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## Clays and clay minerals as the natural barriers for heavy metals in pollution mechanisms — illustrated by Polish rivers and soils

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With 10 figures and 2 tables

### Abstract

The content and phase specific bonding forms of heavy metals in the clay fraction of river sediments and soils from Southern Poland were investigated. The clay fraction especially of high polluted sediments is enrich in heavy metals. Association types of metals can be divided into two groups: (1) highly mobile elements — Cd, Zn, Cu; (2) metals more strongly bound to sediment particles — Cr, Pb, Ni. The content of metals found in the residual fraction is higher in the soils and in the less contaminated sediments. The sediments and clays containing carbonates show better buffering properties.

The sorption/desorption "batch" experiments of Cd, Cu, Zn and Pb performed for illite and smectites show that the sorption as well as the capability of clay minerals for exchange of metal ions decreases in the sequence: Montmorillonite > Beidellite > Smectite/Illite > Illite. Lead was sorbed in greatest amount, and cadmium in the smallest. For smectites the amounts of sorbed metals depends on the type of cation in the interlayer. Na-smectite sorb more metals than K- and Ca-smectites. Clay soils sorb relatively great amount of heavy metals; in the soils containing calcite sorption and precipitation take place.

### Introduction

For some time now much consideration has been given to the detrimental effect of the resistant substances such as heavy metals. Once they have become introduced into the environment they cannot be removed from it or their amount reduced. In many areas, especially in highly industrialized regions the rivers and soils are strongly polluted with heavy metals.

The content of heavy metals in river sediments, chiefly in the clay fraction, is a very good indicator of environmental pollution. In the finest fractions of sediments due to the active surface of their components there takes place a continuous enrichment with heavy metals (FÖRSTNER & WITTMANN 1981, HELIOS-RYBICKA 1985).

Solid surfaces play an important role in mediating the physicochemical behaviour of heavy metals. Interactive processes between dissolved metals and solid surfaces in a natural aquatic system involve in a considerable portion the clay minerals, partly as substrates, but also as direct medium.

The ability of heavy metals for mobilization depends very strongly on their chemical forms, also on the properties of the particular constituents of the sediment. An important

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role play pH changes. Among the solid components which play an important role are those characterized by an active surface such as clay minerals, Fe-Mn-oxyhydrates, carbonates and organic matter (BURG & FILBY 1974, JENNY 1976, SALOMONS 1980, HELIOS-RYBICKA & CALMANO 1989).

The river sediments as well as the typical more or less permeable soils containing calcite exhibit good buffer capacities binding relatively strongly the heavy metals (FÖRSTNER et al. 1986, HELIOS-RYBICKA & KYZIOL 1990).

### Heavy metals in the clay fraction of river sediments and soils

The content and the binding forms of heavy metals in a clay fraction of river sediments and soils from Southern Poland were investigated. This is a region of a very active mining and metallurgical industry.

The heavy metals were determined by the method of atomic absorption spectroscopy in solution after their extraction with boiling concentrated nitric acid. The chemical speciations of metals were determined by the following chemical extraction method (FÖRSTNER et al. 1981):

1. Exchangeable cations  
1 M ammonium acetate, pH 7, solid:solution ratio=1:20, 2 h shaking
2. Carbonates and easily reducible phases (e.g. Mn-oxides)  
0.1 M hydroxylamine hydrochloride+0.01 M nitric acid, pH 2, solid: solution ratio=1:100, 2 h shaking
3. Moderately reducible phases (e.g. amorphous Fe-oxides)  
0.2 M ammonium oxalate+0.2 M oxalic acid, pH 3, solid: solution ratio=1:100, 24 h shaking
4. Organic fraction and sulphides  
30% H<sub>2</sub>O<sub>2</sub>+nitric acid, pH 2, extracted with 1 M ammonium acetate, solid: solution ratio=1:100, 24 h shaking
5. Residual fraction (e.g. silicates)  
Boiling concentrated nitric acid

The investigations of the bottom sediments of the Upper Vistula river have shown that the content of metals in the clay fraction of the sediments is higher than that in the fraction < 60 $\mu$ m the sediments as well as the suspended matter of Vistula river are particularly rich in heavy metals (Fig. 1).

It has been found that the bottom sediments are to a high degree polluted mainly with Cd, Pb, Cr, Zn and Cu, especially in the river section upwards of Krakow. With a growing distance from the industrial region the metals content in the sediments decreases. The amount of heavy metals in the clay fraction and the suspended matter is several times and occasionally some tens of times higher than in the fraction < 60 $\mu$ m.

In the soils the content of heavy metals is considerably smaller than in the bottom sediments and is equal to: Cd-8, Zn-420, Pb-220, Cu-80 and Ni-50 ppm (Table 1). Also in soils the clay fraction is the one mostly enriched with metals (Fig. 2).

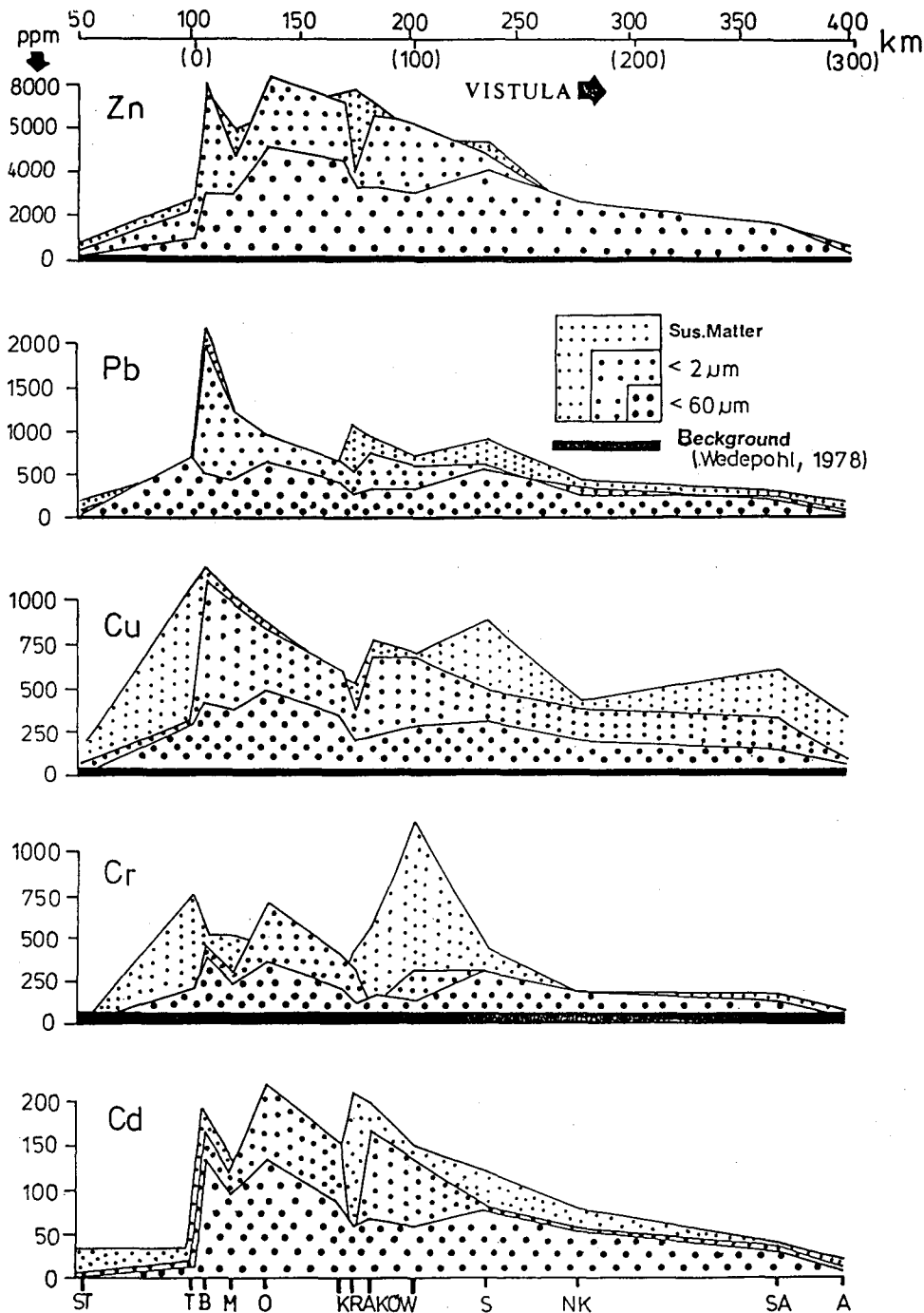


Fig. 1: Content of heavy metals in the bottom sediments and suspended matter of Vistula river.

Table 1: Metals concentration (ppm) in the clay fraction and fraction  $<60\mu\text{m}$  of the soils (ppm) from Kraków Region.

Soils	Ni	Cr	Cu	Cd	Zn	Pb	Mn	Fe %
Alluvial								
< 60	50	40	80	8	420	80	620	2.4
< 2	90	70	150	10	800	150	900	4.6
Loess								
< 60	30	30	50	8	140	50	310	1.4
< 2	90	80	380	11	395	130	616	7.1
Clay								
< 60	40	20	40	3	140	220	870	1.9
< 2	60	40	80	4	280	230	900	4.2

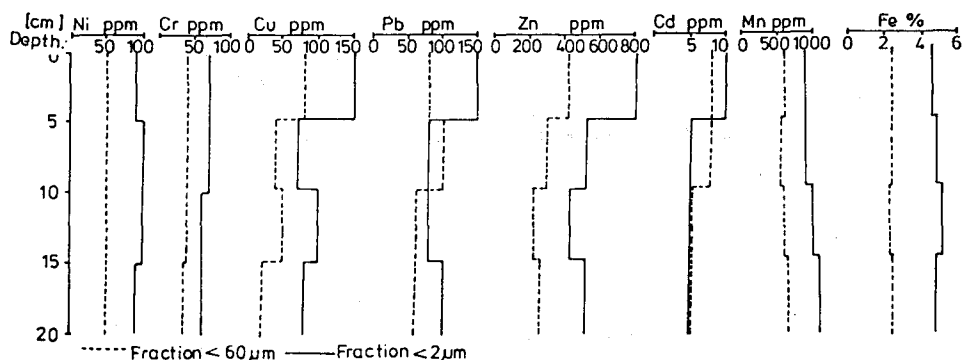


Fig. 2: Content of heavy metals in the fractions:  $<60\mu\text{m}$  and  $<2\mu\text{m}$  of alluvial soil from Krakow Region.

The results of selective chemical extraction have shown that the phase specific bonding forms of metals are differentiated depending on the type of the metal, the character of the sediment and the degree of its contamination. In the clay fraction of sediments a distinct increase in the amount of metals, especially Zn and Cd in a cation exchangeable form can be observed (Fig. 3), and as it seems, these metals form a sorption complex of the clay minerals.

Association types of heavy metals can be divided into two groups: the ones showing relatively high mobility — Cd, Zn, Cu; and metals more strongly bound to sediment particles — Cr, Pb, Ni. Heavy metals in the river sediments are mainly associated with carbonates and Mn-Fe-oxyhydrates. An important carrier of metals are also the clay minerals, especially in the soils. The content of metals found in the residual fraction — mainly bound with clay minerals — is variable but higher in the soils and in the less contaminated sediments. In the soils the less mobile forms of metals were observed.

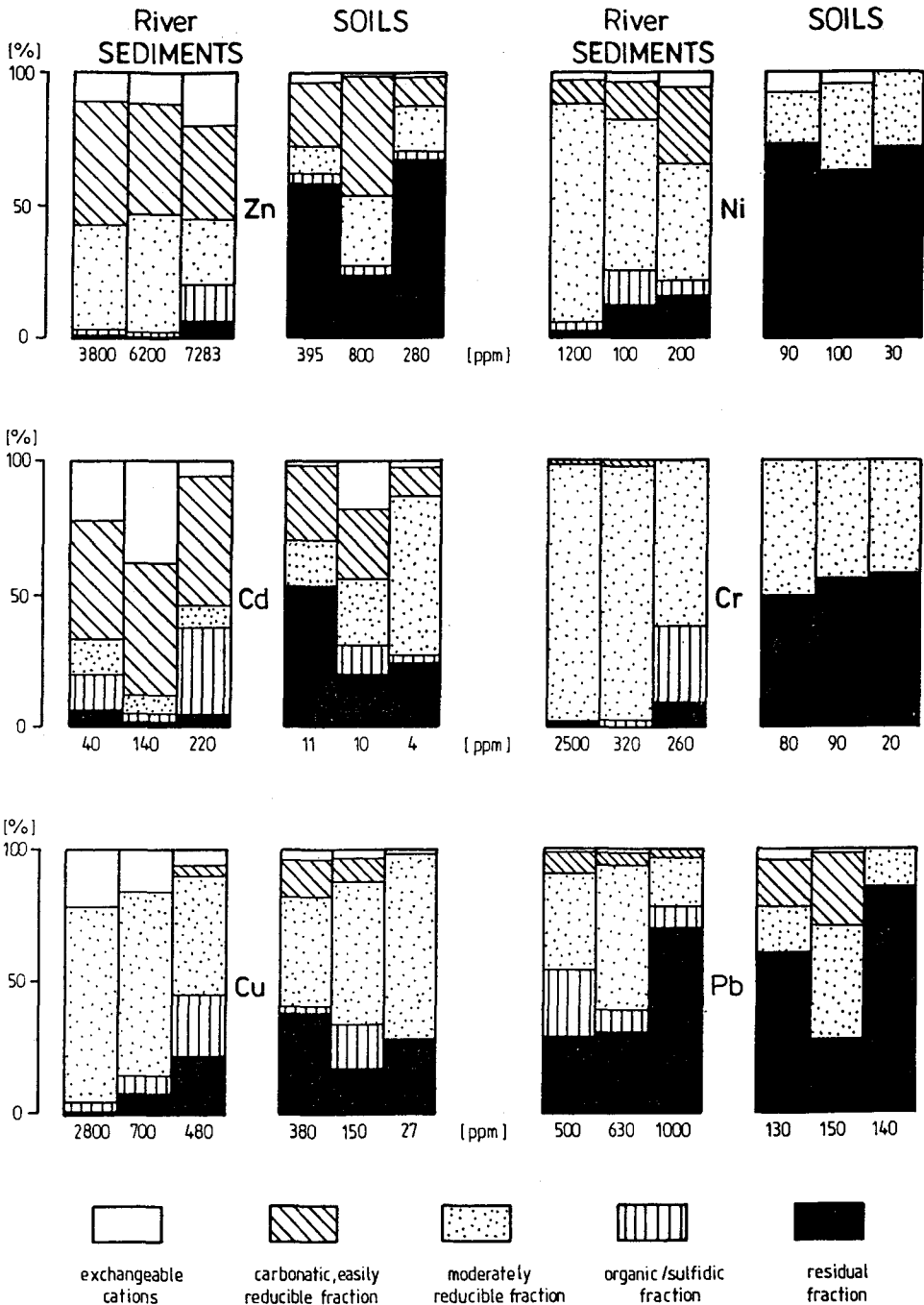


Fig. 3: Chemical extraction results of zinc, cadmium, copper, nickel, chromium und lead from river sediments and soils.

### Buffer capacity of river sediments and typical soils

According to many investigations, for some metals a linear relationship has been found to exist between the pH values and the dissolved metal concentrations. Accordingly, the mobility of metals from bottom sediments with decreasing pH was examined for selected, most important four rivers of Poland: The Vistula, the Oder, the Bug and the Warta.

Nitric acid in the amounts of 10, 20, 30, 40, 50, 60 and 70 ml was added to 10 per cent suspension of the bottom sediments. The samples were shaken for 1 h, and the pH value of the suspension measured; in the solution the amount of dissolved metal was determined. The obtained results are shown in Fig. 4.

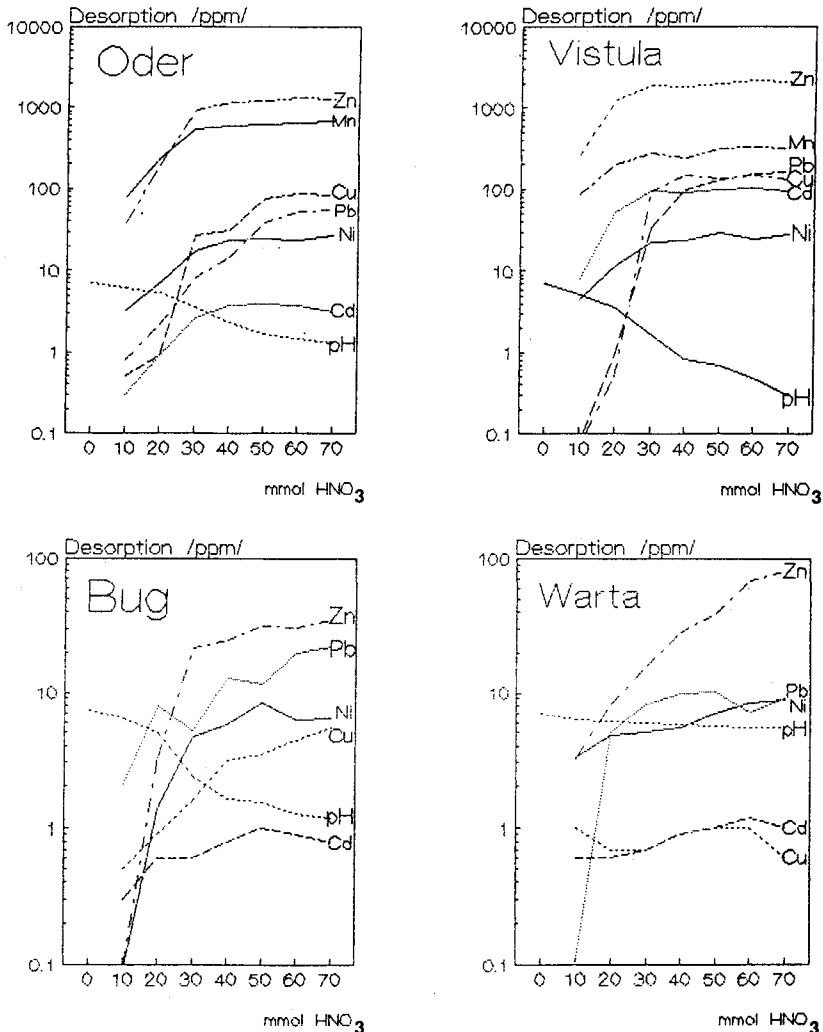


Fig. 4: Mobility of heavy metals from river sediments by lowering of pH after additions of nitric acid.

The bottom sediments of the examined rivers are polluted to different degrees. The most polluted ones are the sediments of the Vistula and the Oder, to a less extent those of the Warta and Bug.

For most metals the highest mobility is observed at the additions of 10 and 20 mmol of the acid. With greater acid additions the differences between the amounts of metals passing into solution are smaller.

Except for zinc very low mobility of metals has been observed in the sediment from the Warta river. With increasing amount of acid added this sediment shows small changes of pH within the range 6.9-5.4. In case of the other river sediments the pH changes are similar, but they are considerably greater and fall within the limits: Vistula: 7.1-0.4; the Oder: 7.1-1.3; the Bug: 7.3-1.2

With regard to the mobility of metals, the buffer capacity of the sediments and typical soils is of prime importance. According to the method of FÖRSTNER et al. (1986), titration experiments, applying different concentrations of nitric acid, were performed on 10 per cent suspensions of typical clays and bottom sediments of four rivers (Fig. 5).

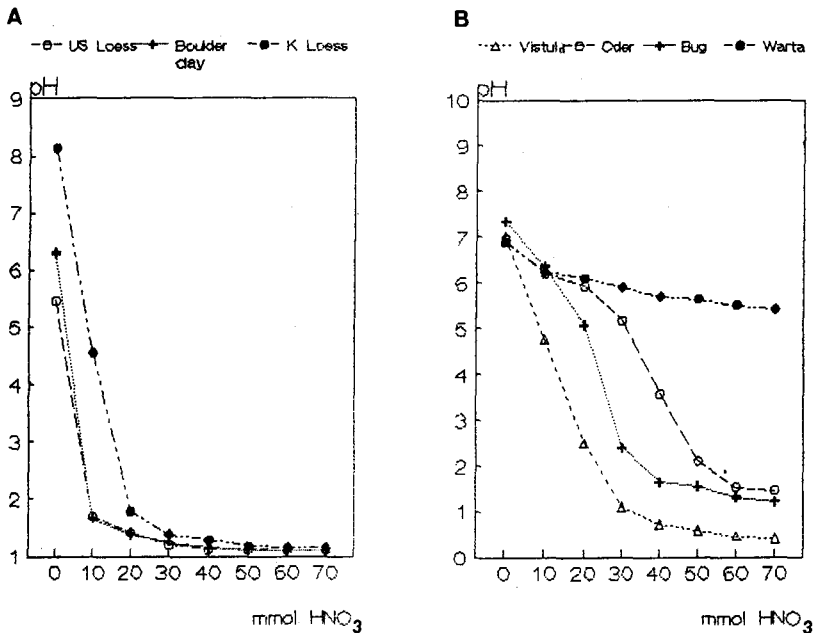


Fig. 5: pH changes of 10 per cent suspensions of clay soils (A) and river sediments (B) from additions of nitric acid in different concentrations.

The examined clay soils exhibited poor buffer capacities. The behaviour of the buffer curves for the loess sample US and for boulder clay is almost identical; an addition of 10 mmol of acid causes a decrease in pH to less than 2. Better buffer capacity is exhibited by loess sample K (from the Krakow region). This loess contains a small amount of calcite, hence high pH value of the water suspension; with an addition of 10 mmol of acid the pH value drops to 4.6 (Fig. 5A).

The considerably greater differentiation in the buffer capacity is shown by bottom sediments of the examined rivers. An addition of 10 mmol of acid brings a decrease of pH only by about one unit in the sediment suspensions from the Oder, the Warta and the Bug; hence these sediments can be regarded as good buffers (Fig. 5B). In the sediments suspension from the Warta river, over the entire range of acid additions, pH changes from 6.9 to 5.4. The bottom sediments from the Vistula river belong to medium buffers, as an addition of 10 mmol of acid causes a drop of pH by more than 2 units. It should be noted here that the applied concentration of the acid was rather high, hence in case of Vistula river sediment as well as loess from Krakow region the decrease in pH was considerable, in spite of the fact that calcite was found in the samples.

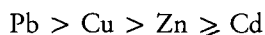
### Sorption/desorption of heavy metals by clays and clay minerals

The sorption of copper, lead, zinc and cadmium was performed on the following clay minerals (fraction  $< 2\mu\text{m}$ ): illite Montana, smectite/illite Konin (Poland), montmorillonite Chmielnik (Poland) and beidellite (South Africa).

The particular metals were sorbed at various initial concentration of the solutions: 0.5, 1, 5, 10 and 20 ppm. The samples of the clay suspensions of a concentration 10 g/l with the additions of metals (pH 6) were shaken for 12 h, then the solution was separated from the sediment through centrifugation. The amount of metal in the equilibrium solution was determined.

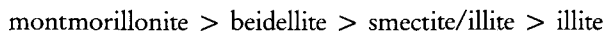
Loess and boulder clay from region of Upper Silesia were selected as typical soils. 10 ml of a metal solution with the initial concentration of 1, 10, 20 and 50 ppm was added to a 4 g sample.

From the sorption curves shown in Fig. 6 it can be seen that the greatest amount sorbed was that of lead, and the smallest — that of cadmium. Sorption decreases in the following order:



It depends also on the clay mineral. At the maximal initial concentration (50 ppm of the metal), the greatest amount of lead — 1765 ppm (88 per cent) is sorbed on illite, that of copper — 1475 ppm (74 per cent) — on smectite/illite, that of cadmium — 1215 ppm (61 per cent) and zinc — 1345 ppm (67 per cent) on montmorillonite.

Except for lead the highest sorption is observed for smectites. For cadmium and zinc sorption decreases in the order:



The differences in the amount of the sorbed metals between smectites and illite are very distinct for Zn and Cd, less distinct for Cu. The sorption of Cd and Zn on illite increases with increasing concentration of the metals in the solution only up to 20 ppm. Increased sorption in the whole range of the used concentrations of the metals was observed for Cu and Pb.

Metals were sorbed, moreover, on monoionic forms of montmorillonite with the Na, K, Ca and Zn cations. As it is seen in Fig. 7 sorption decreases in the following sequence:





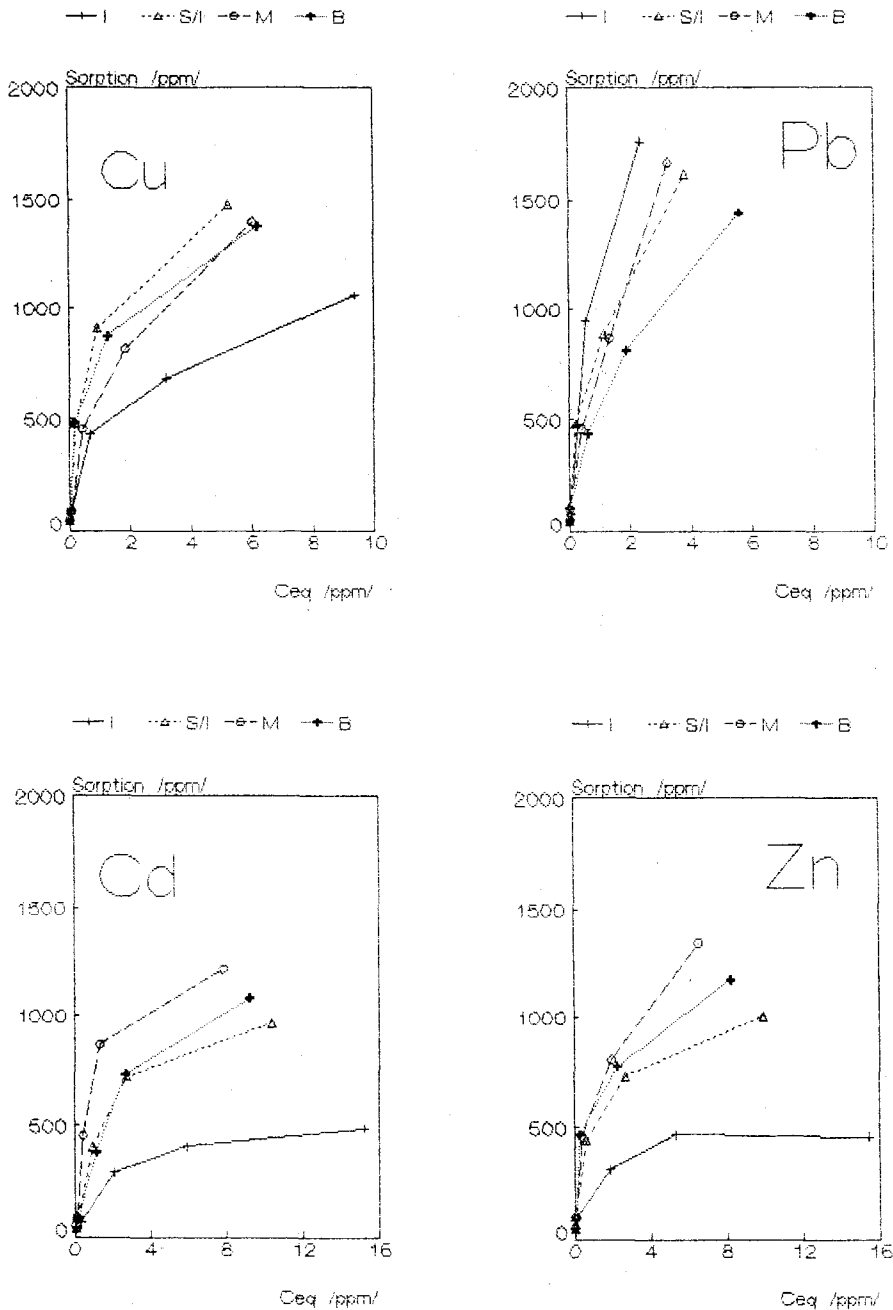


Fig. 6: Sorption of copper, lead, cadmium and zinc on clay minerals: Illite — I, Smectite/Illite — S/I, Montmorillonite — M and Beidellite — B.

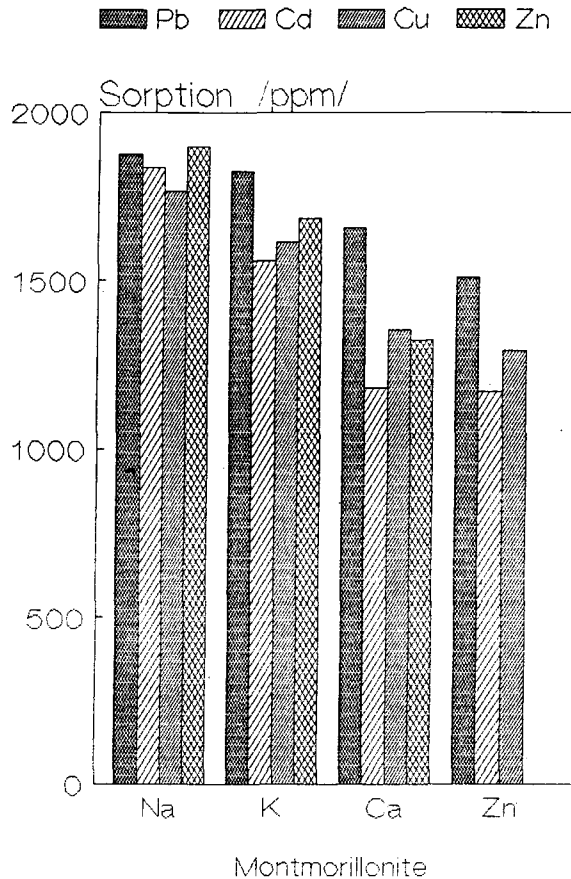


Fig. 7: Sorption of copper and zinc on monoionic (Na, K, Ca, Zn) forms of montmorillonite. Initial concentrations of metals: 20 ppm.

Differences between the metals were also observed. Lead was almost always sorbed in the greatest amounts. Zinc is also sorbed in greater quantities. Except for Na-montmorillonite cadmium is sorbed in the smallest amounts.

The metals were sorbed also on typical soils: loess and boulder clay. The obtained results of the sorption of cadmium and copper are shown in Fig. 8. In general, copper is sorbed more readily than cadmium, and in a greater extent by the boulder clay. With maximal concentration in the initial solution (50 ppm) boulder clay sorbs 360 ppm (72 per cent) of Cu and 195 ppm (39 per cent) of Cd, and loess — 300 ppm (60 per cent) of Cu and 130 ppm (26 per cent) of Cd, respectively. By the loess and boulder clay samples zinc and lead were sorbed in amounts greater than 95 per cent.

The metal sorption was carried out also on a loess sample K — contains calcite, hence it shows good buffering properties. After addition of the metals to the suspensions their sorption and precipitation occur simultaneously, thus in equilibrium solutions a very small amount or complete absence of these metals is observed.

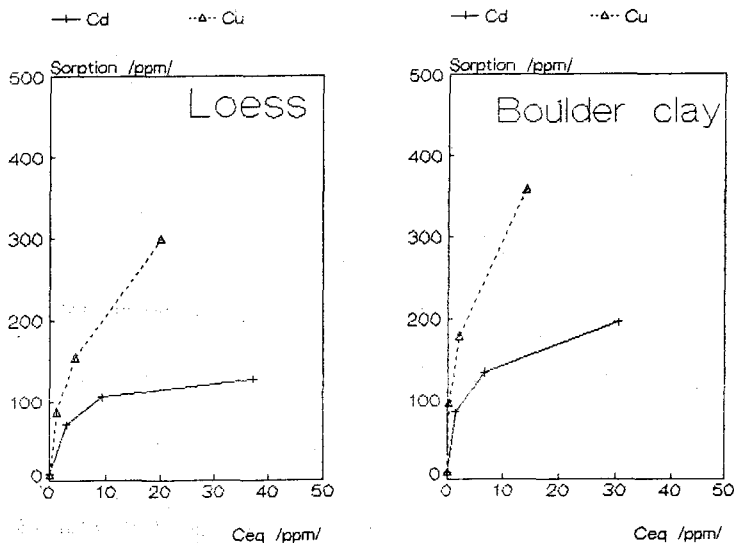


Fig. 8: Sorption of cadmium and copper on loess and boulder clay.

Desorption of metals from clay minerals was performed with 1N ammonium acetate, pH 7, solid/solution ratio = 1:100 and the shaking time 2 h. The obtained results are shown in Fig. 9 and Table 2. The highest exchange capacity is shown by cadmium and zinc from illite, lead from beidellite, copper from montmorillonite. After desorption of metals with ammonium acetate a considerable amount of copper and lead is bound with the particles of clay minerals. The capability of the clay minerals for exchange of Cd and Pb ions decreases in the sequence:

Montmorillonite > beidellite > smectite/illite > illite

Table 2: Sorbed and desorbed (1N  $\text{CH}_3\text{COONH}_4$ ) amount (ppm) of metals by clay minerals. Initial concentration: 20ppm. S-Sorption; D-Desorption.

Minerals	Cd		Zn		Cu		Pb	
	S	D (%)	S	D (%)	S	D (%)	S	D (%)
Montmorillonite	1216	1043 (86)	1346	1067 (79)	1399	1136 (81)	1675	1231 (73)
Beidellite	1080	919 (85)	1178	841 (71)	1380	927 (67)	1443	1266 (87)
Smectite/Illite	966	792 (82)	1007	819 (81)	1476	1154 (78)	1619	1258 (77)
Illite	488	386 (79)	458	424 (92)	1063	606 (57)	1765	1308 (74)

The desorption — with ammonium acetate — of cadmium and lead adsorbed on the grains of loess and boulder clay has shown that in case of loess 50 per cent of cadmium and in case of boulder clay 47 per cent of that element is bound in cation exchangeable sites, whereas the desorption of lead resulting from ionic exchange is only 8 per cent in loess and 6 per cent in boulder clay.

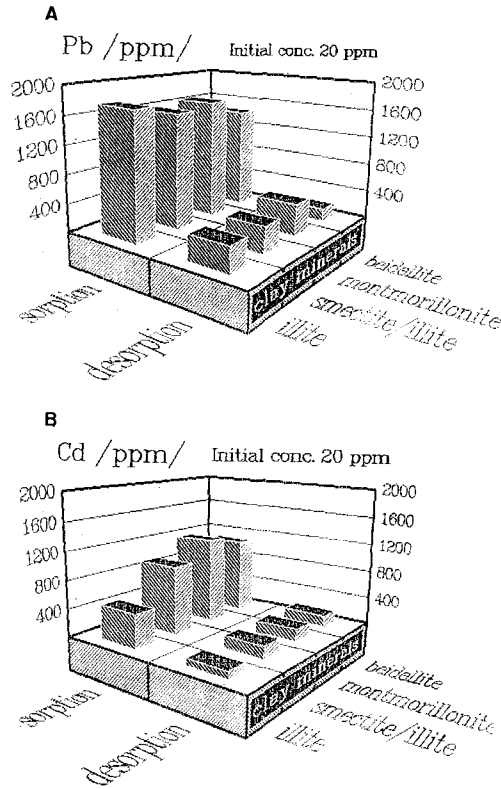


Fig. 9: Sorbed and bound (after desorption) on clay minerals amount of lead (A) and cadmium (B).

### Conclusions

The clay fraction of contaminated river sediments and soils is to a considerable extent enriched with heavy metals. Increased amounts of ion-exchangeable metals such as Zn and Cd are especially noticeable. Hence it can be concluded that these metals form the sorption complex of the clay minerals.

The heavy metals are mainly associated with the Fe-Mn-hydroxides and carbonates. Clay minerals are the important carrier of metals. The amount of metals found in the silicate phase varies and it depends mainly on the degree of contamination, type of the sediment as well as on the metals.

The phase specific bonding forms of metals in the soils are more stable. As it seems, in comparison with the bottom sediments, the soil particles remain in a more quiet and longer

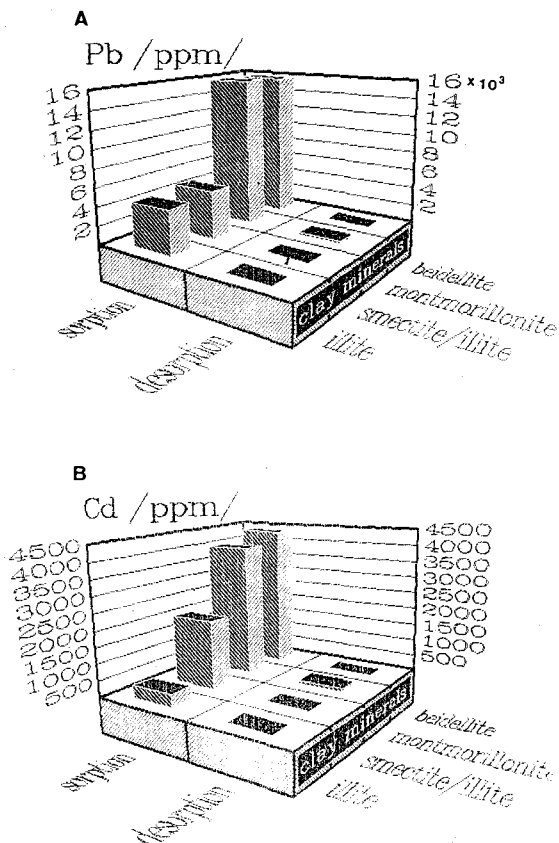


Fig. 10: Sorbed and bound (after desorption — by pH 1) on clay minerals amount of lead (A) and cadmium (B); the data from the sorption/desorption experiments in the “Multichamber Device” (HELIOS-RYBICKA & CALMANO, 1989).

contact with heavy metals in relatively stable environmental conditions (pH, Eh and others). The heavy metal ions may undergo fixation in the interlayer spaces or with time those possessing appropriate ionic radius may become incorporated into the octahedral layer of clay minerals (HELIOS-RYBICKA & FÖRSTNER 1986).

The clay and river sediments containing carbonates show good buffering properties, acting as effective scavengers. Such sediments and soils as a result of their acidification release relatively small amounts of metals.

The sorption “batch” experiments indicated that smectites sorbed a higher than illite amount of metals; the greatest amounts of lead and the smallest of cadmium. In smectites the amount of sorbed metals depends on the type of cation in the interlayer spaces. Na-smectite sorb more metals than the Ca-smectite.

Loess soils, in particular boulder clay, also sorb relatively great amounts of heavy metals. In soils containing calcite, as a result of their buffering activity both sorption and precipitation take place.

The adsorbed metals were desorbed with ammonium acetate, i. e. as a result of ionic exchange. The amount of desorbed metals is high, especially in case of cadmium.

A considerable smaller percentage of metals is desorbed from loess and boulder clay; about 50 per cent of cadmium, and only up to 8 per cent of lead.

Worth noticing in comparison with other metals is a high sorption of lead on illite particles, while this metal is desorbed from illite in smaller amounts than when desorbed from smectites.  $Pb^{2+}$  ion has a great ionic radius — 1.32 Å, similar to that of the  $K^+$  ion — 1.33 Å. The lead ions occupy the positions of potassium in the interlayer spaces of illite easier than other metal ions and similarly to  $K^+$  ions are more strongly bound and not so readily exchanged by  $NH_4^+$  ions.

These results confirm the experimental investigations of sorption and desorption of metals performed in a multichamber device (HELIOS-RYBICKA & CALMANO 1989). In this method the sorption of metals proceeds simultaneously of four clay minerals which compete with respect to the bound metals. Lead is sorbed in the greatest amounts (Fig. 10), but after desorption its amount bound with illite particles is relatively the highest.

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