1. INTRODUCTION

Anthropogenic sources of chemical contaminants, especially that of toxic elements and heavy metals may lead to serious ecological and human health hazard. Thus, potentially toxic elements (Sb, As, Cd, Cr, Cu, Pb, Hg, Ni, Se, Ag, Sn, Zn) have come into focus in several research areas, recently, as these elements obviously cause potential environmental risk through their biogeochemical interactions. To have detailed knowledge on complex processes in the environment and ecosystems is also important to be able to reduce the risks of soil and water pollution by controlling the mobility and bioavailability of the considered elements.

There are many chemical forms of an element in the environment, which can be transformed into one another in different equilibria resulting in changing toxicity and mobility depending on the dynamically changing environmental conditions. In order to assess the contaminant transport including infiltration, water and wind erosion as well as accumulation through food chain it is inevitable to know the element concentration that cause environmental risk and the process mechanisms, which control it. Total element concentration does not necessarily equal to the concentration that has biological effects. Basically, the element speciation and geochemical forms determine the behaviour of an element in the environment i.e. mobility and bioavailability.

Risk assessment and evaluation of recultivation technologies of sites where contaminants originate from mining activity and mining waste disposal are considered specific areas. In mine tailings heavy metal concentration may be up to 10^3 mg kg^{-1}, however, the mobile fraction can be relatively low as heavy metals are mostly in the forms of ore or precipitation with low water solubility. At the same time, the mobile fraction is continuously produced when infiltration and dilution take place, which means that water content of the mine tailings has slightly changing heavy metal concentration and relates to the extent being different from the actual equilibrium, resulting in long term effect on the environment. According to our recent knowledge it can be stated from geochemical point of view that the mobility of heavy metals in mine tailings, where sulphide forms are dominant, are strongly dependent on the environmental conditions and different for each element, thus, risk assessment is necessary to be site specific. In addition, considering the distribution of an element between solid and water phases, the soluble heavy metal content is determined by both adsorption-desorption and dissolution-precipitation processes, however their rate can be different in mine tailings than in contaminated soils.

For the recultivation of mine tailings, taking both economical and technological feasibilities into consideration, phytoremediation has been widely evaluated, nowadays. Phytoremediation technology seems to be applicable, since these sites have relatively low environmental impact, namely contaminants do not show high dispersion resulting in hazard of surface and subsurface water pollution as well as human health risk through landuse, in short term. The role of vegetation is significant in changing water balance, erosion control, and landscape. Research on natural vegetation of mining areas provides information applicable in risk assessment and remediation planning, and results are also important from ecological point of view.

Based on the issues mentioned above, the aims of our research are the following:

- Analysis of chemical forms of heavy metals (Cd, Cu, Pb, and Zn) in mine tailings: sequential extraction of solid phase; and speciation analysis in water solution with modelling.
- Evaluation of effects of environmental conditions on heavy metal mobility: examination of leaching kinetics with soil column experiments; analysis of acid-base buffering capacity; analysis of heavy metal solubility and leaching in the function of pH with both one step and multistep extraction experiments and modelling; and analysis of hydrological impact on heavy metal forms, migration and potential bioavailability with SEM/EDX, XRD and extraction methods.
- Analysis of the relationship between heavy metals (Pb, Zn and Cu) and vegetation in a mine tailing: evaluation of certain methods used to estimate the potentially bioavailiable fractions; spatial analysis of relationship among heavy metal distribution, pH and vegetation pattern; analysis of heavy metal accumulation and translocation in certain plant species; and evaluation of erosion risk and the role of vegetation in erosion control.
- Evaluation of the applicability of FPXRF spectrometry to measure Pb, Zn and Cu total concentrations of mine tailings in field: analyses of matrix effect; and that of dependence on water content.

2. MATERIALS AND METHODS

2.1. Study area and sampling

Based on previous qualitative risk assessment, potential sources of heavy metal (Pb, Zn, Cu and Cd) contamination of soil, surface and subsurface water were identified in Gyöngyösoroszi mining site, the study area. Former Pb and Zn mining activities have resulted in acidic oxidation of sulphides leading to potential acid mine/rock drainage of the mine tailings and erosion risk is also considered crucial. At the same time, phytoremediation was taken into consideration to reduce the environmental risk.

Systematically random sampling with GPS was carried out in the surrounding of the ore processing factory to evaluate the contaminants' spatial distribution and identify hot spots. Statistical analysis of both chemical and spatial parameters revealed three types of mining wastes, which were characterised by examining three representative samples (*A*, *B*, and *C*).

2.2. Extractions, soil column and suspension experiments

The total element concentration was measured according to the Hungarian standard MSZ 21470-50 with H_2O_2-HNO_3 wet digestion. Sequential extractions according to GYŐRI[1] et al. (1996) were used to analyse speciation in the mine waste samples having different pH. Buffering capacity was measured in suspensions of 1:10 solid – liquid ratio, according to TIRUTA-BARNA et al.[2] (2004) and buffering minerals were identified. pH was measured according to MSZ 080206/2-1978. Based on the results of the soil column experiments, performed with slow water flow assuming equilibrium, according to ESNAOLA and MILLÁN[3] (1998), and that of multistep extractions with solutions having different pH, in suspensions of 1:2 ratio, according to TACK et al.[4] (1999), and TIRUTA-BARNA et al. (2004), kinetics of Zn, Cd, Cu, and Pb leaching under different pH conditions was evaluated. On the basis of results gained with model calculation using Visual MINTEQ and suspension experiments, the effect of pH on heavy metal concentrations in solution as well as

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[1] Győri Z., Goulding, K., Blake, L., Prokisch J.: 1996. Changes in the heavy metal contents of soil from the Park Grass Experiment at Rothamsted Experimental Station. *Fresenius Journal of Analytical Chemistry* **354**, 699-702.

[2] Tiruta-Barna, L., Imyim, A., Barna, R.: 2004. Long-term predicition of the leaching behavior of pollutants from solidified wastes. *Adv. Environ. Res.* **8**(3-4), 697-711.

[3] Esnaola, M.V., Millán, E.: 1998. Effect of acid precipitation ont he mobilisation and leaching of heavy metals from contaminated soils. *Environ. Technol.* **19**, 567-578.

[4] Tack, F.M.G., Verloo, M.G.: 1995. Chemical speciation and fractionation in soil and sediment heavy metal analysis: a review. *Intern. J. Environ. Anal. Chem.* **59**, 225-238.

determining mechanisms i.e. sorption and/or precipitation were studied. The analytical measurement of element concentrations in solution was carried out with an OPTIMA 3300 DV spectrometer using ICP-OES method.

2.3. Analysis of hydrological impact on heavy metal speciation and mobility

Most of the mining waste was placed in the Szárazvölgy mine tailing. The impact of different hydrological regimes on heavy metal speciation, vertical mobility and geochemical zonality as well as potential bioavailability was analysed examining a site having unsaturated medium (*a*) and another being under water (*b*) The sampling cores extended from 0-290 and 0-240 cm below the surface of the tailings, respectively. The analyses of solid phases including elemental and mineralogical composition were carried out using SEM/EDX and XRD measurements, and water and DTPA extractions and, in addition, particle size distribution profiles were also analysed. For the SEM/EDX analysis a JEOL 5900 LV scanning electron microscope incorporating an Oxford Instruments INCA Energy analytical system was used, while the XRD measurement was carried out using an Enraf-Nonius PDS 120 diffractometer. Water and DTPA extractions were made according to QUEVAUVILLER[5] (1998), and the element concentrations in solution were measured with ICP-OES.

2.4. Evaluation of methods for the estimation of potentially bioavailable element contents

The heavy metal concentrations of Lakanen-Erviö extract were compared to the total heavy metal concentrations. The Lakanen-Erviö extraction was performed according to MSZ 20135:1999. Hot water percolation according to FÜLEKY and CZINKOTA[6] (1993) was used to analyse the kinetics of potentially bioavailable heavy metal leaching from mine tailings. The change of heavy metal concentration and leaching characteristics in the presence of a complexing agent, EDTA were analysed with multistep extractions. The element concentrations in solution were measured with ICP-OES.

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[5] Quevauviller, Ph.: 1998. Operationally defined extraction procedures for soil and sediment analysis I. – Standardisation. *Trends in Anal. Chem*. **17**(5), 289-298.

[6] Füleky Gy., Czinkota I.: 1993. Hot water percolation (HWP) a new rapid soil extraction method. *Plant and Soil* **157**, 131-135.

2.5. Analysis of plant – heavy metal relationship

The relationship among vegetation pattern, heavy metal distribution and pH was analysed at one of the sampling sites, situated among the Toka-stream using GIS. The aim of the analysis was to identify the factor that potentially determines the presence/absence of vegetation. The accumulation and translocation features were characterised for the most abundant plant species: *Rubus ceasius*, *Echium vulgare*, *Poa annua*, *Plantago lanceolata* and *Anagallis arvensis.* The element concentrations of plants for dry material were measured with ICP-OES after wet digestion.

2.6. Evaluation of erosion risk and role of vegetation in erosion control

On the basis of the Smith-Wischmeier universal soil loss equation, the erosion risk was analysed and the role of vegetation in erosion control was evaluated at the Szárazvölgyi mine tailing using GIS technique and considering field and laboratory measurement results.

2.7. Evaluation of the applicability of FPXRF spectrometry in mining areas

The applicability of FPXRF spectrometry in mining areas was evaluated. The use of this analytical tool makes the in situ measurement of heavy metal concentrations possible in high scale, which is essential for the environmental risk assessment and remediation planning. The measured concentrations were analysed in the function of matrice (mine tailing material, soil and plant samples) as well as water content in case of the mine tailing material. The non-destructive FPXRF measurements were carried out using a NITON-700 XL spectrometer with a Cd-109 X-ray radiation source.

2.8. Spatial data processing

The processing of analytical data connected to spatial coordinates in the unified Hungarian projection system (EOV) was carried out using the programs SURFER 8, ArcView 3.2 and Idrisi 32.

2.9. Statistical methods

The statistical analyses of data sets were performed using the programs SPSS 11, Minitab 14, Idrisi 32, Excel and Grapher 3. The sample classification on the basis of both analytical and spatial characteristics was proved using the Mann-Whitney-Wilcoxon probe. The normality test with Ryan-Joiner probe (N<30) revealed that the data sets' are not normally distributed, thus non-parametric correlation analyses with the indication of Spearman coefficients were applied. The relationship among vegetation pattern, heavy metal distribution and pH was evaluated with multiple regression analysis. Linear regression analyses were used to estimate the relationship between results of FPXRF and ICP-OES methods, and that of FPXRF results and water content of samples.

3. RESULTS AND DISCUSSION

3.1. Chemical forms of heavy metals in mine tailings

At the Gyöngyösoroszi Pb and Zn mining site high heavy metal concentrations can be measured. The chemical parameters of the representative samples for the identified three types of mining wastes are summarised in *Table 1.*

Table 1: **pH and heavy metal concentrations of the representative samples (mg kg^{-1})**

sample code	*pH*	*Cd (mg kg^{-1})*	*Cu (mg kg^{-1})*	*Pb (mg kg^{-1})*	*Zn (mg kg^{-1})*
A	1.96	8.55	106	2026	442
B	6.70	25.4	217	264	3806
C	6.44	31.8	1386	6376	7271

Chemical forms of heavy metals at mining sites are greatly determined by pH. Sequential extraction results revealed that the rate of different chemical forms in mining wastes having same pH do not differ significantly. At the same time, acidic oxidation of sulphide minerals in acidic mining wastes determines the secondary minerals, and increases the solubility of heavy metal compounds leading to increased leaching, which is confirmed by the relative extracted element contents in the sequential extraction fractions (*Figure 1-2*).

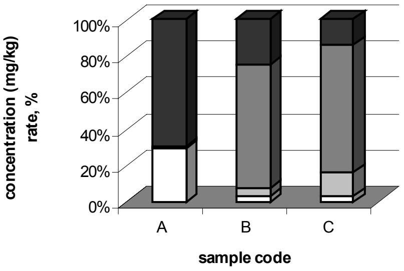


Figure 1: **Relative Zn-distribution in sequential extraction fractions**

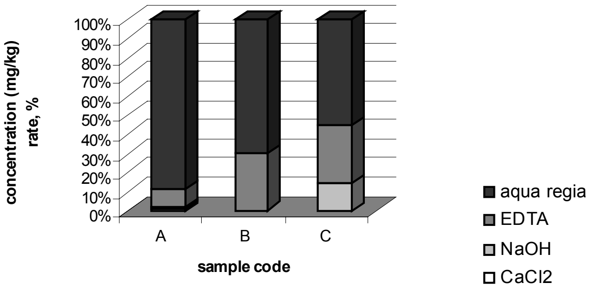


Figure 2: **Relative Pb-distribution in sequential extraction fractions**

Based on the results of sequential extractions it can be stated that the relative heavy metal content is the highest in the aqua regia soluble fraction in case of the acidic mining waste sample (*A*) for all the examined heavy metals (Cd 88.1%, Cu 76.1%, Pb 93.0% and Zn 69.3%), however, the absolute Cd, Cu and Zn concentrations are low, which means intensive weathering and leaching. In case of the two neutral mining waste samples (*B* and *C*) the rates of the relative element contents in the aqua regia fraction are also high and similar for Cd, Zn and Cu. For sample *B* the concentration rates are 64.3%, 67.3%, and 76.0%, while in case of sample *C* 69.8%, 69.7%, and 70.2%, respectively. At the same time, Zn concentration rates in the EDTA fraction are much higher than in sample *A*. For sample *B* it is 67.3%, for sample *C* it is 69.7%, however, presence of Zn-carbonate was not proved in previous SEM and EDX analyses, thus further examinations are required to identify the chemical form represented by the EDTA fraction, in case of mining wastes. Pb distributions in neutral samples are different. In case of sample *C*, where vegetation can be found, the NaOH soluble Pb fraction is also significant (14.5%) comparing to that of sample *B*, where vegetation is absent.

3.2. Effect of environmental conditions on heavy metal mobility and leaching in mining wastes

3.2.1. Results of soil column experiments

Results of the soil column experiments aiming kinetics analysis proved that after the assumed initial desorption, nearly constant heavy metal concentration can be measured in case of mining wastes (*Figure 3*).

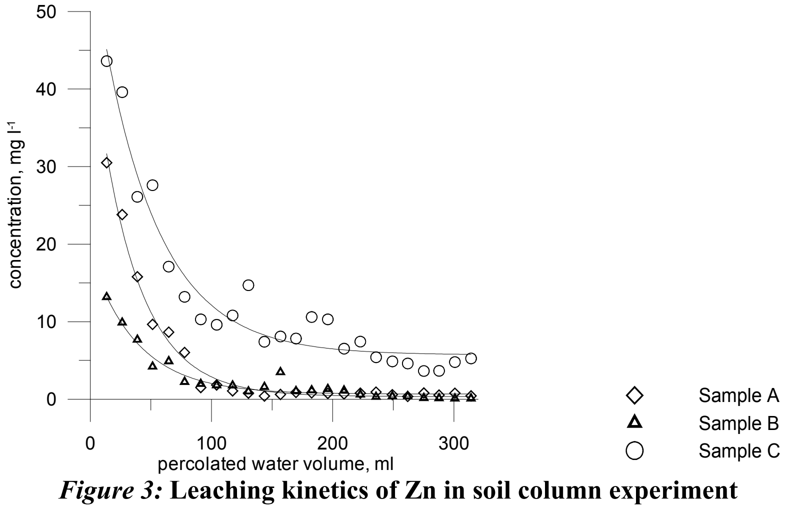


Figure 3: **Leaching kinetics of Zn in soil column experiment**

The heavy metal leaching, in the function of hydraulic parameters, can be expressed according to first order kinetics (*Equation 1*).

$$y = y_0 + A\, e^{-x/k} \qquad (1)$$

The constants and determination coefficients are listed in *Table 2*.

Table 2: **Constants and determination coefficients for Equation 1**

	A				*B*				*C*			
	Cd	***Cu***	***Pb***	***Zn***	***Cd***	***Cu***	***Pb***	***Zn***	***Cd***	***Cu***	***Pb***	***Zn***
asymptote (y_0), mg l^{-1}	0.01	0.46	0.03	0.35	0.00	0.01		0.67	0.00	0.02		5.71
maximum (A), mg l^{-1}	0.28	322	0.89	46.4	0.09	0.13		17.8	0.21	0.07		52.4
rate constant (k)	38.3	9.26	20.1	34.4	122	15.6		38.9	199	24.7		47.6
r^2	0.89	0.99	0.92	0.98	0.78	0.87		0.95	0.65	0.90		0.94

3.2.2. Effect of pH on the heavy metal concentration in solution

Considering the dissolution – precipitation equilibria, changes of Cd, Zn, Pb and Cu concentration in solution were modelled in the function of varying pH with iteration. In addition, laboratory experiments were carried out to evaluate the role of dissolution – precipitation and adsorption – desorption processes in controlling heavy metal concentrations in solution, for mining wastes. Based on the calculated and measured values, it can be stated that Zn and Cd concentration in solution is greatly determined by dissolution – precipitation equilibria, while in case of Cu and Pb, Fe-hydroxide precipitation has significant role, precipitation and adsorption together reduce Cu and Pb concentration in solution with increasing pH. Model calculations and experimental results show that Cd and Zn concentrations in the solution of acidic mining waste decrease significantly only pH above 7. Cu and Pb concentrations tend to decrease together with Fe concentration pH above 3, which may indicate adsorption on and co-precipitation with Fe-hydroxide.

According to the model calculations, the dominant species in water solution are free heavy metal ions and sulphates, $MSO_{4(aq)}$ resulting from the weathering of sulphides. To prove it, further analytical speciation analyses are required.

3.2.3. Acid-base buffering capacity

Results of multistep extractions with 10^{-2} M acid or basic solutions show that the pH of the suspensions does not change significantly in the presence of the above mentioned acid or base, and does not result in increase of heavy metal concentrations, which is in good agreement with the model calculations. It can be explained with the remarkable measured buffering capacity of the neutral waste samples and the high H^+-concentration in solution in case of the acidic waste sample, which is 0.12 mmol g^{-1} in equilibrium (*Figure 4*).

The multistep extraction also shows that the dissolution of heavy metals is continuous and tends to a certain saturation value.

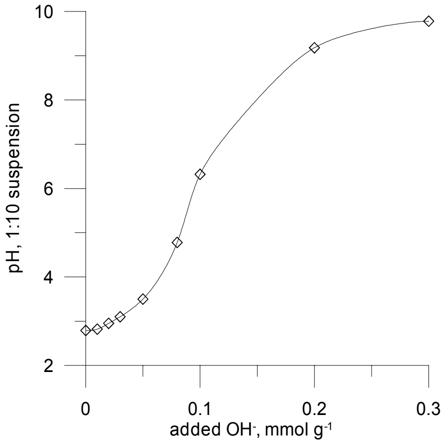


Figure 4*: Buffering capacity of sample *A

Mineralogical components of the neutral mining waste samples determine the buffering capacity against acidic treatment. The curves representing the buffering capacity show that carbonates buffer in the pH range of 5.5-7, while Al-silicates buffer at pH 2-3, and the presence of FeOOH as a buffering agent cannot be proved (*Figure 5-6*).

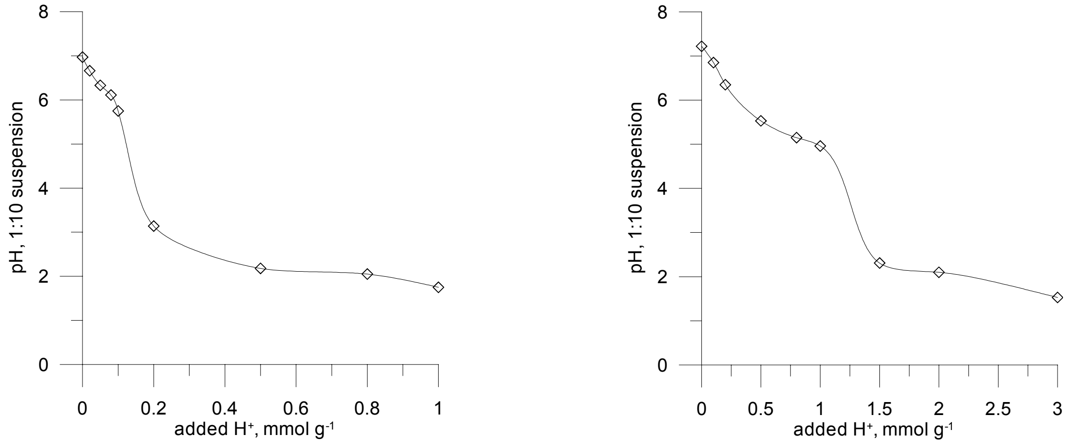


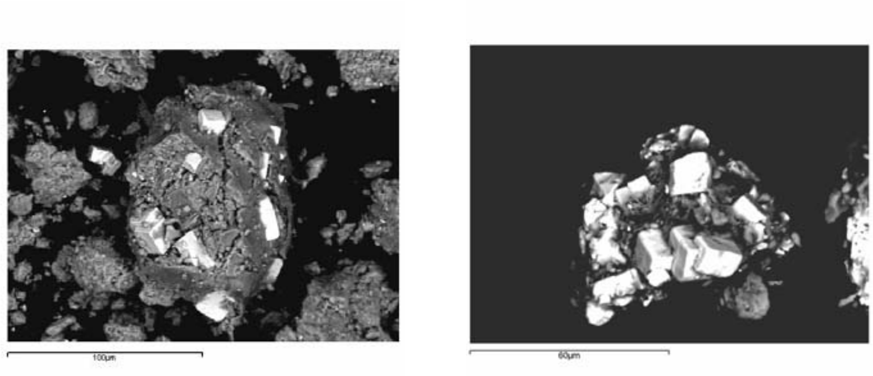
Figure 5:* Buffering capacity of sample *B

Figure 6*: Buffering capacity of sample *C

3.2.4. Evaluation of hydrological impact on heavy metal speciation and migration

Dominant minerals identified with XRD are the same comparing the samples of the site being unsaturated, exposed to only precipitation to that being saturated. Based on SEM/EDX results, pyrite, galena and sphalerite potentially weathering minerals are in less reactive form having relatively small specific surface in both cases (*Figure 7*).

The presence of buffering carbonate and Al-silicate minerals, and some secondary minerals, particularly gypsum, can be identified with SEM/EDX as well as water extractions.



(*a*) **(*b*)**

***Figure 7*: Cubic pyrite in K-aluminium-silicate at the sampling site *a* and *b*, SEM**

Vertical zonality in the saturated and unsaturated systems was evaluated on the basis of the pH, particle size distribution and heavy metal profiles measured in water suspension of 1:10. Based on these profiles, a geochemical barrier was found in both cases. The neutralization zone, where formation of secondary minerals results in low permeability and decreased intensity of acidic oxidation leading to neutral pH held by carbonates and low heavy metal solubility, is in deeper layer in the saturated sampling site (*Figure 8*).

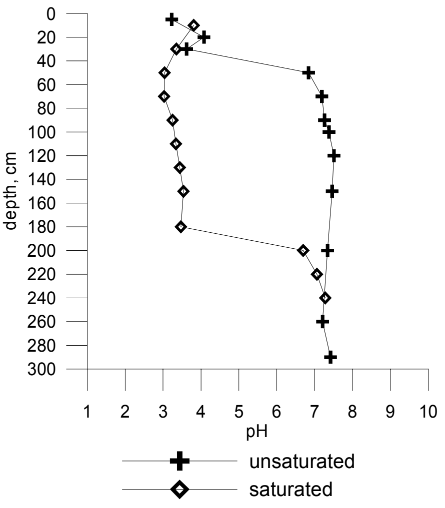


***Figure 8:* pH in 1:10 water suspension**

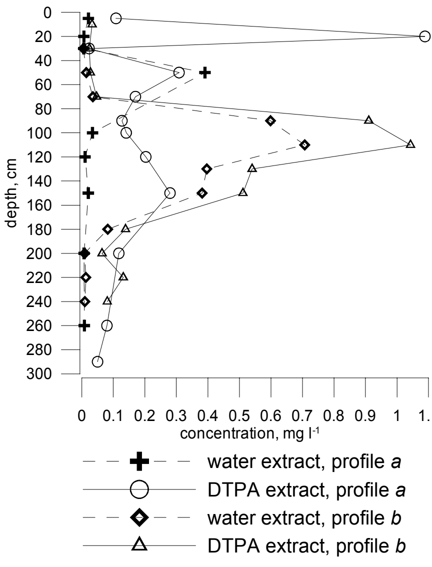


***Figure 9:* Cd concentration in water and DTPA extracts**

The neutralization zone in the saturated system is in depth of 200-210 cm, while in the unsaturated one it is in depth of 50-60 cm. Layers above it have acidic pH (3.5) and higher heavy metal concentration (*Figure 9*).

In the literature, water cover is often recommended to reduce the intensity of acidic oxidation and heavy metal leaching, however, results of our study show that in the saturated system the pH is highly acidic in deeper layers and heavy metal concentration is also high, while at the unsaturated site pH is acidic only in the upper layer and heavy metal concentration is low below it. Water soluble Fe concentration profiles also indicate the intensity of the acidic oxidation of pyritic ore (*Figure 10*). Based on it, the applicability of the above mentioned technology to slow weathering should be evaluated site specifically, considering primarily the water balance.

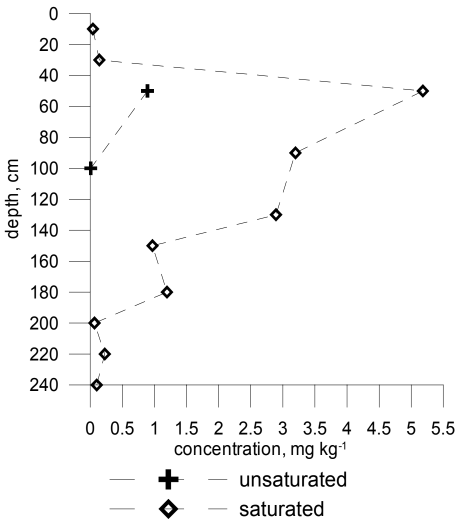


Figure 10: **Fe concentration in water extract**

3.3. Evaluation of methods used for estimation of potentially bioavailable heavy metal concentration

The concentrations of Zn, Cd, Pb and Cu in the Lakanen-Erviö extract used for the evaluation of potentially bioavailable element concentration are in good correlation with the total element, in mine tailings (for the Ércelőkészítő sampling site the correlation coefficients are as follows: r_{Zn}= 0.89, r_{Cd}= 0.75, r_{Cu}= 0.91; for the mining waste from Mátraszentimre: r_{Zn}= 0.97, r_{Pb}= 0.93, r_{Cd}= 0.76, r_{Cu}= 0.94; and for sampling site among the Toka stream: r_{Pb}= 0.91, r_{Cd}= 0.85, r_{Cu}= 0.91). It can be explained by the same heavy metal forms characteristic of the certain sample sets, i.e. the buffered EDTA soluble element content is expected to be similar resulting from the similar weathering processes, in each case.

The hot water percolation was worked out also for the estimation of potentially bioavailable element concentration showing the adsorbed fraction. The results of the experiment performed using the mine tailing samples can be describe by Freundlich desorption isotherms (*Equation 2*) with the constants and determination coefficients listed in *Table 3*.

$$y = a + bx^c \tag{2}$$

***Table 3*: Constants and determination coefficients for Equation 2**

sample		*A*			*B*			*C*	
element	***Cd***	***Cu***	***Zn***	***Cd***	***Cu***	***Zn***	***Cd***	***Cu***	***Zn***
a	0.00	0.09	0.34	0.00	0.00	0.00	0.00	0.00	0.00
b	6.22	603.8	1607	2.2	3.21	4.40	4.08	0.28	23.51
c	-1.54	-2.31	-1.98	-0.81	-1.15	-0.34	-0.93	-0.87	-0.97
r^2	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.95	0.98

The multistep extraction with non-buffered EDTA was applied to estimate the leachable heavy metal concentration in the presence of a complexing agent at the pH characteristic to a given mining waste material, and the kinetics of leaching. In case of the acidic sample, the leachable heavy metal concentration is of the same order of magnitude in the presence and in the absence of EDTA, at the same pH. In neutral samples, EDTA soluble Zn and Cd concentrations exceed the water soluble ones with one order of magnitude, while Cu and Pb with more than one order of magnitude, at a given pH. In addition, concentrations measured step by step converge to constant values. The results are considerable for the evaluation of phytoremediation, especially chelate induced phytoextraction technologies.

3.4. Plant – heavy metal relationships

Cenological survey of the mine tailing among the Toka stream carried out yearly in the same period of time provides useful information to evaluate succession processes in long term, and additional information on potentially applicable plant species for phytoremediation. The relationship among vegetation pattern, spatial distribution of heavy metal, and pH was examined both in GIS and with statistical analyses. Results show that presence of vegetation is significantly dependent on pH, which confirms that phytotoxicity is a function of element concentration in solution, which is primarily controlled by pH (*Table 4-5*).

***Table 4*: Results of statistical analysis of vegetation pattern – heavy metal distribution – pH relationship, Mann-Whithey-Wilcoxon probe**

	N	*median*	*95% confidence interval*	*99% confidence interval*	*Mann-Whitney test, P*
$pH_{covered}$	215	6.38	6.27-6.48	6.23-6.51	
$pH_{uncovered}$	101	5.19	4.95-5.65	4.88-5.79	***0.0000****

*significant at P<0,01

***Table 5*: Results of regression analyses for vegetation pattern – heavy metal distribution – pH relationship,** y(*presence of vegetation*)= a [Pb] + b [Zn] + c [Cu] + d pH + e

	n	*value*	*standard error*	*T*	*P*	*r*
model 1	312					0.431
a		-0.000015	0.000008	-1.80	0.073	
b		-0.000005	0.000003	-1.80	0.074	
c		-0.0000007	0.000013	-0.05	0.956	
d		0.156	0.023	6.84	**0.000***	
e		-0.083	0.134	-0.62	0.538	
model 2	316					0.439
d		0.13	0.02	6.53	**0.000***	
e		-0.086	0.12	-0.72	0.474	

*significant at P<0,01

Considering the element concentration in the most abundant plant species at study area, information can be gain on which are accumulating ones and for what element, in addition to their heavy metal toleration. Results show that dewberry (*Rubus caesius*), vipersbugloss (*Echium vulgare*), scarlet pimpernel (*Anagallis arvensis*) and narrowleaf plantain (*Plantago lanceolata*) accumulate significant amount of Pb, Cu, Zn and Cd, while in case of annual bluegrass (*Poa annua*) only Pb can be measured in elevated concentration.

Analyses of translocation features provide data on plant species potentially applicable for phytoextraction. According to the results, the scarlet pimpernel, the narrowleaf plantain, and the dewberry accumulate heavy metals primarily in their roots, while accumulated heavy metal concentration in the vipersbugloss and the annual bluegrass is higher in the shoots (*Table 6*).

***Table 6:* Average rate and standard deviation of heavy metal concentrations in shoot and root (c_{root}/c_{shoot}; N=5)**

species	*Cu*	*Zn*	*Pb*	*Cd*
scarlet pimpernel (*Anagallis arvensis*)	0.20±0.07	0.36±0.15	0.14±0.04	0.38±0.08
vipersbugloss (*Echium vulgare*)	2.14±0.99	0.93±0.51	1.30±0.74	1.24±0.60
narrowleaf plantain (*Plantago lanceolata*)	0.69±0.44	0.58±0.32	0.79±0.62	0.58±0.33
dewberry (*Rubus ceasius*)	0.40±0.27	0.62±0.09	0.37±0.16	0.42±0.08
annual bluegrass (*Poa annua*)	1.44±1.21	1.56±0.78	3.18±2.70	1.21±1.55

Our research does not include the microbiological aspects of plant – heavy metal relationships, which also play role in weathering processes and heavy metal mobilization, however. This approach is a subject of further studies.

3.5. Erosion risk at a mining site and the role of vegetation in erosion control

The risk of heavy metal contamination of the environment by erosion at mining sites can be reduced with vegetation, thus it has important role in erosion control. The calculation of the heavy metal load of the environment of the mine tailing revealed that extreme values of particle size, slope length and slope angle result in differences of more than a magnitude, in space. In case of 1 t ha^{-1} y^{-1} waste material loss considering the average heavy metal losses are as follows: Zn 292 g ha^{-1} y^{-1}, Pb 181 g ha^{-1} y^{-1}, Cu 113 g ha^{-1} y^{-1}, and Cd 17,9 g ha^{-1} y^{-1}. However, the role of vegetation is still significant, having at least medium cover factor can reduce the above mentioned values with one order of magnitude.

3.6. Applicability of FPXRF spectrometry in environmental assessment

The field portable X-ray fluorescence spectrometry is a useful and efficient method to provide great amount of data for risk assessment, and choosing adequate clean up technology, measured in situ, without sample preparation. Comparing results of FPXRF spectrometry and that of ICP-OES, linear relationship was found for the examined elements for each matrice. The determination coefficients are listed in *Table 7* for mine tailing materials. Results prove that in situ FPXRF measurements can be corrected using the equations calculated on the basis of data gained by limited number of laboratory analyses, for a certain matrice.

Table 7: **Linear regression analyses of element concentrations measured with FPXRF and ICP-OES in mining wastes; Y=a+bX**

element	*equation*	*N*		*standard error*	*T*	*P*	*r^2*
Zn	(ICP) = 66 + 0.998 (XRF)	55	a	142.8	0.46	*0.644*	**0.94**
			b	0.035	28.53	*0.000*	
Pb	(ICP) = - 62.4 + 1.21 (XRF)	42	a	52.41	-1.19	*0.241*	**0.90**
			b	0.065	18.62	*0.000*	
Cu	(ICP) = 58.9 + 0.664 (XRF)	34	a	43.53	1.35	*0.185*	0.60
			b	0.096	6.92	*0.000*	

Dependence of measured concentrations with FPXRF spectrometry is also linear from water content in the mining waste so that total element content can be estimated with extrapolation based on the calculated equations for each element (*Table 8*).

Table 8: **Linear regression analyses of dependence of element concentrations on water content in mining wastes; Y=a+bX**

element	*equation*	*N*		*standard error*	*T*	*P*	*r^2*
Zn	(Zn) = 15520 - 316 water %	30	a	510.7	31.59	*0.000*	**0.81**
			b	49.07	-9.52	*0.000*	
Pb	(Pb) = 2000 - 37.2 water %	30	a	24.43	81.89	*0.000*	**0.90**
			b	2.347	-15.86	*0.000*	
Cu	(Cu) = 1306 - 17.7 water %	27	a	72.66	77.97	*0.000*	0.18
			b	7.484	-2.36	*0.026*	

4. NEW SCIENTIFIC RESULTS

1. Sequential extraction results show that Zn, Cu, Cd and Pb are mostly in the aqua regia soluble fraction of acidic mining waste, which means that these heavy metals are mainly in sulphide forms. At the same time, considerable amount of Zn can be measured in the EDTA soluble fraction in neutral mining wastes. In addition, neutral mining wastes, where vegetation is present, contain significant amount of Pb in the NaOH soluble fraction.
2. According to the results of soil column experiments, constant heavy metal concentration of leaching solutions was measured after the initial desorption, which can be described with first order kinetics.
3. Comparing measured heavy metal concentrations in the function of pH in water solution to the results of model calculations considering only dissolution-precipitation processes, concentrations of Zn and Cd were found to be controlled by dissolution-precipitation, basically, while Cu and Pb concentrations are controlled by both sorption on the precipitating Fe-hydroxide above pH 3 and precipitation.
4. On the basis of pH, particle size distribution and heavy metal concentration profiles, zonality was found in both the unsaturated and saturated site of the studied mine tailing. At the same time, neutralization zone was formed in deeper layer in case of the saturated sample core.
5. Based on the results gained by the examination of the relationship among vegetation pattern, pH and heavy metal distribution in space in GIS and with statistical analyses, pH was found to control the absence/presence of vegetation at the mine tailings.
6. Significant correlation has been found between the element content of Lakanen-Erivö extract worked out for the estimation of potentially bioavailable element content and total element concentration, in mining wastes.
7. In case of acidic mining wastes the soluble heavy metal concentrations in the presence of the chelating agent were found not to exceed the measurable ones in the absence of it, at the same pH. While, in case of neutral mine wastes Zn and Cd concentrations are higher with one order of magnitude, Cu and Pb with more than one order of magnitude in the presence of chelating agent and converge to certain values. The findings are useful to evaluate the feasibility of phytoremediation, especially chelate induced phytoextraction technologies.

8. Additional data and information have been provided with the annual cenological survey of a mine tailing and quantification of the accumulation and translocation characteristics of the most abundant native plant species considered potentially applicable in phytoremediation is also important.
9. Method has been recommended for the in situ application of FPXRF spectrometry in mine tailings taking into consideration the matrice effect and water content. For different matrices (mining waste, soil and plant) mathematical relations have been given for Zn, Pb and Cu between FPXRF and ICP-OES results.

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