The role of cation exchange in the sorption of cadmium, copper and lead by soils saturated with magnesium

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ABSTRACT

The displacement of Ca^{2+}, Mg^{2+}, K^+ and Al^{3+} from the A and Bw or Bt horizons of two soils developed over serpentinized amphibolites when equilibrated in Cu^{2+}, Cd^{2+} or Pb^{2+} solutions was determined, together with the concomitant sorption of the heavy metal. The contributions of Mg^{2+} to the effective cation exchange capacities of the A and Bt horizons of the Endoleptic Luvisol were 57% and 94%, respectively, and its contributions to those of the A and Bw horizons of the Mollic Cambisol were 70% and 77%, respectively. In all four horizons, cation exchange, chiefly with Mg^{2+} and Ca^{2+}, was the process chiefly responsible for sorption of Cd^{2+}, Cu^{2+} and Pb^{2+}. Al^{3+} and K^+ were hardly implicated, especially in the case of Cd^{2+}.

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1. Introduction

Soils have great capacity to immobilize metals by sorption of metal species from the soil solution onto "solid" phases through processes that can involve physical and chemical adsorption, precipitation on the solid surface, and diffusion into the interior of the solid phase [1,2]. The sorption capacity of a soil may be defined as the total amount of sorbate needed to occupy all sorption sites per unit mass of the soil, and its buffering capacity as the excess amount of sorbate over the amount in solution [3]. Since the distribution of a metal between solid and solution phases controls its bioavailability, its availability for transport towards surface or underground waters, and the capacity of the soil to act as a sink for it, an understanding of sorption processes should aid prediction of these parameters [4–7].

The capacity of a soil to retain or release macroelements and trace metals is largely determined by its cation exchange capacity (CEC), i.e. its ability to give up the native cations of its solid phase in exchange for extraneous cations bound in outer-sphere complexes or present in the surrounding diffuse ion swarm [3,8]. Ion exchange is generally diffusion-controlled, reversible and stoichiometric [9]. Its extent depends on the types and quantities of organic and mineral materials present, which also determine selectivity for one or another kind of extraneous ion. There are studies in soils with low swelling clay contents in which CEC has been determined before and after the removal of organic matter [10–12]. In another studies CEC was regressed on clay and organic matter contents in large series of soils or soil fractions with widely differing values of these components [13,14]. All of these results have shown that it is organic matter content that largely determines CEC.

The relatively few studies that have examined exchange of heavy metals for exchange complex cations have concerned sorption on oxides or natural or synthetic clays, with or without associated humic compounds. For example, an important mechanism in cation sorption by sepiolite is the replacement of structural Mg at the edges of octahedral sheets has been reported for sorption of Cd [15,16], Zn [15,17], Pb [16], Co [18] and Cu [17], although binding to silanol groups has also been invoked for Cd, Pb, Cu and Zn [16,17], and exchange with Na for Cu and Zn [17]. The binding of Cd, Pb, Cu and Zn to silanol groups may also be the chief mechanism of their sorption by palygorskite [19]. The presence of humic acids has been reported to increase the capacity of kaolinite to sorb Cd, and the presence of iron to increase its capacity to sorb humic acids, which make sorption more irreversible by replacing ionic interactions by complexation [20]. Desorption from sepiolite and palygorskite appears only to have been studied in the case of Cd [21].

In view of the lack of studies on the replacement of exchangeable cations by heavy metals in whole soil horizons, and mindful that metal immobilized by cation exchange is more available for uptake by plants than metal immobilized by precipitation or incorporation in insoluble complexes, in the work described here we investigated

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the replacement of Ca^{2+}, Mg^{2+}, K^+ and Al^{3+} by Cu^{2+}, Cd^{2+} or Pb^{2+} in the A and B horizons of two soils developed over serpentinized amphibolites.

2. Materials and methods

We studied the A and Bt horizons of an Endoleptic Luvisol (EL), and the A and Bw horizons of a Mollic Cambisol (MC). Samples were dried in air, passed through 2 mm sieves, and homogenized in a Fritsch Laborette 27 rotary sample divider. Subsamples were taken for analysis and sorption experiments. All analyses were performed in triplicate.

2.1. Soil analyses

Soil pH and particle size distribution were determined as per Guitián y Carballas [22]. Organic carbon was quantified by the method of Walkey and Black [23], and free Fe, Al and Mn oxides by extraction with dithionite-citrate [24] followed by quantification in the extract by inductively coupled plasma optical emission spectrometry (ICP-OES) in a PerkinElmer Optima 4300 DV apparatus (results are expressed as Fe_2O_3, Al_2O_3 and MnO). Exchangeable Ca^{2+}, Mg^{2+}, K^+ and Na^+ contents were determined by saturating the sample with 0.2 M ammonium chloride buffered at the soil pH [25–27] followed by determination of the analytes by ICP-OES. Exchangeable Al^{3+} was extracted by shaking the sample with KCl and determined by titration against NaOH with phenolphthalein as indicator [28]. Effective cation exchange capacity (CECe) was calculated as $Ca^{2+} + Mg^{2+} + K^+ + Na^+ + Al^{3+}$ in $cmol_{(+)} \, kg^{-1}$. All analyses were performed in triplicate.

2.2. Sorption/exchange experiments

The sorption of Cd, Cu and Pb was determined by the method of Alberti et al. [29] and Gomes et al. [30] as modified by Harter and Naidu [31]. Soil samples (6 g) were added to 100 mL of "sorption solutions" containing 0.01 M $NaNO_3$ as background electrolyte and 0.01, 0.03, 0.05, 0.08, 0.10, 0.20, 0.30, 0.40, 0.50, 1.00, 2.00 or 3.00 mmol L^{-1} cadmium nitrate, copper nitrate or lead nitrate. The concentrations chosen were such that, if the metal contents of the solutions were totally sorbed by the soil samples, the resulting soil metal contents would range from normal values to values representative of severe pollution; nitrates were used on account of their great solubility in water. The soil-and-solution mixtures were shaken for 24 h at 25 °C in polyethylene centrifuge tubes in a rotary shaker, and were then centrifuged at 5000 rpm, after which the supernatant was filtered through Whatman 42 paper and analysed by ICP-OES for Cd, Cu or Pb and also, for evaluation of cation exchange, Ca, Mg, Na, K and Al. To take exchange with the background electrolyte into account, the concentrations of the latter metals were corrected by subtraction of the values determined in an additional experiment in which the sorption solution contained only 0.01 M $NaNO_3$. All experiments were performed in triplicate.

2.3. Statistical analyses

The significance of differences among means was estimated by analysis of variance (ANOVA), followed by least significant difference (LSD) tests. The occurrence of cation exchange was investigated by means of pairwise Pearson correlation analyses between amounts of sorbed metal and released exchange complex cations, and by least squares regressions of the latter on the former. All statistical calculations were performed using SPSS for Windows, version 14.0.

Table 1
Characteristics of the horizons studied.

Property	Soil EL		Soil MC	
	A	Bt	A	Bw
pH H_2O	5.73 c	6.4 bc	6.87 a	6.83 ab
Organic matter (g kg^{-1})	68.23 a	10.03 d	47.34 b	16.5 c
Al oxides g kg^{-1}	7.47 b	3.5 c	6.4 b	10.08 a
Fe oxides (g kg^{-1})	52.16 b	30.07 c	31.72 c	64.69 a
Mn oxides (g kg^{-1})	0.39 b	0.36 b	0.34 b	1.16 a
CECe ($cmol_{(+)} \, kg^{-1}$)	7.95 b	62.16 a	23.24 a	14.81 ab
Na ($cmol_{(+)} \, kg^{-1}$)	0.25 c	0.69 a	0.31 b	0.24 c
K ($cmol_{(+)} \, kg^{-1}$)	0.25 a	0.22 ab	0.25 ab	0.19 b
Ca ($cmol_{(+)} \, kg^{-1}$)	1.13 d	1.35 c	3.27 a	1.42 b
Mg ($cmol_{(+)} \, kg^{-1}$)	2.27 c	29.17 a	8.02 b	5.72 bc
Al ($cmol_{(+)} \, kg^{-1}$)	0.21 a	0.07 b	0.03 c	0.03 c
Sand (%)	54.0 a	21.3 c	49.8 ab	46.9 b
Silt (%)	303 b	12.6 c	27.9 b	39.6 a
Clay (%)	15.7 c	66.1 a	22.3 b	13.5 d

In each row, values with different associated (a–c) letters differ significantly at the $p = 0.01$ level.

3. Results and discussion

The CECe of the A horizon of the Endoleptic Luvisol EL (hereinafter "EL.A", with analogous notation for the other horizons studied) was 7.95 $cmol_{(+)} \, kg^{-1}$ (57% due to Mg^{2+}, 29% to Ca^{2+}), and that of EL.Bt 62.16 $cmol_{(+)} \, kg^{-1}$ (94% due to Mg^{2+}). The CECe of MC.A was 23.24 $cmol_{(+)} \, kg^{-1}$ (69% due to Mg^{2+}, 28% to Ca^{2+}), and that of MC.Bw 14.81 $cmol_{(+)} \, kg^{-1}$ (77% due to Mg^{2+}, 20% to Ca^{2+}) (Table 1). The only horizon in which Al^{3+} made any appreciable contribution to CECe was EL.A (8%). The high CECe of EL.Bt is in keeping with its high clay content, 66% as against 14–22% in the other horizons studied. Of the other major contributors to CEC, organic matter was, as was to be expected, more abundant in the A horizons (6.8% in EL.A as against 1.0% in EL.Bt, and 4.7% in MC.A as against 1.7% in MC.Bw); and the highest oxides contents (Al, Fe and Mn) were the Al and Fe of MC.Bw (10 and 65 g kg^{-1}, respectively) and the Mn oxides content of MC.A (1.16 g kg^{-1}). The oxides of Fe, Mn and Al have been described as those with greatest influence on heavy metal sorption [32–34]. Doubtless due in part to their development over serpentinites, both soils were of nearly neutral pH, ranging from 5.7 in EL.A to 6.9 in MC.A.

Figs. 1–3 plot, for Cd, Cu and Pb, respectively, the amount of heavy metal sorbed and the amount of native exchangeable metallic cations released ($\Sigma = Ca^{2+} + Mg^{2+} + K^+ + Al^{3+}$), both expressed in $\mu mol_{(+)} \, g^{-1}$, against the concentration of heavy metal in the initial sorption solution. Released Na^+ is not included in Σ because it was negligible (there is only a little amount of Na^+ in the soils compared
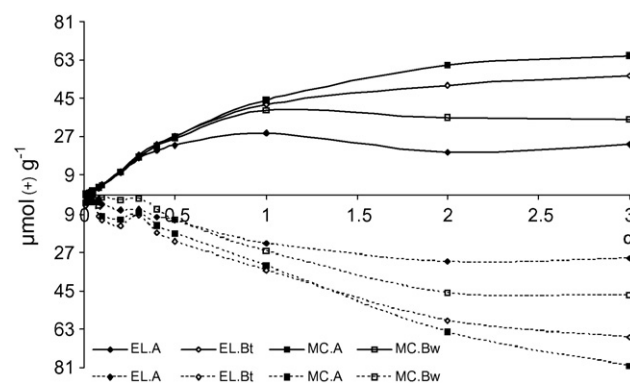

Fig. 1. Plots of sorbed Cd (top, continuous lines) and released exchangeable metallic cation ($\Sigma = Ca^{2+} + Mg^{2+} + K^+ + Al^{2+}$) (bottom, dotted lines) against the concentration of Cd in the initial sorption solution (C_0, in mmol L^{-1}). The lines joining data points are merely visual aids.
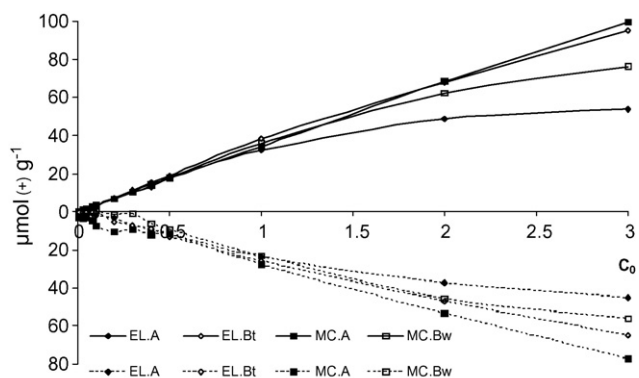
Fig. 2. Plots of sorbed Cu (top, continuous lines) and released exchangeable metallic cation ($\Sigma = Ca^{2+} + Mg^{2+} + K^+ + Al^{2+}$) (bottom, dotted lines) against the concentration of Cu in the initial sorption solution (C_0, in mmol L^{-1}). The lines joining data points are merely visual aids.

Fig. 3. Plots of sorbed Pb (top, continuous lines) and released exchangeable metallic cation ($\Sigma = Ca^{2+} + Mg^{2+} + K^+ + Al^{2+}$) (bottom, dotted lines) against the concentration of Pb in the initial sorption solution (C_0, in mmol L^{-1}). The lines joining data points are merely visual aids.
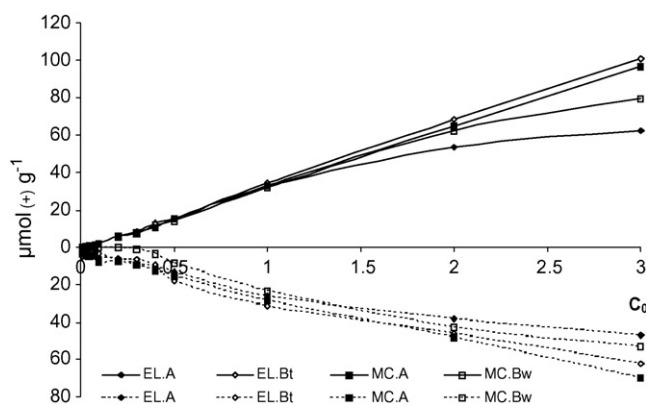
with the concentration of Na$^+$ provided by background electrolyte (0.01 M NaNO$_3$). This is also in consonance with reports that Na$^+$ is hardly displaced at all by Cu^{2+}, Cd^{2+} or Pb^{2+} [16–18], and with NaNO$_3$ having been used, on the basis of a series of preliminary experiments, as background electrolyte (this choice is further justified by the exhaustive review by Goldberg et al. [35], who found

that metal ion sorption was independent of ionic strength in NaNO$_3$ but not in other electrolytes).

Horizons EL.Bt and MC.A both sorbed more of each heavy metal than the other horizons, and showed no sign of saturation with Pb or Cu over the concentration range employed; the other horizons showed slight signs of saturation at initial Cu or Pb concentrations of 2000 μmol$_{(+)}$ g^{-1} or more, and all four horizons began to become saturated with Cd at concentrations exceeding 500–1000 μmol$_{(+)}$ g^{-1}.

For Pb and Cu, the sorption curves were closely mirrored by the corresponding curves of Σ against initial heavy metal concentration, except that heavy metal sorption exceeded Σ. In fact, in each horizon Σ correlated extremely closely with sorption of both Cu ($r = 0.989–0.999$) and Pb ($r = 0.988–0.998$) (Table 2). The inference that sorption depended to a large extent on CECe agrees with previous results obtained in soils [4,34,36] and soil fractions [6,16,37]; see also Neal and Sposito [38], Kalbitz and Wennrich [39] and the review by Bradl [32]. However, Σ accounted for only 66–79% of sorption (Table 2). At high initial heavy metal concentrations the four horizons generally showed the same order with respect to sorption as with respect to metallic cation release (EL.A < MC.Bw < EL.Bt < MC.A). Nevertheless, the horizon with by far the greatest CECe, EL.Bt, sorbed less Cu, and released less exchangeable cation in Cu solutions, than did MC.A, which had a CECe almost three times smaller but almost five times as much organic matter.

Sorption of Cd began to level off at lower initial sorption solution concentrations than Σ, especially in EL.A and MC.Bw, the horizons with the smallest CECe values. Furthermore, although Cd sorption exceeded Σ in solutions with initial Cd concentrations of up to 1000 μmol$_{(+)}$ g^{-1}, the reverse was the case at 3000 μmol$_{(+)}$ g^{-1}. Nevertheless, the general trend was for Σ to increase with Cd sorption; in fact, the corresponding regression coefficients (Table 2) are larger than for Pb and Cu, although the correlation is not so close ($r = 0.806–0.952$). Also the fact that all four horizons began to become saturated with Cd at concentrations higher than 500 μmol$_{(+)}$ g^{-1}, indicated that after these concentrations data of Cd sorption and Σ close to the same concentration. Cd sorption is thus also probably largely due to cation exchange.

Figs. 4–6 show, for each initial concentration of each heavy metal, and each horizon, the proportions of Σ due to each of the exchangeable metallic cations except Na$^+$ (release of which was, as noted above, negligible in all cases). As the concentration of de added solution increases (Figs. 4–6) the percentage of Al^{3+} and K$^+$ decreases and the one of Mg^{2+} becomes to be the most important. In general, the ion contributing most to Σ was Mg^{2+}, at least at

Table 2
Results of regressing released exchangeable metallic cation (y) on sorbed heavy metal (x) (only regressions that are significant at the $p = 0.01$ level are shown).

Horizon	Metal sorbed	Cation released									
		Total (Σ)		Mg^{2+}		Ca^{2+}		K$^+$		Al^{3+}	
		a	R^2	a	R^2	a	R^2	a	R^2	a	R^2
EL.A	Cd	0.85	0.65	0.62	0.68	0.22	0.6				
	Cu	0.79	0.99	0.47	0.99	0.20	0.99	0.02	0.75	0.01	0.66
	Pb	0.75	0.99	0.43	0.96	0.18	0.99	0.02	0.76	0.02	0.53
EL.Bt	Cd	1.04	0.90	0.99	0.91	0.05	0.88				
	Cu	0.68	1.00	0.64	0.99	0.03	0.99	0.01	0.64		
	Pb	0.66	0.98	0.62	0.98	0.03	0.98	0.01	0.94		
MC.A	Cd	1.01	0.91	0.82	0.92	0.19	0.88				
	Cu	0.79	0.99	0.62	0.99	0.15	0.98	0.01	0.63		
	Pb	0.74	0.99	0.58	0.99	0.15	0.98	0.01	0.79		
MC.Bw	Cd	0.85	0.71	0.69	0.73	0.16	0.71				
	Cu	0.71	0.98	0.57	0.99	0.13	0.98	0.01	0.65		
	Pb	0.66	0.99	0.51	0.99	0.14	0.99	0.01	0.92		

Regression lines were constrained to pass through the origin ($y = ax$) following verification that the ordinates at the origin of unconstrained regressions ($y = b + ax$) did not differ significantly from zero.
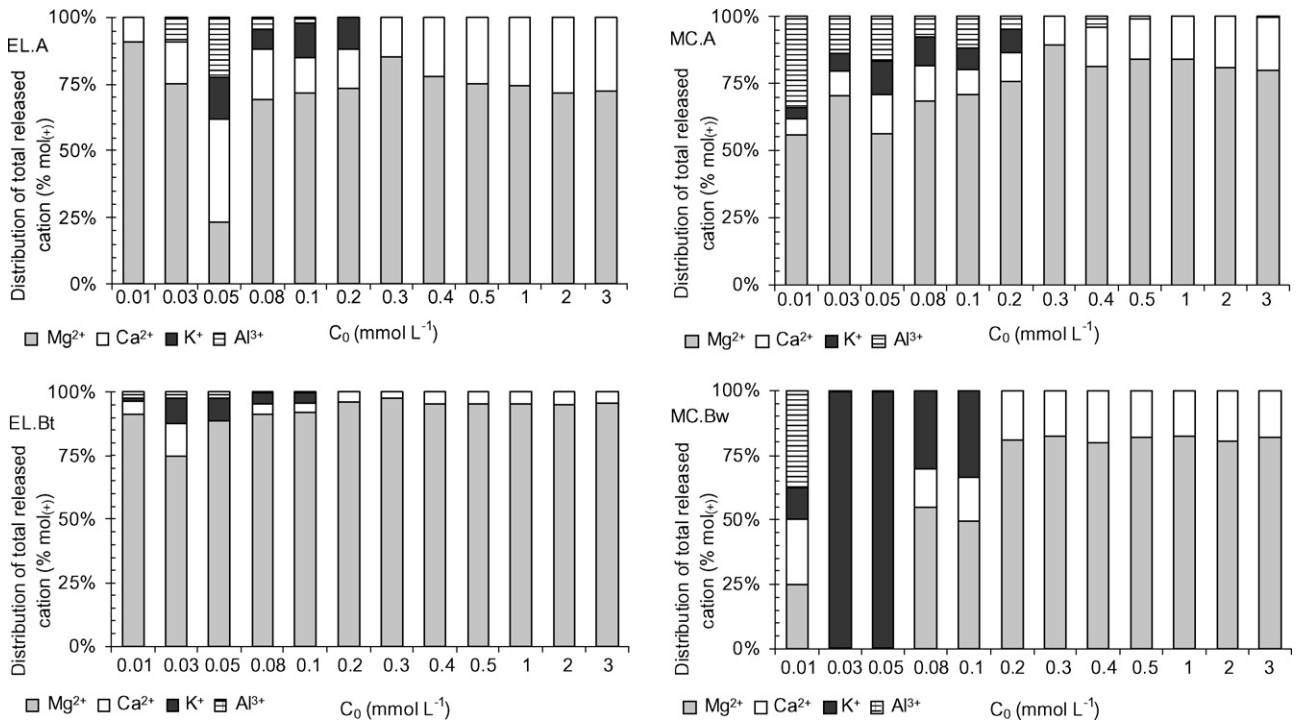
Fig. 4. Release of exchangeable metallic cation in Cd^{2+} solution: distribution of total released cation ($\Sigma = Ca^{2+} + Mg^{2+} + K^+ + Al^{2+}$) among its four components.

high heavy metal concentrations, in keeping with the correlations between heavy metal sorbed and Mg^{2+} released, they are very similar to those found for Σ (Table 2). Al^{3+} and K^+ only contribute significantly to the total amount of displaced exchangeable cation at low exchange levels in weak heavy metal solutions, especially in the case of Cd^{2+} sorption (Fig. 4). These findings suggest that the sorption, especially in the cases of Cu and Pb; was largely determined in all horizons by the replacement of Mg^{2+}, and similarly, the

release of Ca^{2+} seems also to influence the heavy metal sorption. In the case of K^+, however, cation release only correlated with metal sorption in the cases of Pb^{2+} and Cu^{2+}; while release of Al^{3+} was only associated with heavy metal sorption in soil EL, in which it correlated with Cu^{2+} sorption in both horizons and with Pb^{2+} sorption in the A horizon. That Cd^{2+} sorption did not correlate with release of K^+ or Al^{3+} in any of the four horizons studied suggests that the sites at which exchangeable K^+ and Al^{3+} are bound in these soils are
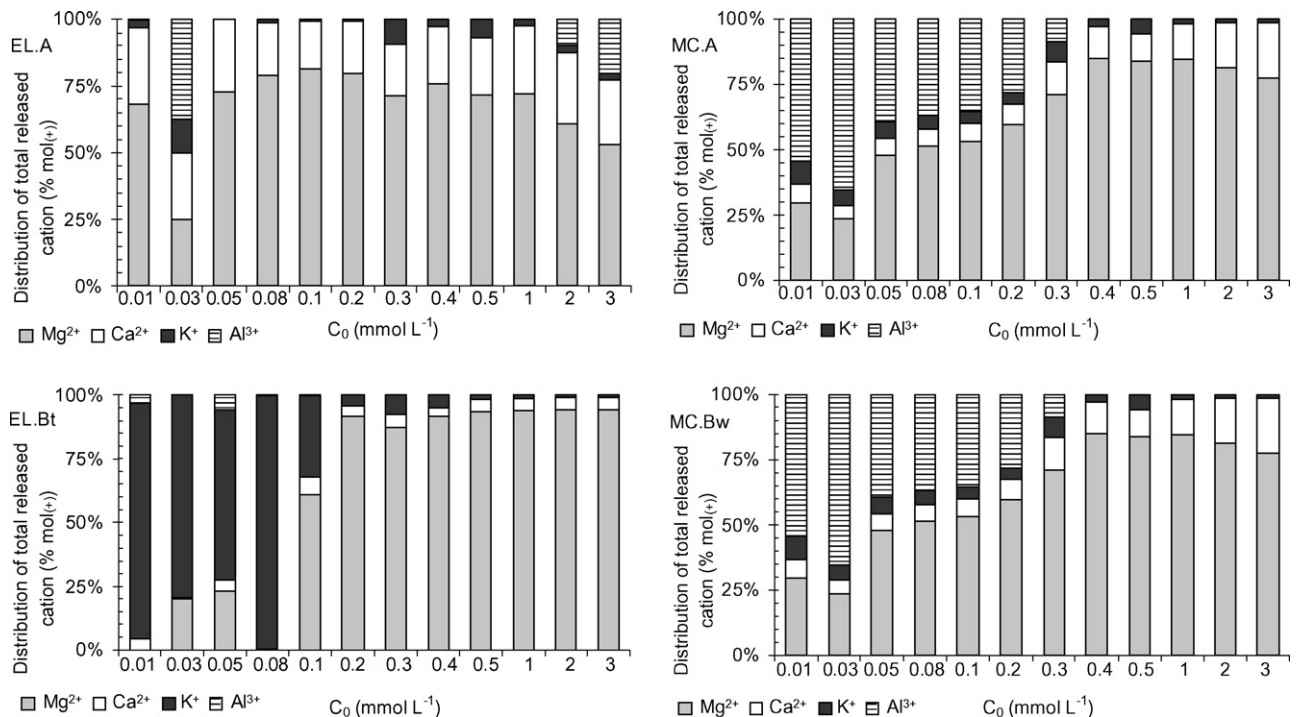

Fig. 5. Release of exchangeable metallic cation in Cu^{2+} solution: distribution of total released cation ($\Sigma = Ca^{2+} + Mg^{2+} + K^+ + Al^{2+}$) among its four components.
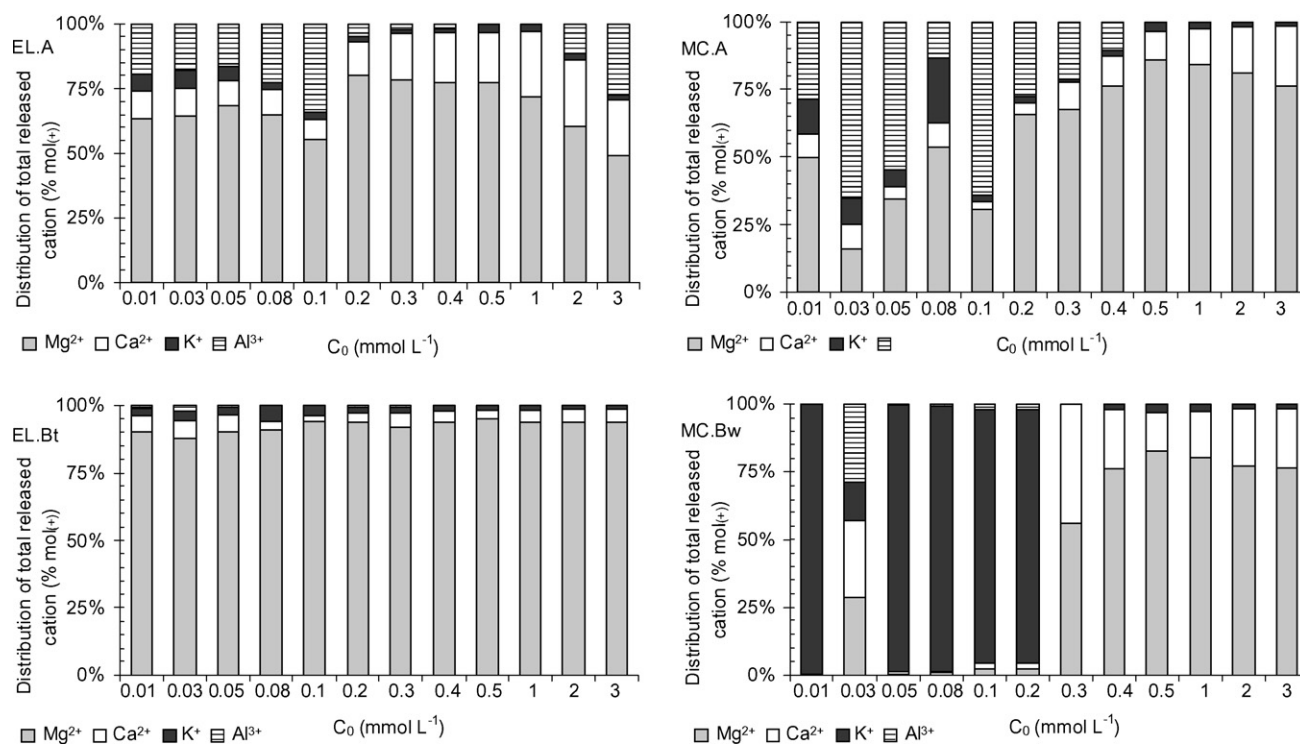
Fig. 6. Release of exchangeable metallic cation in Pb^{2+} solution: distribution of total released cation ($\Sigma = Ca^{2+} + Mg^{2+} + K^+ + Al^{2+}$) among its four components.

not available for Cd^{2+} binding, i.e. that Cd^{2+} binding is more specific than the binding of Cu^{2+} or Pb^{2+}; and similarly, the Al^{3+} sites in soil MC appear not to be available for any of the three heavy metals considered in this work.

4. Conclusions

The sorption of Cd^{2+}, Cu^{2+} and Pb^{2+} by the A and Bt or Bw horizons of soils EL and MC is largely a cation exchange process in which most of the replaced cation is Mg^{2+}, followed by Ca^{2+}; Al^{3+} and K^+ only contribute significantly to the total amount of displaced exchangeable cation at low exchange levels in weak heavy metal solutions, especially in the case of Cd^{2+} sorption.

Acknowledgements

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