

A Model Experiment: Competitive Sorption of Cd, Cu, Pb and Zn by Three Different Soils

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Abstract

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The aim of this study was to evaluate and compare the competitive and individual sorption of Cd, Cu, Pb and Zn on three natural soils: a Gleyic Fluvisol (content of Cd 30, Cu 25, Pb 2297 and Zn 3718 mg/kg), a Gleyic Cambisol (content of Cd 5, Cu 29, Pb 1158 and Zn 180 mg/kg) and a Chernozem (content of Cd 0.4, Cu 36, Pb 75 and Zn 67 mg/kg). For evaluation of the sorption and desorption, the Freundlich isotherms were used. The results of the model experiment confirmed that the sorption from single-metal solution was more effective than sorption under multi-metal conditions, due to competitive effects. In all tested soils sorption of Cd, Cu and Zn decreased with the rate of other competitive metals; the Pb sorption was not affected by other competitive metals in solutions. Moreover, during multi-metal sorption, Zn was significantly desorbed in Cambisol. In general, sorptions of Cu, Pb and Zn were greater in uncontaminated soil compared to contaminated soils. Clear trend of impact of the contamination on Cd sorption was not observed. The results showed the sorption decreasing in order Chernozem > Fluvisol > Cambisol. The sorption was the greatest in uncontaminated soil with low mobility of studied metals.

Keywords: desorption; contamination; heavy metals; isotherm; single- and multi-metal solutions

Soil pollution by heavy metals has received considerable attention during the last decades (ADRIANO *et al.* 2004). The contaminations of soil with heavy metals even at low concentrations are known to have potential impact on environmental quality and human health as well as posing a long-term risk to groundwater and ecosystems (SLACK *et al.* 2005).

The capacity of soils to retain and release metals can be an important factor to predict environmental impact (SILVEIRA *et al.* 2003).

Some of the heavy metals are essential in small concentrations for plants and heterotrophic organisms in soil, e.g. Cu and Zn. These elements must therefore be available in the soil. On the other hand, Cd and Pb, are non-essential and belong to the most toxic among the heavy metals (MAKOVNÍKOVÁ & BARANČÍKOVÁ 2009). Behavior of heavy metals in

a soil is governed largely by their sorption and desorption reactions with different soil constituents (SINGH *et al.* 2001).

Sorption of trace element ions by soil is a complex process involving different mechanisms, and is controlled by different variables that can interact (GUANSHU & BAOSHAN 2001). It is a major process responsible for the fate of trace elements in soils, since the mobility of trace elements is directly related to their partitioning between the soil solid phase and soil solution in equilibrium (VIDAL *et al.* 2009). This process is often described by the sorption isotherm, which describes the equilibrium of the sorption of a material at a surface at constant temperature. These isotherms are often used as empirical models (VELIEV *et al.* 2006). The most important factors influencing trace elements accumulation in soils and isotherm

shape are: soil pH; Eh (redox potential) (BRADL 2004); clay minerals; cation-exchange capacity (CEC); oxides of Fe, Al, and Mn; calcium carbonate and humic substance associated with natural organic matter (SPARKS 2005; FONTES & DOS SANTOS 2010).

Contaminated soils often contain more than one trace element, a factor that can have potential impact on the adsorption behaviour of each trace elements present. Currently there is limited information in the literature about determining the maximum amount of chosen trace elements sorbed from single- and multi-element solutions, and evaluating the potential for these elements to migrate through the soils (MARKIEWICZ-PATKOWSKA *et al.* 2005; FONSECA *et al.* 2011).

MATERIAL AND METHODS

Objective of this study was to determine the sorption behaviour of contaminated and uncontaminated soil. Consequently in this study sorption of selected metals was compared: Cd, Cu, Pb and Zn in the two contaminated and one uncontaminated soils with different physicochemical properties. We compare sorption of these metals in three soil types (Gleyic Fluvisol, Gleyic Cambisol and Chernozem). Batch test was undertaken using single- and multiple-metal solutions with equimolar concentrations of the aforementioned metals in order to study their mutual effects. Sorption isotherms of the selected metals were also obtained, to elucidate the each other effects on the sorption.

Soil samples. The soil samples used in this study were collected from different areas in the Czech Republic and represented a range of different chemical and physical properties. The soils were rated into the taxonomic groups: (i) heavily polluted Gleyic Fluvisol from the alluvium of the Litavka river (main contamination was caused by the floods of water contaminated by wastes from smelter tailings); (ii) Gleyic Cambisol Příbram with moderate contamination

mainly by atmospheric emissions from the same smelter (Kovohutě Příbram); and (iii) unpolluted Chernozem of Suchdol. The soil samples were collected from three places and depths of 0–20 cm of each soil. The samples were pooled, air-dried, sieved through a 2 mm sieve, and homogenized prior to laboratory analysis and sorption model experiment.

Analytical methods. The pH values of the soils were measured in deionized water and 0.01M CaCl₂ in ratio (1:1.25 w/v). Cation exchange capacities (CEC) of soil samples were determined in suspension of soil and 0.1M BaCl₂ (1:50 w/v). The organic carbon (C_{org}) was determined spectrophotometrically after the oxidation of organic matter by K₂Cr₂O₇ (SIMS & HABY 1971). Measurement of the extract was performed by segmental flow-analysis using a colorimetric method on a SKALAR (San⁺System, Breda, Netherlands) apparatus. Available contents of nutrients, such as Ca, K and Mg, were determined by the Mehlich III soil extraction procedure (MEHLICH 1984) using flame atomic absorption spectroscopy (F-AAS, VARIAN 280FS, Varian, Australia).

Total concentrations of Cd, Cu, Pb and Zn in the soils were determined according to SZÁKOVÁ *et al.* (2009). Quality control of Cd, Cu, Pb and Zn determination in the soil samples was evaluated using the certified reference material (RM) 7003 Silty Clay Loam. Available metal fractions were determined using extraction 0.11M CH₃COOH (NOVOZAMSKY *et al.* 1993). Metals in the digests and extracts were analyzed using ICP-OES (Varian VistaPro, Varian, Australia).

Selected chemical properties of three soils studied are shown in Table 1.

Desorption and sorption experiments. The batch sorption/desorption model experiments were conducted according to TRAKAL *et al.* (2011). The sorption isotherms of Cd, Cu, Pb and Zn for each soil were obtained by adding 20 ml of the metal solution (disolved metal-nitrate salts in the 0.01M KNO₃

Table 1. Selected chemical characteristics and total initial metal concentration in the studied soils

	pH (–)	CEC (mmol(+)/kg)	C _{org} (%)	Available form of nutrients			Total metal content			
				K	Ca	Mg	Cd	Cu	Pb	Zn
Fluvisol	5.3	57 ± 4	1.8	155 ± 4	995 ± 68	125 ± 0.1	30 ± 3	25 ± 1	2297 ± 42	3718 ± 317
Cambisol	6.1	134 ± 3	2.1	67 ± 0.3	2242 ± 109	42 ± 0.3	5 ± 1	29 ± 0.8	1158 ± 51	180 ± 16
Chernozem	7.2	258 ± 4	1.8	294 ± 3	7826 ± 92	209 ± 4	0.4 ± 0.02	36 ± 0.4	75 ± 0.8	67 ± 3

CEC – cation-exchange capacity; C_{org} – organic carbon

background electrolyte) to 1.0 g of the soil. A series of single- and multi-element solutions were prepared at varying concentrations: Cu, Pb, Zn (0.1, 0.5, 1, 2, 4, 8 mmol/l) and Cd (0.05, 0.25, 0.5, 1, 2, 4 mmol/l). All samples and concentrations were in triplicate. The suspensions of soil samples in sorption/desorption were shaken according to BOUDESOCQUE *et al.* (2007) on an end-over-end shaker for 48 h in order to reach equilibrium and centrifuged at 4000 rpm for 10 min at temperature of 25°C. The supernatants were analyzed by ICP-OES (Varian VistaPro, Varian, Australia). All the chemicals used were of analytical grade (Lach-Ner, Neratovice, Czech Republic).

The sorption of Cd, Cu, Pb and Zn was described by non-linear Freundlich equation (1), which was

chosen for isotherm parameter evaluation in order to avoid limitations associated with the linearization of sorption isotherms (HANAFI & SJIAOLA 1998; CHEN *et al.* 1999):

$$S = K_f C^n \quad (1)$$

where:

S – trace elements adsorbed

C – equilibrium concentration

K_f – adsorption coefficient

n – constant

The Freundlich K_f constant describes the partitioning of a metal between solid and liquid phases and implies trace elements sorptive capacity (GRAY

Table 2. Values of Freundlich parameters and model efficiencies (E) determined in the individual and multi-metal experiments

Experiment		E	Freundlich parameters	
			K	n
Cd	Fluvisol	> 0.99	0.06	0.48
	Chernozem	0.97	0.9	0.35
	Cambisol	0.94	3.40	0.32
Cd _{multi-metal}	Fluvisol	0.74	0.003	0.16
	Chernozem	0.60	1.15	0.14
	Cambisol	0.45	2.05	0.11
Cu	Fluvisol	0.99	0.05	0.43
	Chernozem	0.99	0.20	0.41
	Cambisol	0.93	9.40	0.36
Cu _{multi-metal}	Fluvisol	0.97	0.02	0.33
	Chernozem	0.95	0.05	0.30
	Cambisol	0.77	10.2	0.18
Pb	Fluvisol	0.96	0.07	0.36
	Chernozem	0.98	0.04	0.40
	Cambisol	0.80	26.9	0.27
Pb _{multi-metal}	Fluvisol	0.96	0.06	0.30
	Chernozem	0.95	0.05	0.29
	Cambisol	0.90	6.45	0.28
Zn	Fluvisol	0.95	0.02	1.15
	Chernozem	0.94	0.06	0.78
	Cambisol	0.98	0.71	0.63
Zn _{multi-metal}	Fluvisol	0.90	0.004	0.19
	Chernozem	n.a.	n.a.	n.a.
	Cambisol	n.a.	n.a.	n.a.

K – sorption coefficient; n – empirical coefficient ; n.a. – results not available

Table 3. Desorption of Cd, Cu, Pb and Zn in experimental soils (in nmol/g)

Soil	Desorption			
	Cd	Cu	Pb	Zn
Fluvisol	3.3 ± 0.3	4.5 ± 0.2	48.0 ± 2.4	667 ± 25.0
Cambisol	1.3 ± 0.07	3.0 ± 0.2	55.5 ± 4.8	18.2 ± 3.4
Chernozem	-0.016 ± 0.0005	-0.1 ± 0.002	0.8 ± 0.016	12.3 ± 2.1

et al. 1998). For evaluation of non-linear isotherm parameters and fitting models efficiencies (E) the model of BOLSTER and HORNBERGER (2007) using unweighted nonlinear least squares regression by Microsoft Excel was used (Table 2).

Statistical Analysis. All data were processed by Microsoft Excel (Microsoft 2007) and the linear correlation (R^2) was performed by using the program of Statistica 9.1 (StatSoft, Tulsa, USA).

RESULTS AND DISCUSSION

The results obtained from the model experiment showed a low desorption of Cd and Cu and a relatively low desorption of Pb for all tested soils (Table 3). Cd is easily desorbed in the presence of more competitive metals, e.g. Cu and Pb due to their weaker binding in the soil (MARKIEWICZ-PATKOWSKA *et al.* 2005). The Zn desorption was high in Fluvisol and low in other soils in the background electrolyte (0.01 mol/l KNO_3). These desorption results were related to the initial Cd, Cu, Pb and Zn total contents in tested soils (Table 1). The high Zn total content in Fluvisol and the high Pb total contents in Fluvisol and Cambisol significantly affected desorption of both elements. According to PÉREZ-NOVO *et al.* (2011) zinc is much more easily desorbed for its weak binding into the soil and its chemical characteristics.

pH of all experimental soils decreased with increased metal concentrations in single-metal and multi-metal solution. In single-metal solution strong negative correlation between decrease of pH and sorption quantity of all tested elements and soils were determined (Table 4). The same effect was found in multi-metal solution, except Fluvisol. Effect of pH decrease was caused by the hydrolysis and loose of H^+ cation from soil sorption sites (MOUTA *et al.* 2008; TRAKAL *et al.* 2011).

Figure 1a shows the isotherm curves obtained for Cd sorption in competitive (multi-metal) and non-competitive (single-metal) systems. The Cd sorption in multi-metal solution was 10-times lower in contrast to sorption in single-metal solution for all soil

types. The sorption from the single-metal solution was much more effective than sorption of the same element from the multi-metal solution, agreeing with work of CAY *et al.* (2004).

The sorption of Cu was higher in single-metal solution in contrast to sorption in multi-metal experiment (Figure 1b). Strong competition between Cu and Cd during the sorption was observed by CERQUEIRA *et al.* (2011). Our results of the model experiment confirmed

Table 4. Results of linear correlation between change pH and sorption quantity

Experiment		R^2
Cd	Fluvisol	-0.98
	Chernozem	-0.98
	Cambisol	-0.94
Cd _{multi-metal}	Fluvisol	-0.43
	Chernozem	-0.76
	Cambisol	-0.90
Cu	Fluvisol	-0.87
	Chernozem	-0.96
	Cambisol	-0.99
Cu _{multi-metal}	Fluvisol	-0.91
	Chernozem	-0.98
	Cambisol	-0.90
Pb	Fluvisol	-0.99
	Chernozem	-0.96
	Cambisol	-0.98
Pb _{multi-metal}	Fluvisol	-0.96
	Chernozem	-0.93
	Cambisol	-0.93
Zn	Fluvisol	-0.99
	Chernozem	-0.98
	Cambisol	-0.85
Zn _{multi-metal}	Fluvisol	0.50
	Chernozem	-0.90
	Cambisol	-0.98

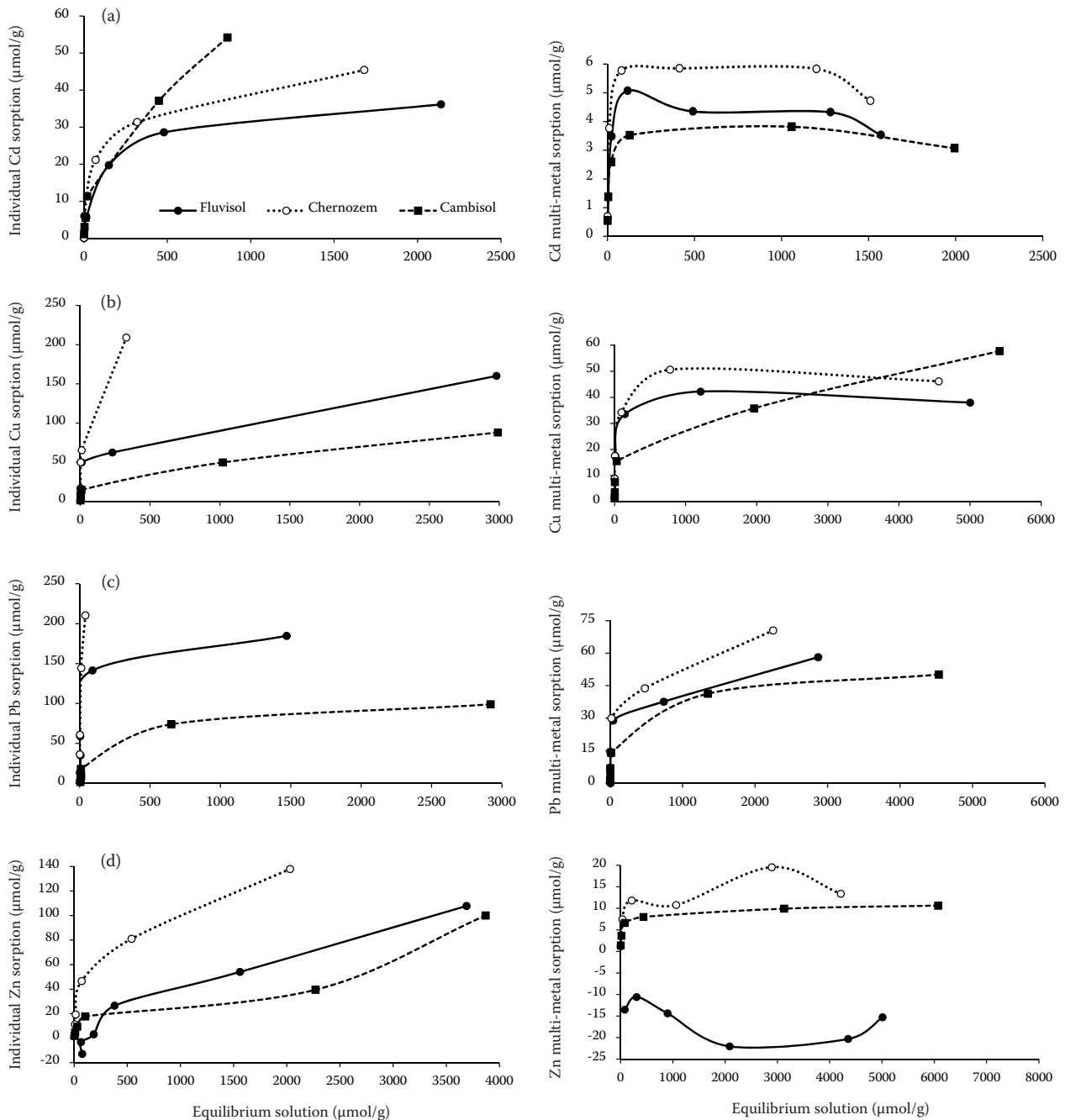


Figure 1. Individual and multi-metal sorption isotherms of Cd (a), Cu (b), Pb (c) and Zn (d)

the finding of these authors and showed increased Cu sorption in multi-metal solution in Cambisol (Figure 1b). The other metal Pb has a similar trend of the sorption behavior as Cu (Figure 1c). The results of the model experiment indicate the highest Pb sorption in single-metal experiment as well as in multi-metal one in Chernozem. In general, the sorption of Pb and Cu was higher than Cd and Zn sorption (COVELO *et al.* 2008).

The sorption concentration of Zn was 10-times lower in the presence of other competitive metals.

The different Zn behavior was observed in Fluvisol, where Zn was desorbed during multi-metal sorption (Figure 1d). According to TRAKAL *et al.* (2011) this effect caused probably due to (i) extremely high initial Zn content in the soil and (ii) its high desorption efficiency caused by other competitive metals.

The results of the model experiment from single-metal sorption in Chernozem and Fluvisol confirmed the well-known fact that soil sorption decreased in the order Pb > Cu > Zn > Cd, which was previously

reported by other authors (VIDAL *et al.* 2009; TRAKAL *et al.* 2011). In Cambisol sorption decreased in order $Pb \approx Zn > Cu > Cd$. These results are in accordance with the initial content of metals in this soil. The results of the model experiment showed high sorption of all soil types, the sorption decreased in order Chernozem > Fluvisol > Cambisol. The sorption was the greatest in uncontaminated soil – Chernozem with low mobility of these tested metals and higher pH (7.2). The greater sorption of metals with increased pH is well known (RAGHUPATHI & VASUKI 1993; ECHEVERRÍA *et al.* 1998; MARKIEWICZ- PATKOWSKA *et al.* 2005). The reason for this enhanced metal sorption with increased soil solution pH is due to a decrease in competition with H^+ for binding sites and an increase in the negative charge of the soil surface.

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