

Effect of Ca on the Solubility and Molecular Size Distribution of DOC and Cu Binding in Soil Solution Samples

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Flocculation of soil-derived dissolved organic carbon (DOC) was used as a tool to study the molecular size distribution of DOC and the native amount of copper bound to different size fractions. DOC was extracted from arable soils that had received varying amounts of animal manure, inorganic fertilizer, or CuSO_4 . Addition of calcium to the DOC extracts resulted in flocculation of up to 50% of the DOC originally present in the samples. High performance size exclusion chromatography (HPSEC) analysis revealed that the DOC removed mainly consisted of high molecular weight (HMW) organic acids. Low molecular weight (LMW) substances remained soluble even at high calcium concentrations. Copper solution concentrations decreased almost linearly with decreasing DOC levels, suggesting that copper remained bound to the flocculated material despite increasing calcium concentrations. The amounts of copper bound to both LMW and HMW components depended on the copper content of the soil and were described by two Langmuir sorption equations. Maximum binding capacities varied between 250 μmol of copper g^{-1} of C for HMW components and 450 μmol of copper g^{-1} of C for LMW components, but binding affinities were higher for HMW components. The Langmuir equation described the measured copper solution concentrations from the batch experiments very well ($R^2 = 0.994$). The observation that up to 50% of the DOC in solution was not removed by calcium indicates that a significant part of copper is potentially highly mobile in soils and can be prone to DOC-facilitated transport.

Introduction

During the last few decades, the average trace metal content of soils has increased as a result of increased input from industry, traffic, and agriculture (1). In the Netherlands, especially, animal manure has been an important source of copper (2). In order to predict metal solubility and transport in relation to the increased soil metal content, adsorption and complexation processes have been studied in great detail. In most laboratory studies, metal solubility is controlled by pH-dependent adsorption with cation sorption diminishing at low pH (3, 4). Apart from adsorption, also, complexation in solution strongly affects solubility and speciation. Metals that form stable complexes with DOC (e.g., Cu and Pb) are

mobilized in the presence of DOC (5–7): total dissolved copper concentrations in both terrestrial and aquatic environments were positively correlated with DOC (8–12).

Processes that control the DOC solution concentration, therefore, are of utmost importance with respect to both metal solubility and speciation in soils. However, DOC in soils contains a wide range of organic substances as well as reactive groups, and copper binding to different components varies according to specific surface charge or the presence of specific binding sites. Aside from differences in the chemical composition, humic acids (HAs) and fulvic acids (FAs) differ in binding capacity and molecular size. FA proton binding capacities are higher than HA binding capacities (13) but HAs have a larger molecular weight than FAs (14). The chemical differences between low molecular weight (LMW) FAs and high molecular weight (HMW) HAs make that HMW HAs are less soluble than LMW FAs (14). Soil parameters that decrease the solubility of HMW HAs as a result of flocculation are pH and the concentration of polyvalent cations (15–17) like calcium (in soils containing CaCO_3) and aluminum (e.g., in acid forest soils).

In contrast to the well-known phenomenon of proton and/or aluminum-induced precipitation of HAs below pH 4 and the removal of DOC from wastewater and river water by polyvalent ions (15–17), little is known about the potential removal of DOC and the trace metals attached to it, from solution at near neutral pH by calcium in soils. Results from a previous study showed that calcium reduced both DOC and copper solution concentrations, probably as a result of ternary complex formation in combination with flocculation (18). Although it was impossible to distinguish between flocculation and ternary sorption processes, the results still revealed that DOC removal by calcium was quantitatively more important for copper solubility than calcium-copper exchange.

In order to study the effect of calcium on the solubility of DOC without the interference of adsorption processes onto the solid matrix, the study described here was performed with solutions containing DOC from various soils without soil material being present. Although calcium could potentially increase the free copper solution activity (Cu^{2+}) as a result of calcium-copper exchange on DOC, it is believed that the importance of direct ion exchange is limited due to the large differences in binding affinity between calcium and copper for DOC (19).

The goals of this study are (i) to study the effect of calcium addition on the solubility of DOC in soil extracts from nonpolluted and copper-polluted soils, (ii) to determine which molecular size fraction of the DOC is affected by flocculation (application of high performance size exclusion chromatography), (iii) to measure the amounts of copper bound to both HMW HAs and LMW FAs, and (iv) to develop a model describing the binding of copper to DOC on a macromolecular basis that can be used to predict copper solution concentrations under field conditions.

Material and Methods

Site Description. The soils used in this study originate from two experimental plots, one located in Haren and one in Wageningen (the Netherlands). Both soils are sandy soils [spodosols (20)] with a low clay content and have been used for arable crop production for several decades. General soil characteristics are listed in Table 1. The Haren samples originate from an experimental field at the Research Institute for Agrobiology and Soil Fertility in Haren. The experimental plots were amended with different amounts of animal manure

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TABLE 1. General Soil Characteristics

site	CEC (cmol _c kg ⁻¹)	organic matter (%)	particle size distribution (%)			pH KCl soil
			<2 μm	2–50 μm	>50 μm	
Wageningen ^a	5.6	3.8	3.0	10.0	87.0	4.7
Haren	8.8	3.9	2.7	15.5	81.8	4.7–5.5 ^b

^a Characteristics of the nonamended plots (0 Cu, pH 6 plots). ^b 4.7, manured plot; 5.5, fertilizer plot.

(H16 sample) or inorganic fertilizer (H11 sample) from 1971 to 1982. The H16 plot received an annual dose of 160 Mg ha⁻¹ whereas the H11 plot received the equivalent of that amount (with respect to N, P, and K) using inorganic fertilizer. The soils have been used for conventional cropping in a crop rotation of forage maize, potatoes, and sugar beets. A detailed description of the experimental conditions and soil treatments is given elsewhere (21, 22).

The Wageningen samples originate from an experimental field of the Agricultural University. In 1982, the experimental field (approx. 1 ha) was divided into 128 plots, 6 × 11 m each. Four copper levels were established by applying CuSO₄·5H₂O at rates of 0, 250, 500, and 750 kg Cu ha⁻¹ (23). Simultaneously, soil pH was adjusted to values ranging from 4 to 6 using either CaCO₃ or elemental sulfur. Lime and sulfur applications were repeated every 6 years to maintain soil pH at the desired level. Common agricultural practice was maintained from 1978 onward and continued during the experiment; the soil has been used in a maize, wheat, potato rotation. In this study, only samples from the 0, 250, and 750 kg Cu ha⁻¹ plots were used (referred to as W0, W250, and W750).

Soil Sampling and Soil Treatment. Sampling at the Wageningen and Haren site was carried out in spring 1994 just before lime and sulfur application (at the Wageningen plots). From both the Haren and Wageningen plots, soil samples were obtained from the topsoil (0–20 cm), each consisting of 15 separate subsamples. The soil was sieved on a 2 mm sieve after drying for 24 h at room temperature, and was stored at 10 °C in a dark room in plastic containers until further use. In case of the Wageningen soil, care was taken to avoid cross-contamination of copper-treated and noncontaminated soil samples.

DOC Extraction. The DOC used in this study was obtained by a NaNO₃ extraction at pH 7.5 as described below. Strictly speaking, the soluble carbon thus obtained is not entirely equal to real DOC as obtained in lysimeters, by centrifugation or present in aquatic environments. The DOC used here probably represents the potentially soluble part of the soil organic matter fraction under the conditions imposed here (pH 7.5). Nevertheless we feel confident that the soluble carbon obtained in our extracts matches DOC in soil solutions more closely than the classically prepared humic and fulvic acids that are obtained by alkaline extractions at pH 14. In the remainder of the text, we will, therefore, use the term DOC for the soluble carbon extracted, unless we compare our "DOC" with DOC from soils (use of quotation marks).

Forty grams of soil and 130 mL of 0.05 M NaNO₃ was equilibrated on a table-top shaker at a speed of 50 rpm. The pH of the solution was slowly raised from the initial soil pH (approx. 5.0) to 7.5 using small amounts of 0.1 M NaOH to promote DOC desorption from the soil. After 20 h, the soil-solution mixture was centrifuged for 15 min (3000g) to separate the soil from solution. After decantation, the supernatant was centrifuged again (18000g) for 15 min to remove silt and coarse clay particles. After centrifugation,

all solutions were filtered through 0.4 μm HTP Millipore filters. To prevent microbial decay of the DOC, small amounts of a 2% NaN₃ solution were added to the stock solutions. Final DOC concentrations ranged from approx. 370 mg of C L⁻¹ in the H11 and Wageningen soils (inorganic fertilizer) to 490 mg of C L⁻¹ in the H16 soil (organic manure). The pH of all stock solutions was brought to 6.0 ± 0.1 using small amounts of 0.1 N HNO₃. Working solutions were obtained by dilution of the stock solution with 0.05 N NaNO₃. All stock solutions and working standards were stored at 4 °C until further use; all experiments were carried out within 1 week after extraction of the DOC. Repeated analysis of the organic carbon concentration in the stock solution after several days indicated that no mineralization of the DOC had occurred. Proton titrations revealed that the charge density of the "DOC" thus extracted (ranging from 8.5 to 11.2 mequiv g⁻¹ of C (24) was approximately equal to that of DOC in soils (25, 26).

Flocculation Experiment. The effect of calcium on DOC flocculation was studied in a batch experiment by adding 5 mL of stock DOC solution (H16, 4 mL) to 15 mL (H16, 16 mL) of 0.05 M NaNO₃ in acid-washed 50 mL tubes. Between 0 and 200 μL of a 1 M CaCl₂ solution was added to the DOC solutions to obtain a range in calcium concentrations between 0 and 10 mM. After equilibration on a table-top shaker for 20 h the samples were centrifuged (15 min at 3000g) and filtered (0.4-μm HTP Millipore filter). Total dissolved carbon concentrations as well as inorganic carbon concentrations were measured within 1 day after filtration. The addition of calcium slightly lowered the final pH of the solution compared to samples without calcium addition, but the measured differences were less than 0.25 pH units. The humic to fulvic acid ratio was also determined by addition of 1 M HNO₃ (Merck Suprapur) to the diluted DOC samples (without calcium addition). The pH of the solution was lowered to 1 and the carbon remaining in solution was measured. After decantation of the solution containing the fulvic acids, the precipitates on the filters were rinsed twice with unbuffered 0.05 N NaNO₃ and subsequently dissolved separately using 1 N NaOH. The pH of the separate solutions containing humic and fulvic acids was brought back to 6. The solutions thus obtained were used in the HPSEC analyses to determine the molecular size distribution of both humic and fulvic acids.

High Performance Size Exclusion Chromatography. High performance size exclusion chromatography (HPSEC) was used to determine the effect of calcium on the composition of the DOC remaining in solution. The HPSEC system consisted of a Waters 510 HPLC pump equipped with a Rheodyne manual injection valve, a 20 μL injection loop, a Bio-SIL SEC 250 preparative column (600 × 7.5 mm), and a Waters 994 Programmable Photodiode Array Detector (wavelength variable between 200 and 500 nm). Peak analysis was carried out using a Baseline 810 work station (Millipore). In this study, both 200 and 250 nm were used to detect the signals. Furthermore, a scan between 200 and 450 nm was made on each peak detected. The samples were eluted at ambient temperature (20 ± 2 °C) at a flow rate of 1 mL min⁻¹ in either a 0.05 M NaNO₃ solution or in demineralized, degassed water at pH 6. The samples were not concentrated prior to injection, and input concentrations ranged between 40 and 110 mg of C L⁻¹. To determine possible salt peaks or effects related to ionic strength (e.g., in the humic and fulvic acids samples) blanks were injected with an ionic composition similar to that of the samples. The pH of the eluent closely matched that of the samples.

Solid Phase Analyses. The total copper content of the soil samples was determined by hot acid extraction. One gram of air-dried, sieved (<2 mm) soil from each plot was digested for 1 h using 15 mL of a boiling 1:4:0.1 mixture (v/v) of concentrated H₂SO₄, HNO₃, and HClO₄ with repeated

additions of HNO₃ until white fumes remained visible. After boiling with 10 mL of distilled water, the digested mixture was diluted to 100 mL with distilled deionized water. Copper concentrations in the mixtures were measured on a Perkin-Elmer model 5000 flame atomic absorption spectrophotometer. Total carbon (TC) and inorganic carbon (IC) in solution were measured on a Shimadzu TC-500 Total Carbon Analyzer. DOC was calculated as the difference between the total carbon content and the inorganic carbon content. pH in all experiments was determined using a ROSS sure flow pH combination electrode in combination with a ROSS pH 290 measuring device. Calcium solution concentrations were determined using ICP spectrophotometry (Perkin-Elmer model 2000); copper solution concentrations were determined by atomic absorption spectrophotometry (AAS) on a Perkin-Elmer Graphite Furnace model 5000 using standard addition methods.

Model Development

Copper Binding to DOC: Two-“site” Langmuir Equation.

The quantity of DOC removed upon calcium addition was calculated as the difference between the initial DOC concentration in the sample without calcium addition (Ca₀ sample) and the DOC concentration remaining in solution at the highest calcium addition (Ca₂₀₀ sample). A similar approach was used to calculate the amount of copper bound to the dissolved and precipitated DOC fractions: the amount of copper bound to the flocculated DOC (Cu_{DOC-HMW}) was calculated as the difference between the copper concentration in the Ca₀ sample and the copper content remaining in solution in the Ca₂₀₀ sample:

$$\text{Cu}_{\text{DOC,HMW}} = \frac{\text{Cu}_{\text{Ca0}} - \text{Cu}_{\text{Ca200}}}{\text{DOC}_{\text{Ca0}} - \text{DOC}_{\text{Ca200}}} \quad (\mu\text{mol of Cu g}^{-1} \text{ of C}) \quad (1)$$

In the equations, the abbreviations HMW (high molecular weight) and LMW (low molecular weight) are used, this in accordance with the results of the HPSEC analyses. In a similar way, the amount of copper bound to the dissolved fraction at the highest calcium level was calculated as the amount of copper in solution in the Ca₂₀₀ sample relative to the amount of DOC remaining in solution:

$$\text{Cu}_{\text{DOC,LMW}} = \frac{\text{Cu}_{\text{Ca200}}}{\text{DOC}_{\text{Ca200}}} \quad (\mu\text{mol of Cu g}^{-1} \text{ of C}) \quad (2)$$

The amounts of copper bound to DOC was a function of the copper content of the soil. The relation between the soil copper content and the amount of copper bound to both fractions was described by

$$\text{Cu}_{\text{DOC},i} = \frac{Q_{\text{max},i} k_i \text{Cu}_{\text{soil}}}{1 + k_i \text{Cu}_{\text{soil}}} \quad (3)$$

where

Cu_{DOC,i} = copper bound to DOC in either the dissolved or the precipitated fraction (μmol of Cu g⁻¹ of C)

Q_{max,i} = maximum amount of copper bound to fraction *i* (μmol of Cu g⁻¹ of C)

k_i = affinity parameter (kg_{soil} mmol⁻¹ of Cu)

Cu_{soil} = copper content of the soil (mmol of Cu kg_{soil}⁻¹)

Equations 1 and 2 were used to calculate the amounts of copper bound to the dissolved and precipitated fraction for each soil. The copper concentration in solution was calculated according to

$$\text{Cu}_{\text{solution}} = \alpha \text{DOC}_{\text{total}} \frac{Q_{\text{max,HMW}} k_{\text{HMW}} \text{Cu}_{\text{soil}}}{1 + k_{\text{HMW}} \text{Cu}_{\text{soil}}} + \beta \text{DOC}_{\text{total}} \frac{Q_{\text{max,LMW}} k_{\text{LMW}} \text{Cu}_{\text{soil}}}{1 + k_{\text{LMW}} \text{Cu}_{\text{soil}}} \quad (4)$$

where

Cu_{solution} = Cu concentration in solution (μM Cu)

α = HMW fraction of DOC_{total} that can be removed by calcium (0 ≤ α ≤ 1)

β = LMW fraction of DOC_{total} not removed by calcium (0 ≤ β ≤ 1)

DOC_{total} = total amount of DOC in solution (g of C L⁻¹)

The values of α and β are based on the amount of DOC flocculated by calcium

$$\alpha = \frac{\text{DOC removed by Ca}}{\text{DOC}_{\text{total}}} \quad (5)$$

$$\beta = 1 - \alpha \quad (6)$$

In the calculation, no correction was made for the amount of free ionic copper or other inorganic copper species. However, at the pH in the experiment (6.0 ± 0.1), the sum of the free metal activity (Cu²⁺) and inorganic complexes (e.g., CuCO₃, CuNO₃⁺) is less than 1% of the total copper solution concentration (5–7). Therefore, it was assumed that more than 99% of copper in solution is bound to either HMW or LMW DOC, and no significant errors in the estimates of copper bound to DOC are introduced by neglecting the free metal activity or inorganic copper complexes.

Results

Impact of Calcium on Solubility of DOC. Addition of calcium to solution samples resulted in precipitation of DOC (Figure 1). DOC concentrations decreased from initial levels of around 90 mg of C L⁻¹ to about 60 mg of C L⁻¹ in the samples from Wageningen and to less than 50 mg of C L⁻¹ in the Haren samples. Figure 1 shows that, following an initial small DOC removal at calcium concentrations around 0.5 mM (< 10 mg of C L⁻¹ DOC removed), flocculation strongly decreased DOC concentrations starting at calcium concentrations of 2.5 mM in the W750 soil to 6 mM in the W0 soil.

Impact of Calcium on Size Distribution of DOC. The partial precipitation of DOC upon calcium addition led us to hypothesize that this fractionation reflects the mixed composition of DOC. In general, two classes of DOC are distinguished: a high molecular weight/size (HMW) “humic”-type fraction, and a low molecular weight/size (LMW) “fulvic”-type fraction (14). HPSEC chromatograms of DOC not amended with calcium indeed showed two distinct, but broad response areas that eluted between, respectively, 7 and 13 min and 15 and 22 min (Figure 2). The second peak (15–22 min) appeared roughly identical to the LMW fulvic fraction when compared with a chromatogram of a fulvic acid prepared from the same soil. The first (HMW) peak area, which actually consisted of two subpeaks 1A and 1B (in Figure 2A), signifies the humic fraction.

Addition of calcium to the samples did not affect the retention time nor the size of the LMW peak, but induced

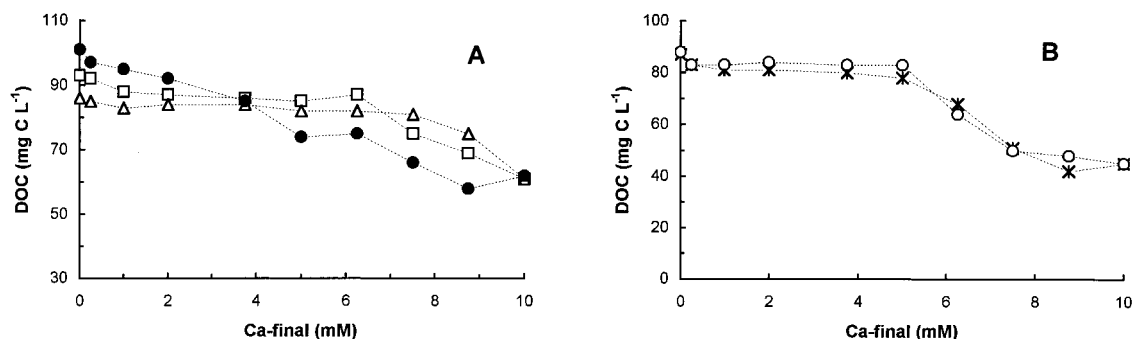


FIGURE 1. DOC removal from solution as affected by calcium addition (panel A, Wageningen plots; panel B, Haren plots; \square , WO; \triangle , W250; \bullet , W750; $*$, H11; \circ , H16).

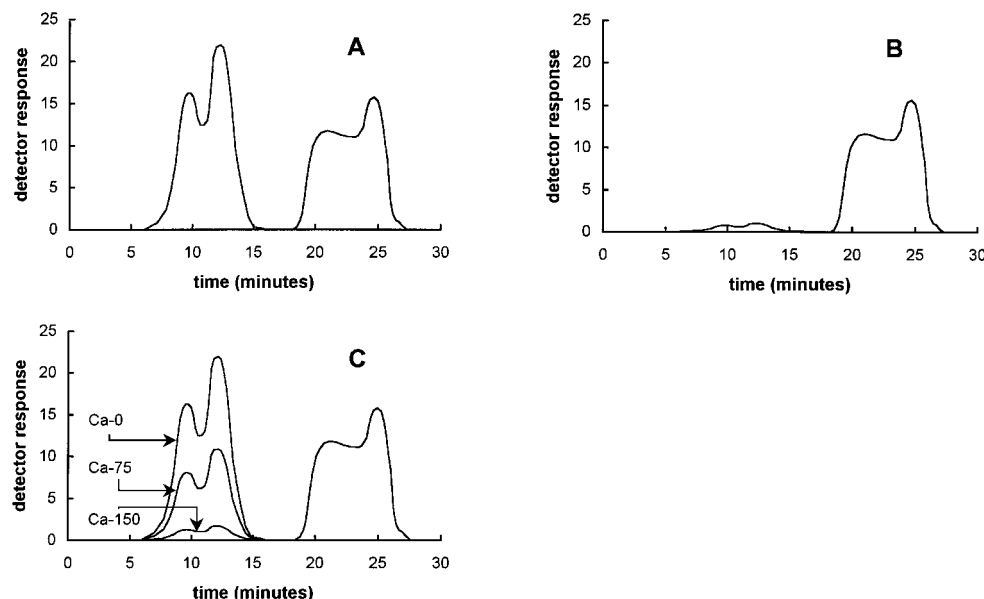


FIGURE 2. HPSEC results H11 soil. (A) Chromatogram soil derived DOC, no calcium added. (B) Chromatogram soil fulvic acid. (C) Effect of calcium addition, respectively, without Ca (Ca-0), 75 μ L (Ca-75), and 150 μ L 1 M CaCl_2 (Ca-150) addition.

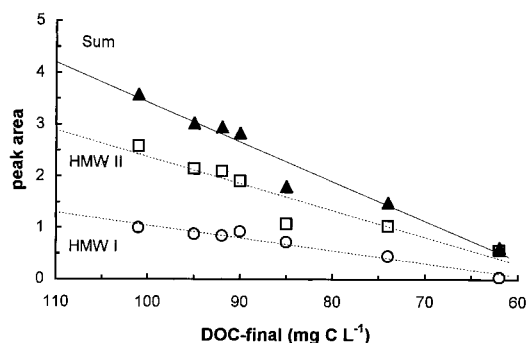


FIGURE 3. Relation between DOC and HPSEC-HMW peak area of DOC from W750 soil (\circ , HMW-I peak; \square , HMW-II peak; \blacktriangle , sum of HMW I + II).

a slight shift for the two humic (HMW) peaks: retention times decreased from 12.1 and 8.5 min in the samples without added calcium to 11 and 7.2 min for samples with the highest calcium concentration. Since calcium is expected to induce a decrease of the average DOC molecule size, the observed shift toward shorter elution time (=larger size) is most likely related to changes in the elution characteristics of the column. The most drastic effect of calcium addition was the gradual decrease of the first two HMW peaks (Figure 2) that correlated linearly with the decrease in the DOC concentration (Figure 3, $R^2_{\text{DOC-Sum}} = 0.96$). From these observations we conclude that the addition of calcium resulted in a preferential precipitation/flocculation of HMW humic acids.

Effect of Calcium on the Solubility of Copper Bound to DOC. The copper content in the DOC extracts of the five soils reflected the range of copper present in the solid phase of the soils: the DOC extract from the Wageningen soil from field plots to which no copper had been added contained 3.4 μM copper versus 7.2 and 14.1 μM copper from plots to which copper had been added at a load of 250 and 750 kg ha^{-1} , respectively. Similarly, extracts from the Haren soil that had been treated with inorganic fertilizer contained less copper than extracts from plots that had been treated with animal manure (1.1 μM Cu vs 3.0 μM Cu). Addition of calcium to these extracts resulted in a removal of 40% of the copper from the extracts of the Wageningen soils and of 60% from the extracts of the Haren soils (Figure 4). The removal pattern of copper (in percent, Figure 4, panels C and D) was similar to that of DOC (Figure 1) in all extracts.

Discussion and Model Application

Impact of Calcium on the Solubility and Size Distribution of DOC. The data in Figure 1 indicate that, at calcium concentrations ranging from 2.5 to 8 mM, a significant part of the HMW "DOC" present in solution is removed as a result of flocculation. The amounts of DOC removed from solution in the Haren samples by calcium are in good (qualitative) agreement with the amount of humic acids in solution: the ratio of HMW to LMW components varied around 1 for all soils ($\alpha \approx \beta \approx 0.5$). Only the field plot that received animal manure (H16) has a slightly higher HMW HA content ($\alpha \approx$

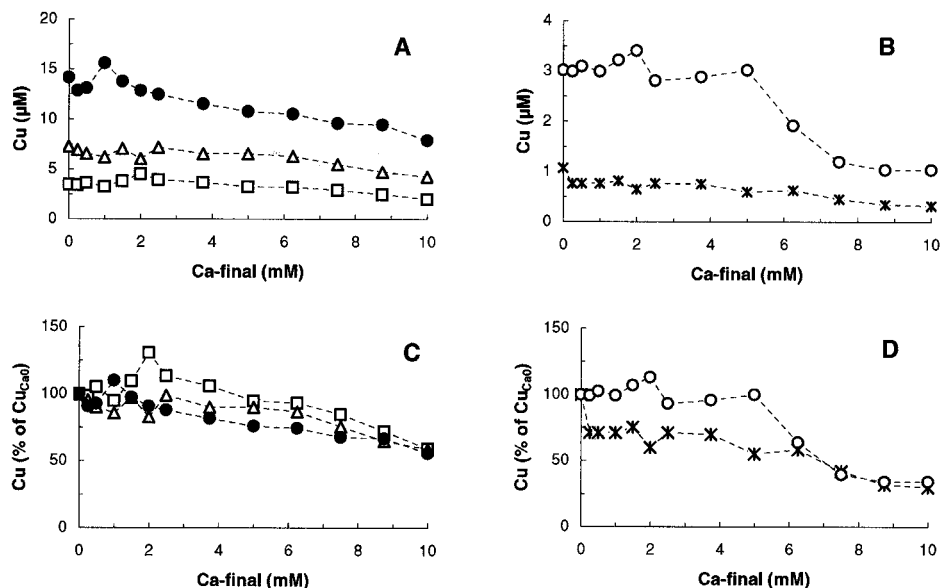


FIGURE 4. Copper concentration in solution and percentage of copper remaining in solution upon calcium addition (panels A and C, Wageningen plots; panels B and D, Haren plots; \square , W0; Δ , W250; \bullet , W750; $*$, H1; \circ , H16).

0.6), which is probably related to the application of manure in the past (10).

Previous measurements of the $C\text{-}f_{\text{crit}}$ (critical flocculation concentration, defined here as the minimum concentration at which flocculation starts) of DOC resulted in values for $C\text{-}f_{\text{crit}}$ ranging from 0.5 to 1 mM calcium for natural humic substances in river and lake waters (15–17) to 30 mM calcium in peat extracts obtained by shaking in 0.1 N NaOH (27). This range probably reflects differences in charge density and molecular size distribution of DOC from soils and aquatic systems (see below); values for $C\text{-}f_{\text{crit}}$ obtained in this study (between 2.5 and 6 mM) are in line with the reported values.

The preferential removal of HMW components is in agreement with observations on the behavior of humic substances in waste water treatment plants: a preferential removal of humic acids relative to fulvic acids was observed in flocculation experiments where aluminum was used as a coagulant (28). The complete removal of “humic” HMW components at calcium concentrations exceeding 7.5–10 mM (data not shown here) is, however, in contrast with data obtained for aquatic humic substances where only partial removal of humic substances was achieved upon addition of polyvalent cations (16, 29, 30). This difference is most likely due to the difference in molecular weight and chemical nature between aquatic humic substances and the “DOC” used in this study. Aquatic humic and fulvic acids contain a higher amount of reactive acidic functional groups (mainly carboxyl and phenol groups) than soil humic acids (31). Also, the ratio of carboxyl to phenol groups is higher in aquatic humic than in terrestrial humic substances (32). Since the pK_a for carboxyl groups ranges from 3 to 6 and from 8 to >10 for phenol groups (33), a higher carboxyl content will lead to higher molecular charges under near neutral pH conditions. Both the higher total charge and the higher contribution of carboxyl groups will decrease the propensity of aquatic humic substances from flocculation.

The differences in chemical characteristics of DOC from various environments (soils, lakes, rivers, and oceans) imply that it will be difficult to extract general rules on $C\text{-}f_{\text{crit}}$ values. Apart from the inherent differences in chemical characteristics of DOC in natural systems, the mode of extraction probably affects $C\text{-}f_{\text{crit}}$ values even more. Extraction under highly alkaline conditions probably leads to an overestimation of the $C\text{-}f_{\text{crit}}$ as was indicated by the rather high $C\text{-}f_{\text{crit}}$ in peat soils (27).

However, the significant impact of polyvalent ions such as calcium on the solubility and size distribution of organic components in solution implies that the process of flocculation plays an important role in carbon dynamics in soils. The ultimate impact of cations on the solubility of DOC, however, also depends on system conditions. In acid forest soils, for example, the ration HA:FA (or, approximately, HMW: LMW) is much lower than in soils with near neutral pH values (14). An increase in the polyvalent cation solution concentration that would induce flocculation in an arable soil at pH 6 might, therefore, not affect DOC dynamics in a forest soil.

Copper Binding to LMW and HMW DOC: Data and Model Results. The present research shows (i) that calcium can be used to selectively precipitate the HMW humic fraction of DOC and (ii) that this precipitation and/or flocculation results in a partial removal of copper from the extracts of a given soil. This gives us a tool to estimate and describe the DOC-normalized amount of copper bound to the humic HMW and fulvic LMW fractions in soil extracts. Figure 5A shows the relationship between the total copper content of the soil and the amounts of copper bound to the HMW and LMW fractions from the five soils calculated with eqs 1 and 2.

Strictly speaking, such data cannot be interpreted directly as isotherm data, since they have not been obtained in adsorption experiments, but the amount of copper bound to LMW DOC and HMW DOC could nevertheless be described very well by a Langmuir-type relationship as explained earlier ($R^2 = 0.991$ for LMW DOC and 0.983 for HMW DOC). Q_{max} was 251 μmol of Cu g^{-1} of C for HMW components and 450 μmol of Cu g^{-1} of C for LMW components. Values for k were 0.1376 $\text{kg}_{\text{soil}} \text{mmol}^{-1}$ of Cu for LMW components and 0.6419 $\text{kg}_{\text{soil}} \text{mmol}^{-1}$ of Cu for HMW components. This shows that (i) LMW components have a higher binding capacity for copper than HMW components and (ii) HMW components have a higher binding affinity for copper.

The measured copper solution concentration (depicted in Figure 4, panels A and B, as a function of calcium in solution) in all samples was subsequently simulated using eq 4 in order to test the hypotheses that (i) copper is bound to both HMW and LMW components in the extracts of the present study and (ii) calcium mainly removes HMW components. An assumption was that the measured decrease in the total DOC concentration was entirely due to the removal of HMW components. The values for α and β were

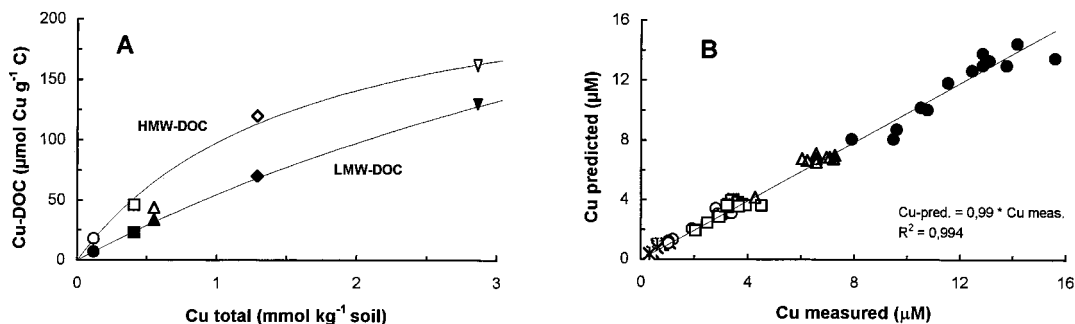


FIGURE 5. Measured versus predicted copper distribution using the Langmuir equation for HMW- and LMW-DOC: (A) Copper bound to DOC (○, H11; □, H16; △, W0; ◇, W250; ▽, W750, open symbols, HMW-DOC; closed symbols, LMW-DOC). (B) Copper solution concentrations (□, W0, △, W250; ●, W750; *, H11; ○, H16).

0.5 for all soils except for the H16 soil ($\alpha = 0.6$, $\beta = 0.4$), values for Q_{max} and k were kept constant for all soils (data given previously).

As is shown in Figure 5B, the predicted copper solution concentrations match the measured data very well ($R^2 = 0.994$). Thus, under the defined experimental conditions of constant pH, ionic strength, and solution composition, a two-species Langmuir equation is able to accurately predict copper solution concentrations based on the soil copper content and the amount of DOC in solution.

The results indicate that, in arable soils with copper contents ranging from 5 to 150 mg of Cu kg⁻¹ of soil, the contribution of HMW "humic" acids to the copper solution concentrations will be more important than that of LMW "fulvic" acids. But it also indicates that a significant amount of copper will remain in solution bound to LMW "fulvic" acids after removal of humic acids from solution by flocculation. This stresses the potential role of LMW components in the mobilization and potential transport of copper in soils.

Impact of Calcium on Contaminant Solubility under Field Conditions: Relevance of Calcium-Induced Flocculation of DOC. The observed removal of DOC by calcium has implications for the behavior of copper under field conditions: in addition to the direct effect of "macroions" (Ca, Al, or Fe) on trace metal chemistry (mainly by cation exchange), the results presented here show that the "indirect" effect of DOC-flocculation, induced by an increase in calcium solution concentration, has an important impact on copper solution geochemistry. An increase in the calcium solution concentration, e.g., induced by lime application, flooding with sea water or evaporation, reduces the solubility of DOC which results in a decrease in the solution concentration of contaminants that are tightly associated with DOC such as copper (this study) and hydrophobic pesticides like DDT and Chlordane (34).

However, aside from studies on wastewater treatment and trace metal dynamics in seawater, virtually no information exists on the quantitative importance of flocculation processes on contaminant solubility and mobility in soils. The data presented here suggest that, at calcium concentrations commonly encountered in arable soils, flocculation of DOC will occur, e.g., after lime application or in summer when solution concentrations increase due to evaporation. Furthermore, in soils with a high natural CaCO₃ content, dynamics of calcium in solution will affect the composition of DOC: on the basis of the outcome of the present study, it can be expected that the contribution of soluble LMW components is higher than that of HMW components. Thus, depending on soil conditions, a substantial part of the total contaminant load attached to DOC in solution can be "immobilized" as a result of the removal of DOC from solution.

Since both DOC and calcium dynamics are largest in the topsoil, flocculation of HMW components is a mechanism

by which part of the DOC-bound contaminants can be retained in the topsoil. However, until now, the effect of calcium on contaminant solubility and the effect on the chemical composition of DOC are not incorporated in chemical equilibrium models. The Langmuir-type model presented here can serve as a tool to assess the distribution of metals over labile and nonlabile dissolved organic substances in the soil solution, which, in turn, yields information on the tendency of metals to leach to lower soil horizons and the groundwater.

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