Dynamics of Cu, Zn, Cd, and Hg release from sediments at surface conditions

Martin Komárek – Josef Zeman

Masaryk University, Brno, Faculty of Science, Institute of Geological Sciences, Kotlářská 2, 611 37 Brno, Czech Republic.
E-mail: komarek@zoner.cz, jzeman@sci.muni.cz

Abstract. Sediments and soils have a high capacity for binding heavy metals from contaminated waters. However, these sediments become a potential source of water contamination by subsequently releasing the metals into the water when environmental conditions change.
Samples of typical sediments from the Vienna Basin were collected for the experimental study of Cu, Cd, Zn, and Hg release from sediments to water. These sediments were characterized using chemical analysis, XRD analysis, the measurement of sediment sorption parameters, grain and pore analysis, and sequential analysis.
Initially, a set of sediment samples was placed into batch reactors, each containing 0.1 M solution of $CuSO_4$, $CdSO_4$, $ZnSO_4$, or $HgCl_2$, and kept there for two months. These artificially contaminated sediments were subsequently leached by distilled water in flow-through reactors.
Described experiments show that a significant proportion of the metal remains strongly bound to the sediment after the leaching process, suggesting that the reactions by which they are bound to the sediment are not completely reversed. The rate of metal release is significantly affected by sediment composition and bond type. Geochemical modeling and sequential analysis have confirmed that the metals are not only bound to sediments by sorption, but also by the precipitation of secondary minerals such as brochantite, tenorite (Cu^{2+}), hydrozincite (Zn^{2+}), and otavite (Cd^{2+}). Significant quantities of the metals are releasable from the sediments only in extreme conditions (Cd, Zn, and Cu in strongly acidic reducing conditions, and Hg in acidic oxidizing conditions). The presence of calcite in the sediment decreases the rate of Hg, Zn and Cu release through pH buffering by calcite dissolution (in solutions with pH values ranging from 7 to 7.5). Under these conditions the metals are not released, and can remain bound to the sediment.

Key words: flow-through reactors, sequential analysis, system sediment-water, interactions, geochemical modeling, dynamics of heavy metal release, calcite dissolution

Introduction

Heavy metals are released into water by natural processes and through human activities. The weathering of minerals containing these metals is the primary natural source. Metals are mainly bound in silicates such as feldspars and Fe-Mn micas by replacing Ca^{2+}, Fe^{2+}, and other cations in the structure of such minerals. They may also be released into the environment by the weathering of minerals in which they are a main compositional component, especially metallic sulphides. This process occurs in natural sulphide deposits even in the absence of mining (Alpers and Blowes 1994). Concentrations of heavy metals released into water by natural processes are usually low, approximately 10^{-7}–10^{-11} M (Stumm and Morgan 1996).

The input of heavy metals into the environment from human activity is often higher than that from nature (Nriagu 1990). Natural waters often become contaminated as a result of such activities. The burning of fossil fuels and the smelting of ores releases metals into the atmosphere, where they are removed by rain or dry deposition into surface waters. Metals are also released into surface and subsurface waters through mining activities, waste disposal, industrial effluent, and municipal sewage (Drever 1997).

Increased concentrations of some chemical forms of released metals in groundwater, rivers, lakes, oceans, sediments and soils may become dangerous for organisms (Smith 1992). Biological availability depends on the speciation of a metal, which is affected by a wide range of environmental conditions such as pH, Eh, the presence of dissolved organic carbon, and the composition of the surrounding rocks or soils (Stumm and Morgan 1996).

Metal migration and speciation in natural waters is significantly affected by interactions between water and bedrock. It is through these reactions that metals may become bound to rocks or released into waters during weathering.

There are many ways by which metals may become bound in soils and sediments:

1. Through waters occupying the pore spaces of rocks. In such cases the metal is weakly bound and remains mobile.
2. At the exchange positions of clay minerals (Pacáková et al. 2000).
3. By complexing with organic materials (Tipping and Hurley 1992).
4. By sorption and co-precipitation onto Fe-Mn oxyhydroxides (Stumm and Morgan 1996) and onto Al oxyhydroxides (Lee et al. 2002).
5. By adsorption and coprecipitation onto the surfaces of other minerals, such as carbonates (Tesoriero and Pankow 1996).
6. By precipitation of their secondary minerals, especially carbonates, sulphates, and oxides.
7. By the substitution of other cations at tetrahedral and octahedral positions in the structure of clay minerals (Nagy et al. 1999).
8. By the settling of weathered rock particles consisting of primary minerals such as feldspars, micas, quartz, and other silicates. Metals are often bound in tetrahedral and octahedral sites in the structures of these minerals.

Sediments and soils that contain substantial proportions of clay minerals, Fe, Mn, and Al oxyhydroxides, organic matter and other reactive substances, play an important part in these processes (Veselý 1995). Additionally, reactions between water and sediments are environmentally important because they occur in the reservoirs of drinking water. Contaminated sediments become a potential source of pollution: when conditions in the system change, metals may be released from sediments into natural waters.

Materials and procedures

Two samples of typical sediments of varying porosity and composition were collected from the Vienna Basin (Table 1). These sediments were characterized using XRD, petrographical analysis, complete chemical analyses (including minor compounds, heavy metals, and organic compounds), and grain and pore size analyses at the Brno branch of the Czech Geological Survey and at the Institute of Geological Sciences, Masaryk University Brno. The chemical analysis methods we used are listed in Table 2.

The mineralogical composition of crystalline fraction of the sediments was quantitatively determined by diffraction analysis developed on the STOE diffractometer by transmission with a Ge monochromator and a Cu anticathode (in latitude 2 theta = 10–90 with step 0.01). These sorption parameters of sediments were measured: exchangeable H, hydrolytic acidity, the capacity of exchangeable bases, maximum sorption capacity, and the degree of sorption saturation. These parameters were measured by the Mehlich method for sediments containing carbonates, and by the Kappen method for sediments without carbonates.

The laboratory simulation of the release of heavy metals from sediment consists of two parts:

1. The artificially contaminated sediments. 100 g of sediment was placed into a glass column. Four columns of each of the two sediments were prepared, for a total of eight columns. 100 ml of distilled water was added to each column, and the mixtures were regularly stirred twice daily. The solutions were drained from the columns after seven days. A 0.1 M solution of the selected metal was then added by use of the following salts: $3CdSO_4 . 8H_2O$, $ZnSO_4 . 7H_2O$, $HgCl_2$, or $CuSO_4 . 5H_2O$. Thus, one column of each sediment was devoted to an individual metal. The mixtures were stirred regularly during the following two months. Samples of the solutions were taken on the 60th day of the experiment for the determination of pH, Eh, and metal concentration.

2. These same sediment samples (100 g) were then placed in flow-through reactors (Fig. 1) and leached by distilled water. The reactors were made from laboratory glass; the columns were 35 cm high, with an internal diameter of 2.5 cm. The height of the sediment layer in the reactors was approximately 25 cm. On the 28th day of leaching the input solutions were acidified with H_2SO_4 to pH 4–4.5. Metal concentration, pH, and Eh were measured in the input and output solutions. Eh and pH were measured by the Hanna 8314 membrane mV-pH meter, using combined platinum and glass electrodes (the reference electrode was a Ag/AgCl electrode). The glass electrode was calibrated in buffers of pH 7 and 10 (from the company Russell) before every measurement. The platinum electrode was calibrated in a Zo-Bell's solution (Nordstrom 1977). Cu, Zn, Cd, and Hg concentrations were determined by the ICP method. After the experiment 10 g of sediment were removed from the upper part of the columns for sequential sediment analysis. This method is based on the sequential dissolution of sediments in the following five steps (Tessier et al. 1979, Clevenger 1990):

I. Exchangeable metals: 2 g of sample were treated with 20 ml 1M CH_3COONa (pH = 8.2). Metals bound by sorption are released during this step.

II. Metals bound in carbonates: the residuum from step I was leached in a CH_3COONa solution with pH = 5 (the pH was set by adding CH_3COOH). This releases metals bound in carbonates.

III. Metals bound by Fe-Mn oxyhydroxides: the residuum from step II was treated with 20 ml of 0.04 M $NH_2OH.HCl$ in 25% CH_3COOH (T = 96 °C). Metals that co-precipitate with Fe-Mn oxyhydroxides are released during this step.

IV. Metals bound by organic matter: the residuum from step III was leached in 3 ml of 0.02M HNO_3 + 5 ml 30% H_2O_2 (pH = 2, T = 85°C) for two hours. 3 ml of 30% H_2O_2 (pH = 2) was then added, and the sediment was leached for an additional three hours. After cooling, 5 ml of 3.2 M CH_3COONH_4 (in 20% HNO_3) was added

Table 1. Locality, age, and petrographical classification of the sediments

Locality	Age	Petrographic classification
Hevlín	Eggenburgian	Sandy silt to siltstone
Staré Město	Pannonian	Sandy silt to siltstone

Table 2. Analytical methods used for the determination of sediment composition

Component	Analytical technique
H_2O^-	drying at 110 °C
H_2O^+	penfield method
Si, S	gravimetry
Ti, Fe^{3+}, P	photometry
Al, Ca, Mg	titration with complexone III
Fe^{2+}	titration with $K_2Cr_2O_7$
Mn	atomic absorption spectrometry (AAS)
K, Na, Li	flame photometry
CO_2	absorption
Cu, Ni, Zn, Hg	ICP
Organic carbon, non sulphate sulphur	eltra Analyzer

Table 3. The silicate analysis of the sediments, the mineralogical composition of their crystalline fraction determined by XRD, and the open porosity and maximum sorption capacities of the sediments

Locality	Hevlín	Staré Město
Mineral (wt%)		
Quartz	75.7	96.5
Illite-montmorillonite	1.8	1.7
Calcite	8.0	0.0
Halloysite	2.8	1.8
Albite	11.6	0.0
Component (wt%)		
H_2O^-	0.93	3.05
H_2O^+	2.72	3.54
SiO_2	59.48	73.31
TiO_2	0.53	0.63
Al_2O_3	11,25	11,1
Fe_2O_3	1.73	2.52
MnO	0.05	0.01
CaO	6.48	0.62
MgO	3.18	0.88
K_2O	2.36	2.76
Na_2O	1.42	0.16
S	0.17	0.00
CO_2	6.41	0.00
P_2O_5	0.17	0.07
Organic carbon	0.49	0.08
Total	99.83	99.86
Maximum sorption capacity (mval/100 g)	19.1	10.44
Open porosity (%)	24.90	20.85

to the solution, diluted to 20 ml, and stirred for 15 minutes. Metal mainly bound by organic matter is released during this step.

V. Metals bound in silicates: The residuum from step IV was dissolved in a HF-$HClO_4$ mixture, causing the release of metals bound in the tetrahedral and octahedral positions in silicates.

The extracted solutions were centrifuged. The concentrations of metals were determined by ICP.

Results and discussion

Characterization of the sediments

The XRD analysis (see Table 3) determined that the predominant mineral of the crystalline fraction of the sediments is quartz (75.7% in the Hevlín sediment, and 96.5% in the Staré Město sediment). The proportions of clay minerals in the crystalline fraction of these sediments are low (to 4.6%). Albite (11.6%) and calcite (8%) were found to be abundant components in the Hevlín sample, but were not identified in the Staré Město sample. The absence of calcite in the latter sample is consistent with its chemical analysis, in which the content of CO_2 was below the detection limit.
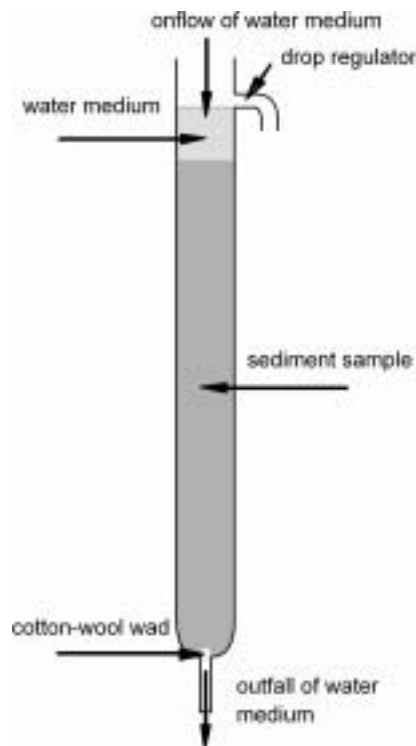

Figure 1. Schematic diagram of the flow-through reactors. The solution in these reactors flows through the sediment column only once (Zeman et al. 1997).

By comparing the chemical analysis (see Table 3) to the mineral composition in the Staré Město sediment, we found that much of the Al^{3+}, Fe^{3+} and other components are bound in non-identified substances: presumably in weakly crystalline and amorphous minerals (primarily Fe-Al-Si oxyhydroxides), which cannot be determined by XRD. The proportion of these components is important because of their high sorption capacity. The sorption potentials of the sediments were characterized by maximum sorption capacities T_m (see Table 3). The T_m values of these sediments are high, varying from 10.44 mval/100 cm^3 (Staré Město) to 19.1 mval/100 cm^3 (Hevlín).

The preparation of contaminated sediment samples in batch reactors

First, the sediment samples were enriched with Cu, Zn, Hg and Cd in batch reactors. These processes correspond to the contamination of sediment deposits as it occurs in tailing piles and sludge beds (Zeman et al. 1997).

The total amounts of metals in the sediment samples are calculated using the concentrations of metals in solutions measured after a two-month experimental run. This calculation uses the following relation:

$$n(Me^{2+})_{sed} = V_{solution} \, [c_{input} \, (Me^{2+}) - c_{output} \, (Me^{2+})],$$

where $n(Me^{2+})_{sed}$ is the amount of metal bound to the sediment (mol), $V_{solution}$ is the volume of the reaction medium (100 ml), and c_{input} and c_{output} are the initial and final concentrations of metal in the solution. In the Hevlín sample most of the Cu, Zn, and Hg passed into the sediment, and
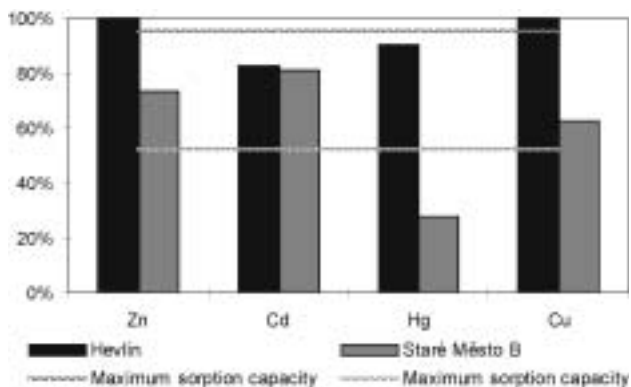
101

Figure 2. Percentage of metals bound in the sediment from 0.1 M Me^{2+} solutions in batch reactors, compared to the maximum sorption capacities of the sediments.
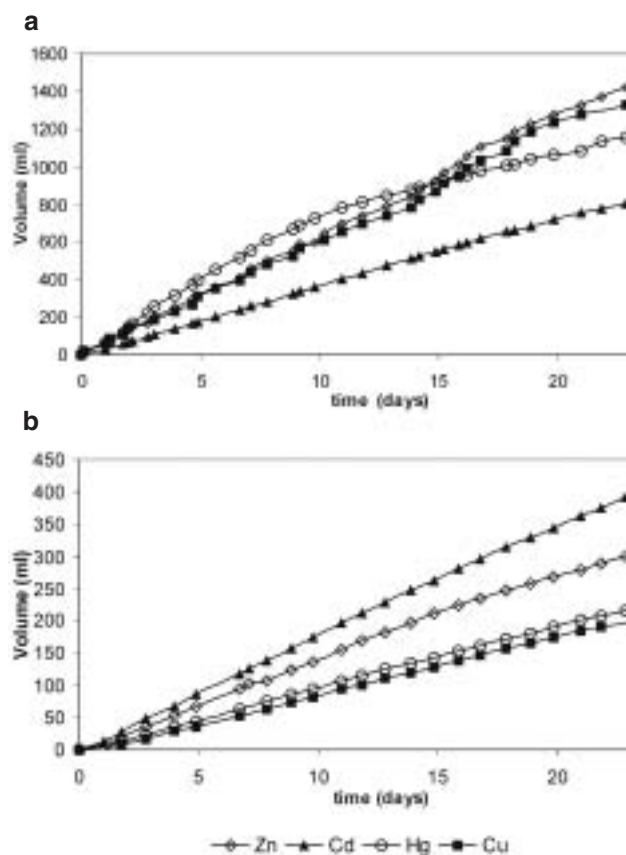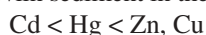

Figure 3. Total volume of distilled water that filtered through the contaminated sediments during the leaching process. a – Hevlín, b – Staré Město.
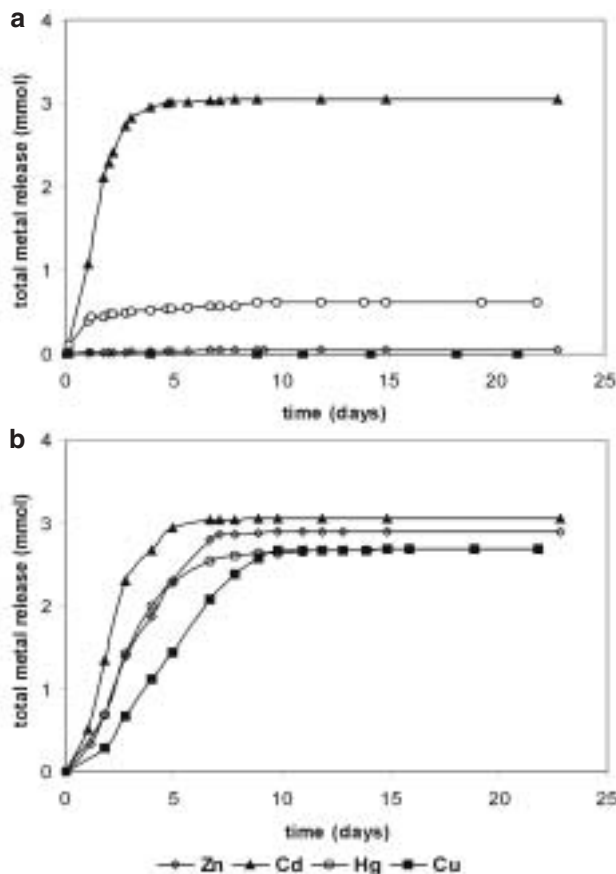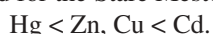

Figure 4. Total amounts of the metals (mmol) released from the sediments during the leaching process. a – Hevlín, b – Staré Město.

The leaching of sediments with distilled water

The rate of water infiltration through sediments depends not only on porosity and on the bonding properties of the specific metal involved. The following order of permeability was found for the Hevlín sediment:

Cd < Hg < Zn, Cu (Fig. 3a).
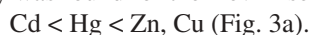
The average permeability of the Hevlín sediment ranges from 35.5 to 58.8 ml/day. The Staré Město sediment samples were found to be permeable to the metal-carrying solutions in the following order:

Cu < Hg < Zn < Cd (Fig. 3b).
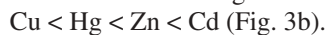
The average permeability of the Staré Město sediment ranges from 8.5 to 17.1 ml/day. In the Hevlín sediment samples, the sequence of metal permeability corresponds to the amounts of each metal bound within the sediment. Interactions at the interface between solid surfaces and solutions affect sediment permeability.

The rates by which the metals were released from the sediment samples also varied. The highest concentrations of metals in the output solutions were found in those sampled during the first days of the experiments (see Fig. 4), which decreased during subsequent leaching. This trend was not affected by acidifying the input solutions to pH ~ 4 from the 28th day of the experiments. The concentrations of metals in the earlier output solutions from the Staré Město samples ranged from 0.03 to 0.05 mol/L, which decreased

thus the concentrations of the metals in the resulting solutions were very low (from 0.5 μmol/L of Cu to 1 mmol/L Hg). The amount of Cd bound in this sediment was lower (about 80%), and this value is comparable with that of the Staré Město sample. The amounts of metals caught in the Staré Město sediment were significantly lower, with values ranging from 21% Hg to 80% Cd (see Fig. 2). The amounts of Zn and Cu caught by these sediments exceed their maximum sorption capacities (T$_{max}$). Metals were found to bind to the Hevlín sediment in the following order:

Cd < Hg < Zn, Cu

and for the Staré Město sediments:
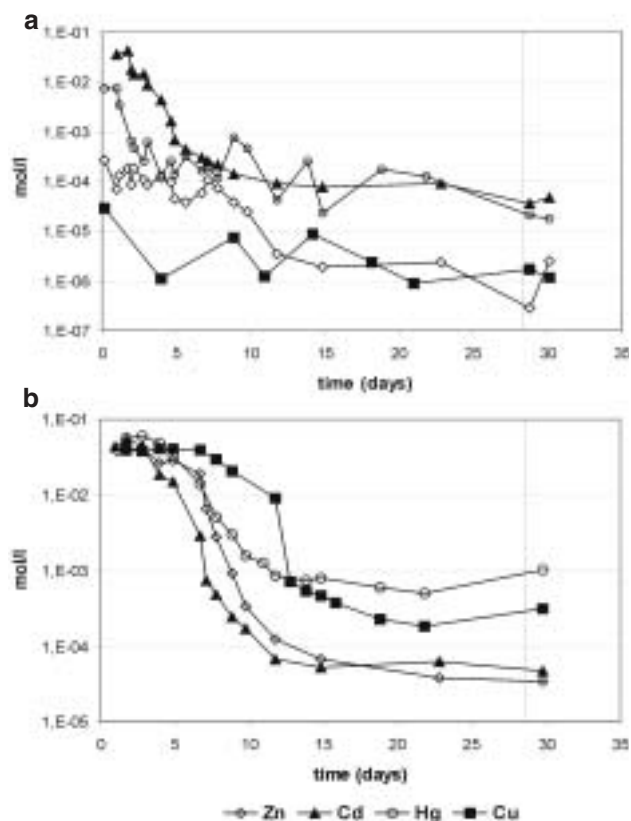
Hg < Zn, Cu < Cd.

Figure 5. Evolution of metal concentrations in the output solutions sampled during the leaching process. The dashed line marks the beginning of leaching by distilled water acidified by H_2SO_4 to pH ~ 4.5. a – Hevlín, b – Staré Město.
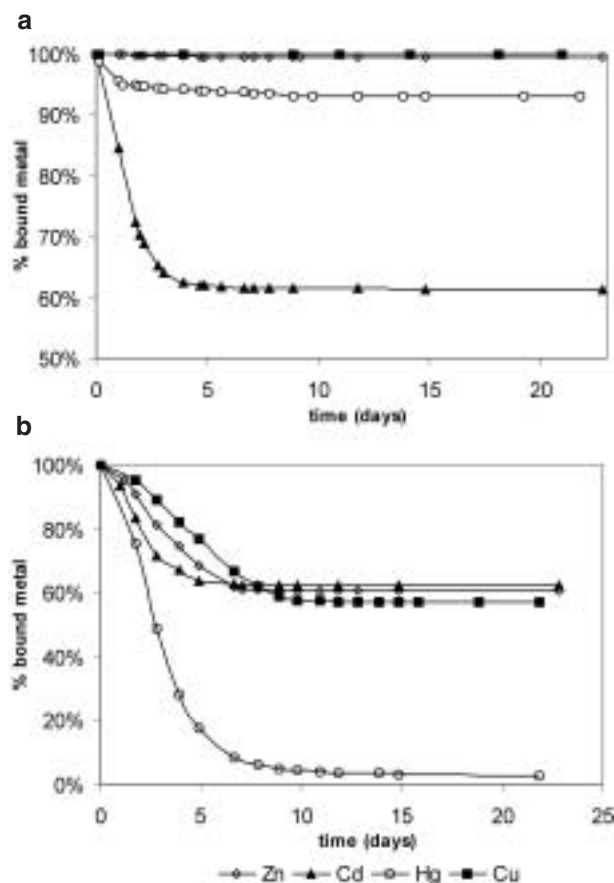

Figure 6. Release of metals during the leaching process: percent of decrease of metal contents in the sediments from the original pre-leaching concentrations. a – Hevlín, b – Staré Město.

to 0.05–0.98 mmol/L during further leaching. The tested metals were found to be released during leaching in the following relative proportions (Fig. 4b):

Hg, Cu < Zn < Cd.

The concentrations of metals in the output solutions from the Hevlín sediments at the beginning of the experiment also differed significantly from those sampled later. Concentrations in the earlier solutions ranged from 0.28 mmol/L to 36 mmol/L, after which they decreased to 1.2–50 μmol/L. The metals were found to be released from the Hevlín sediments in the following relative proportions (Fig. 4a):

Cu, Zn < Hg < Cd.

The above sequences might appear to be in conflict with the metal concentrations of the output solutions (see Fig. 5). However, the degree to which the metals are released depends not only on their concentration in the solution, but also on sediment permeability. The absolute rate of metal release from sediment is the result of chemical and physical interactions in the sediment/water system.

After leaching, about 90% of the Cu, Zn, and Hg, and approximately 60% of the Cd, remained bound within the Hevlín sediment. This latter value also corresponds to the proportion of Cd, Zn, and Cu that remained bound in the Staré Město samples. Only an insignificant amount of Hg remained bound in the Staré Město sediments, while about 98% was released into the output water (Fig. 6). The be-

haviour of these systems suggests that metals become bound to sediments in various ways. The nature of these bonds can be described by thermodynamic modeling and sequential analysis.

Cadmium

The behaviour of Cd was found to be fairly uniform during the leaching experiments of both sediment samples. The output concentrations of Cd^{2+} were relatively high during the first few days of leaching (from 36 to 43 mmol/L Cd^{2+}). Lower pH values (from 3.16 to 3.65) were caused by the complexation of Cd^{2+} in the solutions. Diagrams showing pH - $a(Cd^{2+})$, calculated using the Geochemist WorkBench software (Bethke 1996), suggest that the system gradually tends toward equilibrium with the mineral otavite, $CdCO_3$ (Fig.7). The rate of release decreased during leaching, with Cd^{2+} concentrations in the output solutions dropping to below 0.1 mmol/L. When Cd^{2+} concentrations decreased, the pH increased to around 7. Acidifying the samples from the 28th day of the experiment did not affect this trend. About 60% of the Cd^{2+} remained bound in the sediments after the experiments. Sequential analysis (Fig. 8) has shown that a significant proportion of the Cd^{2+} (about 37% in the Staré Město sample, and about 82% in the Hevlín sample) is re-
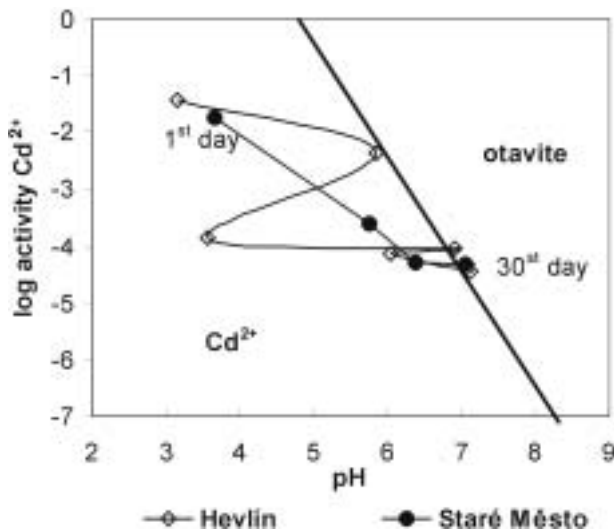
103

Figure 7. Evolution of the systems in a pH – $a(Cd^{2+})$ diagram. Model conditions: $a(SO_4^{2-}) = 0.001$, $Eh = 0.5$ V, partial pressure of $CO_2 = 10^{-3.5}$ (equilibrium with atmospheric CO_2).
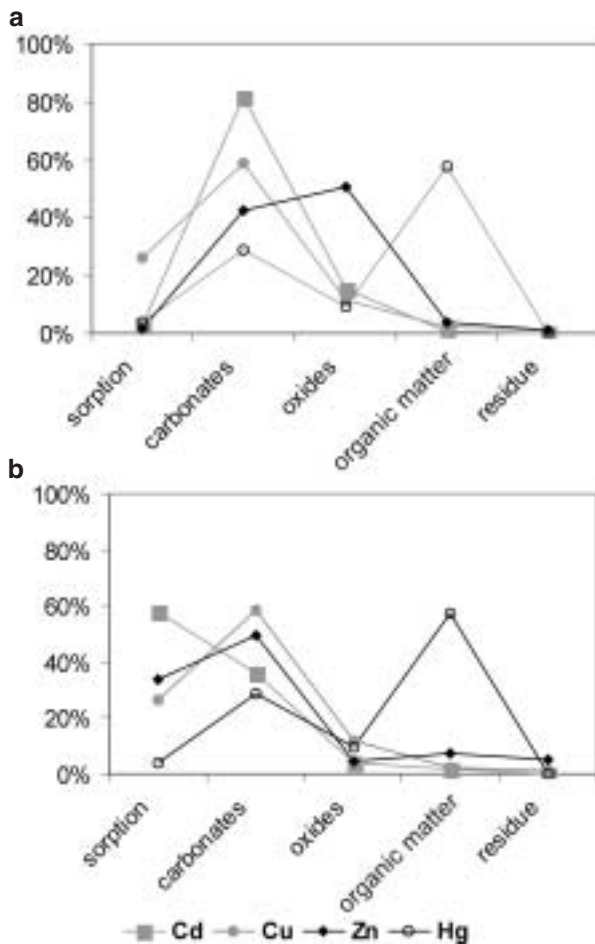

Figure 8. Sequential analysis of the sediment samples after the leaching experiment. a – Hevlín, b – Staré Město.

leasable in step II (leaching in a solution of pH ~ 5). About 58% of the Cd^{2+} in the Staré Město sample was released in step I (leaching in a solution of pH ~ 8.2), although such a proportion was not released by the infiltration of distilled water through the sediment column. This discrepancy may

be explained by the re-binding of released Cd^{2+} to the sediment by sorption. This effect was not observed in the Hevlín sediment. The differences in the behaviour of the sediments may be caused by variable permissivity, as the reaction time in the Staré Město sediment is higher than that of Hevlín. In the Hevlín sediment about 17 % of Cd^{2+} was found in the oxide phase (leaching in pH ~ 2). This fraction would not be released under normal environmental conditions.

Copper

The geochemical modeling of processes by pH – $a(Cu^{2+})$ diagrams, calculated using the Geochemist WorkBench software (Bethke 1996), suggests that the variable behaviour of this metal depends on sediment composition. Cu remained strongly bound during the leaching of the Hevlín sediment. Cu^{2+} concentrations in the output solutions ranged from 28 μmol/L to 1.1 μmol/L. The pH values of these solutions were high (7–7.5) and did not change significantly during the experiment. This system seems to be buffered by calcite dissolution, and the Cu is bound in forms that are not released from the sediment under such conditions. This model has been confirmed by sequential analysis (Fig. 8), as 60% of the Cu was released in step II (pH ~ 5), while only 30% was released during step III (pH ~ 2). About 40% of the Cu^{2+} was released during the leaching of the Staré Město sample. Cu concentrations in the output solutions from this sediment ranged from 38 mmol/L at the beginning of leaching to 0.1 mmol/L at end of the experiment. The lower pH values from the first stage of the experiment (~ 3.85) were due to copper complexation. The evolution of the system in the pH – $a(Cu^{2+})$ diagram shows that the Cu concentrations of the output solutions are controlled by equilibrium with secondary minerals such as brochantite or tenorite (Fig. 9). This was confirmed by the sequential analysis, in which 60% Cu^{2+} was released in step II (leaching at pH ~ 5). A significant part of the Cu^{2+} (about 23%) is released in step I of the sequential analysis (similar to Cd^{2+}), while 17% of the Cu^{2+} was released in step III (pH ~ 2). The proportions of metals released from the solid phase in step III of the sequential analysis are often ascribed to the formation of metallic bonds in Fe-Mn oxyhydroxides (Clevenger 1990). However, metals may also be bound to other substances (such as Al oxyhydroxides) that dissolve in strongly reducing acidic conditions. The contents of Fe(III) and Mn in these sediments are low (see Table 3). Thus, the Cu^{2+} is probably not bound only to Fe-Mn oxyhydroxides, but also to other substances that are unstable in strongly reducing acidic conditions. Cu^{2+} bound to such substances is not released under common environmental conditions.

Zinc

The behaviour of Zn was analogous to that of copper in the samples of both sediments. Zn concentrations in the

output solutions from the Hevlín sample were low from the beginning (0.26 mmol/L) and gradually decreased to 0.28 μmol/L. The pH of those solutions were higher (about 7–7.5), and did not change significantly during the experiment. The buffering of the output solutions was probably caused by calcite dissolution from the sediment. These solutions were undersaturated relative to known Zn minerals (Fig. 10). Sequential analysis (see Fig. 8) of the Hevlín sediment suggests that a major part of the Zn is released only during step III (about 55% Zn^{2+}), the rest (less than 50% Zn^{2+}) being released in step II (pH ~ 5). It is of interest that the behaviour of Zn^{2+} differs significantly from the geochemically similar element Cd. However, the system involving Cd did not become buffered by calcite dissolution as did the Zn system. As mentioned above, the carbonate equilibrium in the Cd system was influenced by the dissolution of otavite.

No significant variations were observed during Zn leaching from the Staré Město sample. The Zn concentrations in the output solutions were high (about 0.06 mol/L Zn^{2+}) during the first few days of the experiment. Lower pH values (about 3.5) were caused by Zn^{2+} complexation. The decrease of Zn^{2+} concentration (48.9 mmol/L) in the output solutions led to an increase in pH (to 7.03). The system tended towards equilibrium with hydrozincite. The sequential analysis of Zn^{2+} is analogous to that of Cu^{2+}: a significant part of the Zn (about 58%) was released in step II (pH ~ 5), with the rest being released in steps I (38%) and III (5%).

Mercury

The quantity of Hg bound in the sediment samples did not exceed the maximum sorption capacity of the sediment. The difficulty of obtaining thermodynamic data for mercury species and minerals complicated such attempts to model the compositions of the output solutions. The thermodynamic database of the Geochemist WorkBench software (Bethke 1996) was supplemented by thermodynamic data for Hg^{2+} hydroxocomplexes (Stumm and Morgan 1996). Diagrams of pH – $a(Hg^{2+})$ were calculated by the Geochemist WorkBench software in the following model conditions (Fig. 11): Eh = 0.5 V, $a(Cl^-)$ = 0.002, and partial pressure of CO_2 = $10^{-3.5}$ (equilibrium with atmospheric CO_2).

Only about 10% of the Hg was released during the leaching of the Hevlín sample, though almost 100% was released from the Staré Město sample. Sequential analysis shows that most of the Hg (about 60% in the Hevlín sample, and about 80% in the Staré Město sample) is released only during the oxidation of the sediment (step IV). The metal fractions released from the solid phase in this step are often ascribed to metal being bound to organic matter (Clevenger 1990) and in Fe-Mn rock forming minerals. The contents of organic carbon in the sediments are negligible (see Table 3); thus, the Hg^{2+} is not bound to organic matter, but to substances that are unstable in oxidizing
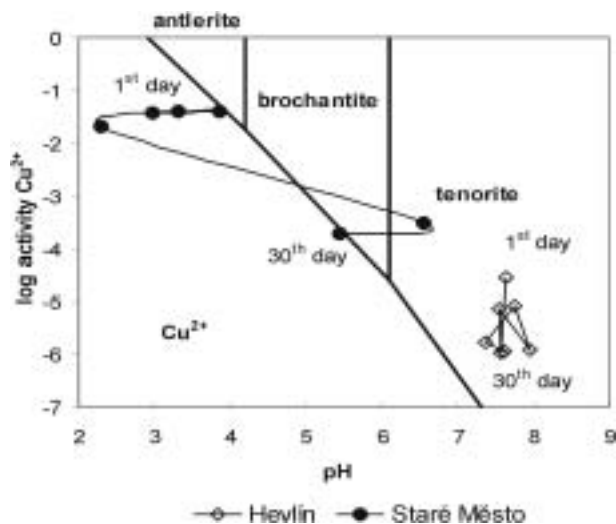

Figure 9. Evolution of the systems in a pH – $a(Cu^{2+})$ diagram. Model conditions: $a(SO_4^{2-})$ = 0.001, Eh = 0.5 V, partial pressure of CO_2 = $10^{-3.5}$ (equilibrium with atmospheric CO_2).

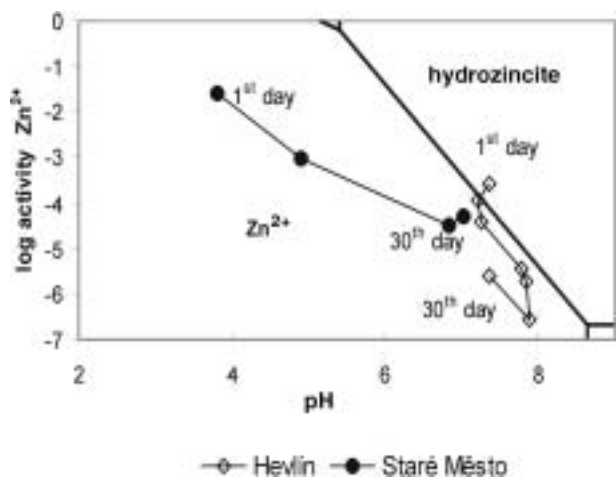
Figure 10. Evolution of the systems in a pH – $a(Zn^{2+})$ diagram. Model conditions: $a(SO_4^{2-})$ = 0.001, Eh = 0.5 V, partial pressure of CO_2 = $10^{-3.5}$ (equilibrium with atmospheric CO_2).
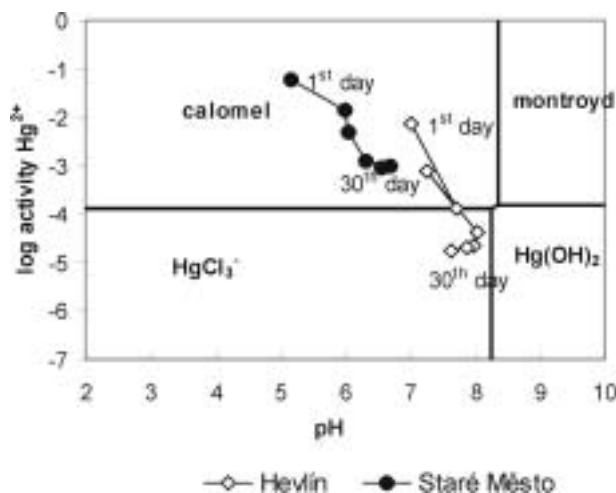

Figure 11. Evolution of the systems in a pH – $a(Hg^{2+})$ diagram. Model conditions: $a(Cl^-)$ = 0.002, Eh = 0.5 V, partial pressure of CO_2 = $10^{-3.5}$ (equilibrium with atmospheric CO_2).

acidic conditions (see Fig. 8). A smaller proportion was released in step II (about 25% in the Hevlín sediment, and about 5% in the Staré Město sediment).

In the pH – $a(Hg^{2+})$ diagram, the systems moved along a line in the stability field of calomel and $HgCl_3^-(aq)$. This line can mark the border between a Hg complex and a Hg mineral, which was not considered in the modeling of these systems.

Conclusions

Sediments and soils contaminated by heavy metals are potential sources of pollution for natural waters. The object of this experimental study was to determine the dynamics of metal release from sediment deposits. The sediment samples used in this study were artificially contaminated by Cu, Zn, Hg, and Cd in the laboratory, and subsequently placed in columns and leached by distilled water.

Our leaching experiments suggest that the reactions by which metals are bound to the sediment are not completely reversed, a significant proportion of the metals remaining in the sediment under normal environmental conditions. The distribution of metals between the sediment and infiltrating water is significantly affected by the sediment solution and by the type of metal involved. Interactions between the sediments and infiltrating water influence the permeability of the sediments: although considerable variability was found between sediment samples, binding of different metals, no dependence on metal concentration in the output solutions was found. Metal release was not affected by acidifying the input solutions to pH ~ 4– 4.5.

Sequential analysis and the geochemical modeling of these systems suggest that metals are bound in sediment by sorption, and by the precipitation of secondary minerals such as hydrozincite (Zn), tenorite or brochantite (Cu), and otavite (Cd). Significant proportions of the metals were released from the sediments only under extreme conditions (Cd, Zn, and Cu in strongly acidic reducing conditions; Hg, on the contrary, in acidic oxidizing conditions). The presence of calcite in the sediment decreases the rate by which Hg, Zn, and Cu are released from the sediment due to pH buffering by calcite dissolution (pH ranging from 7 to 7.5). The metals are not released under such conditions, and remain bound to the sediments.

References

Alpers C. N., Blowes D. W. (1994): Environmental geochemistry of sulphide oxidation. ACS Symposium Series 550. American Chemical Society, Washington DC.

Bethke M. C. (1996): Geochemical reaction modeling. Concepts and applications. Oxford University Press, New York.

Clevenger T. E. (1990): Use of sequential extraction to evaluate the heavy metals in mining wastes. Water, Air Soil Poll. 50, 241–254.

Drever J. I. (1997): The geochemistry of natural waters: surface and groundwater environments. 3rd ed. Prentice Hall. New Jersey.

Lee G., Bigham J. M., Faure G. (2002): Removal of trace metals by coprecipitation with Fe, Al and Mn from natural waters contaminated with acid mine drainage in the Ducktown Mining District, Tennessee. Appl. Geochem. 17, 5, 569–581.

Nagy K. L., Cygan R. T., Hanchar J. M., Sturchio N. C. (1999): Gibbsite growth kinetics on gibbsite, kaolinite and muscovite substrates. Atomic force microscopy evidence for epitaxy and an assessment of reactive surface area. Geochim. Cosmochim. Acta 63, 2337–2351.

Nordstrom D. K. (1977): Thermochemical redox equilibria of Zobell's solution. Geochim. Cosmochim. Acta 41, 1835–1841.

Nriagu J. O. (1990): Human influence on the global cycling of trace elements. Palaeogeogr. Palaeoclimatol. Palaeoecol. 82, 113–120.

Pacáková V., Pockevičiute D., Armalis S., Štulík K., Li J., Veselý J. (2000): A study of the distribution of lead, cadmium, and copper between water and kaolin, bentonite and a river sediment. J. Environ. Monit. 2, 187–191.

Smith R. P. (1992): A primer of environmental toxicology. Lea and Febiger, Philadelphia.

Stumm W., Morgan J. J. (1996): Aquatic chemistry. 3rd ed. Wiley, New York.

Tesoriero A. J., Pankow J. F. (1996): Solid solution partitioning of Sr^{2+}, Ba^{2+} and Cd^{2+} to Calcite. Geochim. Cosmochim. Acta 60, 6, 1053–1063.

Tessier A., Campbell P. G. C., Bisson M. (1979): Sequential extraction procedure for the speciation of particulate trace metals. Anal. Chem. 51, 844–850.

Tipping E., Hurley M. A. (1992): A unifying model of cation binding by humic substances. Geochim. Cosmochim. Acta 56, 3627–3641.

Veselý J. (1995): Drainage sediments in environmetal and explorative geochemistry. Bull. Czech Geol. Surv. 70, 3, 1–8.

Zeman J., Müller P., Komárek M. (1997): Dynamics of heavy metal exchange between sediment and water. Geol. Výzk. Mor. Slez. v Roce 1997, 125–128.