

HEAVY METAL RETARDATION IN SOME SLOVAK CLAYS AND CLAYEY SOILS

RENÁTA ADAMCOVÁ¹ and FRITZ T. MADSEN²

¹Department of Engineering Geology, Faculty of Sciences, Comenius University, Mlynská dolina G, 842 15 Bratislava, Slovak Republic

²Laboratory for Clay Mineralogy, Division of Geotechnical Engineering, Swiss Federal Institute of Technology, CH-8092 Zürich, Switzerland

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Abstract: The natural clayey ground below three old waste sites in the Slovak Republic was mineralogically, chemically and geotechnically investigated. Concentration profiles of both the heavy metal and chloride ions in the soil below the waste sites were established. From these, together with the knowledge about the age of the waste site, the migration velocity of the ions into the clay was estimated. For heavy metal ions the velocity is in the range of a few centimetres per ten years. The migration velocity of chloride ions is five to ten times larger. From all the calculated apparent diffusion coefficients, the values for zinc about $1.2 \times 10^{-11} \text{ m}^2/\text{s}$, for lead about $1 \times 10^{-11} \text{ m}^2/\text{s}$ and for chloride about $3 \times 10^{-10} \text{ m}^2/\text{s}$ seem to be the most realistic. With regard to the mineralogical composition, the most significant retardation processes were estimated. However, a sequence analysis indicated that sometimes the role of the ion exchange can be overestimated. The study also demonstrated the difficulties in gaining undisturbed samples of sufficient quality by drilling, as well as in the interpretation of the established concentration profiles.

Key words: clay and clayey soils, waste sites, heavy metal transport, field study, diffusion coefficient, retardation factor, adsorbents.

Introduction

Clays and clayey soils are often used as bottom liner material for waste sites because of their stability against chemical attack, their low hydraulic conductivity and their ability to adsorb organic and inorganic pollutants and thus protect the environment. The protection is, however, temporally limited. Even in compacted clays and clayey soils with a very low hydraulic conductivity some transport of contaminants will take place due to diffusion. The velocity of transport by diffusion is dependent on the mineralogical composition of the liner material, the content of organic matter, the porosity, the moisture content, pH of the pore water, the redox potential in the system etc. Some dissolved substances may diffuse through the clayey material without being adsorbed, whereas others are adsorbed at least for some time and thus retarded (Lu et al. 1985).

A simple mathematical modelling using the parameters of the adsorption capacity of the material, the apparent diffusion coefficient and the retardation factor, allows an approximate calculation of the barrier-thickness for a desired break-through time. These parameters are normally determined in laboratory tests of rather short duration. Several different laboratory methods have been developed

during the last 10 to 15 years (Wagner 1991, 1992). It is, however, questionable how well processes which in nature are going on for many years can be described by laboratory tests. A way of calibrating the laboratory tests results with findings from "in situ" field testing has therefore been desired.

Crooks & Quigley (1984), Quigley & Rowe (1986), and Wagner (1991, 1992) used old waste sites to study leachate migration through clays and to compare laboratory and field investigations. The investigations yield the calculation of the transport velocity of various chemical compounds from the waste into the clay below for a known age of the waste site. Careful sampling taken into account, the apparent diffusion coefficient and the retardation factor may be calculated.

During the present study the clayey layers beneath three old waste sites in the Slovak Republic have been investigated in a joint venture project between the Comenius University in Bratislava and the Swiss Federal Institute of Technology in Zürich. Drilling cores from different depths below the waste have been chemically analysed. Concentration profiles of different ions were used to calculate the apparent diffusion coefficient and the retardation factor.

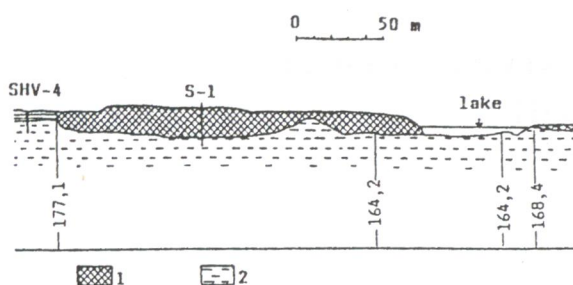


Fig. 1. Schematic geological profile through the waste site in Stupava. 1— waste, 2— Miocene clay.

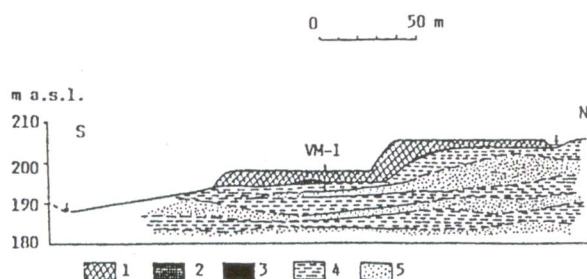


Fig. 2. Schematic geological profile through the waste site in Modra. 1— waste, 2— anthropogene soil deposit, 3— humus, 4— Miocene clay, sandy clay, 5— Miocene sand, clayey sand.

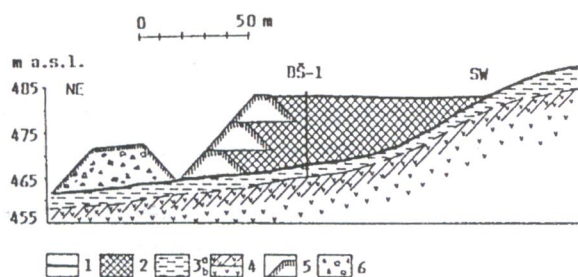


Fig. 3. Schematic geological profile through the settling lagoon in Banská Štiavnica. 1— humus, 2— sludge deposit, 3— Quaternary slope sediments and eluvium, 4— Neogene andesite: a) weathered, b) weakly weathered to unweathered, 5— dam, 6— deposit of slag from ore dressing.

Characteristics of the sites

The waste site "Stupava" is situated 10 km west of Bratislava in an old clay pit (Fig. 1). The clay belongs to the formations of the Vienna Basin and contains grey Miocene marine clays (Badenian), practically without sandy layers (Vaškovský et al. 1988). The clay is about 30 m thick. The waste site is about 10 years old and contains up to 14 m of municipal waste, slag and demolition debris. According to an unpublished archival source, temperatures higher than 100 °C were measured at the depth.

The waste site "Modra" is situated about 30 km NE of Bratislava on the border of the Danube Basin. The site (Fig. 2) is located in an old clay pit in freshwater deposits of the upper Miocene (Buday et al. 1962). The composition is vertically and horizontally variegated from clay to sandy clay and clayey sand. For about 20 years the pit has been used as deposit for the solid municipal waste of the city of Modra. The waste has a thickness of between 4 and 8 m.

The 30 to 40 years old waste site "Banská Štiavnica" (Fig. 3) is located about 160 km E of Bratislava on a Quaternary clayey soil above porphyric Miocene andesites of the "Studenská Formation" (Konečný et al. 1983). The andesite is hydrothermally altered and deeply weathered. The change from the weathered rock into the eluvial layer is continuous. The composition of this about 1.5 m thick layer varies from sandy gravel to clayey sand. The uppermost layer is a slope sediment, brown clay with a higher content of organic matter, about 0.4 m thick. The waste site is a settling lagoon with a local name Lintich containing up to 17 m of sludge remaining from ore dressing. The site has not been in use for about 20 years and the sludge has converted into a silty sand (geotechnical classification) covered with a thin humus layer. The ore with the main minerals pyrite, chalcopyrite, galenite, sphalerite etc. is the reason for the pollution of the underlying strata and the surroundings with heavy metals, especially with lead, zinc, and copper.

Methods

Sampling and laboratory tests

After selecting the waste sites according to clayey underlying strata, high concentration of heavy metals and age, drillings through the waste into the clay were carried out. The cores had a diameter of 127 to 137 mm. The outer 2 cm of the clay cores were dismissed and the remaining core cut in slices of 1 to 2 cm thickness. Only the upper half meter was probed continuously. Below the upper half meter, the clay was probed in larger intervals to keep the amount of samples at a reasonable level. The slices were immediately packed and sealed in lidded polysterol boxes and sent to the laboratory. Larger pieces of drilling cores were packed in plastic bags and used for geotechnical testing. Leachate was collected in PVC bottles and HNO_3 was added to lower the pH to 2.

The solid samples were divided into two parts. One part was used to establish geotechnical parameters such as moisture content, Atterberg limits, and grain size distribution. Larger samples allowed the determination of the hydraulic conductivity according to Darcy in consolidometers or triaxial test cells according to Hermanns (1993).

The mineralogical composition was determined by X-ray diffraction technique (XRD) and Infrared technique (FTIR). The carbonate content was determined either by the method of Janko (STN 72 1022) or by using the "car-

bonate-minibomb" (Maha 1994). Swelling clay minerals like illite, smectite and mixed-layer illite/smectite were identified by adding ethyleneglycol to the oriented smear-slides. Samples were X-rayed in calcium form. The <2µm fraction samples were also preheated to 150°C and 200°C. Obtained X-ray diffractograms did not enable a quantitative analysis. In general, the type of smectite or mixed-layer illite/smectite was not studied at this level of research and they were not differentiated in the results of the quantitative analysis by FTIR; illite, smectite and mixed-layer have been put together. Therefore, as well as because the quantitative analysis was restricted only to a few samples, the differences in the smectite content have been considered according to the external surface area and cation exchange capacity, also using information about the clay mineralogy from archival sources. The external surface area was determined by the nitrogen gas adsorption method according to Brunauer, Emmett and Teller (BET). The cation exchange capacity (CEC) was determined by exchanging the double-layer cations with ammonium-ions at pH 7 and determining the amount of ammonium-ions by Kjeldahl-distillation. The authors are conscious of the fact, that the analysis of the clay minerals is not complete. But the research was aimed at the geotechnical application of natural clays and clayey soils. And, there is usually only the content of the <2µm fraction determined in the geotechnical practice, so that even the estimate of the swelling clay content as a whole exceeds the traditional geotechnical methods.

The metal ions were determined as follows. A part of the dried sample was dissolved according to DIN 38 414/7 and the cations determined by atomic adsorption spectroscopy (AAS). The water-soluble ions were dissolved according to DIN 38 414/4 and chloride determined by high pressure liquid chromatography (HPLC). Because the DIN 38 414/7-method was shown to be rather time consuming, the method was slightly changed and the samples later dissolved in concentrated HCl or in one part concentrated HCl to three parts concentrated HNO₃. This method yielded similar results to the DIN-method.

Two samples have undergone a stepwise investigation as follows: 1) treatment in distilled water yielded water soluble ions; 2) treatment in KCl solution yielded ions in exchange position; 3) treatment with 0.02 M HNO₃ and 30% H₂O₂ (2:3) dissolved the organic bound heavy metals; 4) treatment with Na₂S₂O₄ and citrate buffer yielded the heavy metals connected to iron oxides. The remaining heavy metal ions are mainly sulphides and silicates including those con-

nected firmly to the clay minerals. The carbonate content of those samples were below 1% or zero. Heavy metal ions connected to carbonates were thus not determined.

Evaluation of the results

The concentrations of chloride and heavy metal ions in the samples were used to produce concentration profiles which show the dependency of the ion concentration in the clay as a function of the depth below the waste. The apparent diffusion coefficients D_a for various ions were determined according to Madsen & Kahr (1993) for either constant source (Stupava and Modra) or for decreasing source (Banská Štiavnica). Chloride was used as a tracer to calculate the retardation factor assuming that chloride ions diffuse through the clay without being adsorbed. The tortuosity factor τ for chloride was calculated assuming that the effective diffusion coefficient D_e of chloride in the porous media is equal to the apparent diffusion coefficient D_{aCl} . Is D the diffusion coefficient in solution, then is $D_e = \tau D$. The retardation factor R_f for a heavy metal ion M_e is then calculated from its apparent diffusion coefficient D_{aMe} as:

$$R_f = \frac{D_{Me} \cdot \tau}{D_{aMe}}$$

D_{Cl} and D_{Me} are taken from the tables by Li & Gregory (1974).

Results and discussion

Stupava

The 18 m deep drilling in Stupava reached the clay in a depth of 13.8 m below the surface of the waste site. The chemical analysis of the leachate found in the well showed that except of chloride the ion content was below the limit of Slovak drinking water regulations STN 75 7111. The results are shown in Table 1. A sample from the small lake at the border of the waste site showed values about twice as high. However, the concentration of heavy metals was still below the limits of STN 75 7111. The concentration profiles are contained in Fig. 4. Fig. 5 shows the concentration profile in a 40 cm thick soft clay layer found about 0.8 m above the contact between the waste and the underlying strata. The clay is described according to STN 73 1001 as a highly plastic (CH), stiff carbonate and fossil containing

Table 1: Metal ion concentrations (µg.l⁻¹) and pH of leachates.

Waste site	Pb	Cd	Cr	Ba	Al	Be	Co	Ni	Mo	Hg	As	Cu	Zn	pH
Stupava	x	<20.0	25.6	x	x	x	x	41.3	x	x	6.3	9.3	25.0	7.9
B. Štiavnica	150.3	8.7	x	28.9	226.0	<0.1	<10.0	x	<30.0	<1.0	5.0	35.2	440.0	6.9

x - not analysed

Table 2: Average physical properties of clays in the ground.

Waste site	Stupava	Modra	B. Štiavnica
<2µm fraction (%)	51	57	30
external specific surface area (BET) (m ² .g ⁻¹)	32	42	11
bulk density ρ _n (g.cm ⁻³)	2.18	1.96	1.89
dry bulk density ρ _d (g.cm ⁻³)	1.76	1.56	1.57
water content w _n (%)	22.3	25.0	33.2
liquid limit w _L (%)	65	55	43
plastic limit w _p (%)	22	19	23
plasticity index I _p (%)	43	36	20
cation exchange capacity (meq./100g)	19	32	25
permeability k _r (m.s ⁻¹)	1.10 ⁻⁸	7.10 ⁻⁹	9.10 ⁻⁹
	consolid	consolid	triaxial

Table 3: Main adsorbents s. l. in clays.

Waste site		Stupava	Modra	B. Štiavnica
adsorbents		content in whole samples (%)		
clay	illite+smectite	40	45	28
minerals	+I/S mixed layer			
	chlorite	5	5	3
	kaolinite	3	5	3
carbonate		20	5	<1
Fe ₂ O ₃ (goethite, limonite)		(+)	+	4
sulphide		+	(+)	+
organic matter		+	+	<9

+ present, amount not analysed, (+) probably present

material, the colour is grey. Results from the geotechnical classification are shown in the Table 2 and 3.

Due to the highest carbonate content (Table 3), adsorbtion and precipitation probably takes place mainly in the carbonates and in the swelling clay minerals. According to the archival sources, the main clay mineral at this site is illite (our X-ray diffractograms also indicated a certain content of illite/smectite mixed-layer). In spite of the relatively high content of the <2µm fraction, this is the reason for the lowest CEC from all three compared sites, as well as for the highest hydraulic conductivity, also influenced by the clay structure (“fissured clay”) (Table 2).

Only copper and cadmium showed a certain accumulation in the upper 6 cm of the clay. The concentration of the other heavy metal ions is practically constant over the depth and in the range of the natural background concentration. The waste site Stupava did not allow the calculation of diffusion coefficients and retardation factors. This because of the rather young age of the site, the small amount of heavy metal ions in the leachate, and the clay layer which was found in the waste above the natural clay. This clay layer seems to have protected the natural clay by adsorbing and thus delaying the transport of the pollutants downwards into the natural clay. A simplified estimate of the apparent diffusion coefficient of chlorides 16.10⁻¹⁰ m²/s and

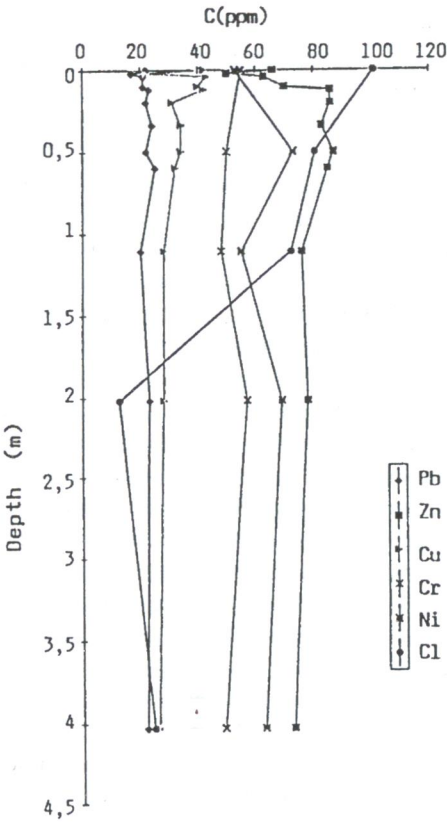


Fig. 4. Concentration profiles of both, heavy metal and chloride, ions in the natural clayey ground of the waste site Stupava.

tortuosity $\tau = 0.5$ seems to be too high. It can be partly explained by the fissured structure of the clay. Obviously, convection should also be taken into account by the calculation. The study, however, showed that the underlying strata have not been polluted by heavy metals.

Modra

The drilling in Modra was 6.54 m deep. The thickness of the waste was 4.34 m. The well stayed dry during the operation. The geotechnical classification shows the clay as a highly plastic (CH), fairly stiff material with carbonate. The carbonate is normally finely divided. The weathered zone is of yellowish-brownish colour due to iron oxides. The concentration profiles are contained in Fig. 6.

The clay in Modra contains about 5 % more clay fraction than the clay in Stupava. According to unpublished archival data, this clay consists mainly of montmorillonite, less of illite. All this correlates well with the highest CEC and the least hydraulic conductivity (Table 2). We have also identified illite/smectite mixed layer by XRD. Besides the clay minerals as adsorbents, the clay also contains carbonates, which act as a buffer and retard the migration of heavy metal ions by precipitation. Another possible adsorbents are —according to the colour of the clay— the

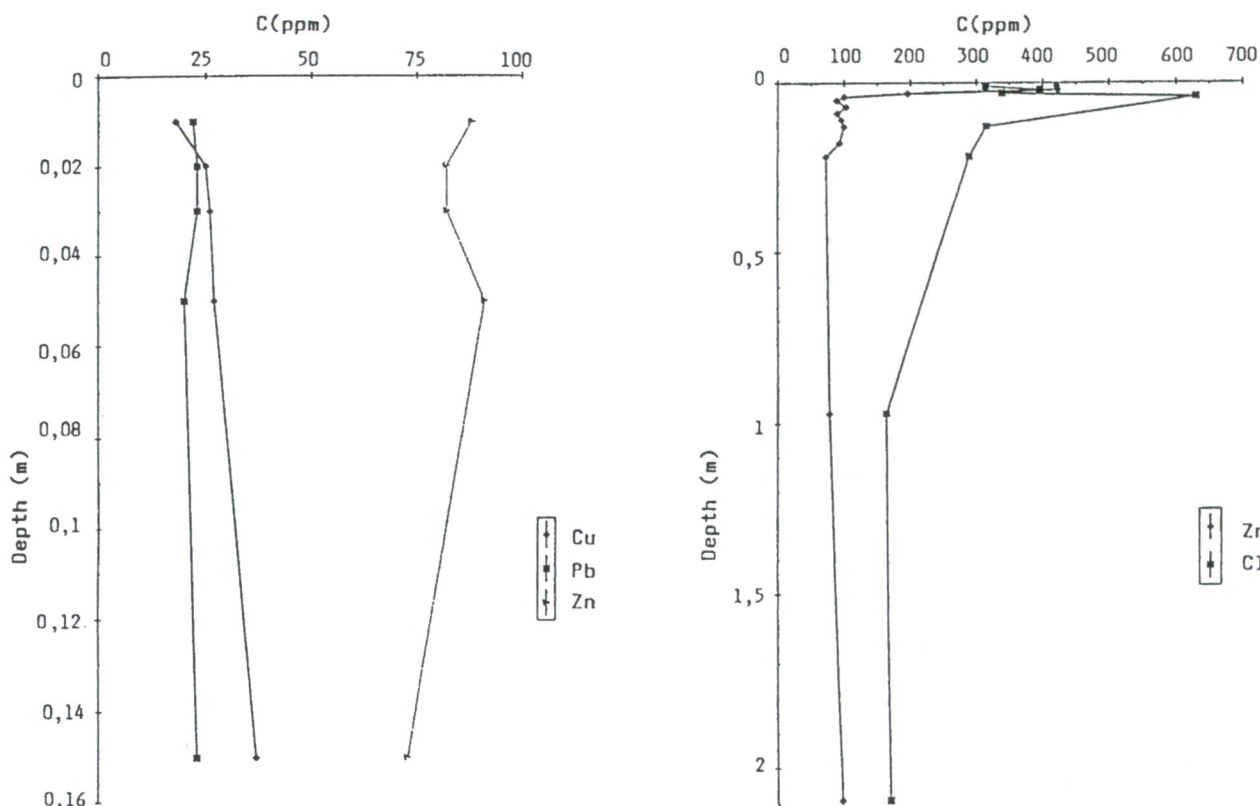


Fig. 5. Some concentration profiles of heavy metal ions in the clay layer found in the waste in Stupava.

hydrated iron oxides. Regarding the mineralogical composition of the clay, fairly good adsorption and retardation is expected. The upper 2 cm of the clay contains large amounts of heavy metals. The values of copper and lead are above the allowed value for soils (Decision 1994). The concentration decreases very rapidly below the upper 2 cm. Only zinc showed elevated values up to a depth of about 10 cm. The apparent diffusion coefficient was calculated for zinc ions to $1.2 \times 10^{-11} \text{ m}^2/\text{s}$ for a migration time of 18 years. The apparent diffusion coefficient of chloride was calculated to $3 \times 10^{-10} \text{ m}^2/\text{s}$ (Fig. 7). The tortuosity was calculated to $\tau = 0.15$ and the retardation factor for zinc to about 9.

Banská Štiavnica

The 17.8 m deep drilling in Banská Štiavnica reached the clay after penetration through 15.6 m of sludge. The clayey material is classified as a medium plastic clay (CI) according to STN 73 1001. The clay changes gradually into sandy clay with depth. A leachate sample was collected at a depth of 8.5 m and the content of heavy metals was determined (Table 1). The leachate was expected to be acid because of high pyrite content in the sludge and the pyrite oxidation that can be observed on the deposit surface. However, the leachate was about pH-neutral, probably

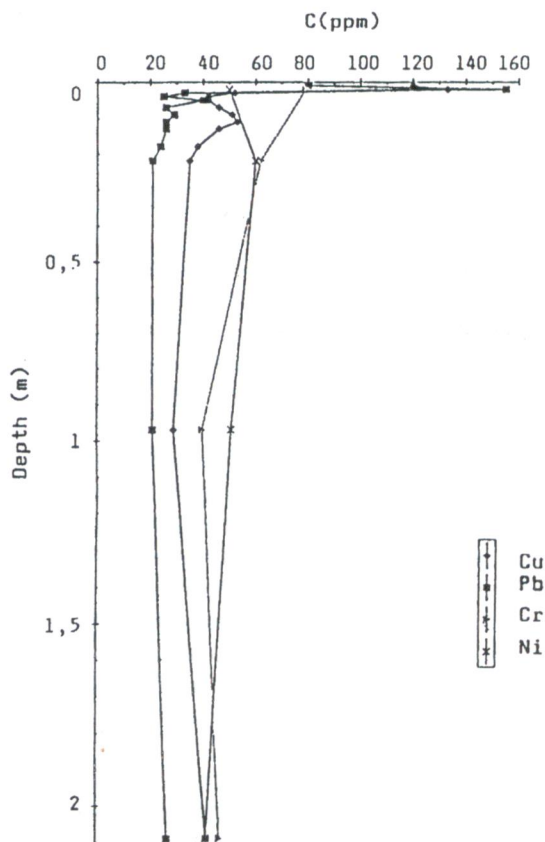


Fig. 6. Heavy metal ion and chloride ion concentration profiles in the clay beneath the waste site in Modra.

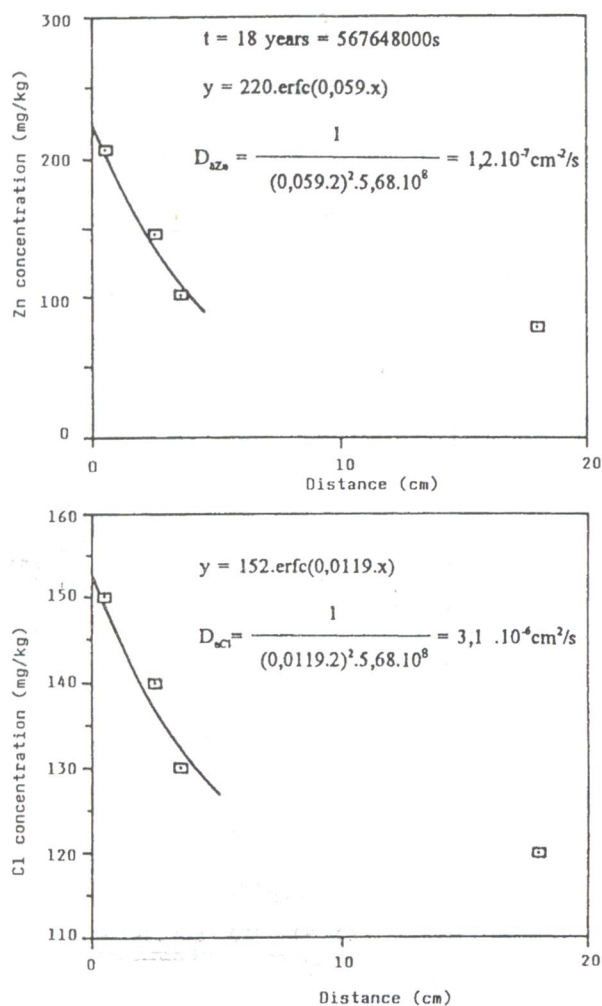


Fig. 7. Calculation of apparent diffusion coefficients for both, zinc and chloride, ions in the clay from Modra.

because of unknown flotation chemicals, certain carbonate content in the sludge, and the age of the deposit may also be significant. The leachate showed a fairly high content of heavy metal ions, especially of lead with three times the allowed concentration according to STN 75 7111. The concentration of aluminium, zinc and copper are at or below the limit. The dry sludge contained high amounts of lead (3500 mg per kg clay), zinc (2100 mg per kg clay) and copper (920 mg per kg clay). According to the regulation act in the Slovak Republic (Decision 1994) these values are between five and two times above the limits for remedial actions. The chemical analysis of the clay samples were restricted to the metals lead, zinc and copper. The concentration profiles are shown in Fig. 8.

The content of swelling clay minerals in Banská Štiavnica is lower than in Stupava. But here, the main swelling clay mineral is smectite (without type identification), illite was classified as a minor mineral (unpublished archival data). Therefore, the clay in Banská Štiavnica exhibits

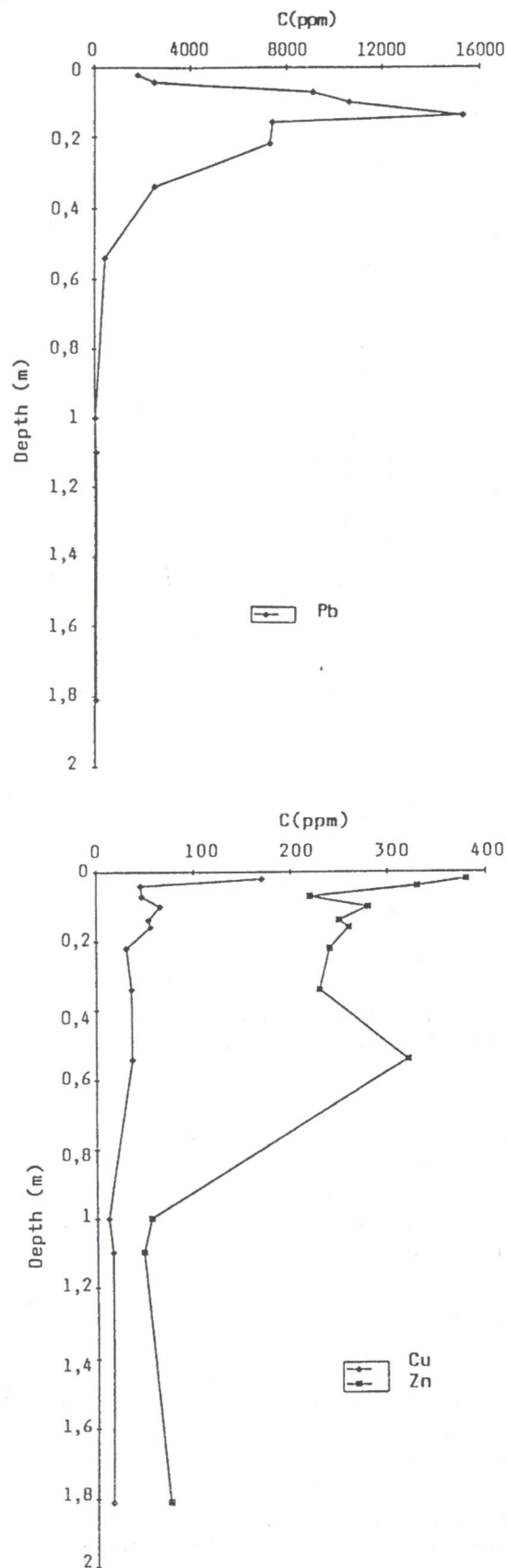


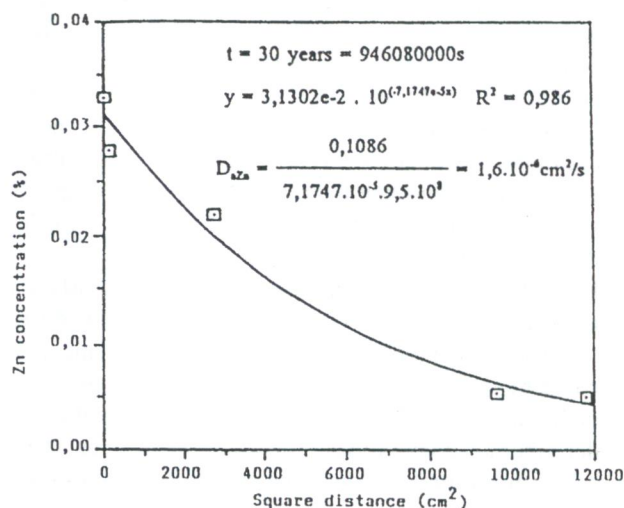
Fig. 8. Heavy metal ion concentration profiles in the clayey soil beneath the settling lagoon in Banská Štiavnica.

Table 4: Sequence analysis of the metal ion content in the clay from Banská Štiavnica.

Depth below the sludge (m)	0.0–0.02				0.08–0.10			
	Pb		Zn		Pb		Zn	
	(mg/kg)	(%)	(mg/kg)	(%)	(mg/kg)	(%)	(mg/kg)	(%)
water soluble compounds	1.5	0.1	8.1	2.1	19.6	0.2	7.3	2.6
ion exchange	129.6	7.2	71.4	18.8	1280.6	12.1	18.9	6.8
fixation on organic matter	381.7	21.2	92.5	24.4	3038.7	28.7	56.5	20.2
adsorption on hydrous Fe-oxides	202.7	11.3	76.5	20.1	57.7	0.5	53.7	19.2
difficult soluble compounds	1084.5	60.2	131.5	34.6	6203.4	58.5	143.6	51.2
together	1800.0	100.0	380.0	100.0	10 600.0	100.0	280.0	100.0

higher CEC. The mineralogical composition of the clay also influenced the hydraulic conductivity, which is less than in Stupava, even though the $<2\mu\text{m}$ fraction content in Banská Štiavnica is lower. In contact with water, expanding smectite closes the pores in the soil better than illite in Stupava (Table 2). (The influence of the fissured clay structure in Stupava has already been mentioned). A part of the swelling clay minerals was identified by XRD as hydroxy-interlayered smectite/vermiculite (HIS/HIV) according to Barnhisel & Bertsch (1989), also characterized generally by less CEC than smectite. This type of clay mineral (HIV) was also found in the deposit and in its vicinity. Near to the deposit, this is the second main clay mineral. The content of HIV is decreasing with increasing distance from the deposit and it turns from minor, trace to zero values (unpublished archival source). We suppose the same below the deposit, i.e. the content of these minerals is higher close to the contact between the waste sludge and clay. This could be one explanation why CEC was increasing up to the depth of 10 cm with a constant content of the $<2\mu\text{m}$ fraction, with the maximum CEC value in the depth of 10 to 14 cm below the contact. We expect the highest smectite content at this level. Next samples show decreasing CEC again; kaolinite is increasing (XRD) and the whole content of the $<2\mu\text{m}$ fraction is slowly decreasing with the depth. Besides the clay minerals, hydrated iron oxides, sulphides and organic matter act as adsorbents. Carbonates were found only in small amounts ($<1\%$).

The concentration profiles show extremely high values for lead —up to 15g/kg— in the upper few cm of the clay below the waste. The concentration decreases rapidly with increasing depth and reaches the background value below 50 cm. The background value of 70 to 80 mg lead/kg clay is fairly high due to hydrothermal processes (Forgáč et al. 1995). The concentrations of zinc and copper also show elevated values above 50 cm depth. Regarding the age of the waste site (30 to 40 years), this transport velocity of heavy metal ions through the clay seems to be normal. A first calculation of the diffusion coefficient for zinc ions from incomplete analytical data gave a value of $1.6 \times 10^{-10} \text{ m}^2/\text{s}$ (Fig. 9) which seems to be too high. The estimated value of the apparent diffusion coefficient for lead ions $1.10^{-11} \text{ m}^2/\text{s}$ in the decreasing part of the concentration profile seems to be more realistic.

**Fig. 9.** Calculation of the apparent diffusion coefficient for zinc ions in the Quaternary clayey soil from Banská Štiavnica.

The concentration profiles show the highest concentration of heavy metals 10–15 cm deep, in the layer with the expected highest smectite content. It was then suggested that adsorption on clay minerals was the most important adsorption factor. Results from the stepwise analysis of the clay, however, showed that higher amount of heavy metals was found connected to the organic matter (Table 4), even when this regarding the weight is much less abundant than clay minerals. The water soluble amount of heavy metals is very small and the more or less insoluble chemical compounds are in the majority. It is at present not clear how much heavy metal is fixed firmly to the clay. It seems, however, that the retardation of heavy metals by clay minerals is somewhat smaller than expected.

Conclusions

The quality of the concentration profiles from field studies of this kind, as well as their interpretation, are affected by many factors:

- High quality of drilling cores is necessary to ensure representative and undisturbed samples of a soil profile.

Double or triple core barrels are necessary. These kinds of core barrel were not available at the time of the study. But, the expensive drilling gear is endangered by drilling through the domestic waste that mostly contains larger hard objects (in Stupava and Modra blocks of concrete and engine parts destroyed the drilling gear).

- For the interpretation of the migration velocity, the border between the waste and the underlying soil must be exactly detected. Because the heavy metals are usually concentrated in the upper few centimetre of the soil profile a misdetection would result in completely wrong concentration profiles. According to our experience, it is not easy when dealing with domestic waste sites. There was often a contact zone with the waste particles pressed into the clay.
- Geological conditions (grain size distribution, mineralogical composition etc.), together with the difference in age of the waste site and in content of ions in the leachates are the most important factors influencing the migration velocity and thus the shape of the concentration profiles. At our three waste sites, they were very different.
- Even if a "nice" concentration profile is established, it represents a heterogeneous soil body, affected by different processes in the waste site history (their enumeration could be quite long). It means, the migration processes under natural conditions are far more complex than under laboratory conditions. Therefore, calculation of the heavy metal migration into the soil from field results is difficult and only possible with simplifications.

The presented values of diffusion coefficients and retardation factors are thus to some extent questionable as is the proper calibration of the laboratory values, too. Because of the very slow migration of the ions, and the difficulty in identifying and probing the upper part of the clay, the oldest waste sites gave the best values of diffusion coefficients and retardation factors. The research will continue with laboratory experiments on uncontaminated soil samples from these sites. Mathematical modelling using results from both field and laboratory investigations will be carried out to approach the real values of migration parameters.

The present results, however, showed that heavy metal ions migrate very slowly in clayey soil and that there is also a considerable amount of retardation in the organic matter. The determined velocity of migration from the concentration profiles and the calculated diffusion coefficients are in fair agreement with values reported in the literature by Wagner (1992) and by Madsen & Kahr (1993).

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