

Competitive sorption and desorption of trace elements by Tunisian Aridisols Calcorthids

Hamdi Sahraoui · María Luisa Andrade ·
Mohamed Hachicha · Flora Alonso Vega

Received: 8 December 2014 / Accepted: 26 February 2015 / Published online: 14 March 2015
© Springer-Verlag Berlin Heidelberg 2015

Abstract The sorption and retention processes play an important role in determining the bioavailability and fate of trace elements in soils. Sorption and desorption of Pb^{2+} , Zn^{2+} , Ni^{2+} , Cu^{2+} , and Co^{2+} in three Tunisian Aridisols Calcorthids (AR1, AR2, and AR3) were studied using batch experiments. Sorption and retention capacities were determined by means of K_r parameter and they were related to soil properties. The results showed that in all studied soils, K_r values for Pb^{2+} and Cu^{2+} were higher than those of Zn^{2+} , Ni^{2+} , and Co^{2+} indicating that soils have higher affinity for the first ones. The high sorption and retention capacity of the three studied soils is ascribed to their alkaline pH and their high carbonates contents favoring the precipitation of these elements. Moreover, bivariate correlation analysis showed that sorption and retention of the studied cations was also strongly correlated with clay fraction and Fe oxides contents. All soils show high sorption irreversibility of Pb^{2+} , Zn^{2+} , Ni^{2+} , Cu^{2+} , and Co^{2+} . The soils with highest sorption capacity show also the highest irreversibility.

Keywords Competitive sorption/retention · Trace elements · Aridisol · Sorption capacity · Selective sequences · Hysteresis

Responsible editor: Philippe Garrigues

H. Sahraoui (✉) · M. L. Andrade · F. A. Vega
Departamento de Biología Vexetal e Ciencia do Solo, Facultade de Biología, Universidade de Vigo, Lagoas, Marcosende, 36310, Vigo Pontevedra, Spain
e-mail: hamdi.sahraoui@gmail.com

H. Sahraoui · M. Hachicha
Institut National de Recherche en Génie Rural Eaux et Forêts,
Université de Carthage, Rue Hédi Elkarray, Elmenzah IV,
Tunis, Tunisia

Introduction

Recently, numerous investigations connected with trace elements in soils have been conducted in order to assess their availability or to point out the contamination of soils. The trace elements contamination for soil is mainly from the mining activities, tanneries, atmospheric deposition, reuse of wastewater, disposal of tailings, sewage irrigation, and use of pesticides and fertilizers (Alloway 2013).

The existence of trace elements in the solid phase is a result of many processes with sorption being the most important (Evans 1989; Harter and Naidu 2001; Selim 2012; Alloway 2013). Thus, it is important to study the sorption behavior and mechanism of trace elements on soils, which may help to assess risks to the environment and manage remedial activities. Many studies on individual sorption and retention of trace elements have been conducted by different type of soil or different components such clay minerals, acid soils, organic matter, and oxides (McKenzie 1980; McLaren et al. 1998; Gomes et al. 2001; Bradl 2004; Papageorgiou et al. 2009). However, there are few studies focusing on competitive component sorption and retention (Selim 2012). Furthermore, individual sorption studies may not adequately predict the behaviors of multiple trace elements in soil (Fontes et al. 2000). It is, therefore, desirable to study the competitive sorption and desorption for better predicting the mobility, bioavailability, and fate of trace elements in soil.

Soil contains complex mixture of components and characterized by varied physicochemical properties that could be involved in trace elements sorption process. Soil pH, the amount and type of clay minerals, carbonate contents, organic matter, oxides, and eventually simultaneous presence of competing trace elements affect sorption processes and their fate in soils (McGrath et al. 1988; Harter and Naidu 2001; Veeresh et al. 2003; Bradl 2004; Cerquiera et al. 2011a, 2011b). Despite the sorptive aspect that gives these properties and

components to the soil, trace elements can be desorbed from the surface of the soil colloid to the soil solution, and thus absorbed by plants or released to lower soil horizons and groundwater (Evans 1989; Backes et al. 1995; Selim 2012).

Sorption and desorption isotherms provide useful information about the soil retention capacity and show therefore whether sorption is reversible or irreversible (hysteresis). Vega et al. (2008) stated that K_f is a useful parameter for comparing sorption and retention capacity and hysteresis of different soils or materials for trace elements. K_f parameter has been used on previous studies of sorption and desorption of trace elements (Vega et al. 2009; Cerquiera et al. 2011a; Cerquiera et al. 2011b; Asensio et al. 2014).

The majority of the agricultural soils in Southern Tunisia are Aridisols type, characterized by rich-carbonate contents, poor organic matter (content is often lower than 1%), and sandy texture. Reuse of treated wastewater, spreading of different amendments like composts and sewage sludge, were used for striving water scarcity, and remediation to poor organic matter and poor-nutrients on southern Tunisian agricultural soils. Although these effluents generally display low concentrations of trace elements, their long-term use often results in the build-up of trace elements content in soils (Alloway 2013). Accumulation of these elements in agricultural soils constitutes a major environmental concern given that the trace elements translocation into crops and ultimately into the food chain has already been recorded (Bruemmer et al. 1986; Cheng 2003; Rattan et al. 2005; Solis et al. 2005; Zhao et al. 2014).

Therefore, studying their sorption and desorption became essential to assess their availability and fate in the soil.

Many trace elements, such as Pb, Zn, Cu, Ni, and Co, were more focused because of their accumulation in soil,

contamination to groundwater, and endangerment to safety of agricultural products (Alloway 2013). These elements are highly toxic and cumulative, causing risks to humans and the ecosystem, even at low dosages. They also often occur simultaneously in contamination soil and compete with each other for sorption sites (Echeverria et al. 1998; Veeresh et al. 2003; Papageorgiou et al. 2009; Cerquiera et al. 2011a, 2011b).

The competitive sorption of trace elements in soil may influence their retention, mobility, and the ultimate fate in the environments.

While numerous studies has been conducted to understand competitive sorption and desorption of trace elements in clay minerals, organic matter, oxides, and natural soils, less is known about their competitive sorption and desorption in calcareous soils. Soil carbonates may control sorption and retention of trace elements in calcareous soils (Hussein et al. 2002; Maftoun et al. 2002; Jalali and Moharrami 2007).

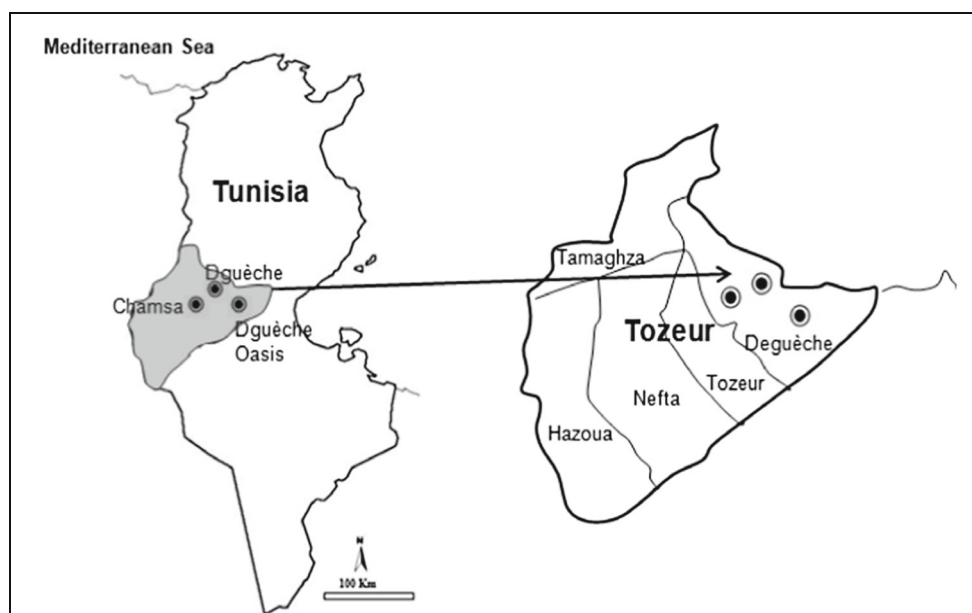
Thus, the objectives of the present study are to evaluate and compare the Pb^{2+} , Zn^{2+} , Ni^{2+} , Cu^{2+} , and Co^{2+} competitive sorption and desorption capacity and sorption hysteresis in three Tunisian Aridisols. The relationship between soil properties and the sorption capacities of these elements were also studied.

Materials and methods

Soil sampling

Soil samples from the surface layer (horizon A) were collected from three areas of Tozeur Province, southwestern Tunisia (Fig. 1). The three soils were classified as Aridisols Calcorthids soils. They were analyzed and extensively

Fig. 1 Location of sampling areas (AR1, AR2, and AR3) in Tozeur province (Southwestern Tunisia)



characterized to assess the influence of their components and properties on Pb^{2+} , Zn^{2+} , Ni^{2+} , Cu^{2+} , and Co^{2+} sorption and retention. Using an Eijkelkamp sampler, the samples were collected from the surface horizon of each soil and then stored in polyethylene bags. The samples were pooled, air dried, passed through a 2 mm sieve, homogenized, and stored until analysis. Subsamples were used for determining soil properties and for sorption and desorption experiments.

Soil characterization

Soil pH was determined with a pH meter in 2:1 water/soil extracts (Gutián and Carballas 1976). Particle-size distribution was determined following oxidation of organic matter with hydrogen peroxide; the fraction down to 50 μm was separated by sieving, and the lower fraction was characterized as Kroetsch and Wang (2008). The carbonate content was determined with a LECO-100 analyzer connected to a LECO-CN-2000. Effective cation exchange capacity (CEC) was determined by the method of Hendershot and Duquette (1986).

Total organic carbon (TOC) was determined in a module for solid analysis (SSM-5000, Shimadzu, Japan) coupled with a TOC analyzer (TNM-1, Shimadzu, Japan).

Oxides were determined using the method of Mehra and Jackson (1960); samples were shaken in a solution of sodium hydrogen carbonate and sodium citrate. Fe, Al, and Mn contents were determined in the extracts by inductively coupled plasma optical emission spectrometry (ICP-OES) in a Perkin-Elmer Optima 4300DV apparatus.

Clay mineralogy was determined by powder X-ray diffraction in a SIEMENS D-5000 Bragg–Brentano ($\theta/2\theta$) apparatus with a Cu anode, using 0.05 steps and 10 s per step (Brindley and Brown 1980).

Total dissolved trace elements were determined using the method of Houba et al. (2000) by calcium chloride extraction. Available trace elements were extracted with diethylenetriaminepentaacetate (DTPA) as described by Lindsay and Norwell (1978). Total contents were determined following acid digestion with a mixture of concentrated nitric, hydrochloric, and hydrofluoric acids (Marcet et al. 1997). Trace elements concentrations on the extractions were determined by ICP-OES.

Sorption and desorption experiments

Batch equilibrium experiments were constructed using the methods of Fontes et al. (2000), as modified by Harter and Naidu (2001). Sorption experiments were evaluated using single-trace element solutions containing equal mass concentrations of Pb^{2+} , Zn^{2+} , Ni^{2+} , Cu^{2+} , and Co^{2+} nitrates (0.05, 0.1, 0.2, 0.4, 0.5, 1, 2, 3, 4, and 5 $mmol L^{-1}$). Competitive sorption was evaluated using multi-trace element solutions of Pb^{2+} ,

Zn^{2+} , Ni^{2+} , Cu^{2+} , and Co^{2+} nitrates, each element had the same concentration (0.05, 0.1, 0.2, 0.4, 0.5, 1, 2, 3, 4, and 5 $mmol L^{-1}$).

In both experiments, the solutions contained 0.01 M $NaNO_3$ as background electrolyte. In each experiment, triplicate suspensions of 3 g of soil were equilibrated in 50 mL of sorption solution in polyethylene tubes. The solutions were shaken in a rotary shaker for 24 h at 25 °C in order to ensure sorption equilibrium. After equilibration, the samples were centrifuged at 4000 rpm for 5 min and the supernatant was filtered through Whatman 42 paper. Trace element concentrations in the supernatant were determined by ICP-OES. The pellet was set aside for use in the desorption stage of the experiment. The amount of each element sorbed was calculated from the difference between its concentration in solution before making contact with the soil and after equilibration.

Based on Madrid and Diaz-Barrientos (1992), desorption isotherms were constructed using the pellets obtained in the sorption experiments. The pellets were dried at 45 °C, weighed, resuspended in 100 mL of 0.01 M $NaNO_3$ solution, and shaken in a rotary shaker for 24 h in polyethylene tubes at 25 °C. The solutions were centrifuged at 4000 rpm for 5 min, and the supernatant was filtered through Whatman 42 paper. Finally, the concentration of Pb^{2+} , Zn^{2+} , Ni^{2+} , Cu^{2+} , and Co^{2+} in the supernatant was analyzed by ICP-OES in a Perkin-Elmer Optima 4300DV apparatus.

The quantities of each element that had been retained on the soil sample were calculated from the difference between the concentrations sorbed in the sorption experiments phase and the concentrations of the trace element in solution following desorption. Each sorption and desorption experiment was performed in triplicate.

Isotherms were constructed for each element by representing the amount of trace element sorbed or retained upon desorption by the soils ($\mu mol/g$ of dry soil), and the concentrations in the equilibrium solution at each added concentration ($\mu mol L^{-1}$).

Sorption and desorption isotherms were classified, whenever possible, as belonging to one or other of the profile types described by Giles et al. (1974).

Sorption and retention capacities and hysteresis

Sorption and retention capacity of soils was estimated as the slope K_r in the regression equation $C_{s,i} = K_r C_{p,i}$ (Vega et al. 2008), where $C_{s,i}$ is sorbed element i (μmol) per gram of soil at equilibrium, and $C_{p,i}$ is potentially sorbable element i , i.e., the amount of element i in the solution before contact with the soil, likewise per gram of soil.

As proved by Vega et al. (2008) and mentioned by Cerquiera et al. (2011a, 2011b), K_r is a useful parameter for comparing the sorption and retention capacities of different

soils or materials for trace elements under the same experimental conditions.

K_r is dimensionless and ranges from 0 to 1; otherwise, K_r adopts a null value for a soil that liberates all sorbed trace elements to the value 1 corresponding to a soil that releases no element during the desorption experiment phase. On other hand, a high K_r value indicates a high trace element sorption and retention by soil components; similarly, a low K_r value indicates that a high trace element amount is in the solution.

The irreversibility of sorption was obtained by calculating the hysteresis index (HI) defined as the ratio between the K_r values for retention and sorption (Vega et al. 2008). HI varies from 1 for a totally irreversible sorption and rather 0 for a non-irreversible sorption.

$$HI = K_{r,retention} / K_{r,sorption}$$

Statistical analysis

All results were statistically analyzed using the software SPSS v. 20.0 for Windows (SPSS, Inc., Chicago, IL). The statistical significance of differences was determined by one-way analysis of variance (ANOVA) and the least-significant difference (LSD) test. The influence of soil properties on sorption and retention capacity and on HI was investigated by means of pairwise Pearson correlation analysis.

Results and discussion

Characterization of the soils

Basic chemical and physical properties of the soils are shown in Table 1. The three soils have contrasting physical and chemical characteristics.

The highest clay percentage is detected in AR1 soil, whereas AR2 has poor clay contents and has the lowest sand and carbonate contents. AR3 has the highest sand percentage, whereas clay fraction is inexistent. For this reason, mineralogical analysis was realized only for AR1. The mineralogical analysis of the clay fraction of AR1 showed that the most abundant mineral is halite, and contains in addition, moderate kaolinite content and small quartz and mica contents. In general, all soils have a low CECE; the AR1 exhibits slightly higher values than AR2 and AR3. The sand content is significantly different between soils and varied between 90 % (AR1) and 60 % (AR2). The TOC is not detected for the three studied soils.

The pH of the soils is alkaline, and they have very similar pH values. Carbonate content, the major defining characteristic of Aridisols, is the most abundant component in the studied

soils, and there are no significant differences between AR1 and AR3 contents.

The AR1 soil has the highest proportion of Fe and Mn oxides. Fe oxide concentrations differ significantly between soils, whereas Mn and Al oxides concentrations are very low.

Total concentration of Pb^{2+} , Zn^{2+} , Ni^{2+} , Cu^{2+} , and Co^{2+} is within the range of the limits established in some reference guides (ICRCL 1987). Trace elements concentrations are significantly different among all studied soil, and the highest values for Zn^{2+} , Ni^{2+} , and Co^{2+} are detected in AR1 while the ones of Pb^{2+} and Cu^{2+} are in AR2 (Table 1). The contents extracted with DTPA and $CaCl_2$ methods are zero or close to zero.

Competitive sorption and retention isotherms

Figures 2 and 3 show the amounts of Pb^{2+} , Zn^{2+} , Ni^{2+} , Cu^{2+} , and Co^{2+} sorbed by AR1, AR2, and AR3 and retained upon desorption, as well as the concentrations in the equilibrium solution at each added concentration. Sorption and retention isotherms were described by the four general types of isotherms (L, H, S, and C) using the classification of Giles et al. (1974). Most are irregular because of difference on the soils' physicochemical properties and between-element competition for binding sites, especially in the case of retention isotherms on AR1 for the cations Zn^{2+} , Ni^{2+} , and Co^{2+} .

The sorption and retention isotherm shapes of Pb^{2+} , however, were identifiable for all soils. In most cases except for retention on AR1, they were almost vertical lines overlapped y-axis and close to C-type isotherms. Sorption and retention of Pb^{2+} increased vertically with very low initial concentration in the sorption solution, whereas this fact did not occur with Zn^{2+} , Ni^{2+} , and Co^{2+} which increased almost constantly and linearly with their initial concentration in the sorption solution and thus presented L curve type, except AR1. The constant slope, suggesting constant partitioning of the adsorbate between the solid interface and soil solution, characterized the Zn^{2+} , Ni^{2+} , and Co^{2+} sorption and retention isotherm on the studied soils except for AR1 retention case (Fig. 3).

The competitive sorption and retention isotherms of Cu^{2+} produced in almost all of the cases a C-type isotherm. The characteristic steep slope of the Cu^{2+} and Pb^{2+} sorption and retention isotherms in contrast to the linear and gentle slope of the Zn^{2+} , Ni^{2+} , and Co^{2+} sorption and retention isotherms indicated a stronger affinity for Cu^{2+} and Pb^{2+} than Zn^{2+} , Ni^{2+} , and Co^{2+} . The steep slope of Pb^{2+} and Cu^{2+} isotherms could have been produced by inner-sphere complexation (Sposito 1989).

Sorption and desorption capacities

Table 2 lists the equation regression, calculated K_r of sorption and retention and the corresponding coefficient of

Table 1 Chemical and physical properties of the studied soils

	Characteristic	AR1	AR2	AR3
	pH (H ₂ O)	8.76a	8.38a	8.27a
	TOC (g kg ⁻¹)	nd	nd	nd
	CECe cmol ₍₊₎ kg ⁻¹	2.34a	1.11b	0.73c
	Carbonates (%)	14a	3b	15a
	Sand (%)	78b	60c	90a
	Silt (%)	12b	37a	10b
	Clay (%)	10a	3b	nd
	Halite	XXXX	nd	nd
	Kaolinite	XX	nd	nd
	Quartz	X	nd	nd
	Mica	X	nd	nd
Oxide contents	Fe oxides (g kg ⁻¹)	0.88a	0.42c	0.70b
	Mn oxides (g kg ⁻¹)	0.02a	0.01b	0.01b
	Al oxides (g kg ⁻¹)	0.01a	nd	nd
Total content (mg kg ⁻¹)	Pb	4.20c	5.52a	4.52b
	Zn	8.40a	4.52c	6.70b
	Ni	22.03a	0.17c	14.73b
	Cu	2.35b	2.51a	2.51a
	Co	2.35a	1.34c	1.67b
CaCl ₂ fraction (mg kg ⁻¹)	Pb	nd	nd	nd
	Zn	nd	nd	nd
	Ni	0.06a	0.03b	0.04b
	Cu	0.00b	0.00b	0.02a
	Co	0.07a	0.05c	0.06b
Available (mg kg ⁻¹)	Pb	0.27a	0.01c	0.07a
	Zn	0.64a	0.02c	0.07b
	Ni	0.01	nd	nd
	Cu	0.10b	0.09b	0.30a
	Co	nd	0.01b	0.05a

X 3–10 %, XX 10–30 %, XXX 30–50 %, XXXX >50%, nd not detected. Values followed by different letters in each column differ significantly with *P* <0.05

determination (*R*²) for Pb²⁺, Zn²⁺, Ni²⁺, Cu²⁺, and Co²⁺ for the three studied soils.

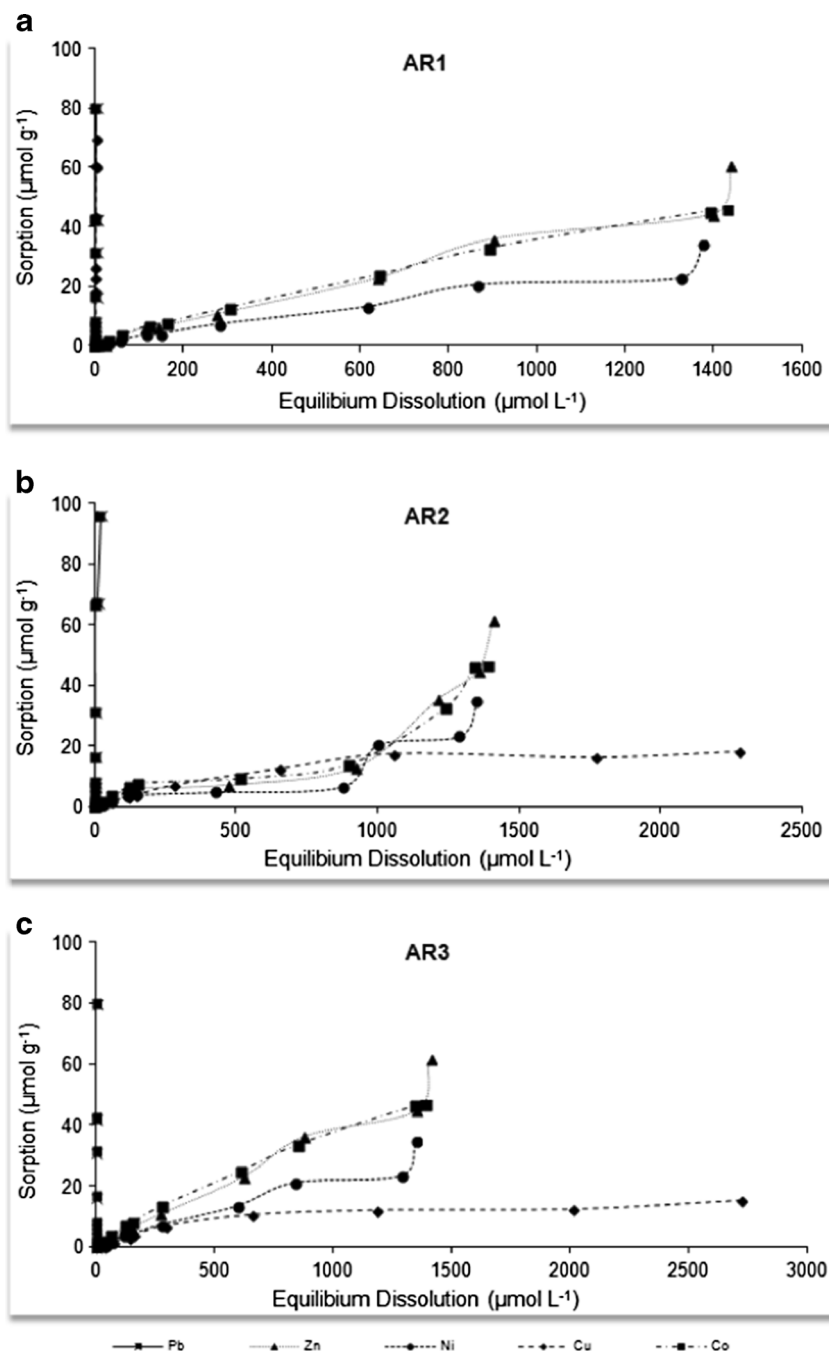
Regarding the studied soils, *K_r* values reveal that both AR1 and AR3 sorbed and retained larger amounts of all cations than AR2 does. By far, a high cations amount was sorbed and retained by AR3 which contain the highest carbonate contents (up to five times more than AR2) and despite the fact that it was characterized by the lowest CECE (0.73 cmol kg⁻¹) (Table 1).

The three studied soils sorbed and retained Pb²⁺ and Cu²⁺ more than twice as the lowest fixed cation (Ni²⁺). However, the AR1 had the highest sorption and retention capacity for Pb²⁺ and Cu²⁺, followed by AR3 and AR2 (Table 2). This trend was consistent essentially with the carbonate contents, and less markedly the percentage of clay and CECE (Table 1). Obviously, sorption of Pb²⁺ and Cu²⁺ increased with increasing clay, carbonate contents, and CECE of the

soil, which was in accordance with the result obtained by Echeverria et al. (1998) for soils with a range of chemical and physical properties.

Following McGrath et al. (1988) and Veeresh et al. (2003), in carbonated and alkaline soils and with no or little contents of Fe, Al, and Mn oxides, clays fraction and TOC, sorption, and retention are regulated by three different mechanisms: surface adsorption of colloids, complexation with surface functional groups, and the precipitation with hydroxides and carbonates. For Pb²⁺, fixation process is mainly regulated by strong covalent bonds (Bradl 2004) as well as the probability of formation of PbCO₃ (Lindsay 1979). Eventually, AR1 and AR3 had a sufficient amount of carbonate, clay, and Fe oxide to be able to form strong bonds that permitted the sorption and retention of Pb²⁺ regardless of the presence of the other cations.

Fig. 2 Competitive sorption isotherms of Pb^{2+} , Zn^{2+} , Ni^{2+} , Cu^{2+} , and Co^{2+} on AR1 (a), AR2 (b), and AR3(c)



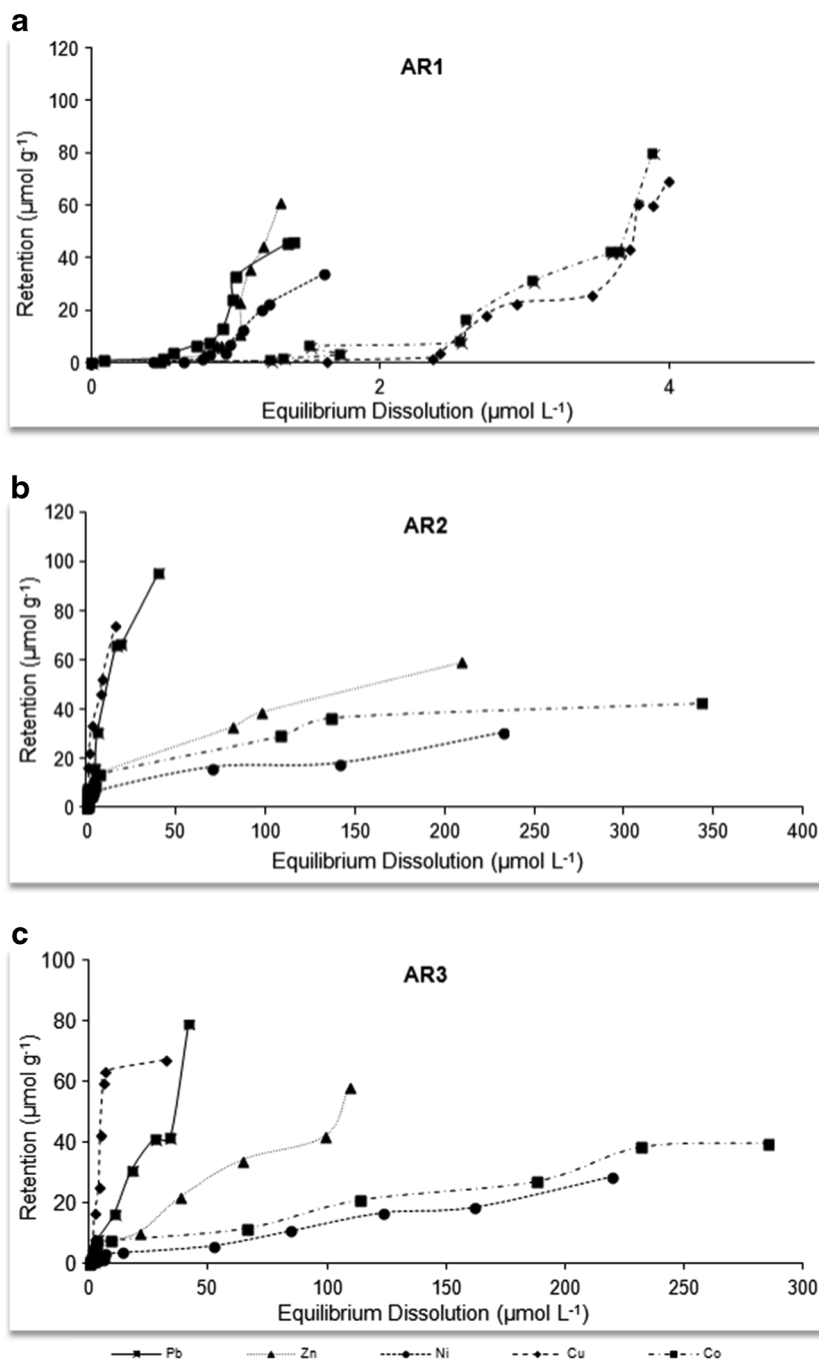
According to ion activity production of $\text{M}(\text{OH})_2$, Cu may be precipitated as an anionic hydroxyl complexes ($\text{Cu}(\text{OH})_2$, $\text{Cu}(\text{OH})_3^-$ and $\text{Cu}(\text{OH})_4^{2-}$) which are the dominant copper species in the soil solution with a pH above 8. Also, copper carbonate (CuCO_3) is the dominant inorganic soluble form of Cu^{2+} in alkaline soils and high carbonate soils like Aridisols.

Similarly to Pb^{2+} , the amount of Zn^{2+} sorbed and retained by AR1 and AR3 is greater than for AR2. The high capacity of these soils to sorb and retain Zn^{2+} could be also revealed to the high carbonate contents as described by Hussein et al. (2002). However, since the carbonate contents in AR1 and AR3 were

significantly the same and were much higher than that in AR2, higher sorption and retention capacities of Zn^{2+} is therefore presented in these two soils. On the other hand, because AR3 clay fraction was very low and not detected (Table 1), its sorption and retention capacities of Zn^{2+} were lower than AR1. These results are quite consistent with those obtained by Hussein et al. (2002) in Zn^{2+} sorption tests on Sudanese Aridisol.

Also as explained by Alloway (2013), in alkaline soils, zinc hydrolyses and the hydrolyzed species are strongly adsorbed to soil surfaces. Zn sorption increases due to the higher surface

Fig. 3 Competitive retention isotherms of Pb^{2+} , Zn^{2+} , Ni^{2+} , Cu^{2+} , and Co^{2+} on AR1 (a), AR2 (b), and AR3 (c)



charge density and precipitation of Zn^{2+} as $Zn(OH)_2$ is more prevalent. These formed compounds are more soluble than those formed for Pb^{2+} .

As to Co^{2+} and Ni^{2+} , the three soils present a low affinity to the two cations, which might indicate that the binding sites of studied soils had a larger affinity and selectivity for Pb^{2+} , Zn^{2+} , and Cu^{2+} than for Co^{2+} and Ni^{2+} (Table 2).

Nickel and Co^{2+} does not form insoluble precipitates in soils, and their retention are, therefore, exclusively regulated through sorption processes. Dähn et al. (2003) and Kim et al. (2006) found that the greatest amount of Ni^{2+} and Co^{2+} in

soils was associated with clays, Fe, and Mn oxides. However, since these contents in the three soils are low and approximately the same, the two cations are the lowest sorbed and retained and present the same order in the selectivity sequences (Table 2).

Overall the high sorption and retention capacities of studied soils containing low proportion of known components that most commonly influence trace elements fixation (i.e., oxides, organic matter, and clay fraction), we suggest that trace element fixation may be due to the formation of element-precipitates, since the pH of the soils is alkaline. These sorption

Table 2 K_f for sorption and retention of Pb^{2+} , Zn^{2+} , Ni^{2+} , Cu^{2+} , and Co^{2+}

		Sorption			Retention		
Pb^{2+}	Regression equation	AR1	AR2	AR3	AR1	AR2	AR3
	R^2	$y=0.999x$ 1	$y=0.846x$ 0.984	$y=0.999a$ 1	$y=0.997x$ 1	$y=0.839x$ 0.983	$y=0.982x$ 1
	K_f	0.999a ^a	0.846b	0.999a	0.997a	0.839c	0.982b
	Curve type	C	C	C	-	C	C
	Soil ranking		AR1≈AR3>AR2			AR1>AR3>AR2	
Zn^{2+}	Regression equation	$y=0.692x$	$y=0.673x$	$y=0.548x$	$y=0.691x$	$y=0.627x$	$y=0.662x$
	R^2	0.996	0.971	0.953	0.996	0.965	0.994
	K_f	0.692a	0.673b	0.548c	0.691a	0.627c	0.662b
	Curve type	L	-	L	-	L	L
	Soil ranking		AR1>AR2>AR3			AR1>AR3>AR2	
Ni^{2+}	Regression equation	$y=0.566x$	$y=0.701a$	$y=0.577a$	$y=0.565x$	$y=0.468x$	$y=0.470x$
	R^2	0.987	0.996	0.987	0.987	0.944	0.982
	K_f	0.566b	0.701a	0.577b	0.565a	0.468c	0.470b
	Curve type	L	-	L	-	L	L
	Soil ranking		AR2>AR3>AR2			AR1>AR3>AR2	
Cu^{2+}	Regression equation	$y=0.999x$	$y=0.731x$	$y=0.999a$	$y=0.997x$	$y=0.728x$	$y=0.993x$
	R^2	1	0.992	1	1	0.991	1
	K_f	0.999a	0.731b	0.999a	0.997a	0.728c	0.993b
	Curve type	C	L	L	-	C	L
	Soil ranking		AR1≈AR3>AR2			AR1>AR3>AR2	
Co^{2+}	Regression equation	$y=0.669x$	$y=0.646x$	$y=0.682a$	$y=0.668x$	$y=0.567x$	$y=0.573x$
	R^2	0.998	0.971	0.997	0.998	0.968	0.994
	K_f	0.669b	0.646c	0.682a	0.668a	0.567c	0.573b
	Curve type	L	-	L	-	L	L
	Soil ranking		AR3>AR1>AR2			AR1>AR3>AR2	
Selective sequences	$Pb \approx Cu > Zn > Co > Ni$	$Pb > Cu > Ni > Zn > Co$	$Pb > Cu > Co > Ni > Zn$	$Pb \approx Cu > Zn > Co > Ni$	$Pb > Cu > Zn > Co > Ni$	$Pb > Cu > Zn > Co > Ni$	

^a Values of same parameter followed by different letters in each line differ significantly with $P < 0.05$

Table 3 Correlations between soil characteristics and the K_r for sorption and retention of Pb^{2+} , Zn^{2+} , Ni^{2+} , Cu^{2+} , and Co^{2+}

	Sorption					Retention				
	Pb^{2+}	Zn^{2+}	Ni^{2+}	Cu^{2+}	Co^{2+}	Pb^{2+}	Zn^{2+}	Ni^{2+}	Cu^{2+}	Co^{2+}
pH	–	–	–	–	–	–	0.700*	0.972**	–	0.963**
Fe oxide	0.700*	–	–	0.702*	–	0.724*	0.761*	0.535*	0.704*	0.556*
Clay contents	–	–	–	–	–	–	–	0.941**	–	0.930**
CECe	0.609*	0.759*	0.798**	–	0.788*	0.978**	0.850**	0.609*	0.985**	0.629*
Carbonate contents	0.988**	0.967**	0.943**	0.987**	0.954**	–	–	–	–	–
Halite	–	–	–	–	–	–	0.837**	0.999**	–	0.998**
Kaolinite	–	–	–	–	–	–	0.835**	0.998**	–	0.997**
Quartz	–	–	–	–	–	–	0.829**	0.991**	–	0.989**
Mica	–	–	–	–	–	–	0.829**	0.991**	–	0.989**

*The correlation is significant at the level of 0.05 (bilateral). **The correlation is significant at the level of 0.01 (bilateral)

characteristics are in good agreement with previous studies on sorption of trace elements on Aridisols which have approximately the same characteristics as our selected soils (Elkhatib et al. 1991; Plassard et al. 2000; Fontes et al. 2000).

In addition, Bruemmer et al. (1986) has demonstrated that not only the alkalinity of soils lead to metal precipitation but also the high trace element concentrations in the added dissolution used in batch experiment can also be the reason to the low element’s solubility and also the small number of specific sorption sites. In our case, studied soils are characterized by their alkalinity due essentially to the presence of carbonates (Table 1) and also high trace element concentrations in sorption phase were used eventually which reached 5 mmol L⁻¹. Those both factors may have led to trace element carbonate precipitation reactions.

Bivariate correlation analysis was carried out to study the correlations between the properties and components of the soils and the competitive sorption and retention of Pb^{2+} , Zn^{2+} , Ni^{2+} , Cu^{2+} , and Co^{2+} (Table 3). As can be seen above, the sorption of Pb^{2+} , Zn^{2+} , Ni^{2+} , Cu^{2+} , and Co^{2+} was strongly correlated with carbonate contents indicating that this component is the major contributor on sorption and retention of these trace elements (Table 3). Also, significant correlations were found between the sorption and retention of Pb^{2+} , Zn^{2+} , Ni^{2+} , Cu^{2+} , and Co^{2+} and with CECe, except for Cu^{2+} sorption. Fe oxide presented a significant correlation mainly between all studied soils and retention capacity. The lack of a correlation between clay contents (except for Ni^{2+} and Co^{2+} retention) and Pb^{2+} , Zn^{2+} , Ni^{2+} , Cu^{2+} , and Co^{2+} sorption and retention capacities was probably related to the fact that the soil samples had poor clay contents (Table 1). Significant correlations have been established between the K_r for the competitive retention of Zn^{2+} , Ni^{2+} , and Co^{2+} and halite, kaolinite, quartz, and mica. Significant correlations have been established between the K_r for the competitive retention of Zn^{2+} , Ni^{2+} , and Co^{2+} and

halite, kaolinite, quartz, and mica. The positive correlation (Table 3) established between the studied trace elements content with the halite, kaolinite, quartz, and mica contents demonstrates that these minerals have a high capacity to retain Zn^{2+} , Ni^{2+} , and Co^{2+} , which agrees with the results obtained by several authors (Miranda-Trevino and Coles 2003; Agoubordea and Navia 2009).

Selectivity sequences of trace elements

Regarding the studied trace elements, Pb^{2+} and Cu^{2+} have been arranged in the first order of the sorption and retention sequences showing that their binding is much greater than coexisting elements binding and that Pb^{2+} and Cu^{2+} were less sensitive to the presence of the other cations. Abdelfattah and Wada (1981) reported that trace element affinity for 11 soil samples were in the order $Cu \approx Pb > Zn > Co$. Results of the study on sorption onto quartz at different pH values revealed the following sequence of sorption: $Pb > Zn > Ni > Cu$ (Honghai et al. 1999).

Jalali and Khanlari (2006) studied the sorption of trace elements on calcareous soils receiving spiked sewage sludge, and found that Pb^{2+} sorption was greater than coexisting elements.

Table 4 Hysteresis indices HI

	Soil	Pb^{2+}	Zn^{2+}	Ni^{2+}	Cu^{2+}	Co^{2+}
HI	AR1	0.998a	1a	0.998a	0.998a	0.999a
	AR2	0.992b	0.994b	0.854b	0.996ab	0.878b
	AR3	0.992b	0.998a	0.815c	0.994b	0.840c

Values of same parameter followed by different letters in each column differ significantly with $P < 0.05$

Table 5 Correlations between soil characteristics and hysteresis indices

Hysteresis indices HI					
	Pb ²⁺	Zn ²⁺	Ni ²⁺	Cu ²⁺	Co ²⁺
pH	0.905**	–	0.999**	0.846**	0.999**
Fe Oxide	–	0.747*	–	–	–
Clay contents	0.906**	–	0.985**	0.918**	0.987**
Carbonate contents	–	0.908**	–	–	–
Halite	0.957**	0.715*	0.979**	0.769*	0.973**
Kaolinite	0.952**	0.709*	0.978**	0.761*	0.972**
Quartz	0.933**	0.691*	0.971**	0.737*	0.965**
Mica	0.933**	0.691*	0.971**	0.737*	0.965**

*The correlation is significant at the level of 0.05 (bilateral). **The correlation is significant at the level of 0.01 (bilateral)

Alternatively, an interchange was found in the order of Zn²⁺, Ni²⁺, and Co²⁺ in the obtained sequences (Table 2). Similar result was also reported by Jalali and Moharrami (2007), who measured the sorption of trace elements on ten Iranian calcareous soils and found that Cu²⁺ are always sorbed to a large extent than Zn²⁺ and Ni²⁺ which presented, as the sequences in our study, an interchange on their order on the sorption selectivity sequence based on K_d distribution parameter. Furthermore, similarly to the obtained selectivity sequence in our study, some studies showed a Zn²⁺ and Ni²⁺ interchanging orders in the selectivity sequence of sorption, as indicated by the results of Antoniadis et al. (2007) for soils treated with sewage sludge and Fontes et al. (2000) for seven Brazilian soils.

In turn, McLaren et al. (1998) found that Co²⁺ was the most desorbed cations to soil solution on a binary sorption. According to the sequences reported by Backes et al. (1995), Co²⁺ is always desorbed to a large extent than coexisting elements on poor Fe and Mn oxide soils and soil clay minerals.

Hysteresis

Table 4 depicts the values of the hysteresis indices calculated from the sorption and retention capacity of the studied cations. Generally, the three soils presented high sorption irreversibility for Pb²⁺, Zn²⁺, Ni²⁺, Cu²⁺, and Co²⁺. The hysteresis of the sorption of Ni²⁺ and Co²⁺ on AR2 and AR3 is lower than on AR1, indicating their reversibility in these soils. On other hand, reversibility occurs in the soils with lowest clay fraction and oxides (Table 1). Respectively to the K_r values, the soils which have the highest sorption and retention capacity present the higher hysteresis indices.

A correlation analysis was carried out between the characteristics of the soils, and HI was studied (Table 5). The hysteresis of Pb²⁺, Ni²⁺, Cu²⁺, and Co²⁺ is correlated with pH, Fe oxide clay fraction, and carbonate contents meaning that these soils' characteristics influence the irreversibility of

the sorption of these cations. Apart from these soil characteristics, all the clay minerals present in it are also highly correlated with the irreversibility of the sorption of Pb²⁺, Ni²⁺, Cu²⁺, and Co²⁺ (Table 5).

Conclusion

In this study, sorption and desorption of Pb²⁺, Zn²⁺, Ni²⁺, Cu²⁺, and Co²⁺ in three Tunisian Aridisols were assessed with batch experiments at varying concentrations. The sorption and desorption isotherms, even the selective sequences of the trace element sorption based on the K_r , showed that Pb²⁺ and Cu²⁺ are the most strongly sorbed trace elements by these soils, whereas Zn²⁺, Ni²⁺, and Co²⁺ were the least sorbed ones. The correlation analysis indicated that for the competitive sorption and retention, the soil properties that were most strongly related to trace element sorption were carbonate contents and CECE of soils. More studies, eventually microscopic, are required to understand which process is controlling the sorption on these soils.

Acknowledgments This work was supported by the research project: A/029394/09. Interuniversity Cooperation Program and Scientific Research between Spain and Mediterranean countries (Spanish Ministry of Foreign Affairs and Cooperation). We also thank the Spanish Ministry of Science and Innovation for the research foundlings (Project CGL2010-16765/BTE).

References

- Abdelfattah A, Wada K (1981) Adsorption of lead, copper, zinc, cobalt and cadmium by soils that differ in cation exchange materials. *J Soil Sci* 32:271–283
- Agoubordea L, Navia R (2009) Heavy metals retention capacity of a non-conventional sorbent developed from a mixture of industrial and agricultural wastes. *J Hazard Mater* 167:536–544

- Alloway BJ (2013) Environmental pollution: heavy metals in soils: trace metals and metalloids
- Antoniadis V, Tsadilas CD, Ashworth DJ (2007) Monometal and competitive adsorption of heavy metals by sewage sludge amended soil. *Chemosphere* 68:489–494
- Asensio V, Forján R, Vega FA, Covelo EF (2014) Planting trees and amending with waste increases the capacity of mine tailings soils to retain Ni, Pb and Zn. *Span J Soil Sci* 4:225–238
- Backes CA, McLaren RG, Rate AW, Swift RS (1995) Kinetics of cadmium and cobalt desorption from iron and manganese oxides. *Soil Sci Soc Am J* 59:778–785
- Bradl HB (2004) Adsorption of heavy metal ions on soils and soils constituents. *J Colloid Interface Sci* 277:1–18
- Brindley GW, Brown G (1980) Crystal structures of clay minerals and their X-ray identification, Mineralogical Society (Eds.), London pp 495
- Bruemmer GW, Pflanzenemaehr Z, Gerth J, Herms U (1986) Heavy metal species, mobility and availability in soils. In *The Importance of Chemical “Speciation” in Environmental Processes*. Dahlem Workshop Reports 33: 169–192
- Cerqueira B, Covelo EF, Andrade ML, Vega FA (2011a) Retention and mobility of copper and lead in soils as influenced by soil horizon properties. *Pedosphere* 21:603–614
- Cerqueira B, Covelo EF, Andrade ML, Vega FA (2011b) The influence of soil properties on the individual and competitive sorption and desorption of Cu and Cd. *Geoderma* 162:20–26
- Cheng S (2003) Effects of heavy metals on plants and resistance mechanisms. *Environ Sci Pollut Res* 10:256–264
- Dähn R, Scheidegger AM, Manceau A, Schlegel ML, Baeyens B, Bradburry MH, Chateigner D (2003) Structural evidence for the sorption of Ni(II) atoms on the edges of montmorillonite clay minerals: a polarized x-ray absorption fine structure study. *Geochim Cosmochim Acta* 67:1–15
- Echeverria JC, Morera MT, Mazkiarin C, Garrido JJ (1998) Competitive sorption of heavy metals by soils. Isotherms and fractional factorial experiments. *Environ Pollut* 101:275–284
- Elkhatib EA, El-Shebiny G, Balba AM (1991) Lead sorption in calcareous soils. *Environ Pollut* 69:269–276
- Evans LJ (1989) Chemistry of metal retention by soils—several processes are explained. *Environ Sci Technol* 23:1046–1056
- Fontes MPF, Matos AT, Costa LM, Neves JCL (2000) Competitive adsorption of zinc, cadmium, copper and lead in three highly-weathered Brazilian soils. *Commun Soil Sci Plant Anal* 31:2939–2958
- Giles CH, Smith D, Huitson A (1974) A general treatment and classification of the solute adsorption isotherm: I. Theoretical. *J Colloid Interface Sci* 47:755–765
- Gomes PC, Fontes MPF, da Silva AG, Mendonça EDS, Netto AR (2001) Selectivity sequence and competitive adsorption of heavy metals by Brazilian soils. *Soil Sci Soc Am J* 65:1115–1121
- Gutián F, Carballas T (1976) *Técnicas de Análisis de Suelos* (In Spanish). Editorial Pico Sacro, Santiago de Compostela
- Harter RD, Naidu R (2001) An assessment of environmental and solution parameter impact on trace metal sorption by soils. *Soil Sci Soc Am J* 65:597–612
- Hendershot WH, Duquette M (1986) A simple barium chloride method for determining cation exchange capacity and exchangeable cations. *Soil Sci Soc Am J* 50:605–608
- Honghai W, Daqing W, Jinlian P (1999) Experimental study on surface reactions of heavy metal ions with quartz-aqueous ion concentration dependence. *Chin J Geochem* 18:201–207
- Houba VJG, Temminghoff EJM, Gaikhorst GA, Van Vark W (2000) Soil analysis procedures using 0.01 M calcium chloride as extraction reagent. *Commun Soil Sci Plant Anal* 31:1299–1396
- Hussein AA, Elamin EA, ElMahi YE (2002) Zinc sorption in two vertisol and one aridisol series as affected by electrolyte concentration and sodium adsorption ratio. *U K J Agric Sci* 10:1–13
- ICRCL (1987) International committee on the redevelopment of contaminated land. *Guidance on the Assessment and Redevelopment of Contaminated Land*. Departement of the Environment Interdepartmental Committee on the Redevelopment of Contaminated Land, Guidance Note 59/83. London
- Jalali M, Khanlari ZV (2006) Mobility and distribution of zinc, cadmium and lead in calcareous soils receiving spiked sewage sludge. *Soil Sediment Contam* 15:603–620
- Jalali M, Moharrami S (2007) Competitive adsorption of trace elements in calcareous soils of western Iran. *Geoderma* 140:156–163
- Kim JK, Jung JY, Kim JH, Kim MG, Kashiwagi T, Kang YT (2006) The effect of chemical surfactants on the absorption performance during NH₃/H₂O bubble absorption process. *Int J Refrig* 29:170–177
- Kroetsch D, Wang C (2008) Particle size distribution. In: Carter, MR and Gregorich, EG (eds.) *Soil sampling and methods of analysis* (2nd 411 Ed). Canadian Society of Soil Science, CRC Press, Boca Raton, FL 713–726
- Lindsay WL, Norwell WA (1978) Development of a DTPA soil test for zinc, iron, manganese and copper. *Soil Sci Soc Am J* 42:421–428
- Lindsay WL (1979) *Chemical Equilibria in Soils*. Wiley, New York
- Madrid L, Diaz-Barrientos E (1992) Influence of carbonate on the reaction of heavy metals in soils. *J Soil Sci* 43:709–721
- Maftoun M, Karimian N, Moshiri F (2002) Sorption characteristics of copper (II) in selected calcareous soils of Iran in relation to soil properties. *Commun Soil Sci Plant Anal* 33:2279–2289
- Marcet P, Andrade ML, Montero MJ (1997) Efficacité d’une méthode de digestion par microondes pour la détermination de Fe, Mn, Zn, Cu, Pb Cr Al et Cd en sédiments (In French). In: R. Prost (Ed.), *Contaminated soils: Third International Conference on the Biogeochemistry of Trace-Elements*
- McGrath SP, Brookes PC, Giller KE (1988) Effect of potentially toxic metals in soil derived from past application of sewage sludge on nitrogen fixation by *Trifolium repens* L. *Soil Biol Biochem* 20: 415–424
- McKenzie RM (1980) The adsorption of lead and other heavy metals on oxides of manganese and iron. *Aust J Soil Res* 18:61–73
- McLaren RG, Backes CA, Rate AW, Swift RS (1998) Cadmium and cobalt desorption kinetics from soil clays: effect of sorption period. *Soil Sci Soc Am J* 62:332–337
- Mehra OP, Jackson ML (1960) Iron oxide removal from soils and clays by a dithionite–citrate system buffered with sodium bicarbonate. In: *Clays Clay Min. Seventh Conference*, pp 317–327
- Miranda-Trevino JC, Coles CA (2003) Kaolinite properties, structure and influence of metal retention on pH. *Appl Clay Sci* 23:133–139
- Papageorgiou SK, Katsaros FK, Kouvelos EP, Kanellopoulos NK (2009) Prediction of binary adsorption isotherms of Cu²⁺, Cd²⁺ and Pb²⁺ on calcium alginate beads from single adsorption data. *J Hazard Mater* 162:1347–1354
- Plassard F, Winiarski T, Petit-Ramel M (2000) Retention and distribution of three heavy metals in a carbonated soil: comparison between batch and unsaturated column studies. *J Contam Hydrol* 42:99–111
- Rattan RK, Datta SP, Chhonkar PK, Suribabu K, Singh AK (2005) Long term impact of irrigation with sewage effluents on heavy metal content in soils, crops and groundwater—a case study. *Agric Ecosyst Environ* 109:310–322
- Selim HM (2012) *Competitive sorption and transport of heavy metals in soils and geological media*. CRC Press
- Solis C, Andrade E, Mireles A, Reyes-Solis IE, Garcia-Calderon N, Lagunas-Solar MC, Pina CU, Flocchini RG (2005) Distribution of heavy metals in plants cultivated with wastewater irrigated soils during different periods of time. *Nucl Inst Methods Phys Res B* 241:351–355
- Sposito G (1989) *The chemistry of soils*. Oxford Univ. Press

- Veeresh H, Tripathy S, Chaudhuri D, Hart BR, Powell MA (2003) Competitive adsorption behavior of selected heavy metals in three soil types of India amended with fly ash and sewage sludge. *Environ Geol* 44:363–370
- Vega FA, Covelo EF, Andrade ML (2008) A versatile parameter for comparing the capacities of soils for sorption and retention of heavy metals dumped individually or together: results for cadmium, copper and lead in twenty soil horizons. *J Colloid Interface Sci* 327:275–286
- Vega FA, Covelo EF, Andrade ML (2009) Hysteresis in the individual and competitive sorption of cadmium, copper and lead by various soil horizons. *J Colloid Interface Sci* 331:312–317
- Zhao Y, Yan Z, Qin J, Xiao Z (2014) Effects of long-term cattle manure application on soil properties and soil heavy metals in corn seed production in Northwest China. *Environ Sci Pollut Res* 21:7586–7595