Effects of clay minerals, hydroxides, and timing of dissolved organic matter addition on the competitive sorption of copper, nickel, and zinc

a column experiment


DOI
10.1016/j.jenvman.2016.11.056

Publication date
2017

Document Version
Final published version

Published in
Journal of Environmental Management

License
Article 25fa Dutch Copyright Act (https://www.openaccess.nl/en/in-the-netherlands/you-share-we-take-care)

Link to publication

Citation for published version (APA):

General rights
It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use, unless the work is under an open content license (like Creative Commons).

Disclaimer/Complaints regulations
If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: https://uba.uva.nl/en/contact, or a letter to: Library of the University of Amsterdam, Secretariat, Singel 425, 1012 WP Amsterdam, The Netherlands. You will be contacted as soon as possible.
Effects of clay minerals, hydroxides, and timing of dissolved organic matter addition on the competitive sorption of copper, nickel, and zinc: A column experiment

Yasser Refaeya, b, *, Boris Jansen a, John R. Parsons a, Pim de Voogta, Simone Bagnis a, c, Adriaan Markusa, d, Abdel-Hamid El-Shaterb, Abdel-Aziz El-Haddadb, Karsten Kalbitza, e

a Institute for Biodiversity and Ecosystem Dynamics (IBED), University of Amsterdam, P.O. Box 94240, 1090GE, Amsterdam, The Netherlands
b Geology Department, Faculty of Science, Sohag University, P.O. Box 82524, Sohag, Egypt
c Biogeochemistry Research Centre, Portland Square, Plymouth University, Drake Circus, Plymouth, Devon, PL4 8AA, United Kingdom
d Deltares, P.O. Box 177, 2600 MH, Delft, The Netherlands
e Soil Resources and Land Use, Institute of Soil Science and Site Ecology, Faculty of Environmental Sciences, Technical University Dresden, Pienner Strasse 19, 01737, Tharandt, Germany

ABSTRACT

Infiltration of heavy metal (HM) polluted wastewater can seriously compromise soil and groundwater quality. Interactions between mineral soil components (e.g. clay minerals) and dissolved organic matter (DOM) play a crucial role in determining HM mobility in soils. In this study, the influence of the timing of addition of DOM, i.e. concurrent with or prior to HMs, on HM mobility was explored in a set of continuous flow column experiments using well defined natural soil samples amended with goethite, birnessite and/or smectite. The soils were subjected to concurrent and sequential additions of solutions of DOM, and Cu, Ni and Zn. The resulting breakthrough curves were fitted with a modified dose-response model to obtain the adsorption capacity ($q_0$). Addition of DOM prior to HMs moderately enhanced $q_0$ of Cu ($8\text{e}^{-25\%}$) compared to a control without DOM, except for the goethite amended soil that exhibited a 10% reduction due to the blocking of binding sites. Meanwhile, for both Zn and Ni sequential addition of DOM reduced $q_0$ by 1–36% for all tested soils due to preferential binding of Zn and Ni to mineral phases. In contrast, concurrent addition of DOM and HMs resulted in a strong increase of $q_0$ for all tested metals and all tested soil compositions compared to the control: 141–299% for Cu, 29–102% for Zn and 32–144% for Ni. Our study shows that when assessing the impact of soil pollution through HM containing wastewater it is crucial to take into account the presence of DOM.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Heavy metals (HMs) are considered potentially highly toxic pollutants and may pose a serious threat to environmental quality (e.g. Qin et al., 2006; Usman, 2008). Soil contamination with HMs may occur due to irrigation with contaminated water, the addition of fertilizers and metal based pesticides. Such problems are especially acute in arid developing countries such as Egypt where wastewater reuse could be a reasonable choice to mitigate the shortage and scarcity of fresh water resources (Radwan and Salama, 2006; Alfarra et al., 2011).

The fate and transport of HMs in soils and subsequently in groundwater aquifers are mainly controlled by the sorption capacity of soil constituents and aquifer materials (Alloway, 1995; McBride et al., 1997, 1999). Smectite and hydro-oxides minerals are known to exhibit high adsorption capacities for HMs owing to their high reactivity and large specific surface area (SSA) (Klaine et al., 2008; Hashim et al., 2011; Tang and Lo, 2013; Uddin, 2017). Several studies to date have addressed the sorption of HMs under equilibrium conditions onto different mineral surfaces (e.g., Serrano et al., 2005; Arias et al., 2006; Covelo et al., 2007; Refaey et al., 2014). However, to quantify the fate and distribution of HMs in different mineral surfaces, proper transport-related parameters of HMs in groundwater or wastewater treatment
technology need to be evaluated (Chotpantarat et al., 2012). Column experiments have been conducted for this purpose but most of these studies were focused on a single metal (e.g., Gupta and Sharma, 2002; Liu et al., 2006; Miretzky et al., 2006; Chotpantarat et al., 2011). For instance, Abollino et al. (2008) reported that the adsorption capacity of smectite minerals for individual metal ions was 3.04, 3.61, and 3.63 mg/g for Cu, Zn and Ni, respectively. Only few studies addressed the competitive adsorption of Cu, Zn and Ni onto soil minerals under dynamic conditions. For instance, Seo et al. (2008) studied sorption of As, Cd, Cr, Cu, Hg, Pb and Zn onto sediments containing > 58% clay under dynamic conditions. This study reported that the sorption capacities of Cu and Zn were lower under competitive conditions (2.5 mg/g for Cu and 1.5 mg/g for Zn) than when sorption of individual metals was considered (13.4 mg/g for Cu and 9.3 mg/g for Zn). Likewise, Chaari et al. (2011) found that the adsorption capacity of Cu and Ni in competitive adsorption experiments were 0.033 and 0.024 mg/g, respectively.

In addition to competition between HMs, the adsorption behavior of metal ions from contaminated water is influenced by the presence of other components that may either impede or enhance adsorption and thus HM mobility. Of particular importance in the context of soil pollution with HM rich wastewater is the presence of dissolved organic matter (DOM). DOM is often found in considerable concentrations either in the wastewater itself (e.g., industrial and agricultural effluents) or in the soil (e.g. due to manuring). Such presence of DOM can exert a significant influence on the fate and transport of HMs in soil. Sorption of DOM to mineral surfaces is considered an important pathway for the retention and also the stabilization of OM (e.g., Kaiser and Guggenberger, 2000; Kalbitz et al., 2005; Mikutta et al., 2007). Therefore, the influence of DOM on HM mobility not only concerns the interaction of DOM with HMs, but also processes altering the mobility of the DOM itself in the soil. Understanding the mechanisms controlling the interactions of HMs with both mineral surfaces and DOM is therefore essential to get insight into transport and fate of metals in soils (Arshad et al., 2008; Cecchi et al., 2008).

DOM was previously found to either hinder or promote HM adsorption to mineral surfaces in soils depending on the affinity of metal-ligand complexes for adsorbents (Kalbitz and Wennrich, 1998; Shuman et al., 2002; Jansen et al., 2003; Lackovic et al., 2004; Abollino et al., 2008; Refaey et al., 2014). However, most of the studies looking at the effects of DOM on the adsorption HMs by clay and hydroxide have been conducted in batch setups where DOM was in equilibrium with the HMs.

In a recent study employing batch experiments to investigate the competitive adsorption of Cu, Zn and Ni on several mineral phases, we discovered that the timing of the addition of DOM to soils, i.e. concurrent with or sequential to HM addition, most likely plays a significant role in regulating the mobility of HMs in soils (Refaey et al., 2014). While providing this valuable, novel insight, our previous batch study only yielded a snapshot at particular liquid to solid ratios and is unsuitable for capturing the dynamics of a realistic soil system where flow kinetics should be taken into account (Maszkowska et al., 2013). To study these dynamics a column approach is needed to enable time-dependent monitoring of contaminant leaching from soil and waste materials under more realistic environmental conditions (Maszkowska et al., 2013). As also recently acknowledged by other scientists, this knowledge gap has yet to be addressed (e.g. Chotpantarat et al., 2012; Anna et al., 2015). Addressing this knowledge gap is urgently needed in particular in the context of designing appropriate strategies for the remediation of HMs contamination in soils (Chotpantarat et al., 2012).

Following from the foregoing, the objectives of the present study were to build on the results of our recent batch adsorption study (Refaey et al., 2014) in order to (1) unravel the effect of the timing of the addition of DOM on the competitive adsorption of Cu, Ni and Zn onto different soil compositions in a kinetic system, (2) quantify the fate and transport of metals in different mineral surfaces and (3) gain insights into leaching behavior under actual environmental conditions. For this a column approach was used in order to accommodate the dynamic characteristics of metals interaction with DOM and soil minerals.

2. Materials and methods

2.1. Sampling area and soil selection

Soils were sampled in Southern Limburg, The Netherlands at 50° 53’37.61” N lat; 5° 53’34.56” E long. The samples were collected from the C horizons according to their variations in soil composition (e.g. grain size, color, and organic material) after removing the A horizons on the top (up to 45 cm depth). The A horizon has a silty loam texture and is characterized by angular blocks, more sticky, brown to dark grey, and clay-rich. The A horizon has a sharp boundary to the B horizon. The B horizon (up to 75 cm depth) is yellowish brown, soft, silty, burrows traces, less blocky, less permeable, and contains brownish rich materials. The B horizon changes gradually downward to the C horizon. The C horizon is rich in Fe-oxide, has a silty loam texture, and low clay fraction content (28%).

The soil was selected based on a previous application in a different study focusing on soil-water interactions. Selection criteria were that the C horizon is of uniform grain size texture (silty texture), lacks native HMs, and is poor in native OM content. Samples of the C horizon were therefore used in the current column approach. The C horizon was extensively characterized before its application in the present study (see 2.2).

2.2. Physico-chemical and mineralogical characteristics of the studied soil

Field water content was determined by drying soil samples at 105° C for 24 h. The soil pH H2O was also measured (1:2.5 ratio). The cation exchange capacity (CEC) of soils was measured using the method of Hendershot and Duquette (1986). Major cations (Ca²⁺, Mg²⁺, K⁺, and Na⁺) and major anions (Cl⁻ and SO₄²⁻) were measured using inductively coupled plasma optical emission spectrometry ICP-OES (PerkinElmer-Optima 3000XL) and San⁺⁺ Automated Wet Chemistry Analyzer-Continuous Flow Analyzer (Skalar), respectively. Total carbon (TC) content was determined with a C/N analyzer (Elementar Vario EL). Total content of pedogenic (hydr)oxides was estimated as dithionite-citrate-bicarbonate extractable iron (Fed) (AA, PerkinElmer) using the method of Mehra and Jackson (1960). Mn-oxide and active (oxalate extractable) Fe- and Al-(hydr)oxide (Feo and Alo) contents were measured using the method of Searle and Daly (1977). For mineralogical identification, X-ray diffraction analysis was performed using a Philips (now PANalytical) PW 1830 instrument, with a Philips PW 3710 control unit (Cu Ka radiation with wavelength 1.54056 Å produced at 50 mA and 40 kV) to identify the clay minerals present in the clay fraction (Brindley and Brown, 1980; Refaey et al., 2015).

2.3. Column experiments

2.3.1. HMs solution, DOM solution, and soil preparation

Mixed solutions of chloride salts of Cu, Ni, and Zn (~25 mg L⁻¹) were used. DOM was prepared by aqueous extraction from soil with added natural manure following the method described by Refaey et al. (2014). The same source of DOM was used in our previous
and current studies for reasons of comparison (Refaey et al., 2014). The HM and DOM solutions were adjusted to pH 6 before starting the experiments by adding appropriate amounts of 0.1 and 0.01 M NaOH to avoid precipitation of HMs and DOM.

Previously, smectite, goethite and birnessite were found to play a prominent role in regulating the binding affinity of Cu, Ni, and Zn to soil (Refaey et al., 2014). Therefore, in our current study the original soil was amended with these three minerals. Na-smectite (montmorillonite) of Wyoming (SWy-2) was obtained from the Source Clays Repository of The Clay Minerals Society, West Lafayette, USA; SWy-2 Na-rich Montmorillonite, Crook County, Wyoming, USA. Goethite (α-FeOOH) was synthesized according to the method of Schwertmann and Cornell (1991). Birnessite (6-MnO₂) was synthesized according to the method of Handel et al. (2013).

The mineral amendments were used to create five different soil compositions as described in Table 1. Each was mixed with 5.00 g of sand (50–70 mesh particle size, SiO₂, Sigma-Aldrich) to increase the hydrological conductivity of the soil once packed in the column, so the final weight of each prepared soil was 10.0 g (Table 1).

2.3.2. Experimental set-up

Continuous flow sorption experiments were conducted in 12 cm high and 2.5 cm internal diameter glass columns (Glassinstrumentmakerij, FNWI, University of Amsterdam). 10 g dry weight of each prepared soil was placed in the column to yield the desired bed height (Fig. 1).

Soils were packed in the columns by a series of additions in thin layers. Additionally, two sand layers of 35 g each were used to guarantee consistent flow through the soil bed. The soil sample was retained in the column by means of adaptors on the top and bottom of the column containing two paper retents. To further stabilize the soil bed, a layer of glass wool of ~ 3 g was placed on top of the upper sandy filter (Fig. 1). To prevent preferential flow-paths and for precise control of the flow rate, the HMs and DOM solutions were pumped upwards against gravity by means of peristaltic pumps (Minipuls 3, Gilson). The flow rate was set at 0.333 ml/min. To saturate the soil sample and eliminate air bubbles, demineralized water was pumped for 12 h prior to the experiment.

The experiments consisted of the following three scenarios (A, B and C); conducted on each of the five soil compositions (see 2.3.1) and carried out in quadruplicate:

(i) Scenario A (Control experiment): A total amount of ~9.41 L of HMs solution without DOM was pumped through all soil columns (~0.47 L for each soil column). Samples of the effluent solution were collected at a fixed volume/time interval (15 ml/45 min). This volume was used to determine the HMs in the collected effluents in each sample.

(ii) Scenario B (DOM and HMs added sequentially): The soil columns were first amended with DOM by continuous pumping of DOM solution (170 mg C/l) overnight (~5.00 L; ~250 ml for each soil column), followed by ~ 10.50 L of HM solution (~0.53 L for each column). Samples of the effluent solution were collected at a fixed volume/time interval (35 ml/105 min). About 15 ml was used to determine HMs using ICP-OES and 20 ml of this volume was used to investigate DOC and ultraviolet absorbance (see 2.3.3. for specification of the analyses and equipment used).

(iii) Scenario C (DOM and HMs added simultaneously): ~13.73 L of a solution containing DOM and HMs solution was pumped through the soil columns (~0.70 L for each column). Samples of the effluent solution were collected and analyzed using the same scheme as for scenario B. The pH of the effluents was monitored in all scenarios.

2.3.3. Analysis

Dissolved organic carbon (DOC) was determined by a TOC analyzer (TOC-VCPH, Shimadzu, Kyoto, Japan) while TOC contents in solid OM were determined with a C/N analyzer (Elementar Vario EL). Ultraviolet absorbance (UVA) was measured at λ = 254 in effluents with a UV–Vis spectrometer (Spectroquant Pharo 300, Merck). Specific ultraviolet absorbance (SUVA) values for each leached sample were obtained by dividing the UV absorbance value by the DOC concentration (mg/l) in the leachate and reported in the units of liter per milligram carbon per meter (L mg⁻¹ m⁻¹). SUVA is related to the average molecular weight of the DOM and provides a rough estimation of the aromaticity per unit of carbon concentration (Weishaar et al., 2003; Piirsoo et al., 2012). Effluent samples (35 ml) were collected from the exit of the column at different intervals for a total time of 18 h and analyzed for Cu, Ni, Zn, Fe, Mn and cations (Ca²⁺, Mg²⁺, K⁺, and Na⁺) using ICP-OES (PerkinElmer-Optima 3000XL).

2.3.4. Modeling of adsorption of heavy metals

A variety of mathematical models have been used recently instead of experimental determination for simulation of breakthrough curves (BTCs) data and prediction of parameters such as the capacity of adsorbent (Meng et al., 2012; Yi et al., 2012). The obtained data are presented in the form of BTCs which in turn were analyzed using the modified dose-response model (Araneda et al., 2011).

Yan et al. (2001) used the modified dose-response model to more adequately describe the breakthrough data of the Bohart-Adams and Thomas models (Araneda et al., 2011; Xu et al., 2013). In the current study linear regressions of the modified dose-response model by Yan et al. (2001) were performed in order to simulate the BTCs [Eq. (1)].

\[
\ln(C_t/C_0 - C_t) = a \ln(t) + a \ln(C_0 Q/q_0 X)
\]

where \(C_t\) is the concentration of HM in the effluent, \(C_0\) is the concentration of HM in the influent (mg/l), \(a\) is the modified dose-response model constant, \(t\) is time (min). \(Q\) is the flow rate (L/min), \(q_0\) is the sorption capacity per unit mass of adsorbent (mg/g), and \(X\) is the mass of adsorbent (g). The values of \(a\) and \(q_0\) were derived from the plot of \(\ln(C_t/C_0 - C_t)\) against \(\ln(t)\). The \(q_0\) of adsorbents for toxic HMs is generally seen as an important indicator for the environmental hazards HMs in the environment (Silveira et al., 2003).

3. Results

3.1. General properties of the tested soils

Table 2 summarizes the main physicochemical and mineralogical characteristics of the studied soil. It had a moderate CEC value (23.4 cmol, kg⁻¹), low soil organic carbon (2.5 g kg⁻¹) and moderate crystalline Fe-oxide content (15.9 g kg⁻¹) (Table 2). The particle-size distribution was dominated by silt (67%) with a moderate contribution of clay (28%) and a minor contribution of the sand fractions (5%) (Table 2). Illite (10.4, 5.1, 3.4, and 3.3 Å), kaolinite (7.2 and 3.6 Å), and smectite (14.4 Å) were the most common clay minerals in the studied soil (Table 2; XRD patterns in Fig. S1 in the supplementary materials). Chlorite was scarce in the studied soil as a very weak peak appeared in the position of the kaolinite peak (7.2 Å) after heating treatment to 550 °C. The clay fraction was dominated by illite (68%) with a moderate amount of kaolinite (32%) and minor amount of smectite (3%) (Table 2). The dominant exchangeable cation was Ca²⁺, while Na⁺, Mg²⁺, and K⁺ provided minor contributions (Table 2).
3.2. Outflow concentrations of major cations and DOC

In all scenarios the major cation concentrations (Ca$^{2+}$, K$^{+}$ and Na$^{+}$) in the column outflows varied depending on the soil composition (Fig. 2; Fe and Mn cations in Fig. S2 in the supplementary materials). Soil-smectite-oxides and soil-smectite released the largest amount of Na$^{+}$ while the largest amounts of K$^{+}$ and Ca$^{2+}$ were released from soil-birnessite and soil-control (Fig. 2a, b, c).

Low DOC concentrations were recorded in the effluents in scenario A compared to those in scenario B and C (Fig. 3a). The UV254 values generally followed the trend, C > B > A in all scenarios (Fig. 3b). The average SUVA$_{254}$ values of DOM in the effluents were 6.46, 4.55, and 4.41 L mg$^{-1}$ m$^{-1}$ in scenario A, B, and C respectively (Fig. 3). The largest OC leaching was from soil-goethite and soil-control (Fig. 2a, b, c).

3.3. Sorption capacities of metals

The BTCs show that Cu took the most time to reach breakthrough in all three scenarios compared to Zn and Ni (Fig. 4). This indicates a higher removal capacity for Cu than Zn and Ni (Fig. 4). The breakthrough point of both Zn and Ni was much closer to each other (Fig. 4). The time intervals in BTCs between Cu on one side and Zn and Ni on the other side was higher in scenario C compared to scenario B and A (Fig. 4).

The adsorption capacity generally followed the trend, Cu > Zn > Ni ($q_0$ values; mg HM/g soil, Table 3). Both Zn and Ni cations displayed quite similar $q_0$ values in the studied soils; however, $q_0$ for Zn was relatively higher than that of Ni. The differences in $q_0$ of tested soils were reported to indicate the goodness of fit of the model (Table 3).

3.3.1. Scenario A (control experiment)

Differences in the sorption behavior of the studied metals were observed in scenario B (exp. B) compared to the control experiment. The highest value of $q_0$ observed in all the metals in all scenarios was reported to indicate the goodness of fit of the model (Table 3).

3.3.2. Scenario B (prior addition of DOM)

Differences in the sorption behavior of the studied metals were observed in scenario B (exp. B) compared to the control experiment. The highest value of $q_0$ observed for all the metals in all

---

**Table 1** Composition of the tested soils.

<table>
<thead>
<tr>
<th>Soil compositions</th>
<th>Original soil (g)</th>
<th>SiO$_2$ (g)</th>
<th>Smectite (g)</th>
<th>Goethite (g)</th>
<th>Birnessite (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil-control</td>
<td>5.00</td>
<td>5.00</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Soil-smectite</td>
<td>4.50</td>
<td>5.00</td>
<td>0.50</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Soil-goethite</td>
<td>4.92</td>
<td>5.00</td>
<td>-</td>
<td>0.08</td>
<td>-</td>
</tr>
<tr>
<td>Soil-birnessite</td>
<td>4.80</td>
<td>5.00</td>
<td>-</td>
<td>-</td>
<td>0.20</td>
</tr>
<tr>
<td>Soil-smectite-oxides</td>
<td>4.22</td>
<td>5.00</td>
<td>0.50</td>
<td>0.08</td>
<td>0.20</td>
</tr>
</tbody>
</table>

---

**Fig. 1.** Schematic diagram of single column apparatus.
studied soils was for Cu (Table 3). Much lower values of \( q_0 \) were obtained for Zn and Ni (Fig. 5a). Soil-birnessite had the highest value of \( q_0 \) for Cu, while soil-goethite showed the lowest one. For both Zn and Ni, soil-control showed the highest \( q_0 \) values while soil-smectite-oxides showed the lowest values.

The differences in \( q_0 \) of Cu for different soils were statistically significant only between soil-goethite and soil-birnessite (\( p < 0.05 \)). The relative increases in \( q_0 \) for Cu in all tested soil samples augmented by prior addition of DOM amounted to 8–25% except for soil-goethite which showed a 10% reduction in \( q_0 \) compared to the control experiment (Fig. 5b). On the other hand, the relative changes in \( q_0 \) for both Zn and Ni showed larger reductions for Zn (11–36%) than for Ni (1–21%) (Fig. 5b). Between individual soil samples, a statistically significant difference was observed between Cu & Zn and Cu & Ni (\( p < 0.05 \)) but no statistically significant difference was observed between Zn & Ni (\( p > 0.05 \)).

3.3.3. Scenario C (simultaneous addition of DOM and HMs)

Analogously to scenarios A and B, soil-birnessite had the highest \( q_0 \) for Cu while soil-goethite showed the highest \( q_0 \) for Zn and Ni. On the other hand, soil-smectite-oxides showed the lowest \( q_0 \) for Cu, Zn, and Ni (Fig. 5a). Concurrent addition of DOM and HMs to soil columns resulted in a large enhancement in \( q_0 \) for Cu (141–299%), Zn (17–102%), and Ni (32–144%) (Fig. 5b). In general, the differences in \( q_0 \) for Cu, Zn, and Ni in the tested soils were statistically significant (\( p < 0.05 \)). Also, differences in \( q_0 \) for Cu, Zn, and Ni in all tested soils were statistically significant (\( p < 0.05 \)) between scenarios C & A and scenarios C & B.

4. Discussion

4.1. Metal sorption and competition in the absence of DOM (scenario A)

The adsorption (both exchange and specific adsorption) capacity of a soil is determined by the number and kind of binding sites available (Boulding, 1996). Since sorption of Cu depends on cation–ligand interactions (inner-sphere complex) with the soil constituents, Cu was more strongly adsorbed than Zn and Ni, which are predominantly retained through electrostatic interactions (outer-sphere complex) (Anderson and Christensen, 1988; Gomes et al., 2001; Lafuente et al., 2008). This finding confirms the sorption results for Cu, Zn, and Ni in our previous batch study (Refaey et al., 2014). The adsorption of the metal that has a higher affinity for sorbent sites is less affected by other metals with weaker affinities (Chen, 2012). Accordingly, Cu was found to be the most strongly sorbed and the strongest competitor for soil constituents and OM in all scenarios (Fig. 4). That Zn exhibited a higher \( q_0 \) than Ni ions could be due to the fact that Zn outcompetes Ni in occupying sites available for both metals (Trivedi et al., 2001; Xu et al., 2006). Consistent with Xu et al. (2006), Zn adsorption onto goethite was found to be greater than for Ni because Zn ions have a higher affinity than Ni ions for this mineral surface.

The CEC value of the original soil was low (23 cmolc/kg), which is consistent with its low soil organic matter content (2.5 g C/kg soil) and the predominance of illite (10–40 cmolc/kg) and kaolinite (2–15 cmolc/kg) that both possess low-moderate CEC values (Grim, 1968; Ghosh and Bhattacharyya, 2002). Compared to the other soil constituents, birnessite has a higher CEC (247 cmolc kg\(^{-1}\)), higher SSA (76.5 m\(^2\)/g) and holds a negative charge in a wider pH range (Puppa et al., 2013). Consequently, Mn-oxide is a more effective sorbent for Cu ions than the other soil constituents (Bradl, 2004; Fernandez et al., 2015). Soil-birnessite showed the highest \( q_0 \) for Cu of all soils, probably due to penetration of metal cations into the birnessite layer structure, while soil-goethite showed higher \( q_0 \) for Zn and Ni (Fig. 5a). This might be attributed to strong retention of Cu by soil-birnessite (McKenzie, 1980) reducing the free binding sites for Zn and Ni, while in soil-goethite the competition between Cu, Zn and Ni was lower. However, this conclusion should be the subject of further research.

In addition, the presence of large competitive cations such as Ca\(^{2+}\) can affect HM adsorption in soils. Ca\(^{2+}\) competes effectively with metals for adsorption sites, and this competition is greater for Zn and Ni than for Cu because Zn and Ni are predominantly retained in the soil by exchange reactions, while Cu forms inner-sphere complexes with soil constituents (Pierangeli et al., 2003). Furthermore, the presence of Ca\(^{2+}\) ions as the dominant cation in the tested soils suppresses adsorption of metal on Fe-oxide and this also can explain the superiority of soil-birnessite for adsorption of Cu compared to soil-goethite (Cowan et al., 1991). The fact that soil-birnessite showed a higher \( q_0 \) for Cu, Ni and Zn than the soil-smectite-oxides may be attributed to the following: in the weakly acidic to neutral pH range, the surface of birnessite becomes more negatively charged than that of goethite. Moreover, the Point-of-Zero Charge (PZC) of birnessite is lower than that of goethite, and consequently there are more hydroxy groups available for binding metal ions on birnessite (Xu et al., 2015). The lower PZC of birnessite is less favorable for the protonation of its surface (Xu et al., 2015), thereby enhancing the attraction forces between the sorbent surface and the metal ions (Zhang et al., 2009). As a result, the removal ability of HMs from their solution by the soil amended with birnessite was higher than other amended soils in all pH conditions (Xu et al., 2015).

4.2. The effect of the (timing of) DOM addition on metal sorption (scenario B and C)

4.2.1. Effects of timing of DOM addition on Cu retention

Cu is more extensively complexed than Zn and Ni by DOM due to the formation of strong and stable (inner-sphere) complexes with DOM (e.g., McBride, 1998; Refaey et al., 2014; Fernandez et al., 2015). The time interval between breakthrough of Cu and that of both Zn and Ni in the BTCs was longer in the presence of DOM, reflecting the high affinity of Cu for DOM (Figueira et al., 2000) (Fig. 4). The timing of DOM addition had a great influence on the mobility of the tested HMs in current study. Following prior addition of DOM to soil constituents, DOM ligands can form a bridge between the soil surface and the HMs (Bradl, 2004; Refaey et al., 2014) and a moderate 8–23% enhancement in \( q_0 \) for Cu was thus
Fig. 2. Effluent concentrations of Ca$^{2+}$, K$^+$ and Na$^+$ (mg/l) at different soil compositions in experiments A, B and C.
Fig. 2. (continued).
Fig. 2. (continued).
molecular weight, aromatic compounds (Chorover and Amistadi, 2001; Chin et al., 1997; Hur et al., 2006), which is consistent with being blocked by OM (Kothawala et al., 2009; Refaey et al., 2014). For DOM complexation which can result in binding sites for Cu (slightly acidic) the Cu-DOM complex becomes unstable since Fe complexes with DOM (Senesi et al., 1986; Zhang et al., 2016), thereby occupied by Fe as this metal also forms strong inner-sphere complexes formed in solution prior to adsorption as a result of their cation bridging and precipitation as a result of metal-DOM complexes joined by prior addition of DOM due lower amounts of DOM being adsorbed on the birnessite surface. Both DOM and birnessite are negatively charged at pH 6 while goethite is net positively charged at the same pH (Chorover and Amistadi, 2001). As a result, the birnessite surface is less coated with adsorbed DOM than goethite is due to repulsion of “like” charges.

In contrast, concurrent addition of DOM and HMs to all tested soils (scenario C) showed remarkable enhancement in \( q_0 \) for all metals, probably due to cation bridging and precipitation (Bradl, 2004; Refaey et al., 2014). The \( q_0 \) for Cu was greatly enhanced (141–299%) by concurrent addition of DOM and HMs compared to the control situation (Fig. 5b). Soil-birnessite consistently exhibited a higher \( q_0 \) for Cu than other soils and this can be attributed to birnessite and DOM being the most likely to bind Cu in a non-exchangeable form. In addition, the presence of DOM increases the hydrolysis of Mn ions, thereby increasing the likelihood of Mn precipitation, and the negative charge on the exchange complex (Bradl, 2004).

4.2.2. Effects of timing of DOM addition on Zn and Ni retention

Both Zn and Ni were significantly affected by prior addition of DOM (scenario B) to soil constituents. The largest reduction in \( q_0 \) for Ni (1–36%) for all tested soils compared to the control experiment can be attributed to blockage of active sites on the soil constituents by OM (Refaey et al., 2014). In general, the statistically significant \( p < 0.05 \) reduction of \( q_0 \) for Ni and Zn compared to the control experiment confirms that electrostatic binding mechanisms and mineral phases dominate for these two metals resulting in a weaker association with OM (Refaey et al., 2014). Mineral phases such as clay minerals and hydroxides predominantly controlled the \( q_0 \) for Zn and Ni (Fujiyoshi et al., 1994; Li et al., 2009).

In contrast, all tested soils showed a remarkable enhancement of \( q_0 \) for both Zn and Ni by concurrent addition of DOM and HMs (scenario C). The \( q_0 \) for Ni was higher (32–144%) than for Zn (17–102%), probably due to the low stability of organic complexes with Zn (Kalbitz and Wennrich, 1998; Zhang et al., 2016) and higher affinity of Ni than Zn for DOM (McBride, 1989). Soil-goethite consistently exhibited a higher \( q_0 \) for both Zn and Ni than soil-birnessite. This can be explained by the pH of the effluents from soil-goethite being below 5.7 (slightly acidic) which resulted in Cu-DOM complexes becoming unstable as Fe displaces Cu (Bradl, 2004) and forms strong inner-sphere complexes with DOM (Senesi et al., 1986).

The enhanced leaching of OC induced by sequential addition of HMs in scenario B (Fig. 3a) was probably due to the competition of added HMs for adsorption sites in the soil solids with the previously adsorbed OM (Weng et al., 2009; Zhang and Zhang, 2010). In scenario C, concurrent addition of DOM and HMs (Fig. 3a) showed a remarkable increase of OC in the leachate. This is probably due to cation bridging and precipitation as a result of metal-DOM complexes formed in solution prior to adsorption as a result of their concurrent addition (Seo et al., 2008; Bradl, 2004).

4.2.3. Effects of differences in mineralogical composition on HM retention

Clay minerals in soils play a minor role in the sorption of HMs to soil compared to (oxyhydr)oxides and DOM (Fernandez et al., 2015). In our experiments, clay minerals influenced the mobility of the tested metals in the presence of DOM to some extent. The mineral kaolinite was detected in a considerable amount (32%) in the soil-control and contributed to adsorption of a large amount of DOM (Fig. 3a); thereby enhancing \( q_0 \) for Cu, Zn, and Ni (Stevenson and Fitch, 1981). The observation that soil-smectite and the ternary complex soil (soil-smectite-oxides) had a lower \( q_0 \) for Cu, Zn and Ni in presence of DOM could be attributed to smectite reducing the

---

![Graph](image-url)
Fig. 4. Selected breakthrough curves (BTCs) of Cu, Zn, and Ni in experiments A, B and C.

Table 3
Estimated parameters of modified dose-response model for the sorption of Cu, Zn and Ni.

<table>
<thead>
<tr>
<th>Experiment (Scenario)</th>
<th>Soil</th>
<th>Cu</th>
<th>Zn</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>q₀ (mg/g)</td>
<td>a</td>
<td>r²</td>
<td>q₀ (mg/g)</td>
</tr>
<tr>
<td>Exp. A</td>
<td>Soil-control</td>
<td>1.13</td>
<td>3.06</td>
<td>0.85</td>
</tr>
<tr>
<td></td>
<td>Soil-smectite</td>
<td>0.82</td>
<td>2.44</td>
<td>0.82</td>
</tr>
<tr>
<td></td>
<td>Soil-goethite</td>
<td>1.12</td>
<td>2.47</td>
<td>0.75</td>
</tr>
<tr>
<td></td>
<td>Soil-birnessite</td>
<td>1.22</td>
<td>2.43</td>
<td>0.88</td>
</tr>
<tr>
<td></td>
<td>Soil-smectite-oxides</td>
<td>0.88</td>
<td>2.68</td>
<td>0.73</td>
</tr>
<tr>
<td>Exp. B</td>
<td>Soil-control</td>
<td>1.22</td>
<td>2.42</td>
<td>0.78</td>
</tr>
<tr>
<td></td>
<td>Soil-smectite</td>
<td>1.03</td>
<td>2.10</td>
<td>0.84</td>
</tr>
<tr>
<td></td>
<td>Soil-goethite</td>
<td>1.01</td>
<td>2.09</td>
<td>0.83</td>
</tr>
<tr>
<td></td>
<td>Soil-birnessite</td>
<td>1.36</td>
<td>2.32</td>
<td>0.74</td>
</tr>
<tr>
<td></td>
<td>Soil-smectite-oxides</td>
<td>1.08</td>
<td>2.32</td>
<td>0.74</td>
</tr>
<tr>
<td>Exp. C</td>
<td>Soil-control</td>
<td>3.34</td>
<td>1.14</td>
<td>0.83</td>
</tr>
<tr>
<td></td>
<td>Soil-smectite</td>
<td>2.17</td>
<td>1.32</td>
<td>0.90</td>
</tr>
<tr>
<td></td>
<td>Soil-goethite</td>
<td>3.01</td>
<td>1.36</td>
<td>0.84</td>
</tr>
<tr>
<td></td>
<td>Soil-birnessite</td>
<td>4.87</td>
<td>1.58</td>
<td>0.90</td>
</tr>
<tr>
<td></td>
<td>Soil-smectite-oxides</td>
<td>2.12</td>
<td>1.85</td>
<td>0.82</td>
</tr>
</tbody>
</table>
DOM contribution to binding Cu (Stevenson and Fitch, 1981). Smectite minerals tend to strongly bind hydrophilic organic material from solution (Meleshyn and Tunega, 2011) but bind the hydrophobic DOM used in the current study less strongly and thus removes little HMs from the solutions. This conclusion is also supported by the fact that a large amount of OC in scenario C was leached in the effluent from soil-smectite (Fig. 3a). In the ternary soil, DOM could fail to form stable complexes with birnessite in presence of goethite and Ca\(^{2+}\) because both Fe and Ca can substitute for Mn (Norvell and Lindsay, 1972).

4.3. Comparison between the batch and column experiments

The column experiments generally confirmed and substantiated the preliminary results from our previous batch study (Refaey et al., 2014) with respect to the timing of addition of DOM in retention of HMs. The adsorption of Cu, Zn and Ni in both experiments in general showed stronger adsorption of Cu compared to similar sorption of Zn and Ni. In addition, in both studies, Cu showed strong sorption to DOM and mineral phases by forming strong complexes (inner-sphere) whereas both Zn and Ni preferred mineral-phase by forming outer-sphere complexes.

In theory, the batch approach would be expected to overestimate sorbed amounts because various kinetic reactions are studied under equilibrium conditions, while under natural conditions they could be too slow to reach equilibrium. This could lead to inappropriately optimistic predictions of metal retention (Plassard et al., 2000; Antoniadis et al., 2007). However, in our case the column study showed a larger metal retention compared to our batch
experiments. This could be attributed to adsorption mechanism being predominant in the batch experiments whereas in the column study other additional retention mechanisms besides adsorption, such as surface precipitation, may have been involved (Seo et al., 2008). It is worth mentioning that in both batch and column studies, the timing of the DOM addition (concurrent with or prior to HM addition) had a large effect on metal retention. Also, it seems that in both batch and column studies, previously added DOM (scenario B) blocked the binding sites for Cu, Zn and Ni on soil-goethite and hence reduced their adsorption capacity.

5. Conclusions

In our study, an important role in regulating the mobility of HMs in soils was played by the timing of DOM addition (concurrent with or prior to HM addition). All tested metals showed strong enhancement of adsorption with concurrent addition of DOM (scenario C) compared to prior addition of DOM (scenario B). Both Zn and Ni showed reduced retention to soil components following prior addition of DOM, confirming our previous findings that mineral-phases are preferential sorbents for these two metals. Conversely, Cu exhibited higher sorption to both DOM and mineral phases by forming stable inner-sphere complexes. Timing of DOM addition with respect to that of HM therefore has to be taken into account when assessing the influence of HM pollution of soils through polluted irrigation- or wastewater in a system where Zn also enters the soil (e.g. agricultural irrigation in combination with manuring). Similarly, both the presence of DOM and timing thereof should be taken into account in design of strategies where soil constituents, e.g. clay minerals, are used to clean-up HM polluted waste water.

Acknowledgments


Appendix A. Supplementary data

Supplementary data related to this article can be found at http:// dx.doi.org/10.1016/j.jenvman.2016.11.056.

References

metal contamination of a calcic cambisol by fallout from a lead-recycling plant. Geoderma 144, 287–296.
Chorpantarat, S., Ong, S.K., Sukthirat, C., Otsathip, K., 2011. Effect of pH on transport of Pb(II), Mn(II), Zn(II) and Cd(II) through lateritic soil: column experi-

The reference list is a detailed compilation of all the sources cited in the document. It includes various types of scientific articles and books, covering topics such as heavy metals in soils, adsorption mechanisms, and the effects of DOM on metal retention. The references are cited throughout the text to support the findings and conclusions presented. The use of a comprehensive reference list is crucial in academic writing to provide credibility and traceability of the information presented.