Mobility of Cd, Pb, Cu, and Cr in some Estonian soil types

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Abstract. The sorption capacity of selected heavy metals (Cd, Pb, Cu, Cr) to five Estonian soils was evaluated using spiked subsoil samples in laboratory experiments. The experimental sorption data fitted well to the linear Freundlich isotherm. The sorption of metals in subsoil depended on the soil type, e.g., mineral composition. The results indicate that the content of quartz and carbonates is important in affecting the metal sorption capacity of subsoil. On the basis of our data the possibility of penetration in depth and accumulation of mobile metals was evaluated. It was concluded that increase in dissolved Cd and accumulation of other metals in the subsoil of Podzol is expected. The accumulation of Pb could be the main process for soils with a high amount of dolomite.

Key words: heavy metals, soil, leaching, sorption, contamination.

INTRODUCTION

Contamination of soil with heavy metals is a common environmental problem related to industrial activity and agricultural practices, i.e. wastewater irrigation and composts, application of fertilizers and agro-chemicals, disposal of sewage sludge (Punning & Varras 1993; Sterckeman et al. 2000; Han et al. 2001; Twardowska 2004; Weber et al. 2007). Heavy metals discharged to soil are generally characterized by long residence times (Alloway 1995; Selim & Amacher 1997). Metals can be accumulated in the upper layer of the soil or penetrate in different forms into surface water (Keller & Domergue 1996; Citeau et al. 2003; Lepane et al. 2007). Sorption and precipitation are fundamental chemical reactions of trace elements that greatly affect metal availability in aerobic terrestrial systems (Bradl 2004). The infiltration of surface water is one possible way of contamination of soil and groundwater by mobile metals (Singh & Steinnes 1994; Qiang et al. 2006). Metals in dissolved forms are more bioavailable and consequently constitute the greatest environmental hazard (Kalbitz &Wennrich 1998; Kookana & Naidu 1998; Turner et al. 2008). Metals can be transported along the soil profile by colloids or in dissolved forms depending on the metal concerned (Citeau et al. 2003; Zhao et al. 2009). In general, metal mobilization depends on the concentration of the parent metal in the soil solution, which in turn depends on the sorption and retention of the same metal in soil (Singh & Steinnes 1994; Alloway 1995; Sterckeman et al. 2000).

It is well known that basic soil characteristics influencing the sorption of metals are pH, redox potential, contents of organic matter, clay, Fe and Mn oxides and hydroxides, and metal carbonates (Selim & Amacher 1997; Bradl 2004; Vega et al. 2006; Usman 2008). Recent studies have established significant impact of mineral components such as carbonates on the sorption and retention of metals (Shirvani et al. 2006; Ahmed et al. 2008; Sipos et al. 2008). However, the role of carbonates in affecting the fate of toxic metals in soils is not yet fully clear.

As a rule, soil properties and composition change with depth. Consequently, the characteristics of subsoil could be different from those of the surface layer. The subsoil layer has been shown to be an important geochemical barrier against the migration of metals in the soil system, including penetration into groundwater (Elliott et al. 1986; Hooda & Alloway 1998; Sterckeman et al. 2000).

An abundant literature is available on the sorption of heavy metals by surface soils, but data concerning the whole soil system are lacking. The estimation of the risk derived from heavy metals contamination in soils requires better knowledge about metal interaction in soil.

The aim of the present work is to evaluate the capacity of subsoil for selected heavy metals (Cd, Pb, Cu, Cr) using experimentally derived distribution coefficients (K_d). Five soils, representing four important soil types in Estonia, Rendzic Leptosol (Rendzinas),

Table 1. Characterization of the studied soil types. Classification of parent matter according to Petersell et al. (1997). Samples of soil 5 were collected from the B–C horizon because monolithic Silurian dolomite occurs deeper than 60 cm

Sample No.	Soil type	Site	Parent matter	Depth, cm
1	Podzoluvisol	Tooma-15	Sand and silt	100–120
2	Podzol	Tartu-41	Sandy till	100–120
3	Podzolic Gleysols	Kasari-26	Till and silt	110–130
4	Rendzic Leptosol	Papiaru-1	Till	90–110
5	Rendzic Leptosol	Arase-1	Local till	50–60

Podzol (Sod-podzolic), Podzoluvisol (Brown pseudo-podzolic), and Podzolic Gleysols (Gley-podzols), were investigated (Table 1). The paper is an extension of our previous study (Alumaa et al. 2001) on topsoil (A horizon) samples from the parent soil types.

MATERIALS AND METHODS

Sampling

Samples of soils were taken from the C horizon in different locations in Estonia (Table 1). A detailed sampling procedure is described in Petersell et al. (1996).

The subsoil samples were wrapped in plastic bags and transported to the laboratory. All samples were air-dried, crushed, and sieved through a 2 mm mesh. The fraction less than 2 mm was taken for the sorption experiments.

Procedures

Soil pH was measured using a $1:2$ suspension of soil/water. The content of soil organic matter (OM) was found by the mass difference (weight loss) upon heating air-dry soil ($105\,°C$ for 3 h) to $340\,°C$ in a muffle furnace for 2 h.

Sorption experiments

Batch equilibrium experiments were used in order to compare metal affinity differences between the subsoil matrices. The experiments were carried out using 50 mL test tubes. Two grams of the air-dried sample was added to each test tube along with 10 mL of parent metal solution in 0.01 M $CaCl_2$. The ranges of initial concentrations of Cd, Pb, Cu, and Cr are presented in Table 2.

After 16 h of shaking at room temperature ($21\,°C$), the samples were separated by centrifugation at 3000 rpm for 10 min and the supernatant was analysed by graphite furnace AAS. The metal solutions were prepared from the stock solution of metal salts (chlorides) by adding the required amount of the stock solution to 0.01 M $CaCl_2$.

The native amount of the metal involved in the sorption process was characterized by extracting the soil sample with 0.01 M $CaCl_2$. The amount of the metal adsorbed was calculated from the difference between concentrations in the initial and the equilibrium solution. Blank tests without a sample but applying the same procedure for the sorption were carried out in parallel for each set of analysis.

Table 2. The ranges of initial concentrations of metals ($\mu g\ mL^{-1}$; for Cd, $ng\ mL^{-1}$) in sorption experiments

Metal	The range of initial concentrations
Cd	7–74
Pb	6–129
Cu	1–61
Cr	0.2–15.6

RESULTS AND DISCUSSION

Soil properties (C horizon)

The main properties of subsoil samples are presented in Table 3. The pH values were almost neutral. The mineral composition of samples was characterized by high variation of quartz, clay, calcite, dolomite, and Fe/Mn content.

Sorption experiments

Isotherms of metal sorption by subsoil were calculated by plotting equilibrium concentrations of the metal against adsorbed amounts. The data fitted well to the linear Freundlich isotherm. The distribution coefficient (K_d) was then found using the relation $K_d = C_s/C_w$, where C_s is the concentration of the metal adsorbed in the soil at equilibrium and C_w is the concentration of the metal in the solution at equilibrium. The K_d values for each metal

Table 3. The characteristics of subsoil samples (data on the mineral composition and Fe/Mn content after Petersell et al. 1996). For the numbering of soil types see Table 1

Composition, %	Soil sample				
	1	2	3	4	5
Clay	7	16	4	12	15
Quartz	35	69	31	16	22
Calcite	37	2	31	56	7
Dolomite	9	1	17	3	44
OM	0.2	1.2	0.2	0.7	0.1
Mn*	176	440	278	425	464
Fe	0.62	2.21	0.99	1.03	1.58
pH (H_2O)	7.1	6.9	7.2	7.2	7.1

* Mn in ppm; OM, organic matter.

Table 4. Adsorption of metals in subsoil samples according to K_d values (mL g^{-1}) with standard deviations. For the numbering of soil types see Table 1

Soil sample	Cd	Pb	Cu	Cr
1	1 040 ± 63	9 660 ± 434	2 360 ± 340	6 010 ± 92
2	33 ± 2	4 090 ± 230	1 220 ± 144	7 780 ± 558
3	1 060 ± 457	21 500 ± 142	10 090 ± 1 253	1 820 ± 178
4	2 390 ± 104	>61 600	3 670 ± 529	269 ± 53
5	1 350 ± 170	61 600 ± 471	1 640 ± 94	870 ± 55

are presented in Table 4. The sequence of sorption affinity of metals toward subsoils was found to be the following: Pb > Cr > Cu > Cd for Podzoluvisol, Cr > Pb > Cu >> Cd for Podzol, Pb > Cu >> Cr > Cd for Podzolic Gleysols, Pb >> Cu, Cd >> Cr for Rendzic Leptosol.

As expected, the results obtained revealed an important role of the soil type, i.e. pH and composition in immobilization of Cd, Pb, and Cu in subsoil samples. Cd and Pb demonstrated high affinity towards subsoils, which had the highest content of carbonates and Mn-containing components (Table 3). Hooda & Alloway (1998) observed similar trends when investigating the sorption of Cd and Pb in different soils in England.

A positive significant correlation was detected between Cr adsorption and content of quartz ($R = 0.90$, $p < 0.05$), whereas for Cd the relationship was negative ($R = -0.92$, $p < 0.05$). It means that Cr had the highest affinity to subsoil (sample 2) with the highest content of OM and quartz.

The results of the present study on heavy metal sorption in subsoils were compared with early data obtained for parent topsoil samples. The main characteristics of topsoil samples are presented in Table 5. The data demonstrated higher affinity of Cd, Pb, and Cu towards topsoil samples (Table 6), with a high content

of carbonates and Fe/Mn components. Cr sorption was affected by the significant amount of OM and quartz in topsoil samples. A significant ($p < 0.05$) positive correlation was estimated between Cd ($R = 0.94$), Pb ($R = 0.93$), Cu ($R = 0.93$) and the content of Mn, which indicated the prevalent role of Mn oxides in the accumulation of these metals.

On the basis of the adsorption characteristics it is possible to evaluate in-depth penetration of each metal (Carlon et al. 2004; Sastre et al. 2007). In general, soils with a high sorption affinity and retention for a trace metal have a significant capacity for surface accumulation of the metal concerned. The metal pollution of topsoil may have long-lasting effect on the mineralization of OM and nutrient cycling in the soil ecosystem via change in the microbiological properties of soil (Kandeler et al. 2000).

Metal leaching through the boundary between topsoil and subsoil increases soil-bound and/or dissolved metal in subsoil (Citeau et al. 2003). If subsoil has a high affinity for a metal, the retention of the metal leached from the surface soil is efficient and its further penetration to groundwater could be prevented. On the contrary, if the adsorption is low, subsoil is an inefficient barrier against groundwater contamination. Finally, if the adsorption capacity of both topsoil and subsoil is low, soil as a whole

Table 5. The characteristics of topsoil samples (after Petersell et al. 1996). For the numbering of soil types see Table 1

Composition, %	Soil sample				
	1	2	3	4	5
Clay	8	15	21	13	12
Quartz	60	34	32	29	26
Calcite	5	nd	9	15	2
Dolomite	2	nd	6	nd	14
OM	6.64	4.88	18.64	6.86	6.93
Mn*	330	280	470	688	880
Fe	0.93	1.24	2.34	2.28	2.26
pH (H$_2$O)	7.4	6.5	5.0	7.1	7.12

* Mn in ppm; nd, not determined; OM, organic matter.

Table 6. Adsorption of metals in topsoil (A horizon) samples based on values of the distribution coefficient, K_d ($n \pm$ SD), mL g^{-1}, for parent metal. In parentheses: $n - K_d$ value, SD – standard deviation. For the numbering of soil types see Table 1. (Data adopted from Alumaa et al. 2001)

Soil sample	Cd	Pb	Cu	Cr
1	486 ± 34	6 250 ± 125	473 ± 52	1 020 ± 92
2	88 ± 6	308 ± 6	58 ± 6	537 ± 48
3	1 260 ± 88	5 420 ± 108	235 ± 26	1 100 ± 99
4	1 250 ± 236	>61 600	4 150 ± 1 743	577 ± 190
5	2 650 ± 186	>61 600	11 200 ± 1 561	295 ± 86

offers low protection against groundwater contamination by metals deposited to the soil surface from air pollution, fertilizer application, or other sources.

The great difference between the Cd and Cu sorption ability of topsoil and subsoil of Podzoluvisol (sample 1) (Tables 4 and 6) could be an indicator of the following processes: the metals leached from the surface soil layer could be accumulated in subsoil. This soil has high affinity for both Pb and Cr and consequent possible accumulation of metals in soil.

The low Cd sorption capacity of Podzol (sample 2) indicates that the metal present in the surface layer could be readily leached to groundwater. The observed behaviour of Cd is in good agreement with the study of Keller & Domergue (1996), who also found that the metal could be transported in depth through a Podzolic soil. On the other hand, the much higher adsorption capacity of subsoil for Pb, Cr, and Cu (Table 4) compared to topsoil (Table 6) show that these metals could be readily accumulated in subsoil.

Podzolic Gleysols (sample 3) exhibit a certain affinity in subsoil for Cu and only moderate affinity for Pb and Cd (Tables 4 and 6). This soil has only moderate retention capacity for Pb and Cu in the surface layer, but much higher values in the subsoil, where accumulation

of these metals would be expected. The low affinity of soil towards Cr indicates the risk of contamination of groundwater with this metal.

It is interesting to compare the different behaviour of metals in two Rendzic Leptosol samples. Cu in sample 4 would be retained mainly in the surface layer, whereas in sample 5 this metal could penetrate into deeper layers and accumulate there. Sample 5 has a sufficiently high Cd adsorption capacity of the surface layer to predict accumulation there. In sample 4 the leaching of the metal from the surface layer and its subsequent retention in subsoil with a high content of calcite is a more likely outcome. The adsorption capacity for Cr is low in both samples and water could be easily contaminated by this metal. As a consequence, plants growing in contaminated soils could represent a significant pathway for human exposure to toxic metal (Kabata-Pendias 2004; Khan et al. 2008).

The two Rendzic Leptosol soils (samples 4 and 5) exhibit a higher sorption affinity for Pb and Cd than the other soils. The very high sorption capacity of Pb in these soils would indicate an extremely high possibility of metal accumulation and retention, which affect metal mobility and toxicity. Several studies on the sorption of heavy metals added to soils and minerals have inferred

a higher Pb affinity relative to other metals (Elliott et al. 1986; Anderson & Christensen 1988; Veeresh et al. 2003; Vega et al. 2006; Sastre et al. 2007; Zhang & Zheng 2007; Usman 2008). This phenomenon is explained by specific properties of the metal concerned, i.e., higher ionic radius, atomic weight, greater hydrolysis constant, etc., and the formation of hydrolysis products of $(MeOH^+)$. The removal of OH^- ions from the solution by the precipitation of the metal as $Me(OH)_2$ is also an important issue (Usman 2008).

CONCLUSIONS

The adsorption of selected heavy metals (Cd, Pb, Cu, and Cr) in four soil types was studied. An important role of calcites and dolomites in the immobilization of metals in soils was revealed. Due to different sorption affinity of topsoil and subsoil for toxic metals in Podzol, an increase in dissolved Cd in the surface layer and accumulation of other metals in subsoil could be expected. The accumulation of toxic lead could occur in soils with a high content of dolomite. The results indicate the potential risk of groundwater contamination with toxic metals in every studied soil type.

REFERENCES

Ahmed, I. A. M., Crout, N. M. J. & Young, S. D. 2008. Kinetics of Cd sorption, desorption and fixation by calcite: a long-term radiotracer study. *Geochimica et Cosmochimica Acta*, **72**, 1498–1512.

Alloway, B. J. 1995. Soil processes and the behaviour of metals. In *Heavy Metals in Soils* (Alloway, B. J., ed.), pp. 38–57. Blackie Academic and Professional, London.

Alumaa, P., Steinnes, E., Kirso, U. & Petersell, V. 2001. Heavy metal sorption by different Estonian soil types at low equilibrium solution concentration. *Proceedings of the Estonian Academy of Sciences, Chemistry*, **50**, 104–115.

Anderson, P. R. & Christensen, T. H. 1988. Distribution coefficients of Cd, Co, Ni and Zn in soils. *Journal of Soil Science*, **39**, 15–22.

Bradl, H. B. 2004. Adsorption of heavy metal ions on soils and soils constituents. *Journal of Colloid and Interface Science*, **277**, 1–18.

Carlon, C., Dalla Valle, M. & Marcomini, A. 2004. Regression models to predict water-soil heavy metals partition coefficients in risk assessment studies. *Environmental Pollution*, **127**, 109–115.

Citeau, L., Lamy, I., van Oort, F. & Elsass, F. 2003. Colloidal facilitated transfer of metals in soils under different land use. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **217**, 11–19.

Elliott, H. A., Liberati, M. R. & Huang, C. P. 1986. Competitive adsorption of heavy metals by soils. *Journal of Environmental Quality*, **15**, 214–219.

Han, F. X., Kingery, W. L. & Selim, H. M. 2001. Accumulation, redistribution, transport and bioavailability of heavy metals in waste-amended soils. In *Trace Elements in Soil: Bioavailability, Flux and Transfer* (Iskandar, I. K. & Kirkham, M. B., eds), pp. 141–168. CRC Press, Boca Raton, FL, USA.

Hooda, P. S. & Alloway, B. J. 1998. Cadmium and lead sorption behaviour of selected English and Indian soils. *Geoderma*, **84**, 121–134.

Kabata-Pendias, A. 2004. Soil–plant transfer of trace elements – an environmental issue. *Geoderma*, **122**, 143–149.

Kalbitz, K. & Wennrich, R. 1998. Mobilization of heavy metals and arsenic in polluted wetland soils and its dependence on dissolved organic matter. *Science of Total Environment*, **209**, 27–39.

Kandeler, E., Tscherko, D., Bruce, K. D., Stemmer, M., Hobbs, P. J., Bradgett, R. D. & Amelung, W. 2000. Structure and function of the soil microbial community in microhabitats of a heavy metal polluted soil. *Biology and Fertility of Soils*, **32**, 390–400.

Keller, C. & Domergue, F.-L. 1996. Soluble and particulate transfers of Cu, Cd, Al, Fe and some major elements in gravitation waters of a Podzol. *Geoderma*, **71**, 263–274.

Khan, S., Aijun, L., Zhang, S., Hu, Q. & Zhu, Y.-G. 2008. Accumulation of polycyclic aromatic hydrocarbons and heavy metals in lettuce grown in the soils contaminated with long-term wastewater irrigation. *Journal of Hazardous Materials*, **152**, 506–515.

Kookana, R. S. & Naidu, R. 1998. Effect of soil solution composition on cadmium transport through variable charge soils. *Geoderma*, **84**, 235–248.

Lepane, V., Varvas, M., Viitak, A., Alliksaar, T. & Heinsalu, A. 2007. Sedimentary record of heavy metals in Lake Rõuge Liinjärv, southern Estonia. *Estonian Journal of Earth Sciences*, **56**, 221–232.

Petersell, V., Mõttus, V., Täht, K. & Unt, L. 1996. *Bulletin of the Geochemical Monitoring of Soil 1992–1994*. Department of Environmental Geology, Geological Survey of Estonia, Tallinn, 68 pp.

Petersell, V., Ressar, H., Carlsson, M., Mõttus, V., Enel, M., Mardla, A. & Täht, K. 1997. *The Geochemical Atlas of the Humus Horizon of Estonian Soil*. Geological Survey of Estonia, Tallinn–Uppsala, 75 pp.

Punning, J.-M. & Varvas, M. 1993. Influence of natural and manmade processes on the geochemical composition of lake sediments, northeast Estonia. *Applied Geochemistry*, **8**, Suppl. 2, 75–77.

Qiang, X., Bing, L., Hui-yun, W. & Lei, L. 2006. Numerical simulation of trace element transport on subsurface environment pollution in coal mine spoil. *Journal of Trace Elements in Medicine and Biology*, **20**, 97–104.

Sastre, J., Rauret, G. & Vidal, M. 2007. Sorption–desorption tests to assess the risk derived from metal contamination in mineral and organic soils. *Environment International*, **33**, 246–256.

Selim, H. M. & Amacher, M. C. 1997. *Reactivity and Transport of Heavy Metals in Soils*. Lewis Publishers, Boca Raton, FL, 201 pp.

Shirvani, M., Kalbasi, M., Shariatmadari, H., Nourbakhsh, F. & Najafi, B. 2006. Sorption–desorption of cadmium in aqueous palygorskite, sepiolite, and calcite suspensions: isotherm hysteresis. *Chemosphere*, **65**, 2178–2184.

Singh, B. R. & Steinnes, E. 1994. Soil and water contamination by heavy metals. In *Soil Process and Water Quality* (Lal, R. & Stewart, B. A., eds), pp. 233–270. Lewis Publisher, Boca Raton, FL, USA.

Sipos, P., Németh, T., Kis, V. & Mohai, I. 2008. Sorption of copper, zinc and lead on soil mineral phases. *Geoderma*, **73**, 461–469.

Sterckeman, T., Douay, F., Proix, N. & Fourrier, H. 2000. Vertical distribution of Cd, Pb and Zn in soils near smelters in the North of France. *Environmental Pollution*, **107**, 377–389.

Turner, J. N., Brewer, P. A. & Macklin, M. G. 2008. Fluvial-controlled metal and As mobilisation, dispersal and storage in the Río Guadiamar, SW Spain and its implications for long-term contaminant fluxes to the Doñana wetlands. *Science of the Total Environment*, **394**, 144–161.

Twardowska, I. 2004. Assessment of pollution from solid waste. In *Solid Waste: Assessment, Monitoring and Remediation 4* (Twardowska, I., Allen, H. E., Kettrup, A. F. & Lacy, W. J., eds), pp. 173–205. Elsevier, Amsterdam.

Usman, A. R. A. 2008. The relative adsorption selectivities of Pb, Cu, Zn, Cd and Ni by soils developed on shale in New Valley, Egypt. *Geoderma*, **144**, 334–343.

Veeresh, H., Tripathy, S., Chaudhuri, D., Hart, B. R. & Powell, M. A. 2003. Competitive adsorption behavior of selected heavy metals in three soil types of India amended with fly ash and sewage sludge. *Environmental Geology*, **44**, 363–370.

Vega, F. A., Covelo, E. F. & Andrade, M. L. 2006. Competitive sorption and desorption of heavy metals in mine soils: influence of mine soil characteristics. *Journal of Colloid Interface Science*, **298**, 582–592.

Weber, J., Karczewska, A., Drozd, J., Licznar, M., Licznar, S., Jamroz, E. & Kocowicz, A. 2007. Agricultural and ecological aspects of a sandy soil as affected by the application of municipal solid waste composts. *Soil Biology and Biochemistry*, **39**, 1294–1302.

Zhang, M. & Zheng, S. 2007. Competitive adsorption of Cd, Cu, Hg and Pb by agricultural soils of the Changjiang and Zhujian deltas. *Journal of Zhejiang University – Science A*, **8**, 1808–1815.

Zhao, L. Y. L., Schulin, R. & Nowack, B. 2009. Cu and Zn mobilization in soil columns percolates by different irrigation solutions. *Environmental Pollution*, **157**, 823–833.

Cd, Pb, Cu ja Cr mobiilsus mõnedes Eesti muldades

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On hinnatud viie Eesti mulla sorptsioonivõimet raskmetallide suhtes, kasutades raskmetallilisanditega mullaproove. Eksperimentaalsetest sorptsiooniandmetest on koostatud lineaarne Freundlichi isoterm. Metallide sorptsioon alusmullas sõltub mulla tüübist, s.o mineraalsest koostisest. Kvartsi ja karbonaatide sisaldus võib olulisel määral mõjutada alusmulla sorptsioonivõimet raskmetallide suhtes. Katsetulemustele ja meie eelnevalt avaldatud andmetele tuginedes on analüüsitud võimalusi, kas metallid võivad jõuda sügavale pinnasesse või kogunevad need pinnalähedastes kihtides. Võib järeldada, et Podzoli-tüüpi alusmullas võib tekkida lahustunud Cd suur kontsentratsioon, kuid teised metallid akumuleeruvad. Mullad, mis sisaldavad palju dolomiiti, võivad suurel määral Pb-d akumuleerida.