Sorption of Pb and Cd by sediments of the polygenetic river valleys of the eastern part of the Polish Lowland

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Sediments, filling the polygenetic, melt-out river valleys of the eastern part of the Polish Lowland and adjacent areas are characterised by various sorption capacities in relation to Pb and Cd. Valley bottoms and ice-dammed basins within the morainic plateau are built of peats, mucks and warps, which bond 98% of the added heavy metals from the input solution with concentrations of 1 to 20 mg/dm^3. These sediments, occurring also in the form of horizontal and continuous layers, form natural isolation barriers protecting the groundwaters against pollution with lead and cadmium. Deposits which build the adjacent morainic plateau and which contain over 20% of clay fraction also possess very high sorption capacities in relation to Pb and Cd. Sandy sediments of kames and kame terraces are characterised by the lowest sorption capacities to lead and cadmium. The content of organic matter and to a lesser extent the clay mineral composition determines the sorption capacities of lacustrine and marsh sediments. In the case of the clastic deposits of the morainic plateau, the value of this parameter depends on the quantity and composition of the clay fraction, and on the presence of $CaCO_3$ and oxides and hydroxides of Fe, Al and Mn. The sorption of lead by peats and warps for delivered input solutions (5–100 mg/dm^3), in most cases, are described by Henry's isotherms whereas the sorption of cadmium is described by Freundlich's isotherms. The sorption of lead as well as cadmium by mineral and organic-mineral sediments are described by Freundlich's isotherms.

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INTRODUCTION

The health hazard to large human populations, since industrialisation, has increased as regards pollution of air, near-surface soils, surface waters and groundwaters. Further development in industrialised areas must be based in the light of knowledge of their sensibility to specific contamination, when they are of key economic importance. Such areas are for example river valleys.

Investigations carried out in the Polish Lowland area (Straszewska, 1968; Falkowski, 1971; Baraniecka, 1974; Baraniecka *et al*., 1978; Falkowski *et al*., 1988; Klajnert and Rdzany, 1989; Musiał, 1992; Nitychoruk, 1995; Falkowski, 1995; Kobojek, 1996; Falkowska, 1998, 2001), indicate that most river valleys are polygenetic forms. Rivers adopted postglacial depressions, mainly of melt-out origin, for their course.

Sediments filling these polygenetic river valleys are mainly peats and organic warps. They are characterised by high sorp-

tion capacities in relation to heavy metals. They form a near-surface isolation layer, protecting the underlying sediments and groundwaters against contamination. The existence of such protective layers provides natural protection against contamination, especially where highly toxic compounds of heavy metals are concerned.

The marked protective potential of organic soils, particularly peats, has been noted and utilised in other countries. In the United States and in Canada (Irvine and Barsotti, 1994; fide Olkowicz-Paprocka *et al*., 1994), sorbents obtained from peat oil are typically used in industry instead of clays or zeolites. Peats are also utilised in ecological catastrophes, in cases of pollution with liquid toxins (Olkowicz-Paprocka *et al*., 1994). They have been also tested as effective filtration agents for the removal of toxic pollutants from industrial and urban sewage as well as absorbents of pungent, unpleasant odours. Application of this type amounts to 15% of the utilisation of peat in the United States (Olkowicz-Paprocka *et al*., 1994).

Binding of heavy metals in soils proceeds as a result of ion exchange and chemical, physical, mechanical and biological sorption (Velde, 1995; Jackson, 1998). Heavy metals are re-
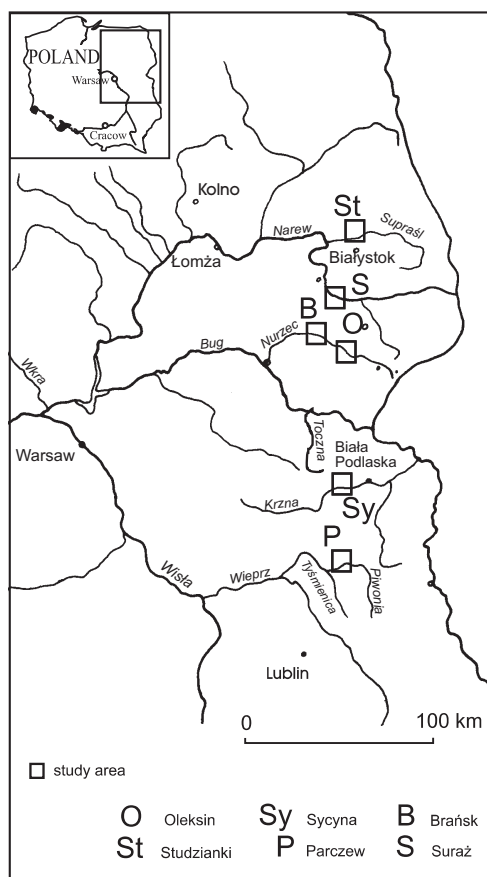
Fig. 1. Location of sampling sites

tained in sediments mainly by clay minerals, organic matter, oxides and hydroxides of iron and manganese (Helios-Rybicka, 1986; Pittman and Lewan, 1994; Pettersson *et al.*, 1993; Kyzioł, 1994; Shine *et al.*, 1995; Velde, 1995; Twardowska *et al.*, 1997).

GEOLOGY

The eastern part of the Polish Lowland is a postglacial area, upon which polygenesis of river valleys is a common phenomenon (Falkowska, 1997, 1998, 2001). Frequently, they have an "inherited" character (Falkowski, 1971), because these rivers adopted glacial melt-out depressions for their flow paths (Falkowski, 1971; Różycki, 1972; Falkowska, 2001). Thus, valley bottoms of polygenetic melt-out rivers, primarily forming overflow lakes, have been totally filled with lacustrine and marsh sediments such as lake marl, gyttja, organic warps and peats. The proportion of channel facies deposits in polygenetic sections of river valleys is small in relation to their area. Sandy alluvial sediments are embedded within organic sediments. These glacial melt-out depressions formed during regional deglaciation. Results of detailed investigations, which showed polygenesis of several river valleys in the eastern part of the Polish Lowland was presented by Falkowska (2001).

In the Polish Lowland, stretches revealing features of melt-out river valleys were described by Falkowski (1971) in some parts of the valleys of Narew, Bug and Krutynia (NE Poland). These features were described by Różycki (1972) and Galon (1972). Mojski (1972) revealed that the Narew River followed marginal depressions. Falkowski *et al.* (1988) described features of the areal deglaciation in the Biała Podlaska district area (eastern Poland), where a river system of polygenetic, melt-out character was created. Klajnert and Rdzany (1989) noted traces of melt-out origin of the river valley in the case of Rawka River (Central Poland). These authors showed that the Rawka River followed postglacial depressions. Klajnert and Wasiak (1989) indicated that the NE part of the Łódź Plateau has formed as a result of areal deglaciation and that postglacial features characterise the rivers. Kobojek (1996) noted the influence of glacial processes on the morphogenesis of the Rawka River valley. Traces of areal deglaciation and melt-out origin of river valleys in the Polish Lowland were shown also by Straszewska (1968); Baraniecka and Sarnacka (1971); Baraniecka (1974); Baraniecka *et al.*, (1978); Bałuk (1991); Klatkowa (1989); Musiał (1992); Błaszkiewicz and Krzemińska (1992); Nitychoruk (1994); Falkowski (1995) and others. All these authors described the occurrence of organic sediments in the bottoms of these polygenetic rivers valleys.

During the areal deglaciation characteristic geomorphological units were formed. These are shown on the schematic transverse cross-section through the polygenetic river valley (Fig. 2) Falkowska (2001). This cross-section was based on analyses of the geological setting of several river valleys in the eastern part of the Polish Lowland (Falkowska, 2001). The wide valley bottoms, are filled with a thick and continuous cover of organic sediments (warps and peats), while locally valley kames, which form sandy (locally with gravel) hills, also occur. The valley bottom typically forms a flood terrace, while marginal to the morainic plateau are local kame terraces, commonly showing glacigenic disturbance (Falkowska, 2001). Slopewash deposits occur locally on the plateau slopes and on the kame terrace. Within the adjacent morainic plateau areas and tributery valleys there occur commonly ice-dammed basins, filled with post-glacial peats, mucks and warps (Falkowska, 2001).

RESEARCH MATERIAL

RESEARCH AREAS

Research was carried out on selected, representative sections of these polygenetic melt-out river valleys: those of the Narew, Piwonia, Supraśl, Krzna and Nurzec rivers (Fig. 1) sited within deposits of the Odranian and Wartanian glaciations (Lindner and Marks, 1995). They contain all the geomorphological forms mentioned above (Falkowska, 2001) and comprise the geological context of the Cd and Pb sorption studies.

The valley bottoms are underlain by peat ranging in thickness from 0.5 to 4.2 m. Their area ranges from 10.5 ha (Narew in the vicinity of Suraż) to 2163 ha (Nurzec in the vicinity of Oleksin). These areas have mostly been long drained.
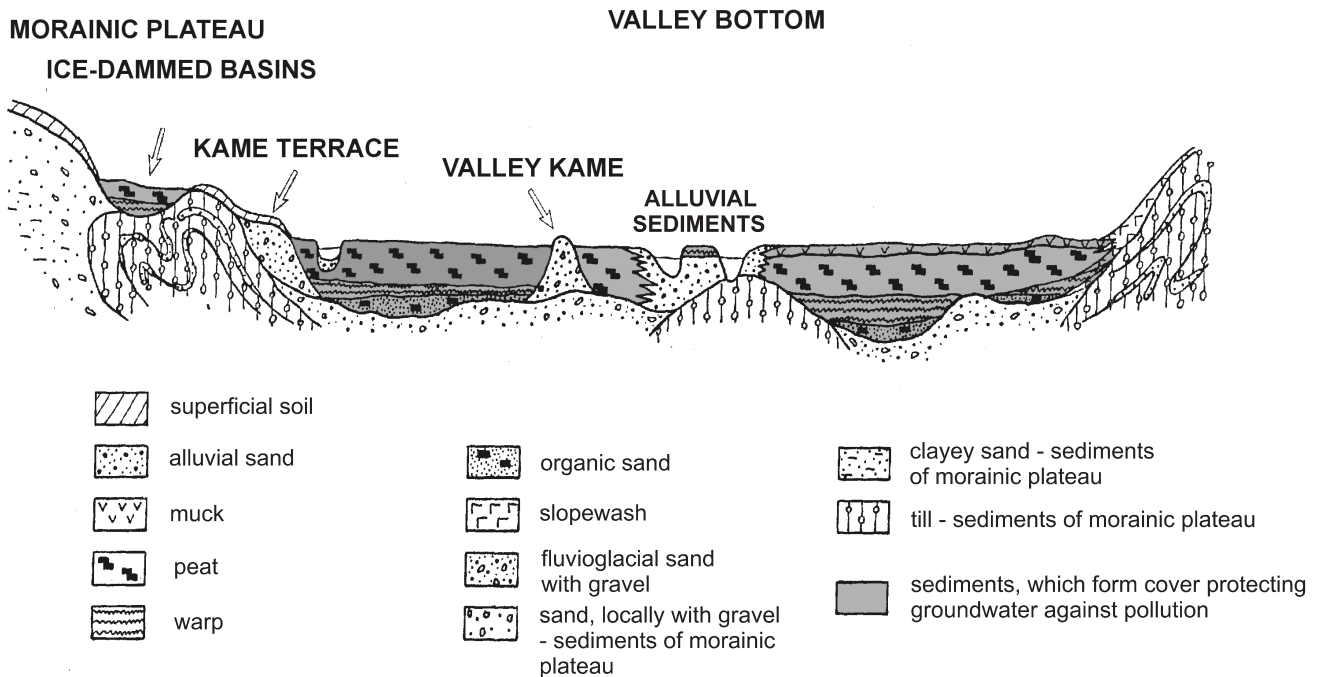
MORAINIC PLATEAU

ICE-DAMMED BASINS

VALLEY BOTTOM

KAME TERRACE

VALLEY KAME

ALLUVIAL SEDIMENTS

superficial soil

alluvial sand

muck

peat

warp

organic sand

slopewash

fluvioglacial sand with gravel

sand, locally with gravel - sediments of morainic plateau

clayey sand - sediments of morainic plateau

till - sediments of morainic plateau

sediments, which form cover protecting groundwater against pollution

Fig. 2. Schematic cross-section through a polygenetic, melt-out river valley after Falkowska (2001)

SAMPLED MATERIAL

144 sediment samples from the geomorphological units investigated were collected, and 37 were analysed for sorption of Cd and Pb. Among them there were 9 samples of peats 9 samples of warp 17 samples of clastic sediment (including 3 organic-rich samples) and 3 samples of superficial soil.

METHODS

LITHOLOGICAL CHARACTERISTIC

Grain-size composition, mineral composition, calcium carbonate content, organic content, organic carbon content and sediment pH were determined in laboratory tests. Some samples were also analysed as regards clay mineral composition and Fe, Mn oxide/hydroxide content. For analysis of grain-size composition hydrometer analysis was used for cohesive soils and sieve analysis for non-cohesive soils (Myślińska, 2001a). Calcium carbonate content was determined using the Scheibler (Myślińska, 2001b) and thermal analysis methods. Organic matter content was determined as ash content by roasting at a temperature of 550°C. For samples with low contents of organic matter (< 10%) the organic carbon content was also determined using the Tiurin method (Myślińska, 2001b). Mineral composition was determined by thermal analysis and X-ray diffraction analysis. Thermoanalytical curves of whole soil samples and also of the clay fractions were obtained (Wyrwicki, 1988). X-ray diffraction analysis was made through registration of oriented samples (sedimented, after glycolling and roasted), using the *DRON 1.0* diffractometer with a computer system of data logging ("*DRONEK*"). The pH was also determined, in an aqueous extract, for all samples using a microcomputer pH-meter (Ostrowska *et al*., 1991).

The following classification of organic soils was used: peat-marsh sediment with ash content up to 70%; muck (peat-earth) — weathered peat with a similar content of organic matter; warp (aggraded mud) — soil deposited subaqueously ash contents from 95 to 70%. In soils with ash contents from 92 to 95% the prefix "organic" in used.

CATION EXCHANGE CAPACITY

The real cation exchange capacity (CEC) was determined by measurement of copper sorption (Sapek, 1979, 1986). Control determinations of the sum of alkali cations and hydrolytic acidity of sands revealed difference in values not exceeding 4 meq/100 g of soil.

SORPTION OF LEAD AND CADMIUM

The Cd^{2+} and Pb^{2+} sorption was conducted by means of the "BATCH" method (Osmęda-Ernst and Witczak, 1991a) using solutions of nitrates of these metals with variable input concentrations — c_0. For lead, concentrations of 5, 10, 20, 50, 100 mg/dm^3 Pb, and in some cases also 500 mg/dm^3 were used in order to obtain a state of saturation. Solutions of 1, 5, 10, 20, 50 mg/dm^3 Cd were used during examination of cadmium sorption. A suspension of 50 ml of the input solution with adequate concentration and 1 g of air-dried soil samples was shaken for 4

hours (after Sapek, 1980). After 24 hours, metal-equilibrium concentrations (c_R) in solution were determined by the AAS (Atonic Absorption Spectrometry) method. Sorption of heavy metalions (S, $S\%$) was calculated from the difference of the input concentration and the concentration in the equilibrium state. Experimental heavy metal sorption isotherms were prepared for each sample, using also Henry's or Freundlich's model on the assumption that the concentrations of the heavy metals investigated in equilibrium solutions, in relation to uncontaminated soil are so low that they can be neglected (Buchter *et al.*, 1989; Osmęda-Ernst and Witczak, 1991; Appelo and Postma, 1993).

The formula of Freundlich's isotherm (Osmęda-Ernst and Witczak, 1991*a*) is:

$$N^X = K^F \times c_R^{\frac{1}{n}} \qquad [1]$$

where: N^X — equilibrium concentration of the sorbed component in soil (mg/kg), c_R — equilibrium concentration of the sorbed component in aqueous solution (mg/dm^3), K^F — constant characterising the sorbing surface of the soil (dm^3/kg), n — constant characterising interaction: soil — component undergoing sorption (nondimensional).

Alternatively, the equation of Henry's isotherm (Osmęda-Ernst and Witczak, 1991*a*) is:

$$N^X = K_d \times c_R \qquad [2]$$

where: K_d — coefficient of division (dm^3/kg).

Sorption during migration of contaminants may usefully be described by the retardation factor (R). The rate of migration of a component undergoing sorption is R times slower than the real of groundwaters (Osmęda-Ernst and Witczak, 1991). For Henry's model there is the following relation:

$$R = 1 + \frac{\rho_d}{n_0} K_d \qquad [3]$$

where: R — retardation factor, ρ_d — dry density (Mg/m^3), n_0 — active porosity of the soil (non dimensional).

Effective porosity was not determined during the investigations, total porosity being used in calculations:

$$n = \frac{\rho_s - \rho_d}{\rho_s} \qquad [4]$$

where: ρ_s — particle density (Mg/m^3).

Obtained values of retardation factor were low, because the porosity in the formula is in the denominator. However, for estimated evaluations, this influence does not cause major changes.

Estimation of the retardation factor R for the process described by Freundlich's isotherm is possible for a concrete equilibrium concentration of a component undergoing sorption

in solution. For this aim it is necessary to determine a substitute division coefficient — K_d^F (Witczak, 1984).

Then the retardation factor R is calculated from the formula:

$$K_d^F = K^F \times c_R^{\frac{1}{n}-1} \qquad [5]$$

Knowledge of values of retardation calculated on the basis of sorption isotherms parameters allows estimation of the degree of hazard from the substance undergoing sorption, and sorption intensity, understood as soil property, can be classified on the basis of calculated retardations (Osmęda-Ernst and Witczak, 1991*b*). A classification of sorption intensity was given by Witczak (1984), who suggested 5 degrees of sorption intensity: low ($R = 1$–2), medium ($R = 2$–10), high ($R = 10$–100), very high ($R = 100$–1000) and unlimited ($R > 1000$).

In some samples, the content of the ions Na, K, Ca, Mg, dislodged by heavy metals was also determined in equilibrium solutions.

DESORPTION

On selected soil samples, desorption of lead and cadmium was carried out with distilled water and ammonium ions using a 1n solution of ammonium acetate (NH_4COOH) at pH 7. Use of NH_4^+ allowed evaluation of the quantity of bonded heavy metal in cation-replaceable positions (Helios-Rybicka and Kyzioł, 1991). To determine this parameter 50 ml of H_2O was added to sediments enriched with heavy metals. This suspension was then shaken for 2 hours. After 24 hours, when the equilibrium state was reached, the aqueous solution was separated in a centrifuge. The content of the element investigated (Dw) was determined by spectrophotometric and AAS methods. The remaining soil was treated with 20 ml of ammonium acetate and that solution was shaken for 2 hours (Helios-Rybicka and Kyzioł, 1991). Concentration of Cd and Pb (Dp) was determined after one day, after separation of soil also by centrifuging. The results are also shown as percentages of Cd and Pb released in relation to metal ($D\%$) absorbed earlier.

RESULTS OF INVESTIGATIONS

LITHOLOGICAL CHARACTERISTICS OF THE INDIVIDUAL GEOMORPHOLOGICAL UNITS

The bottoms of postglacial melt-out river valleys are mainly built of peats and mucks with ash contents from 18.8 to 66.1% (Table 1), warps with ash contents from 74.0 to 91.8% and organic sands and organic silts with ash content ranging between 95.4–97.8%. In warps the content of organic carbon reaches an average of 5%, and in organic-mineral sediments it averages 2%. Because the pH of peats and mucks reached values from 4.6 to 6.9 (Table 1), they showed acid reactions. The pH of warps and organic-mineral sediments was a little higher — from 5.0 to 7.2. The composition of the clay fraction of cohe-

Table 1

Characteristic of samples

Geomorpho-logic unit	Samples number	Sediments	Content of particle <0.002 mm [%]	Ash content [%]	Organic carbon content [%]	Content of CaCO$_3$ [%]	CEC meq/100 g of soil	pH
Valley bottom	S6/1	peaty warp	–	76.9	–	0.0	105	5.0
	S10/2	organic slightly cayey sand	7	97.8	2.0	0.0	55	7.2
	P1/2	warp	19	91.8	–	0.0	63	6.4
	P2/4	organic fine-grained sand	–	95.4	2.2	0.0	25	6.2
	P3/2	poorly decomposed peat	–	53.4	–	0.0	104	5.3
	P$_A$4/1	peaty warp	–	79.1	–	0.0	49	5.0
	St7/4	warp	5	89.6	–	1.3	50	6.3
	St7/5	warp	–	88.3	–	3.3	58	7.2
	St8/1	well-decomposed peat	–	62.5	–	0.0	107	4.6
	Sy4/1	muck	–	66.1	–	0.0	72	5.4
	Sy4/2	poorly decomposed peat	–	21.0	–	0.0	122	5.1
	Sy4/4	warp	12	91.0	5.5	0.0	46	6.7
	B5/1	muck	–	30.0	–	0.0	123	5.5
	B5/2	poorly decomposed peat	–	24.3	–	0.0	156	5.6
	O5/3	peaty warp	–	74.0	–	1.8	59	6.8
	O6/1	poorly decomposed peat	–	18.8	–	0.0	148	6.2
	O7/1	poorly decomposed peat	–	28.4	–	0.0	152	6.9
Morainic plateau	S1/2	clay	57	98.0	0.9	0.0	79	7.5
	S13/4	slightly clayey sand	10	99.1	–	15.3	154	8.5
	P5/4	clayey and sandy silt	12	98.8	–	0.0	51	8.2
	St11/2	slightly clayey sand	5	98.2	3.2	0.0	41	5.8
	Sy1/3	clayey sand	12	98.7	–	0.0	50	6.6
	Sy1/4	clayey sand-gravel mix	4	99.3	–	23.2	144	8.3
	Sy5	slightly clayey sand	9	99.1	–	0.0	23	5.7
	B1/3	clay/sandy and silty clay	30	98.1	–	12.1	152	8.1
	O1/1	sandy and silty clay	25	98.5	–	4.3	74	8.1
Side valley and ice-dammed basin within plateau	S2/1	warp	6	94.1	3.2	0.0	44	6.5
	S2/2	clayey sand	11	97.6	1.8	0.0	38	7.5
	St1/3	organic clay	54	96.9	2.9	24.9	157	8.0
	St2/2	warp	4	91.1	5.3	2.2	37	7.1
	B4/1	muck	–	48.8	–	0.0	119	6.0
	O2/2	clayey sand	12	98.4	–	0.0	59	7.1
Slopewash	S3/1	fine grained sand	–	97.4	2.2	0.0	25	6.5
	S12/1	clayey sand	18	97.6	–	18.1	149	7.7
	B2/1	sandy and silty clay	23	98.1	–	5.4	99	8.6
Superficial soil	S7	organic clayey sand	16	94.1	–	0.0	35	5.9
	P$_A$2/1	organic fine grained sand	–	96.8	–	0.0	19	5.6
	Sy1/1	organic medium grained sand	–	96.8	–	0.0	28	4.7

Mineral composition of the selected sediments

Geomorphologic unit	Sample number	Mineral composition determined with X-ray diffraction analysis*	Content of minerals determined with thermal analysis [%]					
			beidelite	kaolinite	illite	goethite	CaCO₃	other carbonates
Valley bottom	Sy4/4	–	0.7	6.7	–	3.4	–	–
Morainic plateau	S13/4	Q, I, S, Kt, C, Cl, P	2.2	–	21.2	1.0	–	–
	P5/4	Q, I, S, Kt, K, P	8.2	2.1	–	2.8	–	–
	Sy1/3	Q, I, S, Kt, C, K	7.0	4.7	–	1.6	–	–
	B1/3	Q, I, S, Kt, Cl, C, D, K, P	17.0	0.8	4.6	3.9	12.1	1.3
	O1/1	–	23.0	–	–	–	4.3	0.7
Side valley and ice-dammed basin within plateau	S2/2	–	4.0	4.8	–	1.9	–	–
	St1/3	Q, I, S, Kt, Cl, K, P	34.5	8.6	–	2.1	24.9	2.6
	O2/2	Q, I, S, Kt, P	5.4	3.6	–	2.9	–	–
Slopewash	S12/1	–	10.0	7.2	–	2.3	–	–
	B2/1	–	19.0	2.3	–	2.9	5.4	1.4

* Q — quartz, I — illite, S — smectite, Kt — kaolinite, Cl — chlorite, C — calcite, D — dolomite, K — feldspar, P — plagioclase

sive soils consists mainly of beidelite and kaolinite (Table 2). The content of oxides of Fe and Al is rather low in these organic-mineral sediments. Sample S10/2 includes only 0.36% of these compounds (Table 3).

Sediments of the morainic plateau are characterised by the largest variation in grain-size (Falkowska, 2001). Sands (fine-, medium-grained, well-graded and gravel) as well as clays occur there. Cohesive soils contain beidelite, kaolinite, illite and admixtures of chlorite. It was observed that in most regions investigated, beidelite is the main component in the clay mineral group within sediments of the morainic plateau (Table 2). Only in the Suraż area, soils were characterised by a higher content of illite in relation to beidelite. In some cases sediments of the morainic plateau also contain geothite and calcium carbonate (Tables 1 and 2). The pH of these sediments reached from 5.7 to 8.5, but in most cases they had an alkaline reaction (Table 1).

In side valleys and ice-dammed basins within the plateau the type of sediment is similar to those in the valley bottom. Peats and mucks with ash contents averaging 50% and warps with ash contents from 91 to 94% occur there. Cohesive soils with contents of clay fraction up to 54% represent the lower parts of the sequences. In these cohesive soils the clay minerals include mainly kaolinite-beidelite (Table 2). Soils in side valleys and ice-dammed basins contain also goethite (2%). The admixture of CaCO₃, inducing alkaline reactions (pH > 7), is also common (up to 24%).

The lithology of the slopewash sediments is closely linked with the geological setting of the morainic plateau, with associated regional variations in grain-size and mineral content. Slopewash sediments composed exclusively of cohesive soils occur in the Nurzec valley. They are genetically connected with mudflows, rather than with downwashed deposits. As in the case of the plateau, a typical lithological succession has not been recognised for the slopewash. Slopewash sediments are formed by different soils from sands with various grain-size distributions to clayey and sandy silt (loam) with a beidelite-kaolinite clay mineral composition (Table 2). A characteristic phenomenon is also the occurrence of laminae of organic matter. The pH of these sediments ranges from 6.5 to 8.6 (Table 1).

Kames and kame terraces are built of fine- and medium-grained quartz-feldspar sands locally with gravel. The presence of illuvial zones in the lithological column observed in this area is a very important element from the environment protection point of view. These horizons are cemented with Al, Fe, Mn oxides and SiO_2 (hardpan — sample Sy5), and they are characterised by a larger chemical activity (Apello and Postma, 1993). They form continuous covers and are about 7 cm thick.

Content of Fe and Al oxides and ions of Na⁺, K⁺ in the selected samples

Geomorphologic unit	Sample number	Content [%]			
		Fe₂O₃	Al₂O₃	Na⁺	K⁺
Valley bottom	S10/2	0.12	0.24	–	–
Morainic plateau	S1/2	2.31	4.01	0.05	0.23
	S13/4	0.73	0.41	0.09	0.19
Side valley	S2/1	0.05	0.11	–	–
	S2/2	0.46	0.65	0.47	0.10

Superficial soil forms a relatively compact cover with an average thickness of 0.3 m. It contains up to *ca*. 7% organic matter. The superficial soil occurring in the regions discussed is both cohesive and sandy. Fine-grained sands and organic medium-grained sands as well as slightly clayey sands and clayey sand (sandy loam) with clay contents from 5 to 16% (Table 1) build these covers. In some cases superficial soils also contain calcium carbonate, though, mostly in small quantities. The pH of these deposits reached values from 4.7 to 5.9, therefore their reaction is acid.

CATION EXCHANGE CAPACITY

Examinations of the real cation exchange capacity (CEC) occurring in natural conditions of pH were investigated. This parameter influences the sorption capacities of the sediments (Bache, 1976; Bolt, 1979), thus it was determined for all samples examined. For peats, the pH ranged within 4.8 and 7.3, and for mineral sediments from 5.8 to 8.6.

Peats and mucks occurring in valley bottoms are characterised by the highest values of cation exchange capacity, with the parameter equalling to 120 meq/100 g of soil on average (max. over 150 meq/100 g of soil; Table 1). A trend of CEC in peats increasing linearly with an increase in organic content was observed (Falkowska, 2001). Warps also present in valley bottoms are characterised by a slightly lower values of cation exchange capacity than peats. Their CEC reached values up to of 62 meq/100 g of soil on average (max. 110 meq/100 g of soil — Table 1). Only fine- and medium-grained organic sands showed lower values of CEC (25 meq/100 g of soil).

The morainic plateau is the area with the greatest lithological variation, on which soils characterised by both high and low values of CEC occur. For clays, values of this parameter range from about 80 meq/100 g of soil to 152 meq/100 g of soil (Table 1). Slightly clayey sands, clayey and sandy silts, clayey sands that are mainly boulder clay (till), are characterised by cation exchange capacities averaging about 50 meq/100 g of soil. The CEC of sands building the morainic plateau are about 8 meq/100 g of soil (Helios-Rybicka and Kyzioł, 1991; Małecki, 1998). Among sandy sediments of the morainic plateau there occur hardpan horizons (sample K5), which also show a higher cation exchange capacity than do the sands: 23 meq/100 g of soils. Thus, as continuous layers within sandy soils, they can play an important role in preventing the spreading of contamination.

Peats and warps building side valleys and ice-dammed basins within the plateau reach similar values of cation exchange capacity to the organic valley bottom sediments. The CEC of peats averages 115 meq/100 g of soil, whereas the CEC of warps averages 56 meq/100 g of soil. Clayey and sandy silts (loams) and clays, constituting the lower parts of the sequence in this geomorphological unit, reveal high values of cation exchange capacity: from 38 to 157 meq/100 g of soil (Table 1).

The CEC of slopewash sediments ranges from 23 to 149 meq/100 g of soils (Table 1). This variation is caused by the variability of mineral and grain-size composition of soils building the morainic plateau, from which the slopewash sediments come.

Table 4

Sorption of Pb and Cd by the sediments of the valley bottom

Input solution [mg/dm^3]	Sorption [mg/100 g of soil]		
	peats and mucks	warps	mineral-organic sediments
Pb			
5	24.7–25.0	24.4–24.7	24.5–24.8
10	49.5–49.9	49.1–49.6	49.2–49.6
20	99.4–99.8	99.1–99.4	98.6–98.9
50	243.6–249.6	248.4–249.2	246.5–247.8
100	498.3–499.6	498.2–498.8	489.9–499.2
500	2481.0–2498.8	2239.0–2492.6	630.0–2494.6
Cd			
1	4.9–5.0	4.9	4.8–4.9
5	24.7–24.9	24.8–24.9	23.2–24.8
10	49.5–49.8	49.2–49.8	47.3–49.6
20	99.1–99.8	98.2–99.8	93.2–98.8
50	243.6–249.5	241.0–247.6	216.7–241.3

Sediments of kame terraces and kames reveal the lowest values of CEC. For sands this parameter from 2 up to 15 meq/100 g of soil (Helios-Rybicka and Kyzioł, 1991; Małecki, 1998).

In superficial soils the cation exchange capacity values range from 19 to 100 meq/100 g of soil, averaging about 30 meq/100 g of soil.

SORPTION OF LEAD AND CADMIUM

VALLEY BOTTOM SEDIMENTS

Peats and mucks (O6/1, O7/1, St8/1, P3/2, Sy4/1, Sy4/2, B4/1, B5/1, B5/2), which are characterised by exceptionally good sorption capacities for heavy metals, are the dominant sediments in the bottoms of inherited river valleys. Even though their pH is lower than 7, they bond over 99% lead and cadmium from each added input solution, not achieving a state of saturation even for solutions of 500 mg/dm^3 Pb. The range of results obtained for Pb and Cd sorption is also narrow for these sediments (Fig. 3). Only two samples (K4/1, B4/1) absorbed 98.8% from a solution of 5 mg/dm^3 Pb. However, it is necessary to emphasize that in this case only 0.06 mg/dm^3 Pb remained in the equilibrium solution. This is a lower value in comparison to that obtained after the application of higher concentrations, for which S% was higher. An exception was the sample of well-decomposed peat (St8/1), containing 37% of organic matter. It sorbed 97% from a solution of 50 mg of Cd/dm^3 concentration, which is equivalent to 243.6 mg of Cd/100 g of soil (Table 4). c_R equal to 1.28 mg/dm^3 was determined in the equilibrium solution.
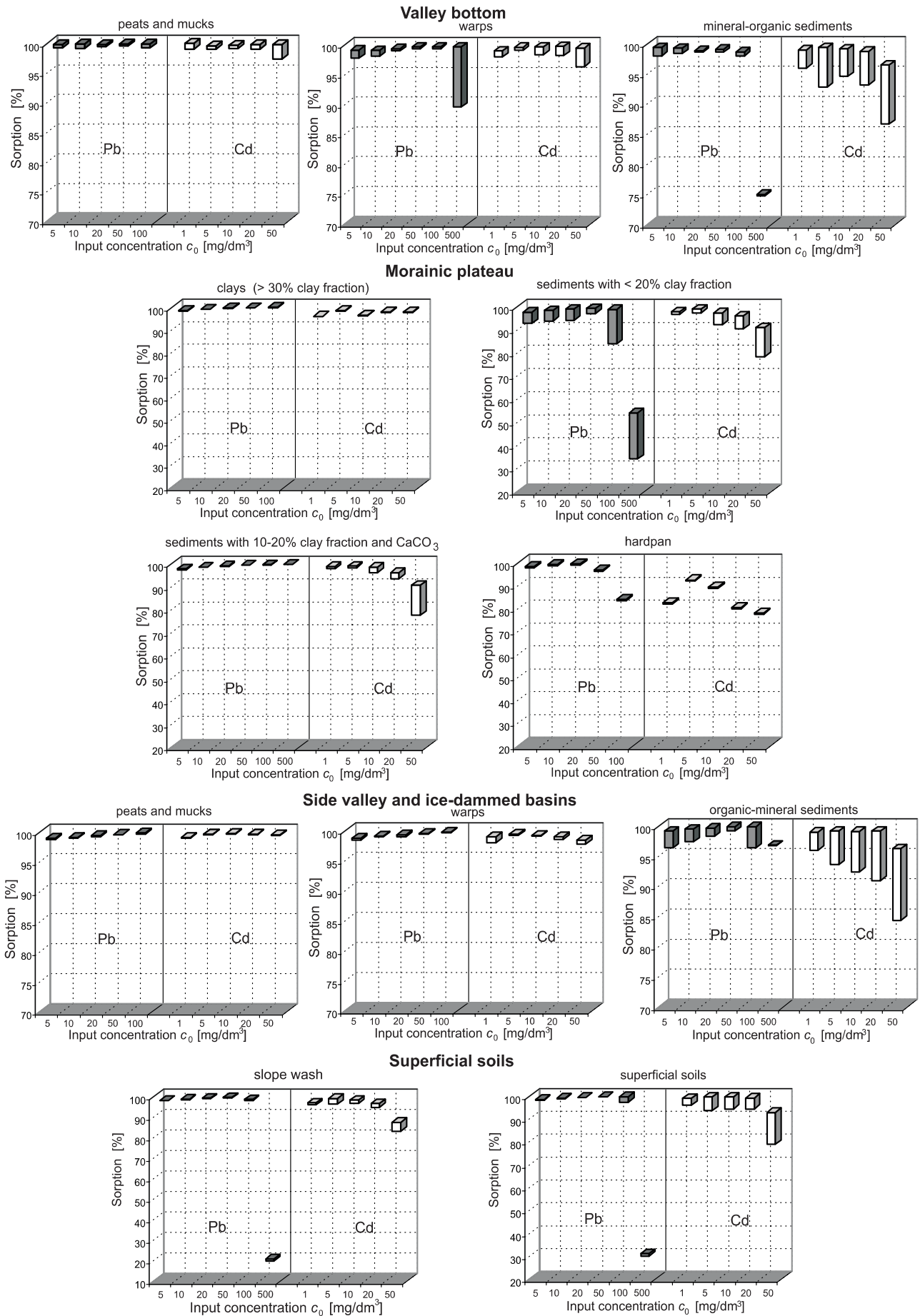
Fig. 3. Sorption of Pb and Cd by the sediments of the polygenetic river valley, expressed in percent

Sorption of Pb and Cd by the sediments of the morainic plateau

Input solution [mg/dm^3]	Sorption [mg/100 g of soil]			
	clays (>30% clay fraction)	sediments with 10–30% clay fraction +CaCO$_3$	sediments with < 20% clay fraction	hardpan
Pb				
5	24.6	24.4–24.5	23.2–24.4	24.4
10	49.5	49.3–49.4	47.0–49.3	49.2
20	99.4	98.9–99.3	94.2–99.2	99.0
50	249.4	248.7–249.3	243.1–248.6	241.1
100	499.1	497.9–499.2	420.0–495.1	417.0
500	–	2489.7	855.0	–
Cd				
1	4.8	4.9	4.8–4.9	4.1
5	24.6	24.6–24.8	24.4–24.8	23.0
10	48.2	48.2–49.4	46.2–48.8	44.4
20	97.6	93.6–99.0	90.5–96.2	80.0
50	244.0	194.0–227.0	196.3–228.0	193.9

For peats and mucks, the organic matter is a crucial feature in determining the capacity to bond heavy metals. As in the case of the CEC, this sorption potential of organic sediments increases with an increasing content of organic matter (Falkowska, 2001).

Warps, because of their lower organic matter content, are characterised by slightly weaker sorption capacities for heavy metals than are peats and mucks (Table 4). Lead and cadmium was bonded in quantities higher than 95% of the input state (Fig. 3). Although lower sorption values were found for lower concentrations, one must underline that much less of these determined elements remained in the equilibrium solution. The sorption of Pb was lower only for the input solution with a concentration of 500 mg/dm^3 Pb. The S% achieved values from 88 to 99%. Generally, the sorption of Cd by warps was lower than the sorption of Pb. The range of values of the bonded heavy metals was also larger for Cd than for Pb, especially for the input solution of 50 mg/dm^3 (Fig. 3). The pH of equilibrium solutions approaches and even sometimes exceeds 8 which is favourable for sorption.

Mineral soils containing small quantities of organic matter usually underlie the peats. They bond lead to a larger extent than they bond cadmium (Table 4, Fig. 3). S% for Pb for these sediments exceeded 97%. Only the sample S10/2 achieved the saturation condition, albeit, after applying the solution of 500 mg/dm^3 Pb. In this case S was equal to 630 mg/100 g of soil Pb, that is 75% of added lead. S% for Cd achieved a wider range of values than for Pb. For the input solution 50 mg/dm^3 Cd, sorption of this heavy metal ranged from 86 to 91% (Fig. 3).

These results show that the soils, especially organic soils, filling the valley bottoms, are characterised by very good sorption capacities to bond cadmium and lead. These sediments form a natural isolation barrier to the passage of heavy metals.

The sorption capacity of valley bottom sediments is, to a larger extent, determined by the content of organic matter (organic carbon). Lead is sorbed to a greater degree than cadmium by these soils.

SEDIMENTS OF THE EDGE ZONE OF THE MORAINIC PLATEAU

Sediments building the morainic plateau sorb varied quantities of heavy metals, which reflects their varying clay contants and range of mineralogical composition. The pH, content of calcium carbonate and content of Fe, Mn, Al oxides also have a great influence on sorption capacities. Despite this variety, the S% of clays (> 30% clay fraction) for lead as well as for cadmium equals about 98% of added heavy metals in most cases (Fig. 3). A state of lead saturation was reached only for a solution of initial concentration of 500 mg/dm^3 Pb in the case of samples which contain less than 20% of clay fraction (e.g. clayey and sandy silt P5/4, which contains 8% beidelite, 2% kaolinite and almost 3% goethite). They also bonded from 80 to 98% Pb for the input solution of 100 mg/dm^3 (Fig. 3) and from 32 to 53% for the input solution of 500 mg/dm^3. Cadmium was sorbed by these sediments to a slightly lesser degree (Table 5). They bonded from about 90 to 99% of added heavy metals from the solution with an input concentration of 1 to 20 mg/dm^3 Cd. From the input solution of 50 mg/dm^3 Cd, these sediments sorbed from 77 to about 87% of this element (Fig. 3). The oc-

Table 6

Sorption of Pb and Cd by the sediments of the side valley and ice-dammed basins within the plateau

Input solution [mg/dm^3]	Sorption [mg/100 g of soil]		
	peats and mucks	warps	mineral-organic sediments
Pb			
5	24.7	24.6–24.7	24.1–24.4
10	49.5	49.5–49.6	48.1–49.1
20	99.2	99.1–99.3	98.4–98.7
50	248.8	248.4–248.8	248.1–248.2
100	498.4	498.3–498.5	482.0–491.7
500	–	–	1242.0
Cd			
1	4.9	4.9	4.8
5	24.9	24.8	23.4–24.4
10	49.9	49.5–49.6	46.2–46.82
20	99.6	98.6–99.0	91.0–94.0
50	248.6	244.4–246.0	211.0–240.0

currence of calcium carbonate within the sediments of the morainic plateau increases the pH (about 8) and also of sorption capacities. S% reached values of over 95% for lead and over 90% for Cd for the input solution of 1–20 mg/dm^3. The range of results obtained for the input solution of 50 mg/dm^3 Cd was smaller, lying between 76 and 89% for sediments containing CaCO$_3$.

Hardpans, both on the morainic plateau and on kames and kame terraces, deserve particular consideration with respect to their common occurrence as continuous layers. In the case of sample Sy5, representing this type of sediment, lead was sorbed to a greater degree than cadmium, though saturation conditions were reached for both metals. Sample Sy5 bonded 98% of lead and 92% of cadmium after applying the input solution of 5 mg/dm^3.

Decidedly lower values of Pb and Cd sorption, equal to 193.9 mg/100 g of soil, that is 78% of the added element, were obtained in the case of cadmium for an input solution of 50 mg/dm^3 Cd, and equal to 241.1 mg/100 g of soil Pb, that is 96% in the case of lead. However, S% decreased to 84% for the input solution of 100 mg/dm^3 Pb (Fig. 3). Precipitation of Cd and Pb hydroxides can take place in sediments with a variable clay content depending on environmental pH.

These results show that very cohesive sediments (fi > 20%) on the edge of the morainic plateau are characterised by high sorption capacities to bond lead and cadmium. Capacities to hold these heavy metals by mineral soils of the morainic plateau depend on the quantity and mineral composition of the clay fraction (levels of smectite), and on the levels of calcium carbonate and oxides and hydroxides of Fe and Mg.

SEDIMENTS OF SIDE VALLEYS AND ICE-DAMMED BASINS WITHIN THE PLATEAU

Mineral sediments, of pH higher than 6 and often enriched in organic matter, occurring within the boundaries of this geomorphological unit, sorb heavy metals in the series Pb > Cd. Lead was bonded by these soils at the level of 90% — (clayey sand /sandy loam) to over 99% (organic clay) (Fig. 3); for the input concentration of 100 mg/dm^3 Pb. The saturation state was reached for a sample of clayey sand (O2/2), which contains 12% of clay fraction (beidelite — 5.4% and kaolinite — 3.6%), only after application of the input solution of 500 mg/dm^3 Pb. S% was equal to about 90% in these conditions which means that the sediment bonded 1242 mg/100 g of soil Pb (Table 6). In the case of cadmium, the saturation condition is reached for solutions with a lower input concentration. S% achieved values from 84% (216.7 mg/100 g of soil) to 92% (241.3 mg/100 g of soil) for the solution of 50 mg/dm^3 Cd. The greatest quantities of cadmium (from 96 to 98%) were retained from the solution of 1 mg/dm^3 Cd.

Warps occurring in side valleys and ice-dammed basins are characterised by relatively high sorption capacities to bond heavy metals. Their saturation state with respect to lead and cadmium was not reached during these studies. They bonded from 97 to 99% of added lead from the solutions applied.

Mucks occurring in side valleys and ice-dammed basins, were characterised by very high sorption capacities, as to 98% to bond lead and cadmium.

Laboratory tests showed that organic sediments of side valleys and ice-dammed basins were characterised by very high sorption capacities to hold Pb and Cd and can be considered as natural isolation barriers to heavy metals.

SEDIMENTS OF SLOPEWASH

Investigations of Cd and Pb sorption as regards slopewash sediments were conducted on both non-cohesive and cohesive soils. Fine-grained organic sand (S3/1) sorbs 98%, that is 24.5 mg/100 g of soil Pb from the input solution of 5 mg/dm^3 Pb (Table 7). The percentage of absorbed Pb increases up to the input concentration of 50 mg/dm^3 Pb, for which it reaches a maximum of 99% (Fig. 3), which gives S equal to 248.4 mg/100 g of soil. For the concentration of 100 mg/dm^3 Pb, sorption is equal to 491.5 mg/100 g which soil, what constitutes 98% of the added quantity of lead. This value is close to saturation, because for the solution with a concentration of 500 mg/dm^3 Pb, S is equal to 495.0 mg/100 g of soil Pb , and S% is equal to 20%. Cadmium is bonded to a lesser degree by sample S3/1. S% does not exceed 97% of the maximal value obtained for the solution with the concentration of 10 mg/dm^3 Cd. The percentage of absorbed cadmium decreased significantly to 87% when applied as a solution with an input concentration of 50 mg/dm^3. Slopewash cohesive soils showed very high effectiveness during the examination of lead sorption. From the input solution with an initial concentration of 5 mg/dm^3, they bonded 24.5 mg/100 g of soil Pb, constituting 98% of the primarily added element, and from the solution of 50 mg/dm^3 Pb, they bonded 99.7% of lead, that is about 249 mg/100 g of soil (Table 7). The maximum of 99.8% (B2/1) was reached for an input concentration equal to 100 mg/dm^3 Pb. Samples of slopewash sediments

are characterised by weaker sorption capacities to bond cadmium. The maximum value of sorption was obtained for the input concentration of 5 mg/dm^3 Cd. It equalled from 98%, that is 24.6 mg/100 g of soil for sample S12/1, to 99%, that is 24.8 mg/100 g of soil Cd for sample B2/1. For the input solution of 50 mg/dm^3 Cd, sorption is weaker in the case of these soils, because S% ranges from 83 (S12/1) to 85% (B2/1).

Sorption capacities of slopewash sediments to bond Pb and Cd are very variable. However, these sediments can be utilised in protecting ground water against the migration of heavy metals.

SUPERFICIAL SOILS

Pb is sorbed best by these sediments, in quantities exceeding 99% (Fig. 3). Only a single sample (Sy1/1 — organic medium-grained sand) from the input solution with a concentration of 100 mg/dm^3 Pb, bonded 487.2 mg/100 g of soil, which constitutes 97% of the added element. Conditions of saturation were obtained after applying the input concentration of 500 mg/dm^3 Pb. S% achieved a value of 30%. Sorption of cadmium was variable for these sediments. The sample of cohesive superficial soils (S7) using input solutions with concentrations ranging from 1 to 20 mg/dm^3 Cd, banded over 99% of cadmium, and only 93% from the input solution of 50 mg/dm^3 Cd. The sample of sandy superficial soil (Sy1/1) showed weaker capacities. From the input solution of 1 mg/dm^3 Cd it bonded 96%, that is 48 mg/100 g of soil, leaving about 10 mg/dm^3 Cd in the equilibrium solution (Table 7).

These results showed that, with input concentration increasing, sorption values in each sample of each type of sediment increased with a decrease in the percentage of the metal sorbed. This is consistent with the observations of Sapek (1980) for sorption of copper by muck soils.

IONS DISPLACED

Besides pH, the content of Ca^{2+}, Mg^{2+}, Na$^+$, K$^+$ (Table 8) displaced from the sorption complex was also determined, in selected equilibrium solutions, following sorption of Pb. In the case of peats, the pH of equilibrium solutions exceeded the value, at which precipitation of lead hydroxides occurs. It ranges from 8.39 to 8.04 (sample O7/1) and from 7.28 to 7.01 (sample Sy4/2). However, the presence of organic matter and therefore of a strong complexing factor can counteract the formation of these compounds. Moreover the shape of the sorption isotherm indicates the lack of precipitation of lead hydroxides. Along with the increase of concentration of the applied input solution, the pH of the equilibrium solution decreases after sorption of peats. This indicates an increasing number of dislodged hydrogen ions. This pattern was observed by Twardowska *et al.* (1999) during investigation of sorption of Zn by peats from peatlands in Poland and Israel.

Similarly to H$^+$ ions, the concentration of Ca^{2+} and Mg^{2+} ions in equilibrium solution increased whereas the quantity of replaced ions of Na$^+$ and K$^+$ stabilised, this being independent of the initial concentration. During the sorption of heavy metals by warps, as in the case of peats, the pH of the equilibrium solution decreased as the input concentration increased, and the content of magnesium and calcium ions in it increased; the

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Sorption of Pb and Cd by the slopewash sediments and superficial soils

Input solution [mg/dm^3]	Sorption [mg/100 g of soil]	
	slopewash	superficial soils
Pb		
5	24.5	24.5–24.6
10	49.2–49.4	49.4–49.5
20	99.0–99.4	99.3–99.5
50	248.4–249.3	249.0–249.2
100	491.5–499.2	487.2–498.9
500	495.0	755.0
Cd		
1	4.8	4.8–4.9
5	24.1–24.8	23.4–24.6
10	48.4–49.2	47.2–49.8
20	94.8-96.8	94.4-99.2
50	207.0–219.0	197.2-237.5

quantity of sodium and potassium determined remained relatively constant.

In equilibrium solutions following Pb sorption, a pH decreasing from 8.0 to 7.6 (for an input concentration of 100 mg/dm^3) was determined for a sample from the morainic plateau, indicating an increase in H$^+$ content. An increasing concentration of Ca^{2+} ions, as well as Mg^{2+} ions was found, together with a slight increase in Na$^+$ and K$^+$ concentrations.

SORPTION ISOTHERMS OF LEAD AND CADMIUM

The sorption of lead and, in part, cadmium by peats and warps occurring in valley bottoms, side valleys, ice-dammed basins within the plateau and by superficial soils, for added input solutions, is described by Henry's isotherms (B5/2; Fig. 4). The initial stretch of the curve characterises the sorption phenomenon, as the increase of added solution causes a proportional increase in the quantity of sorbed heavy metal. The cadmium sorption by this type of sediment, especially in side valleys and in ice-dammed basins within the plateau, is described by the curvilinear Freundlich isotherm (S2/1) showing, in many cases, that saturation conditions of this element will be reached significantly earlier than in the case of lead. Application of higher concentrations of the input solution will not cause an increase in the quantity of cadmium retained in the sediment. Similar patterns were also observed for the majority of very cohesive sediments of the all the geomorphological units analysed. Sorption of both lead and cadmium by clay only (S1/2) is described by Henry's isotherms (Fig. 4). On the other hand,

Ions dislodged from the sorption complex after Pb sorption

Sample number (soils)	Input concentration Pb[mg/dm^3]	pH of equilibrium solution	Dislodged ions [mg/dm^3]			
			Ca^{2+}	Mg^{2+}	Na$^+$	K$^+$
S1/2 (clay)	5	8.00	5.11	1.53	2.45	0.52
	10	7.97	5.39	1.59	2.47	0.56
	20	7.92	6.36	1.90	2.51	0.56
	50	7.78	9.35	2.71	2.59	0.63
	100	7.58	14.6	4.31	2.79	0.98
S2/1 (mud)	5	8.03	7.94	1.12	1.30	0.83
	10	7.99	8.23	1.16	1.21	0.62
	20	7.90	8.93	1.26	1.37	0.68
	50	7.80	13.0	1.70	1.32	0.66
	100	7.52	20.6	2.35	1.40	0.83
Sy1/3 (clayey sand)	5	7.78	15.3	2.20	2.41	1.23
	10	7.64	16.8	2.18	2.27	1.20
	20	7.60	16.3	2.11	2.30	1.33
	50	7.43	10.8	0.99	1.57	1.39
	100	6.80	21.7	1.26	1.31	1.44
Sy4/2 (peat)	5	7.28	38.2	3.55	1.60	0.50
	10	7.26	36.7	3.62	1.86	0.55
	20	7.22	37.9	3.56	1.66	0.50
	100	7.01	51.9	4.70	1.80	0.52
Sy5 (slightly clayey sand — slopewash)	5	7.31	2.12	0.53	0.98	1.05
	10	7.07	2.46	0.53	1.15	1.16
	20	6.98	3.77	0.75	1.19	1.27
	50	6.46	7.62	1.39	1.21	1.52
	100	6.22	12.9	2.14	1.23	1.69
B1/3 (clay/sandy and silty clay)	5	8.50	8.74	1.39	1.39	1.18
	10	8.37	9.58	1.43	1.22	1.15
	20	8.32	11.1	1.65	1.39	1.24
	50	8.28	16.6	2.31	1.34	1.39
	100	8.22	25.7	2.97	1.33	1.58
O7/1 (peat)	5	8.39	37.0	3.83	1.77	0.67
	10	8.30	37.6	3.83	1.70	0.65
	20	8.25	37.7	3.82	1.54	0.62
	50	8.15	40.4	4.12	1.63	0.63
	100	8.04	47.6	4.82	1.67	0.63

sediments with low clay contents (clayey and sandy silts /loams and slightly clayey sands) occurring on the morainic plateau, sorb lead as well as cadmium according to Freundlich's isotherm (P5/4). The value of sorption, as well as the form of the curve describing its dynamics for cohesive sediments, is dependent not only on the clay content, but also on the mineral composition. The sorption of cadmium and lead by sediments containing kaolinite as the main component of the clay fraction is best described by Freundlich's isotherms. Henry's isotherms, though, apply for sediments containing illites and smectites (B1/3, O1/1). This parameter is best influenced by the contents of organic matter, oxides/hydroxides of iron and aluminium and calcium carbonate. For sample S13/4, containing only 10% clay, sorption of Pb and Cd was described by Henry's isotherm, suggesting an initial stage in this phenomenon. This resulted from a content of calcium carbonate in excess of 16%. The lead and cadmium sorption of mineral-organic sediments occurring in the valley bottom, in side valleys, in ice-dammed basins within the plateau, in non-cohesive organic sediments of the morainic plateau, in slopewash and in kames is described by Freundlich's isotherms. Samples of these soils, for the applied concentrations, approach conditions of saturation with respect to cadmium and lead. The curve of sample Sy1/1 for higher concentrations is approximately parallel to the axis of equilibrium concentrations, what means that the value of sorption is constant under these conditions. In Figure 4 examples of sorption isotherms, characteristic for selected lithological types, are shown.

Results of the investigation indicate that sorption of lead by peats and warps as well as sorption of cadmium and lead by the mineral sediments containing illite or clay minerals from the group of smectite are described in most cases in the way most approximated to reality by Henry's isotherms. Lead and cadmium sorption by mineral-organic sediments, mineral sediments containing kaolinite as the main component of clay fraction as well as sorption of cadmium by peats and warps are described by Freundlich's isotherms.

SORPTION INTENSITY OF LEAD AND CADMIUM

According to Witczak (1984), sorption intensity for lower concentrations of input solutions of Cd and Pb is unlimited for most sediments, because the retardation factor R is greater than 1000 (Table 9). Only sands occurring on the morainic plateau,
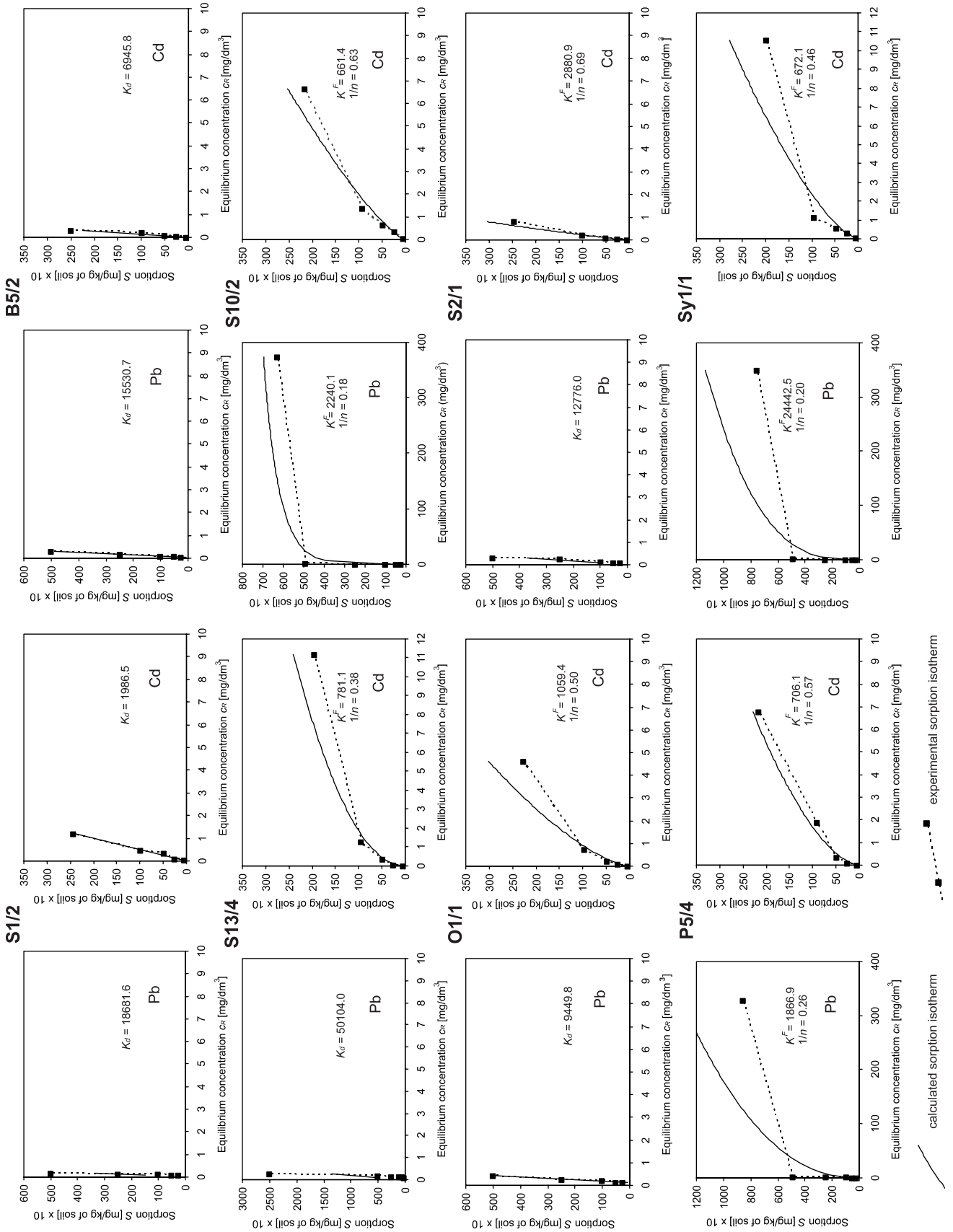
Fig. 4. Examples of experimental and calculated sorption isotherms for the selected sediments

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Retardation factor and Pb, Cd sorption intensity of the selected sediments

Geomorphologic unit	Sample number	Heavy metal	Correlation coefficient	Retardation factor R/sorption intensity[1]						
				1	5	10	20	50	100	500
Valley bottom	S10/2	Pb	0.71	–	86430*/u	58800/u	38300/u	26140/u	7350/u	103/v
		Cd	0.95	60300/u	32260/u	18400/u	9860/u	3550/u	–	–
	P1/2	Pb	0.96	–	40570/u	33620/u	30460/u	25140/u	19370/u	890/h
		Cd	0.89	60340/u	32260/u	18400/u	9860/u	6520/u	–	–
	Sy4/1	Pb	0.99	11300**/u						
		Cd	0.96	10200/u	8420/u	6940/u	5700/u	3750/u	–	–
	B5/2	Pb	0.99	4350/u						
		Cd	0.97	1950/u						
	O6/1	Pb	0.98	18530/u						
		Cd	0.99	2000/u						
Morainic plateau	S13/4	Pb	0.98	421900/u						
		Cd	0.88	114300/	48400/u	12400/u	5640/u	1470/u	–	–
	P5/4	Pb	0.72	–	23900/u	16000/u	9840/u	8650/u	6170/u	150/v
		Cd	0.97	22300/u	12300/u	6440/u	3150/u	1820/u	–	–
	St11/2	Pb	0.74	–	29200/u	26400/u	21800/u	12400/u	1110/u	–
		Cd	0.91	17140/u	8221/u	3091/u	2141/u	760/vh	–	–
	Sy5	Pb	0.81	–	58330/u	47800/u	39800/u	9780/u	2350/u	–
		Cd	0.98	5360/u	3870/u	2930/u	2080/u	1570/u	–	–
	O1/1	Pb	0.99	21400/u						
		Cd	0.93	17006/u	8500/u	5380/u	2840/u	1120/u	–	–
Side valley and ice-dammed basin	S2/1	Pb	0.96	31300/u						
		Cd	0.98	29400/u	20900/u	15400/u	11600/u	7560/u	1350/u	–
	St1/3	Pb	0.99	632700/u						
		Cd	0.91	99800/u	70600/u	47100/un	34200/u	10400/u	–	–
	B4/1	Pb	0.95	6970/u						
		Cd	0.98	10200/u	8100/u	7620/u	5700/u	4700/u	–	–
Slopewash	S3/1	Pb	0.35	–	47200/u	30600/u	23900/u	16500/u	3900/u	38/h
		Cd	0.92	12300/u	7100/u	4340/u	2620/u	988/vh	–	–
	B2/1	Pb	0.89	87200/u						
		Cd	0.88	44000/u	37000/u	16100/u	7010/u	1640/u	–	–
Superficial soil	$P_A2/1$	Pb	0.98	55300/u						
		Cd	0.94	18500/u	13800/u	10400/u	7050/u	3260/u	–	–
	Sy1/1	Pb	0.71	–	45100/u	38400/u	33600/u	24800/u	3100/u	62/h
		Cd	0.83	10300/u	3230/u	2470/u	1700/u	507/vh	–	–

Sorption intensity (Witczak, 1984); [1]: vh — very high, h — high, u — unlimited; * — values calculated using Freundlich isotherms , ** — values calculated using Henry isotherms

Desorption of Pb on selected soil samples with distilled water and with ion NH$_4^+$

Input solution	Superficial soil Sy1/1		Morainic plateau Sy1/4		Valley bottom Sy4/1	
[mg/dm^3]	[mg/dm^3]	[%]	[mg/dm^3]	[%]	[mg/dm^3]	[%]
Pb — H$_2$O dest.						
5	0.05	1.02	0.12	2.4	0.04	0.81
10	0.07	0.71	0.17	1.7	0.05	0.51
20	0.09	0.45	0.29	1.4	0.08	0.40
50	0.12	0.24	0.61	1.2	0.14	0.28
100	0.15	0.15	0.76	0.7	0.26	0.28
Pb — NH$_4^+$						
5	0.97	19.96	0.85	17.45	0.67	13.6
10	2.53	25.76	2.64	27.22	1.67	16.9
20	9.55	48.28	8.81	44.89	4.47	22.5
50	35.6	71.64	39.0	79.20	15.2	30.6
100	88.8	91.26	97.0	97.93	40.2	40.4

kames and kame terraces showed sorption intensity ranging from low to very high. This was caused by variations in contents of organic carbon oxides and hydroxides of iron and aluminium and clay. Samples of cohesive sediments with clay contents of < 20%, for example slightly clayey sand St11/2 (morainic plateau) and sands containing organic matter on the morainic plateau and slopewash (e.g. S3/1), as well as some superficial soil samples (e.g. Sy1/1) are characterised by lower sorption intensities of cadmium, for input concentrations greater than 20 mg/dm^3. Their retardation fraction R ranged from 100 to 1000. In the case of lead, lower values of R were obtained only for the input solution with a concentration of 500 mg/dm^3 (Falkowska, 2001). In the case of samples occurring in the valley bottom, of organic slightly clayey sand (S10/2), R reached a value of 103, and 887 for warp (P1/2), showing sorption intensities in these conditions to be very high. Sample S10/2 has a low clay content (7%), a high ash content (97.8%) and a low organic carbon content (2%), whereas the sample P1/2 contains 19% clay and its ash content is 91.8%. Similarly, a clay poor (12%) sample of clayey and sandy silt (loam) P5/4 from the morainic plateau showed an R of 151, indicating a very high sorption intensity. This sample contains beidelite as the main clay mineral (8%) and 2.8% of goethite.

These results show that, the sorption intensity for organic sediments composing the valley bottoms, side valleys and ice-dammed basins, and cohesive sediments of the morainic plateau, was unlimited. High and very high sorption intensities ($10 < R < 1000$) are shown by sandy sediments of kames, kame terraces and the morainic plateau for input concentrations over 20 mg/dm^3.

DESORPTION OF LEAD AND CADMIUM

Desorption of NH$_4^+$, an ion commonly delivered to soils in the form of fertilisers and farming wastes, was conducted on samples of superficial soil (Sy1/1), of clayey sandy-gravel from the morainic plateau (Sy1/4), of mucks in the valley bot-

tom (Sy4/1) and on samples of sandy and silty clay (clay loam) from the morainic plateau and of peat from the valley bottom (B5/1, O7/1).

From samples enriched with lead there were released, by means of H$_2$O, quantities of this element not exceeding 0.76 mg/dm^3 (Table 10). Pb was most strongly bonded by muck (Sy4/1): which yield low concentrations of lead in the solution following description, equivalent to 0.04 mg/dm^3 for an input solution of 5 mg/dm^3, which constitutes 0.81% of the absorbed metal, and 0.26 mg/dm^3, that being 0.28% for an input concentration of 100 mg/dm^3 Pb. Similar results were obtained for soil (Sy1/1). Desorption ranged, in this case, from 0.05 (1.02%) for a solution of 5 mg/dm^3 Pb to 0.15 mg/dm^3 (0.15%) for a solution of 100 mg/dm^3 Pb. The greatest quantity of lead was released from the sample Sy1/4 of clayey sandy-gravel. With an input concentration of 5 mg/dm^3, desorption equalled 0.12 mg/dm^3, which comprised as much as 2.45%, and in the case of input concentration of 100 mg/dm^3, 0.76, that being 77% (Table 11). As the concentration of the input solution of Pb increased, so did the value of desorption Dw, while the percentage of desorbed metal decreased. In the case of desorption of lead from samples enriched with this element, using ammonium ions, values of Dp and $D\%$ increase as input concentration increases (Table 11). Pb^{2+} ions were removed most easily and in greatest quantities from clayey sandy-gravel (Sy1/4). For the input solution of 5 mg/dm^3 Pb, desorption equalled 0.85, that constitutes 17.5%, while for the solution of 100 mg/dm^3 it equalled 97.0 mg/dm^3, that is 97.9% of previously bonded metal. Similar results were obtained for superficial soil (Sy1/1), though Dp in the case of the input solution of 100 mg/dm^3 Pb did not exceed 88.8 mg/dm^3 (91.3%). The lowest quantities of lead were released from muck (Sy4/1). In the case of the input solution of 5 mg/dm^3, Dp was equal to 0.67 mg/dm^3, which constitutes 13.67%, whereas for input solution of 100 mg/dm^3 it was 40.2 mg/dm^3 and thus 40.44% of absorbed heavy metal. Desorption from muck was approximately half that of desorption of other samples.

Table 11

Desorption of Cd on selected soil samples with distilled water and with ion NH_4^+

Input solution	Superficial soil Sy1/1		Morainic plateau Sy1/4		Valley bottom Sy4/1	
[mg/dm³]	[mg/dm³]	D% [%]	[mg/dm³]	D% [%]	[mg/dm³]	D% [%]
Cd — H_2O						
1	0.00	0.00	0.00	0.00	0.00	0.00
5	0.00	0.00	0.01	0.20	0.01	0.20
10	0.01	0.11	0.12	1.21	0.11	1.10
20	0.04	0.21	1.08	5.54	0.26	1.31
50	0.72	1.83	2.67	5.61	0.84	1.69
Cd — NH_4^+						
Input solution	Valley bottom B5/1		Valley bottom O7/1		Morainic plateau O1/1	
	[mg/dm³]	[%]	[mg/dm³]	[%]	[mg/dm³]	[%]
1	0.63	63.64	0.20	20.20	0.89	90.82
5	2.80	56.34	1.00	20.08	4.72	95.93
10	5.20	52.21	2.80	28.08	9.57	97.65
20	12.50	63.00	7.20	36.14	18.45	95.70
50	37.00	74.60	21.05	42.34	44.21	97.38

During desorption with distilled water, cadmium behaved differently to lead. For cadmium, both percentages of released metal and also concentrations in solution expressed in mg/dm³ increased (Table 11). This element was least removed from the sample of muck (Sy4/1). *Dw* was 0.84 mg/dm³, and *D*% was 1.7% for the input concentration of 50 mg/dm³ Cd. The highest desorption was obtained for the clayey sandy-gravel (Sy1/4). Under application of the input solution of 50 mg/dm³ Cd it was equal to 2.67 mg/dm³ that is 5.61% of the element initially absorbed. These values are higher than those obtained for lead for input solutions with concentrations over 10 mg/dm³. Lower contents of cadmium were determined from solutions of lower concentration. Desorption from cadmium, conducted with use of ammonium ions, reached especially high values for the sample of sandy and silty clay (clay loam) from the morainic plateau (O1/1) containing 95% clay. It equalied to 4.72 mg/dm³ that is 95.9%, for the input solution of 5 mg/dm³ Cd and 44.21 mg/dm³ for the input solution of 50 mg/dm³, constituting 97.4% of previously bonded metal. Cadmium was desorbed from peats in the lowest quantities. Similar values, though slightly higher than obtained in the case of lead, were obtained for sample O7/1. At the input concentration of 50 mg/dm³, *Dp* was 21.05 and *D*% was 4.23%. However, the sample of medium-distributed peat B5/1 shows worse features as regards environmental protection. For the input solution of 50 mg/dm³, desorption was 37.00 mg/dm³ which constitutes 74.6% of the originally bonded element. This phenomenon is similar to that described by Sapek (1980), where of easier release of copper can take place from mucks which are moderately decomposed. Heavy metals are bonded there mainly on cation-exchangeable positions.

These results show that cadmium is more easily from such soils than lead. The widespread organic soils are characterised by relatively low resistance to desorption, lower than in mineral soils.

Many factors influence the value and dynamics of desorption. The most important of these are: composition of the solid phase, clay mineral structure, buffering capacity kinds of metal ions, redox potential and quantities of absorbed elements (Helios-Rybicka and Kyzioł, 1991; Kyzioł, 1994). With greater levels of sorption and greater concentrations of input solutions, so the release of heavy metals takes place to a greater degree. More powerful bonding of metal with the solid phase takes place when apart from sorption proceeding in the course of ion-exchangeable reactions, it takes place by precipitation and co-precipitation of sparingly soluble compounds (Kyzioł, 1994). These elements are then less mobile, and are released only with a pH change. Lead, a more stable heavy metal than cadmium, is released in higher quantities only at pH = 5.0 (Urban *et al.*, 1990). A reduction in pH promotes exchange between H^+ ions and ions of heavy metals absorbed earlier. In those conditions, carbonates and hydrated oxides of iron and manganese dissolve (Hudson-Edwards *et al.*, 1999). Decomposition of organic matter also takes place, causing activation of environmentally damaging elements bonded with it.

CONCLUSIONS

1. Peats, mucks and warps, filling valley bottoms, side valleys and ice-dammed basins within the plateau, are character-

ised by very high sorption capacities in relation to lead and cadmium. They bond up to 98% of the added Pb and Cd from input solutions with concentrations of 1 to 20 mg/dm^3.

2. Very high sorption capacities to bond lead and cadmium are shown by very cohesive sediments of the morainic plateau (fi > 20%). They sorb up to 98% of added Pb and Cd from input solutions with concentrations of 1 to 20 mg/dm^3.

3. The sorption intensity for organic sediments building the valley bottoms, side valleys and ice-dammed basins within the plateau, as well as cohesive sediments of morainic plateau, is unlimited. High and very high sorption intensities (10 < R < 1000) are indicated by sandy sediments of kames, kame terraces and the morainic plateau for input concentrations over 20 mg/dm^3.

4. Within the area of melt-out river valleys of the eastern part of the Polish Lowland there occur natural isolation barriers (in the valley bottoms), protecting groundwaters and lower-lying soils from contamination by the heavy metals Cd and Pb. These barriers are built of marsh and lacustrine sediments.

5. Organic content determines the sorption capacities of organic sediments. In mineral sediments, on the other hand, the quantity and mineral composition of the clay fraction and levels of admixtures of calcium carbonate and oxides and hydroxides of Fe and Mg are important.

6. Lead is bonded, both in the case of mineral and organic sediments, to a greater degree than the cadmium.

7. Lead sorption by peats and warps as well as cadmium and lead sorption by the mineral sediments containing illite or smectite are mostly best approximated by Henry's isotherms. Sorption of lead as well as cadmium by mineral-organic sediments, mineral sediments containing kaolinite as the main clay mineral as well as sorption of cadmium by peats and warps are described by Freundlich's isotherms.

8. The value of desorption by H_2O increases as the input solution of Pb increases, whereas the percentage of metal decreases. In desorption of lead from samples enriched with this element, by ammonium ions, both the value of desorption and the percentage of desorbed metal increase with increase in input concentration.

9. For cadmium, the percentage of released metal as well as the concentration in solution expressed in mg/dm^3 increase during desorption by distilled water and NH_4^+.

10. Mineral sediments are more susceptible to desorption than organic sediments.

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