DETERMINATION OF PHYTOREMEDIATION POTENTIAL OF DESERT BROOM GROWN IN A MINE TAILINGS RECLAMATION PROJECT[1]

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Abstract: This research was conducted out at a copper mine tailings reclamation project (CMTRP) located in the Globe-Miami mining district near Claypool, AZ, USA. Desert broom (*Baccharis sarothroides*) is a very environmentally friendly and available plant that might have phytoremediation potential, grows at the CMTRP. Therefore, in this research metal concentrations both in the tailings and plants (elemental ratio from soil to plant) were investigated. The metal concentrations in the soil cover and tailings were determined using ICP-OES. Based on the concentration, the elements were classified as high level elements (HLE): (K > Al > Fe > S> Ca > Mg > Na > Cu > P) and low level elements (LLE): (Mn > Pb > Mo > Cr > Vn > Zn > As > Ni > Co). The concentration of Cu, Pb, Mo, Cr, Zn, As, Ni, and Co in tailings was 454.9, 209.7, 89.32, 85.6, 51.2, 49.2, 39.3, and 36.3 mg/kg, respectively. The concentration for HLE and LLE in the soil cover was 10~15% higher than that of the tailings except for Cu and Mo. The concentration of Cu, Pb, Mo, Cr, Zn, As, Ni, and Co in desert broom (*Baccharis sarothroides*) was 819.3, 152.7, 74.3, 56.7, 39.9, 43.1, 97.3, and 26.3 mg/kg for roots and 1212.7, 102.2, 106.7, 104.4, 56.12, 34.3, 31.2, and 10.1 mg/kg for shoots, respectively. Considering the translocation factor (TF), enrichment coefficient (EC), and the concentration of elements in shoots 10 – 500 times more than those in a normal plant, desert broom could be a potential hyperaccumulator of Cu, Pb, Cr, Zn, As, and Ni for application in phytoremediation of copper mine tailings.

Additional Key Words: Phytoremediation, Hyperaccumulator, Heavy metals, Mine tailings, Desert broom.

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Introduction

Utilization of the earth's natural resources is fundamental to the survival and prosperity of society. However, removal of natural resources from one environment to another for utilization impacts both environments to some extent. Tailings from mining activities are one of the best examples of such a scenario. Heavy metals and metalloids released from mine tailings may cause severe damage to ecosystems including plants, animals, micro-organisms and human health (Kim et al. 2003). Uncontrolled mining activities can generate a large amount of particulate emissions and waste containing heavy metals and metalloids that can contaminate the surroundings—soil, water and air. Such effects may be particularly serious and may pose a severe ecological and human health risk when mining activities are located in the vicinity of urban environments. Therefore, it is necessary to minimize or mitigate the impacts of resource utilization to the extent reasonably feasible.

A range of technologies has been used for the removal of metals for soil remediation. Many of these methods have high maintenance costs and may cause secondary pollution. A promising approach is phytoremediation technology, where living plants are used to remove trace metals from impacted sites. Significant research has been conducted on phytoremediation for metal-sorption capacity (US EPA, 2000; Meagher, 2000; Mitch, 2002; Glick, 2003; Pulford and Watson, 2003). A series of fascinating scientific discoveries combined with an interdisciplinary research approach has allowed the development of this idea into a promising, low-cost and environmentally friendly technology (Chaney et al. 1997, 2000; Baker et al., 1991; Eapen and Dsouza, 2005; Krämer 2005). Phytoremediation can be applied to both organic and inorganic pollutants, present in soil substrates (e.g. soil), in liquid substrates (e.g. water), and in the air (Salt et al., 1998; Adler et al., 1994). Phytoremediation is currently divided into many types: phytoextraction (hyperaccumulator), phytodegradation, rhizofiltration, phytostabilization and phytovolatilization (Salt et al., 1998).

Hyperaccumulators that are often found growing in impacted areas can naturally accumulate higher quantities of heavy metals in their shoots than in their roots. There are numerous references concerning hyperaccumulating plants (Berti and Cunningham, 1993; Brown et al., 1995; Shen and Liu, 1998; Ozturk et al., 2003). A hyper-accumulator has been defined as a plant that can accumulate, Cu >1000 mg/kg, Pb >1000 mg/kg, or Zn >10,000 mg/kg in their shoot dry matter. In hyper-accumulator plants, the metal concentrations in shoots are invariably greater than that in roots, demonstrating a special ability of the plant to absorb and transport metals and store them in their above-ground components (Baker and Brooks, 1989; Baker et al., 1994; Brown et al., 1994; Wei et al., 2002). Also, a hyper-accumulator is regarded as a plant in which the concentration of heavy metals in its above ground components is 10–500 times more than that in normal plants (Shen and Liu, 1998). It will be useful to identify plants having the ability to hyperaccumulate heavy metals. The first hyper-accumulators to be characterized were members of the Brassicaceae and Fabaceae families (Salt et al., 1998).

There are numerous tailings impoundments containing Cu and other metals in the vicinity of Claypool, Arizona, USA. Many plants [including desert broom (*Baccharis sarothroides*), mesquite (*Prosopis spp.*), desert Willow (*Chilopsis linearis*), and whitethorn acacia (*Acacia constricta*)] are established at the Cu mine tailings reclamation project (CMTRP) near Claypool. Since these plant species are surviving at the CMTRP, it is important to identify the phytoremediation potential of these plants. To achieve this goal, the concentration of heavy metals and metalloids in the tailings and soil cover from the mining areas were analyzed. Then the concentration of those metals and metalloids was determined in the roots and shoots of desert broom which was collected from the five different locations. The main objectives were as follows: (1) determine the ability of desert broom to accumulate and tolerate heavy metals such as Cu, Pb, Cr, Zn, As, and Ni in tailings; and (2) identify desert broom as a hyperaccumulator having the potential to remediate of metal and metalloid impacted tailings at this CMTRP.

Materials and Methods

Site Description

The CMTRP is situated north of Claypool, Gila County, Arizona approximately 80 miles East of Phoenix, Arizona, USA in the Globe-Miami mining district. The reclamation project, comprised of 6 tailing impoundments covering an area of approximately 1,100 acres, was initiated in 1989. Copper is the primary product mined in the Globe-Miami mining district.

Sampling

Sampling was carried out during March 2005 and among many plants, desert broom was collected from the mine tailings. At the CMTRP, there are 5 reclaimed tailing impoundments (Sites 2 to 6). Each site was divided into a geometrical shape as shown in Fig. 1. Then samples were collected from each intersection of Fig. 1. Three soil and plant samples were collected from each intersection location (A to E in Fig. 1) for enhanced statistical analysis. Samples were preserved and transported properly for analysis in the lab.

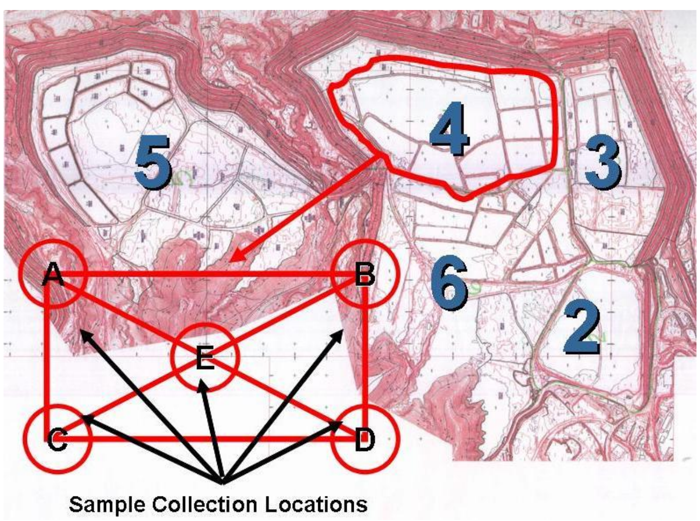

Figure 1: CMTRP sites (2 to 6) and sampling locations (A to E) at Claypool, AZ, USA.

Soil Analysis

On the surface of the sites, the top 8" layer was considered soil cover overlaying the tailings. Collected soil cover and tailing samples were air-dried at 70ºC for 3 days, ground (only soil cover was ground because tailings were fine enough to sieve) and then sieved through a 2 mm mesh to yield a homogeneous mixture. The pH value was determined in a 1:2.5 (w:v) soil: deionized water slurry. Samples were then run in X-ray fluorescence (XRF) instrument to determine the elemental concentration of the available elements in the soil. Based on the concentration level, samples were classified as high and low level elements. To obtain a total extraction of high and low level elements, 0.5 g soil samples were digested by HNO_3 using the 3051 EPA Method in a CEM Microwave oven. The total concentrations of all the elements were then determined by inductively coupled plasma optic emission spectroscopy (ICP-OES).

Plant Analysis

Prior to analysis, plant samples were carefully washed with tap water and thoroughly rinsed with deionized water to remove any soil particles attached to the plant surfaces. After washing, the samples were oven-dried at 60º C for 24 h. The dried tissue were weighed and ground into fine powder for the determination of elemental concentration. A similar digestion procedure was followed as like as for soil digestion. Finally, total concentration of all elements of interest was determined by utilizing ICP-OES.

Translocation Factor and Enrichment Coefficient

Translocation factor (TF) of heavy metals from roots to shoots and enrichment coefficient (EC) of heavy metals in a plant are calculated as follows:

$$TF = [Metal]_{shoot}/[Metal]_{root} \quad (1)$$

$$EC = [Metal]_{shoot}/[Metal]_{soil} \quad (2)$$

Shoot concentration time level was defined as the ratio of heavy metals in plant shoots to that in plants from non-impacted environments (Zu et al., 2005). All of these factors can be used to evaluate the heavy metal accumulation capacity of plants.

Statistical Analysis

The experiments were run in triplicate in order to evaluate the experimental reproducibility. The confidence level of the data generated in the present investigations has determined by standard statistical methods to determine the mean values and standard deviation. Each data set was calculated at the 95 % confidence level ($P < 0.05$) to determine the error margin (Gardea et al., 1996). The correlation coefficient for the calibration curve of 0.986 or greater was obtained and computed as required to confirm the linear range for a minimum of 12 data points.

Results

Concentration of the Heavy Metals and Metalloids in the Tailings and Soil Cover

A range of elements was identified in the tailings and soil cover collected from the CMTRP. The elements were classified based on the concentration as high level elements (HLE): K, Al, Fe, S, Ca, Mg, Na, Cu, P and low level elements (LLE): Mn, Mo, Pb, Cr, Vn, Zn, Co, As, Ni based on the concentration. The concentrations of all the HLE and LLE are shown in Table 1. As shown in Table 1, concentrations of Cu, Mo, and As were 454.9, 89.32, and 49.2 mg/kg, respectively, which were higher than those in normal soils (Table 2). The concentrations of HLE and LLE in soil cover were higher (Appx. 10~15%) than that of the tailings except for Cu (209.5 mg/kg) and Mo (96.5 mg/kg). The pH value of soil cover samples was slightly alkaline (6.1~7.3) and the pH conditions were favorable to plant growth.

Table 1. Concentration of the high and low level elements in the tailings and soil cover*.

Tailings			
HLE	Concentration (mg/kg)	LLE	Concentration (mg/kg)
K	118790.1 ± 412.6	Mn	154.5 ± 2.1
Al	23279.1 ± 89.3	Pb	209.7 ± 1.3
Fe	17860.5 ± 192.2	Mo	89.32 ± 1.1
S	3356.9 ± 25.6	Cr	85.6 ± 2.3
Ca	1197.2 ± 12.9	Vn	57.9 ± 1.1
Mg	1203.5 ± 16.3	Zn	51.2 ± 2.1
Na	1152.8 ± 11.9	As	49.2 ± 2.9
Cu	454.9 ± 2.3	Ni	39.3 ± 1.6
P	176.4 ± 3.9	Co	36.3 ± 1.1

* Concentration of all elements in soil cover**:** 10 ~15% ± Tailings Concentration

Table 2. Normal concentration range of elements (mg/kg) in the soil and plants.

Elements	Normal range in soil	Normal range in plants
Cu	2 – 250*	5 – 25†
Mo	0.1 – 40**	5‡
Pb	2 – 300*	0.1 – 5†
Cr	5 – 1500*	0.2 – 5†
Zn	1 – 900*	20 – 400†
Co	0.05 – 65**	0.03 – 2†
As	0.1 – 40**	0.01 – 5§
Ni	2 – 750*	1 – 10†

* Alloway, 1995; ** Bowen, 1979; § Ma et al., 2001
† Reeves and Baker, 2000; ‡ Lavado et al., 2001

Accumulation of Heavy Metals and Metalloids in Plants

The concentration of HLE and LLE in desert broom is shown in Table 3. The uptake of Cu, Mo, Pb, Zn, Co, Ni, As, and Cr in the roots and shoots of desert broom was significant. The accumulation of Cu in the shoots (1212.7 mg/kg) tops the list, followed by Mo (106.7 mg/kg), Cr (104.4 mg/kg), Pb (102.2 mg/kg), Zn (56.1 mg/kg), As (34.3 mg/kg), Ni (31.2 mg/kg), and Co (10.1 mg/kg). There were significant differences ($P<0.05$) in the average concentrations of the above elements, except for Zn, Mo, and As.

Table 3. Accumulation of HLE and LLE in roots and shoots of desert broom from the CMTRP and a comparison of shoot concentration (CST) of desert broom collected from the CMTRP with other plants collected from non-impacted environments*.

HLE	Concentration (mg/kg)			LLE	Concentration (mg/kg)		
	Root	Shoot	CST		Root	Shoot	CST
K	89711	284104	--	Mn	348.54	2193.12	--
Al	5470.2	1484.3	--	Pb	152.7	102.2	20.4
Fe	6065.5	3365.1	--	Mo	74.3	106.7	21.3
Ca	87678	378460	--	Vn	38.26	83.41	--
Mg	3940.4	3475.0	--	Cr	56.7	104.4	20.9
Cu	819.31	1212.7	48.5	Zn	39.9	56.1	0.1
				As	43.1	34.3	6.9
				Ni	97.3	31.2	3.1
				Co	26.3	10.1	5.19

* Concentration of plants from non-impacted environments is shown in Table 2.

Translocation Factor and Enrichment Coefficient

Figure 2 shows the translocation factor (TF) and enrichment coefficient (EC) of Cu, Pb, Mo, Cr, Zn, As, Ni, and Co. As shown in Fig. 2, the TF values for Cu, Mo, Cr, and Zn are greater than 1, which indicates that these metals move more easily in the plants than Pb, As, Ni, and Co. The EC values for Cu, Mo, Cr, and Zn were greater than 1 as well. Cu had the highest EC value (Fig. 2b) of all elements and Cr had the highest TF value (Fig. 2a).

Discussion

Uptake and Accumulation

Table 2 shows the general trend that desert broom could exist within a broad range of metal and metalloid (Cu > Mn > Pb > Mo > Cr > Vn > Zn > As > Ni > Co) concentrations in the soil. The concentration of Cu, Mo, and As in the soil of the CMTRP greatly exceeded the ranges which were considered toxic to normal plants (Kabata-Pendias and Pendias, 1984), so desert broom growing in the impacted site exhibited strong metal adaptability. Wei et al. (2005) concluded in their research that the exclusion of metals from aboveground tissues has been regarded as a metal tolerant strategy. The excessive metal and metalloid concentration did not affect desert broom; nevertheless, it seemed that it possessed metal resistance capability according to Pichtel et al. (2000). Resistance of plants to heavy metals can be achieved by an avoidance mechanism, which includes the immobilization of a metal in roots and in cell walls (Garbisu and Alkorta, 2001). As shown in Fig. 2a, Pb, As, Ni, and Co accumulated by desert broom was retained in the roots and TF values less than 1 demonstrates the limited mobility of Pb, As, Ni, and Co in desert broom. Each plant species might have a unique mechanism against any metal; however, similar results were found in other research for Pb (Fitzgerald et al., 2003), As (Geng et al., 2006), Ni (Nkoane et al., 2005), and Co (Page et al., 2006). The elevated metal concentrations in roots and low translocation to the aboveground tissues in some investigated species might also suggest that they are capable of rather well-balanced uptake and translocation of metals under heavily metal-polluted conditions (Nkoane et al., 2005, Deng et al., 2004).

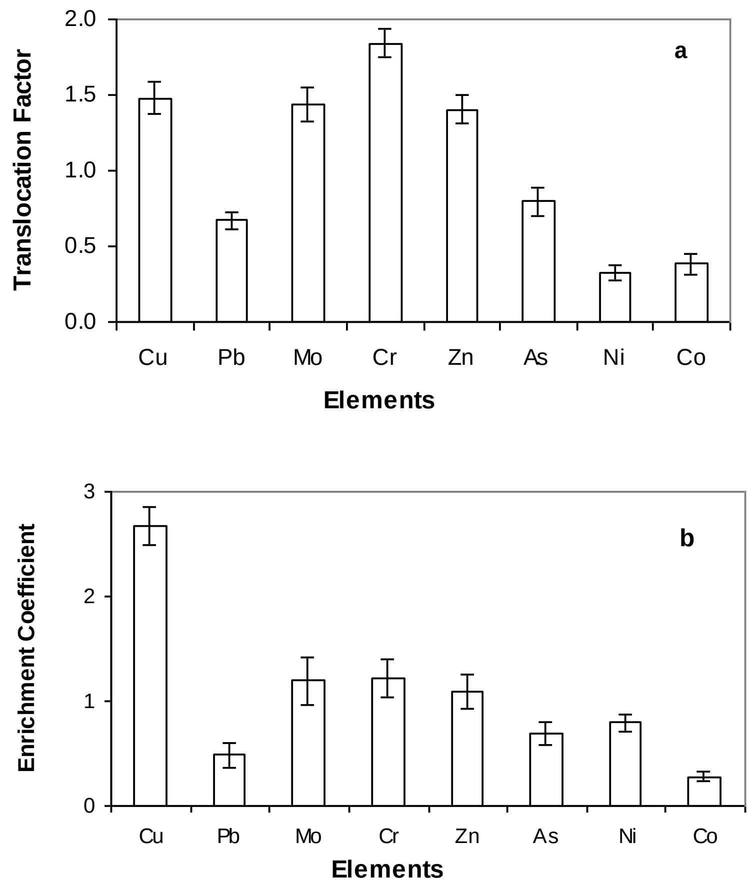

Figure 2. Translocation factor (a) and enrichment coefficient (b) of desert broom.

On the other hand, the TF values for Cu, Mo, Cr, and Zn were greater than 1, which clearly illustrates that the translocation of Cu, Mo, Cr, and Zn was higher from the roots to the shoots. TF values greater than 1 indicated a very efficient ability to transport metal from roots to shoots, most likely due to efficient metal transporter systems (Zhao, et al, 2002) and probably sequestration of metals in leaf vacuoles and apoplast (Lasta et al., 2000). This high metal accumulation in desert broom indicates that an internal metal detoxification tolerance mechanism might exist in addition to its exclusion strategies (Baker, 1981).

Enrichment coefficients were a common important factor when considering the potential of phytoremediation of a given species (Zhao et al., 2003). In this study, EC values of Cu, Mo, Cr, and Zn were greater than 1 (Fig. 2b) which indicated the phytoremediation potential of these heavy metals from the CMTRP. On the other hand, EC values for Pb, As, Ni, and Co were found to be less than 1 in this research. The decrease in enrichment coefficients may be due to the saturation of metal uptake and/or root to shoot transport when internal metal concentrations were high. Baker (1981) concluded that any species may act as an accumulator, an indicator and excluder over different ranges of soil metal concentration and this seems to be the case for desert broom for Pb, As, Ni, and Co. Desert broom might behave differently with a higher concentration of Pb, As, Ni, and Co in the soil.

The normal concentrations of Cu, Mo, Pb, Cr, Zn, Co, As, and Ni are shown in Table 2. The concentrations of all these elements, except Zn, in desert broom (Table 3) were higher than that of the normal plants (Table 2), which showed that desert broom had a strong ability to tolerate these elements. Detoxification tolerance to heavy metals and metalloids is based on the sequestration of heavy metal ions in vacuoles, on binding them by appropriate ligands like organic acids, proteins and peptides and on the presence of enzymes that can function at high levels of metallicions (Garbisu and Alkorta, 2001).

Hyperaccumulator and Potential Applications to Phytoremediation

Presently, there is no standard rule to determine whether any plant is a hyperaccumulator or not. However, four rules are being used successfully to determine hyperaccumulator criteria: (1) the concentrations of heavy metal in plant shoots reach hyperaccumulating level, Pb and Cu >1000 mg/kg (Baker et al., 1994), Zn >10,000 mg/kg (Brown et al., 1994), As >1000 mg/kg (Ma et al., 2001), Ni and Co >1000 mg/kg (Brooks, 1998), Cr >1000 mg/kg (Reeves and Baker, 2000) and Mo >1500 mg/kg (Lombi et al., 2001); 2) the concentrations of heavy metals in shoots are 10-500 times as much as those in a normal plant (Table 2) (Shen and Liu, 1998); 3) the metal concentration in shoots are invariably greater than that in roots (Baker et al., 1989, 1994); and 4) an enrichment coefficient >1 (Brown et al., 1994;Wei et al., 2002).

In this research, hyperaccumulation of Cu in desert broom satisfied all the above mentioned criteria. For Mo, Cr, and Zn, desert broom can be considered as a hyperaccumulator considering the TF and EC value. Finally, according to the accumulated concentration in plant shoots and the concentration time levels compared to plants from non-impacted environments, desert broom had hyperaccumulation capacity for Pb, although the TF and EC value were less than 1. The response of desert broom as a hyperaccumulator against Cu, Mo, Cr, Zn, and Pb might be by employing the strategy of accumulation and sequestration of metals because plants have an extremely high capacity to take up metals by roots and translocate and store them in the shoots (Baker et al., 2000; McGrath et al., 2001).

Based on the results of this research, two distinct strategies of phytoremediation can be applied at the CMTRP, phytoextraction and phytostabilizaition (Salt et al., 1998). Phytoextraction is the utilization of metal accumulating plants to transport and concentrate metals from impacted soils to shoots, followed by gathering the aboveground tissues by conventional methods. In phytostabilization, plants can stabilize pollutants in the soil by rendering them harmless (Eapen and Dsouza 2005). According to this field investigation, desert broom exhibited a strong accumulative ability to Cu, Mo, Cr, Zn, and Pb and therefore it might be used to phytoremediate impacted soils at the CMTRP after further research in the accumulation mechanism.

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