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COMPARISON OF BIO - AND MINERAL - SOLIDS FOR THE MOBILITY OF HEAVY METALS IN A HUNGARIAN MINE SPOIL

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Abstract: Biosolids (peat and FYM) and mineral solids (clay and zeolite) were compared for their effects on the mobility of six heavy metals: Cr, Ni, Pb, Cu. Zn and Ni under progressive acidification in a Hungarian mine spoil. Successive decline in pH enhanced the mobility of the heavy metals due to dissolution. Solubility behaviors of heavy metals followed the order Cd = Zn > Pb = Cu > Ni = Cr showing that metal ion pairs Zn – Cd, Pb – Cu and Ni – Cr had almost similar mobilities ranging between 29.34 – 34.54, 61.89 – 63.35 and 68.94 – 70.73 %, respectively under extremely acidic environment. Biosolids enhanced the mobility (by 1.16 – 11.69 %) in the order: FYM > peat over control owing to the dissolution of stable metal complexes; whereas mineral solids reduced it (by 3.39 – 14.05%) following the order: zeolite > clay due to retention of metals. The results suggested that polluted mine spoils should be amended with mineral solids like zeolite to reduce the risk of heavy metal contamination.

Key words: bio- and mineral - solids, heavy metals mobility, mine spoil

1. INTRODUCTION

Mining, metal processing, burning of fossil fuels, traffic, wastes disposal, and using sewage sludge, fertilizers and agro-chemicals in crop production enrich the soil with heavy metals (Weber et al., 2007). These metals may accumulate to phytotoxic levels, reducing plant growth and/or enhancing their concentrations in plants, and when such plants are consumed by animals and human beings, they can enter the food chain affecting their health (Lee et al., 2005). If these metals leach rapidly through soil, they can pollute the ground water supplies, creating the risk of environmental contamination (Alloway, 1995).

Mobility is a concept used to estimate the risk of environmental contamination by heavy metals (Domergue & Vedy, 1992). Nand Ram & Verloo (1985) characterized the mobile fraction of a metal as the sum of the soluble amount in the liquid phase and the amount retained by the solid phase that can be transferred to the liquid phase of the soil. Rieuwerts et al. (1998) emphasized the importance of mobility of metals to predict their concentrations in solution from the total concentrations. In general, metal mobilization depends on the concentration of the parent metal in the solution, which in turn depends on the sorption and retention of the same metal in soil (Sterckeman et al., 2000).

An understanding of the factors affecting mobility is essential to evaluate environmental quality. Therefore, the present study is focused with a mine spoil from Gyöngyösoroszi in Hungary, where mining of sulphide ores of heavy metals was in operation for about 4-decadres till 1985 (Simon et al., 2006). Careless handling of the mine spoils in this area caused serious heavy metal contamination of the local environment (Horváth & Gruiz, 1996). In view of this, the present investigation was conducted to compare the effects of bio- and mineral- solids on the mobility of six heavy metals viz.: Cr, Ni, Pb, Cu, Zn and Cd in a mine spoil from Gyöngyösoroszi enabling to devise means for remediation.

2. MATERIALS AND METHODS

2.1. Description of the study area

The study area - Gyöngyösoroszi (latitude – 47°50'34" N, longitude – 19°54'44" E and latitude-352 m above the Baltic sea level) is situated in Toka

– valley near the South-West part of Mátra Mountains in North Hungary lying about 90 km North-East of Budapest (Fig. 1). This area has former mines of Pb-Zn-Cu sulphides (Feigl et al., 2007). The climate of the region is temperate with continental features.

2.2. Sampling, amendments and chemical analysis

Composite sample of mine spoil (approximately 25 kg) was collected from 10 randomly selected spots, mixed well after grinding and packed into polyethylene bags. It was dried at 25°C to constant weight and sieved through 2-mm nylon mesh. Total contents of heavy metals i.e. Cr, Ni, Pb, Cu, Zn and Cd in the mine spoil were measured by inductively coupled plasma - mass spectrometry (ICP-MS) after digesting 0.1 g of mine spoil with aqua-regia (HNO_3 : HCl = 1:3).

For studying the mobility of heavy metals in the mine spoil, two solid amendments i.e. bio -and mineral - solids were used. For this, there were five treatments consisting of peat and farmyard manure (FYM) as biosolids; and clay (separated from soil) and zeolite as mineral solids, and a control (no amendment). Two kg of mine spoil for each treatment in duplicate was filled in plastic pots and treated with the amendments @ 1.5 % (equivalent to normal application rates of FYM and zeolite in agriculture). The treated samples were mixed homogeneously and incubated for a fortnight at optimal moisture level. The pH of each treatment was determined.

Change in pH results in a transfer of the metal from one phase to another, thus permits the estimation of mobility in the soil. Therefore, potentially mobilizable fraction of heavy metals in different treatments was determined under progressive acidification (Original pH, pH 4.0, pH 2.0 and pH 0.5), by following the procedure of Nand Ram & Verloo (1985). For this, 40 ml distilled water was added to 10 g mine spoil and the desired pH was adjusted by adding HNO_3 with the help of an automatic titrator; which recorded the milliequilents (me) of HNO_3 needed at each specified pH. The suspensions were constantly stirred for 30 min. and volumes were made up to 50 ml with distilled water. After centrifuging and filtration, the concentrations of Cr, Ni, Pb, Cu, Zn and Cd in each of the treatment were determined in the filtrate by ICP-MS.

Mobility of heavy metals was computed as:

$$\text{Mobility (\%)} = \frac{\text{Soluble concentration of metal (mg kg}^{-1}\text{)}}{\text{Total content of the metal (mg kg}^{-1}\text{)}} \times 100$$

Figure 1. Location of Gyöngyösoroszi, near south-west of Mátra Mountain in North Hungary

3. RESULTS AND DISCUSSION

3.1 Total content of heavy metals

The total contents of heavy metals extractable with aqua-regia in the mine spoil from Gyöngyösoroszi are shown in table 1. Concentration of all the heavy metals under study except Cr exceeded the Hungarian permissible tolerance limits for heavy metals (Várallyay, 1993) Therefore, this mine spoil was polluted with heavy metals. Extremely high contents of Pb, Cu and Zn in the mine spoil are attributed to the previous mining of galena, chalcopyrite and sphalerite ore minerals of the respective metals in the study area. The original pH of mine spoils under different treatments ranged from 7.7 to 7.9.

Table 1. Total content of heavy metals (mg kg^{-1}) in mine spoil from Gyöngyösoroszi

Heavy metals	Total content (mg kg^{-1})
Cr	14.4
Ni	123.8
Pb	3879.0
Cu	4553.9
Zn	12685.0
Cd	15.4

3.2. Mobility of heavy metals under progressive acidification

Mobility of the heavy metals under progressive acidification was measured at four pH values (original pH, pH 4.0, pH 2.0, and pH 0.5) adjusted by adding HNO_3. to various treatments of the mine spoil The mobility (%) of heavy metals is given in table 2 whereas their mobility patterns at various pHs are illustrated in figure 2 The buffering capacity of the mine spoil as affected by addition of bio - and mineral - solids gave some variation in the me of HNO_3 needed to bring the pH of the mine spoil to a desired value. At lower pH values, the presence of biosolids i.e. peat and FYM produced brown color in the equilibrium solution.

At the original pH of the mine spoil, the soluble amounts all the heavy metals were not at all detected. Moreover, Cr up to pH 2.0, and Pb and Cu up to pH 4.0 were completely retained by the mine spoil, while Ni, Zn and Cd were slightly soluble having mean mobilities of 2.81, 7.62 and 10.29, respectively. At pH 2.0, about 20% of Pb and Cu, and 40% of Zn and Cd were brought into solution, whereas 88% of Ni was still adsorbed on the mine spoil. Further acidification to pH 0.5 led to a tremendous increase in the mobility of Cr (67-fold) and about 2–3 times improvement in the mobilities of all other metals as compared to those at pH at 2.0. This is attributed to differential dissolution rates of heavy metals at various pH. Moreover, metal ion pairs Ni-Cr, Pb-Cu and Zn-Cd resulted in almost identical patterns with mean mobility in the range of 29.34–34.54, 61.98–63.35 and 68.94–70.73 %, for the respective metal – pairs under extremely acidic condition (pH 0.5). Oborn & Linde (2001) also reported that Cd and Zn were easily extractable as compared to Cu and Pb. More over the solubility behavior of heavy metals followed the order: Cd = Zn > Pb = Cu > Ni = Cr; which agreed to the order of metal retention (Ok et al., 2007).

It is evident from the results that the mobilizable fraction of heavy metals increased with progressive acidification i.e. from the original pH to pH 0.5 of the mine spoil corroborating the findings of Thornton (1996). It is partly ascribed to competition of H^+ (and Al^{3+}) ions for adsorption sites at low pH leading to decreased metal retention (Nand Ram & Verloo, 1985), as well as metal hydrolysis at higher pH levels followed by strong, preferential adsorption of resulting metal hydroxide complexes (Basta & Tabatabai, 1992).

3.3. Relationship between mobility and pH

For the relationship of mobility and various pH, the regression equations and the correlation coefficients (R^2) were computed between natural logarithm (ln) of mobility (%) and varying pHs (Table 3). Highly significant value of R^2 (0.83^{**}–0.99^{**}) revealed the existence of linear relationship between the solubility of heavy metals and pH. In addition, negative value of the regression coefficients i.e. slope (b) in the linear regression equations also implied that progressive acidification (decline in pH from original pH to pH 0.5) increased the mobilizable fraction of all the heavy metals. Xian & Shokohifard (1989) also observed increased levels of exchangeable Pb, Cd and Zn with decrease in soil pH.

3.4. Effect of bio- and mineral - solids on the mobility of heavy metals

The effects of bio - and mineral - solid amendments on the heavy metals mobility (Relative to control) are given in table 4; whereas the patterns of mobility under different treatments are depicted in figure 3. The results revealed that amending mine spoil with biosolids, the solubility of the heavy metals enhanced; whereas with mineral solids it declined under progressive acidification.

Table 2. Mobilty (%) of heavy metals under different treatments with progressive acidification of Gyöngyösoroszi mine spoil

Treatments	me HNO_3 (to adjust pH)	Cr	Ni	Pb	Cu	Zn	Cd
pH 4.0							
Control	1.6	0.13	2.90	0.65	0.85	7.94	10.40
Peat	1.5	0.14	3.00	0.76	0.90	8.50	10.96
FYM	1.5	0.15	3.14	0.81	0.95	9.21	11.50
Clay	1.4	0.12	2.74	0.60	0.70	6.45	9.40
Zeolite	1.3	0.12	2.28	0.57	0.65	6.00	9.20
Mean		**0.12**	**2.81**	**0.68**	**0.81**	**7.62**	**10.29**
pH 2.0							
Control	4.8	0.40	12.00	24.82	19.75	40.25	37.63
Peat	5.4	0.50	12.50	25.30	20.62	42.17	38.87
FYM	5.6	0.60	13.16	27.30	23.08	44.30	42.37
Clay	5.2	0.35	11.63	21.30	17.93	37.84	35.23
Zeolite	5.0	0.32	11.12	20.22	15.88	35.91	33.10
Mean		**0.43**	**12.08**	**23.79**	**19.45**	**40.09**	**37.44**
pH 0.5							
Control	40.0	28.18	36.00	63.89	64.22	72.50	70.90
Peat	41.6	31.30	37.72	65.05	66.92	75.80	72.50
FYM	38.4	38.98	39.65	75.58	69.62	77.66	75.50
Clay	41.0	24.79	30.37	55.07	60.77	65.40	65.30
Zeolite	39.6	23.68	28.96	49.84	55.20	62.30	60.50
Mean		**29.39**	**34.54**	**61.89**	**63.35**	**70.73**	**68.94**

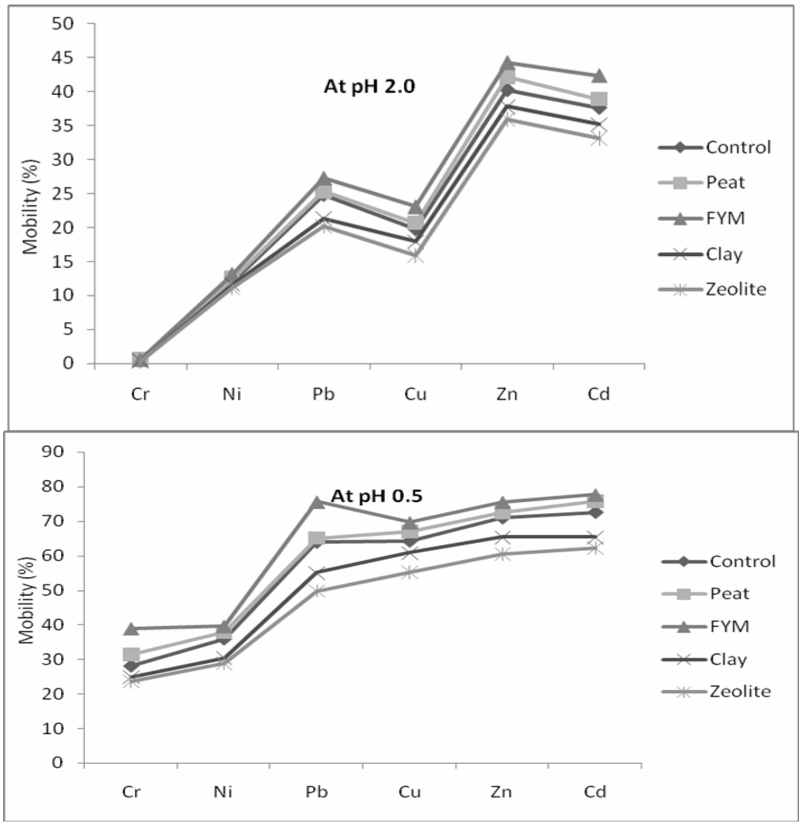

Figure 2. Mobility patterns of heavy metals at various pH

Amending mine spoil with biosolids, the mobility (%) of heavy metals rose by + 1.16 (Pb) to + 3.30 (Zn) for peat and by +3.65 (Ni) to +11.69 (Pb) for FYM over control at extremely acidic conditions. It may be attributed to reduced stability of complexes of heavy metals with humic substances of biosolids under progressive acidification. Nand Ram & Verloo (1985) also noticed highly increased contents of dissolved heavy metals in soil amended with various sources of organic matter owing to the decomposition of organo-metallic complexes. The heavy metals among biosolids followed the order: FYM > Peat. Relatively greater mobility with FYM in comparison to peat is owing to the enhanced synthesis of fulvic acid (FA) fraction of humic substances using FYM being more hydrophilic and less humified (Das & Nand Ram, 2006) resulting in formation of soluble metal–FA complexes with lesser stability (Nand Ram & Raman, 1984).

Table 3. Regression equations and correlation coefficients (R^2) between natural logarithm (ln) of mobility (%) and varying pH

Heavy metals	**Treatments**	**Regression equation** (y = a+ b x) where y = ln mobility (%) , and x = pH	**Correlation coefficient (R^2)**
Cr	Control	y = 3.34 – 1.48 x	0.84**
	Peat	y = 3.50 – 1.50 x	0.86**
	FYM	y = 3.75 – 1.54 x	0.87**
	Clay	y = 3.20 – 1.47 x	0.84**
	Zeolite	y = 3.12 – 1.45 x	0.83**
Ni	Control	y = 3.93 – 0.72 x	0.99**
	Peat	y = 3.99 – 0.72 x	0.99**
	FYM	y = 4.05 – 0.73 x	0.99**
	Clay	y = 3.75 – 0.66 x	0.99**
	Zeolite	y = 3.77 – 0.73 x	0.99**
Pb	Control	y = 5.21 – 1.34 x	0.94**
	Peat	y = 5.18 –1.29 x	0.94**
	FYM	y = 5.34 – 1.32 x	0.95**
	Clay	y = 5.04 – 1.32 x	0.94**
	Zeolite	y = 4.95 – 1.30 x	0.94**
Cu	Control	y = 5.04 –1.25 x	0.97**
	Peat	y = 5.08 – 1.25 x	0.97**
	FYM	y = 5.14 – 1.25 x	0.96**
	Clay	y = 5.01 – 1.30 x	0.97**
	Zeolite	y = 4.99 – 1.31 x	0.98**
Zn	Control	y = 4.74 – 0.64 x	0.97**
	Peat	y = 5.32 – 0.93 x	0.97**
	FYM	y = 5.35 – 0.93 x	0.97**
	Clay	y = 4.69 – 0.67 x	0.96**
	Zeolite	y = 4.64 – 0.68 x	0.95**
Ni	Control	y = 4.61 – 0.55 x	0.99**
	Peat	y = 4.62 – 0.55 x	0.99**
	FYM	y = 5.35 – 0.92 x	0.96**
	Clay	y = 4.54 – 0.56 x	0.98**
	Zeolite	y = 4.45 – 0.54 x	0.99**

Table 4. Effects of bio- and mineral solids on heavy metals mobility (%) over control

Treatments	**Cr**	**Ni**	**Pb**	**Cu**	**Zn**	**Cd**
pH 4.0						
Peat	+0.01	+0.10	+0.11	+0.05	0.56	+0.56
FYM	+0.02	+0.24	+0.26	+0.10	+1.27	+1.10
Clay	–0.03	–0.16	–0.05	–0.15	–1.49	–1.00
Zeolite	–0.03	–0.62	–0.08	–0.20	–1.94	–1.20
pH 2.0						
Peat	+0.01	+0.50	+0.48	+0.87	+1.92	+1.24
FYM	+0.20	+1.16	+2.48	+3.33	+4.05	+4.74
Clay	–0.05	–0.39	–3.52	–1.82	–2.41	–2.40
Zeolite	–0.08	–0.88	–4.60	–3.87	–4.34	–4.53
pH 0.5						
Peat	+3.12	+1.72	+1.16	+2.70	+3.30	+1.60
FYM	+10.80	+3.65	+11.69	+5.40	+5.16	+4.60
Clay	–3.39	–5.63	–8.82	–3.45	–7.10	–5.60
Zeolite	–4.50	–7.04	–14.05	–9.02	–10.20	–10.40

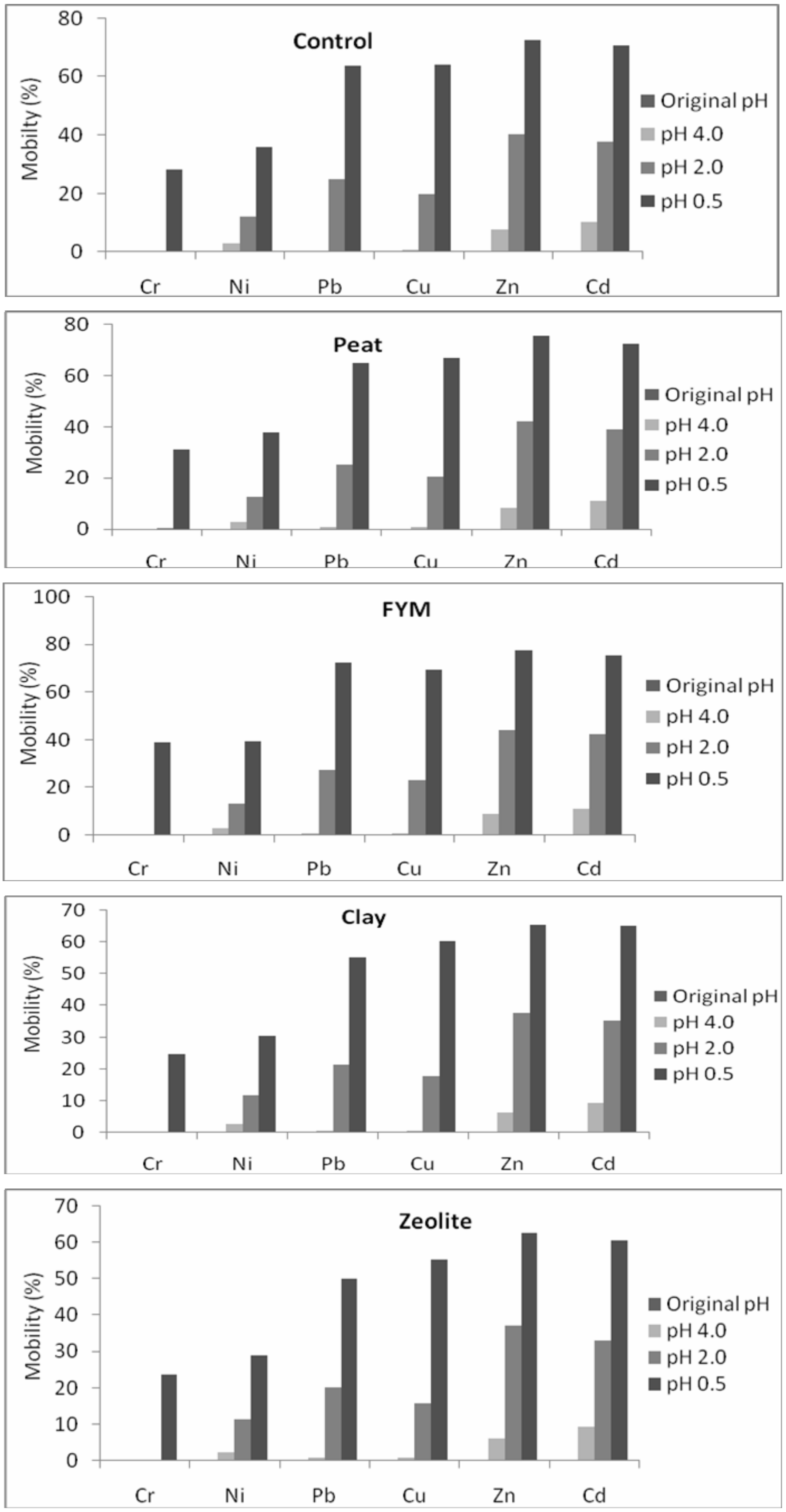

Figure 3. Effect of bio-and mineral-solids on the mobility of heavy metals

The magnitude of drop in metals mobility with mineral solids was to the tune of - 3.39 (Cr) to - 8.82 (Pb) % for clay and - 4.5 (Cr) to - 14.05 (Pb) % for zeolite as compared to control at the same pH showing the order: zeolite > clay. Garcia-Sanchez et al. (1999) also observed larger reduction in heavy metals mobility by zeolite, whereas clay showed lesser decline due to poor adsorption capacity. The Pb was evenly distributed within zeolite particle but Cd accumulated on particle surfaces because of low hydration energy (Yuan et al., 1999). Moreover, zeolites have been reported effective adsorbent for removing heavy metals from aqueous solutions (Cabrera et al., 2005). From the results it evident that mineral solid amendments especially zeolite should be used for decreasing the risk of heavy metal contamination to remediate the mine spoils. Alternatively, it is suggested that the polluted mine spoils may be used in heavy clayey soils to reduce their heavy metals toxicity.

4. CONCLUSIONS

The study has revealed the pollution of Hungarian mine spoil with Pb, Cu and Zn owing to the previous mining of the respective metal sulphide ore minerals in Gyöngyösoroszi area. Progressive acidification of mine spoil enhanced the mobilities of heavy metals and followed the order Cd = Zn > Pb = Cu > Ni = Cr due to differences in their dissolution rates

Amending mine spoil with biosolids enhanced the mobility of the heavy metals over control in the order of FYM > Peat as a result of reduced stability of heavy metal-complexes with humic substances of the biosolids. Whereas using mineral solid amendments, heavy metals mobility declined in order of zeolite > clay. Therefore, it is suggested that mineral solids especially zeolote should be used for decreasing the risk of heavy metal contamination to remediate the mine spoils. Alternatively, polluted mine spoils may be used in heavy clayey soils to reduce their heavy metals toxicity.

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