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Influence of amendments and aided phytostabilization on metal availability and mobility in Pb/Zn mine tailings

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ABSTRACT

A greenhouse experiment was conducted to evaluate the effect of four different amendments, bone mill, bottom ash, furnace slag, and red mud, as immobilizing agents and the plant species *Miscanthus sinensis* and *Pteridium aquilinum* in aided phytostabilization of Pb/Zn mine tailings. The effects of amendments and plants on the availability and mobility of heavy metals were evaluated using single extraction, sequential extraction, pore-water analysis, and determination of heavy metal concentrations in plants. The application of Fe-rich amendments significantly reduced the amount of soluble and extractable heavy metals in the tailings ($p < 0.05$). Furnace slag and *M. sinensis* reduced $CaCl_2$-extractable heavy metals by 56–91%, red mud and *P. aquilinum* treatment was the most effective at decreasing bioaccessible Pb, reducing it to 34% of the total Pb. Compared to control, water soluble Cd, Cu, Pb, and Zn were reduced by 99, 99, 98, and 99%, respectively, in the red mud and *P. aquilinum* tailings. *M. sinensis* accumulated heavy metals mainly in the root, and had lower translocation factors compared with P. *aquilinum*. The results of this study suggest that *M. sinensis* can be used in aided phytostabilization for these types of mine tailings and Fe-rich amendments are effective for the in situ immobilization of metals.

1. Introduction

When mining ceases, large industrial mines are often abandoned, leaving behind a legacy of abandoned tips and tailings (Tordoff et al., 2000). According to Ministry of Trade, Industry and Energy of Korea (KMoTIE), there are ~2200 metallic mines in Korea, >96% of which are now closed and may be long-term sources of environmental pollution (KMoTIE, 2010).

Among mine wastes, tailings are known to have the largest environmental impact, as they have the highest concentrations of toxic elements and are the most susceptible to wind dispersal and water erosion (Dudka and Adriano, 1997; Wong et al., 1998), which are the main mechanisms for the loss of metals from mine tailings. The effects of these pollutants can reach local and, in some cases, regional scales (Rybicka, 1996), affecting urban and agricultural areas. Consequently, these pollutants can pose a risk to human health (Conesa et al., 2007).

Conventional technologies used in the management of mine tailings have focused on physical and chemical stabilization. Physical stabilization involves covering unstable mine waste with innocuous materials to reduce wind dispersion and water erosion. Chemical stabilization aims to prevent the loss of heavy metals by applying chemical agents that provide a crust that is resistant to the effects of wind and water. The use of chemical methods is restricted due to their lack of permanence and the need for regular inspections. Moreover, the widespread application of these physico-chemical techniques is limited by the availability of suitable materials and the high costs of transportation (Tordoff et al., 2000).

Phytostabilization, the establishment of a vegetation cap on mine tailings using plants, is a remediation strategy that is currently being explored to ameliorate wind dispersion and water erosion of tailings in a cost-effective manner (Mendez and Maier, 2008; Alvarenga et al., 2009a,b; Cunningham et al., 1995). Many abandoned and post-operative mine tailing dams are barren or have minimal to slow natural vegetative colonization. Common

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physicochemical limitations to plant growth on mine tailings include extreme pH, high salt content, lack of required nutrients, metal toxicities, high bulk density, lack of structure, slow water infiltration, poor water retention, and low air permeability (Wong, 2003). To overcome these limitations, amendments may be added. In situ stabilization of metals can be combined with phytostabilization to overcome the physicochemical limitations and establish a green cover. If such revegetation is performed in combination with immobilizing agents, it can be considered as aided phytostabilization (Alvarenga et al., 2009a,b).

The selection of appropriate plant species is crucial to achieving successful phytostabilization. The plants chosen should develop an extensive root system and a large amount of biomass in the presence of high concentrations of heavy metals while keeping the translocation of metals from roots to shoots as low as possible and thereby limiting the propagation of metals into the food chain (Pulford and Watson, 2003; Rizzi et al., 2004). In some cases, plant growth may enhance metal leaching due to soil acidification and the production of dissolved organic matter (Mayer, 1998). Hence, with respect to risk control, it is very critical to select plant species, for phytostabilization purposes, that cause low soil acidification and minimal translocation of metals to their leaves (Mertens et al., 2007).

The aim of the current study was to assess the effects of four different amendments as immobilizing agents and to evaluate the potential use of two plants that are native to Korea, *M. sinensis* and *Pteridium aquilinum*, in aided phytostabilization of heavy-metal-contaminated mine tailings. Based on these results, it will be possible to further elucidate the benefits and/or potential risks, derived from the application of different types of amendments and plant species, in the remediation of contaminated mine tailings.

2. Methods

2.1. Experimental set-up

Mine tailings were obtained from the Suseong Pb/Zn mining area in Chungnam Province, Korea. Four kinds of amendments were examined: bone mill (BM), furnace slag (FS), bottom ash (BA), and red mud (RM); these were obtained from a commercial fertilizer vendor, a steel plant, a coal power plant, and an alumina smelter, respectively. Numerous amendments have been proposed and tested for in situ stabilization of heavy metals including for industrial products such as furnace slag and red mud. Their use also achieves reduction of waste disposal through revalorization of industrial wastes into industrial co-products. Examples are the use of red mud and furnace slag. Red mud is produced in large quantities during the extraction of alumina from bauxite annually; 0.2 Mt of red mud are produced in Korea. Huge amounts of furnace slag are also produced; 9 Mt slags are annually produced in Korea. Subsamples of tailings and amendments were air dried, passed through a 2-mm sieve, and subjected to chemical characterization. The pH and electrical conductivity (EC) of each sample were determined by the glass electrode method (1:5 solid:liquid ratio; Thomas, 1996). Pseudo-total heavy metal (Cd, Cu, Pb, Zn) concentrations were determined by inductively coupled plasma optical emission spectrometry (ICP-OES) following the digestion of samples with aqua regia according to ISO 11466 (1995). The main chemical characteristics of the experimental tailings and amendments are listed in Table 1. The tailings contained 32.46, 388.31, 3,889, and 2210 mg kg^{-1} Cd, Cu, Pb, and Zn, respectively.

The amendments were added to the tailings at 2% (w/w), and the combination was mixed thoroughly to obtain homogeneity with cement mixer, followed by equilibration for 40 d. *M. sinensis* and *P. aquilinum* seedlings were then transplanted into the tailings (one seedling/pot, three pots/treatment). The pot used in this experiment was 1 kg capacity, 20 cm diameter and 25 cm height. The trials were conducted under controlled greenhouse conditions (temperature: 15–25 °C; relative humidity: 60–70%) and a daily watering schedule.

M. sinensis is a flowering species in the grass family Poaceae and is native to Korea. It is an herbaceous perennial grass that grows to 0.8–2 m tall, forming dense clumps from an underground rhizome. *P. aquilinum* is a species of fern that is found in temperate regions. It is an herbaceous perennial plant that is deciduous in winter. The large, roughly triangular fronds are produced singly, rising upward from an underground rhizome, and growing to 1–3 m in length. Both plants tested in this study have well-developed root systems.

Table 1
Chemical properties and total metal concentrations of the tailing and amendments.

Parameter	Tailing	BM[a]	FS	BA	RM
pH[b]	7.64	8.91	10.57	9.23	11.32
Total carbon (%)	–[d]	13.7	–	–	–
Total nitrogen (%)	–	4.27	–	–	–
Cd (mg kg^{-1})[c]	32.46	0.08	1.70	0.14	2.12
Cu (mg kg^{-1})	388.31	1.88	10.70	11.61	6.83
Pb (mg kg^{-1})	3889.13	5.81	78.20	2.82	78.21
Zn (mg kg^{-1})	2210.85	115.11	60.60	11.00	60.61

Mean values of three replicates.
[a] BM, bone meal; FS, furnace slag; BA, bottom ash; RM, red mud.
[b] pH of tailing and amendments measured at the ratio of soil to H_2O as 1:5 (mass:volume).
[c] Aqua regia extractable metal concentration.
[d] "–"means not determined.

2.2. Heavy metal availability and mobility

The effect of plants and amendments on contaminant extractability was evaluated by extraction with a 0.5 M $CaCl_2$ solution according to the procedure of Esnaola and Millan (1998). Briefly, 3 g of tailings was added to 30 mL of 0.5 M $CaCl_2$ in 40-mL polypropylene centrifuge tubes. The tubes were shaken on a wrist-action shaker for 2 h, centrifuged for 20 min at 5100 g, and then filtered through Whatman GF/F 0.7-μm borosilicate glass filters. The availability of Pb to the human gastrointestinal (GI) system via ingested soil was estimated using the modified physiologically based extraction test (PBET) described by Geebelen et al. (2003). Briefly, 0.35 g of tailings was shaken (30 rpm) with synthetic gastric solution (0.4 M glycine; pH 2.2) for 1 h at 37 °C and then filtered through a Whatman GF/F 0.7-μm borosilicate glass filter. Changes in the fraction of heavy metals were determined by sequential extraction, as described by Tessier et al. (1979). Briefly, heavy metals were separated into five operationally defined fractions: extractable with 1 M NH_4OAc at pH 7 (exchangeable, F1), extractable with 1 M NH_4OAc at pH 5 (associated with carbonate, F2), extractable with hydroxylamine (associated mainly with Fe–Mn oxides, F3), extractable with H_2O_2 in 1 M HNO_3 (strongly complexed with organic matter, F4), and $HClO_4$ and HF-extractable (residual, F5).

Using the sequential extraction results, the mobility factor (MF) value was calculated based on the following equation (Narwal et al., 1999):

$$MF = \frac{F1 + F2}{F1 + F2 + F3 + F4 + F5} \times 100$$

2.3. Heavy metal leachability

To evaluate the effects of amendments and plants on heavy metal leachability, substrate pore-water samples were collected