

# Sorption of Zn(II) and Cu(II) by four Argentinean soils as affected by pH, oxides, organic matter and clay content

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**Abstract** Increasing heavy metal applications to agricultural soils in the form of phosphatic fertilizers and/or atmospheric deposition have led to extensive research on the chemistry of Zn and Cu in soils. Cu(II) and Zn(II) sorption onto different soil fractions of three Mollisols and one Entisol from the southwest of Buenos Aires Province, Argentina, was studied. Different variables affecting the sorption capacity such as pH, cation exchange capacity, specific surface area (SSA), type and amount of clay minerals present, content of Fe-, Al-, and Mn-oxides and oxohydroxides, organic matter and electric charge parameters were investigated. To assess the monometal sorption, batch equilibrium experiments were performed using Cu(II) and Zn(II) metal solutions over a pH range from 4.0 to 7.0. The increase in metal sorption with increasing pH for both metal cations was attributed to an increase in the negative surface charges. At pH 5.0, Cu(II) showed more affinity than Zn(II) for reactive surface soil sites. Removal of organic matter via H<sub>2</sub>O<sub>2</sub> treatment (<2-mm OMR fraction) dramatically decreased the sorption of both cations; however, Cu(II) was sorbed more than Zn(II). The variation in SSA (obtained by water vapor adsorption) in <2- $\mu$ m (clay fraction) and <2-mm (whole soil fraction)

after Zn(II)/Cu(II) sorption at pH 4 and 6 reflected a different interaction between both cations and binding surface sites. Sorption isotherms correlated better with Langmuir than Freundlich equations. Sorption capacities ( $q_{\max}$ ) in <2- $\mu$ m fraction, ranged from 166 to 111 mmol kg<sup>-1</sup> for Cu(II), and from 62 to 31 mmol kg<sup>-1</sup> for Zn(II). This study extends the understanding of the sorption mechanisms of Cu(II) and Zn(II) to agricultural soils from the semi-arid Pampean region of Argentina. An understanding of the local soil environment is important in order to reduce or prevent contamination of this valuable resource, especially from fertilizers and other such anthropogenic additions to the soil.

**Keywords** Sorption processes · Heavy metals · Clay minerals · Agricultural soils

## Introduction

It is well known that the levels of heavy metals in the environment have greatly increased, mainly in the last few decades, due to human activities causing serious pollution problems in different aquatic, atmospheric, and terrestrial systems. In fact, although many heavy metals are essential in small amounts for the optimal functioning of biological cycles, most of them exert toxic effects at the concentrations encountered in polluted environments (Sarfrazi et al. 2007). Several studies have indicated a direct relationship between the concentrations of heavy metals in crops and the contamination levels found in soils (Nabulo et al. 2008). This is a concern because elevated levels of heavy metals in edible crops pose a serious threat to human health. Human intake of excessively large doses of Cu leads to neurological disorders (Eren and Afsin 2008), and

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excessive Zn intake may contribute to elevated blood pressure and brain damage (Yanagisawa et al. 2004). The bioavailability of metal ions depends not only on their total concentration, but also on their mobility and reactivity with other components of the ecosystem (Abollino et al. 2002).

In addition to pollution problems originating from anthropic activities, soils naturally contain innate background levels of Cu and Zn at concentrations dependent on the nature of the parent material, but which are generally higher in basic soils than in acid soils.

Highly significant positive correlations have been found between the ratio of metal concentration in the solid phase to that in the equilibrium solution (distribution coefficient) and the maximum sorption capacity of metal ions, pH and the cation exchange capacity of soils, suggesting that these are the key parameters controlling the solubility and mobility of metal ions in soils (Lu and Xu 2008).

Metal mobility and bioavailability through a given soil depends on the sorption/desorption behavior of soil components, where “sorption” encompasses adsorption, surface precipitation and fixation (Ming-Kuí et al. 2006; Covelo et al. 2008; Cerqueira et al. 2011; Lafont et al. 2013). The soil property that most affects the sorption of heavy metals is organic matter content (Bradl 2004), and the binding of metal ions to organic matter often controls the concentration of free ions in the soil solution and the toxicity of the metal (Abollino et al. 2003). Consequently, this property is of immediate relevance to the bioavailability of the metal ion considered.

Another soil property that also significantly affects metal sorption processes is the type and amount of clay minerals present. Clay minerals are good sorbents for metal ions from aqueous solutions owing to their high cation exchange capacity and high specific surface area associated with their small particle sizes (Gupta and Bhattacharyya 2012; Li et al. 2013). In addition, the surfaces of Fe, Al and Mn oxides contain functional groups that are capable of interacting with species in solution. These mineral surfaces are amphoteric (able to act as both acids and bases), and thus, are associated in sorption–desorption processes.

Heavy metals in soils may be inherited from the parent material, but the background levels can be elevated by a range of anthropic activities including agricultural, mining and industrial operations all of which can produce a decrease in soil quality (Pérez-Novo et al. 2008; Nabulo et al. 2008; Waterlot et al. 2013; Zhuang et al. 2013). In addition, heavy metals are influenced by the soil physicochemical properties, and soil and crop management practices. Among the anthropic agricultural activities, the use of organic and chemical fertilizers and pesticides are common. Fertilizers used as carriers of macro and micronutrient and other amendments used in agriculture also contribute to heavy metal additions to the surface soil. In general, in

fertilizers carrying N, P and K, Zn and Cu exist as main impurities. Phosphate fertilizers are among the main sources of heavy metal inputs to agricultural systems (Srinivasarao et al. 2014) while mineral fertilizers containing nitrogen in the form of N-NO<sub>3</sub>, N-NH<sub>4</sub> or N-NH<sub>2</sub> also can cause an increase of Cu and Zn concentrations affecting the buffer properties of the soils (Smolén and Sady 2007).

Few studies on heavy metals in Argentina have been carried out in soils of Buenos Aires city and neighboring agricultural areas (Lavado et al. 1998) and industrial areas (Lafont et al. 2013). However despite this, the semi-arid Pampean region is one of the major agricultural regions of Argentina and there is a need to assess the response of different soil subgroups to potential contamination from agricultural, and other, sources of pollution. Wheat, barley, oat, soybean, sunflower, garlic, and onion are relevant species grown in the southwest of the Buenos Aires Province. These crops have great economic importance, especially as a result of changing consumer habits towards healthy eating and increased awareness of their healing properties, in the Argentinean region studied. The intensification of agriculture, without crop rotation, has caused the loss of nutrients in many soils of this region. To avoid this chemical degradation and in order to compensate the extraction of nutrients by crops, fertilizers are added. Furthermore, these soils are characterized by a genetically very low total and available P content. P deficiencies are a limiting factor for crop growth, whereby the phosphate fertilization practice is widespread. In this region phosphate or mixtures of phosphate-sulfur and nitrogen fertilizers are used. The addition of these fertilizers involves involuntary Cu and Zn inputs to the soil system. Adding fertilizers to soils could cause a potential situation of soil contamination.

Then, a more detailed understanding of the soil environment, and more specifically the behavior of likely soil contaminants, is required. In this study, Cu(II) and Zn(II) sorption onto four soil subgroups from the semiarid Pampean region of Argentina was investigated. Although sorption isotherms are used extensively to characterize the nature of soil retention phenomena, information regarding sorption behavior on soils from this region is very limited. Sorption studies were carried out on three subsamples: whole soil (<2-mm), soil samples where organic matter was partially removed (<2-mm OMR), and soil clay fraction (<2- $\mu$ m). Adsorption isotherms are reported and the effects of pH, organic matter, specific surface area, oxides and clay content are investigated. Therefore, our main objectives were (1) to investigate the effects of the major physicochemical soil properties on the sorption of Cu(II) and Zn(II), (2) to provide a more detailed understanding of the sorption mechanisms between typical agricultural soils

and selected metals, and (3) to provide knowledge in order to reduce the risk of contamination of the soils in this region. Furthermore, the results of the detailed analysis of the parameters involved in sorption processes will be useful for other soils with similar physicochemical characteristics in other regions of the world.

## Materials and methods

### Soil samples

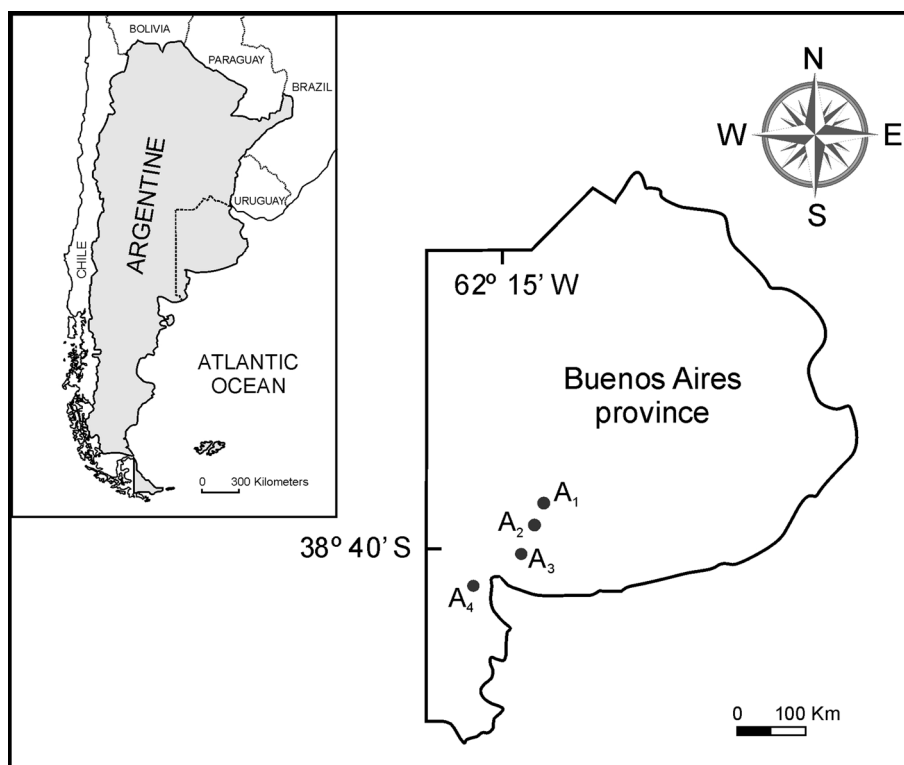
Four agricultural surface soil subgroups (0–12 cm depth), representing the A<sub>p</sub> horizon, were collected from the southwest of the Province of Buenos Aires in the Pampean Region of Argentina, denoted A<sub>1</sub>, A<sub>2</sub>, A<sub>3</sub>, and A<sub>4</sub> (Fig. 1).

At each site, 20 topsoil samples were randomly taken from an area of approximately 0.1 ha and mixed to form a composite topsoil sample and stored in polyethylene bags. Soils of this region contain mainly quartz, Na-rich feldspars and plagioclase in the sand fraction, and illite, interstratified illite–smectite, quartz, Na-rich feldspars and mica in the silt and clay fraction, with Ca<sup>2+</sup> and Mg<sup>2+</sup> as the main exchangeable cations (Acebal et al. 2000). Soils were classified following the Soil Taxonomy system (USDA 1999) as three Mollisols and one Entisol: Typic Argiudoll (A<sub>1</sub>), Pachic Argiudoll (A<sub>2</sub>), Petrocalcic Paleustol (A<sub>3</sub>), and Typic Ustipsament (A<sub>4</sub>). These soils

were chosen according to their chemical and mineralogical characteristics in order to elucidate different behaviors on heavy metal sorption. Characteristics of the soil surfaces are the final determinative factors affecting sorption of metals. Generally, the ability of the soil to sorb heavy metals depends upon the type (mainly, smectites) and the amount of clay, as well as organic matter content. Soil samples were air-dried at room temperature, ground, and passed through a 2-mm stainless steel sieve to obtain the <2-mm size fraction. The clay fraction (<2-μm) was obtained by sedimentation techniques using Stoke’s law: a 1:3 <2-mm-soil sample/deionised water suspension was mixed thoroughly for 16 h, and then centrifuged at 500 rpm for 6 min. The <2-μm clay fraction was siphoned from the suspension. The procedure was repeated 4–5 times until the suspension was clear or only slightly cloudy following centrifugation (Aguirre 1987). In order to verify the validity of the extraction method a hydrometer Bouyoucos (Fisherbrand Model # 14-331-5c) was used. To prevent contamination by inorganic components deionised H<sub>2</sub>O, as a dispersing agent, was used. No adverse effects on oxide solubilities with wet sedimentation techniques were observed. The solubility of Fe<sup>3+</sup> oxides is low and Fe<sup>2+</sup> oxides are sparingly soluble in water, Mn oxides are present in small amounts, and Al<sup>3+</sup> occurs in appreciable extent as aluminosilicates in these soils.

In many natural systems, organic matter exists in close association with hydrous aluminum and iron phases

**Fig. 1** Location of sampling stations in Argentina



showing particularly high affinity with mineral phases. As soil organic matter plays an important role in sorption processes, and in order to evaluate the sorption behavior of the other phases present, subsamples of each soil (<2-mm) were treated with  $\text{H}_2\text{O}_2$  at 65–70 °C to remove most of the organic matter (Kunze and Dixon 1986). It is well known that organic matter cannot be completely removed from soils by wet oxidative treatments, the removal efficiency being dependent on reaction conditions and sample properties. The presence of carbonates, chemically resistant organic compounds, and the protection of organic matter by mineral surfaces are responsible factors for incomplete C removal (Mikutta et al. 2005). These subsamples were labeled as organic matter removal (<2-mm OMR). All subsamples were homogenized and stored in polyethylene bags for further analysis.

### Soil samples characterization

Particle size distributions were evaluated using the hydrometer method (Gee and Bauder 1986). Soil pH was determined in a 1:2.5 soil/deionised water suspension and in a soil/KCl suspension using a glass pH electrode in an Orion digital ion analyzer (Model 701A). Total organic carbon (TOC) was measured by dry combustion using a LECO CR-12 Carbon System Analyzer (Model 781-600). Soil sampling areas were selected to cover a range in TOC (from 0.71 to 4.78 %). Cation exchange capacity (CEC) was obtained by exchanging the soils with  $\text{NH}_4\text{OAc}$  at pH 7 (Sumner and Miller 1996). The specific surface area (SSA) was determined using the EGME (ethylene glycol monoethyl ether) method ( $S_{\text{EGME}}$ ) (Carter et al. 1965), and also by water vapor adsorption ( $S_w$ ) at a relative humidity of 56 % (Torres Sánchez and Falasca 1997). Samples were dried in a vacuum at room temperature prior to  $S_{\text{EGME}}$  or  $S_w$  measurements. In addition, total Fe, Al and Mn were determined by fusion with  $\text{Na}_2\text{CO}_3$  (Hossner 1996), amorphous Fe, Al and Mn oxides by acid oxalate extraction (OX) (McKeague and Day 1966), and crystalline Fe, Al and Mn oxides by the dithionite-citrate-bicarbonate (DCB) method (Mehra and Jackson 1960). Fe, Al and Mn contents were measured by flame atomic absorption spectrometry (FAAS) (G.B.C. 932 B Australia). Fe, Al and Mn oxides are involved in adsorption–desorption processes. Fe oxides (hematite and goethite) are present at low concentrations occurring with varying degrees of crystallinity and Al substitution,  $\text{Al}^{3+}$  occurs in Al-substituted sites in the soil iron oxides, and Mn oxides are scarce and very sensitive to pH changes (Acebal et al. 2000).

The point of zero charge (PZC) was evaluated by the addition method (Regazzoni 1984); while the isoelectric point (IEP) was determined by the diffusion potential method (Tschapek et al. 1989). Both PZC and IEP are the

pH value at which the surface charge balance is zero, in the absence or presence of specific adsorption, respectively (Taubaso et al. 2004).

The mineralogy of the clay fraction of each soil sample was performed by X-ray diffraction (XRD) on semioriented (powder) samples in a Philips PW 1011/00 diffractometer operated with a power supply at 40 kV and 30 mA, 1° divergence and detector slits, 0.02° ( $2\theta$ ) step size, counting time of 10 s per step and patterns collected from 3° to 65° ( $2\theta$ ). The Rietveld (Rietveld 1969) quantitative method was applied to the soil's clay fractions. A profile matching program (“FULLPROF”; Rodríguez-Caravajal 1990) was used to obtain the refinement and subsequent quantitative analysis to compensate for the existence of phases with incomplete structural data (Taubaso et al. 2004). The starting crystallographic data for each phase were extracted from card data of powder diffraction files compiled by JCPDS. For smectite quantification, the fitting was carried out without taking into account the atomic positions. The structure factors were calculated based on the measured intensities of a sample containing 99 % of Na-montmorillonite (Lombardi et al. 2002) whose pattern matched closely with that present in the samples studied.

All analyses were performed in duplicate, and the mean values of the data are presented.

### Sorption experiments

#### Effect of pH on Cu(II) and Zn(II) sorption

Solutions containing 0.50 mM  $\text{Cu}(\text{NO}_3)_2$  or  $\text{Zn}(\text{NO}_3)_2$  in 0.10 M  $\text{KNO}_3$  as a background solution were prepared. The pHs of the solutions were adjusted with dilute  $\text{HNO}_3$  or  $\text{KOH}$  to obtain a pH range from 4.0 to 7.0. All the experiments were performed in duplicate. Sealed acrylic centrifuge tubes containing the soil suspensions (0.5 g/50 mL) for the different subsamples (<2-mm, <2-mm OMR, and <2- $\mu\text{m}$ ) were continuously shaken on an end-over-end shaker within a water bath for 24 h at room temperature ( $25 \pm 2$  °C). The suspensions were always in contact with the metal solutions. After shaking, samples were removed from the shaker and centrifuged at 5000 rpm for 10 min and an aliquot of supernatant solution (40 mL) removed from each tube using a plastic syringe, and filtered immediately through 0.22- $\mu\text{m}$  polycarbonate filters (Nucleopore Corp.) before pH measurement using the digital ion analyser.

Residual metal content in the supernatant liquid were analysed by FAAS and the metal ions sorbed by the soils were calculated as the difference between initial concentration and that remaining in the supernatant at equilibrium.

### Cu(II) and Zn(II) sorption isotherms

Solutions containing 0.10, 0.25, 0.80, 1.00 and 2.50 mM of either Cu(NO<sub>3</sub>)<sub>2</sub> or Zn(NO<sub>3</sub>)<sub>2</sub> in 0.10 M KNO<sub>3</sub> were prepared and sorption experiments were carried out at pH 5.0 as described above. All results are expressed on an oven-dry basis (105 °C for 72 h). Sorption isotherms, obtained by plotting equilibrium metal ion solution concentrations versus the sorbed metal concentration, were fitted to the Langmuir and Freundlich equations which have, although derived from adsorption on solid–gas systems, been extensively applied to describe metal sorption in soils (Mesquita and Vieira e Silva 2002; Ponizowsky and Tsadillas 2003). The Langmuir model assumes (1) uniform sorption energies onto a homogeneous sorbent surface, (2) no migration of the sorbate in the surface plane, (3) a monolayer formed on the surface and a sorption maximum achieved as the monolayer becomes saturated by the sorbate, (4) no interaction between sorbed species, and (5) identical sorption energy at each sorption site, i.e. equal activity of all surface sites. The Langmuir isotherm equation is defined as follows:

$$q = \frac{q_{\max} \times K_L \times C_{\text{eq}}}{(1 + K_L \times C_{\text{eq}})}$$

where  $C_{\text{eq}}$  is the equilibrium concentration in solution (mmol L<sup>-1</sup>),  $q$  represents metallic ion sorbed by soil (mmol kg<sup>-1</sup>),  $K_L$  is the constant related to the binding strength associated with the pH dependent equilibrium constant and to the maximum sorption capacity ( $q_{\max}$ ) determined by the number of reactive surface sorption sites in an ideal monolayer system, and  $q_{\max}$  is the sorption capacity (mmol kg<sup>-1</sup>).

The Freundlich model represents a much simpler situation in which metal sorption maximum is not defined because the model does not consider saturation of sorption

sites. The Freundlich isotherm equation is defined as follows:

$$C_s = K_F C_e^{1/n}$$

where  $C_s$  (mmol kg<sup>-1</sup>) is the amount of cations adsorbed at the equilibrium concentration  $C_e$  (mmol L<sup>-1</sup>),  $K_F$  is the constant describing the relative adsorption capacity, and  $n$  is also a constant indicating the heterogeneity degree of the sorption sites when its value approaches 0 (Selim 1992).

### Statistical analysis

All data are presented as mean values of duplicate experiments. Statistical analysis of the data was carried out using analysis of variance (ANOVA). The regression and other statistical analyses were conducted using the statistical program (StatSoft, Inc. 1995).

## Results and discussion

### Samples characterization

The soil classification and relevant properties are presented in Table 1.

Bioavailability and mobility of metal ions vary significantly with soil properties. Soil pH has historically been considered one of the most important criteria for soil classification because of the number of co-varying properties which are related to it. In this work, two measures of acidity were determined: pH (H<sub>2</sub>O) which measures the acidity of the soil solution, and pH (KCl) which measures the acidity of the soil solution plus the reserve acidity of the soil colloids. It is generally found that pH (KCl) is lower, usually from 0.5 to 1.0 pH units, than pH (H<sub>2</sub>O)

**Table 1** Soil classification and some chemical and physical properties

Sample	Soil classification	Sand (g/kg)	Silt (g/kg)	Clay (g/kg)	Soil fractions	pH (H <sub>2</sub> O)	pH (KCl)	$S_{\text{EGME}}$ (m <sup>2</sup> /g)	$S_w$ (m <sup>2</sup> /g)	TOC (%)	CEC (cmol <sub>e</sub> /kg)			
A <sub>1</sub>	Typic Argiudol	185	512	303	<2-mm (whole)	5.9	5.2	88.7 ± 8.8	200 ± 20	3.35	20.0			
					<2-mm (OMR)	4.5	4.0					96 ± 9	1.58	23.0
					<2-μm	6.4	5.7					370 ± 30	5.45	48.2
A <sub>2</sub>	Pachic Argiudol	420	440	140	<2-mm (whole)	6.4	5.2	78.7 ± 8.8	130 ± 10	4.78	15.0			
					<2-mm (OMR)	4.4	4.0					110 ± 10	1.37	16.3
					<2-μm	6.8	6.1					368 ± 37	6.50	51.7
A <sub>3</sub>	Petrocalcic Paleustol	504	278	218	<2-mm (whole)	7.5	6.3	69.9 ± 6.9	176 ± 17	2.90	17.1			
					<2-mm (OMR)	5.1	5.5					88 ± 8.8	1.32	20.1
					<-2-μm	6.5	5.6					463 ± 45	3.44	51.5
A <sub>4</sub>	Typic Ustipsament	656	219	125	<2-mm (whole)	7.7	7.4	49.6 ± 5.0	94 ± 9.5	0.71	9.6			
					<2-mm (OMR)	6.6	6.1					47 ± 5.0	0.23	7.8
					<2-μm	8.3	7.2					393 ± 40	2.86	49.7

**Table 2** Total and extractable -iron, -aluminum and -manganese contents

Sample	Soil fractions	Fe <sub>T</sub> (% Fe <sub>2</sub> O <sub>3</sub> )	Fe <sub>OX</sub> (% Fe <sub>2</sub> O <sub>3</sub> )	Fe <sub>DCB</sub> (% Fe <sub>2</sub> O <sub>3</sub> )	Al <sub>T</sub> (% Al <sub>2</sub> O <sub>3</sub> )	Al <sub>OX</sub> (% Al <sub>2</sub> O <sub>3</sub> )	Al <sub>DCB</sub> (% Al <sub>2</sub> O <sub>3</sub> )	Mn <sub>T</sub> (% MnO <sub>2</sub> )	Mn <sub>OX</sub> (% MnO <sub>2</sub> )	Mn <sub>DCB</sub> (% MnO <sub>2</sub> )
A <sub>1</sub>	<2-mm	3.47	0.34	1.50	11.62	0.20	0.35	0.18	0.09	0.14
	<2- $\mu$ m	3.65	0.68	1.45	19.07	0.52	0.70	0.20	0.13	0.18
A <sub>2</sub>	<2-mm	3.42	0.21	1.25	12.81	0.25	0.30	0.10	0.05	0.07
	<2- $\mu$ m	3.86	0.68	2.20	18.07	0.51	0.82	0.16	0.10	0.15
A <sub>3</sub>	<2-mm	4.20	0.14	0.72	13.30	0.24	0.45	0.09	0.04	0.08
	<2- $\mu$ m	5.83	0.53	1.43	22.80	0.69	0.83	0.17	0.13	0.15
A <sub>4</sub>	<2-mm	4.04	0.19	0.82	13.40	0.15	0.23	0.08	0.03	0.06
	<2- $\mu$ m	4.97	0.55	1.59	19.20	0.18	0.65	0.16	0.09	0.15

Fe<sub>T</sub> total iron, Al<sub>T</sub> total aluminum, Mn<sub>T</sub> total manganese, OX Oxalate-extractable Fe, Al and Mn, DCB Dithionite-citrate-bicarbonate-extractable Fe, Al and Mn

(Benton Jones Jr. 1971), observation which is supported here (Table 1).

Soils with high amounts of clay and/or organic matter will typically have higher CECs and buffering capacities than silty or sandy soils. The higher amount of TOC found in <2- $\mu$ m compared to the <2-mm fractions is consistent with the values found by Haile-Mariam et al. (2008) and indicates the high affinity of organic compounds for clays.

The CEC values in the <2-mm soil fraction samples are influenced by the different TOC and clay contents. CEC values follow the trend of TOC content (for whole soil and for soil fraction <2  $\mu$ m,  $R^2$  were 0.84 and 0.88, respectively), where mainly the humic substances of the soil organic matter could contribute with up to 50 % of the CEC value (Urbano Terrón and Rojo Hernández 1992). The lowest CEC value was observed for sample A<sub>4</sub>, in line with the low TOC and low clay-size fraction percentage present in that sample (Table 1).

In <2-mm OMR fractions, CEC values showed a slight increase (within the method error  $\pm 2.8$  cmol<sub>c</sub>/kg, Dohrmann and Kaufhold 2010) compared to <2-mm soil fractions, except in sample A<sub>4</sub>. As CEC depends on TOC and clay content, some reactive sites occupied by organic matter in <2-mm soil fraction would now be available to exchangeable cations in <2-mm OMR fraction. Among all soils, TOC content in the <2-mm OMR samples ranged from 28 to 48 % of that in the whole soil fractions, indicating that organic matter could not completely be removed from whole soils by H<sub>2</sub>O<sub>2</sub> wet oxidative treatment. The presence of chemically resistant organic compounds and some protection of organic matter by mineral surfaces may be responsible factors for incomplete C removal.

The higher observed CEC in clay-soil fractions compared to those of <2-mm and the <2-mm OMR soil fractions was mainly attributed to the presence of higher relative amounts of clay minerals of large surface area in the clay fractions.

Specific surface area for the whole soil fractions, determined by the EGME method ( $S_{EGME}$ ), were directly correlated ( $R^2 > 0.85$ ) with the TOC content. However,  $S_w$  was better correlated ( $R^2 = 0.90$ ) to the soil clay-fraction and consequently to the CEC, as previously shown by Torres Sánchez and Falasca (1997). The higher  $S_w$  values, with respect to  $S_{EGME}$ , had been thought to be a more realistic value of soil specific surface areas (Torres Sánchez and Falasca 1997, and references therein). The decrease in  $S_w$  in the <2-mm OMR fraction was most likely due to loss of some portion of the fine fraction together with organic matter removal.

The aluminum, iron and manganese contents in different soil fractions, expressed as percent oxides (%) are summarized in Table 2.

The oxalate extractable metal fraction (OX) has been shown to be a selective reagent for the dissolution of non-crystalline and poorly crystalline aluminosilicates, oxides, and oxohydroxides of Al, Fe, and Mn (McKeague and Day 1966). While the dithionite-citrate-bicarbonate extractable metal fraction has been primarily associated with the determination of free Fe, Al and Mn oxides and the removal of amorphous coatings and crystals of free oxides acting as cementing agents, although Al/Mn-substituted crystalline hematite and goethite are also dissolved by the DCB treatment (Mehra and Jackson 1960); (Schwertmann and Taylor 1989).

The Al, Fe, and Mn total content increased as the soil particle size decreased. While substantial amounts of Fe and Al were not extracted by either OX or DCB treatments, the amount of DCB-extracted Mn was quite similar to that of Mn<sub>T</sub> (Table 2). Less than 40 % of the total Fe was associated with crystalline and amorphous oxides and/or oxohydroxides. Fe<sub>OX</sub> accounted for <20 % of the total Fe, indicating that all the samples contained small amounts of poorly crystallized oxalate soluble Fe-oxides. Al<sub>OX</sub> and Al<sub>DCB</sub> were very low, indicating only a small amount of poorly crystalline and crystalline OX-soluble and DCB-

**Table 3** Mineral composition (Rietveld method) of the soil clay fractions

Sample	Quartz (%)	Illite (%)	Smectite (%)	Feldspar (Na–Ca) (%)	Hematite + Goethite (%)
A <sub>1</sub>	16.0 (0.5)	61.9 (2.2)	n.d.	17.7 (0.9)	3.0 (0.2)
A <sub>2</sub>	11.6 (0.4)	71.7 (2.9)	1.6 (2.0)	13.6 (0.8)	1.4 (0.4)
A <sub>3</sub>	9.1 (0.5)	71.4 (2.4)	5.7 (1.5)	12.3 (0.8)	1.4 (0.1)
A <sub>4</sub>	9.8 (0.4)	68.6 (2.3)	4.8 (1.6)	15.2 (0.7)	1.6 (0.1)

Estimated standard deviations, in parentheses, were derived from the estimated standard deviations on individual scale factors for the respective phases, excluding other error contributions  
*n.d.* means not detected

soluble Al compounds were present. However, Mn<sub>T</sub> and Mn<sub>DCB</sub> were quite similar, suggesting the presence of crystalline Mn-oxides/oxohydroxides, although Mn<sub>T</sub> contents were low or very low in all soil samples. Also, Mn<sub>DCB/OX</sub> ratios were indicating small amounts of crystalline Mn-oxides were present.

The mineral composition of the clay fractions of the studied soil subgroups is presented in Table 3.

The mineral composition for all clay fractions was quite similar. Soils from this region principally contain hematite and goethite with varying degrees of crystallinity and Al-substitution. Maghemite and magnetite are negligible, especially in the fine fractions of the soil (Acebal et al. 2000). The linear correlations ( $R^2 = 0.80$ ) between  $S_w$  value of the <2- $\mu$ m fractions (Table 1) and the surface calculated for same fractions, taking into account the mineralogical contents of illite, feldspar, hematite, goethite and smectite (Table 3) and the respective mineral- $S_w$  values (67, 85, 100, 68, and 472 m<sup>2</sup>/g, respectively; Taubaso et al. 2004; Rueda et al. 1992), is indicative of negligible interactions among different soil components (Torres Sánchez et al. 2001). Thus while soil A<sub>1</sub> had the greatest percentage of clay-size fraction and no detectable levels of smectite, it exhibited a lower  $S_w$  than A<sub>4</sub>, which had the lowest clay-size fraction content but the greatest percentage of smectite. Furthermore,  $S_w$  value of soil A<sub>3</sub> was two times higher than value obtained for soil A<sub>1</sub>, which was again related to the higher smectite content.

The close agreement between PZC and IEP values (Table 4) among all different soil fractions (within an experimental error  $\pm 0.3$  pH units) indicated a lack of significant sorbed species on the soil surfaces (Torres Sánchez et al. 2001). In particular, for clay size fraction the high coincidence between the PZC and IEP values and the correlation between calculated (as the sum of surface area contribution by each component, Torres Sánchez et al. 2001) and experimental  $S_w$  is a clear evidence of the inexistence of sorbed species.

Both PZC and IEP, in all soil samples, decreased as follows: clay fraction > whole soil > OMR. Besides,  $S_w$  values showed the same behavior: the smaller particle size the greater  $S_w$ . This order was in agreement with a

**Table 4** PZC and IEP of all soil fractions

Sample	Soil fraction	PZC (pH)	IEP (pH)
A <sub>1</sub>	<2-mm (whole)	6.1	6.4
	<2-mm (OMR)	5.2	4.4
	<2- $\mu$ m	7.0	7.0
A <sub>2</sub>	<2-mm (whole)	5.9	6.1
	<2-mm (OMR)	5.3	5.2
	<2- $\mu$ m	6.6	6.4
A <sub>3</sub>	<2-mm (whole)	6.4	6.8
	<2-mm (OMR)	5.8	6.5
	<2- $\mu$ m	6.8	6.6
A <sub>4</sub>	<2-mm (whole)	6.4	5.5
	<2-mm (OMR)	6.5	5.7
	<2- $\mu$ m	6.9	6.5

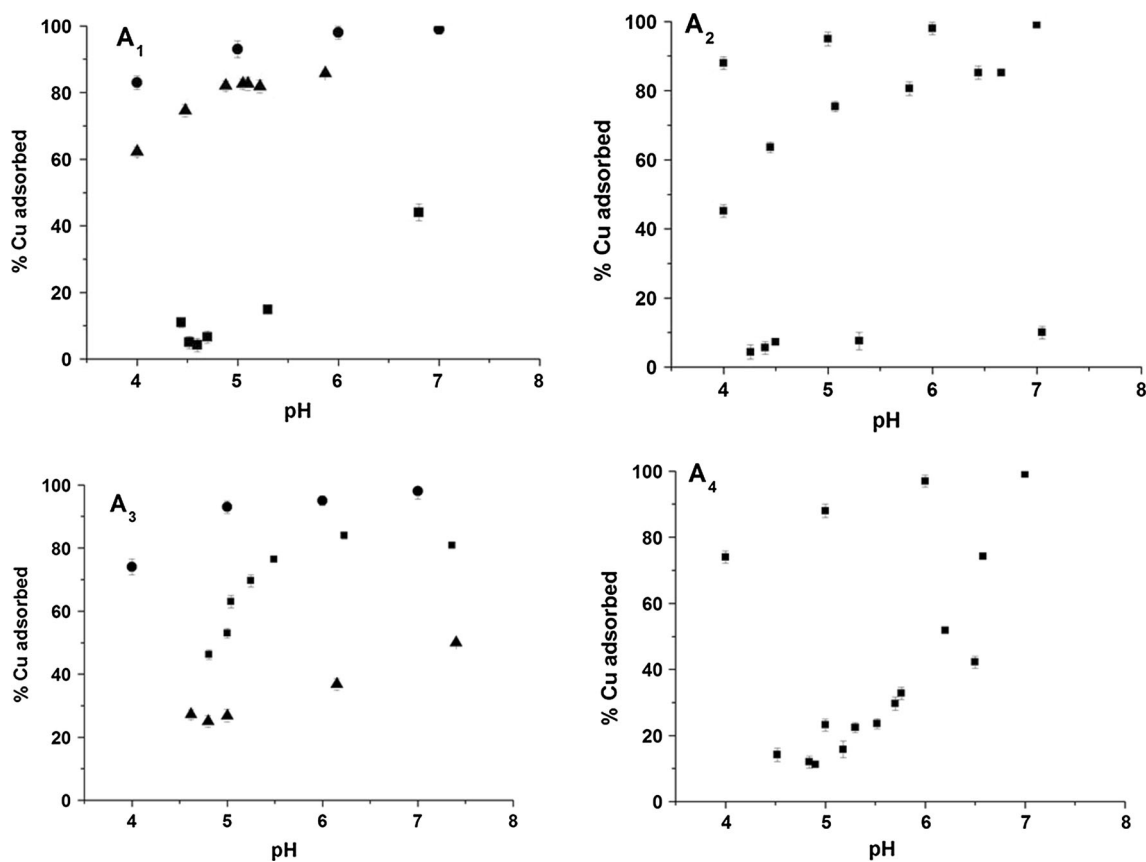
mathematical model designed for oxides and mineral mixtures, and also successfully applied to treated soils with low percentage (or without) of specific adsorption sites (Taubaso et al. 2004).

The decrease in PZC-IEP for <2-mm OMR fractions could be due to partial oxides/oxohydroxides loss during the OMR treatment since Fe, Al and/or Mn compounds may be organically bounded forming metal–organic matter complexes (Me-OM). Generally, Fe, Al and Mn oxides have PZCs in a pH range between pH 6 to 10 (Cornell and Schwertmann 2003); so their presence in a mixture tends to favor higher PZC values, and consequently when Me-OM complexes are partially removed together with organic matter, the resultants PZCs should decrease, as was observed in this study. Compared with other samples, A<sub>4</sub> also showed the lowest IEP values, and also IEPs values between the whole soil and the <2-mm OMR fraction are similar, this behavior could be attributed to the low TOC content in both fractions (Table 1).

**pH effect on Cu(II) and Zn(II) sorption**

The percentage of Cu(II) sorption varied as a function of pH for all soil-size fractions (Fig. 2).

In all samples the same trend was observed, Cu(II) sorption decreased in the following order: clay



**Fig. 2** Sorbed Cu(II) as a function of pH, for all the studied soils,  $[Cu(II)] = 5 \times 10^{-4}$  M; 25 °C. (filled circle) <2- $\mu$ m; (filled triangle) <2-mm; (filled square) <2-mm OMR

fraction > whole soil > OMR fraction in agreement with that found by Huang et al. (2014) for red paddy soils. The <2-mm fraction also exhibited an increase in sorption with pH, mainly attributed to an increase of the negative surface charge of soil particles. In comparison, the clay fraction showed only a minor dependency on pH, and the percentage of Cu(II) sorption for A<sub>1</sub>, A<sub>2</sub> and A<sub>3</sub> clay fractions were very similar.

In sample A<sub>4</sub> a similar sorption percentage profile for Cu(II) for both whole soil and <2-mm OMR fractions was observed, which could be attributed to the lower TOC content of these fractions with respect to higher TOC contents in the Mollisols A<sub>1</sub>, A<sub>2</sub> and A<sub>3</sub>. The low Cu(II) sorption exhibited by the whole soil and <2-mm OMR fractions of sample A<sub>4</sub> was assigned to preferential Cu(II) sorption to organic compounds associated with fine clay fractions (Wu et al. 1999). Some authors (Fernández Covelo 2005; Vega et al. 2008, 2010) proposed that the maximum sorption toward Cu(II) among soil components decreased in the following order: Mn oxides > organic matter > Fe oxides > clay minerals. Since in these soils the presence of Mn-oxides (see Table 2) is very low; therefore, the other soil components are more likely responsible for the observed sorption phenomena.

The percentage of Zn(II) sorption varied as function of pH for all the soil-size fractions (Fig. 3).

As observed with Cu(II), Zn(II) sorption generally increased with increasing pH, but with an affinity for the surface of the different soil fractions that was always lower than that of Cu(II). At pH 4 the percentage of sorbed Zn(II) did not exceed 20 % in any soil. Although the metal binding sites available in organic matter are more selective towards Cu(II) than Zn(II), sorption of Zn(II) in the <2-mm OMR fraction still dropped to negligible levels in agreement with Agbenin and Olojo (2004). Pérez-Novio et al. (2008) found a decrease in competitive sorption for both metal cations after H<sub>2</sub>O<sub>2</sub> treatment, indicating that Cu(II) was more efficient than Zn(II) in competing for binding sites on sorbing surfaces.

In the clay fractions of all the studied soils [Fig. 2 and 3, (●) symbol], Zn(II) showed a larger pH dependence than Cu(II), which suggested more electrostatic bonding of Zn(II) to soil-clay surfaces, this observation is in agreement with data reported by Egirani et al. (2005) for mixed mineral systems and for Gu et al. (2010) for smectite. Egirani et al. (2005) indicated that Cu(II) and Zn(II) were sorbed as outer and inner sphere surface complexes. In agreement with data reported by Usman (2008) for



different Egyptian soils, Cu(II) was sorbed preferentially to the organic matter associated with the clay fraction (Fig. 2), whereas Zn(II) formed more mobile complexes at greater distance from soil surface reactive sites. Zn(II) sorption is much more closely related with the mineralogy (type and class) of the fine soil fractions than with organic matter (Fig. 3).

**Sorption isotherms**

Sorption isotherms of Cu(II) and Zn(II) on the different soil fractions at pH 5 are shown in Figs. 4 and 5, respectively.

For the soils studied, although Cu(II) consistently exhibited a higher affinity for the whole soil fractions than Zn(II), both cations followed the same sequence:  $A_1 > A_2 > A_3 > A_4$ . However, for the clay fraction, where a higher selectivity was observed, the order of sorption was  $A_2 > A_1 > A_3 > A_4$ , and  $A_2 > A_1 > A_4 > A_3$ .

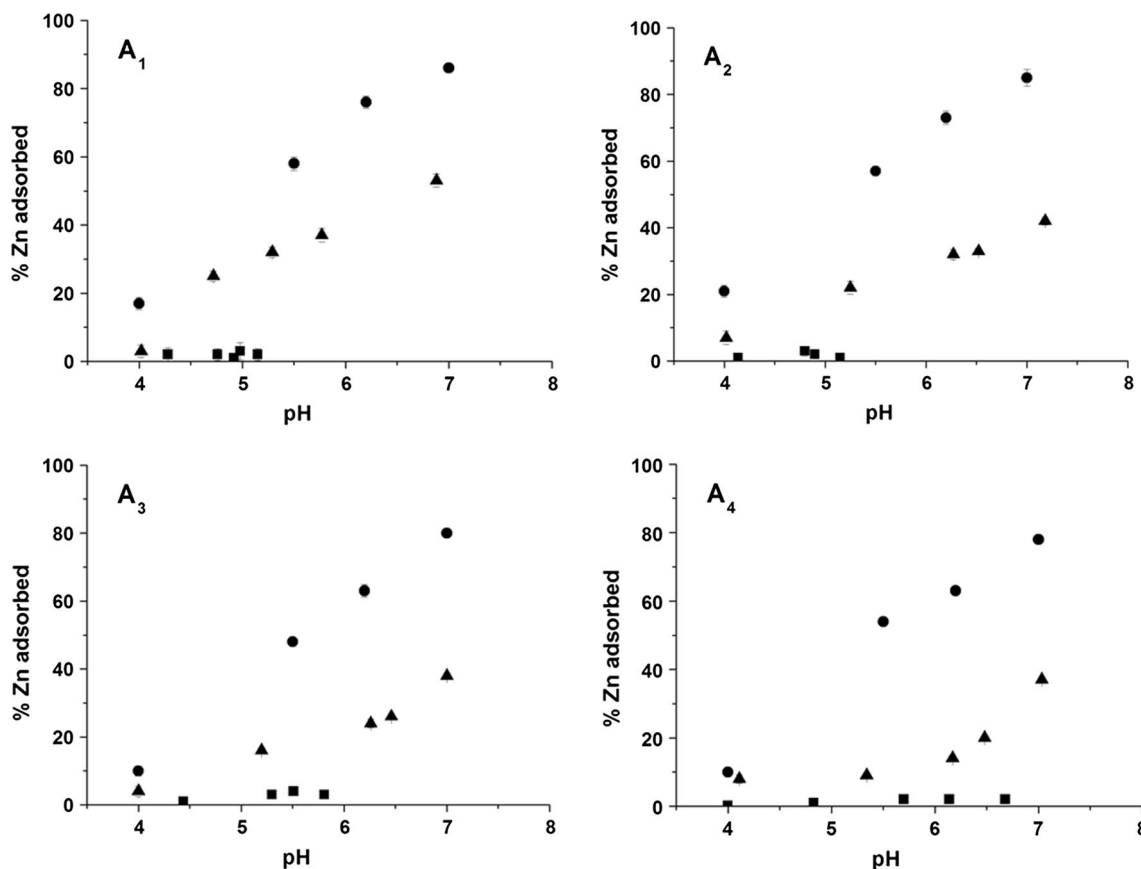
As was pointed out previously, the mineralogy of the clay fraction of these soils suggested that smectite content was an important factor in the sorption behavior, being more evident for Zn(II) than for Cu(II). This was consistent with the strong tendency of Zn(II) to sorb on smectitic

surfaces. In soil  $A_4$ , the presence of low clay content but with a high proportion of smectite, was responsible for the different order of cation affinity observed.

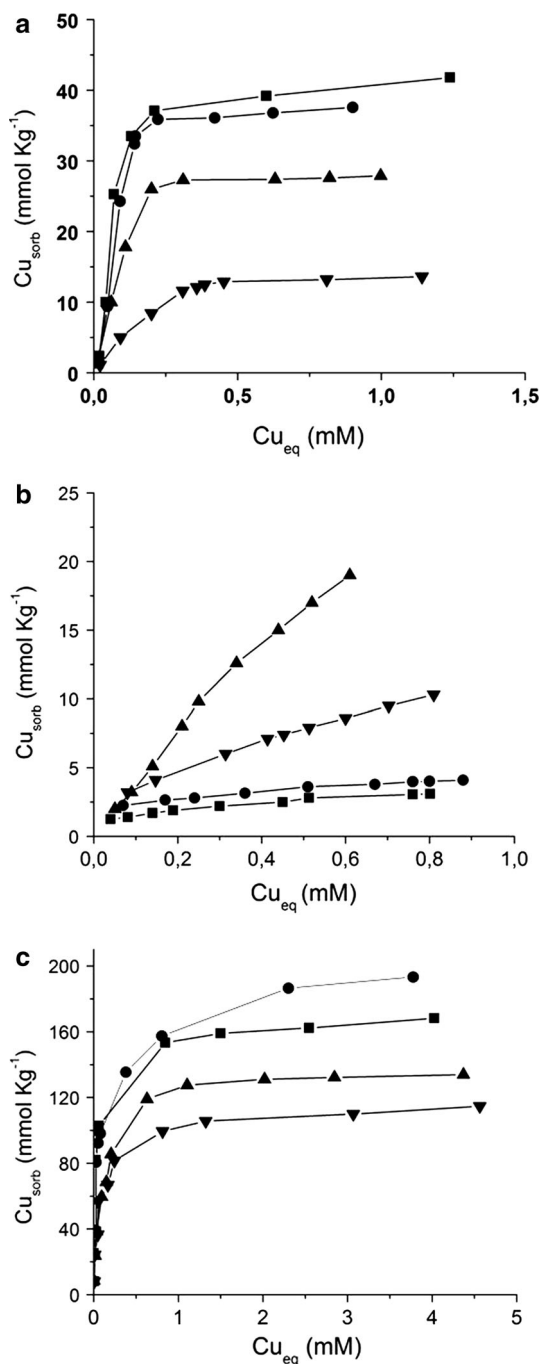
Cu(II) displayed a sequential sorption ( $A_3 > A_4 > A_2 \geq A_1$ ) that was consistent with the high affinity of Cu for organic matter.  $H_2O_2$  treatment produces a more evident impact on soils with a higher TOC content, because the greater organic matter removal the lesser adsorption was observed. For the <2-mm OMR fraction, Zn(II) showed a different sorption sequence ( $A_3 > A_1 > A_2 > A_4$ ) from that observed for Cu(II), which was in agreement with the preference of Zn(II) for clay binding sites.

The sorption behavior of Cu(II) and Zn(II) at pH 5 onto two fractions (<2-mm and <2- $\mu$ m) of soil samples was well described by either Langmuir or Freundlich isotherms (Table 5).

In the <2-mm soil fraction, the  $q_{max}$  values followed the sequence  $A_1 \geq A_2 > A_3 > A_4$  for both Zn(II) and Cu(II). The  $K_L$  values for Cu(II) sorption were consistently higher than those for Zn(II) for all soils in agreement with the general higher affinity of Cu(II) than Zn(II) for reactive adsorption soil sites. As indicated by the larger  $q_{max}$  values (Table 5), sorption of both cations was much greater for the

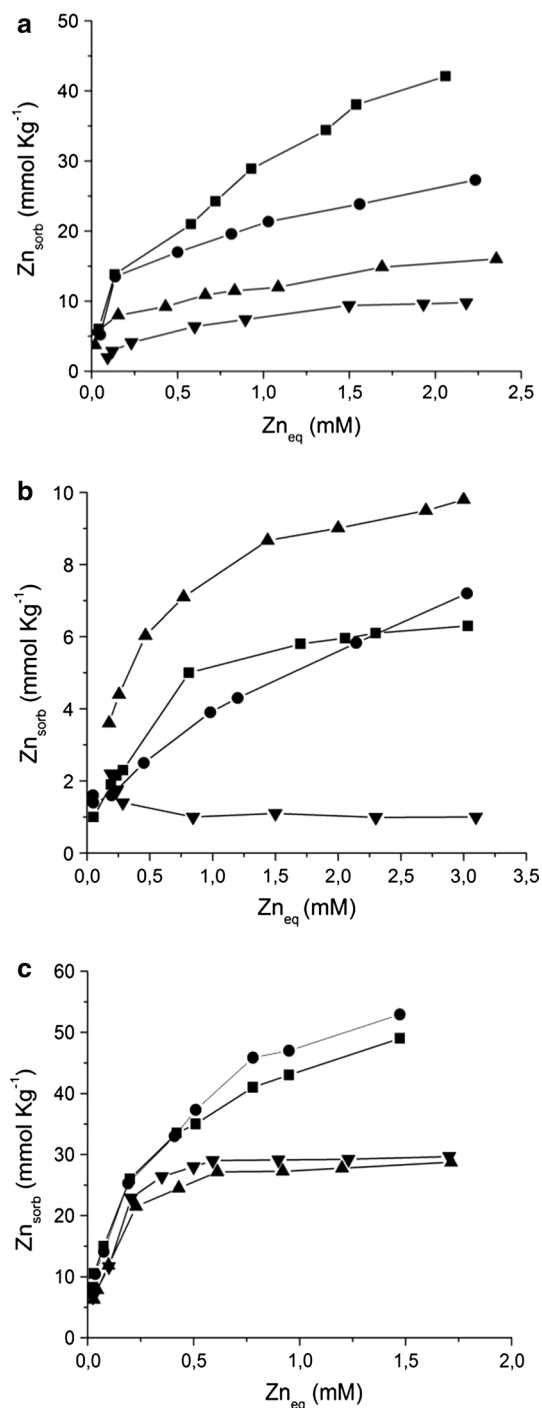


**Fig. 3** Sorbed Zn(II) as a function of pH for all the studied soils,  $[Zn(II)] = 5 \times 10^{-4}$  M; 25 °C. Symbols indicated: (filled circle) <2- $\mu$ m; (filled triangle) <2-mm; (filled square) <2-mm OMR



**Fig. 4** Cu(II) sorption isotherms at pH 5 on: **a** <2-mm; **b** <2-mm OMR fraction; **c** <2- $\mu$ m. Symbols indicated: (filled square) A<sub>1</sub>; (filled circle) A<sub>2</sub>; (filled triangle) A<sub>3</sub>; (filled inverted triangle) A<sub>4</sub>

clay fraction (<2- $\mu$ m) than for the whole soil fraction (<2-mm). Also, in the clay fraction, for Zn(II), samples A<sub>1</sub> and A<sub>2</sub> presented the highest value of  $q_{\max}$  and the lowest affinity (lowest  $K_L$ ). The highest affinities for Zn(II) sorption were observed for the clay fraction of samples A<sub>3</sub> and A<sub>4</sub> ( $K_L = 7.70$  and  $8.52$ , respectively) and was related to the presence of smectitic clay minerals in the soil. For the



**Fig. 5** Zn(II) sorption isotherms at pH 5 on: **a** <2-mm; **b** <2-mm OMR fraction; **c** <2- $\mu$ m. Symbols indicated: (filled square) A<sub>1</sub>; (filled circle) A<sub>2</sub>; (filled triangle) A<sub>3</sub>; (filled inverted triangle) A<sub>4</sub>

clay fractions of these soils, the highest Cu(II) affinity ( $K_L = 21.69$ ) was displayed by soil A<sub>1</sub>, which although it contained no detectable amounts of smectite, contained the largest amounts of clay fraction of any soil samples (Table 1) which are most likely responsible for the higher observed sorption.

For all samples studied the Langmuir equation fit the experimental data better than the Freundlich equation as indicated by the  $R^2$  values (Table 5). The Freundlich isotherm does not predict any saturation of the sorbent by the sorbate. Instead, infinite surface coverage is predicted, indicating multilayer sorption on the surface and  $K_F$  shows the affinity of the sorbate/sorbent for this condition and the observed  $n$ , ranging from 0.20 to 0.48, reflected a different heterogeneity degree of the sorption sites.

The occupancy of soil surface sites by metal cations can be inferred from the changes in SSA values (Supplementary Material, Fig. S<sub>1</sub> and S<sub>2</sub>, for sorbed Cu(II) and Zn(II), respectively). In order to aid clarity only  $S_w$  values were analyzed.

As previously noted, Cu(II) sorption was higher than Zn(II) sorption, and both metal ions can form surface complexes with organic matter (Me-OM). For the whole soil fraction, at pH 4, after metal sorption  $S_w$  of soil samples decreased, but at pH 6 a low  $S_w$  increase was observed. This increase was less for Cu(II) than for Zn(II) sorption. As  $S_w$  was obtained by H<sub>2</sub>O adsorption, the presence of surface Me-OM complexes became clay mineral surfaces restricted for the entry of H<sub>2</sub>O molecules consequently  $S_w$  decreased. In addition, Zn(II) have a higher capacity to form surface complexes at pH 4 than at pH 6 (Wong et al. 2007). Mainly at 5–7 pH range, the formation of soluble Zn(II)-OM complexes is favored, causing the release from clay binding surface sites, which become more available to sorbed H<sub>2</sub>O molecules, so a small increase in  $S_w$  values was observed.

The  $S_w$  values of the clay fraction samples after metal sorption at two different pHs (4 and 6) are shown in Fig. 6.

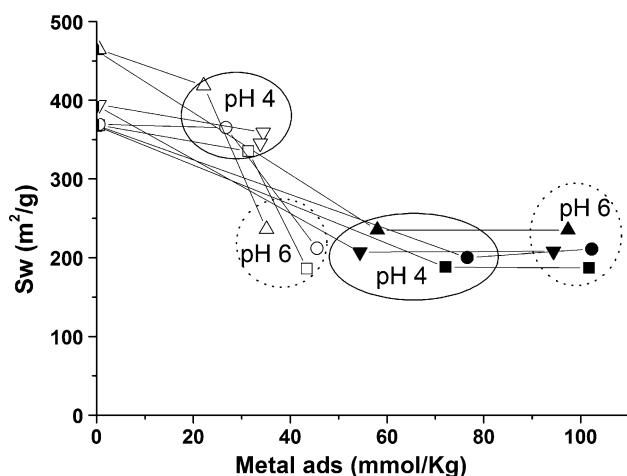
For the clay fraction, increasing pH decreased  $S_w$  values for sorbed Zn(II), but  $S_w$  remained almost constant for sorbed Cu(II) (Fig. 6). In this particle size, the observed  $S_w$  values would be mainly related to the smectite content since the ionic radius of Cu(II) ( $r = 0.073$  nm) and Zn(II) ( $r = 0.074$  nm) (Dean 1999) are almost equal, then a similar sorption behavior would be expected for both metal ions. Moreover, the smaller organic matter particle size increases the reactivity which favors the solubilization, thus the formation of surface Me-OM complexes is restricted.

As  $S_w$  measurement involves H<sub>2</sub>O adsorption, these values were compared with H<sub>2</sub>O activity data measured at the same relative humidity (56 %). Two different amounts of sorbed Cu(II) (from Fig. 6) were compared with H<sub>2</sub>O activity results reported for adsorption of Cu(II) on smectite (Zhou et al. 2008). A low decrease of H<sub>2</sub>O activity from pH 4 to 6 was observed. These results are in agreement (within experimental error) with  $S_w$  values in the soil samples. The low decrease of H<sub>2</sub>O adsorption with increasing pH was assigned to the Cu(II) hydrated shells. At lower pH, smectite interlayers present two H<sub>2</sub>O sheets, and Cu(II) is more hydrated; whereas at higher pH (6.5) only one H<sub>2</sub>O sheet exists between smectite interlayers being CuOH<sup>+</sup>, with a less hydrated shell, the predominant species.

$S_w$  behavior after Zn(II) sorption also can be explained through changes in smectite basal spacings being ZnOH<sup>+</sup>

**Table 5** Langmuir and Freundlich sorption isotherm best fit parameters for Cu(II) and Zn(II) sorption to A<sub>1</sub>, A<sub>2</sub>, A<sub>3</sub> and A<sub>4</sub> (<2-mm and <2-μm) at pH 5

Soil fraction/metal	Langmuir isotherm parameters			Freundlich isotherm parameters		
	$q_{max}$ (mmol kg <sup>-1</sup> )	$K_L$ (L mmol <sup>-1</sup> )	$R^2$	$K_F$ (mmol kg <sup>-1</sup> )	$n$	$R^2$
<b>&lt;2-mm (whole soil)</b>						
A <sub>1</sub> /Cu	46.68	12.50	0.910	44.57	0.29	0.715
A <sub>2</sub> /Cu	43.86	12.85	0.900	45.05	0.29	0.705
A <sub>3</sub> /Cu	31.95	11.40	0.947	31.38	0.30	0.794
A <sub>4</sub> /Cu	16.66	6.01	0.963	15.06	0.35	0.829
A <sub>1</sub> /Zn	57.79	1.15	0.981	29.63	0.48	0.980
A <sub>2</sub> /Zn	26.73	4.97	0.957	21.22	0.33	0.926
A <sub>3</sub> /Zn	17.57	3.70	0.988	11.29	0.30	0.879
A <sub>4</sub> /Zn	11.82	2.19	0.991	7.44	0.42	0.979
<b>&lt;2-μm (clay fraction)</b>						
A <sub>1</sub> /Cu	166.40	21.69	0.982	135.59	0.21	0.866
A <sub>2</sub> /Cu	180.87	16.98	0.990	152.21	0.24	0.905
A <sub>3</sub> /Cu	138.25	8.45	0.999	107.64	0.24	0.908
A <sub>4</sub> /Cu	111.47	12.72	0.999	90.79	0.22	0.888
A <sub>1</sub> /Zn	62.75	4.76	0.904	39.47	0.20	0.852
A <sub>2</sub> /Zn	60.68	3.63	0.980	47.52	0.42	0.983
A <sub>3</sub> /Zn	31.58	7.70	0.988	27.29	0.30	0.879
A <sub>4</sub> /Zn	33.30	8.52	0.994	29.38	0.25	0.795



**Fig. 6**  $S_w$  changes in  $<2\text{-}\mu\text{m}$  fraction for sorbed: Cu(II) full symbols and Zn(II) empty symbols at pH 4 and 6 (filled square) A<sub>1</sub>; (filled circle) A<sub>2</sub>; (filled triangle) A<sub>3</sub>; (filled inverted triangle) A<sub>4</sub>

and Zn(II) the present species at high and low pH, respectively. Similar results were obtained by Ma and Uren (1998), and Zhou et al. (2008) for bentonites saturated with Zn(II).

In the clay fraction the higher  $S_w$  decrease for Zn(II) than for Cu(II) in both pHs was indicative of the different affinity between metal ions and the adsorbent soil surfaces (Table 5), and also could be related to different sorption behavior between  $\text{H}_2\text{O}$  molecules and soil binding surfaces.

## Conclusions

Given the increasing anthropogenic input of potentially harmful elements (PHEs) to soil, both in urban environments and in agriculture, further research on the behaviour of PHEs in soils is important. In order to assess the influence of selected soil parameters on the mobility and sorption characteristics of Cu(II) and Zn(II), a number of Argentine soils were physicochemically characterized.

Type and amount of Fe, Al and Mn oxide/oxohydroxides and clay minerals were evaluated in three soil fractions ( $<2\text{-mm}$ ,  $<2\text{-mm OMR}$  and  $<2\text{-}\mu\text{m}$ ) in order to determine Cu(II) and Zn(II) sorption capacity. Several important electric surface charge parameters (PZC, IEP, CEC) decreased in the following order: clay size fraction  $> 2\text{-mm} > \text{OMR}$  fraction. The lower particle size and higher pH values the greater sorption. The increase in both Cu(II) and Zn(II) sorption was attributed to an increase in negative surface charges, as indicated by PZC and IEP values. The lower affinity exhibited by Zn(II) relative to Cu(II) for different soil fraction surfaces showed that Cu(II) interacted more strongly with soil surface binding sites.

$S_w$  values after Cu(II)/Zn(II) sorption showed a preferential occupancy for different reactive surface sites. In whole soil fractions  $S_w$  values after Cu(II)/Zn(II) sorption could be mainly attributed to the formation of complexes with organic matter, being this Me-OM complexes strongly pH-dependent.

In soil clay fractions  $S_w$  values could be mainly related to Cu(II)/Zn(II) sorption on reactive sites of randomly interstratified illite-montmorillonite and expandable clays of the smectite group, inhibiting the entrance of  $\text{H}_2\text{O}$  molecules.

All these results should be taken into account when fertilizers are added to agricultural soils for limiting heavy metal fixation in order to prevent pollution in this valuable resource.

This study extends the understanding of the sorption mechanisms of Cu(II) and Zn(II) to agricultural soils from the semi-arid Pampean region of Argentina. An understanding of the local soil environment is important in order to reduce or prevent contamination of this valuable resource, especially from fertilizers and other such anthropogenic additions to the soil.

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