Thesis of Doctoral (PhD) Dissertation

EVALUATION OF NATURAL REMEDIATION TECHNOLOGIES

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1. INTRODUCTION

Risk assessment and evaluation of remediation technologies of sites where contaminants originate from mining activity and mining waste disposal are considered interdisciplinary areas. In mine spoils and flotation sludge reservoirs, heavy metal concentration with large spatial distribution may be up to 10^3 mg kg^{-1} which possesses important environmental risks both locally and diffusively by erosion. At the same time, the mobile fraction can be relatively low in mine spoils, since heavy metals are mostly in the form of insoluble precipitation. The presence of pyritic minerals can cause serious problems, because acidic weathering could mobilise the heavy metals. Thus the mobilised element content can enter to the food chain and can be leached to the ground water.

Fast determination of mineral properties and spatial distribution of mine spoils wastes and its minerals has an emphasized role in environmental state assessment of heavy metal contaminated sites. Based on the above mentioned, those sites, which requires further detailed investigation, could be separated. Thus so-called „hot spots" can be determined, which can only be remediated by conventional physical-chemical technologies. On the other hand, phytoremediation seems to be the optimal technology for the remediation of diffusively polluted mining sites with moderate heavy metal content in large spatial distribution (*Tamás, 2002; Simon, 1999; Simon, 2004*). The presence and the form of vegetation has also significant role in water management, landscaping of the contaminated site and it slows down erosion processes. Based on vegetation analysis, plant species can be determined for recultivation a phytoremediation.

2. THE OBJECTIVES OF THE RESEARCH

The main goals of my researches were to develop environmental state assessment methods and to reduce environmental risk with biological processes. My research field was the heavy metal polluted Szárazvölgyi flotation sludge reservoir in Gyöngyösoroszi (Hungary). Main objectives are the followings:

I. Possibilities of airborne hyperspectral environmental state assessment methods at the Szárazvölgyi flotation sludge:

- determination of the mineral properties of the site and mapping the spatial distribution of the minerals;
- determination of the vegetation types and analysing the spatial distribution of it.

II. Possibilities of phytostabilization at heavy metal contaminated mine spoils:

- applicability of sewage sludge compost, as an amendment for amelioration, in phytostabilization;
- determination of feasible plant species for phytostabilization based on its bioaccumulation properties;
- determination of feasible plant species for phytotoxicological tests based on its bioaccumulation properties.

III. Rhizofiltration possibilities of heavy metal contaminated waste:

- applicability of CMS[1] (industrial by-product), as complexing agent;
- quantification and qualification of the CMS for rhizofiltration;
- determination of heavy metal tolerant plant species with enhanced accumulation;
- Rhizofiltration possibilities of acid waste water leached from mine spoils.

IV. Applicability of new FPXRF[2] method at mine spoils:

- evaluation of data accuracy measured in mine spoils and plant tissues;
- evaluation the effect of water content on measurement accuracy in soils and mine spoils, and estimation of the real heavy metal content with different water content.

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[1] Conensed Molasses Soluble – by-product of lysine fermentation

[2] Field Portable X-Ray Fluorescence spectrometry

3. MATERIALS AND METHODS

3.1. The examined site and the contaminated matrix

The study area is a flotation sludge reservoir (Szárazvölgyi reservoir) of an abandoned Pb-Zn mining site, severely polluted by heavy metals. The mining site is situated in the northern part of Hungary, in Heves County in the Mátra Mts. near the village of Gyöngyösoroszi, in the valley of Toka stream. At the examined site the properties, structure of the mine spoil and the spatial distribution of heavy metals are different due to different technological origin (*Tamás* and *Kovács, 2003; Záray, 1991*).

Two mine spoils with different structure and physical –chemical characteristics were examined as a mean sample of the site. Physical properties were determined by direct sieving. After that the fine-grained part was separated by sedimentation in fluid bed based on the sedimentation speed of different grain sizes. The physical properties were also determined by the „Arany[3]" method. Based on the above mentioned methods, physical characteristics of the samples are sandy loam and sand.

In the case of pot and acid waste water experiments mine spoils with the sandy loam and sand physical characteristics were examined separately in seed germination tests and bioaccumulation tests. Sandy loam and sandy mine spoils in 1:1 ratios were used in complex induced rhizofiltration.

3.2. Airborne hyperspectral state assessment of the examined site

Applicability of hyperspectral mapping of minerals was evaluated for preparing *in-situ* phytoremediation technologies.

The spatial distributions of galena (PbS), goethite (FeO(OH)), jarosite ($KFe_3(SO_4)_2(OH)_6$), sphalerite ((Zn, Fe)S), pyrite (FeS_2) minerals were determined by SAM[4] mapping method at barren places. Parallel to the flight campaign heavy metal content of soil samples were examined from the area of the flotation sludge. The analysis of hyperspectral data was verified by the examination of mine tailing samples by a field portable X-ray fluorescence spectrometer, namely the NITON XL-700 gauge.

The role of airborne hyperspectral canopy analysis was examined for supporting phytoremediation by classifying the differences between vegetation types and plant species. Training sites with different spectral features were used to distinguish 8 vegetation types:

[3] Arany value * 1.15 ~ saturation percentage
[4] Spectral Angle Mapper

forest (*Quercus sp.*), young deciduous forest, common reed (*Phragmites sp.)* and aquatic plants, false indigo (*Amorpha fruticosa*), Australian pine (*Pinus nigra*), shrub – mainly sloe (*Prunus spinosa*) and dog rose (*Rosa silvestre*), blackberry (*Rubus caesius*), low biomass.

3.3. Characteristics of CMS complexing agent and sewage sludge compost

The chosen extracting agent is the CMS (Condensed Molasses Soluble), which is an environment friendly waste of lysine fermentation produced in large quantity with permanent availability.

Complexing agent was used to support rhizofiltration and sewage sludge compost was applied as an amendment for stabilizing the examined mine spoil.

To stabilize the examined mine spoil, such a sewage sludge compost was added, which fulfills the requirements of the 36/2006 (V. 18.) Ministry of Agriculture and Rural Development edict. Nutrients for plants were provided by Due to its the nutrient content, the sewage sludge compost could improve individually the nutrient capacity of the mine spoils.

3.4. Phytotoxicological surveys

Before examining complex induced rhizofiltration, toxicological tests, which consisted of *Lemna minor* growth inhibition test and *Lactuca sativa* seed germination test, were carried out in order to optimize the quantity of the CMS complexing agent.

Pot scale seed germination tests were established to suggest the quantity of sewage sludge to be utilized. The chosen test plants were lettuce (*Lactuca sativa*) "King of May", cabbage (*Brassica oleracea L. convar. Capitata provar. alba*) "giant of June", common sorrel (*Rumex acetosa*) and rye grass (*Lolium perenne*).

In the case of all tests (reproduction tests, pot scale and laboratory scale seed germination tests) the root length (mm) of the seedlings and the duckweed were measured at the end of the experiment, and descriptive statistics (arithmetic mean, median, modus and standard deviation) were calculated.

In case of reproduction test student's t-test was applied to examine significant differences between the root lengths of the control and the treated plant species

In case of pot and laboratory scale seed germination variance analysis with Tukey's test was applied to examine significant differences between the root lengths of plants, grown on different treatments. The effect of treatments on germination ability of the plant species was expressed in the percentage of the controls.

3.5. Heavy metal accumulation from water

Based on the CMS quantities, previously defined by toxicological test, small scale, model experiment was established to examine rhizofiltration. Applicability of common reed (*Phragmites australis*), sedge (*Carex flacca*) plant species as a potential heavy metal accumulator species were examined for complex induced rhizofiltration. The analytical measurements, such as acidity, electric conductivity, salt content, of the liquid phase were determined on the 2nd, 4th and 6th weeks. The heavy metal concentration of the matrix, the root and the shoot of common reed and sedge were determined on the 6th week. The effect of the complexing agent on bioaccumulation was also assessed. The non- toxic, optimal extracting agent concentration were determined as well to obtain maximum heavy metal bioaccumulation.

The sandy loam and sandy solid phases were extracted till equilibrium with deionised water in ratio of 1:2.5 to examine the rhizofiltration of acid heavy metal waste water. *Pistia stratiotes*, and *Eichhornia crassipes* pleustophyta, hydrocharoid species among aquatic plants to treat industrial waste water containing heavy metals have been chosen for biotransformation and translocation tests. The growth intensity was also monitored by measuring the biomass at week 1 and 6 for both species.

Accumulation properties of plant species were determined by calculating bioaccumulation and translocation factors. According to *Anton* and *Máthé-Gáspár* (*2005*), *Renoux et al.*, (*2001*) studies, bioconcentration factors (*BCF*) were calculated based on the element concentration in the liquid phase (*l*) and the plant element concentration (*p*) (Eq. 1).

$$BCF = element\ concentration_{(p)} / element\ concentration_{(l)} \qquad (1)$$

The translocation factors (*TLF*) were calculated from the root and shoot element concentrations (*r* and *s*, respectively) to examine the root accumulation properties of the plants (Eq. 2).

$$TLF = element\ concentration_{(r)} / element\ concentration_{(s)} \qquad (2)$$

3.6. Heavy metal accumulation from mine spoils

Based on the previously defined in toxicological tests, experiments were taken to select feasible plant species for phytostabilization. Four plant species (lettuce, cabbage, rye grass and common sorrel) were examined in pot scale and field scale experiments. Each treatment contained sandy and sandy loam mine spoil – sewage sludge compost mixtures with different compost rates. The bioavailable element content of the mixture was also measured. The acidity and electric conductivity of sandy and sandy loam mine spoil – sewage sludge mixtures were determined on the first and the last day of the experiments. Heavy metal concentrations of the plant roots and shoots were determined separately to determine the bioaccumulation. Bioaccumulation and translocation factors were calculated based on the element content of the mixtures and plants (root, shoot). The fresh biomass weight of the plant species was also measured at the last day of the experiment.

3.7. Applied analytical methods

Field portable and laboratory scale measurement tools were used to determine the heavy metal content of plant species, solid and liquid phases, as well as other environmental parameters such as pH and EC[5].

The applicability of field portable X-ray fluorescence (FPXRF) spectrometry in mining areas was evaluated, by comparing the non destructive FPXRF data to ICP-OES results. The samples had to be prepared by HNO_3 -H_2O_2 wet destruction in the case of ICP-OES. The examined mine spoil samples originated from the flotation sludge reservoir in Gyöngyösoroszi. Plant samples were taken from the biomass of bioaccumulation experiments.

The effect of water content on measurement accuracy was evaluated in 21 soil and mine spoil samples. Equitations were also determined to calibrate the disturbing effect of water content in solid phase.

[5] Electric conductivity

4. RESULTS AND DISCUSSION

4.1. Airborne hyperspectral survey of heavy metal contaminated flotation sludge reservoir

First the NDVI image is defined. The area with NDVI values lower than 0,3 is found to be mainly the uncovered slopes of the mine tailings, whereas the surrounding forests, shrubs are represented with an NDVI value above 0,3 based on the histograms of NDVI values. After that image masks were composed based on NDVI image for further investigations.

After masking the spatial distribution of the examined minerals (galena, goethite, jarosite, sphalerite, pyrite) were determined on the barren places (0-0.3 NDVI). Correlation analysis was carried out between the reflectance values of the sampling points and the SAM values. The results suggest, that 1.5-1.8 and 2-2.2 µm wavelength intervals are appropriate for mineral analysis (figure 1.), in correspondence with statements of *Kardeván et al.* (*2003*).

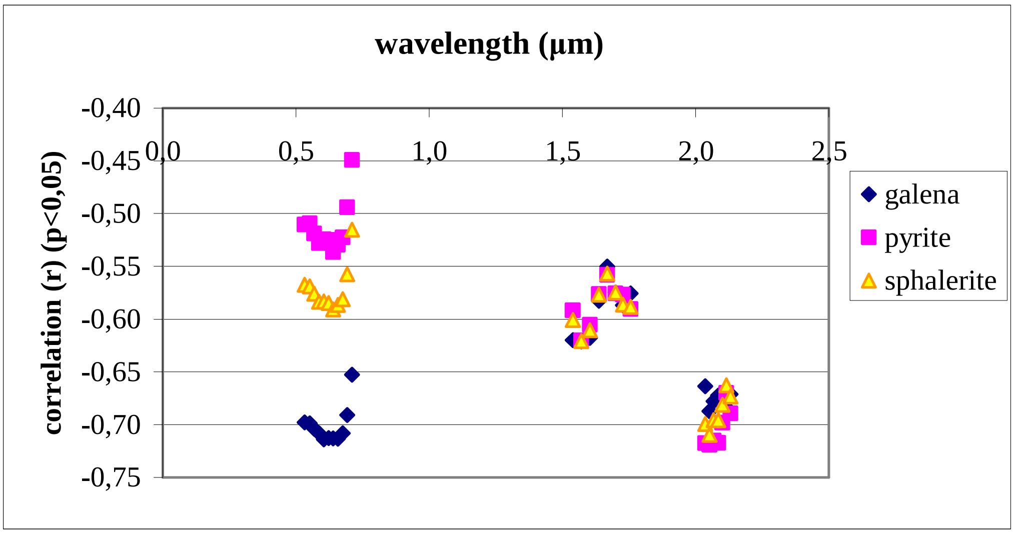

Figure 1. Relationship between reflectance and mineral mapping

Based on the SAM results, calculated from 1.5-1.8 and 2.0-2.2 µm wavelength intervals, galena, sphalerite and pyrite has similar spatial distribution. Strong (r=0,952) and significant ($P^6<0.05$) correlation has been found between galena and sphalerite between pyrite and sphalerite (r=0,950) as well as between pyrite and galena (r=0,999).

Besides the hyperspectral mapping, samples is found to be strongly polluted by heavy metals. Correlation coefficients between the different metal content of the samples were calculated.

[6] Level of significance

The highest correlations were found between Pb-Zn, Fe-Zn Fe-Pb, which show similar spatial distribution of these heavy metals as well (table 1.). These results prove the accuracy of hyperspectral analysis. .

Table 1. Correlations between heavy metals

	Pb-Zn	***Zn-Fe***	***Pb-Fe***	***Ni-Cr***	***Pb-As***	***Pb-Cu***	***Zn-Cu***	***As-Fe***	***As-Zn***	***Ni-Cu***	***Cu-Cr***
R	0.90*	0.88*	0.83*	0.33*	0.23*	0.41	0.17	0.18	0.21	0.12	0.06

*significant P<0.01

Correlations were also measured between zinc content and sphalerite, lead content and galena at sampling points, severely contaminated by Zn an Pb (Zn>1000 mg kg^{-1}; Pb>600 mg kg^{-1}). Moderate correlation (r=0.514) has been found between Pb content and galena at P<0.1 significance level. Fair correlation (r=0.615) has been found between Zn and sphalerite at P<0.01 significance level. Based on the results it can be stated, that it is possible to determine the accurate spatial distribution of the examined minerals by airborne hyperspectral analysis.

In the case of vegetation analysis training sites are selected based on ortophoto, topographic map, and GPS based field data collections. Supervised classification methods were used to distinguish 8 vegetation types. Using SAM classification moderate agreement is achieved, especially in case of using 496-727 nm wavelength intervals. This result shows that the pigments of plant biomass are sensitive for adsorption at this wavelength interval, in correspondence with *Berke et al.* (*2004*) statements.

Two kinds of accuracy indices, producer accuracy index and user accuracy index were used to measure the classification accuracy of one class. Producer accuracy is the probability that a pixel in the classification image is put into class x given the ground truth class is x. User Accuracy is the probability that the ground truth class is x given a pixel is put into class x in the classification image. Analyzing the producer and user accuracy of the classification using 496-727 nm spectral range, the classification resulted good, very good agreements in the case of Australian pine, forest mainly oak tree, shrub sites (table 2.) because of their stronger homogeneity more closed canopy, and lack of other vegetation disturbance. Owing to similar ecological demands, common reed and false indigo scattered and has mixed spectral features in one pixel which explains the moderate results of the classification. In addition, water has disturbing effect as well. The distribution of the shrubs is also very diffusive at the site of young deciduous forest. The weak user's accuracy of the shrub class also contributed to the moderate results.

Table 2. Results of classification for each group

Classes	*Producer's accuracy %*	*User's accuracy %*
Australian pine	66.5	99.5
False indigo	43.7	50.4
Low biomass	67.9	47.3
Shrub	69	47.0
Common reed	51.1	20.1
Blackberries	54,0	89.7
Oak forest	71.4	91.9
Young deciduous forest	44.2	42.4

4.2. Phytotoxicological tests

The frond number of duckweed (*Lemna minor*) has not changed during the reproduction test. Based on the root elongation of the duckweed and their statistical analysis, no feasible results were found regarding the applicable CMS concentration in phytotoxicological test.

In the case of 200 times diluted CMS + mine spoil treatment, lettuce (*Lactuca sativa*) germinated in 65% and was slightly poisonous, contrary to the poisonous results of the 100 times diluted CMS + mine spoil (table 3.).

Table 3. Root elongation of lettuce at 12th day

12th day	*Arithmetic mean*	*Standard deviation*	*Median*	*Modus*
Control	40.25^{e}	5.34	40	35
CMS 100	1.60^{a}	0.55	2	2
CMS 200	10.0^{b}	2.37	10	10
CMS 300	22.6^{c}	4.80	23	23
CMS 500	29.1^{d}	7.99	30.5	32
CMSm 100	7.42^{ab}	2.75	8	9
CMSm 200	22.2^{c}	2.91	22	20
CMSm 300	26.5^{cd}	5.58	28	30
CMSm 500	32.6^{d}	8.85	32	35

CMSm: CMS + mine spoil

There are no significant differences between treatments involved in one specified (a, b, c, d, e) group, ($P<0.05$)

In case of both sandy and sandy loam mine spoil treatments, rye grass, lettuce, cabbage and sorrel germination ability in the percentages of control plants, decreased till the addition of sewage sludge compost in 10 percentages. The maximal germination rate was achieved by application of sewage sludge compost in 5 percentages (table 4.). Based on the toxicological results of the four plant species, sewage sludge compost in 5 % ratio markedly decreased the toxicity of the mine spoils. The most outstanding positive effect of sewage sludge compost was observed on the germination of the rye grass (*Lolium perenne*), which was 110 and 112 % at 5 % compost addition. The results correspond to the high heavy metal tolerance of the rye grass. The sandy physical characteristics of the mine spoil supported the mobilization and bioavailability of the nutrient mobilization from sewage sludge compost. Owing to this and the less heavy metal content the germination ability of the examined plant species were larger in case of the sandy mine spoil.

Table 4. Germination ability of the examined plant species (in the percentages of the control)

	Lettuce[1]		*Cabbage*[2]		*Rye grass*[3]		*Sorrel*[4]	
Compost rate (%)	***Sandy loam***	***Sand***	***Sandy loam***	***Sand***	***Sandy loam***	***Sand***	***Sandy loam***	***Sand***
0	84.2	77.6	63.1	70.4	106	103	68.9	69.7
5	**91.4**	**88.6**	**76.4**	**73.3**	**110**	**112**	**80**	**93.2**
10	84.2	63.9	54.9	50	87.5	93.8	66.7	76.4
15	68.9	48.2	55.6	67.1	54.1	87	46.8	86.8
20	75.4	60.3	66.7	68.7	89.6	97.2	77.8	83.2
25	40.3	40.3	45.1	37.2	*102*	*102*	46.7	46.7
50	39.6	26.3	15.7	7.84	81.2	72.9	35.6	28.9
75	52.6	17.5	15.7	9.8	81.2	77.1	51.1	33.3
100	5.26	0	5.88	0	33.3	50	11.1	17.7

1: The control has germinated in 95 %.; 2: The control has germinated in 85 %.; 3: The control has germinated in 80 %.; 4: The control has germinated in 75 %.

Root elongations of the rye grass, common sorrel, lettuce and cabbage seedlings were differed between sandy and sandy loam mine spoil – sewage sludge compost treatments. (table 5.).

Table 5. Root elongation of the examined plant species (mm)

Compost rate (%)		***Lettuce***	***Cabbage***	***Rye grass***	***Sorrel***
sl	***0***	13.7^{c}	11.6^{bc}	20.3^{bc}	9.16^{cd}
	5	**18.4^{e}**	**18.6^{e}**	**22.9^{cd}**	**10.7^{bc}**
	10	15.7^{d}	15.7^{d}	25^{d}	7.37^{ab}
	15	13.9^{c}	16.9^{de}	19.1^{b}	6.36^{a}
	20	13.9^{c}	12.92^{c}	17.7^{b}	5.83^{a}
	25	3.88^{b}	1.76^{a}	13.6^{a}	5.67^{a}
	50	2.3^{a}	1.7^{a}	11.1^{a}	5.37^{a}
	75	2.09^{a}	1.3^{a}	12.7^{a}	7^{a}
control		16,2^{d}	9.76^{b}	22.2^{c}	12.4^{d}
s	***0***	12.6^{cd}	16.2^{d}	18.3^{c}	6.28^{b}
	5	**19.1^{f}**	**19.9^{e}**	**30.5^{f}**	**11.3^{a}**
	10	13.5^{d}	13.1^{c}	24.4^{e}	6.04^{a}
	15	10.5^{b}	14.4^{cd}	20.9^{cd}	6.08^{a}
	20	11.5^{bc}	16^{d}	18.5^{c}	5.44^{a}
	25	2.36^{a}	3^{a}	14.3^{b}	6.09^{a}
	50	2.76^{a}	0.67^{a}	9.46^{a}	5.31^{a}
	75	1.33^{a}	0.86^{a}	9.97^{a}	5.47^{a}
control		16.2^{e}	9.76^{b}	22.2^{de}	12.4^{b}

- sl –sandy loam; s- sand

There are no significant differences between values with the same letter index in one box (boxes (8 pieces are separated by thick lines), ($P<0.05$)

On both kinds of mine spoils the root elongations of the four plant species were significantly increased by the addition of sewage sludge compost in 5 % ratio, compared to the untreated mine spoil and control treatments. Compared to the control, only the common sorrel (*Rumex acetosa*) showed higher sensitivity for heavy metal toxicity

4.3. Results of bioaccumulation from water

Hydroponic experiments also prove the effective use of the extract of 200 times diluted CMS for complex induced rhizofiltration technology in correspondence with the ecotoxicological experiments. However, toxic effects of the CMS in 100 times dilution were not observed on common reed and sedge. The accumulation of As and Zn by sedge, Cd and Pb by common reed, Cu by both plant species is more efficient with extract of 100 times diluted CMSm. If the contamination properties of the matrix are specified to the abovementioned toxic metals, the optimal application would be the extract of 100 times diluted CMS with the given plant species.

Selection of the applicable plant species for complex induced rhizofiltration is based on the bioconcentration factors and the translocation factors (table 6.).

Table 6. Bioaccumulation and translocation factors of common reed and sedge in case of CMS + mine spoil treatments

Element	Dilution CMS+mine spoil	Bioconcentration factor		Translocation factor	
		Common reed	Sedge	Common reed	Sedge
Zn	Control	*	*	2.50	2.12
	100	388	329	2.33	5.63
	200	406	258	1.74	3.27
	500	500	174	4.96	1.47
Cu	Control	*	*	1.88	1.2
	100	502	371	20.9	3.34
	200	1853	332	9.54	3.26
	500	683	420	3.77	1.98
Pb	Control	*	*	3.47	*
	100	1046	1685	14.9	12.8
	200	*	*	*	29.1
	500	*	*	*	5.49
Cd	Control	*	*	*	*
	100	463	401	8.17	10.8
	200	937	1068	34.0	33.3
	500	548	127	*	2.99
As	100	295	2227	14.4	36.2
	200	668	1835	15.5	5.79
	500	2326	1339	4.96	3.10

* not calculated, because of below detection limit

Common reed accumulated the heavy metals (Zn, Cu and Cd) into its rhizome in higher extent than sedge, and the bioaccumulation of the common reed was also exceeded the sedge's one. Common reed and sedge are root accumulators in correspondence with the results found by *Jacob* and *Otte* (*2003*) *Soltz* and *Greger* (*2002*). Based on the bioconcentration factors and the translocation factors sedge is the optimal plant species for the rhizofiltration of Pb and As. In this study, the properties of the mine tailing, regarding to the element contents, are complex, so application of common reed is recommended with the extract of 200 diluted CMS.

Based on the heavy metal accumulation properties water lettuce (*Pistia stratiotes*) and water hyacinth (*Eichhornia crassipes*) are suitable for rhizofiltration of acidic waste water leached from mine spoil (table 7.) in correspondence with the results of several researches (*Tewari et al., 2008; Toppi et al., 2007*).

Especially Zn was accumulated in high extent, namely in 0.5% of the plant tissue due to the properties of the plants and the acidic pH.

Table 7. Element content of the examined plant species (mg kg^{-1})

		Pb	***As***	***Zn***	***Cu***	***Mn***	***Cd***
c	***water lettuce-root***	64.0	34.2	1174	*	284	*
	water lettuce-shoot	*	*	836	*	*	*
s	***water lettuce-root***	426	24.0	3480	245	2140	23.0
	water lettuce-shoot	70.6	5.12	367	23.0	256	3.31
	water hyacinth-root	680	71.0	4290	473	1000	17.4
	water hyacinth-shoot	297	34.0	1560	143	171	8.13
sl	***water lettuce-root***	1890	25.8	6100	378	744	82.4
	water lettuce-shoot	158	*	1070	28.3	64.2	9.60
	water hyacinth-root	1670	123	5080	363	1080	30.3
	water hyacinth-shoot	437	26.2	1600	143	200	12.9

* not detectable (ICP-OES)
s: sandy mine spoil; sl: sandy loam mine spoil; c: control

4.4. Results of bioaccumulation from mine spoils

The adaptability of rye grass and common sorrel were examined for phytostabilization based on the toxicological tests. The sensitivity of lettuce and cabbage was also examined against heavy metals in pot-experiments and field-experiments.

The pH of mining waste and sewage sludge compost was acidic (4.8-5.5) during the whole period of the experiment which increased the solvability of the heavy metals. Meanwhile, the pH increasing effect of the sewage sludge compost was obvious. According to the electric conductivity all the experiments had medium salt content (EC: 3.91-6.19). The utilization of the compost did not mainly affect (except the Cu content) the biological accessibility of the heavy metals (table 8.).

Table 8. The biologically accessible microelement content of mine spoil – compost treatments (mg kg^{-1})

	Cd	*Cu*	*Pb*	*Zn*	*As*
Control soil	0.19	*	*	1.58	*
Compost ratio (%)	***Sandy loam mine spoil – sewage sludge compost treatments***				
0	1.95	*	*	32	*
5	1.72	0.065	*	22.4	*
10	1.8	0.1	*	26.1	*
15	1.12	0.28	*	17	*
20	2.01	0.28	*	30.6	*
25	1.98	0.418	*	30.2	*
	Sandy mine spoil – sewage sludge compost treatments				
0	0.57	0.1	*	8.61	*
5	0.74	0.28	*	10.6	*
10	0.69	0.37	*	8.74	*
15	0.64	0.74	*	7.8	*
20	0.77	0.59	*	9.51	*
25	0.34	0.77	*	4.85	*

*: below detection limit (ICP-OES)

At the same time, with the increasing sewage sludge compost content of the treatments, the Cu content showed trend-like increase caused by the complexation ability of the compost.

The lettuce accumulated markedly more Cd compared to other plant species, and also accumulated a large amount of Pb, Zn and As as well. This result shows the sensitivity of this plant for heavy metals corresponding to the results of *Lehoczky et al.* (*2002*) and *Vér* (*2006*). The cabbage was more sensitive for the accumulation because the Pb, Zn, As and Cu concentration outnumbered the measured concentration in the lettuce species. Due to the results, the utilization of cabbage is advised for toxicity measurements although the lettuce can also give confidential results. The rye grass and the common sorrel accumulated less Pb, As and Zn in their tissues, which is advantageous for the phytostabilization and recultivation of contaminated (with certain metals) areas.

In case of both sandy and sandy loam mine spoils, the rye grass achieved its maximal fresh biomass weight by application of sewage sludge compost in 5 percentages. Same result was observed in case of common sorrel as well, although in the case of sandy loam mine spoil – sewage sludge mixture there were no higher biomass weight than in case of the control, probably because of the toxicity of high element content. Without any compost addition, growth of plants was inhibited because of the heavy metal toxicity (table 9.).

Table 9. Biomass of the examined plant species (g)

	Lettuce	*Cabbage*	*Rye grass*	*Sorrel*
Control	33	40	10	13
Compost ratio (%)	***Sandy loam mine spoil – sewage sludge compost treatments***			
0	2	4	4	4
5	**56**	**77**	**11**	**9**
10	38	49	9	6
15	47	44	5	5
20	32	38	6	7
25	33	39	6	4
Compost ratio (%)	***Sandy mine spoil – sewage sludge compost treatments***			
0	3	12	8	2
5	**78**	**51**	**10**	**17**
10	44	44	8	14
15	46	45	9	2
20	61	33	6	2
25	30	38	4	*

Based on field experiments *Rumex acetosa* germinated and grew very slightly on contaminated mine spoil – sewage sludge compost mixtures thus common sorrel is not recommended in itself to utilize for phytostabilization and recultivation.

4.5. Applicability of new FPXRF spectrometry in environmental state assessment

The methodological possibilities of field heavy metal detection were basically changed by the product of the NITON Corporation, as an accurate measurement tool to support phytoremediation. In 2008 the first generation equipment using a Cd-109 X-ray radiation source was exchanged at my institute to a new, second generation one using a miniaturized X-ray-tube. The experiments were set by the results of *Kovács* and *Tamás* (*2002*) on the calibration experiences of the first generation equipment. The correlation analysis between the microelement contents of soil, mine spoil samples measured by the FPXRF and ICP-OES showed that the NITON XLt 700 FPXRF equipment is appropriate for accurate determination of the total heavy metal content in prepared solid samples, especially to examine the Pb and Zn content. The NITON XLt 700 FPXRF is also suitable for the accurate determination of Pb, Zn and Mn concentration in plant samples.

On field, the heavy metal concentrations measured with FPXRF can diverge from the real concentrations depending on the moisture content of the sample. Linear estimative equations were set between moisture contents of the samples and the measured heavy metal contents at certain moisture to precise the measurement results in the case of Pb, Zn, Fe, Cu and Mn (table 10.).

Table 10. Relationship between the element content determined by FPXRF and the moisture content of the samples

categories		*equitations (Y=b+ax)*	*Standard deviation of the slope (a)*
element	***element content (mg/kg)***		
Pb	***0-600***	$Pb_{(moisture\%)}$=b-1.18(moisture%)	0.31
	600-2500	$Pb_{(moisture\%)}$=b-8.17(moisture%)	3.36
Zn	***0-1000***	$Zn_{(moisture\%)}$=b -4.16(moisture%)	1.28
	1000-4500	$Zn_{(moisture\%)}$=b -14.9(moisture%)	2.72
	4500<	$Zn_{(moisture\%)}$=b -65.2(moisture%)	27.8
Cu	***0-400***	$Cu_{(moisture\%)}$=b -3.34(moisture%)	0.81
	400-2500	$Cu_{(moisture\%)}$=b -10.5(moisture%)	3.07
Fe	***20000-55000***	$Fe_{(moisture\%)}$=b -377(moisture%)	73.6
Mn	***<2500***	$Mn_{(moisture\%)}$=b -25.5(moisture%)	7.45

According to the validation of the estimative equations, belonging to certain concentration-ranges, equitations are feasible for the precise determination of heavy metals in case of environmental state assessment.

5. NEW SCIENTIFIC RESULTS

The results are related to the scientific background of phytoremediation and environmental state assessment of heavy metal contaminated mining spoils in Gyöngyösoroszi and similar types of mine wastes.

1) The applicability of airborne hyperspectral remote sensing was certified to be feasible for the vegetation and mineralogical examination of heavy metal contaminated sites, which prove its role in the environmental state assessment.
2) The sewage sludge compost is determined to be utilized in 5% ratio for the amelioration of the heavy metal contaminated mine spoil in Gyöngyösoroszi to support phytostabilization.
3) Among the examined plant species the rye grass (*Lolium perenne*) has been found to be the most appropriate plant species for phytostabilization of heavy metal contaminated mine spoils and white cabbage (*Brassica oleracea L. convar. capitata provar. alba*) for toxicological surveys.
4) The complexation characteristics of the CMS lysine-fermentation waste and its feasibility in rhizofiltration technologies with 200 times dilution are certified.
5) According to the results, common reed (*Phragmites australis*) for the Zn, Cu, Cd, Ni, Cr, sedge (*Carex flacca*) for Pb and As can be applied in 200 times diluted CMS complex induced rhizofiltration technologies
6) Based on the heavy metal accumulation properties water lettuce (*Pistia stratiotes*) and water hyacinth (*Eichhornia crassipes*) are suitable for rhizofiltration of acidic waste water leached from mine spoil.
7) In order to precise the measurement results of the field portable X-ray fluorescent spectrometry, estimative equations were established to consider the moisture content of the samples. Thus the calculated heavy metal contents can be equal to element content, measured by ICP-OES with liquid destruction.

6. RESULTS, APPLICABLE IN PRACTISE

1. The examinations of the vegetation and the results of mineralogical researches ensured that the hyperspectral remote sensing is an applicable tool for the precise and cost-effective environmental state assessment of heavy metal contaminated areas. The hyperspectral technology gives large amount of information of the contaminated areas in very short time and may give the basics of sampling strategies and support environmental engineering.

2. Contrary to the widespread and expensive chemical and physical remediation technologies methodological improvement of cost-effective rhizofiltration technology was carried out in liquid phase. Common reed, sedge with the CMS complexing agent and water lettuce, water hyacinth can be applied for the rizofiltration of potential toxic heavy metals.

3. Phytostabilization seems to be the optimal cost effective technology for the remediation of diffusively polluted mining sites in large spatial distribution According to the results the rye grass (*Lolium perenne*) has been found to be the most appropriate plant species for phytostabilization with the utilization of the sewage sludge compost in 5% ratio.

4. Seed germination test with white cabbage is recommended to examine the phytotoxicology of heavy metal contaminated solid phases. Since the white cabbage possesses higher heavy metal bioaccumulation properties and sensitivity on stress than the lettuce, it gives more correct and more accurate toxicological results.

5. Based on the results of the NITON XLt 700 FPXRF the calculated estimative equations are applicable for accurate determination of heavy metals in case of environmental state assessment. This method has severely lower sampling costs than the ICP-OES. According to this, higher sampling-density can be used which makes the work of environmental engineers much more precise.

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