HEAVY METAL SORPTION BY DIFFERENT ESTONIAN SOIL TYPES AT LOW EQUILIBRIUM SOLUTION CONCENTRATIONS

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Abstract. Batch sorption experiments were conducted with heavy metal solutions in 0.01 M $CaCl_2$ at low equilibrium concentrations of Cu, Pb, Cd, and Cr in 10 different intact soil samples. Metal solid/liquid distribution coefficients K_d were determined from the adsorption isotherms obtained. Their values varied over a range from 57 to 53 000 mL/g. The soils used in the experiment were chosen according to their organic matter content and origin to represent differential behaviour with regard to heavy metal sorption. Correlations of K_d with soil parameters were observed together with varying sorption behaviour of metal cations to different soil types. Desorption of metals from soil phase to solution was found to be very small, suggesting that at least during the initial period after the metal pollutants have reached the soil surface they accumulate in the top humus layer. Heavy metal desorption into the water phase also depends on the character of the metal and on soil type.

Key words: soil, Cu, Pb, Cd, Cr, sorption, distribution coefficients, organic matter, correlations.

INTRODUCTION

Sources of technogenic pollution release large amounts of heavy metals into the atmosphere and subsequently into surface water, soil, and plants. Upper layers of soil receive most of the pollutants and processes occurring there determine their further spreading and environmental impact. Emissions of heavy metals to the environment [1] make it relevant to observe the changes in the concentrations and distribution of these elements in soil, to study the regularities and causes of their migration, and to predict the changes in the state of the soil layers. One factor relevant to the behaviour of metal cations in soil systems not yet satisfactory explained is related to the competition between organic and

oxidic adsorption processes. There is a considerable amount of literature published regarding the sorption behaviour of heavy metals with soil components [2–5] but not so much with intact soils [3, 6, 7]. In particular no such information is yet available on typical Estonian soils.

The mobility of heavy metals in soil is frequently described by a distribution coefficient, K_d, defined as the ratio of metal concentration in the solid phase to that in the liquid phase at equilibrium [8]. Distribution coefficients can be determined from the slope of the linear part of the adsorption isotherms. This means that if the distribution coefficients in soil systems are to be predicted accurately, they should be obtained from measurements made at sufficiently low concentrations to get linear isotherms.

The aim of the present study is to report experimental results on adsorption–desorption behaviour of four heavy metals on Estonian soil samples. These soils were chosen according to their organic matter content and soil type to represent substantially different behaviour as regards to heavy metal sorption.

MATERIALS AND METHODS

Determination of soil characteristics

Soil samples were collected from A_0 and A_1 horizons at ten sites in different locations of Estonia (Fig. 1). The soils were air dried and the fraction <3 mm was used. The main characteristics of the soils are presented in Tables 1 and 2.
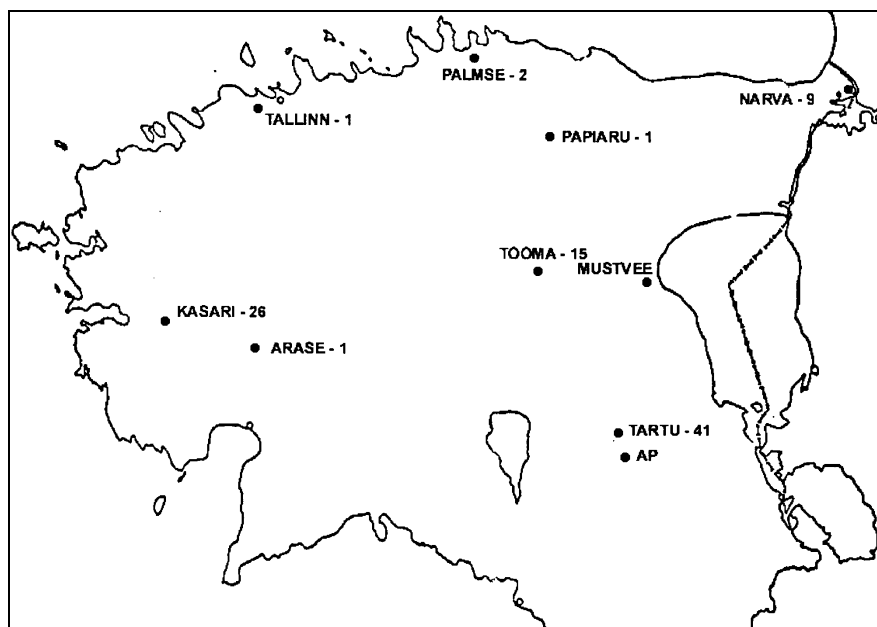

Fig. 1. Locations of observation fields.

Table 1. Geometric mean concentrations of major and trace elements in the humus horizon of soil from different sites (organic matter (OM), Ca, Fe, K, Mg in %; Cd, Cu, F, Mn, P, Pb, Zn in ppm; Hg in ppb; – not detected)

Site	OM	Ca	Fe	K	Mg	Cd	Cu	F	Mn	P	Pb	Zn	Hg
Tallinn-1 5-001 H	22.94	5.16	3.89	1.77	0.65	0.7	9.52	578	1700	2400	25.1	80.1	59
Tartu-41 5-041 H	4.88	0.57	1.24	2.23	0.28	0.16	7.58	200	280	350	15.5	25.1	26
Narva-9 5-009 H	19.92	5.25	4.40	3.93	1.03	0.60	10.38	1280	4660	5090	29.8	90.4	100
Palmse-2 5-002 H	10.00	1.26	3.25	1.59	0.30	0.36	10.22	700	1400	2600	19.3	29.0	46
Kasari-26 5-026 H	18.64	5.30	2.34	1.61	1.36	0.56	18.54	374	470	970	25.3	79.9	96
Tooma-15 5-015 H	6.64	1.84	0.93	1.43	0.32	0.35	7.36	130	330	300	18.3	23.4	22
Arase-1 98 H	6.93	5.50	2.26	1.40	2.96	0.19	12.0	460	880	830	17.7	48.4	–
Papiaru-1 98 H	6.86	7.55	2.28	2.49	0.65	0.20	13.2	530	688	1180	17.5	53.8	–
Average of soil [9]		1.37	3.80	1.36	0.63	0.50	20	200	850	800	10	50	10

Table 2. Composition of the mineral part of soil samples, estimated by X-ray diffraction analysis

Site	Mineral, %										
	Q	Fs	Pl	Ca	Do	G	Ap	Fe-site	Am	Clay	AF
AP	58	23	12	–		–			5	<1	–
Mustvee	61	23	10	–		–			–	–	–
Tallinn-1	36	13	7	8	4	–	–	–	2	30	2
Palmse-2	74	16	10	–	–	–	–	–	2	19	20
Narva-9	17	13	4	8	4	3	4	4	–	27	17
Tooma-15	60	14	9	5	2	–	–	–	1	8	1
Kasari-26	32	11	6	9	6	3	–	–	–	21	12
Tartu-41	34	13	6	–	–	–	–	–	1	15	31
Arase-1	26	8	5	2	14	–	–	–	–	12	32
Papiaru-1	29	11	5	15	–	–	–	–	–	13	26

Symbols: Q – SiO_2 quartz; Fs – $K(AlSi_3O_8)$ ortoclase (K-feldspar); Pl – $Na(AlSi_3O_8)$ plagioclase (albite); Ca – $CaCO_3$ calcite; Do – dolomite (calcium magnesium carbonate); G – goethite; Ap – $Ca_5(PO_4CO_3)_3F$ apatite; Fe-site – $Fe(PO_4) \cdot H_2O$ phosphosiderite; Am – $(Na, Ca)_2(Mg, Fe, Al)_5$ $[(Si_{7-6}Al_{1-2})O_{22}](OH,F)_2$ amphibol; AF – amorphous phase, basically inorganic; – not detected.

For all soil samples the following parameters were determined: pH, soil organic matter content (OMC), total nitric acid soluble amounts of various heavy metals, and composition of major minerals.

The soil pH was determined by shaking 5 g of air-dry soil with 10 mL of deionized water for 60 min, letting the solution rest overnight, and then

measuring the solution with a pH meter. The pH was also determined in 0.01 M $CaCl_2$ solution, which resulted in slightly lower values (0.5–1 pH units).

To determine the total OMC of soil, weighted amounts of air-dry soil samples were heated at $105\,°C$ (3 h) and then at $340\,°C$ (2 h). The residue was weighed and OMC determined as the difference.

The major mineral composition of soil samples was determined by X-ray diffraction analysis. Results are presented in Table 2. The total acid-soluble amounts of Mn, Cu, Zn, Cd, Cr, Ni, and Fe in soil were determined by flame AAS (Cd with graphite furnace AAS), after digestion of soil samples with concentrated HNO_3, see Table 1.

Sorption measurements

One- or two-gram soil samples were shaken for 2 h in polypropylene centrifuge tubes at room temperature with 10 or 5 mL of 0.01 M $CaCl_2$, respectively, containing from 1.0 ppb to 30 ppm of metal ions (chloride salts). After 16 or 24 h equilibration time the tubes were centrifuged at 3000 rpm for 10 min and the supernatant solution was analysed.

For desorption measurements the soil was re-suspended several times in 10 or 5 mL $CaCl_2$ and the metal concentrations were determined in all dilutions by graphite furnace AAS. Knowing the amount of metal added to the system and the concentration in each supernatant solution the amount of sorbed or desorbed metal could be calculated.

Basic properties of soil samples

At different sites the concentrations of elements in the humus horizon of soil varied within wide limits. Especially high concentrations of most elements were recorded at Narva-9, while in the humus horizon at the Tallinn-1 and Kasari-26 sites only some elements displayed increased values. The elevated concentrations described are caused by heterogeneity of soil parent rocks and soil type as well as by the location of the actual sampling site, groundwater level, etc. The Ca concentration is close to the average value of that element (1.37%) in Estonian soils or higher only in the humus horizons of soils formed on tills in the North Estonian plateau of carbonaceous rocks and carbonate-rich glaciolacustrine or marine deposits. At most sites the humus horizon of the soil is characterized by increased concentrations of Pb. Cu occurs in the humus horizon of observation fields in a lower than the average concentration in soil.

RESULTS AND DISCUSSION

An equilibration period of at least 16 h was chosen in the experiments to ensure that the sorption will be essentially complete for all heavy metals under study. All experiments were carried out in the presence of a large excess of Ca

ions (0.01 M CaCl$_2$ solution). The background electrolyte solution was used to simulate natural soil conditions where there is often a large excess of Ca ions. This background electrolyte was intended to minimize the nonspecific sorption (i.e. ion-exchange) of heavy metals so that specific sorption will predominate. The pH value was not adjusted because at the low concentration of metal ions the pH decrease after sorption was small (< 0.5 pH units). The soil pH values as measured were: Tartu, 6.50; Kasari, 5.00; Tallinn, 7.52; Tooma, 7.40; Palmse, 6.20; Narva, 7.64; Mustvee, 7.00; AP, 7.54; Papiaru, 7.10; and Arase 7.12; that is mostly neutral to basic, which is typical of soils in many parts of Estonia.

It must be also taken into account that solute heavy metal ions are complexed with soluble organic matter (fulvic and humic acids) [3, 5]. This fact may influence not only the sorption behaviour, but also the pH. In this study soluble organic matter and pH were treated as a non-variable background to the exchange processes. It was assumed that heavy metals in solution are in equilibrium with the solid phase and total concentrations were used to determine the isotherms.

After the equilibration the ranges of metal concentration in solution were: for Cu 3.33–208.29 µg/L (initial added Cu concentration IAC = 1.00–30.00 mg/L), for Cr 0.659–2.591 µg/L (IAC = 0.025–1.000 mg/L), for Cd 0.036–1.005 µg/L (IAC = 0.001–0.050 mg/L), for Pb 1.41–21.99 µg/L (IAC = 4.00–30.00 mg/L).

The corresponding ranges for the concentrations of added metals in the soils after equilibration were: for Cu 4.90–149.70 µg/g, for Cr 0.124–4.995 µg/g, for Cd 0.004–0.249 µg/g, for Pb 19.99–149.91 µg/g.

The concentrations of CaCl$_2$ extractable heavy metals in solution for unaltered, natural soil samples were from 0.016 to 0.147 µg/L for Cd and 1.92–89.8 µg/L for Cu. Pb and Cr concentration values were below the detection limits of our method.

Isotherms tended to be rectilinear at equilibrium solution concentrations lower than ~0.015–0.03 µg/mL, whereas at higher concentrations curvilinear isotherms were obtained. There were some exceptions for Cu, as in some cases linear isotherms were obtained even at equilibrium solution concentrations of about 0.5 µg/mL. All adsorption isotherms can be described by the Langmuir equation

$$S = \frac{N_T K C^{1-n}}{1 + KC},$$

where S is the equilibrium concentration in the soil, n is an adjustable parameter, N_T is the maximum adsorption, K is a binding constant, and C is the equilibrium concentration of metal cation in solution.

Isotherms obtained belong mainly to the types of H and L according to the classification by Giles et al. [10]. L-type isotherms correspond to great affinity between the metallic cation and the soil surface. Further increase in affinity results in H-type isotherms. S-type isotherms were obtained in the case of Pb (AP) and Cu (Mustvee). S-type isotherms can be due to precipitation or competition between heavy metal and Ca cations [6]. The values of the obtained distribution coefficients are presented in Table 3.

Table 3. Distribution coefficients (K_d) of heavy metals for different sites

Site	OMC, %	K_d, mL/g			
		Cu	Cd	Cr	Pb
Tartu-41	4.88	58	88	537	308
AP	5.83	3665	224	Not measured	6868
Tooma-15	6.64	473	486	1023	6252
Papiaru-1	6.86	4149	1247	577	Not measured
Arase-1	6.93	11173	2651	295	Not measured
Palmse-2	10.00	309	386	1505	2941
Mustvee	14.58	2104	289	2314	6828
Kasari-26	18.64	235	1263	1098	5418
Narva-9	19.92	656	Not measured	2806	52618
Tallinn-1	22.94	1102	741	2860	24413

Efforts to relate the potential of soils to adsorb heavy metals to individual soil properties have been made by many researchers [3, 6, 8, 11–16]. On the basis of these studies it has been suggested that the specific sorption of heavy metals by soils is dominated by hydrous oxides of Fe and Mn and organic matter, though in some studies [3, 8] no correlation has been found between OMC and the distribution of metals. In Fig. 2 the dependence of K_d on OMC of soil is shown.

Correlations between distribution coefficients and soil characteristics are shown in Table 4. Surprisingly, for each of the individual metals the most highly correlated parameter was different: clay for Cr; Ca + Do for Cd; and Cu, Fe, and Mn for Pb. For Cr and Pb also a significant correlation to OMC and clay content was evident. From the soil characteristics OMC, clay, and Fe correlated very well with one another. Fe and Mn content also showed significant correlation at the 1% level.

Table 4. Correlation coefficients between K_d and soil parameters (* – correlation is significant at the 0.05 level, two tailed; ** – correlation is significant at the 0.01 level, two tailed)

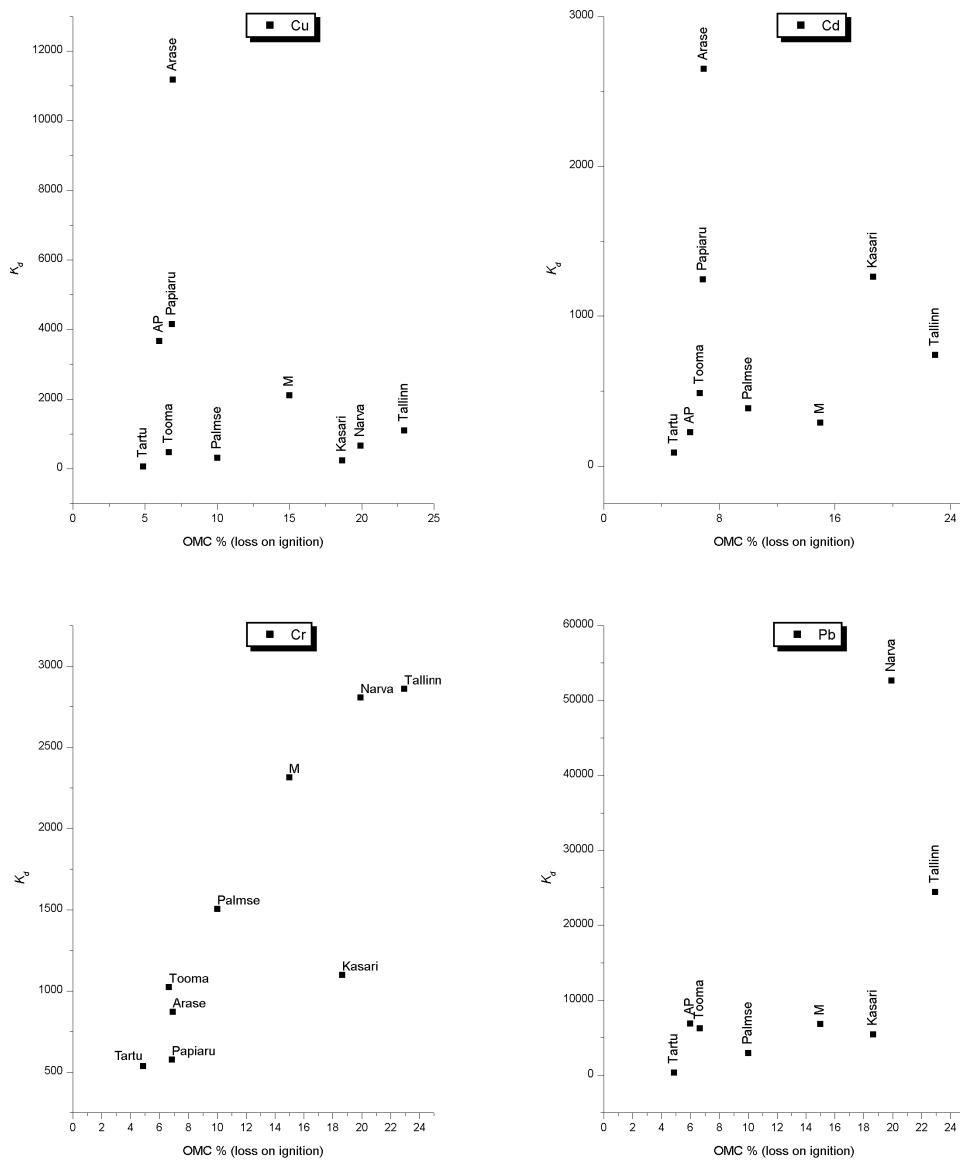|	K_d	OMC	Clay	Ca + Do	Mn	Fe
K_d Pb	1.000	0.640	0.668	0.528	0.767*	0.971**
K_d Cr	1.000	0.846**	0.876**	0.044	0.646	0.743*
K_d Cu	1.000	–0.355	–0.367	0.535	–0.131	–0.086
K_d Cd	1.000	0.011	–0.171	0.795*	0.229	0.102
OMC	–	1.000	0.918*	0.370	0.572	0.724*
Clay	–	0.918*	1.000	0.133	0.656	0.869*
Ca + Do	–	0.370	0.133	1.000	0.201	0.239
Mn	–	0.572	0.656	0.201	1.000	0.804*
Fe	–	0.724*	0.869*	0.239	0.804*	1.000

Fig. 2. Distribution coefficients K_d versus organic matter content (OMC).

In evaluating the data in Table 4 it must be mentioned that weak correlations of K_d and OMC in the case of Cu and Cd are probably due to a non-linear relationship between those parameters (Fig. 2), so the Pearson correlation coefficient may not be an appropriate measure in this situation.

Heavy metals can be ranged according to the K_d values, i.e. their affinities for the soil. This resulted in the following relative sequence:

$$Pb > Cr \geq Cu > Cd,$$

which is similar to analogous sequences by [14] for intact soil:

$$Pb \geq Cu > Zn > Co > Cd$$

and to some extent to the observed sequence for organic matter [16]:

$$Pb \gg Zn = Cd > Ca > Cu = Ag.$$

K_d values for the same metal in different soil types differed greatly. Of the five soil types studied, the ratio between the largest and smallest K_d was 120 for Cu, 91 for Cd, 80 for Pb, and 16 for Cd.

The results of desorption experiments are summarized in Figs. 3 through 6. The resulting desorption isotherms show that the amounts of heavy metals readily desorbed from the soil were very small. The heavy metal concentrations of the equilibrium solution decreased with little corresponding change in the amount of heavy metals retained by the soil. The desorption of Cd was more intensive than for the other metals. There were two distinctly different desorption patterns: one for Cd, Cr, and Cu (Mustvee), and the other one for Pb and Cu (AP, Härjapea).
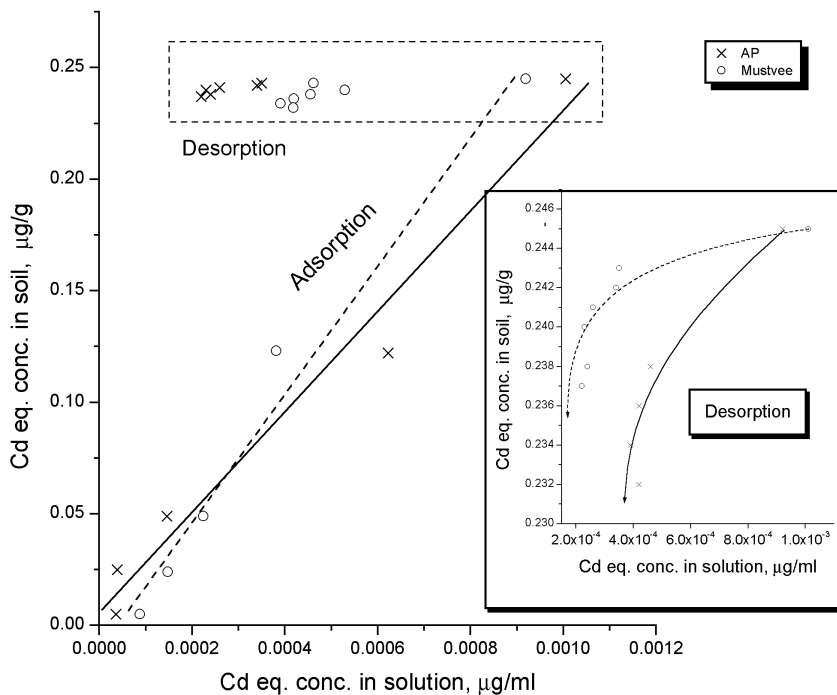

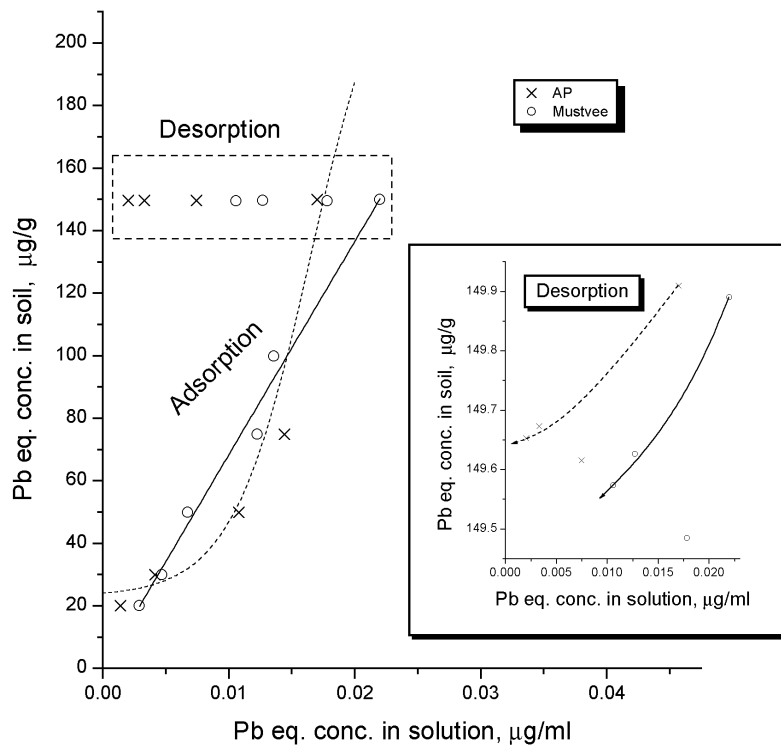**Fig. 3.** Sorption/desorption isotherms of Cd.

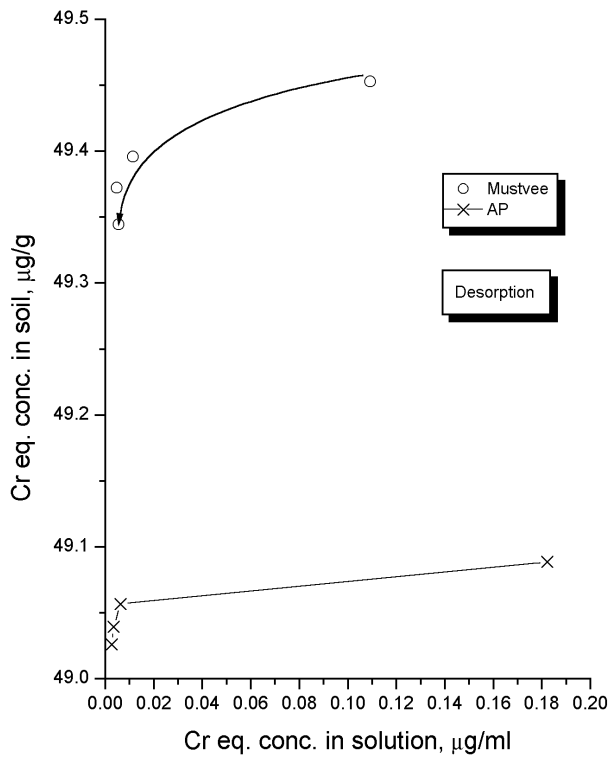**Fig. 4.**
Sorption/
desorption
isotherms
of Pb.

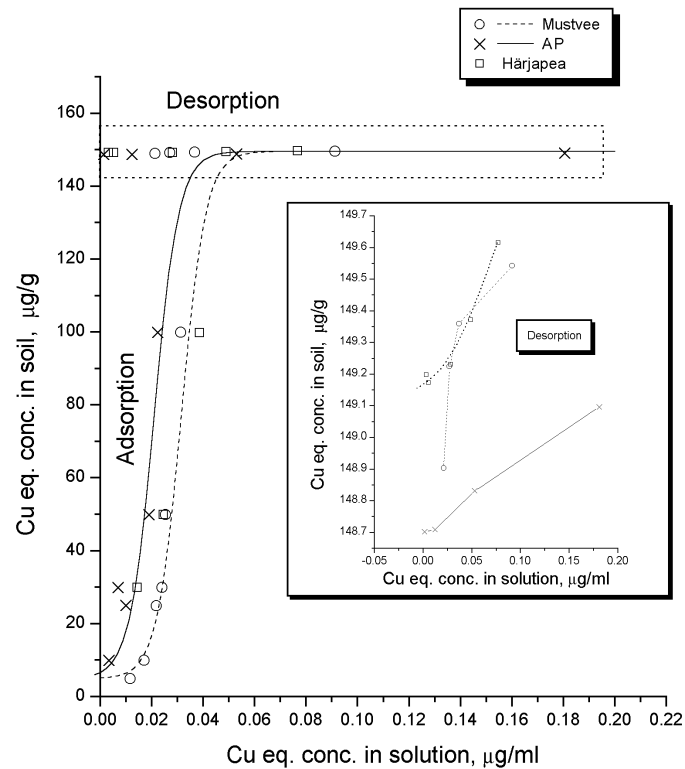**Fig. 5.** Sorption/desorption
isotherms of Cr.

Fig. 6. Sorption/desorption isotherms of Cu.

The limited desorption of the heavy metals suggests that the sorption reactions taking place are only slowly reversible or a high activation energy is required for desorption. This emphasizes the role of organic matter in the soil heavy metal adsorption, because as previously stated by Jarvis [6], heavy metals added to soils in the field will be strongly adsorbed by the first component to which they make contact, i.e. organic matter as the upper part of undisturbed soil horizons. Subsequent redistribution to lower soil layers probably takes a very long time due to the slow desorption, and heavy metal concentrations in the upper soil humus layers will tend to increase with time.

CONCLUSION

The association of the studied heavy metal cations with soils depends upon many soil parameters, most significantly on its organic matter and clay content, but also other parameters such as concentrations of Fe and Mn oxides are important. Pb and Cr are adsorbed to a greater extent to soils with a high organic matter content. Cu and Cd sorption tends to be significantly affected by the

mineral part of the soils, especially the calcite-dolomite content. For that reason their K_d–OMC relations are different from those obtained for Pb and Cr.

The observed desorption of metals from soil to the solution phase was very small. This suggests that at least in the first stage after the heavy metals are emitted to the soil environment they remain mainly in the upper A horizons of the soils. Heavy metal desorption (or leaching of adsorbed compounds) into the water phase also depends on the character of the metal and on the soil type.

The results obtained confirm that it is basically possible to create a correlation model for the heavy metal sorption process based on the soil type and characteristic parameters. Construction of such a model system covering all Estonian soil types would presumably be of great importance in predicting pollutant distribution and accumulation effects. A possible application would be a computer simulation program. A prerequisite for a statistically valid model system of sorption processes is a study of a sufficiently large amount of different soil samples. All prerequisites for such a study are met with the geochemical monitoring study of Estonian soils carried out by the Geological Survey of Estonia in 25 well-characterized monitoring points over Estonia [9].

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RASKMETALLIDE SORPTSIOON ERINEVATEL EESTI MULLATÜÜPIDEL MÕÕDETUNA LAHUSE MADALA TASAKAALULISE KONTSENTRATSIOONI JUURES

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On hinnatud erinevate raskmetallide (Cu, Pb, Cr ja Cd) mobiilsust ja jaotumist süsteemis tahkefaas–vesifaas. Selleks määrati mudelkatses eraldi iga metalli adsorptsiooni–desorptsiooni isotermid, mille põhjal arvutati jaotuskoefitsient K_d. K_d väärtused olid vahemikus 57–53 000 ml g^{-1}. Kõrged K_d väärtused näitavad metalli suurt siduvust mullaga, seevastu madala koefitsiendiga ained esinevad eelistatult vesifaasis. Katsetes kasutati Eesti litosfäärile iseloomulikke loodus-likke mullatüüpe, mis olid võetud riikliku monitooringu seitsmelt geoloogiliselt hästi kirjeldatud mullaväljakult. Määrati mullaproovide mineraloogiline koostis, orgaanilise aine ja ekstraheeruvate ioonide (Na, Ca, Mg ja K) sisaldus ning mulla vesilahuse pH väärtus. Tulemuste põhjal võib väita, et esineb korrelatsioon rask-metallide jaotuskoefitsientide ning mulla orgaanilise aine sisalduse ja anorgaani-lise osa koostise vahel.

Raskmetallide desorptsioon ehk adsorbeerunud ühendi leostumine tagasi vesi-faasi sõltub samuti metalli iseloomust ja mullatüübist, kuid üldjuhul on tegu suhteliselt aeglase protsessiga. Seetõttu võib oletada, et vähemalt saastumise alg-perioodil akumuleeruvad raskmetallid pinnase ülemises huumuskihis.