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The role of dissolved organic matter in adsorbing heavy metals in clay-rich soils

* Yasser B. Refaey_{a,b}, Boris Jansen_a, Abdel-Hamid El-Shater_b, Abdel-Aziz El-Haddad_b,

Karsten Kalbitz_a

Abstract

Heavy metals (HMs) are toxic to human life and the environment when present in excessive concentrations. Therefore, determining the interactions of HMs with soils and dissolved organic matter (DOM) is essential to predict their fate. To find out the effect of DOM and soil properties (Clay minerals, oxides, and bulk organic matter) on the uptake of Cu, Ni, and Zn, batch adsorption experiments were conducted using five soils sampled from Egypt. The sorption isotherms were well described by the initial mass (IM) isotherm model. The amount and timing of DOM addition was found to play a pivotal role in determining the affinity of the HMs for soil. When DOM and HMs were added simultaneously, the affinity of Cu decreased in Fe-(hydr)oxide rich soils (by 7%) and increased in soils poor in Fe-(hydr)oxide (by 6-10%). When DOM was added first, followed by HMs the affinity of Cu strongly increased. In contrast, affinity of both Ni and Zn was enhanced (3-18%) in presence of DOM regardless of the timing of DOM addition. The difference is explained by Cu binding to the solid phase and DOM through strong inner-sphere complexes, whereas Ni and Zn adsorbed predominantly through weaker electrostatic interactions. As a result Cu was able to bind more strongly to previously adsorbed DOM on the solid phase in case of smectite, while this effect was counteracted by the coating of available specific binding sites on Fe-(hydr)oxides. The study has revealed that Egyptian soils hold great potential to remove HMs from aqueous solutions.

^a Earth Surface Science, Institute for Biodiversity and Ecosystem Dynamics, University of Amsterdam, P.O. Box 94240, 1090 GE Amsterdam, The Netherlands

^b Geology Department, Faculty of Science, Sohag University, P.O. Box 82524 Sohag, Egypt

*Corresponding author (y.b.refaey@uva.nl); K.Kalbitz@uva.nl; B.Jansen@uva.nl; hshater@yahoo.com; elhaddad_abdelaziz@yahoo.com

1. Introduction

Industrial activities release significant quantities of different pollutants including heavy metals (HMs). In particular in developing countries, like Egypt, such pollution can be severe, and the removal of HMs from (waste)waters is important to protect public health (Mellah and Chegrouche, 1997).

Methods that are commonly used to remove HMs from waste water solutions include precipitation, ion exchange, solvent extraction, phytoextraction, ultrafiltration, reverse osmosis, electrodialysis, and adsorption onto activated carbon (Donat et al., 2005). Of these the adsorption of HMs on a variety of substances such as activated carbon (Kadirvelu et al., 2001) and clay minerals (Erdem, 2004; Chen et al., 2007; Bhattachayya and Gupta, 2008; Motsi et al., 2009) are generally seen as the most powerful tools for wastewater cleanup.

Soils have been shown to play a pivotal role in mitigating the environmental and health effects of HM pollution originating from (waste)waters, in particular when polluted water sources are used to irrigate crops (Zeid, 2013). On the one hand, adsorption processes in the soil may remove HMs from the dissolved phase. On the other hand, infiltrating water may stimulate the release of HMs that were previously adsorbed (Ahlberg et al., 2006). Clay minerals play an

important role in retaining HMs through adsorption. As a result, the types and amounts of clay minerals present are of considerable importance in determining the distribution and mobility of HMs in soils (Spark et al., 1995; Doula et al., 1999; Al-Qunaibit et al., 2004; Srivastava et al., 2005). Because of their adsorption potential for HMs, many clay minerals are even actively used to remove HMs from polluted wastewater. For example, consider the use of smectite clays, a family of common 2:1 phyllosilicates with a large permanent negative charge through isomorphic substitution, and a large specific surface area resulting in a large cation exchange capacity (CEC) (e.g., Ikhsan et al., 2005; Gu, et al., 2010). Other constituents of the mineral soil phase that are important for the adsorption of HMs include Fe-, Al-, and Mn-(hydr)oxides (e.g. Sprynskyy, et al., 2011).

Due to its high specific surface area and CEC, soil organic matter (SOM) also plays a significant but complicated role in affecting the mobility of (heavy) metals in soils (Stevenson, 1982). When present as part of the solid phase, SOM can serve as adsorption medium for HMs. However, when bound to the mineral phase, SOM can also alter the physicochemical properties of clay minerals by decreasing their specific surface area (SSA) and thus their HM adsorption capacity (Kaiser and Guggenberger, 2003; Wang and Xing, 2005). When present as dissolved organic matter (DOM), SOM influences the mobility of (heavy) metals by forming soluble organo-metal complexes with organic ligands (e.g. Chairidchai and Ritchie, 1990; Kalbitz and Wennrich, 1998; Alvim and Lourenco, 2000). The resulting organo-metal complexes may remain dissolved, be weakly adsorbed to the soil surface, or form strong inner-sphere complexes that are bound even more strongly than would the free metal ion (e.g., Benjamin and Leckie, 1982; Udom et al., 2004).

In general, a complex interplay of different inorganic and organic soil constituents is involved in the adsorption of HMs in soils through a continuum of reactive sites, ranging from weak physical (Van der Waals) forces and electrostatic outer-sphere complexes (e.g. ion exchange) to the formation of strong chemical bonding (inner-sphere complexation) and precipitation (Sposito, 1989). Previous work shows that the complex interplay between i) clay minerals and metal oxides in the solid mineral phase, ii) organic matter in the solid phase, and iii) DOM together determine the mobility and translocation of Al and Fe in podzols (Jansen et al., 2004; 2005). However, the timing of the addition of DOM is an aspect that has received little research attention so far. When a metal binds to solid phase OM, it is immobilized. In contrast, when it is bound to DOM, its immobilization on the solid soil phase may be actively prevented if the resulting dissolved organic metal complex remains in solution. Multidentate coordinative binding of multicharged HMs such as Zn, Cu and Ni to oxygen, containing functional groups on both dissolved and solid phase organic matter, is often largely irreversible (Stevenson, 1982; Karlsson et al., 2006). Consequently, one could expect that the timing of when metal-rich (waste)waters pass through soils (before, concurrently with, or after application of DOM-rich solutions) can significantly affect mobility of such HMs. The net influence of adding DOM to a certain soil system depends on a complex interplay of interactions with the DOM and soil properties in the solid phase (Harter and Naidu, 1995). For example, several mechanisms exist through which complexation of HMs with DOM leads to immobilization of the HMs. Apart from precipitation of the complex, which only occurs upon its saturation (Jansen et al., 2004), a first important mechanism is cation bridging, i.e. formation of S-HM-DOM complexes where S represents the adsorption site on soil surface and HM is the metal ion (Stumm, 1992). This will not only lead to immobilization of DOM itself, but can also result in enhanced binding of metals

when metals subsequently bind to the adsorbed DOM in a second layer as: S-HM-DOM-HM. This will be particularly important for metals, such as Cu, that bind to DOM through inner sphere complexes; it should not be influenced by the timing of addition of DOM. A second mechanism is adsorption of DOM on specific solid phase sorption sites not involved in the binding of HMs, followed by adsorption of HMs on the DOM that is thus adsorbed. Again, this is expected to be most pronounced for metals, like Cu, that bind through inner-sphere complexation. However, in this case, timing would have an influence: addition of DOM followed by later addition of HMs would be expected to have a larger immobilizing influence on HMs than concurrent addition. In spite of a vast body of literature dealing with the interactions of (heavy) metals with DOM, surprisingly little attention has been paid so far to such possible timing effects and to interactions between HMs, soil mineral constituents, SOM, and DOM.

Therefore, the main purpose of this study was to increase the understanding about the combinations of Cu, Ni, and Zn with clay minerals, oxides, bulk SOM, and DOM in the context of metal pollution of Egyptian soils. In particular, we focus on the role of organic matter in regulating the mobility of Cu, Ni and Zn in clay-rich soils from Egypt through (i) the influence of OM-coating on soils, and (ii) the influence of the presence of DOM and the timing of its application (prior to or concurrently with the HMs). In all processes, competitive sorption phenomena between the three metals were also explicitly considered.

As an overarching method, we employed the initial mass (IM) isotherm approach of Nodvin et al. (1986) to describe adsorption processes. The IM isotherm model has been widely used to describe DOM adsorption and desorption to mineral soils (e.g., Kaiser et al., 1996).

2. Materials and methods

2.1. Sampling and study area

Twenty eight soil samples (Pliocene clay deposits) were collected at East and West Sohag governorate, Egypt, midway between Cairo and Aswan. Specifically, samples were taken from the Al-Kwamel (KW), El-Kola (KO), Al-Ahayua (AH) and Wadi Qasab (WQ) areas. The study area is represented by the Nile basin stretch extending between 26° 19' 87" to 26° 33' 08" N lat; 31° 39' 04" to 32° 03' 62" E long. In addition, one sample was collected from the Bahariya Oasis (BO) area, Egypt (27° 47' 84" N lat; 28° 31' 68" E long). Five Egyptian soils (KW, KO, AH, WQ and BO) were selected from the larger suite of twenty eight soils sampled in areas representative for irrigation with HM polluted waste water. The selection was based on obtaining a realistic range in physico-chemical characteristics. The soil samples from KW, KO, AH, WQ, and BO were collected along the surface of vertical exposures (i.e. both artificial and natural outcrops in the field that is characterized by irregular surfaces, such as terraces), at heights of 4.0, 2.0, 3.5, 1.0, and 0.5 (m) respectively. We were looking for clay rich soil material that could be potentially used for large scale processing of wastewater. The samples were transported from Egypt to The Netherlands in sealed plastic bags and stored at 4°C until analyzed.

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

For mineralogical identification, X-ray diffraction (XRD) analysis was performed at Van der Waals-Zeeman Institute, University of Amsterdam, The Netherlands, using a Philips (now PANalytical) PW 1830 instrument, with a control unit Philips PW 3710(Cu K_{α} 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). Total carbon (TC) and total nitrogen (TN) contents in the soils were determined with a C/N analyzer (Elementar Vario EL, Hanau, Germany). We assume that TC equals total organic carbon (TOC) since TC equals the sum of organic and inorganic carbon and no carbonates were found in the selected soil samples as tested by addition of 2 M HCl. Total content of pedogenic (hydr)oxides was estimated as dithionite-citrate-bicarbonate extractable iron (Fe_d) (AAS, Perkin Elmer, Waltham, Massachusetts, USA) using the method of Mehra and Jackson (1960) and Holmgren (1967). Mn-oxide and active (oxalate extractable) Fe- and Al- (hydr)oxide (Fe_o and Al_o) contents were measured using the method of Searle and Daly (1977). Field water content was determined by drying soil samples at 105°C for 24 h. The soil pH_{H_2O} was also measured (1:2.5 ratio). The CEC of soils was measured using the method of Hendershot and Duquette (1986). Major cations (Ca^{2+} , Mg^{2+} , and K^{+} , and Na^{+}) and major anions (Cl^{-} , SO_4^{2-} , and PO_4^{3-}) were measured using ICP-OES (Perkin Elmer-Optima 3000XL) and San⁺⁺ Automated Wet Chemistry Analyzer-Continuous Flow Analyzer (CFA) respectively.

2.3. Dissolved organic matter (DOM) preparation

DOM was prepared by aqueous extraction from organic materials (soil with natural manure) obtained from a commercial garden center “Intratuin bemeste tuinaarde” in Amsterdam-

Netherlands. We chose this product because it contains cattle manure representative for wastewater application in an agricultural setting. In addition, to be allowed to be sold as fertilizer in The Netherlands in compliance with Dutch Law, its contents of HM are restricted, as confirmed by the analyses of major cations (Table 1). The extraction was carried out by adding 100 g of OM to 1 liter deionized H₂O. The suspension was stirred for 24 h at 180 rpm. The suspensions were centrifuged at 984xg for 40 min after which they were centrifuged again at high speed (27,586xg) for 40 min at 25°C. The supernatants were filtered over a 0.2-μm cellulose-acetate membrane filter. Dissolved organic carbon (DOC) was determined by a Total Organic Carbon (TOC) analyzer (TOC-VCPH-Shimadzu-Kyoto, Japan). TOC and TN contents in solid OM were determined with a C/N analyzer (Elementar Vario EL, Hanau, Germany). The pH of the DOC extraction was adjusted to pH 6 by adding appropriate amounts of 0.1 and 0.01 M NaOH. The main physico-chemical properties of DOM and extracted manure are presented in table 1.

Table 1. Characteristics of DOM and the extracted manure used in adsorption experiments.

DOM											
Cu mg L ⁻¹	Ni mg L ⁻¹	Zn mg L ⁻¹	Cr mg L ⁻¹	K mg L ⁻¹	Na mg L ⁻¹	Ca mg L ⁻¹	Mg mg L ⁻¹	Al mg L ⁻¹	Fe mg L ⁻¹	S mg L ⁻¹	P mg L ⁻¹
0.02	0.00	0.03	1.04	169	49.7	17.4	5.68	0.10	0.19	13.5	6.01
DOM								Manure			
PO ₄ mg L ⁻¹	Cl mg L ⁻¹	SO ₄ mg L ⁻¹	pH (H ₂ O)	Ec25 μS cm ⁻¹	TC mg L ⁻¹	TOC mg L ⁻¹	IC mg L ⁻¹	C g kg ⁻¹	N g kg ⁻¹	C/N g kg ⁻¹	S g kg ⁻¹
23.3	115	37.0	7.55	926	68.2	65.4	2.83	214	13.1	16.4	2.01

2.4. Adsorption experiments

Mixed solution of nitrate salts of Cu, Ni, and Zn (50 mg L⁻¹) were used in the adsorption experiments. The pH of the HM solution was adjusted to pH 6 by adding appropriate amounts of

0.1 and 0.01 M NaOH. The initial pH of the prepared HM solution was fixed to avoid precipitation of HMs. Batches of 1g of air-dried soil (< 2 mm) were combined with a range of volumes (10, 40, 70, and 100 ml) of HM solution in polypropylene tubes. Temperature was held constant at 20°C. A preliminary study showed that the sorption equilibrium of HMs on the soils under study was reached within 2 h (results not shown). Therefore, this time interval was chosen for subsequent experiments. All experiments were carried out in duplicate.

In all adsorption experiments, the supernatants were passed through 0.2-µm cellulose-acetate membrane filters, the pH was recorded immediately, and then metals in acidified solutions were measured by ICP-OES. The amount of adsorbed HMs was calculated by subtracting the amount of added HMs from the amount remaining in solutions using the mass-balance equation as follows:

$$q_e = V(C_0 - C_e)/M \quad \text{Eq. [1]}$$

where q_e is the adsorbed metal ion concentration (mg kg^{-1}), V is the solution volume (L), C_0 is the initial concentration of metal ions (mg L^{-1}), C_e is the metal-ion concentration in a bulk solution at equilibrium (mg L^{-1}), and M is the adsorbent mass (g). The following four sets of adsorption experiments (A, B, C, and D) were conducted (see also Fig. 1):

Fig. 1. Schematic overview for all adsorption experiments (A, B, C, and D).

A) HM adsorption in untreated soil samples (Control experiment): to evaluate the effect of soil constituents on the adsorption of Cu, Ni and Zn; 10, 40, 70, and 100 ml of the 50 mg L⁻¹ (pH 6) stock solutions were added separately to 1 g soil in 50, 100, 200, and 250 ml volume polyethylene tubes. The tubes were shaken for 2 h on a horizontal reciprocating shaker (130 rpm) and then centrifuged at 2012xg for 30 min.

B) HM adsorption in OM-enriched soil samples (addition of DOM and subsequent re-drying prior to addition of HM): to examine the effect of prior adsorption of DOM on the solid phase of the soils under study on subsequent adsorption of Cu, Ni and Zn. For this, 1 g soil was added to 20 ml of the DOM stock solution (pH 6) in polyethylene tubes. The tubes were

shaken and then centrifuged analogously to Experiment A. The supernatant was collected, filtered, and analyzed for TOC and TC using the TOC analyzer. The residue (i.e. soil material with adsorbed OM) was subsequently freeze-dried to obtain the OM-enriched soil material. After that, 10, 40, 70, and 100 ml of the Cu, Ni and Zn stock solutions (pH 6) were added separately to 1 g of OM-enriched soil in 50, 100, 200, and 250 ml volume polyethylene tubes. The tubes were shaken and then centrifuged analogously to Experiment A.

C) HM sorption of combined HM-DOM solutions (DOM and HM added simultaneously): to examine the effect of simultaneous addition of DOM and HMs on the sorption of the HMs onto the soils under study; 10, 40, 70, and 100 ml of the Cu, Ni and Zn stock solution was added separately to 1 g soil and 20 ml of DOM in 50, 100, 200, and 250 ml volume polyethylene tubes. The tubes were shaken and then centrifuged analogously to Experiments A and B.

D) Adsorption of HMs on soil surfaces with prior adsorbed DOM (first addition of DOM, then addition of HMs, no drying in between): to examine the effect of sequential addition of DOM and HMs on sorption of HMs onto the soils under study. For this, 1 g soil was added to 20 ml of DOM stock solution in 50, 100, 200, and 250 ml volume polyethylene tubes. The tubes were shaken for 2 h and then 10, 40, 70, and 100 ml of the Cu, Ni and Zn stock solutions was added separately to each tube. The tubes were shaken again for 2 h and then centrifuged as previously described.

In all previous experiments the supernatants were collected, filtered, and analyzed for TOC, Cu, Ni, and Zn.

2.5. Modeling of sorption kinetics and statistical analysis

We applied IM isotherms to describe the adsorption of HMs and DOM because, in contrast to traditional Langmuir or Freundlich based approaches, it is specifically designed to describe a net release of indigenous DOM as well (Kaiser and Guggenberger, 2000). In the IM approach (Eq. [2]), the quantity of a substance adsorbed or released (RE [$\mu\text{mol kg}^{-1}$]) is plotted against the initial quantity of the substance added (X_i [$\mu\text{mol L}^{-1}$]):

$$RE = mX_i - b \quad \text{Eq. [2]}$$

The slope (m [unit-less]) of the linear regression isotherms is interpreted as a partitioning coefficient (K_d) (Nodvin et al., 1986). This K_d is a measure of the affinity (ranging between 0 and 1) of the sorbent. From this K_d value, the mobility and fate of competing metals in the soil can be assessed (Gao et al., 1997; Cruz-Guzman et al., 2006). The intercept of the regression line (b) indicates the amount of substance ($\mu\text{mol kg}^{-1}$) released from soil when a solution without sorbent is added. Therefore, the intercept may be defined as a desorption term (Ussiri and Johnson, 2004).

The estimated K_d -values and the correlation coefficients (r^2) for a linear regression were determined with SigmaPlot for Windows 11.0. A one-way ANOVA followed by a least significant difference (LSD) test were employed to determine the significance of the differences between treatments. For this, Origin (version 8 for Windows) was used.

3. Results

3.1. General properties of the tested soils

Clay contents in the studied soils ranged from 11-71%; Clay minerals consisted of smectites and kaolinites, with the former being the dominant type (Table 2). Only in soil-BO smectite and kaolinite contents were almost equal. The studied soils had large CECs ranging from 424 - 654 $\text{cmol}_c \text{ kg}^{-1}$ (Table 2). Crystalline iron-oxide contents were small to moderate ($3.6\text{-}17.5 \text{ g kg}^{-1}$) with the highest contents in soil-KW and soil-WQ, while soil organic carbon (SOC) contents were low in all soils ($0.3\text{-}1.7 \text{ g kg}^{-1}$; Table 2). The pH was always slightly basic (Table 2). Na^+ was the dominant exchangeable cation while Ca^{+2} , Mg^{+2} , and K^+ provided minor contributions (Table 2).

Table 2. Selected physical and chemical properties of soil samples.

Soil Name	Soil pH	CEC $\text{cmol}_c \text{ kg}^{-1}$	SOM mg kg^{-1}	Clay Minerals		CBD ext.	Oxalate ext.	Particle size			Major anions		Major cations			
				Sme. [%]	Kao. [%]	Fe-oxide mg kg^{-1}	MnO_2 mg kg^{-1}	Clay [%]	Silt [%]	Sand [%]	Cl^- mg L^{-1}	SO_4^{2-} mg L^{-1}	Na mg kg^{-1}	Ca mg kg^{-1}	Mg mg kg^{-1}	K mg kg^{-1}
Soil-KW	7.5	642	300.0	95	4.0	14600	3500	18	78	2.7	6504	451	5439	333	112	12
Soil-KO	7.6	654	1700	87	10	9700.0	1300	18	79	1.1	3562	173	2085	677	211	12
Soil-WQ	7.5	588	1200	84	15	17500	1200	11	85	3.8	4179	91.3	2409	970	77.8	23
Soil-AH	7.7	554	900.0	76	22	10600	2100	19	75	2.8	3818	48.0	4071	541	180	12
Soil-BO	7.0	424	700.0	52	45	3600.0	30.00	71	30	0.3	3892	548	2625	68.1	75.3	59

CBD ext. (Citrate Bicarbonate Dithionite extraction); Kao (Kaolinite); Sme (Smectite).

3.2. Adsorption isotherms and adsorption coefficient (K_d)

In all experiments and for all HMs tested, the IM isotherm model was able to fit the data very well ($R^2 = 0.94\text{-}0.99$; Table 3). The trends in the K_d values for the three metals and five soils

in all four experiments are presented in Fig. 2. In general, the great majority of the added HMs was adsorbed regardless of the treatment processes. Specifically, for the lowest HM addition, 95%-100% of the amount of HMs added was adsorbed (i.e., 10 ml HMs solution with 50 mg L⁻¹). For the highest HM addition (i.e., 100 ml HMs solution, 50 mg L⁻¹), the percentage adsorbed still ranged between 55% - 81 % of metal added.

Table 3. Fitted initial mass isotherm parameters for Cu, Ni, and Zn in the four batch adsorption experiments with five different soils (mean of two replicates).

Soil Name	Metal	Experiment A			Experiment B			Experiment C			Experiment D		
		K _d	b	r ²	K _d	b	r ²	K _d	b	r ²	K _d	b	r ²
Soil-KW	Cu	0.77	4344	0.99	0.72	4832	0.98	0.78	3103	0.99	0.78	3211	0.99
	Ni	0.73	5121	0.98	0.68	5935	0.97	0.75	4364	0.99	0.75	4496	0.99
	Zn	0.71	5605	0.98	0.67	5895	0.97	0.73	4173	0.99	0.73	4270	0.98
Soil-KO	Cu	0.69	5420	0.98	0.69	4746	0.98	0.69	4378	0.99	0.72	4217	0.99
	Ni	0.52	6293	0.97	0.56	5750	0.98	0.61	5130	0.99	0.61	5163	0.98
	Zn	0.51	6973	0.97	0.56	5840	0.97	0.61	4855	0.98	0.60	5013	0.98
Soil-WQ	Cu	0.72	4821	0.99	0.68	4808	0.98	0.67	4844	0.98	0.71	4179	0.99
	Ni	0.54	5318	0.98	0.53	6066	0.97	0.56	5723	0.98	0.59	5286	0.98
	Zn	0.52	6117	0.98	0.52	6216	0.97	0.55	5467	0.98	0.57	5137	0.98
Soil-AH	Cu	0.62	6101	0.97	0.64	5303	0.98	0.67	4989	0.98	0.70	4377	0.99
	Ni	0.54	6480	0.97	0.54	6394	0.97	0.60	5785	0.98	0.61	5551	0.98
	Zn	0.53	7004	0.96	0.52	6475	0.96	0.59	5474	0.97	0.60	5262	0.98
Soil-BO	Cu	0.56	7004	0.96	0.57	6068	0.96	0.62	5290	0.98	0.64	5051	0.98
	Ni	0.52	7441	0.95	0.51	7000	0.95	0.58	6442	0.97	0.59	6243	0.97
	Zn	0.50	7975	0.94	0.50	6901	0.95	0.57	5955	0.97	0.57	5805	0.97

3.2.1. Interaction of untreated soils with HMs in absence of DOM (“Control” Experiment A)

In all studied, soil samples the affinity of the three HMs for the solid soil phase as indicated by the K_d values followed the sequence Cu >> Ni ≈ Zn (Table 3). The variation in the

K_d values for the tested soils (Fig. 2a) reflects the influence of the various soil properties (Clay minerals, oxides, and bulk OM) in determining HM affinity to soils. The K_d values for Cu decreased as follows: soil-KW > WQ > KO >> AH > BO (Fig. 2a). The difference between the tested soils was statistically significant for all studied soils ($p < 0.05$). The K_d values for Ni and Zn were similar for both metals and similar for all soils but one (Fig. 2b, c). The exception is soil-KW, which had a much higher affinity for Ni and Zn than all other soils ($p < 0.001$). The variation between the K_d values of the other soils for Ni and Zn was not significant ($p > 0.05$) (Fig. 2b, c).

The results of the correlative exploration of the relation between K_d values (affinity of Cu, Ni and Zn) and relevant soil properties such as clay minerals content, CEC, bulk OM, cations, and oxides revealed a significant effect ($p < 0.05$) of smectite on Cu affinity ($r^2 = 0.90$) and MnO_2 on Zn affinity ($r^2 \text{ Zn} = 0.77$).

Fig. 2. Comparison between distribution coefficients (K_d s) for individual HM in all adsorption experiments.

3.2.2. Interaction of OM-enriched soils with HMs (Experiment B)

The OM enrichment of the soils that was achieved in the preparatory step of Experiment B was always small, with a maximum of $< 1 \text{ g C kg}^{-1}$ soil adsorbed. However, the proportions of adsorbed organic C in total SOC (sum of adsorbed and original OC) were of similar magnitude: 71%, 35%, 39%, and 60% for soils KW, WQ, AH, and BO, respectively. The only exception was soil-KO, which had the highest original OM content (Table 2) and did not adsorb measurable amounts of OM.

Overall, the interaction of the studied HMs with the OM-enriched soils as represented by their K_d values resulted in the same selectivity sequence ($\text{Cu} \gg \text{Ni} \approx \text{Zn}$) as Experiment A. However, the absolute K_d values and their ordering differed from those found in Experiment A (Fig. 3a, b, c).

Fig. 3. Relative changes in K_d values of Cu, Ni, and Zn comparing to control experiment.

For Cu the affinity for the OM-enriched soil surfaces followed the sequence: $\text{KW} > \text{KO} > \text{WQ} > \text{AH} \gg \text{BO}$ soil. This ordering correlates with the smectite content and CEC value of the tested soils (Table 2). Compared to Experiment A, the K_d values for Cu adsorption were significantly reduced in soil-KW and soil-WQ (6.5% and 5.6% respectively; $p < 0.01$). In the other soils, the differences with the control experiment were much smaller (Fig. 3a).

Analogous to Experiment A, the K_d values of Ni and Zn in Experiment B were similar for both metals in all soils tested (Fig. 3b, c). Also analogous to Experiment A, the variation in Ni and Zn affinities for the studied soils was small, with the exception of soil-KW that showed the highest K_d value of all studied soils (Fig. 3b, c). Compared to Experiment A the K_d values for Ni and Zn adsorption were significantly reduced in soil-KW (7% for Ni and 6% for Zn; $p < 0.01$) and increased in soil-KO (7% for Ni and 8% for Zn; $p < 0.01$). The changes were small but significant ($p < 0.01$) in the other soils (Fig. 3b, c).

3.2.3. *Interaction of untreated soils with simultaneously added HMs and DOM (Experiment C)*

In these experiments where HMs and DOM were added simultaneously, a positive correlation was found between the absolute amount of HMs added and the absolute amount of DOM adsorbed. The amount of DOM adsorbed ranged from 0.5 to 1.2 g C kg⁻¹ soil (Fig. 4). A significant difference was observed in the amount of adsorbed DOM between the 10 and 40 ml HM additions ($P < 0.001$) and the 40 and 70 ml HM additions ($p < 0.05$). The difference between the amount of DOM adsorbed after the 70 ml HM addition and the 100 ml HM addition was not significant ($p > 0.05$). No significant difference was observed in the amount of DOM adsorbed and the type of HM added ($p > 0.05$).

As in Experiments A and B, the K_d values for the three metals followed the sequence: Cu >> Ni $\approx$ Zn (Table 3). For Cu, the sequence in K_d values was similar to that in Experiment B and followed the content of smectite and CEC values in tested soils (Fig. 3a; Table 2). However, the differences between soils varied compared to Experiment B (Fig. 3). The highest relative increase in the K_d value for Cu affinity compared to the control Experiment (A) was registered in

soil-AH (6%) and soil-BO (10%). However, underlying the K_d value was a change in the shape of the affinity curve, with the amount of Cu immobilized at the two lowest additions (10 ml and 40 ml) being higher in Experiment A, but the amount of Cu immobilized at the two highest additions (70 ml and 100 ml) being higher in Experiment C. As a result the difference in affinity for the metals in soil-AH and soil-BO proved not statistically significant. In soil-KW and soil-KO (Fig. 3a) the affinity for Cu also increased. While the increase was smaller than in soil-AH and soil-BO it was statistically significant ($p < 0.01$). In soil-WQ the affinity for Cu significantly decreased (7%; $p < 0.01$).

The affinity sequence for Ni and Zn in Experiment C was similar as in the previous experiments (Soil-KW >>> KO > AH > BO > WQ). In all cases the K_d values for Ni and Zn increased with respect to the control experiment (Experiment A). For Ni the increase was significant ($p < 0.05$) for soils KO, BO, AH, and WQ (respectively 15.8 %, 12%, 9.9%, and 4.1%). No significant change was found with respect to the K_d values for Ni in soil-KW ($p > 0.05$) (Fig. 3b). For Zn the increase in the K_d values was significant ($p < 0.05$) for soils KO, BO, AH, WQ, and KW, and was, respectively 17.7%, 13.2%, 10.8%, 5.9%, and 2.9% (Fig. 3c).

3.2.4. *Interaction of soils with DOM and HMs added sequentially (Experiment D)*

As in Experiment C, increasing HM additions correlated with increasing adsorption of DOM still present in solution (i.e. not yet adsorbed after 2 h of shaking; Fig. 4). However, the amount of DOM adsorbed was larger in all studied soils in Experiment D (0.3-20%) than in Experiment C (Fig. 4).

Interactions of DOM and HMs did not change the general pattern of larger K_d values for Cu than for Zn and Ni. Also, as in all previous experiments, soil-KW still had the highest affinity to the tested metals (Fig. 2).

The K_d values for Cu in Experiment D were larger than those in all other Experiments (A, B, and C) with the exception of the soils that are rich in Fe-(hydr)oxide (soil-KW and soil-WQ) (Fig. 3a). In soil-KW, Cu had nearly the same K_d values in Experiments A, C, and D but the differences between them were significant ($p < 0.01$). Also in soil-WQ the differences in affinity were small but significant ($p < 0.01$; $p < 0.05$) (Fig. 3a). The largest relative increase in the K_d value compared to the control experiment (A) was registered in soil-AH (12.5%) and soil-BO (14.2%) (Fig. 3a). However, the larger K_d value was derived from the higher amounts of Cu immobilized at the two highest additions (70 ml and 100 ml) in Experiment D than in Experiment A. The amount of Cu immobilized at the two lowest additions (10 ml and 40 ml) was lower in Experiment D than in Experiment A, but not enough to result in an overall lower K_d value. As such, while appreciable, the overall difference in K_d value between Experiment A and D were not statistically significant.

The adsorption of Ni and Zn was enhanced in Experiment D compared to Experiments A and B, and was similar to that in Experiment C (Fig. 2b, c). Compared to Experiment A, the K_d values for Ni were significantly enhanced ($p < 0.05$) in soils KO, WQ, AH, and BO by respectively 15.4%, 7.7%, 11.7%, and 13.8% (Fig. 3b). No significant change was found in soil-KW ($p > 0.05$). The affinity of Zn was significantly enhanced ($p < 0.001$) in soils KW, KO, WQ, AH, and BO by 3%, 16.5%, 9.7%, 12.8%, and 15.2%, respectively (Fig. 3c).

Fig. 4. DOM adsorption by the studied soils in experiments C and D based on HMs addition.

4. Discussion

4.1. Overview of the adsorption behavior of the HMs in the soils tested in the four experiments

As expected, the adsorption behavior of the studied HMs was greatly influenced by soil properties (clay minerals; iron oxides; SOM originally present). Na^+ was the main exchangeable cation (Table 2) present in the studied soils, and according to the lyotropic series has a much lower affinity for clay surface than the multicharged HMs under study (Bohn et al., 1985; Essington, 2004). This explains the large net absorption of all HMs studied under all treatments. In addition, both the presence of DOM as well as the timing of its addition affected the

adsorption behavior of the HMs under study. An overview of the combined effects of the various treatments on the affinity of Cu, Ni and Zn for the solid phase in the soils tested is presented in Table 4. In general, there was a distinct division in behavior between Cu on the one hand and Ni and Zn on the other (Table 4).

Table 4. Summary of the results regarding the K_d values of the four different experiments. Details of the four experiments are given in figure 1.

Experiment	Cu affinity	Ni affinity	Zn affinity
Experiment A	Higher in Fe-oxide and smectite-rich soils (soil-KW and soil-WQ).	Higher in smectite-rich soils (soil-KW).	
Experiment B	Compared to Experiment A: reduced in Fe-oxide-rich soils (soil-KW and soil-WQ), slightly increased in Fe-oxide poor soils (soil-AH and soil-BO), and no change in the SOM-rich soil (soil-KO)	Compared to Experiment A: enhanced in the SOM-rich soil (soil-KO) and reduced in the other soils (particularly soil-KW, Fe-oxide and Mn-oxide rich soil).	
Experiment C	Compared to Experiments A and B: Enhanced in Fe-oxide-poor soils (soil-AH and soil-BO), slightly enhanced in the SOM-rich soil (soil-KO), and in the soil with high smectite content (soil-KW). Reduced in the Fe-oxide-rich soil (soil-WQ).	Compared to Experiment A and B: enhanced in all studied soils	
Experiment D	Comparing to Experiments A, B and C: enhanced in Fe-oxide-poor soils (soil-AH and soil-BO) and the SOM-rich soil (soil-KO). In the smectite-rich soil (soil-KW) slightly enhanced compared to Experiment A and C and enhanced compared to Experiment B.	Compared to Experiments A, B, and C: enhanced in soils with low smectite content and low CEC values (soil-WQ, soil-AH, and soil-BO). Compared to Experiments A and B also strongly enhanced in soils with high smectite content and high CEC values (soil-KW and soil-KO), but equal to Experiment C.	

4.2. Adsorption of Cu, Ni and Zn in relation to soil composition and (timing of) DOM addition

4.2.1. The influence of inherent differences in soil composition on HM adsorption (Experiment A)

The preferential adsorption of Cu over Ni and Zn (Table 3) was most likely caused by differences in binding type. It is well known that Cu adsorption depends on covalent interactions with the mineral structure while Ni and Zn are predominantly retained through electrostatic interactions with exchange sites in soils (Gomes et al., 2001; Covelo, et al., 2004). Overall similarities in the adsorption affinities of Ni and Zn are in line with previous work (Anderson and Christensen, 1988; Gomes et al. 2001).

Also the observed significant relationship ($p < 0.05$) between Cu adsorption and smectite content is in agreement with previous studies (e.g. Gomes et al., 2001). A large cation content has been reported to result in rapid exchange with Cu on the external clay minerals surfaces followed by a slow reaction in which Cu ions diffuse into the inter-layer of smectite minerals (Al-Qunaibit et al., 2004). In addition, Cu is known to form strong inner-sphere complexes with the surfaces of Fe-(hydr)oxide, although this correlation was not significant in our experiments. The presence of Fe-(hydr)oxide also increased the total surface area of the soils (Feller et al., 1992; Peacock and Sherman, 2004). All this is reflected in the large K_d values, and thus large affinity of Cu for soil-KW and soil-WQ that had the highest smectite and Fe-oxide contents, respectively. Whereas the lowest calculated K_d value was found in soil-BO due to its lowest smectite and Fe-oxide contents of all soils tested (Fig. 2a).

As expected smectite contents proved important for determining the affinity of Zn and Ni to the solid phase as well, given the large permanent negative charge of this family of clay minerals. In contrast to Cu, MnO_2 contents also seem to have played an important role in enhancing the affinities for both Ni and Zn (e.g., Sheng et al., 2011). As a result, soil-KW with the highest smectite and MnO_2 content showed the highest affinity to Ni and Zn (Tables 1 and 2).

In general, the inherently present SOM (Experiment A) had a weak effect on the adsorption of all HMs. Most likely, this was due to the absence of organic metal complexes due to low initial OM contents (Table 2) (Gao et al., 1997).

4.2.2. The influence of prior OM enrichment of the soils (Experiment B)

The successful enrichment of all soils, except soil-KO, with OM was related to the presence of smectite (Wang and Xing, 2005), Al and Fe oxides, and hydroxides (McKnight et al., 1992; Kaiser et al., 1996). Soil-KO did not adsorb measurable amounts of DOM, in spite of it containing large amounts of Al and Fe-(hydr)oxide, because this soil already had by far the largest inherent SOM content (Table 2). As a result, available sorption sites on the Al and Fe-(hydr)oxides were already saturated with OM (Kaiser et. al, 1996; Kaiser and Zech, 1998). This is further supported by the observed inverse relationships between native SOM contents (KO > WQ > AH > BO > KW) and the proportions of OM adsorbed during OM-enrichment (KW > BO > AH > WQ > KO) (Table 2).

The decreased affinity of Cu for the solid phase of most soils after their enrichment with OM as compared to the control experiment (Fig. 3) indicates a dominant role of the mineral phase in Cu binding. This is in line with its expected bonding through inner-sphere complexes, and with findings of Lair et al. (2007) who showed that even in the presence of SOM, Cu is preferentially bound by the mineral phase. Specifically, the decline in Cu affinity in the Fe-(hydr)oxide and smectite rich soils (soil-KW and soil-WQ; Table 2) could be explained by the blockage by OM coating of specific binding sites on the Fe-(hydr)oxides (Feller et al., 1992; Kaiser and Guggenberger, 2000) and of the interlamellar spaces and/or specific inner binding sites of

smectite (Zhuang and Yu, 2002) after enrichment with OM. Apparently, upon its adsorption, the OM did not adsorb enough Cu itself to counter the reduced affinity of the mineral phase. The lack of an appreciable effect in the other soils might be explained by smaller contents of Fe-(hydr)oxide in these soils also indicating an important role of Fe-(hydr)oxide for adsorption of Cu.

Analogous to Cu, the largest reduction of Ni and Zn affinity to the solid phase was observed for soil-KW and can be attributed to blockage of active sites on the mineral phase by OM coating (Fig. 3). This soil had the highest smectite content (Table 2) indicating binding to smectite as a dominant adsorption mechanism for Ni and Zn, albeit most likely through electrostatic interactions instead of inner-sphere complexation. Because Fe-(hydr)oxides do not have large permanent negative charge like smectite, electrostatic interactions will have been much smaller, explaining the smaller reduction of Ni and Zn affinity by OM compared to Cu in soil-WQ (Fig. 3). The statistically significant increase in Ni and Zn affinity in soil-KO upon OM enrichment was not expected given that the SOM content of this soil did not increase significantly upon OM enrichment. A possible explanation is that, while the absolute amount of OM did not increase, its molecular composition and/or steric configuration might have resulted in an increase in specific binding sites on the SOM present (Liu and Gonzales, 1999).

4.2.3. The effect of the timing of DOM on HM adsorption (Experiment C and D)

The affinity of the solid phase for Cu in soil-AH and soil-BO was significantly enhanced upon concurrent addition with DOM (Experiment C), and even more upon sequential addition (Experiment D; Fig. 3). This indicates that Cu was adsorbed on DOM that itself was previously

immobilized on specific solid phase sites not directly involved in the binding of HMs. In addition Cu was probably immobilized concurrently with DOM through cation bridging with the abundant smectite in these soils. The fact that the affinity of Cu was not enhanced in the oxides-rich soils (KW, WQ) suggests that the DOM in our experiments coated the specific binding sites for Cu on the solid phase. The resulting blocking of binding sites counteracted a potentially enhanced affinity through the previously mentioned mechanisms. In addition, in this case binding sites on DOM for Cu may have been occupied by Fe that also forms strong inner-sphere complexes with DOM (Senesi et al., 1986), thereby reducing the occurrence of both mechanisms.

For Ni and Zn, the increased affinity for binding on the solid phase upon OM addition was much smaller than for Cu and always increased regardless of the timing (Fig. 3). This confirms that electrostatic binding mechanisms dominate for these two metals, resulting in weaker association with DOM. The overall affinity to Ni and Zn remained the highest in soil-KW, which correlates to large surface area of its abundant smectite contents even in the face of adsorbed OM. In fact, several authors suggest that interactions between smectite and OM may promote Ni and Zn adsorption (Wattel-Koekkoek et al., 2003; Feng et al., 2005).

5. Conclusion

Our experiments confirmed the influence of the amount and timing of DOM addition on the affinity of Cu, Zn and Ni for the solid phase in the tested soils. The results suggest that Cu was mostly bound through inner sphere complexes on smectite and Fe-(hydr)oxides. Further, we found that association in the case of smectite was enhanced by inner sphere complexation with DOM bound to the solid phase directly and through cation bridges. As a result, in smectite- rich

soils, sequential addition of DOM and Cu resulted in a higher affinity for the solid phase than concurrent addition. In Fe-(hydr)oxides rich soils, the enhanced affinity by DOM addition was counteracted by coating of binding sites on the Fe-(hydr)oxides by OM.

Ni and Zn were found to bind predominantly through electrostatic interactions. As a result, overall affinity for the solid phase was lower than for Cu. Furthermore, the addition of DOM resulted in smaller increase in affinity than for Cu, and the timing of the addition (concurrent with the metals or sequential) had a much smaller effect. As such, our study points to interesting differences in the influence of DOM addition on the retention of Cu, Ni and Zn in clay rich soils that warrant further investigation.

Nevertheless, regardless of the differences found, in all experiments, for all metals and in all soils tested the great majority of the HMs in the system were adsorbed to the solid phase. This has important implications for the use of natural soil material for wastewater treatment. It means that readily available and abundant natural soil material can be used as a cheap and effective way of removing a large percentage of Ni, Cu and Zn from wastewater, regardless of whether the water is rich in DOM, and regardless of whether DOM had previously been added.

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References

- Ahlberg, G., O. Gustafsson, and P. Wedel. 2006. Leaching of metals from sewage sludge during one year and their relationship to particle size. *Environmental Pollution* 144, 545-553.
- Al-Qunaibit, M.H., W.K. Mekhemer, and A.A. Zaghloul. 2004. The adsorption of Cu (II) ions on bentonite-a kinetic study, *J. Colloid Interf. Sci.* 283, 316-321.
- Alvim Ferraz, M.C.M., and J.C.N. Lourenco. 2000. The influence of organic matter content of contaminated soils on the leaching rate of heavy metals. *Environ. Prog.* 19, 53–58.
- Anderson, P.R., and T.H. Christensen. 1988. Distribution coefficients of Cd, Co, Ni and Zn in soils. *J. Soil Sci.*, 39: 15-22.
- Benjamin, M.M., and J.O. Leckie. 1982. Effects of complexation by Cl, SO₄, and S₂ O₃ on adsorption behavior of Cd on oxide surfaces. *Environ. Sci. Technol.* 16:162-170.
- Bhattacharyya, K.G., and S.S. Gupta. 2008. Adsorption of a few heavy metals on natural and modified kaolinite and montmorillonite. A review. *Advances in Colloid and Interface Science* 140, 114-131.
- Bohn, H.L., B.L. McNeal, and G.A. O'Connor. 1985. *Soil Chemistry*. 2nd edition. Wiley Interscience Publication, John Wiley and Sons, New York.
- Brindley, G.W., and G. Brown. 1980. *Crystal Structure of Clay Minerals and their X-ray Identification*. Mineralogical Society, London.
- Chairidchai, P., and G.S.P. Ritchie. 1990. Zinc adsorption by a lateritic soil in the presence of organic ligands. *Soil Sci. SOC. Am. J.* 54, 1242-1248.
- Chen, H., Y. Zhao, and A.Wang. 2007. Removal of Cu(II) from aqueous solution by adsorption onto acid-activated palygorskite. *Journal of Hazardous Materials* 149, 346-354.

- Covelo, E.F., M.L. Andrade, and F.A. Vega. 2004. Heavy metal adsorption by humic umbrisols: selectivity sequences and competitive sorption kinetics. *Journal of Colloid and Interface Science* 280,1-8.
- Cruz-Guzman, M., R. Celis, M.C. Hermosin, W.C. Koskinen, E.A. Nater, and J. Cornejo. 2006. Heavy metal adsorption by montmorillonites modified with natural organic cations. *Soil Sci. Soc. Am. J.* 70, 215-221.
- Donat, R., A. Akdogan, E. Erdem, and H. Cetisli. 2005. Thermodynamics of Pb^{2+} and Ni^{2+} adsorption onto natural bentonite from aqueous solutions. *Journal of Colloid and Interface Science* 286, 43-52.
- Doula, M., A. Ioannou, and A. Dimirkou. 1999. Influence of ionic strength and pH on Cu^{2+} adsorption and on Mg^{2+} , Ca^{2+} , Mn^{2+} , Zn^{2+} release by kaolinite. *Agrochimica* 43, 215-222.
- Erdem, E., N. Karapinar, and R. Dona t. 2004. The removal of heavy metal cations by natural zeolites. *Journal of Colloid and Interface Science* 280, 309-314.
- Essington, M. J. 2004. *Soil and Water Chemistry: An integrative approach*. CRC Press, New York.
- Feller, C., E. Schouller, F. Thomas, J. Rouiller, and A.J. Herbillon. 1992. N_2 -BET specific surface areas and their relation- ships with secondary constituents and organic matter con- tents. *Soil Science* 153, 293-299.
- Feng, X.J., A.J. Simpson, and M.J. Simpson. 2005. Chemical and mineralogical controls on humic acid sorption to clay mineral surfaces. *Organic Geochemistry* 36, 1553-1566.
- Gao, S., W.J. Walker, R.A. Dahlgren, and J. Bold. 1997. Simultaneous sorption of Cd, Cu, Ni, Zn, Pb, and Cr on soils treated with sewage sludge supernatant. *Water, Air, and Soil pollution* 93: 331-345.
- Gomes, P.C., M.P.F. Fontes, A.G. Da Silva, E.S. Mendonça, and A.R. Netto. 2001. Selectivity

- sequence and competitive adsorption of heavy metals by Brazilian soils. Soil Science Society of America Journal 65: 1115-1121.
- Gu, X., Evans, J. Les, Barabash, and J. Sarah. 2010. Modeling the adsorption of Cd, Cu, Ni, Pb and Zn onto montmorillonite. *Geochemical et Cosmochmical Acta* 74, 5718-5728.
- Harter, R.D., and R. Naidu. 1995. Role of metal-organic complexation metal sorption by soils. *Advances in Agronomy*, Volume 55- Copyright 1995 by Academic Press, Inc.
- Hendershot, W.H., and M. Duquette. 1986. A simple bariumchloride method for determining cation exchange capacity and exchangeable cations, *Soil Sci. Soc. Am. J.*, 50, 605-608.
- Holmgren, G.G.S. 1967. A Rapid Citrate-Dithionite-Extractable Iron Procedure. *Soil Sc. Soc. Amer. Proc.* 31: 210.
- Ikhsan, J., B.B. Wells Johnson and M.J. Angove. 2005. Surface complexation modeling of the sorption of Zn(II) by montmorillonite, *Colloids Surf. A*, 252, 33-41.
- Jansen, B., K.G.J. Nierop and J.M. Verstraten. 2004. Mobilization of dissolved organic matter, aluminium and iron in podzol eluvial horizons as affected by formation of metal-organic complexes and interactions with solid soil material. *European Journal of Soil Science*, 55, 287-297.
- Jansen, B., K.G.J. Nierop and J.M. Verstraten. 2005. Mechanisms controlling the mobility of dissolved organic matter, aluminium and iron in podzol B horizons. *European Journal of Soil Science*, 56, 537-550.
- Kadirvelu, K., K. Thamaraiselvi, and C. Namasivayam. 2001. Removal of heavy metals from industrial wastewaters by adsorption onto activated carbon prepared from an agricultural solid waste. *Bioresource Technology* 76, 63-65.
- Kaiser, K., and G. Guggenberger. 2000. The role of DOM sorption to mineral surfaces in the

- preservation of organic matter in soils. *Org. Geochem.* 31:711-725.
- Kaiser, K., and G. Guggenberger. 2003. Mineral surfaces and soil organic matter. *Eur. J. Soil Sci.* 54 (2), 219-236.
- Kaiser, K., G. Guggenberger, and W. Zech. 1996. Sorption of DOM and DOM fractions to forest soils. *Geoderma* 74, 281-303.
- Kaiser, K., and W. Zech. 1998. Soil DOM sorption as influenced by organic and sesquioxide coatings and sorbed sulfate. *Soil Science Society of America Journal* 62, 129-136.
- Kalbitz, K., and R. Wennrich. 1998. Mobilization of heavy metals and arsenic in polluted wetland soils and its dependence on dissolved organic matter. *Science of the Total Environment*, 209 (1): 27- 39.
- Karlsson, T., P. Persson, and U. Skyllberg. 2006. Complexation of Copper(II) in Organic Soils and in Dissolved Organic Matter-EXAFS Evidence for Chelate Ring Structures. *Environ. Sci. Technol.*, 40 (8), pp 2623-2628.
- Lair, G.J., M.H. Gerzabek, and G. Haberhauer. 2007. Sorption of heavy metals on organic and inorganic soil constituents. *Environ. Chem. Lett.* 5, 23-27.
- Liu, A., and R.D. Gonzales. 1999. Adsorption/desorption in a system consisting of humic acid, heavy metals, and clay minerals. *Journal of colloid and interface science* 218, 225-232.
- McKnight, D., K.E. Bencala, G.W. Zellweger, G.R. Aiken, G.L. Feder, and K.A. Thorn. 1992. Sorption of dissolved organic carbon by hydrous aluminum and iron oxides occurring at the confluence of Deer Creek with the Snake River, Summit County, Colorado. *Environmental Science and Technology* 26, 1388-1396.
- Mehra, O.P., and M.L. Jackson. 1960. Iron oxide removal from soils and clays by a dithionite citrate system buffered with sodium bicarbonate. *Clays and Clay Minerals*, 7, 313-317.

- Mellah, A., and S. Chegrouche. 1997. The removal of zinc from aqueous solutions by natural bentonite. *Water Research*, 31, pp. 621-629.
- Motsi, T., N.A. Rowson, and M.J.H. Simmons. 2009. Adsorption of heavy metals from acid mine drainage by natural zeolite. *Int. J. Miner. Process.* 92, 42-48.
- Nodvin, S.C., C.T. Driscoll, and G.E. Likens. 1986. Simple partitioning of anions and dissolved organic carbon in a forest soil. *Soil Science* 142, 27-35.
- Peacock, C.L., and D.M. Sherman. 2004. Copper (II) sorption onto goethite, hematite and lepidocrocite: a surface complexation model based on ab initio molecular geometries and EXAFS spectroscopy. *Geochimica et Cosmochimica Acta* 68, 2623-2637.
- Searle, P.L., and B.K. Daly. 1977. The determination of aluminium, iron, manganese and silicon in acid oxalate soil extracts by flame emission and atomic absorption spectrometry, *Geoderma*, 19, 1-10.
- Senesi, N., G. Sposito, and J.P. Martin. 1986. Copper (II) and iron (II) complexation by soil humic acids: An IR and ESR study. *The Science of the Total Environment*, 55, 351-362.
- Sheng, G., J. Sheng, S. Yang, J. Hu, and X. Wang. 2011. Behavior and mechanism of Ni (II) uptake on MnO₂ by a combination of macroscopic and EXAFS investigation. *J. Radioanal. Nucl. Chem.*, 289: 129-135.
- Spark, K. M., J.D. Wells, and B.B. Johnson. 1995. Characterizing trace metal adsorption on kaolinite. *Eur. J. Soil Sci.* 46, 633-640.
- Sposito, G. 1989. *The Chemistry of Soils*. New York, Oxford University Press, Inc.
- Sprynskyy, M., T. Kowalkowski, H. Tutu, L.M. Cozmata, E.M. Cukrowska, and B. Buszewski. 2011. The Adsorption Properties of Agricultural and Forest Soils Towards Heavy Metal Ions (Ni, Cu, Zn, and Cd), *Soil and Sediment Contamination: An International Journal*, 20:1, 12-29.

- Srivastava, P., B. Singh, and M. Angove. 2005. Competitive adsorption behavior of heavy metals on kaolinite. *J. Colloid Interf. Sci.* 290, 28-38.
- Stevenson, F.J. 1982. *Humus Chemistry. Genesis, composition, reaction.* New York: Wiley.
- Stumm, W. 1992. *Chemistry of the solid-water interface.* New York: John Wiley and Sons. 428p.
- Udom, B.E., J.S.C. Mbagwu, J.K. Adesodun, N.N. Agbim. 2004. Distributions of zinc, copper, cadmium and lead in tropical ultisol after long-term disposal of sewage sludge. *Environ. Int.* 30, 467-470.
- Ussiri, D.A.N., and C.E. Johnson. 2004. Sorption of organic carbon fractions by Spodosol mineral horizons. *Soil Science Society of America Journal* 68, 253-262.
- Wang, K.J., and B.S. Xing. 2005. Structural and sorption characteristics of adsorbed humic acid on clay minerals. *J Environ Qual.* 2005 Jan-Feb; 34(1):342-9.
- Wattel-Koekkoek, E.J.W., P. Buurman, J. van der Plicht, E. Wattel, and N. van Breemen. 2003. Mean residence time of soil organic matter associated with kaolinite and smectite. *European Journal of Soil Science* 54, 269-278.
- Zeid, I.M., S.M. Ghazi, and D.M. Nabawy. 2013: Alleviation of heavy metals toxicity in waste water used for plant irrigation. *International journal of Agronomy and Plant Production.* Vol., 4 (5), 976-983.
- Zhuang, J., and G. Yu. 2002. Effects of surface coatings on electrochemical properties and contaminant sorption of clay minerals. *Chemosphere* 49, 619-628.