 8.2 by NaOH addition. The filtrate obtained at a constant flow rate of 3 ml per minute was immediately passed through a column packed with a proton-saturated cation exchange resin (Amberlite IR-120, Fluka) to prevent oxidation during the filtration and to remove sodium and carbonate from the filtrate. The hollow fibre cartridge was connected to a reservoir to enable circulation of the humic acid solution. The reservoir was kept under nitrogen gas during the entire separation procedure. To compensate for the loss of liquid in the reservoir, the
latter was connected to a second reservoir containing a 1 mM NaHCO₃ solution at pH 8.2 at a constant pressure of 60 kP adjusted by a nitrogen gas bottle. The ultrafiltration was started using 200 ml purified humic acid stock solution, which had a total organic carbon concentration of 2.27 g C l⁻¹. The separation was performed stepwise, beginning with the highest molecular weight cut-off. The filtrate obtained was further separated using the next lower molecular weight cut-off cartridge. All separations were done under identical conditions. The complete separation scheme was repeated three times to assess the reproducibility of the fractionation results using the hollow fibre ultrafiltration technique.

The molecular size distributions of the purified fulvic and humic acid, and the humic acid size fractions were characterized by size exclusion chromatography using a SigmaChrom.
HETEROGENEITY OF HUMIC SUBSTANCES

GFC-1300 column (Supelco). The 30 cm × 7.5 mm column packed with cross-linked polysaccharides was run at a flow rate of 0.5 ml per minute. The solutions injected were adjusted to pH 7.5 by a 50 mM Tris-HCl buffer solution containing 100 mM KCl. Elution of humic substances was measured as absorption of the eluate at 280 nm. A molecular weight calibration was made as a log-linear peak position calibration from 7 kD to 1000 kD using globular proteins of known molecular weight as recommended by the manufacturer.

Elemental composition (carbon, hydrogen, sulphur, and nitrogen) of freeze-dried samples was determined with a CHNS-932 elemental analyzer (LECO). The measured data were corrected for water contents of the samples determined as loss of weight of samples heated to 105°C for 24 hours. Ash contents of the purified fulvic and humic acid were determined gravimetrically by loss of weight on ignition of samples at 650°C for 24 hours.

The UV-VIS absorption spectra of the purified fulvic and humic acid, and the humic acid fractions were recorded with a Cary 1E spectrophotometer (Varian). All samples were diluted to obtain organic carbon concentrations of 120 ± 10 mg C l⁻¹. The measurements were carried out in a 50 mM NaHCO₃ solution, which was also used as the blank. The E₄/E₆ ratios were calculated as the ratio of absorbance at 465 nm and 665 nm (Schnitzer, 1986).

The chemical composition of the fulvic and humic acid, and the humic acid size fractions was further investigated by Fourier-transform infrared (FT-IR) spectroscopy, cross-polarization magic-angle spinning ¹³C nuclear magnetic resonance (CP-MAS ¹³C-NMR) spectroscopy, and fluorescence spectroscopy.

The FT-IR spectra were collected in transmission mode with a FT-IR spectrophotometer (Spectrum One, Perkin Elmer) using potassium bromide pellets (300 mg KBr) containing 0.3 to 0.6 mg of freeze-dried fulvic or humic acid.

Solid state ¹³C-NMR spectra of freeze-dried samples were recorded on a Bruker DSX 200 NMR spectrometer at a resonance frequency of 50.3 MHz using the cross polarization magic angle spinning technique with a spinning speed of 6.8 kHz. A contact time of 1 ms and a pulse delay of 400 ms were used. A ramped ¹H pulse decreasing the
power from 100% to 50% was used to circumvent spin modulation of Hartmann-Hahn conditions (Peersen et al., 1993). At least 18 000 single scans were collected for each sample. For data analysis, the spectra were divided into chemical shift regions assigned to the chemical group classes alkyl C (0 to 45 ppm), O-alkyl C (45 to 110 ppm), aromatic C (110 to 160 ppm), phenolic C (140 to 160 ppm), carboxyl C (160 to 185 ppm), and carbonyl C (185 to 220 ppm), respectively. The relative intensity of these regions was determined by means of integration.

For the collection of fluorescence spectra, a LS 50 B luminescence spectrophotometer (Perkin Elmer) was used. A series of emission spectra was recorded for each sample with excitation wavelengths ranging from 300 to 520 nm. The emission wavelength range was 310 to 530 nm. An excitation wavelength step size of 10 nm was chosen. Humic acid concentrations of the samples were 120 ± 10 mg C l\(^{-1}\). Fulvic acid had to be diluted to 0.6 mg C l\(^{-1}\) to obtain similar fluorescence intensities as for humic acid samples. All emission spectra of a single sample were combined in the form of an excitation-emission matrix, in which the fluorescence intensity is presented as a function of excitation wavelength and emission wavelength. For the graphs shown, the spectra were interpolated linearly between the wavelength steps.

2.3 Results

2.3.1 Size Fractionation of Humic Acid

The fractionation results of the humic acid using the hollow fibre ultrafiltration technique are summarized in Table 2.1. Based on the percentage of carbon recovered in the size fractions, the humic acid exhibited a bimodal molecular weight distribution. All three replicates of the entire fractionation procedure gave similar results. The fraction >300 kD contained 52%, and the fraction 30-100 kD contained 34% of the total carbon of the humic acid, respectively. The other two fractions contributed less than 10% of the total carbon of the humic acid. On average, 96% of the total amount of carbon was recovered in the four fractions. The small loss of carbon (~4%) is likely due to small amounts of humic solutions remaining in the tubings and the reservoir.
### Table 2.1: E/E₆ ratio, elemental composition, ash content, and average molecular weight of fulvic acid (FA), humic acid (HA), and humic acid size fractions isolated from an organic horizon of a Humic Gleysol at Unterrickenzopfen, northern Switzerland. The right column gives the carbon distribution in the different molecular weight fractions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>E/E₆</th>
<th>Elemental composition (g kg⁻¹)</th>
<th>Ash (±0.6)</th>
<th>Mₜ (kDa)</th>
<th>Carbon (%)</th>
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<td></td>
<td></td>
<td>C</td>
<td>H</td>
<td>N</td>
<td>S</td>
</tr>
<tr>
<td><strong>Fulvic Acid</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FA</td>
<td>14.3</td>
<td>526 ± 4</td>
<td>45 ± 1</td>
<td>17 ± 1</td>
<td>3 ± 0</td>
</tr>
<tr>
<td><strong>Humic Acid</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HA</td>
<td>6.6</td>
<td>552 ± 2</td>
<td>53 ± 1</td>
<td>33 ± 0</td>
<td>4 ± 0</td>
</tr>
<tr>
<td>HAₙ300 kDa</td>
<td>6.1</td>
<td>584 ± 4</td>
<td>58 ± 1</td>
<td>40 ± 0</td>
<td>6 ± 0</td>
</tr>
<tr>
<td>HAₙ100-300 kDa</td>
<td>6.2</td>
<td>570 ± 2</td>
<td>50 ± 2</td>
<td>30 ± 0</td>
<td>6 ± 0</td>
</tr>
<tr>
<td>HAₙ10-30 kDa</td>
<td>7.5</td>
<td>566 ± 5</td>
<td>46 ± 1</td>
<td>24 ± 1</td>
<td>4 ± 0</td>
</tr>
<tr>
<td>HAₙ10-30 kDa</td>
<td>8.6</td>
<td>485 ± 3</td>
<td>42 ± 1</td>
<td>16 ± 0</td>
<td>2 ± 1</td>
</tr>
</tbody>
</table>

aStandard deviation calculated from five measurements.

bCalculated as difference to 100 %.

cSince the exclusion peaks of size exclusion chromatograms (Figure 2.2) cannot be included into the calculation, lower limits can only be reported for HA and HAₙ300 kDa.

dStandard deviation calculated from three replications of hollow fiber ultrafiltration cycles.

To assess the efficiency of the hollow fibre ultrafiltration technique for fractionating humic acid into molecular size classes, all obtained fractions were characterized by size exclusion chromatography. The results are shown in Figure 2.2. As the chromatograms of the three replicates obtained by hollow fibre ultrafiltration were nearly identical for each humic acid size fraction, the chromatograms of fractions from one fractionation cycle are presented. The same fractions were used to obtain all other characterization results reported in this chapter. Increasing peak elution volume corresponds to decreasing
molecular weight, as shown by the arrows on top of Figure 2.2. Peak elution volumes of the humic acid fractions increase with decreasing size cut-off of the hollow fibre cartridges used. This demonstrates that the method was successful in separating the humic acid into several fractions of different molecular size. The exclusion peak at 4.2 ml found for the purified humic acid and the largest humic acid size fraction is outside of the calibration range of the column and thus corresponds to molecules with apparent molecular weights greater than 1000 kD. For the estimation of an average apparent molecular weight $M_w$ (Table 2.1) a calibration with globular proteins was used. Since the exclusion peak of the humic acid and the largest humic acid size fraction cannot be included in the calculation we can only report a lower limit for the average molecular weight of the humic acid and the largest humic acid size fraction. It is noteworthy that the estimated average molecular weight of the smallest humic acid fraction is even smaller than the estimated average molecular weight of the fulvic acid.

### 2.3.2 Chemical Characterization

Since the fractionation scheme was very reproducible, detailed chemical characterization was conducted only on the fractions of one of the cycles. The elemental composition of the purified fulvic and humic acid, and the humic acid size fractions are shown in Table 2.1. Since the ash contents of the purified humic and fulvic acid are negligible (Table 2.1), the difference to 100 percent can be assigned to the oxygen content. Contents of all measured elements (C, H, N, and S) are less for the fulvic acid than for humic acid, indicating a higher O content in fulvic acid. Results for humic acid size fractions show a clear trend: C, H, N, and S contents decrease and O content increases with decreasing molecular weight. The composition of the total humic acid sample is consistent with the composition of its molecular size fractions, taking the carbon distribution into account (Table 2.1). The smallest humic acid fraction contains even less C, H, N, and S and more O than the fulvic acid.
The $E_d/E_6$ ratios of the purified fulvic and humic acid, and the humic acid fractions are reported in Table 2.1. The $E_d/E_6$ ratio is much larger for the fulvic acid (14.3) than
for the humic acid (6.6). For the fractions of humic acid, the $E_4/E_6$ values increased steadily from 6.1 to 8.6 with decreasing molecular weight. However, the smallest humic acid size fraction still had a much smaller $E_4/E_6$ ratio than the fulvic acid, despite the similarity of molecular weight.

![Figure 2.3](image.png)

**Figure 2.3.** Cross-polarization magic-angle spinning $^{13}$C nuclear magnetic resonance spectra of fulvic acid (FA), humic acid (HA), and humic acid size fractions isolated from an organic horizon of a Humic Gleysol at Unterrickenzopfen, northern Switzerland.

More detailed information about the structure of the humic substances was obtained by solid-state CP-MAS $^{13}$C-NMR spectroscopy. The spectra of the purified fulvic and humic acid, and the humic acid size fractions are presented in Figure 2.3, and the relative intensities of the chemical shift regions are summarized in Table 2.2. Comparison shows that the fulvic acid contains more carboxyl carbon, slightly more phenolic and carbonyl carbon, but less alkyl and O-alkyl carbon than the humic acid. The percentages of aromatic carbon of humic and fulvic acid are surprisingly similar. $^{13}$C-NMR analysis of the
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Humic acid fractions reveals that the chemical forms of carbon vary between the different size fractions of humic acid. The spectrum of the largest humic acid fraction is dominated by alkyl and O-alkyl carbon. With decreasing molecular weight, the percentage of both, alkyl and O-alkyl carbon decreases. On the other hand, the aromatic character of the humic acid becomes more pronounced in the lower molecular weight fractions. The percentage of carbon in chargeable groups, represented by phenolic and carboxyl carbon, increases with decreasing molecular weight. Although the two smallest humic acid fractions are similar to the fulvic acid in terms of molecular weight as determined by size exclusion chromatography, their chemical composition is significantly different from the fulvic acid in terms of functional group contents. Furthermore, they are less aliphatic and more aromatic than the fulvic acid.

**Table 2.2.** Distribution of carbon in fulvic acid (FA), humic acid (HA), and humic acid fractions determined by solid-state CP-MAS $^{13}$C-NMR spectroscopy. The fulvic and humic acid were isolated from an organic horizon of a Humic Gleysol at Unterrickenzopfen, northern Switzerland.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Percentage distribution of carbon within indicated ppm regions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 - 45</td>
</tr>
<tr>
<td></td>
<td>alkyl C</td>
</tr>
<tr>
<td>Fulvic Acid</td>
<td></td>
</tr>
<tr>
<td>FA</td>
<td>24</td>
</tr>
<tr>
<td>Humic Acid</td>
<td></td>
</tr>
<tr>
<td>HA</td>
<td>28</td>
</tr>
<tr>
<td>HA$_{&gt;300\text{ kD}}$</td>
<td>33</td>
</tr>
<tr>
<td>HA$_{100-300\text{ kD}}$</td>
<td>21</td>
</tr>
<tr>
<td>HA$_{30-100\text{ kD}}$</td>
<td>20</td>
</tr>
<tr>
<td>HA$_{&lt;30\text{ kD}}$</td>
<td>20</td>
</tr>
</tbody>
</table>
In addition to $^{13}$C-NMR spectra, FT-IR spectra of all fractions were recorded to cross-check the results of functional group analysis (Figure 2.4). All fractions exhibit the typical absorption bands of humic substances in the regions of 3430 cm$^{-1}$ (H-bonded OH groups), 2920 cm$^{-1}$ (aliphatic C–H stretching), 1720 cm$^{-1}$ (C=O stretching of COOH and ketones), 1620 cm$^{-1}$ (aromatic C=C and H-bonded C=O), 1400 cm$^{-1}$ (O–H deformation, CH$_3$ bending, C–O stretching of phenolic OH, and COO$^{-}$ antisymmetric stretching), 1250 cm$^{-1}$ (C–O stretching and OH deformation of COOH, C–O stretching of aryl esters), and 1050 cm$^{-1}$ (C–O stretching of polysaccharide or polysaccharide-like substances) (Stevenson, 1994). Although absorption magnitudes of FT-IR spectra cannot be compared directly (Christensen et al., 1998), significant differences between the FT-IR spectra of fulvic and humic acid, and the humic acid fractions can easily be seen (Figure 2.4).

![Figure 2.4](image-url)  
**Figure 2.4.** Fourier-transform infrared spectra of fulvic acid (FA), humic acid (HA), and humic acid size fractions isolated from an organic horizon of a Humic Gleysol at Unterrickenzopfen, northern Switzerland. Spectra were recorded from potassium bromide pellets (300 mg KBr) containing 0.3 to 0.6 mg organic acids.
The FT-IR spectrum of the fulvic acid has more pronounced adsorption bands in the regions of 1720 cm\(^{-1}\) and 1250 cm\(^{-1}\) than that of the humic acid, indicating a larger concentration of carboxyl groups. The comparison of FT-IR spectra of the humic acid fractions reveals similar trends as those shown by NMR results. The aliphatic and polysaccharide-like character represented by absorption bands at 2920 cm\(^{-1}\) and 1050 cm\(^{-1}\) becomes weaker with decreasing molecular weight. The fact that the absorption bands at 1720 cm\(^{-1}\) become more pronounced with decreasing molecular weight suggests that the lower molecular weight fractions contain more carboxyl groups than high molecular weight fractions of the humic acid. These trends accord with the \(^{13}\)C-NMR results. However, the clear parallels between molecular weight and phenolic groups as well as aromatic character can hardly be derived from the FT-IR spectra alone.

Further information about the composition of the purified fulvic and humic acid, and the humic acid fractions was obtained by fluorescence spectroscopy. Excitation-emission matrices are shown in Figure 2.5 for the fulvic and humic acid as well as for the largest and the smallest humic acid size fraction. The fluorescence spectrum of the fulvic acid exhibits a peak maximum at shorter excitation and emission wavelengths than that of the humic acid. Within the humic acid fractions, a further red shift in the fluorescence maxima with decreasing molecular weight is observed. Excitation and emission wavelengths of the fluorescence maximum increase with decreasing molecular weight of the humic acid fractions. A red shift in fluorescence maxima in humic acids relative to fulvic acids from the same source is attributed to the presence of high molecular weight fractions, linearly-condensed aromatic systems with electron-withdrawing substituents, and a greater degree of conjugation in humic acids (Senesi et al., 1991; Mobed et al., 1996). A small degree of aromatic polycondensation, small amounts of conjugated chromophores, and the presence of electron-donating substituents in the fulvic acid structure contribute to the relative short wavelengths of the fluorescence maxima and high fluorescence intensities compared with humic acid (Senesi et al., 1991; Mobed et al., 1996). This suggests that, despite similar percentages of aromatic carbon determined by \(^{13}\)C-NMR spectroscopy for the fulvic and the humic acid, the degree of condensation of aromatic ring systems is less for the fulvic than for the humic acid. In addition, the aromatic ring sys-
tems of the humic acid may bear more electron-withdrawing substituents such as carboxyl groups, whereas carboxyl groups of the fulvic acid may be less often associated to aromatic ring systems. The red shift of fluorescence maxima gradually increases with decreasing molecular weight of the humic acid fractions, which corresponds well with the contents determined by $^{13}$C-NMR spectroscopy. The large difference in fluorescence spectra of the smallest humic acid fraction and the fulvic acid indicates clear chemical differences despite the similar molecular weight distributions of both fractions.

Figure 2.5. Fluorescence spectra of fulvic acid (FA), humic acid (HA), and humic acid size fractions isolated from an organic horizon of a Humic Gleysol at Unterrickenzopfen, northern Switzerland. Relative fluorescence intensities are shown as excitation-emission matrices. Absolute intensities were normalized to maximum intensity of each excitation-emission matrix. Spectra were recorded in a 50 mM NaHCO$_3$ background solution.
2.4 Discussion

The results obtained by size exclusion chromatography confirmed that the hollow fibre ultrafiltration successfully fractionated the soil humic acid into four different molecular size fractions. However, the nominal molecular weight cut-offs of the hollow fibre filtration cartridges did not directly correspond to the average molecular weights obtained by size exclusion chromatography. This result is not surprising, however, considering the differences between globular proteins used for size calibration and humic substances in terms of stereochemistry, charging behaviour, and hydration. Negatively charged humic and fulvic acid molecules can, for example, interact with ultrafiltration membranes by electrostatic repulsion, yielding very large apparent molecular weights. Despite the well-known difficulties in the application of size exclusion chromatography for humic substances (De Nobili et al., 1989; De Nobili and Chen, 1999; Perminova, 1999), the measured peak elution volumes suggest rather large molecular weights for the fulvic and humic acid studied.

The macromolecular nature of humic substances is still subject of controversial discussion (Clapp and Hayes, 1999). Recently, some researchers have proposed that humic substances are self-associates of rather small, uniform humic molecules held together by weak hydrophobic forces (Piccolo et al., 1996). Our results presented in this paper revealed clear chemical differences between the molecular size classes of a soil humic acid. Assuming a self-associates structure of the humic acids would consequently imply the existence of different types of humic building blocks forming self-associates which differ significantly in chemical composition and apparent molecular size. Our results are not consistent with the view that small, uniform humic molecules are the primary building blocks of humic acids with high apparent molecular weights. However, additional research using a combination of techniques is required to indisputably elucidate the macromolecular nature of humic substances, which could well be a combination of several models proposed, e.g., polydisperse macromolecules which additionally tend to form even larger self-associates of some kind.
The detailed analysis of the humic acid size fractions revealed that the elemental composition, the degree of condensation of aromatic units, and the amounts of major functional groups changed with the apparent molecular weight of the fractions. The smaller humic acids may have a more compact structure than that of the larger ones. This may be caused by their larger content of aromatic carbon and a higher degree of condensation, as was indicated by the $E_d/E_g$ ratio, which increased with decreasing molecular weight. Similar findings for a fractionated humic acid have been recently reported (Tomáčz, 1999). The smaller humic acid size fractions also contained larger percentages of chargeable functional groups than the larger humic acid fractions. It is interesting to note that the smallest humic acid size fraction even exhibited a smaller average molecular weight, but a larger percentage of chargeable functional groups than the fulvic acid fraction. The trend that an the amount of chargeable functional groups increases with decreasing molecular size of humic acid fractions has previously been reported by (Tomáčz, 1999).

The results of fluorescence spectroscopy indicate that the aromatic systems of the fulvic acid are likely to be less substituted with electron-withdrawing functional groups, such as carboxyl groups, and be less condensed than in the structures of the humic acid. This is in good agreement with the larger $E_d/E_g$ ratio of the fulvic acid than that of the humic acid (Table 2.1). For most humic substances investigated in the past, the $E_d/E_g$ ratio decreases with increasing molecular weight and degree of condensation (Summers et al., 1987; Stevenson, 1994; Tomáčz, 1999). The combination of all results suggests that the fulvic acid is dominated by aliphatic structures linked by aromatic systems with a small degree of condensation. Functional groups, such as carboxyl and carbonyl groups, are linked to aliphatic units rather than to aromatic ring systems.

The humic and fulvic acids that we investigated in this paper generally exhibited very typical composition when compared with standard soil or peat humic substances. However, the $E_d/E_g$ ratio and the percentage of carboxyl carbon of the fulvic acid determined by $^{13}$C-NMR spectroscopy correspond more closely to results reported for fulvic acids of aquatic origin (Malcolm, 1990; Grøn et al., 1996). This somewhat surprising result may be a consequence of the extraction and purification procedure used. Most soil fulvic ac-
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ids investigated previously were not purified by adsorption on polymer resins such as DAX-8 or XAD-8 (Malcolm, 1990). In contrast, resins are widely used for the isolation of aquatic fulvic acids (Malcolm, 1990). Thus, most analysed aquatic fulvic acids are well purified, whereas most analysed soil fulvic acids still contained major amounts of poly-saccharide-like components and low molecular weight acids (Malcolm, 1990). Data on the chemical composition of well purified soil fulvic acids are rare.

Since the chemical composition of the humic acid was typical for soil humic acids, we expect that humic acids from other soils are likely to exhibit similar chemical heterogeneity. The presented hollow fibre technique proved to be efficient in separating soil humic acid into different molecular weight fractions. The characterization results humic acid size fractions revealed that humic acid is fairly heterogeneous in its chemical composition. The size fractions may exhibit a different environmental behaviour as a result of differences in molecular weight and charge. Studying the proton and metal binding behaviour of different size fractions will provide valuable information about the influence of chemical heterogeneity on the binding of environmentally relevant ions.
Bibliography


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CHAPTER 3
RELATING PROTON BINDING BY FULVIC AND HUMIC ACIDS TO CHEMICAL COMPOSITION AND MOLECULAR SIZE

Abstract

Proton binding to soil fulvic acid, humic acid, and a set of humic acid size fractions was studied as a function of pH and ionic strength by potentiometric titrations. The charge resulting from deprotonation generally increased with increasing pH and increasing ionic strength. For fulvic acid, the charge of fulvic acid is much higher than for humic acid at any given pH and ionic strength. The charge of the humic acid size fractions steadily decreased with increasing apparent molecular weight of the fractions. Differences in proton binding behavior of fulvic acid, humic acid, and humic acid size fractions corresponded very well to differences in elemental composition and $^{13}$C NMR spectra.

The NICA-Donnan model was used for data modeling. When all model parameters were fitted, the values of the parameters were physically and chemically unreasonable. To avoid arbitrary constraints, model parameters were related to characterization results obtained by size exclusion chromatography and solid-state $^{13}$C NMR spectroscopy. For all fractions, excellent descriptions of titration data and reasonable model parameter values were obtained, when characterization results were used for parameter estimation. We propose to relate NICA-Donnan model parameters to characterization results to obtain stable and reliable fitting results. The value of the NICA-Donnan model parameters derived for humic and fulvic acid are similar to values reported previously. Thus, we con-
clude that the proton binding behavior of humic substances may be predicted approximately based on average NICA-Donnan model parameters. The incorporation of characterization results may improve the goodness of predictions.
3.1 Introduction

Humic substances strongly affect the fate of trace metal cations and organic contaminants in soils and aquatic environments (Carter and Suffet, 1982; Marinsky and Ephraim, 1986; Weber, 1988; Cabaniss, 1992; Schlautman and Morgan, 1993; Harter and Naidu, 1995). The mobility of humic compounds in soils and aquifers strongly depends on their charging behavior, since the colloidal stability of humic acids is related to their charge (Hunter, 1986). The charging behavior of humic and fulvic acids is controlled by the types and amounts of functional groups (Tombácz, 1999). Since humic and fulvic acids are polydisperse mixtures of natural organic polyelectrolytes with different functional groups (Benedetti et al., 1996a), it is essential to have information about the chemical composition of humic and fulvic acids to understand their charging behavior. Recently published studies on the chemical characterization of size-fractionated humic acids revealed that physical and chemical properties of the size fractions varied significantly (Tombácz, 1999; Chapter 2 of this thesis). The results proposed that chemical and physical properties of the size fractions were correlated, e.g. the amount of carboxylic and phenolic carbon determined by solid-state $^{13}$C nuclear magnetic resonance (NMR) spectroscopy decreased with increasing apparent molecular size (Chapter 2). But the question how differences in chemical composition of fulvic or humic acid fractions affect proton and metal binding has not yet been answered comprehensively. Since cation binding to humic and fulvic acids is linked to the presence of reactive functional groups (Masini et al., 1998), types and respective amount of reactive functional groups in a humic sample may play a key role.

For a good description of proton and metal binding to humic substances a model is required that accounts for the heterogeneity of the chemical composition (Bartschat et al., 1982; Marinsky and Ephraim, 1986; de Wit et al., 1993b; Kinniburgh et al., 1996). This has been done by establishing models including discrete or continuous affinity distributions to describe the variability of binding sites (Dzombak et al., 1986; de Wit et al., 1993b; Benedetti et al., 1995; Cernik et al., 1996; Bolton et al., 1996; Bryan et al., 1997; Tipping, 1998; Avena et al., 1999). One of the successfully applied models among the
continuous affinity distribution models is the NICA-Donnan model (Kinniburgh et al., 1999). The NICA-Donnan model was chosen for this study as the combination of the NICA model considering the heterogeneity of binding sites and the Donnan model allowing for electrostatic interaction between humic molecules and bulk solution gives a reasonable description of cation binding to humic substances. However, the model needs a large number of fitting parameters to ensure an accurate description of proton binding data. To obtain physically and chemically reasonable parameter sets, parameter constraints are often needed (Christensen et al., 1998). Relating model parameters to characterization results may help to avoid arbitrary contraints.

This chapter is part of a larger study on the chemical heterogeneity of soil humic and fulvic acid and its influence on the proton and metal binding behavior. The objectives of this part are (1) to investigate proton binding to a well-characterized soil fulvic acid, humic acid, and humic acid size fractions differing in chemical composition, (2) to describe the proton binding data using the NICA-Donnan model, and (3) to relate model parameters to characterization results in order to obtain a set of model parameters, which excellently describes the data in consistence with characterization results. Results of metal (Cu(II) and Pb(II)) binding experiments will be presented and discussed in Chapter 4.

3.2 Experimental Section

3.2.1 Preparation of Humic Substances

Humic and fulvic acids were extracted from a well humified organic horizon (H) of a Humic Gleysol at Unterrickenzopfen (northern Switzerland) and further purified following a procedure recommended by the International Humic Substances Society (Swift, 1996). The humic acid fraction was separated into four fractions of different nominal molecular weight (10-30kD, 30-100kD, 100-300kD and >300kD) using a hollow fiber ultrafiltration technique. The detailed extraction, purification and ultrafiltration procedures are described in Chapter 2.
3.2.2 Characterization of Humic Substances

The fulvic acid, humic acid, and the humic acid size fractions were extensively characterized by elemental analysis (C, H, N, and S), size exclusion chromatography, solid-state cross-polarization magic-angle spinning $^{13}$C nuclear magnetic resonance spectroscopy, Fourier transform infrared spectroscopy, UV-VIS spectroscopy, and fluorescence spectroscopy. The characterization results have been discussed in detail in Chapter 2, but for a comprehensive understanding, we will present a short summary of the relevant results.

3.2.3 Potentiometric Titrations

The pH and ionic strength dependent protonation behavior of fulvic and humic acid fractions was studied by potentiometric acid–base titrations. All experiments were performed in a thermostated room at 25 ± 1°C using a computer controlled titration system (Kinniburgh et al., 1995). Four burettes (Dosimat 605, Metrohm), a pH electrode (6.0123.100, Metrohm), and an AgCl reference electrode (6.0733.100, Metrohm) were connected to a personal computer by a Microlink MF18 interface (Biodata, Manchester). The burettes were filled with CO$_2$-free deionized water, 0.05 M HNO$_3$ (Titrisol, Merck), ~0.05 M NaOH, and 2 M NaN0$_3$ (Merck, p.a.). NaOH and NaN0$_3$ solutions were prepared under nitrogen atmosphere using CO$_2$-free deionized water. To keep the solutions CO$_2$-free, the burettes were connected with the atmosphere only through a glass tube filled with NaOH on granulated activated carbon (Merck, p.a.). All experiments were carried out in a 350 mL teflon vessel, which was continuously flushed with water-saturated, CO$_2$-free nitrogen gas. During titrations, the solution was stirred for two minutes after each addition of titrant. Electrode readings were recorded when the potential drift has dropped below 0.02 mV min$^{-1}$ or after a maximum equilibration time of 30 minutes. Acid and base additions were dosed to obtain steps of approximately 10 mV potential difference. The precise base concentration and electrode parameters were obtained from fitting blank titrations of NaN0$_3$ electrolyte solutions. The analysis included ion activity corrections as well as diffusion potentials. Average deviations between the fits and measurements were below 15 µM. The derived parameters such as the dissociation constant of water
and activity coefficients were in good agreement with literature values (Baes and Mesmer, 1976). The amount of adsorbed protons was determined by subtracting theoretical blank titrations from the fulvic and humic acid titrations. Typically, experiments were performed by titrating with base (forward titration) followed by backward titration with acid. During each titration cycle, the ionic strength was kept constant within 1% by adding either water or salt solution (2 M NaNO₃) to correct for changes in ionic strength due to the acid or base additions. After each cycle, the ionic strength was increased to the next higher level by adding salt solution. Several forward and backward titrations at different ionic strengths were obtained within a single experiment. Forward and backward titrations gave identical results, except for a small hysteresis (<0.12 moles kg⁻¹) near pH 7. Here, backward titrations are reported.

### 3.3 Model Description

#### 3.3.1 The NICA-Donnan Model

Modeling ion binding to humic substances requires a model that accounts for the heterogeneity of functional groups in terms of their affinity for protons or metal ions, nonspecific electrostatic interactions, and the macromolecular nature of humic substances in relation to molecular size. One approach taking these aspects into account is the NICA-Donnan model (Benedetti et al., 1996a; Benedetti et al., 1996b; Kinniburgh et al., 1999). This model is a combination of the Donnan model, which describes the electrostatic interactions between bulk solution and negatively charged polyelectrolytes such as humic and fulvic acids, and the Consistent Non Ideal Competitive Adsorption (NICA) model, which describes the specific binding of cations to humic and fulvic acids. In the Donnan model, the humic acids are considered as separate gel-like phase. The volume of the gel phase, the so-called Donnan volume, \( V_D \) varies with the ionic strength to mimic conformational changes of humic molecules. The change of the Donnan volume with ionic strength is described by the empirical relationship:

\[
\log V_D = b (1 - \log I) - 1
\]  

\[ (3.1) \]
where $V_D$ is the Donnan volume, $I$ is the ionic strength, and $b$ is a parameter related to the size of the molecules. The net negative charge of humic substances is compensated by cations in the Donnan phase. This leads to an increase of the concentration of each cation in the Donnan phase, $c_{D,i}$ compared to the concentration in the bulk solution, $c_i$.

The NICA equation describes the specific binding of ions in the Donnan phase to humic substances. A bimodal affinity distribution is commonly used to describe cation binding to humic and fulvic acids to allow for pools of high and low affinity binding sites, each with a quasi-Gaussian affinity distribution. The Henderson-Hasselbalch equation is used as local isotherm for the binding of ion $i$. For a competitive case, the basic equation for specific binding of ion $i$ is given by

$$
\theta_i = \frac{\left(\frac{K_i c_{D,i}}{c_{D,i}}\right)^{n_i}}{\sum_i \left(\frac{K_i c_{D,i}}{c_{D,i}}\right)^{n_i}} \times \frac{1 + \left[\sum_i \left(\frac{K_i c_{D,i}}{c_{D,i}}\right)^{n_i}\right]^p}{1 + \left[\sum_i \left(\frac{K_i c_{D,i}}{c_{D,i}}\right)^{n_i}\right]^p} \quad (3.2),
$$

where $\theta_i$ is the fraction of all sites (of one type) occupied by species $i$, $c_{D,i}$ is the concentration of species $i$ in the Donnan phase, $K_i$ is the median value of the affinity distribution for ion $i$, and $p$ is the width of the affinity distribution. Since $p$ is equal for all binding ions, it is considered to reflect the intrinsic chemical heterogeneity of a humic substance studied. The value of $n_i$, however, varies from ion to ion and is considered to reflect the ion specific heterogeneity or non-ideality. The amount of specifically bound ion $i$, $Q_i$ is given by

$$
Q_i = \theta_{i,1} \left(\frac{n_{i,1}}{n_H,1}\right) Q_{\text{max},1} + \theta_{i,2} \left(\frac{n_{i,2}}{n_H,2}\right) Q_{\text{max},2} \quad (3.3),
$$

where $Q_{\text{max},j}$ is the number of sites of either affinity distribution. By introducing the scaling factor $n_i/n_H$ into eq. 3.3 stoichiometric consistency was obtained (Kinniburgh et al., 1999).

The total amount of ion $i$ bound, $Q_{i,\text{tot}}$, equals the sum of specifically bound ions $i$, $Q_i$, and the amount of ions $i$ bound electrostatically in the Donnan phase

$$
Q_{i,\text{tot}} = Q_i + V_D (c_{D,i} - c_i) \quad (3.4).
$$
3.3.2 Fitting Procedure

The NICA-Donnan model contains a large number of adjustable parameters. For fitting titration data at different ionic strengths, the following eight parameters are adjustable: the Donnan volume parameter \( b \), the initial charge of the humic substance \( Q_0 \), the number of low and high affinity sites, \( Q_{\text{max}1} \) and \( Q_{\text{max}2} \), the median values of both affinity distributions for protons, \( K_{H,j} \), and the heterogeneity parameters \( n_{H1} \) and \( n_{H2} \). In the absence of competing metal ions only \( n_{H,j} \) defined by

\[
m_{H,j} = n_{H,j} p_j
\]

can be derived. In this case, the value of \( p_1 \) and \( p_2 \) is usually fixed to 1 for either affinity distribution. In the presence of competing metal ions the number of adjustable parameters increases by two, namely \( p_1 \) and \( p_2 \). In addition, four parameters have to be included for each additional metal ion, namely its affinity constants for each type of binding site \( K_{M,j} \) and the respective heterogeneity parameters \( n_{Me,j} \). To obtain a consistent set of NICA parameters for protonation and heavy metal binding, we fitted proton, copper, and lead binding data simultaneously, wherever heavy metal binding data were available (Chapter 4). In this chapter, only the results referring to proton binding are reported. Metal ion binding is discussed in Chapter 4.

When all parameters were adjusted in simultaneous fits, the values of some model parameters fitted were chemically unreasonable, e.g. the number of high affinity sites frequently drifted up to unrealistically high values (> 8 moles kg\(^{-1}\)). Reducing the number of adjustable parameters by independently estimating some model parameters may yield more reliable and stable estimates for the remaining adjustable parameters. To avoid arbitrary parameter constraints, we related two model parameters, the number of high affinity sites \( Q_{\text{max}2} \) and the Donnan volume parameter \( b \), to characterization results.

The number of high affinity sites, \( Q_{\text{max}2} \), cannot be derived reliably from acid-base titration data due to limitations of acid-base titrations above pH 10 (Ricart et al., 1996). Unfortunately, metal binding data can hardly provide additional information in this pH range, because experiments are limited by metal hydroxide precipitation. Thus, we fixed
PROTON BINDING TO HUMIC SUBSTANCES

Q\textsubscript{max2} to the calculated amount of phenolic groups determined by \textsuperscript{13}C NMR spectroscopy (Table 3.1) which gives a reasonable guess for Q\textsubscript{max2}.

The stability of the Donnan volume parameter b was studied in preliminary model fits (not shown) where the effect of various arbitrary model parameter constraints on the value of b was tested. Those values of b which were independent of the assumptions made in the preliminary fits were correlated with the results obtained from size exclusion chromatography. The derivation of the correlation equation is explained in the following.

Calibration of the size exclusion chromatography (Chapter 2) gives the relationship between the molecular weight M and the elution time t (eq. 3.6) in the following form

\[ \ln M = \alpha t + \beta \]  (3.6).

The constants \( \alpha \) and \( \beta \) depend on the column used and the experimental conditions. Eq. 6 can only be applied if the humic molecules studies are a homologous series, since elution times of size exclusion chromatography depend more on the shape and size of the substance investigated than on its molecular weight (De Nobili and Chen, 1999). Assuming a spherical geometry of humic molecules, the molecular weight M is given by

\[ M = \gamma r^3 \]  (3.7),

where \( \gamma \) is constant and \( r \) is the radius (de Wit et al., 1993a). Since the volume \( V \) of a sphere is given by

\[ V = \frac{4}{3} \pi r^3 \]  (3.8),
eqs. 3.1, 3.6, 3.7, and 3.8 can be combined resulting in a linear relationship between the Donnan volume parameter b and the elution time t in the form

\[ b = mt + n \]  (3.9).

For a given ionic strength, m and n are constant.

Based on the linear correlation (eq. 3.9), the Donnan parameter values used for the final modeling were estimated from the peak elution times of size exclusion chromatograms.
3.4 Results and Discussion

3.4.1 Characterization of Humic Substances

Selected characteristics of the fulvic acid, humic acid, and the humic acid size fractions are summarized in Table 3.1. The average apparent molecular weights were estimated from size exclusion chromatograms (Figure 3.1) based on a calibration with globular proteins.

Figure 3.1. Size distribution of fulvic acid (FA), humic acid (HA), and humic acid fractions in a 50 mM Tris-HCl buffer solution containing 100 mM KCl measured by gel chromatography. Absorbance of eluates at 280 nm is illustrated as a function of elution time. Scale of molecular weights corresponding to elution times as calibrated with globular proteins is shown on the upper edge.
### Table 3.1. Selected Characteristics of the Soil Fulvic Acid (FA), Humic Acid (HA), and the Humic Acid Size Fractions

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\bar{M}_w$</th>
<th>Elemental Composition [g kg$^{-1}$]</th>
<th>Carbon Distribution$^c$</th>
<th>Carboxylic Carbon$^d$</th>
<th>Phenolic Carbon$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[kD]</td>
<td>C</td>
<td>H</td>
<td>N</td>
<td>S</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fulvic Acid</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FA</td>
<td>10.5</td>
<td>526</td>
<td>45</td>
<td>17</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Humic Acid</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HA</td>
<td>&gt;16.8</td>
<td>552</td>
<td>53</td>
<td>33</td>
<td>4</td>
</tr>
<tr>
<td>HA$_{&gt;300,kD}$</td>
<td>&gt;63.0</td>
<td>584</td>
<td>58</td>
<td>40</td>
<td>6</td>
</tr>
<tr>
<td>HA$_{100-300,kD}$</td>
<td>24.8</td>
<td>570</td>
<td>50</td>
<td>30</td>
<td>6</td>
</tr>
<tr>
<td>HA$_{30-100,kD}$</td>
<td>15.7</td>
<td>566</td>
<td>46</td>
<td>24</td>
<td>4</td>
</tr>
<tr>
<td>HA$_{10-30,kD}$</td>
<td>8.5</td>
<td>485</td>
<td>42</td>
<td>16</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$Average apparent molecular weight determined by size exclusion chromatography.

$^b$Calculated as difference to 100 %.

$^c$Average and standard deviation of three replicated fractionations.

$^d$Calculated from $^{13}$C NMR spectra and carbon contents.

Size exclusion chromatograms show that the humic acid was successfully separated into four fractions of different molecular weight. A carbon mass balance given as carbon distribution in Table 3.1 revealed that the humic acid fractions with apparent molecular weights $>300$ kD and 30–100 kD contribute most to the total carbon of the humic acid mixture. Results of elemental analysis of the humic acid size fractions indicated that the content of carbon, hydrogen, nitrogen, and sulfur decreased with decreasing apparent molecular weight of the fractions, and correspondingly, the oxygen contents increased. The fulvic acid had lower C, H, N, and S contents as compared to the humic acid. Based on carbon contents and $^{13}$C NMR spectra, the amounts of carboxylic carbon and phenolic carbon were estimated for all fractions (Table 3.1). Carboxylic and phenolic carbon contents of the humic acid fractions tended to increase with decreasing average molecular...
weight. A comparison of humic and fulvic acid showed that the fulvic acid contained more carboxylic and slightly more phenolic carbon than the humic acid. It is noteworthy that the fulvic acid and the smallest humic acid size fraction are significantly different from each other in terms of elemental composition as well as carboxylic and phenolic carbon contents, despite similar apparent molecular weight distributions (Figure 3.1) A detailed discussion of characterization results of the fulvic acid, humic acid, and the humic acid size fractions is given in Chapter 2.

3.4.2 Proton Binding

The charging behavior the fulvic acid, humic acid, and the humic acid size fractions determined by acid-base titrations is shown in Figure 3.2. In general, the negative charge increases with increasing pH due to deprotonation of functional groups. Negative charge also increases with increasing ionic strength, as has previously been reported for other humic and fulvic acids (Milne et al., 1995; Benedetti et al., 1996a; Christensen et al., 1998; Avena et al., 1999). The effect of ionic strength on charging behavior was similar for all fractions (Figure 3.2), despite clear differences in apparent molecular weight and chemical composition (Table 3.1). This suggests that the ionic strength effect on charging behavior of humic and fulvic acids is not strongly affected by molecular size and chemical composition.

As illustrated in Figure 3.3, the negative charge on fulvic acid (FA), humic acid (HA), and humic acid size fractions at given proton and salt concentration decreases in the following order: FA \( \gg \) HA\(_{10-30 \text{ kD}} \approx \) HA\(_{30-100 \text{ kD}} \) > HA\(_{100-300 \text{ kD}} \) > HA\(_{>300 \text{ kD}} \). The sum of charge of all humic acid size fractions weighted by their respective weight contributions to the total mass of the humic acid results in a slight underestimation of the charge of the total humic acid (Figure 3.3). Taking into account that about 4 percent of the total carbon was lost during the fractionation procedure (Chapter 2), and assuming that the lost compounds exhibit a charging behavior similar to the small humic acid fractions, the charging behavior of the humic acid can be explained fairly well by the weighted sum of the size fractions (Figure 3.3).
Figure 3.2. Charging behavior of fulvic acid (FA), humic acid (HA), and humic acid size fractions as a function of proton concentration and ionic strength. NaN$_3$ was used as background electrolyte. Symbols represent data calculated from acid titrations. Lines represent fits with the NICA-Donnan model.
Figure 3.3. Charging behavior of fulvic acid (FA), humic acid (HA), and humic acid size fractions as a function of proton concentration in a 0.1 M NaNO₃ background electrolyte. Symbols represent data calculated from acid titrations. The line represents the sum of charge of the humic acid size fractions weighted by their respective contribution to the total mass of the humic acid.

The decrease of charge with decreasing size of the humic acid fractions is in agreement with $^{13}$C NMR data (Table 3.1). Phenolic and carboxylic groups are the functional groups of natural organic acids which contribute most to their proton and metal cation binding behavior (Masini et al., 1998). The sum of phenolic and carboxylic carbon of the humic acid size fractions determined by solid state $^{13}$C NMR spectroscopy decreases in the same order as their charge at any given pH and ionic strength. When comparing the charging behavior with $^{13}$C NMR data, it has to be kept in mind that not only the dissociation of phenolic and carboxylic groups contributes to the total molecule charge (Stevenson, 1994; Stumm and Morgan, 1996), and that a significant percentage of the intensity of the peak in the chemical shift range of 160 to 185 ppm in $^{13}$C NMR spectra of humic substances is due to esters (Malcolm, 1990). A comparison of acid-base titration data and $^{13}$C NMR data of humic and fulvic acids reported in the literature suggests that the intensity of the carboxylic peak in $^{13}$C NMR spectra is primarily due to carboxylic...
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groups for fulvic acids, while esters contribute to at least one third of the intensity of the carboxylic carbon peak for humic acids (Malcolm, 1990). Different percentages of esters and carboxylic groups of humic and fulvic acids may explain why the molecule charge at a certain proton and salt concentration is much higher for fulvic acid than for humic acid, even though the sum of carboxylic and phenolic carbon is only slightly higher for the fulvic acid compared to the humic acid. The fulvic and humic acids studied here exhibited a protonation behavior which is in good agreement with literature data (Milne et al., 1995; Benedetti et al., 1996a; Christensen et al., 1998; Avena et al., 1999). Despite different origin, size, and chemical composition, fulvic acids typically exhibit a charge of about 2.5 to 3.5 moles kg$^{-1}$ at pH 4 and 6.5 to 7.5 moles kg$^{-1}$ at pH 10, while humic acids exhibit a charge of about 1 to 1.5 moles kg$^{-1}$ at pH 4 and 4 to 5 moles kg$^{-1}$ at pH 10.

3.4.3 Modeling

Proton sorption data of all organic acid fractions were fitted with the NICA-Donnan model. To check the stability of the fitted Donnan parameter b, a variety of different parameter constraints was tested in preliminary model fits (not shown). In all cases, very good descriptions of proton binding data were achieved for all fractions ($R^2 \geq 0.996$), however, different sets of model parameters were obtained. This illustrates the great flexibility of the NICA-Donnan model in describing acid-base titration data. It is interesting, that despite large variations in the values of $K_{\text{H}}$ and $K_{\text{D}}$, the fitting results of the Donnan parameter b were rather constant for most humic acid size fractions. The relationship between the Donnan parameter b and the peak elution times from size exclusion chromatograms is shown in Figure 3.4. The plotted b values are averages and the error bars are standard deviations of the b values resulting from fits with different parameter constraints. Since the humic acid mixture is very polydisperse compared to all other fractions (Figure 3.1), it is not surprising that the b values for the humic acid were most variable. For the humic acid fractions HA$_{10-30 \, \text{kD}}$, HA$_{100-300 \, \text{kD}}$, and HA$_{300 \, \text{kD}}$, the values of b were nearly independent of the assumptions made for other model parameters, indi-
cated by standard deviations of 0.01 or less. The fact that the fitted b values for the humic acid fraction HA\textsubscript{30-100 kD} were nearly as low as for PUHA\textsubscript{>300 kD} cannot be explained.

Despite a well-defined size distribution of HA\textsubscript{30-100 kD}, the standard deviation of b values was significantly higher for HA\textsubscript{30-100 kD} than for all other size fractions. This suggests that the average b value is less reliable for HA\textsubscript{30-100 kD} than for all other humic acid size fractions. Thus, only the results for the humic acid fractions HA\textsubscript{10-30 kD}, HA\textsubscript{100-300 kD}, and HA\textsubscript{>300 kD} were used to correlate average Donnan volume parameters with the peak elution times from size exclusion chromatography. As a linear relationship is theoretically expected (eq. 3.9), b values were correlated with peak elution times in a linear way. Then, the Donnan parameter b was calculated from this relationship for all humic acid size fractions. These calculated Donnan parameters were used as fixed input parameters in the final modeling presented (Figure 3.2). For the humic acid mixture, the Donnan parameter was calculated from b values of the size fractions and the mass percentage of each fraction, since the calculation of b from the peak elution time obtained by size ex-

\[ b = 0.0544 \cdot t_{\text{max}} - 0.5321 \]
\[ R^2 = 0.9984 \]

Figure 3.4. Average Donnan volume parameters b for fulvic acid (FA), humic acid (HA), and humic acid size fractions as a function of peak elution times determined by size exclusion chromatography. Average b values and standard deviations were calculated from results of NICA-Donnan model fits with different constraints. Average b values with standard deviations of 0.01 or less (filled diamonds) were used for linear correlation.
clusion chromatography would lead to an overestimation of the small fractions due to the polydispersity of the humic acid (Figure 3.1). For the fulvic acid, the fitted $b$ values were slightly lower than the value calculated from the peak elution time of the size exclusion chromatogram based on the relationship obtained for the humic acid size fractions. The goodness of the fit for fulvic acid was nearly unaffected when $b$ was fixed to the calculated value. For all fits shown (Figure 3.2), the calculated Donnan parameters given in Table 3.2 were used. A comparison of Donnan parameters reported in the literature shows that the values obtained for the humic acid and the humic acid size fractions are within the range of 0.3 to 0.5 reported for other humic acids (Kinniburgh et al., 1999). For fulvic acids, $b$ values between 0.7 and 0.9 are reported (Kinniburgh et al., 1999). Since the fulvic acid studied here exhibits a relatively high average molecular weight compared to other fulvic acids investigated previously (Chapter 2), the relatively low $b$ value for the fulvic acid seems also reasonable.

**Table 3.2. NICA-Donnan Model Parameters for Proton Binding by Soil Fulvic Acid (FA), Humic Acid (HA), and Humic Acid Size Fractions**

<table>
<thead>
<tr>
<th>Sample</th>
<th>$b^a$</th>
<th>$Q_{max1}$</th>
<th>$\log K_D$</th>
<th>$m_H$</th>
<th>$Q_{max2}^b$</th>
<th>$\log K_D$</th>
<th>$m_H$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Fulvic Acid</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FA$^c$</td>
<td>0.57</td>
<td>6.0</td>
<td>2.4</td>
<td>0.44</td>
<td>2.7</td>
<td>8.7</td>
<td>0.24</td>
<td>0.9983</td>
</tr>
<tr>
<td><strong>Humic Acid</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HA$^c$</td>
<td>0.40</td>
<td>3.1</td>
<td>2.8</td>
<td>0.48</td>
<td>2.7</td>
<td>8.0</td>
<td>0.24</td>
<td>0.9978</td>
</tr>
<tr>
<td>HA$_{&gt;100\text{ kD}}$</td>
<td>0.30</td>
<td>2.1</td>
<td>2.9</td>
<td>0.52</td>
<td>2.2</td>
<td>7.3</td>
<td>0.24</td>
<td>0.9986</td>
</tr>
<tr>
<td>HA$_{100-300\text{ kD}}$</td>
<td>0.45</td>
<td>3.0</td>
<td>2.9</td>
<td>0.50</td>
<td>3.0</td>
<td>7.7</td>
<td>0.22</td>
<td>0.9988</td>
</tr>
<tr>
<td>HA$_{30-100\text{ kD}}$</td>
<td>0.51</td>
<td>3.2</td>
<td>2.8</td>
<td>0.49</td>
<td>4.0</td>
<td>9.0</td>
<td>0.17</td>
<td>0.9980</td>
</tr>
<tr>
<td>HA$_{10-30\text{ kD}}$</td>
<td>0.59</td>
<td>3.3</td>
<td>3.0</td>
<td>0.52</td>
<td>4.1</td>
<td>9.8</td>
<td>0.16</td>
<td>0.9979</td>
</tr>
</tbody>
</table>

$^a$Donnan volume parameter $b$ was fixed to the value derived from size exclusion chromatograms.

$^b$ $Q_{max2}$ was fixed to the amount of phenolic carbon derived from $^{13}$C NMR data (Table 1).

$^c$Results were obtained from simultaneous fits of proton, copper, and lead binding data.

$^d$Results were obtained by fitting proton binding data, only.
The NICA-Donnan model provided an excellent description of acid-base titration data for fulvic acid, humic acid, and humic acid size fractions ($R^2 \geq 0.9978$), when $Q_{\text{max}2}$ was fixed to the amount of phenolic carbon determined by $^{13}$C NMR spectroscopy and the Donnan volume parameter $b$ was estimated from peak elution times of size exclusion chromatograms. For all fractions studied, the NICA-Donnan model tended to slightly underestimate the ionic strength effect at high pH values. This might be caused by the fact that the influence of the molecule charge on the Donnan volume is neglected in the NICA-Donnan model (eq. 3.1). The goodness of the fits increased only unsubstantially, when $Q_{\text{max}2}$ and $b$ were fitted, as well. However, the parameter values fitted were not physically and chemically reasonable, when $Q_{\text{max}2}$ and $b$ were also adjustable. It has been reported, previously, that $Q_{\text{max}2}$ or the sum of $Q_{\text{max}1}$ and $Q_{\text{max}2}$ had to be constrained to obtain reasonable results for fulvic and humic acids with the NICA-Donnan model (Benedetti et al., 1996b; Christensen et al., 1998). To reduce the number of fitting parameters and to obtain modeling results, which are in agreement with characterization results, we propose to estimate the values of $b$ and $Q_{\text{max}2}$ from characterization results, if available. Thereby, the need of more or less arbitrary constraints can be avoided. Since the percentage of esters contributing to the carboxyl carbon peak in $^{13}$C NMR spectra widely varies for different humic substances, the number of low affinity site, $Q_{\text{max}1}$, can hardly be derived from $^{13}$C NMR spectra, as long as a large database for humic and fulvic acids is lacking.

The mean proton affinity constants of both distributions, $\tilde{K}_{H}$ and $\tilde{K}_{E}$, derived for fulvic and humic acid (Table 3.2) correspond very well to values reported for fulvic and humic acids in the literature (Benedetti et al., 1996b; Benedetti et al., 1996a; Kinniburgh et al., 1996; Milne et al., 1996; Temminghoff et al., 1997; Christensen et al., 1998; Kinniburgh et al., 1999; Pinheiro et al., 1999). For fulvic acids, literature values range from 2.2 to 3.6 and 7.5 to 9.9 for log $\tilde{K}_{H}$ and log $\tilde{K}_{E}$, respectively. For humic acids, values ranging from 3.0 to 5.1 for log $\tilde{K}_{H}$ and from 8.6 to 9.8 for log $\tilde{K}_{E}$ are reported. The ranges for log $\tilde{K}_{H}$ and log $\tilde{K}_{E}$ correspond well to proton affinity constants of mono- and polycarboxylic acids and phenols (Christensen et al., 1998). This supports the idea
that proton binding to humic and fulvic acids is mainly determined by dissociation of carboxylic and phenolic groups (Masini et al., 1998). It is noteworthy that the fitted value of \( \log K_{mH} \) is nearly constant for all humic acid size fractions. The values derived for \( \log K_{mH} \), however, steadily increase with decreasing molecular weight of the humic acid fractions. Coincidentally, the values of \( m_{Hi} \) of all fractions studied are higher than the values of \( m_{H2} \) (Table 3.2). As \( m_{H} \) is considered to reflect the apparent heterogeneity of the site type (Benedetti et al., 1996a), this indicates that the low affinity proton binding sites (carboxylic type) exhibit a smaller apparent heterogeneity than the high affinity sites (phenolic type). In the literature, values of \( m_{Hi} \) are higher than the values of \( m_{H2} \) for most fulvic and humic acids studied (Benedetti et al., 1996b; Benedetti et al., 1996a; Kinniburgh et al., 1996; Milne et al., 1996; Temminghoff et al., 1997; Christensen et al., 1998; Kinniburgh et al., 1999; Pinheiro et al., 1999). The values of \( m_{H1} \) derived for fulvic acid, humic acid, and humic acid size fractions fit very well into the range of values reported for fulvic and humic acids. The values of \( m_{H2} \) are at the lower end of the range given in the literature.

The number of low affinity sites, \( Q_{max1} \), fitted for fulvic acid is about twice as high as for humic acid (Table 3.2). A comparison of \( Q_{max1} \) derived for the humic acid size fractions reveals that \( Q_{max1} \) increases with decreasing apparent molecular weight. This is in good agreement with \(^{13}\text{C} \) NMR results (Table 3.1). Relating \( Q_{max1} \) (Table 3.2) to the amount of carboxylic carbon (Table 3.1), which gives the sum of esters and carboxylic groups (Malcolm, 1990), the contribution of carboxylic groups to the intensity of the carboxylic carbon peak in \(^{13}\text{C} \) NMR spectra can be estimated. For fulvic acid, about 75 percent of the intensity of the carboxylic peak is due to carboxylic groups, whereas for humic acid, esters and carboxylic groups contribute to the intensity more or less to the same extent (Malcolm, 1990). A comparison of the humic acid size fractions shows that the contribution of the carboxylic groups tends to decrease from about 50 to 33 percent with increasing apparent molecular weight of the fractions. Different percentages of esters and carboxylic groups of the total carboxylic carbon determined by \(^{13}\text{C} \) NMR spectroscopy, which have previously been proposed for humic and fulvic acids (Malcolm,
1990), make carboxylic carbon contents of all fractions investigated correspond very well to $Q_{\text{max1}}$.

The results of this and previous studies show that the NICA-Donnan model parameters derived for different humic and fulvic acids are within a relatively narrow range. NICA-Donnan model parameters such as $b$ and $Q_{\text{max2}}$ may be easily derived from size exclusion chromatograms or viscosimetric measurements (Avena et al., 1999) and $^{13}$C NMR spectra, respectively. To be able to estimate the amount of low affinity sites $Q_{\text{max1}}$ from $^{13}$C NMR spectra, a large base of titration and $^{13}$C NMR data will be required to calculate an average percentage of carboxylic groups contributing to the carboxylic carbon signal in $^{13}$C NMR spectra. Then, the proton binding behavior of soil and aquatic humic and fulvic acids might be predicted, using average NICA-Donnan model parameters values. This may be very useful for the application of geochemical models, since humic substances strongly affect the fate of contaminants in the environment. For an accurate prediction of the proton binding behavior of a certain humic substance, the incorporation of basic characterization results into the NICA-Donnan model would still be necessary.


CHAPTER 4
RELATING METAL BINDING BY FULVIC AND HUMIC ACIDS TO CHEMICAL COMPOSITION AND MOLECULAR SIZE

Abstract

Cu(II) and Pb(II) binding to soil fulvic acid, humic acid, and two different humic acid size fractions as a function of pH and metal concentration was investigated by metal titrations. The humic substances studied exhibited a very similar metal binding behavior despite great differences in their chemical composition. Cu(II) and Pb(II) binding strongly increased with increasing pH. In general, Cu(II) was bound more strongly to the humic substances than Pb(II). Only at extremely high metal concentrations, the amount of metal sorbed was higher for Pb(II) than for Cu(II). The molar proton-metal exchange ratios ranging from 1.0 to 1.8 for Cu(II) and from 0.6 to 1.2 for Pb(II) implied that Cu(II) is bound in monodentate and bidentate complexes while Pb(II) is predominantly bound as monodentate complexes by humic substances.

The NICA-Donnan model excellently described metal binding data when model parameters were related to characterization results. The best description of an entire data set including proton, Cu(II), and Pb(II) binding data was achieved when the entire data set was fitted simultaneously. The NICA-Donnan model parameters derived for the humic substances studied are in good agreement with previously reported values for other humic substances. Since values of NICA-Donnan model parameters for different humic
substances are within a relatively narrow range, we conclude that average model parameters may be useful in geochemical modeling.
4.1 Introduction

Humic and fulvic acids are polydisperse mixtures of natural organic polyelectrolytes containing a large number of different functional groups (Benedetti et al., 1996a). Studies on the chemical characterization of humic and fulvic acids indicate that the amounts of different functional groups vary significantly between humic substances of different origin. However, only few studies have been conducted on chemical differences between molecular size fractions of humic substances (Tombácz, 1999). In Chapter 3, it was demonstrated that differences in proton binding behavior of the fulvic acid and the humic acid size fractions isolated from a surface soil are consistent with chemical characterization results. The NICA-Donnan model excellently described proton binding data of humic acid size fractions when some model parameters were related to characterization results. Since cation binding to humic and fulvic is recognized to be mainly due to the presence functional groups such as e.g., carboxylic and phenolic groups (Masini et al., 1998), it has been hypothesized that the size of humic substances would affect trace metal complexation (Cabaniss et al., 2000). However, detailed investigations on metal ion binding to humic substances in relation to chemical composition are lacking. A better understanding of metal ion binding to humic substances is of fundamental importance in geochemical modeling of near-surface environments, where natural organic matter is always present and represents an important sorbent for metal ions. Development of a generalized database of model parameters for metal ion binding to humic substances has been hampered by the assumption that humic substances are too heterogeneous in nature. However, if the influence of chemical composition on metal binding is only weak, as proposed by Avena et al. (1999), average stability constants for different metal humate complexes derived from previous studies may be useful for predicting the fate of metal cations at contaminated sites. On the other hand, if differences in chemical composition result in large differences in metal ion binding, a generalized database would not be useful in most cases.

The objectives of this chapter are (1) to study the pH-dependent binding of Cu(II) and Pb(II) to a set of well characterized soil fulvic acid and humic acid size fractions
differing in their chemical composition, (2) to model the metal binding data using the NICA-Donnan approach, and (3) to relate model parameters to chemical characterization results for the same humic substances reported in Chapters 2 and 3.

4.2 Experimental Section

4.2.1 Preparation of Humic Substances

Humic and fulvic acids were extracted from a well humified organic horizon (H) of a Humic Gleysol near Unterrickenzopfen (northern Switzerland) and purified following a standard procedure of the International Humic Substances Society (Chapter 2). The humic acid fraction was further fractionated into four molecular size classes with nominal molecular weights of 10-30 kD, 30-100 kD, 100-300 kD and >300 kD using a hollow fiber ultrafiltration technique (Chapter 2). A detailed description of the extraction, purification and ultrafiltration procedures is given in Chapter 2. All fractions were characterized by a combination of methods including FT-IR, CP-MAS $^{13}$C NMR, and elemental analysis (Chapter 2). Characterization results are discussed in relation to proton binding in Chapter 3. It was shown that the amounts of functional groups capable of binding protons increased with decreasing average molecular weight of the humic acid size fractions. Accordingly, the negative charge of the humic acid fractions increased with decreasing average molecular weight. The results further suggested that the amounts of carboxylic and phenolic functional groups determined the charging behavior of the fulvic and humic acid fractions.

For the investigation of Cu(II) and Pb(II) binding, we confined ourselves to the fulvic acid (FA), the total humic acid (HA), and the humic acid size fractions 30-100 kD (HA$_{30-100}$ kD) and >300 kD (HA$_{>300}$ kD). The humic acid fractions 10-30 kD and 100-300 kD were omitted as these fractions contributed less than 10 percent of the total mass of soil humic acid.
4.2.2 Calibration of Ion-Selective Electrodes

Ion-selective electrodes (ISE) for Cu$^{2+}$ (Orion 9429) and Pb$^{2+}$ (Orion 9482) were calibrated by titration of metal salt solutions with an organic ligand. It has been shown that the calibration range commonly reported for sulfide-based solid-state ISEs is extendable to lower metal activities by orders of magnitude by means of titration with a strong ligand compared to simple calibrations using unbuffered solutions of different metal salt concentrations (Ruzicka and Hansen, 1973; Avdeef et al., 1983; Yuchi et al., 1983; Milne et al., 1995; Benedetti et al., 1995). Both, Cu$^{2+}$ and Pb$^{2+}$ sensitive electrodes were calibrated by titrating 50 mL of a 0.15 mM Cu(NO$_3$)$_2$ (Merck, p.a.) and Pb(NO$_3$)$_2$ (Merck, p.a.) solution, respectively, with a 1.787 mM ethylenediamine (p.a., Fluka) solution using a computer controlled titration system (Kinniburgh et al., 1995). The calibration was conducted in a thermostated room at 25 ± 1°C. The ethylenediamine solution was prepared under nitrogen gas atmosphere using CO$_2$-free deionized water. To exclude CO$_2$ during the calibration, the titration vessel was sealed and flushed with water-saturated, CO$_2$-free nitrogen gas. To maintain a constant ionic strength throughout the calibration, metal salt and ethylenediamine solutions were prepared in a 0.1 M NaN$\text{O}_3$ (Merck, p.a.) background. Prior to recording electrode readings, the metal solution was stirred for 2 min after each titrant addition. Readings of a pH electrode (6.0123.100, Metrohm) and the respective ISE were measured against an Ag/AgCl reference electrode (6.0733.100, Metrohm) placed into an electrolyte bridge containing a 0.1 M NaNO$_3$ solution which was continuously replaced by a peristaltic pump. Electrode readings were recorded when both potential drifts had dropped below 0.1 mV min$^{-1}$ or after a maximum equilibration time of 30 minutes. Solution speciation was calculated for each recorded data point using the chemical speciation program ECOSAT (Keizer and van Riemsdijk, 1998). Hydrolysis constants of aqueous metal species were taken from Baes and Mesmer (1976). Critical stability constants of ethylenediamine complexes as well as solubility constants of metal oxide and hydroxide phases were taken from Smith and Martell (1976 and 1990). The calculated free metal activities corresponded to the measured ISE voltage readings in a linear way down to pH 17 and pH 9.5, where pMe is the negative
logarithm of the free metal (Me\(^{2+}\)) activity in solution. The performance of both ISEs used was checked before and after each fulvic and humic acid titration. Fulvic and humic acid titration data were used for further analysis only if the calibration before and after each experiment did not differ significantly and if the response of the electrodes was nearly Nernstian.

### 4.2.3 Copper and Lead Binding to Fulvic and Humic Acid

The binding of Cu(II) and Pb(II) to the fulvic acid and the humic acid size fractions was measured at constant ionic strength (0.1 M NaNO\(_3\)) and constant pH values (pH 4, 6, and 8). All experiments were performed in a thermostated room at 25 ± 1°C using the same titration setup as for ISE calibration (Kinniburgh et al., 1995). The four burettes were filled with 0.05 M HNO\(_3\) (Titrisol, Merck), −0.05 M NaOH, 1 mM Cu(NO\(_3\))\(_2\) (Merck, p.a.) containing 0.1 M NaNO\(_3\) (Merck, p.a.), and 0.1 M Cu(NO\(_3\))\(_2\) (Merck, p.a.) for copper titrations. For lead binding experiments, Pb(NO\(_3\))\(_2\) (Merck, p.a.) solutions were used instead of Cu(NO\(_3\))\(_2\) solutions. NaOH and metal solutions were prepared under nitrogen gas atmosphere using CO\(_2\)-free deionized water. To keep the solutions CO\(_2\)-free, the burettes were connected with the atmosphere only through a glass tube filled with NaOH on granulated activated carbon (Merck, p.a.). All experiments were carried out in a 200 mL glass vessel, which was continuously flushed with water-saturated, CO\(_2\)-free nitrogen gas. Each experiment was started with a 100 mL solution containing 0.1 M NaNO\(_3\) and approximately 100 mg humic or fulvic acid. To ensure complete dispersion of the humic acid, the pH was first increased to pH 10 by NaOH addition and then lowered to the desired value by HNO\(_3\) addition. Before starting metal titrations, the pH was kept constant within a tolerance range of ±0.004 pH units (0.2 mV) for 12 h. This procedure was used to fully equilibrate the humic acid to pH and ionic strength conditions before metal addition was started. During metal titrations, the humic solutions were stirred for four minutes after each addition of titrant. After metal addition, the pH was automatically readjusted to the desired pH value and then kept constant for 20 min within a tolerance range of ±0.004 pH units (0.2 mV). Electrode readings were recorded.
when the potential drift was below 0.05 mV min\(^{-1}\) for the pH electrode and 0.1 mV min\(^{-1}\) for the ISE, or after a maximum equilibration time of 20 minutes. On average, readjustment of the pH value after metal addition took 60 to 75 min. Dose of metal salt additions were gradually increased during the experiments. To cover a large free metal concentration range in one titration experiment without exceeding the maximum volume of the titration vessel, a 1 mM metal solution was used for metal addition prior to a 0.1 M metal solution. Each experiment was automatically stopped at a critical mV reading of the ISE, which corresponded to a free metal activity close to the level where metal (hydr-)oxide precipitation must be expected according to chemical speciation calculations. During each experiment, the ionic strength remained constant within 3 %.

### 4.2.4 Data Analysis

For each titration data point, the amount of inorganic species in solution was calculated using the chemical speciation program ECOSAT (Keizer and van Riemsdijk, 1998). Metal hydrolysis constants and metal (hydr-)oxide solubility constants given by Baes and Mesmer (1976) and Smith and Martell (1976) were used in the calculations. For the calculation, pH, metal activity, and concentration of sodium and nitrate were used as input data. The amount of metal sorbed to the respective humic substance was calculated by subtracting the sum of aqueous metal species from the known total amount of metal in solution. Stoichiometric exchange ratios for proton and metals were calculated from the increase of metal sorption and the amount of base needed to readjust pH after metal addition. The calculation was corrected for hydroxide consumption of the bulk solution due to pH adjustment and formation of hydrolysis species of Cu(II) and Pb(II).

### 4.3 Data Modeling

Experimental Cu(II) and Pb(II) binding data were fitted using the consistent non-ideal competitive adsorption (NICA) model (Kinniburgh et al., 1999). Electrostatic interactions were accounted for using the Donnan gel approach (Benedetti et al., 1996a). The NICA-Donnan model was chosen for this study, because it has been quite successful in
describing proton and metal binding to different humic substances, taking the chemical heterogeneity and the gel structure of humic substances into consideration (Christensen et al., 1998; Kinniburgh et al., 1999; Pinheiro et al., 1999; Chapter 3 of this thesis). A brief summary of the NICA-Donnan model has been given in Chapter 3, and a complete description can be found in Kinniburgh et al. (1999).

Copper and lead sorption data were simultaneously fitted with proton binding data presented in Chapter 3. The NICA-Donnan model contains a large number of adjustable parameters. One of the objectives of this study was to reduce the number of fitting parameters by relating chemical characterization results to proton and metal binding data modeled with the NICA-Donnan model. Thus, the amount of high affinity binding sites, $Q_{\text{max,2}}$, was fixed to the amount of phenolic carbon determined by solid-state $^{13}$C NMR spectroscopy (Chapter 2). In addition, the Donnan parameter $b$ was estimated from size exclusion chromatograms (Chapter 2 and 3).

The stoichiometry of proton-metal ion exchange provides additional information about the dentism of divalent metal cation binding to humic substances. The proton-metal exchange ratio, $r_{ex}$, is given by

$$r_{ex} = -\frac{\partial H_b/\partial H}{\partial M_b/\partial H}$$

(4.1),

where $H$ is the proton concentration in solution, and $H_b$ and $M_b$ are the amount of protons and metal ions bound to the humic substances, respectively. In a system containing only two specifically sorbing ions, e.g. protons and one type of metal ion, $r_{ex}$ can be calculated from the NICA-Donnan model parameters (Kinniburgh et al., 1999):

$$r_{ex} = \frac{n_H}{n_M} \left[ \frac{\bar{K}_{HH}^{n_H}}{1+\left(\bar{K}_{HH}^{n_H} + \bar{K}_{MM}^{n_M}\right)} \right] - p \left(\frac{\bar{K}_{MM}^{n_M}}{1+\left(\bar{K}_{HH}^{n_H} + \bar{K}_{MM}^{n_M}\right)}\right)$$

(4.2),

where $M$ is the metal ion concentration in solution, $n_i$ is the ion-specific heterogeneity parameter of species $i$, $p$ is a parameter reflecting the intrinsic heterogeneity of the humic substances, and $\bar{K}_i$ is the median value of the affinity distribution constants for ion $i$. 
4.4 Results and Discussion

4.4.1 Copper Binding

Binding isotherms of Cu(II) to fulvic acid, humic acid, and two different humic acid size fractions (HA_{30-100 \text{kD}} and HA_{300 \text{kD}}) are presented in Figure 4.1. All binding isotherms plotted on a log-log scale were nearly linear at free Cu(II) concentrations below $10^{-6} \text{M}$. At high concentrations, the isotherms tended to exhibit saturation with a maximum adsorption capacity of roughly 3 moles kg$^{-1}$. Due to proton-metal ion competition for binding sites, metal ion sorption decreased with decreasing pH. In addition, the increase of charge of humic and fulvic acids with increasing pH (Chapter 3) may cause an increase of metal sorption.

*Figure 4.1.* Copper binding to fulvic acid (FA), humic acid (HA), and humic acid size fractions at pH 4, 6, and 8 in 0.1 M NaNO$_3$ plotted against the free metal ion concentration. Symbols represent data calculated from metal titrations. Lines represent fits obtained with the NICA-Donnan model (see Table 4.1 for parameter values).
A comparison of copper binding to humic acid size fractions (Figures 4.1 and 4.2) reveals that the amounts of copper bound by the two size fractions HA_{30-100 \, kD} and HA_{>300 \, kD} are nearly identical although HA_{30-100 \, kD} contains more functional groups and is more negatively charged than HA_{>300 \, kD} (Chapter 3). Only at high copper concentration (non-linear part of isotherms of log-log plots), a significantly greater amount of copper is bound by the lower molecular weight fraction. This demonstrates that the effect of differences in chemical composition of humic acid size fractions is small as long as enough sites are available to bind Cu(II) ions. At high Cu(II) concentrations, differences between the two humic acid size fractions can be observed as the smaller fraction exhibits a higher maximum binding capacity due to a greater number of functional groups.

![Graphs showing copper and lead binding](image)

**Figure 4.2.** Copper and lead binding to fulvic acid (FA), humic acid (HA), and humic acid size fractions at pH 6 in 0.1 M NaNO₃ plotted against the free metal ion concentration. Symbols represent data calculated from metal titrations.

The amounts of copper bound to fulvic and humic acid are fairly similar at pH 4. At pH 6 and 8, Cu(II) is bound more strongly by humic acid than by fulvic acid (Figures 4.1 and 4.2). At high Cu(II) concentrations, the differences between fulvic and humic acid isotherms at pH 6 and 8 become smaller. This result indicates that it is not only the total number of different functional groups that affects the copper binding behavior of humic substances. Structure, that is the linkage of the functional groups to the carbon backbone, may have a strong influence as well. Fluorescence spectra of humic and fulvic acid
suggested that a greater percentage of carboxyl groups in fulvic acid are linked to aliphatic backbones than to aromatic ring systems compared to humic acid. This means that the probability of adjacent carboxyl and phenolic groups on aromatic rings, such as in phthalic or salicylic acid, capable of forming strong complexes with Cu(II) is higher for humic acid than for fulvic acid. The fact that the isotherms of humic and fulvic acid tend to merge at high copper concentrations again may be due to the greater amount of binding sites of fulvic acid compensating for the influence of the structural differences. Overall, copper binding data of fulvic acid, humic acid, and humic acid size fractions indicate that amounts, types, and linkage of functional groups affect copper binding behavior. At high copper concentrations, the total amount of binding sites may be the most important factor.

Proton-copper exchange ratios of fulvic acid, humic acid, and humic acid size fractions derived from copper titration data range from 1.0 to 1.8. The values vary with pH and copper concentration. As an example, proton-copper exchange ratios of humic acid are shown in Figure 4.3. The range of the values implies that protons are exchanged by copper in a 1:1 and in a 2:1 stoichiometry. This suggests that copper is bound by humic

**Figure 4.3.** Molar \( \text{H}^+ / \text{Cu}^{2+} \) exchange ratio for \( \text{Cu}^{2+} \) binding to humic acid at pH 4, 6, and 8 in 0.1 M NaNO\(_3\) plotted against the free metal ion concentration. Symbols represent data calculated from metal titrations. Lines represent predictions obtained with the NICA-Donnan model.
substances as monodentate and bidentate complexes. Similar proton-copper exchange ratios have been found for a purified peat (Benedetti et al., 1995) and a soil humic acid (Robertson and Leckie, 1999).

4.4.2 Lead Binding

Binding isotherms for Pb(II) to fulvic acid, humic acid, and humic acid are shown in Figure 4.4. Again, a decrease in Pb(II) binding with decreasing pH is observed, due to competition of Pb(II) with protons for binding sites. The binding of Pb(II) to humic acid size fractions was almost identical. Even at high Pb(II) concentrations, only small differences in lead binding behavior of humic acid size fractions were observed.

Figure 4.4. Lead binding to fulvic acid (FA), humic acid (HA), and humic acid size fractions at pH 4, 6, and 8 in 0.1 M NaNO₃ plotted against the free metal ion concentration. Symbols represent data calculated from metal titrations. Lines represent fits obtained with the NICA-Donnan model (see Table 4.1 for parameter values).
In contrast to Cu(II) binding, significant differences in Pb(II) binding behavior of humic and fulvic acid were observed at pH 4, but not at pH 6 and 8 (Figures 4.2 and 4.4). A comparison of Pb(II) binding to fulvic and humic acid with other humic and fulvic acids reported in the literature reveals that the results of this study fit very well with results of previous studies (Pinheiro et al., 1994; Mota et al., 1996; Pinheiro et al., 1999). This suggests that lead binding to humic substances is nearly unaffected by differences in chemical composition of humic substances.

Compared to copper binding (Figure 4.1), lead binding is affected more strongly by variations in the metal concentration (Figure 4.4). This means the slope of the isotherms is greater for lead than for copper. Lead isotherms of all humic substances studied intersect the respective copper isotherms at high metal concentrations. This indicates that more lead than copper is bound by humic substances at very high metal ion concentrations, whereas the amount of copper sorbed exceeds the amount of lead sorbed by orders of magnitudes at low, environmentally-relevant metal ion concentrations.

Proton-lead exchange ratios of fulvic acid, humic acid, and humic acid size fractions are fairly similar. The values range from 0.6 to 1.2. As an example, proton-lead exchange ratios of the total humic acid fraction are shown in Figure 4.5. As for copper, proton-lead exchange ratios vary with pH and metal concentration. The values of the exchange ratios agree well to proton-lead exchange calculated for a peat humic acid (Kinniburgh et al., 1999). The range of proton-lead exchange ratios suggests that lead binding reactions follow a 1:1 stoichiometry, predominantly. Differences in the stoichiometry of binding reactions imply that bidentate binding sites are less important for lead binding compared to copper binding. For lead, the total number of binding sites may be the main factor controlling the binding behavior. The structural configuration of binding sites may be secondary for lead binding. This may be the reason why lead binding of humic acid size fractions is nearly not affected by chemical differences between humic acid size fractions, while copper binding is affected. The fact that proton-metal ion exchange ratios of humic substances are lower for lead than for copper may further explain differences in the aggregation of humic substances with lead and copper, respectively. Saar and Weber (1980) found that Pb-fulvate precipitated at much lower mole ratio of metal ion to fulvic
acid than Cu-fulvate. We observed the same phenomenon during our experiments. The stability of fulvic colloids is, like the stability of any other colloid, strongly influenced by the charge of the colloids (Hunter, 1986). Since one proton is exchanged by one Pb(II) ion, on average, whereas one Cu(II) ion exchanges about 1.5 protons, the negative charge of fulvate is compensated by lead binding more than by copper binding. The dependence of the aggregation behavior on the metal cation implies that the mobility of metal-organic compounds in natural systems may be quite different for different metal cations (Kretzschmar and Sticher, 1997).

\[
\text{Figure 4.5. Molar } H^+/Pb^{2+} \text{ exchange ratio for } Pb^{2+} \text{ binding to humic acid at } pH 4, 6, \text{ and } 8 \text{ in } 0.1 \text{ M } \text{NaNO}_3 \text{ plotted against the free metal ion concentration. Symbols represent data calculated from metal titrations. Lines represent predictions obtained with the NICA-Donnan model.}
\]

4.4.3 Modeling

The NICA-Donnan model provided excellent descriptions of copper (Figure 4.1) and lead binding (Figure 4.4) to fulvic acid, humic acid, and humic acid size fractions (R² ≥ 0.9978). Values of R² based on simultaneous fits of proton, copper and lead binding data are shown in Table 4.1. Only, the slope of the pH 4 lead isotherm of fulvic acid differing significantly from the slope of pH 6 and 8 isotherms was not satisfactorily described (Figure 4.4).
**Table 4.1. NICA-Donnan Model Parameters of Soil Organic Acid Fractions Studied**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fulvic Acid</th>
<th>Humic Acid</th>
<th>Humic Acid &gt;300 kD</th>
<th>Humic Acid 30-100 kD</th>
</tr>
</thead>
<tbody>
<tr>
<td>$b^{b}$</td>
<td>0.57</td>
<td>0.40</td>
<td>0.30</td>
<td>0.51</td>
</tr>
<tr>
<td>$Q_{max1}$ [mol kg$^{-1}$]</td>
<td>6.0</td>
<td>3.1</td>
<td>2.1</td>
<td>3.2</td>
</tr>
<tr>
<td>$p_l$</td>
<td>0.67</td>
<td>0.61</td>
<td>0.62</td>
<td>0.53</td>
</tr>
<tr>
<td>log $\tilde{K}_{HH}$</td>
<td>2.4</td>
<td>2.8</td>
<td>2.9</td>
<td>2.8</td>
</tr>
<tr>
<td>$n_{HH}$</td>
<td>0.65</td>
<td>0.79</td>
<td>0.84</td>
<td>0.93</td>
</tr>
<tr>
<td>log $\tilde{K}_{Ca}$</td>
<td>0.0</td>
<td>1.5</td>
<td>1.8</td>
<td>2.0</td>
</tr>
<tr>
<td>$n_{Ca}$</td>
<td>0.50</td>
<td>0.50</td>
<td>0.55</td>
<td>0.58</td>
</tr>
<tr>
<td>log $\tilde{K}_{Ph}$</td>
<td>0.6</td>
<td>1.7</td>
<td>1.8</td>
<td>1.6</td>
</tr>
<tr>
<td>$n_{Ph}$</td>
<td>0.90</td>
<td>0.90</td>
<td>0.79</td>
<td>0.74</td>
</tr>
<tr>
<td>$Q_{max2}$ [mol kg$^{-1}$]</td>
<td>2.7</td>
<td>2.7</td>
<td>2.2</td>
<td>4.0</td>
</tr>
<tr>
<td>$p_2$</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
<td>0.23</td>
</tr>
<tr>
<td>log $\tilde{K}_{H2}$</td>
<td>8.7</td>
<td>8.0</td>
<td>7.3</td>
<td>9.0</td>
</tr>
<tr>
<td>$n_{H2}$</td>
<td>0.80</td>
<td>0.80</td>
<td>0.78</td>
<td>0.74</td>
</tr>
<tr>
<td>log $\tilde{K}_{Ca2}$</td>
<td>8.6</td>
<td>8.1</td>
<td>6.8</td>
<td>8.5</td>
</tr>
<tr>
<td>$n_{Ca2}$</td>
<td>0.44</td>
<td>0.41</td>
<td>0.40</td>
<td>0.44</td>
</tr>
<tr>
<td>log $\tilde{K}_{Ph2}$</td>
<td>6.6</td>
<td>5.8</td>
<td>4.2</td>
<td>5.4</td>
</tr>
<tr>
<td>$n_{Ph2}$</td>
<td>0.70</td>
<td>0.63</td>
<td>0.86</td>
<td>0.93</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.9983</td>
<td>0.9978</td>
<td>0.9986</td>
<td>0.9980</td>
</tr>
</tbody>
</table>

---

$a$ Results were obtained from simultaneous fits of proton, copper, and lead binding data. Fixed NICA-Donnan model parameters are in italics.

$b$ Donnan parameters $b$ were fixed to values derived from size exclusion chromatograms (Chapter 3).

$c$ $Q_{max2}$ was fixed to the amount of phenolic carbon derived from $^{13}$C NMR spectra and carbon contents determined by elemental analysis (Chapter 2).
In addition, high lead loadings of fulvic acid, humic acid and humic acid size fractions at pH 8 were not fitted accurately. This mismatch of the model can not be solved by weighting data points, as the model performance at high metal loadings is strongly limited by the maximum sorption capacity which is the same for each pH value. However, one has also to keep in mind that error of high metal loading data points may be much greater than for low metal loadings (Ricart et al., 1996).

In order to relate the model parameters to chemical characterization results of the fractions investigated and to reduce the number of adjustable parameters, $Q_{\text{max}2}$ was fixed to the amount of phenolic carbon calculated from $^{13}$C NMR spectra and carbon contents. Furthermore, the Donnan volume parameter $b$ was estimated from peak elution times measured by size exclusion chromatography (Chapter 3). Adjusting $Q_{\text{max}2}$ and $b$ did not result in a substantial improvement of the model fits.

All model descriptions presented in Figure 4.1 and 4.4 are the results of simultaneous fits of proton binding data given in Chapter 3, and Cu(II) and Pb(II) binding data. For all humic substances studied, only the simultaneous fits of the entire multidimensional data sets provided excellent description of proton and metal binding. Successive data modeling, that is deriving protonation constants and number of binding sites $Q_{\text{max}1}$ and $Q_{\text{max}2}$ from acid-base titration data, keeping these values fixed and fitting then metal binding data, i.e. first copper and finally lead or vice versa, led to unsatisfactory descriptions of the entire data set. Successive data fitting resulted in $R^2$ values for metal binding of less than 0.85, whereas the simultaneous fitting procedure yielded $R^2$ values above 0.98 (Table 4.1). From our results we conclude that the number of binding sites, $Q_{\text{max}1}$ and $Q_{\text{max}2}$, as well as the median protonation constants of the NICA-Donnan model can not be reliably derived for humic substances from acid-base titration alone. Simultaneous fitting of a data set and deriving model parameters from characterization results as far as possible seems to be the most promising way to obtain good fitting results for the entire data set with physically and chemically reasonable model parameter values. Additional constraining such as relating model parameters to characterization results makes the fitting procedure more stable and the results more reliable.
Based on fits of metal binding data sets, the proton-metal ion exchange ratios were predicted for copper and lead (Eq. 4.2). Proton-metal ion exchange ratios calculated from metal titration data and predicted with the NICA-Donnan model are shown for the total humic acid fraction (Figures 4.3 and 4.5). The predicted proton-metal ion exchange ratios were in good agreement with data calculated from experimental data. This confirms that the NICA-Donnan model can reliably describe metal binding by humic substances.

The complete NICA-Donnan model parameter set for proton, copper and lead binding to fulvic acid, humic acid, and humic acid size fractions are given in Table 4.1. The values of proton binding constants have been discussed in Chapter 3. The values of $\tilde{K}_{Cu}$ and $\tilde{K}_{Pb}$, the median copper and lead affinity constants of low proton affinity sites (carboxylic type) are in the same order of magnitude for humic acid and humic acid size fractions. For fulvic acid, both values are smaller by about one order of magnitude. This seems reasonable because of the differences in linkage of carboxylic groups of fulvic and humic acid (Chapter 2). Since carboxylic groups of fulvic acid are more likely to be linked to aliphatic carbon backbones, while more carboxylic groups are linked to aromatic systems for humic acid, humic acid may contain more salicylate and phthalate like parts which are generally recognized to be predominant metal binding sites of humic substances (Murray and Lindner, 1983; Murray and Lindner, 1984). In general, the affinity of carboxylic type binding sites for copper and lead are similar for the humic substances investigated. Lead binding constants tend to be slightly higher than copper binding constants of carboxylic sites for fulvic and humic acid.

For high proton affinity sites (phenolic type), median metal binding constants are much greater for copper than for lead (Table 4.1). On average, copper binding constants exceed lead binding constants by two orders of magnitudes. In contrast to low proton affinity sites, copper and lead binding constants of high proton affinity sites are greater for fulvic acid than for humic acid. In addition, clear differences in metal binding constants of high proton affinity sites can be seen for humic acid size fractions. Values of $\tilde{K}_{Cu}$ and $\tilde{K}_{Pb}$ are much higher for HA$_{30-100}$ kD compared to HA$_{>300}$ kD.
A comparison of NICA-Donnan model parameters of fulvic and humic acid with parameters reported in the literature (Benedetti et al., 1996b; Kinniburgh et al., 1999; Pinheiro et al., 1999) shows that not only binding constant, but also heterogeneity parameters $p_i$ and $n_i$ fitted are in general agreement with values reported previously for fulvic and humic acids, respectively. However, differences between the parameter sets derived for different humic substances are significant. Thus, investigation of proton and metal binding behavior seems to be essential to obtain model parameters able to accurately describe and predict metal sorption to distinct humic substances. Incorporation of characterization results appears to be a good means for deriving physically and chemically reliable parameters. However, detailed characterization of humic substances and precise investigation of proton and metal binding is very time consuming. Since NICA-Donnan model parameters derived for different humic substances do not differ very widely, average NICA-Donnan parameter may be used to estimate metal binding of humic substances. As organic matter is a major sorbent of metal cations in natural systems, it has to be included in geochemical modeling. For the application of geochemical models to environmental systems, the availability of average model parameters may be valuable to be able to approximately predict the fate of metals at contaminated sites.
Bibliography


METAL BINDING TO HUMIC SUBSTANCES


CHAPTER 5

COMPETITIVE SORPTION OF COPPER AND LEAD AT THE OXIDE-WATER INTERFACE: IMPLICATIONS FOR SURFACE SITE DENSITY

Abstract

The competitive sorption of Cu(II) and Pb(II) to colloidal hematite was investigated as a function of pH and total metal concentration. Acid-base titrations of the hematite and single-metal sorption experiments for Cu and Pb at low to medium surface coverages were used to calibrate two surface complexation models, the triple layer model and a 2-pK basic Stern model with ion-pair formation. The surface site density was systematically varied from 2 to 20 sites per nm². Three different metal surface complexes were considered: (i) an inner-sphere metal complex, (ii) an outer sphere metal complex, and (iii) an outer-sphere complex of singly hydrolyzed metal cations. Both models provided excellent fits to acid-base titration and single-metal sorption data, regardless of the surface site density used. With increasing site density, ΔpK of the stability constants for protonation reactions increased and metal surface complexes decreased steadily. The calibrated models based on different site densities were used to predict competitive sorption effects between Cu and Pb and single-metal sorption at higher total metal concentrations. Precipitation of oversaturated solid phases was included in the calculations. Best predictions of competitive sorption effects were obtained with surface site densities between 5 and 10 sites per nm². The results demonstrate that surface site density is a key parameter if surface complexation models are exposed to more complex, multi-component environ-
ments. We conclude that competitive metal sorption experiments can be used to obtain additional information about the relevant surface site density of oxide mineral surfaces.
5.1 Introduction

Surface complexation models describing ion binding to oxide mineral surfaces have developed rapidly since the pioneering work of Stumm, Schindler, and colleagues, who formulated the constant capacitance model (Schindler and Kamber, 1968; Schindler and Gamsjäger, 1972) and the diffuse layer model (Stumm et al., 1970; Huang and Stumm, 1973). Since then, a number of variations have been proposed, including the site-binding model (Yates et al., 1974), the triple layer model (Davis et al., 1978; Davis and Leckie, 1978), the variable surface charge – variable surface potential model (Bowden et al., 1973; Bowden et al., 1977), the 1-pK basic Stern model (van Riemsdijk et al., 1986; Westall, 1986), and the generalized two-layer model (Dzombak and Morel, 1990). More recently, multi-site approaches have been developed to account for the chemical heterogeneity of oxide surfaces (Hiemstra et al., 1989a, b). All surface complexation models are based on common principles: (i) sorption of ions takes place at specific surface sites, (ii) sorption reactions are described by mass law equations, (iii) surface charge results from the sorption of ions, and (iv) electrostatic effects on ion binding are taken into account (Dzombak and Morel, 1990). Differences between the models include the formulation of surface protonation reactions (e.g., 1-pK or 2-pK approach), the placement of ions at various distances within the electric double layer (Westall, 1986; Goldberg, 1992; Hiemstra and van Riemsdijk, 1996), and their ability to explicitly account for surface heterogeneity (Hiemstra et al., 1989b).

A comparison of the performance of the most commonly used surface complexation models is given by Venema et al. (1996a). Most of the models are able to describe limited data sets of acid-base titration or ion adsorption experiments. However, the more extended a data set becomes, the more challenging it is to model. In general, complex models have greater flexibility to fit extended data sets than simple models, but they also have a larger number of parameters that need to be determined. Consistent sets of model parameters are commonly determined by least-squares fitting, as implemented in the FITEQL program (Herbelin and Westall, 1996). Model parameters determined by fitting must be considered strictly empirical and their predictive capability needs to be tested.
Only recently, theoretical approaches attempting to derive surface complexation model parameters have been proposed (Rustad et al., 1996; Sverjensky and Sahai, 1996; Sahai and Sverjensky, 1997).

The density of reactive surface sites is one of the key parameters in all surface complexation models. The site density of oxide mineral surfaces relevant to proton and ion binding is difficult to determine experimentally, and is therefore often treated as a fitting parameter as well. For hematite, site density estimates obtained with different methods such as proton titration (James and Parks, 1982), tritium exchange (Yates et al., 1977; Hsi and Langmuir, 1985), H$_2$O adsorption (Morimoto et al., 1969), and adsorption of NaOH, CH$_3$OH, CH$_2$N$_2$, and NO$_2$ (Boehm, 1971) range from 2 to 24 sites per nm$^2$. The tritium exchange method, which is acknowledged to give the most reliable results, typically yields values between 15 and 22 sites per nm$^2$ for hematite (James and Parks, 1982). Theoretically derived site densities of different crystal planes of hematite range from 2 to 16 sites per nm$^2$ (Barró and Torrent, 1996; Pivovarov, 1998).

The surface site density relevant to metal cation binding is particularly difficult to determine, since metal cations tend to form polynuclear complexes or surface precipitates at high concentrations. In this paper we demonstrate for the first time that a combined analysis of acid-base titration, single-metal sorption, and competitive metal sorption experiments can provide additional information about the surface site density relevant for metal sorption. We show that the accurate prediction of complex, multi-component systems is sensitive to the surface site density used in the model. Such information is essential if surface complexation models are to be applied to natural, multi-component environments. Our specific objectives were: (i) to model proton and metal cation (Cu(II), Pb(II)) binding to colloidal hematite, (ii) to assess the influence of surface site density on model performance, and (iii) to predict and investigate competitive sorption effects between Cu and Pb at the hematite surface. Model calculations were performed with the modified triple-layer model (Hayes and Leckie, 1987) and a 2-pK basic Stern model, both including surface ion-pair formation with the background electrolyte ions. Since the results obtained with both models were very similar, we limit most of our discussion to the basic Stern model.
5.2 Materials and Methods

5.2.1 Colloidal Hematite Particles

Submicrometer sized, uniform hematite particles of spheroidal shape were synthesized by aging a concentrated iron hydroxide gel (Sugimoto and Sakata, 1992). The gel was prepared by adding 100 mL of 6 M NaOH (Merck, p.a.) to 100 mL of 2 M FeCl₃ (Fluka, p.a.) in a Pyrex glass bottle and mixing with a propeller stirrer for 10 min. The bottle was sealed and the gel was aged for 72 h at 100 °C. After cooling to room temperature, excess salts were removed by washing the particles twice with deionized water by centrifugation and dialyzing against deionized water for 12 days. The resulting stock suspension was stored in a polyethylene bottle in the dark at 4 °C.

The morphology and size distribution of the hematite particles was characterized by transmission electron microscopy (TEM). The size distribution was determined from TEM micrographs by measuring 800 particles and calibrating against a standard diffraction grating. Powder X-ray diffraction analysis was performed for mineralogical characterization. An air-dried sample was scanned from 20-140° scattering angle at 0.04°/min on a Scintag diffractometer (XRD 2000) with a Cu-Kα line as the radiation source. The specific surface area of the hematite particles was determined from multi-point BET analysis of nitrogen gas adsorption isotherms (Gregg and Sing, 1982). Freeze dried samples were outgassed for 20 min at 180 °C. A surface area analyzer (Gemini 2360, Micromeritics) was used to record nitrogen gas adsorption isotherms at −196 °C. The BET isotherm equation was fitted to experimental data in the pressure range of 0.05 to 0.3. A cross-sectional area of 0.162 nm² per nitrogen molecule was assumed for the calculation of specific surface area.

5.2.2 Acid-Base Titration

The pH and ionic strength dependent protonation behavior of the hematite was studied by potentiometric acid–base titrations. All experiments were performed in a thermostated room at 25 ± 1 °C using an automated titration set-up (Kinniburgh et al., 1995). Four burettes (Dosimat 605, Metrohm), a glass electrode (6.0123.100, Metrohm), and an
AgCl reference electrode (6.0733.100, Metrohm) were connected to a personal computer by a Microlink MF18 interface (Biodata, Manchester). The burettes were filled with CO$_2$-free deionized water, 0.05 M HNO$_3$ (Titrisol, Merck), $\sim$0.05 M NaOH, and 2 M NaN$_3$ (Merck, p.a.). NaOH and NaN$_3$ solutions were prepared under nitrogen atmosphere using CO$_2$-free deionized water. To keep the solutions CO$_2$-free, the burettes were connected with the atmosphere only through a glass tube filled with NaOH on granulated activated carbon (Merck, p.a.). All experiments were carried out in a 250 mL Teflon vessel, which was continuously flushed with water-saturated, CO$_2$-free nitrogen gas. Before starting an experiment, solutions were acidified to remove residual CO$_2$. During titrations, the suspension was stirred for two minutes after each addition of titrant. Electrode readings were recorded when the potential drift has dropped below 0.05 mV/min or after a maximum equilibration time of 30 minutes. Acid and base additions were dosed automatically to obtain steps of approximately 10 mV potential difference. The precise base concentration and electrode parameters were obtained from fitting blank titrations of NaN$_3$ electrolyte solutions. The analysis included ion activity corrections as well as diffusion potentials. Average deviations between the fits and measurements were below 15 $\mu$M. The derived parameters such as the dissociation constant of water and activity coefficients were in good agreement with literature values (Baes and Mesmer, 1976).

The amount of adsorbed protons was determined by subtracting theoretical blank titrations from the hematite titrations. The common intersection point of titration curves at different ionic strengths represents the point of zero charge of the hematite surface (PZC). Surface charge densities were calculated on the basis of BET surface area.

Typically, experiments were performed by titrating with base (forward titration) followed by backward titration with acid. During each titration cycle, the ionic strength was kept constant within 1% by adding either water or salt solution to correct for changes in ionic strength due to the acid or base additions. After each cycle, the ionic strength was increased to the next higher level by adding salt solution. Several forward and backward titrations at different ionic strengths were obtained within a single experiment. Forward
and backward titrations gave identical results, except for a small hysteresis (<4 mC/m²) near pH 7. Here, averages of forward and backward titrations are reported.

5.2.3 Metal Sorption
The pH dependent adsorption of Cu(II) and Pb(II) to the hematite particles was investigated separately in batch experiments. The hematite concentration was 2 g/L and the total metal concentration was varied between 4 and 100 μM, resulting in maximum surface coverages (at 100% sorbed) between 0.07 and 1.7 μmoles/m². Preliminary experiments showed that ionic strength (0.003 to 0.3 M NaNO₃) has little effect on Cu or Pb sorption. Therefore, all other experiments were performed at constant background electrolyte concentration in 0.1 M NaNO₃. The pH values were adjusted by adding either HNO₃ or carbonate-free NaOH. All samples were equilibrated under nitrogen gas for 21 h at 25 °C and then centrifuged for 20 min at 6000 g (Mistral 6000). The pH-values of the supernatants were measured using combined pH-electrodes (6.0204.100, Metrohm). The supernatants were passed through 0.1-μm membrane filters (NC10, Schleicher & Schuell), acidified by adding a drop of distilled HNO₃, and analyzed for Cu or Pb by flame atomic absorption spectroscopy.

To investigate competitive sorption effects between Cu and Pb, two additional experiments were carried out in which both metals were added in similar concentrations. The first experiment was designed to yield medium surface coverages (2 g/L hematite, ~100 μM of each metal). The second experiment was conducted at higher surface coverage (1 g/L hematite, ~200 μM of each metal). The sorption of each metal in the presence of the respective competing metal was compared with single-metal experiments conducted under identical conditions.

5.2.4 Surface Complexation Modeling
Acid-base titration and metal sorption data were modeled with the modified triple-layer model (Hayes and Leckie, 1987) and a 2-pK basic Stern model, both including surface ion-pair formation with the background electrolyte ions. The two models are almost identical, except that in the basic Stern model the second layer capacitance is neglected.
and the potentials at the inner and outer Helmholtz planes are set equal (Westall, 1986). In the following, we briefly describe the 2-pK basic Stern model; the modified triple-layer model has been described in detail by Hayes and Leckie (1987).

In the 2-pK approach, proton adsorption is described by two protonation steps of “surface sites” SOH with $K_1$ (eq. 5.1) and $K_2$ (eq. 5.2)

$$\text{SOH}^+ \rightleftharpoons \text{SOH} + \text{H}^+ \quad (5.1)$$
$$\text{SOH} \rightleftharpoons \text{SO}^- + \text{H}^+ \quad (5.2).$$

As demonstrated theoretically by Borkovec (1997), a surface site SOH in 2-pK models represents an assemblage of two neighboring surface hydroxyl groups, while in the 1-pK approach introduced by Bolt and van Riemsdijk (1982) each surface site represents a single surface hydroxyl group. Both models yield identical descriptions of oxide surface charging behavior (Borkovec, 1997), but this difference must be kept in mind when discussing different approaches for estimating surface site densities.

Charged surface sites are assumed to form ion-pairs with the oppositely charged background electrolyte ions

$$\text{SO}^- + \text{Na}^+ \rightleftharpoons \text{SO} \cdot \text{Na} \quad (5.3)$$
$$\text{SOH}^+ + \text{NO}_3^- \rightleftharpoons \text{SOH}_2 \cdot \text{NO}_3 \quad (5.4).$$

Heavy metal cations ($\text{Me}^{2+}$) are allowed to form either inner-sphere (eq. 5.5), outer-sphere (eq. 5.6), or singly hydrolyzed outer-sphere complexes (eq. 5.7)

$$\text{SOH} + \text{Me}^{2+} \rightleftharpoons \text{SOMe}^+ + \text{H}^+ \quad (5.5)$$
$$\text{SOH} + \text{Me}^{2+} \rightleftharpoons \text{SO} \cdot \text{Me}^+ + \text{H}^+ \quad (5.6)$$
$$\text{SOH} + \text{Me}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{SO} \cdot \text{MeOH} + 2\text{H}^+ \quad (5.7).$$

Protons and metal cations forming inner-sphere complexes are placed into the o-plane located directly at the mineral surface, while background electrolyte ions and metal cations forming outer-sphere complexes are placed into the s-plane. Table 5.1 provides a schematic representation of the double layer and the resulting definitions of the intrinsic equilibrium constants corresponding to equations (5.1) to (5.7). Here, $F$ is the Faraday constant, $R$ the ideal gas constant, $T$ the absolute temperature, and $\psi_0$ and $\psi_s$ denote the potentials at the o-plane and s-plane, respectively.
Table 5.1. Surface complexes and definition of the corresponding intrinsic equilibrium constants for the 2-pK basic Stern model with ion-pair formation.

<table>
<thead>
<tr>
<th>o-plane</th>
<th>s-plane</th>
<th>Reaction or Type of Complex</th>
<th>Intrinsic Equilibrium Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\psi_0$</td>
<td>$\psi_s = \psi_d$</td>
<td>SOH$_2^+$ Protonation/Deprotonation of Surface</td>
<td>$K_1 = \frac{[\text{SOH}]^+ [\text{H}^+]}{[\text{SOH}]} \exp(-F\psi_d/RT)$</td>
</tr>
<tr>
<td>SO$^-$</td>
<td></td>
<td>SOH Deprotonation of Surface</td>
<td>$K_2 = \frac{[\text{SOH}]^+ [\text{H}^+]}{[\text{SOH}]} \exp(-F\psi_d/RT)$</td>
</tr>
<tr>
<td>SO$^-$</td>
<td>Na$^+$</td>
<td>Ion-pair</td>
<td>$K_{Na} = \frac{[\text{SOH}]^+ [\text{Na}^+]}{[\text{SOH}]} \exp(-F\psi_d/RT)$</td>
</tr>
<tr>
<td>SOH$_2^+$</td>
<td>NO$_3^-$</td>
<td>Ion-pair</td>
<td>$K_{NO_3} = \frac{[\text{SOH}]^+ [\text{NO}_3^-]}{[\text{SOH}]} \exp(-F\psi_d/RT)$</td>
</tr>
<tr>
<td>SOMe$^+$</td>
<td>Inner-sphere</td>
<td>$K_{\text{SOMe}} = \frac{[\text{SOMe}]^+ [\text{H}^+]}{[\text{SOMe}]} \exp(F\psi_d/RT)$</td>
<td></td>
</tr>
<tr>
<td>SO$^-$</td>
<td>Me$^{2+}$</td>
<td>Outer-sphere</td>
<td>$K_{\text{SO-Me}} = \frac{[\text{SOH}]^+ [\text{Me}^{2+}]}{[\text{SOH}]} \exp(F\psi_d/RT)$</td>
</tr>
<tr>
<td>SO$^-$</td>
<td>MeOH$^+$</td>
<td>Outer-sphere</td>
<td>$K_{\text{SO-MeOH}} = \frac{[\text{SOH}]^+ [\text{MeOH}^+]^0}{[\text{SOH}]} \exp(F\psi_d/RT)$</td>
</tr>
</tbody>
</table>

The electroneutrality condition is given by the fact that the charge at the surface $\sigma_0$ is neutralized by the charge of counter-ions in the Stern layer $\sigma_S$ and diffuse layer $\sigma_d$

$$\sigma_0 + \sigma_S + \sigma_d = 0 \quad (5.8).$$

The charge density at the surface $\sigma_0$ can be related to the Stern layer capacitance $C$ and the potentials by

$$\sigma_0 = C(\psi_0 - \psi_s) \quad (5.9).$$

The diffuse layer charge $\sigma_d$ is given by the Poisson-Boltzmann equation for a symmetrical background electrolyte with ions of charge 1 at 25 °C

$$\sigma_d = -0.1174\sqrt{T} \sinh\left(F\psi_d/2RT\right) \quad (5.10).$$

In a first step, the acid-base titration data were modeled to obtain best-fit parameters for surface protonation constants ($K_1, K_2$) and the Stern layer capacitance ($C$). To assess the influence of surface site density on model performance, the site density was systematically varied between 2 and 20 sites per nm$^2$. For each site density, a different set of best-fit parameters was obtained. Since ion-pair formation and protonation constants are
not independent, they cannot be fitted simultaneously. An increase in ion-pair formation constants results in an increase of $\Delta pK$ for the protonation steps, without significant changes in the model fit. Thus, the ion-pair formation constants were set to $\log K_{N03} = \log K_{Na} = 2.5$, a value which corresponds well with theoretical and experimental values reported in the literature (Sahai and Sverjensky, 1997).

In the second step, the single-metal sorption data at low to medium surface coverage were modeled based on the protonation parameters obtained from acid-base titrations. The site density was again varied between 2 and 20 sites per nm$^2$. The only adjustable parameters were the stability constants for metal surface complexes shown in Table 5.1.

In the third step, the models calibrated by acid-base titration and single-metal sorption data were used to predict competitive sorption of Cu and Pb at different surface coverages. Also, single-metal sorption experiments at higher total metal concentrations and lower solid concentrations were predicted, which basically represents an extrapolation outside the experimental window used for model calibration.

The program FITEQ 3.2 was used for parameter optimization (Herbelin and Westall, 1996), while forward calculations were carried out with the chemical speciation program ECOSAT 4.4 (Keizer and van Riemsdijk, 1998). Solution speciation and precipitation of oversaturated solids was taken into account, adopting stability constants from Lindsay (1979).

5.3 Results and Discussion

5.3.1 Characterization of Hematite

Analysis by X-ray diffraction and TEM showed that the particles were uniform, well-crystallized hematite particles of spheroidal shape (Figure 5.1). No impurities were detected. The surfaces appeared rough and predominant crystal planes could not be identified. The number average particle diameter was $119 \pm 29$ nm. The specific surface area of the hematite was $28.3 \pm 0.7$ m$^2$/g, as measured by the N$_2$-BET method (Schudel et al., 1997).
5.3.2 Acid-Base Titration

Acid-base titrations of the hematite particles are presented in Figure 5.2. Titration curves at different ionic strengths exhibited a common intersection point near pH 9.5, which corresponds to the (pristine) point of zero charge (PZC) of the hematite surface. This value is in the upper range of PZC values reported previously for hematite (Parks and DeBruyn, 1962; Atkinson et al., 1967; Breeuwsma and Lyklema, 1971; Gibb and Koopal, 1990). The relatively high PZC value is probably due to careful exclusion of CO₂ and agrees very well with theoretical predictions (Yoon et al., 1979).
Figure 5.2. Acid-base titration of hematite at various ionic strengths in NaNO₃ electrolyte. Lines represent best-fit description with a 2-pK basic Stern model including ion-pair formation. Surface site density was set to (a) low, (b) medium, and (c) high value.
Figure 5.3. Influence of surface site density on best-fit model parameters obtained from acid-base titrations using the 2-pK basic Stern model. (a) Protonation constants $pK_1$ and $pK_2$, (b) Stern layer capacitance, (c) relative goodness of fit (WSOS/DF).

The solid lines in Figure 5.2a-c represent best-fit descriptions of the titration data with the 2-pK basic Stern model assuming a low (2.2 nm$^{-2}$), medium (7.0 nm$^{-2}$), and high (16.6 nm$^{-2}$) surface site density. Equivalent results were obtained with the triple layer model (not shown). Saturation of the hematite surface with protons at low pH only occurs in the model calculations with very low site density (Figure 5.2a). The experimental data and all other model calculations exhibited no surface saturation in the pH range 3-11 (Figures 5.2b and 5.2c). This titration behavior is typical for oxide minerals, with the consequence that the site density cannot be determined reliably from acid-base titrations. Excellent fits to the experimental data are obtained with all site densities tested ranging from 2 to 20 sites per nm$^2$. Figure 5.3 shows that for each site density, a different set of
model parameters is obtained \( (pK_1, pK_2, C) \). As evident in Figure 5.3c, no clear minimum can be observed for the relative goodness of fit, which is presented as the weighted sum of squares per degree of freedom (WSOS/DF) (Herbelin and Westall, 1996). These results are in good agreement with a sensitivity analysis of various surface complexation models for the acid-base titration behavior of \( \alpha \)-FeOOH, \( \alpha \)-Al\(_2\)O\(_3\), and TiO\(_2\) reported by Hayes et al. (1991). The performance of all models tested (constant capacitance, double layer, and triple layer) was insensitive to surface site density variations between 2 to 20 sites per \( \text{nm}^2 \). Thus, fitting of acid-base titration data is not recommended for determining surface site densities, unless the titration curves exhibit a clear surface saturation with protons.

### 5.3.3 Single-Metal Sorption

The sorption of Cu and Pb to hematite as a function of pH and total metal concentration is shown in Figures 4 and 5, respectively. Sorption of both Cu and Pb increased sharply with increasing pH until 100 percent of the metal was adsorbed. The maximum surface coverage in these experiments (at 100% sorbed) ranged from 0.07 to 1.7 \( \mu \text{moles/m}^2 \). At given pH, Pb was sorbed more strongly to hematite than Cu, which is in accordance with previous results (McKenzie, 1980).

The solid lines in Figures 5.4 and 5.5 represent best-fit descriptions of Cu and Pb sorption obtained with the 2-\( pK \) basic Stern model assuming a low (2.2 \( \text{nm}^2 \)), medium (7.0 \( \text{nm}^2 \)), and high (16.6 \( \text{nm}^2 \)) surface site density. For each site density, the corresponding values for \( pK_1 \), \( pK_2 \), and \( C \) determined from acid-base titrations (Figure 5.3) were used in the calculations. Again, excellent fits are obtained with any site density between 2 and 20 sites per \( \text{nm}^2 \), with no clear minimum in the goodness of fit (Figure 5.6c). The intrinsic stability constants for metal surface complexes decreased with increasing site density (Figures 6a and 6b).

For both metals, different surface species dominated the calculated total amounts adsorbed in different pH regions (Figure 5.7). At very low pH, Cu and Pb were predominantly adsorbed as outer-sphere surface complex \((\text{SO-Me}^+)\). At slightly acidic to high pH, the inner-sphere surface species of both metals \((\text{SOMe}^+)\) dominated the calculated
adsorbed amounts. Hydrolyzed outer-sphere surface complexes (SO-MeOH) only occurred to some extent in model calculations for Cu at slightly acidic to neutral pH conditions.

**Figure 5.4.** Sorption of Cu to hematite at three different total Cu concentrations as a function of pH (in 0.1 M NaNO₃). The solid concentration was 2 g/L. Lines represent the best-fit description with a 2-pK basic Stern model. Protonation constants were obtained from acid-base titration data. Surface site density was set to a (a) low, (b) medium, and (c) high value. Dashed lines represent surface adsorption only.
Figure 5.5. Sorption of Pb to hematite at three different total Pb concentrations as a function of pH (in 0.1 M NaNO₃). The solid concentration was 2 g/L. Lines represent the best-fit description with a 2-pK basic Stern model. Protonation constants were obtained from acid-base titration data. Surface site density was set to a (a) low, (b) medium, and (c) high value.
Figure 5.6. Influence of surface site density on best-fit model parameters obtained from fitting single-metal sorption data with the 2-pK basic Stern model. (a) Constants for Cu surface complexes, (b) constants for Pb surface complexes, (c) relative goodness of fit (WSOS/DF) for Cu and Pb sorption.

Davis and Leckie (1978) obtained good fits of Cu and Pb sorption to amorphous iron oxyhydroxide in the pH range 4-7 using the triple layer model with an outer-sphere metal complex (SO-Me+) and a singly hydrolyzed metal complex (SO-MeOH). Venema et al. (1996a) found that cadmium (Cd) adsorption to goethite could not be satisfactorily described by a 1-pK basic Stern model assuming any of the following combinations: (i) an inner-sphere metal complex, (ii) an outer-sphere metal complex, (iii) two outer-sphere complexes of the metal ion and the singly hydrolyzed metal ion, or (iv) only an outer-
sphere complex of the hydrolyzed metal ion. Therefore, Venema (1996a) suggested that strongly sorbing metal ions should be placed between the o-plane and the s-plane.

![Diagram](image)

**Figure 5.7.** Sorption and surface speciation of (a) Cu and (b) Pb calculated with the 2-pK basic Stern model. The model was calibrated with acid-base titration and single-metal sorption data assuming a surface site density of 7.0 sites per nm². Total metal concentration was 20 µM. Total solid concentration was 2 g/L.

The results of this study demonstrate that pH dependent sorption of Cu and Pb to hematite can be described very well with a simple basic Stern model in which inner-sphere complexes are the predominant surface species of both metals. The surface speciation calculated by the models seems reasonable, however, it must be emphasized that
these results are strongly model dependent and need to be verified spectroscopically. For example, the calculated surface speciation also depended on the ion-pair formation constants used in the model. With decreasing ion-pair formation constants, the hydrolyzed surface species (SO-MeOH) became more predominant while the inner-sphere surface complexes (SOMe+) became less important.

The performance of surface complexation models can in some cases be improved by taking surface heterogeneity into account. For example, the description of Cd adsorption to goethite was improved with a multi-site model which considered the different crystal planes of goethite (Hiemstra and van Riemsdijk, 1996; Venema et al., 1996b). In our study, the multi-site approach of Hiemstra et al. (1989b) seems less promising since the dominating crystal planes of the hematite particles are not known and are difficult to determine. Hiemstra et al. (1989a) suggested describing the titration behavior of hematite that exhibits poorly developed crystal planes with a single type of surface site. Indeed, our results show that the titration behavior of hematite can be described very well with a single surface site, although the TEM images suggest the lack of well formed crystal surfaces (Figure 5.1). Our results further show that excellent descriptions of the adsorption of Cu and Pb to hematite can be obtained with a single-site 2-pK basic Stern or triple layer model.

### 5.3.4 Competitive Metal Sorption

At the lower metal concentrations (2g/L hematite; ~100 μM of each metal), no significant competitive effects between Cu and Pb were observed. The results of the competitive sorption experiment at higher metal concentrations (1g/L hematite; ~200 μM of each metal) are shown in Figure 5.8. The lines are predictions obtained with the 2-pK basic Stern model calibrated with acid-base titration and single-metal sorption data as described above. Solid lines represent the predicted total amounts removed from solution (i.e., adsorption plus precipitation of oversaturated solids), while dashed lines show the amounts of metals adsorbed as surface complexes.
Figure 5.8. Competitive sorption of Cu and Pb to hematite as a function of pH (in 0.1 M NaNO₃). The upper graphs show Cu sorption (1 g/L solids, 200 μM Cu) in the absence and presence of ~200 μM Pb. The lower graphs show Pb sorption (1 g/L solids, 200 μM Pb) in the absence and presence of ~200 μM Cu. The solid lines represent 2-pK basic Stern model predictions of metal sorption (including precipitation) based on a (a) low, (b) medium, and (c) high surface site density. Dashed lines represent surface adsorption only.
Let us first focus on the experimental results. In the macroscopic sorption data, competitive effects between Cu and Pb were only observed in a narrow pH range between pH 4.5 and 6.3. In this pH range, the presence of Pb strongly reduced adsorption of Cu, while the effect of Cu on Pb adsorption was visible, but less pronounced. This is consistent with the observation that Pb is adsorbed more strongly to hematite than Cu. At higher pH values, the macroscopic sorption data for single-metal and competitive metal sorption experiments merge, which is probably due to precipitation of Cu and Pb oxide or hydroxide phases. In batch sorption experiments, it is not possible to distinguish surface adsorption from precipitation. Thus, it appears that as soon as metal precipitation sets in, any competitive adsorption effects occurring at the hematite surface are overshadowed in macroscopic batch sorption experiments. Analysis of selected samples by XAFS spectroscopy confirmed the formation of Cu hydroxide clusters at pH>6.3, which will be discussed in a separate paper.

Let us now examine the model predictions. Figure 5.8a shows predictions based on the 2-pK basic Stern model with 2.2 sites per nm². Although the acid-base titration (Figure 5.2a) and single-metal sorption experiments (Figures 5.4a and 5.5a) were described excellently, the model fails to predict Cu and Pb sorption accurately at higher surface coverage (i.e., extrapolation) and it also tends to overestimate the competitive effects between both metals. In contrast, excellent predictions for single-metal sorption and metal competition were obtained when a site density of 7.0 sites per nm² was used (Figure 5.8b). Note that the model prediction also includes precipitation of Cu and Pb at high pH, which was confirmed by XAFS analysis and explains the apparent lack of sorption competition at high pH values. When the surface site density was increased to 16.6 sites per nm², competitive sorption effects between Cu and Pb were slightly underestimated (Figure 5.8c).

These results demonstrate that the predictive capabilities of surface complexation models cannot be inferred from good fits to simple experimental data sets, such as acid-base titration or single-metal sorption experiments. Instead, calibrated models must be challenged by exposing them to more complex situations and testing their predictive capabilities. Our results show that the surface site density is a key parameter in surface
complexation modeling and deserves careful consideration. Excellent fits of acid-base titration and single-metal sorption data were obtained with any site density between 2 and 20 sites per nm$^2$. However, the combined analysis of acid-base titration, single-metal sorption, and competitive metal sorption experiments suggests that the relevant surface site density using a 2-pK description of the hematite surface is between 5 and 10 sites per nm$^2$. Considering the fact that each SOH group in a 2-pK model represents two neighboring surface hydroxyl groups (Borkovec, 1997), this site density agrees well with values typically obtained by tritium exchange ranging from 15 to 22 sites per nm$^2$ (Yates et al., 1977; Hsi and Langmuir, 1985) and theoretically derived site densities of different crystal planes ranging from 9 to 16 sites per nm$^2$ (Barrón and Torrent, 1996).

5.4 Conclusions

The acid-base titration behavior of colloidal hematite particles and the pH dependent adsorption of Cu and Pb to hematite can be modeled very well with a 2-pK basic Stern model including ion-pair formation with background electrolyte ions. The more widely used triple layer model provides equivalent results, but no further improvements. The performance of both models when fitting simple data sets is nearly independent of the surface site density used (2 to 20 sites per nm$^2$). With increasing site density, $\Delta pK$ of the protonation constants increases and metal surface complexation constants decrease steadily, but no clear minimum in the goodness of fit is observed. Thus, no reliable information about the surface site density of hematite can be obtained from acid-base titration or single-metal sorption experiments.

Exposing the calibrated models to competitive situations in which Cu and Pb were present together revealed that the surface site density is a key parameter when predicting sorption competition in more complex, multi-component systems. Comparison of model predictions with competitive metal sorption experiments suggests that the relevant surface site density is between 5 and 10 sites per nm$^2$. The same result was obtained with the triple layer model. Lower site densities resulted in overestimation of competitive effects, while higher site densities tended to underestimate these effects. We conclude that
valuable information about the relevant surface site density of metal oxides can be obtained from competitive metal sorption experiments, but not from acid-base titrations or single-metal sorption experiments alone.
Bibliography


METAL BINDING TO MINERAL SURFACES


CHAPTER 6

INTERACTION OF COPPER AND FULVIC ACID AT THE HEMATITE-WATER INTERFACE

Abstract

The interaction of Cu(II) and soil fulvic acid at the hematite-water interface was investigated as a function of pH and ionic strength in batch sorption experiments. The sorption of fulvic acid to hematite increased with increasing pH and decreasing ionic strength. The presence of 22μM Cu(II) did not affect the sorption of fulvic acid substantially. Only at low ionic strength, the amount of fulvic acid sorbed to the hematite surface was slightly increased. However, the amount of Cu(II) sorbed to the solid phase was strongly altered in the presence of fulvic acid. Below pH 6, the sorption of Cu(II) to the solid phase is strongly increased. Above pH 6, the presence of fulvic acid resulted in a slight decrease of Cu(II) sorption. With decreasing ionic strength, both effects of the presence of fulvic acid on Cu(II) sorption to the solid phase, the increase at acidic conditions and the slight decrease at neutral to basic pH conditions were intensified.

A linear additivity approach was tested to predict Cu(II) sorption in the ternary system. Based on the pH and ionic strength dependent partitioning of fulvic acid between aqueous and solid phase, the sorption of Cu(II) to the solid phase was predicted using a 2-pK basic Stern model and the NICA-Donnan model to describe the sorption of copper to the hematite surface and the fulvic acid, respectively. Comparison of the predicted sum of the Cu(II) adsorptivities to hematite and adsorbed fulvic acid with the sorbed amount of Cu(II) measured showed that model predictions reflected the general pH and
ionic strength dependent influence of fulvic acid on Cu(II) sorption fairly well. The prediction tended to underestimate Cu(II) sorption between pH 4 and 7. We conclude that metal sorption to mineral surfaces coated with organic matter can be approximately predicted by assuming a simple additive effect of organic coatings. For accurate predictions, the interactions between organic matter and mineral surface need to be considered.
6.1 Introduction

In soils and aquatic environments, mineral surfaces are coated to a large extent with natural organic matter such as humic substances (Davis, 1982; Sposito, 1984; O'Melia, 1989). Humic substances are anionic polyelectrolytes which strongly bind to mineral surfaces by a variety of mechanisms, most importantly, specific adsorption by ligand exchange with protonated surface hydroxyl groups (Gu et al., 1994; Murphy and Zachara, 1995). Adsorbed humic substances profoundly alter the surface charge, zeta potential, and colloidal stability of oxide and clay mineral particles (Tipping and Higgins, 1982; Liang and Morgan, 1990; Kretzschmar et al., 1997).

Despite the wide-spread abundance of organic coatings in natural environments, the influence of surface bound humic substances on the adsorption of heavy metal ions to mineral particles is not fully understood (Murphy and Zachara, 1995; Harter and Naidu, 1995). On iron oxides, singly coordinated hydroxyl groups are the most reactive functional groups for surface complexation of metal ions (Davis and Kent, 1990). The same surface functional groups are involved in specific adsorption of humic substances (Murphy et al., 1994). Due to the high affinity of humic substances for such sites, some researchers have speculated that the adsorption behavior of hydroxylated mineral surfaces in natural environments may be largely controlled by adsorbed natural organic matter (Davis and Leckie, 1978; Dalang et al., 1984; Davis, 1984). In studies with different metals and sorbents, variable and sometimes contrasting effects of humic substances on metal binding have been observed (Dalang et al., 1984; Laxen, 1985; Ho and Miller, 1985; Haas and Horowitz, 1986; Xu et al., 1989; Zachara et al., 1994; Robertson, 1996; Vermeer et al., 1999; Samadfam et al., 2000). On one hand, surface bound humic substances provide additional high affinity complexing functional groups for metals and thus increase metal binding to the solid phase. On the other hand, the hydroxyl groups on the mineral surface may be partially occupied by adsorbed humic substances, which would tend to block the surface and decrease metal binding to the mineral surface itself. In addition, dissolved humic substances can form soluble metal complexes and therefore decrease metal sorption to the solid phase (Murphy and Zachara, 1995; Harter and Naidu,
1995; Christensen et al., 1998). Based on the current state of knowledge, adsorbed humic substances are expected to have the strongest increasing effect on metal sorption at low pH, where humic substances are strongly sorbed to mineral surfaces and metal sorption to mineral surfaces is low (Benjamin and Leckie, 1981).

It has not yet been resolved whether adsorbed humic substances simply contribute additional binding sites without masking the mineral surface, according to a linear additivity model (Zachara et al., 1994), or whether the interactions between mineral surface and adsorbed organic matter, and metal ions are more complex (Murphy and Zachara, 1995; Harter and Naidu, 1995). Some studies suggest that humic substances are fractionated upon adsorption to mineral surfaces (Wang et al., 1997; Vermeer and Koopal, 1998). Metal cations are observed to have a higher binding affinity to surface bound humic substances than to dissolved humic substances (Davis and Gloor, 1981; Davis, 1984; Laxen, 1985). In addition, electrostatic interactions between mineral surfaces and adsorbed humic substances have recently been proposed to affect metal binding to both, mineral surface and adsorbed humic substances (Vermeer et al., 1998; Vermeer et al., 1999). In contrast, Zachara et al. (1994) did not find any specific interactions between the sorption of cobalt and sorption of humic acid to different mineral sorbents. The effect of humic acid on cobalt binding was merely additive, that is the sorption of cobalt to the solid phase could be explained by cobalt binding to the mineral surface and adsorbed humic acid contributing additional high affinity sites without specific interactions between mineral surface and adsorbed humic acid.

The objective of this chapter is to investigate how the presence of fulvic acid affects the binding of copper to iron oxide surfaces (ternary systems) as a function of pH and ionic strength. In previous studies, copper binding to either fulvic acid or hematite (α-Fe₂O₃) has been extensively investigated (binary systems). Copper binding to fulvic acid and hematite was quantitatively described using the NICA-Donnan model (Chapter 4) and a 2-pK basic Stern model (Chapter 5), respectively. Using model parameters obtained from binary data sets, a linear additivity approach will be tested to predict metal sorption in ternary systems.
6.2 Experimental Section

6.2.1 Fulvic Acid
Fulvic acid was extracted from a well humified organic horizon (H) of a Humic Gleysol at Unterrickenzopfen (northern Switzerland) and further purified as recommended by the International Humic Substances Society (Swift, 1996). After separating the fulvic acid from the humic acid fraction, the fulvic acid was further purified by adsorption onto a DAX-8 resin (Supelco) and then transformed into the protonated form by passing it through a column filled with proton saturated cation exchange resin (Amberlite IR-120, Fluka). The purified fulvic acid was stored as aqueous solution, which had a total organic carbon concentration of 4.52 g C/L, at 3°C in the dark. The detailed description of extraction and purification procedures is given elsewhere (Chapter 2). Characterization results of the purified fulvic acid have been discussed in detail in Chapter 2.

6.2.2 Colloidal Hematite Particles
Submicrometer sized, uniform hematite particles of spheroidal shape were synthesized by aging a concentrated iron hydroxide gel (Sugimoto and Sakata, 1992). To remove excess salts, the particles were washed twice with deionized water by centrifugation and then dialyzed against deionized water for 12 days. The resulting stock suspension (64.2 g/L hematite) was stored in a polyethylene bottle in the dark at 4°C. Particle characterization by X-ray diffraction and transmission electron microscopy (TEM) revealed that the particles were well crystallized hematite particles of spheroidal shape exhibiting an average particle diameter of 119 ± 29 nm (Chapter 5). The specific surface area measured by the N$_2$-BET method was 28.3 ± 0.7 m$^2$/g. The point of zero charge of the hematite derived from acid-base titrations at different ionic strengths was near pH 9.5 (Chapter 5).

6.2.3 Sorption Experiments
The pH and ionic strength dependent sorption of Cu(II) to hematite in the presence of fulvic acid was studied with batch experiments. The experiments were conducted at three different ionic strengths (0.01, 0.03, and 0.1 M). Ionic strengths were adjusted by adding
NaNO₃ solutions to diluted hematite solutions. Then, the pH values were adjusted by addition of HNO₃ or carbonate-free NaOH. Finally, diluted fulvic acid and Cu(NO₃)₂ solutions were concurrently added. The resulting hematite concentration was 2 g/L. The resulting concentrations of fulvic acid and Cu(II) were 38 mg/L and 22 μM, respectively. All samples were equilibrated under nitrogen gas for 21 h at 25°C prior to centrifugation for 60 min at 6000 × g. Supernatants were analyzed for total organic carbon (TOC) and total copper contents. TOC measurements were performed immediately after centrifugation using a TOC analyzer (TOC-5000, Shimadzu). Total copper concentrations were determined by flame atomic absorption spectroscopy (AAS). For AAS measurements, subsamples of supernatants were acidified by adding a drop of distilled HNO₃.

In addition to the ternary experiments, the adsorption of fulvic acid to hematite in the absence of Cu(II) and the adsorption of Cu(II) to hematite in the absence of fulvic acid was measured using the same batch technique. Cu(II) binding to fulvic acid alone has been investigated in Chapter 4.

6.2.4 Data Analysis

The sorption of Cu(II) to hematite and fulvic acid was calculated with a 2-pK basic Stern model and the NICA-Donnan model, respectively. For the basic Stern model, model parameters reported for a surface site density of 7 sites/nm² were used (Chapter 5). For the NICA-Donnan model, model parameters given in Chapter 4 were taken. Formation of inorganic aqueous complexes and possible precipitation of metal (hydr-)oxide phases was included into the calculations using stability constants given by Baes and Mesmer (1976) and Smith and Martell (1976). The amount of Cu(II) sorbed to the fulvic acid coated hematite particles was predicted based on the linear additivity assumption. This assumption implies that adsorbed fulvic acid merely adds additional binding sites to the solid phase, without blocking a significant portion of binding sites at the mineral surface itself. It is further assumed that the fulvic acid is not fractionated with respect to its affinity for Cu(II) binding, that is, adsorbed and dissolved humic acid are assumed to have the same affinity for Cu(II) binding. Furthermore, the linear additivity approach implies that elec-
trostatic interactions between fulvic acid and Cu(II) at the hematite surface can be neglected.

6.3 Results and Discussion
6.3.1 Binding of Fulvic Acid to Hematite

The influence of pH and ionic strength on the sorption of fulvic acid to hematite is shown in Figure 6.1a. Sorption of fulvic acid decreased with increasing pH. At low pH, the sorption of fulvic acid was nearly independent of ionic strength, while at high pH, a clear increase in fulvic acid sorption with increasing ionic strength was observed. Even at pH values above the point of zero charge (PZC) of the hematite particles (pH 9.5) a significant amount of fulvic acid was sorbed. This suggests that fulvic acid is specifically sorbed to the hematite surface as proposed previously (Gu et al., 1994; Murphy et al., 1994). In addition, electrostatic interaction may affect the sorption of fulvic acid to the hematite surface. At low pH, the hematite surface is highly positively charged (Chapter 5), whereas fulvic acid molecules are slightly negatively charged (Chapter 3). Thus, strong electrostatic attraction between the fulvic acid molecules and the hematite surfaces is expected at low pH. This may explain the increase of fulvic acid sorption with decreasing pH (Figure 6.1a). Furthermore, the macromolecular conformation of fulvic acid may also play an important role upon fulvic acid adsorption (Lyklema, 1985; Lyklema, 1995). At high pH and low ionic strength, natural organic polyelectrolytes such as fulvic acids have an expanded conformation (Clapp and Hayes, 1999; Swift, 1999). With increasing ionic strength or decreasing pH, the configuration of the polyelectrolytes becomes more and more coiled (Clapp and Hayes, 1999; Swift, 1999). This means that the amount of fulvic acid adsorbed to the mineral surfaces is least at high pH and low ionic strength, which is consistent with our measurements (Figure 6.1a). A further explanation for the ionic strength dependence of fulvic acid adsorption may be electrostatic blocking effects. Mineral surfaces may be blocked by adsorbed fulvic acid due to electrostatic interactions between fulvic acid molecules. Since the charge of the fulvic acid molecules is screened by the background electrolyte (Stumm and Morgan, 1996), the concentration of
the background electrolyte is expected to affect these blocking effects. The mineral surfaces may be blocked at low ionic strength to a larger extent than at high ionic strength (Semmler et al., 1998).

Figure 6.1. Fulvic acid binding to hematite as a function of pH and NaN_3 concentration (a) in the absence of copper and (b) in the presence of 22 μM copper. Symbols represent measured data. Lines represent polynomial fits of fulvic acid adsorption in the absence of copper. Total concentrations of fulvic acid and hematite were 38 mg/L and 2 g/L, respectively.
Compared to previous studies with other humic or fulvic acids and minerals, the observed sorption behavior of fulvic acid is rather typical (Ho and Miller, 1985; Murphy and Zachara, 1995; Kretzschmar et al., 1997; Wang et al., 1997; Vermeer et al., 1998; Au et al., 1999; Lenhart and Honeyman, 1999; Elfarissi and Pefferkorn, 2000). Thus, the fulvic acid-hematite system can be regarded as a suitable model system for other organic polyelectrolyte-oxide mineral systems. The advantage of using fulvic acid instead of humic acid is that even at low pH, dissolved fulvic acid does not form aggregates that are separated from the aqueous phase by centrifugation. This enables a clear discrimination between sorbed and dissolved polyelectrolyte.

The presence of 22 μM Cu(II) in the ternary systems had almost no effect on the sorption of fulvic acid. A comparison of fulvic acid sorption in the absence and presence of Cu(II) is shown in Figure 6.1. The lines in Figure 6.1b are polynomial fits of the data in Figure 6.1a and serve for better comparison. Only at the lowest ionic strength (0.01 M) and at neutral to basic pH, fulvic acid sorption was slightly increased in the presence of Cu(II). The small but significant effect of Cu(II) on fulvic acid adsorption under these conditions may be due to changes in the electrostatic interactions between fulvic acid and hematite, since Cu(II) binding adds positive charge to the hematite surface while decreasing the negative charge of fulvic acid molecules.

6.3.2 Influence of Fulvic Acid on Copper Sorption

The sorption of Cu(II) to the solid phase in the absence and in the presence of fulvic acid is shown in Figure 6.2. The Cu(II) sorption is strongly affected by the presence of fulvic acid. Below pH 6, Cu(II) sorption to the solid phase is strongly increased by the presence of fulvic acid. At neutral to basic pH conditions, however, the amount of Cu(II) sorbed to the solid phase is slightly decreased in the presence of fulvic acid. Qualitatively, the effects of fulvic acid on Cu(II) sorption can be explained by the sorption behavior of fulvic acid and Cu(II). Since the fulvic acid strongly binds to the hematite particles at low pH (Figure 6.1), and is additionally able to bind Cu(II) strongly even at acidic conditions (Chapter 4), the sorption of Cu(II) to the solid phase was increased at low pH as a consequence of Cu(II) binding to surface-bound fulvic acid. In the neutral and basic pH
range, however, sorption of fulvic acid to the hematite particles was much lower (Figure 6.1). In addition, fulvic acid binds Cu(II) very strongly at high pH (Chapter 4). Thus, the formation of dissolved Cu(II)-fulvic acid complexes may explain the decrease of Cu(II) sorption in the presence of fulvic acid at high pH values. The fact that Cu(II) sorption was only slightly decreased by the presence of fulvic acid in the neutral and basic pH range suggests that the Cu(II) binding affinity is higher for hematite than for fulvic acid in the neutral and basic pH range.

**Figure 6.2.** Copper sorption to hematite coated with fulvic acid as a function of pH in 0.1 M NaNO₃. Total Cu(II) concentration was 22 μM. Total concentrations of fulvic acid and hematite were 38 mg/L and 2 g/L, respectively. Symbols represent measured data. Filled symbols refer to the Cu(II)-fulvic acid-hematite system. Open symbols represent copper sorption data in the absence of fulvic acid. The solid line represents the prediction of copper sorption to the fulvic acid-hematite complex based on an additive combination of a 2-pK basic Stern model for copper sorption to the hematite surface and the NICA-Donnan model for copper binding to fulvic acid. The dashed line represents the fraction of copper bound to adsorbed fulvic and the dash-dotted line represents the fraction of copper sorbed to the hematite surface. The description of copper sorption to hematite in the absence of fulvic acid with a 2-pK basic Stern model is represented by the dotted line.
The effect of ionic strength variations on the pH dependent sorption of Cu(II) is shown in Figure 6.3. In the binary system containing only Cu(II) and hematite, a decrease of ionic strength resulted in a slight increase of Cu(II) sorption to hematite, which is described fairly well with a 2-pK basic Stern model (Figure 6.3a). The weak influence of ionic strength on Cu(II) sorption to hematite implies that Cu(II) is bound to the hematite surface predominantly as inner-sphere complex. This in accordance with modeling results reported previously for the Cu(II)-hematite system (Chapter 5). In the presence of fulvic acid (ternary system), the effect of ionic strength variations is clearly different to the binary system (Figure 6.3b). At pH values below 4.7, a decrease of ionic strength resulted in a slight increase of Cu(II) sorption to the solid phase. Above pH 4.7, Cu(II) sorption decreased with decreasing ionic strength. The differences of ionic strength effects between low and high pH range in the presence of fulvic acid may be explained by the ionic strength dependence of fulvic acid adsorption to hematite (Figure 6.1) and the influence of ionic strength on metal binding to humic substances (Robertson, 1996). Let us first focus on the low pH range. On one hand, the fulvic acid strongly sorbed to the hematite surface below pH 4.7. In this pH range, the fulvic acid adsorption appeared to be nearly independent of ionic strength variations (Figure 6.1). On the other hand, metal cation binding to humic substances generally increases with decreasing ionic strength (Robertson, 1996). Since Cu(II) sorption to the solid phase may mainly result from Cu(II) binding to surface-bound fulvic acid at acidic pH conditions, an increase of Cu(II) sorption with decreasing ionic strength is expected at low pH values for ternary systems. Let us now focus on the pH range above 4.7. In this pH range, the sorption of fulvic acid decreases with decreasing ionic strength (Figure 6.1). Since the dissolved fulvic acid fraction competes with the adsorbed fulvic acid fraction and the hematite surface for Cu(II) binding, a decrease of Cu(II) sorption with decreasing ionic strength is expected for pH values above 4.7. In summary, the results from the ternary experiments (Cu(II)-fulvic acid-hematite system) are in good qualitative agreement with observations from binary systems.

Furthermore, the influence of fulvic acid on the Cu(II) sorption behavior is in agreement with observations reported for other metal-humic-mineral systems and seems
to reflect a general trend (Davis, 1984; Zachara et al., 1994; Murphy and Zachara, 1995; Taylor and Theng, 1995; Takahashi et al., 1999). This suggests that the fate of metals in soil and aquatic environments is strongly affected by humic substances. Since the metal binding affinity of minerals is generally low at low pH, the presence of adsorbed humic substances may decrease the mobility of metal cations at low pH. On the other hand, it has to be kept in mind that dissolved or suspended humic substances may enhance metal mobility at neutral to basic pH conditions (Davis, 1984).

**Figure 6.3.** Copper sorption to hematite as a function of pH and NaNO₃ concentration (a) in the absence of fulvic acid and (b) in the presence of 38 mg/L fulvic acid. Total concentrations of copper and hematite were 22 µM and 2 g/L, respectively. Symbols represent measured data. The solid lines represent (a) the description of copper sorption to hematite in the absence of fulvic acid with a 2-pK basic Stern model and (b) predictions of copper sorption to the fulvic acid hematite complex based on an additive combination of a 2-pK basic Stern model for copper sorption to the hematite surface and the NICA-Donnan model for copper binding to fulvic acid.
6.3.3 Prediction of Copper Sorption in the Presence of Fulvic Acid

For the prediction of Cu(II) sorption in the presence of fulvic acid, a linear additivity approach was tested to reveal how important specific interactions between Cu(II) and fulvic acid at the hematite surface are. Let us first focus on the sorption of fulvic acid to the hematite surface. As shown in Figure 6.1b, the pH and ionic strength dependent sorption of fulvic acid to hematite in the presence of Cu(II) is fairly well described by the fits obtained from sorption data in the absence of Cu(II) (Figure 6.1a). Only at high pH values and low ionic strength, the sorption of fulvic acid in the presence of Cu(II) is slightly underestimated. This result supports the assumption of the additivity approach that electrostatic interactions between fulvic acid and Cu(II) at the hematite surface can be neglected.

Let us now focus on the calculated partitioning of Cu(II) between hematite surface and adsorbed fulvic acid shown in Figure 6.2. Compared to the calculated amount of Cu(II) sorbed to hematite in the absence of fulvic acid (dotted line), a strong increase of Cu(II) sorption to the solid phase below pH 5.5 and a slight decrease at pH values above pH 5.5 is predicted for the system containing fulvic acid (straight line). The strong increase of the predicted amount of Cu(II) sorbed to the solid phase below pH 5.5 is attributed to Cu(II) binding to adsorbed fulvic acid (dashed line). At pH values above 5.5, Cu(II) sorption to the solid phase is mainly attributed to surface complexation of Cu(II) at the hematite surface itself (dash-dotted line). With increasing pH, surface complexation reactions at the hematite-water interface dominate the sorption of Cu(II) to an increasing extent. Considering the binding interactions observed in binary systems (Cu(II)-fulvic acid system (Chapter 4), Cu(II)-hematite system (Chapter 5), and fulvic acid-hematite system), the partitioning of Cu(II) between hematite surface and adsorbed fulvic acid predicted by the linear additivity approach seems reasonable.

A comparison of model predictions with the measured amounts of Cu(II) sorbed to the solid phase reveals that the additivity model predictions reflect the general trend that the presence of fulvic acid increases Cu(II) sorption at low pH and decreases Cu(II) sorption at neutral to basic pH values (Figure 6.2). Even the predicted effect of ionic strength variations on the pH dependent Cu(II) sorption, follows the trend observed in
ternary sorption experiments (Figure 6.3b). However, the predictions obtained with the linear additivity approach tend to underestimate the amount of copper sorbed to the solid phase (Figure 6.3b). The mismatch between measurements and predictions exhibits a maximum between pH 4.5 and 5.5. In pH ranges where the sorption of Cu(II) to the solid phase is clearly dominated either by binding to adsorbed fulvic acid (very low pH) or by complexation at the hematite surface (high pH), the predictions are fairly accurate.

To find a reasonable explanation for the non-additive sorption behavior of Cu(II) between pH 4 and 7 in the ternary system, let us reconsider the assumptions of the linear additivity approach. In this approach, electrostatic interactions at the mineral-water interface are neglected. As shown in Figure 6.1, the electrostatic interactions between Cu(II) and fulvic acid at the hematite-water interface may be negligible for the prediction of fulvic acid sorption to hematite in the presence of Cu(II). For the prediction of Cu(II) sorption, however, electrostatic effects may be important. The negative electrostatic field of the adsorbed fulvic acid may interact with the electrostatic field of the hematite surface (Vermeer and Koopal, 1999). At pH values below the PZC of the hematite particles, the positive electrostatic field of the hematite surface may be lowered by the negatively charged fulvic acid in the vicinity of the hematite surface. Concurrently, the negative electrostatic field of the adsorbed fulvic acid will be affected by positively charged hematite surface. Due to this mutual interaction of hematite surface and adsorbed fulvic acid, additional positively charged ions such as protons and Cu$^{2+}$ may be bound to the hematite surface. On the other hand, slightly less cations may be bound to the adsorbed fulvic acid by electrostatic attraction. Depending on the Cu(II) affinity of the hematite surface and the fulvic acid and the respective change of the electrostatic fields, the electrostatic interaction between adsorbed fulvic acid and hematite surface may either decrease of increase the amount of Cu(II) sorbed compared to the predictions with the linear additivity approach (Vermeer et al., 1999). Since the affinity of the hematite surface for Cu(II) binding is very high and Cu(II) binding to fulvic acid is rather due to complexation reactions than due to electrostatic binding, electrostatic interactions between adsorbed fulvic acid and hematite surface are supposed to result in an increase of Cu(II) sorption.
A further assumption of the linear additivity approach is that fulvic acid is not fractionated with respect to its Cu(II) binding affinity upon adsorption. Wang et al. (1997) found that the fraction of fulvic acid sorbed to goethite was larger in size than the fraction not sorbed. From investigation of differences between the fraction of a fulvic acid adsorbed to goethite and the fraction not sorbed Wang et al. (1997) concluded that acidity and aromaticity, factors which were linked to molecular weight distribution, controlled the fractionation behavior of the fulvic acid upon adsorption. Similar results have been reported for the sorption of dissolved organic compounds to alumina by Davis and Gloor (1981). Copper binding experiments to a size-fractionated humic acid revealed that the small size-fraction which contained more reactive functional groups compared to the large size-fraction tended to bind more copper than the large size-fraction (Chapter 4). These observations suggest that fulvic acid might be fractionated with respect to molecular size. Furthermore, chemical properties of size fractions are likely to vary with the molecular size. As the sorption of humic substances to mineral surfaces as well as the complexation of metal cations by humic substances are supposed to be largely controlled by the type and amount of reactive functional groups, it has been hypothesized that adsorbed humic substances exhibit a slightly higher binding affinity for metals than the dissolved fraction (Davis and Gloor, 1981; Davis, 1984; Laxen, 1985). This suggests that neglecting a fractionation of fulvic acid with respect to its Cu(II) binding affinity may be a further reason for the underestimation of Cu(II) sorption with the linear additivity approach.

Compared to attempts to predict metal sorption in ternary systems with a linear additivity approach reported previously (Robertson, 1996; Vermeer et al., 1999), the deviations between data and model predictions reported here are relatively small and limited to the pH range between 4 and 7. Unfortunately, pH values in soils mostly range from 4 to 7. Thus, we propose that predictions of metal cation sorption in aquatic and soil environments with models that do not account for interactions between sorbing organic matter and mineral surface can only provide a rough estimate of metal sorption. But still, for a good estimation of metal fate in ternary systems capable of providing valuable information for risk assessment, outstanding descriptions of binary data sets are
required. For a precise prediction of metal-humic interactions at the mineral-water interface, a more complex approach is needed than the simplifying additivity approach to account for the complexity of mutual interactions. To improve model predictions, we suggest that the two kinds of model modification discussed above, electrostatic interaction between adsorbed polyelectrolyte and mineral surface and fractionation of polydisperse polyelectrolytes upon adsorption, need to be included. It will remain a challenge for the future to keep a model accounting for all these effects as simple as possible in order to make it easy to apply without requiring arbitrary assumptions for model parameters or many time consuming experiments for parameter calibration.
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July 2000, Iso Christl
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