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# ACCEPTED MANUSCRIPT

Riparian Plants on Mine Runoff in Zimapan, Hidalgo, Mexico: Useful for Phytoremediation?

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## Abstract

Dispersion and runoff of mine tailings have serious implications for human and ecosystem health in the surroundings of mines. Water, soils and plants were sampled in transects perpendicular to the stream Santiago in Zimapan, Hidalgo, which receives runoff sediments from two acidic and one alkaline mine tailing. Concentrations of potentially toxic elements (PTE) were measured in water, soils (rhizosphere and non-rhizosphere) and plants. Using DTPA extractable

concentrations of Cu, Zn, Ni, Cd and Pb in rhizosphere soil, the bioconcentration and translocation factors were calculated. Ruderal annuals plants formed the principal element of the herbaceous vegetation. Accumulation was the most frequent strategy to deal with high concentrations of Zn, Cu, Ni, Cd and Pb. The order of concentration in plant tissue was Zn>Pb>Cu>Ni>Cd. Most plants contained concentrations of PTE considered phytotoxic and behaved as metal tolerant species. *Rorippa nasturtium-aquaticum* accumulated particularly high concentrations of Cu. *Parietaria pensylvanica* and *Commelina diffusa*, common tropical weeds, behaved as Zn hyperaccumulators and should be studied further.

**Keywords:** bioaccumulation of metals, hypertolerant plants, mine tailings.

**Introduction**

Industrial mining activities in America have increased very rapidly in the last 10 years. Numerous sites in Mexico are polluted by residues of abandoned as well as active mines. Potentially toxic elements (PTE) as Zn, Cd and Cu, along with sodium and extreme pH, have intense negative effects on ecosystems in mining areas (Hernández and Pastor, 2008). Zimapán, Hidalgo, is an old mining town with both active and historical mines for Au, Ag, Cu, Hg, Pb, Zn and other minerals. Residues contain varying amounts of sulfides (PbS, ZnS, CdS, FeCuS<sub>2</sub>), carbonates and other minerals, which are partly deposited in mine tailings, but also had been scattered into the surrounding areas by wind and water (Moreno-Tovar, Barbanson and Coreño-Alonso, 2009). Oxidation of some of these minerals generates acid drainage and increases the available concentrations of As, Pb, Zn, Cu and Cd. Runoff and leachates of PTE form part of the main environmental problems that require immediate intervention (Sánchez-López *et al.*, 2015; González-Chávez, Sánchez-López and Carrillo-González, 2015).

Phytoremediation can be used to diminish PTE pollution and is cheaper than other traditional remediation procedures (Ali, Khan and Sajad, 2013). Plant species adapted to PTE-contaminated soils can accumulate PTE in their tissues through compartmentalization mechanisms without poisoning (Baker and Brooks, 1989; Ali *et al.*, 2013). Around 400 plant species belonging to 34 families have been documented as having developed strategies that confer the ability to tolerate high concentrations of PTE (Baker and Brooks, 1989). However, knowledge of PTE tolerant plants in Latin America is insufficient. In this region, studies relatives to native vegetation growing on PTE polluted areas are scarce compared with other

regions of the world (Ginocchio and Baker, 2004). PTE-tolerant species used in wetlands for mine waters treatment is restricted to a few species (Batty, 2005). Old polluted areas can be explored in order to identify adapted plants (González and González-Chávez, 2006) especially those useful to phytoremediation that naturally occurred in wetlands. This research aims to determine which species in the area of influence of runoff from the mines of the study area, if any, could be useful for stabilization or phytoextraction of PTE in mining waste and/or bodies of contaminated water. Identification of tolerant species for revegetation is a secondary goal.

## **Materials and Methods**

### *Description of Area*

The study area is located in the mining region of Zimapan, Hidalgo, Mexico, between 20° 44' 30" N 99° 22' 30" W, altitude 1780 m. Its climate is temperate and relatively dry, with an average annual temperature of 18.3 °C, and rainfall of 391 mm on average from May to July (INEGI, 2014). The mining waste has been left in open-air deposits (at least nine) in the lower part of the basin that flows into the Toliman River. Santiago is the side stream of the river that has been receiving runoff materials and leachates from the following deposits for the last 55 yr: Los Gomez, La Purisima, Preisser, Pal, and San Antonio. The zone between the creek and the Preisser, Pal and San Antonio deposits constitutes the study area, a strip approximately 600 m long (Figure 1). The Preisser and Pal residues exhibit a reddish orange color due to advanced oxidation. The residues of the San Antonio deposit are less obvious as they have been covered intentionally with ground rock and soil as mitigation measure.

### *Sampling*

Six sampling sites (I-VI) were chosen upstream for their abundance of plants and their location relative to the tailings (Figure 1). The approximate distance between sites was 100 m. They were located only on the northern side of the creek, which received mine tailing runoff and leachates. At each site, a 10 x 5 m transect perpendicular to the Santiago creek was established from its midpoint. Five composite samples of river water were collected in duplicate from each site (except site VI) and stored according to the procedures described by the USEPA (1996). The study sites were sampled in November 2012, May 2013, June 2014 and October 2014 to include both dry and rainy seasons.

Three individuals of each identifiable plant species found in the transect were sampled, both shoot and roots, and for both chemical analysis and taxonomic determination (plant without flowers or fruits were not collected). Composite soil samples were collected from the rhizosphere of plants naturally established and nearby non-rhizosphere soil. These samples were air dried and sieved with a 2 mm mesh sieve. The plants were identified with Rzedowski and Rzedowski (2001 and 2008) and Vibrans (2009), and voucher specimens deposited at the National Herbarium (MEXU).

### ***Analytical Procedures***

**Water.** The water samples were analyzed for pH, electrical conductivity (EC), redox potential (pE), and concentration of  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $K^+$ ,  $Na^+$ ,  $Cl^-$ ,  $HCO_3^-$  and  $SO_4^{2-}$  ions following the procedures proposed by APHA-AWWA-WPCF (2000). Total concentrations of Cu, Zn, Ni, Cd and Pb were measured according to the USEPA (1996) method.

**Soil.** Soil pH and pE were determined in a suspension of 1:2.5 fresh soil: distilled water (w/v) as soon as the samples arrived at the laboratory. Particle size distribution was analyzed by standard procedure. Organic matter content (OM) was measured by the dichromate method (Rowell, 1994). Total concentration of Cu, Zn, Ni, Cd and Pb was determined by method 3050 (USEPA, 1992) and DTPA-extractable concentration according to Lindsay and Norvell method (1978). PTE were quantified by atomic absorption spectrometry using the flame technique (FAAS; Perkin Elmer 3100). Certified standards ( $1000 \text{ mg L}^{-1}$ ; Purity®) were used to prepare the appropriate calibration curves. All analyses were done in triplicate including a blank reagent as part of the QA/QC protocol. The bioavailability index (BI) (Chen, Shan and Qian, 1996) was calculated in soil for each PTE as the ratio of extractable and total PTE concentration and it was expressed as a percentage.

**Plants.** Presence or absence of herbaceous species was registered at each site on each of the fourth soil sampling dates (mentioned above). Vegetation was extremely variable because of frequent flooding and changes in the riverbed. The surface of the plant tissue was washed with tap water, phosphate-free detergent (2% Extran), distilled water, a solution of 10% HCl (10 min) and deionized water (Sánchez-López *et al.*, 2015) to remove soil particles. Leaves, stems, flowers, fruit and roots were separated and dried in a forced air oven at  $65^\circ \text{ C}$  for 72 h. Each sample was ground to powder separately in a stainless steel mill. Samples of 500 mg were digested in a mixture of  $\text{HClO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}_2$  (4:1:1). Once cooled, samples were diluted to 25

mL with deionized water and filtered through fine porosity paper (Whatman 42). The concentration of Cu, Zn, Ni, Cd, Pb and As was determined by FAAS.

The bioconcentration factor (BCF) was calculated according to Zhuang *et al.* (2007) for the root, stem, leaf, flower and fruit, considering the concentration of extractable PTE in the rhizosphere soil. The translocation factor (TF; Stoltz and Greger, 2002) was also calculated as an indicator of the ability of the plant to move PTE from the root to the aerial part.

### ***Statistical analysis***

A one way analysis of variance (ANOVA) test was used to determine significant differences among sample means of soil characteristics in each site ( $\alpha = 0.05$ ). All results were analyzed with Pearson's correlation ( $r$ ) ( $p < 0.01$ ).

## **Results and Discussion**

### ***Water Quality***

The physicochemical characteristics studied as well as concentration of PTE in the water were mostly within the quality parameters proposed by the Mexican Official Norm for water sources (Table S1). In general, the order of metal content concentration in the water was as follows: Zn>Pb>Cu>Ni>Cd, which correspond to the extractable concentrations found in sampled soils (Tables S2 and S3). The pH varied from neutral to slightly alkaline (7.1- 7.8); therefore, the acidic leaching and runoff from the oxidized mine tailing was neutralized in the water stream.



The water was slightly oxidant, but the pE was within the limits of redox stability. CE indicated as scarce dissolved salts in water.

### *Plants Found in the Area of Influence of the Creek*

During the rainy season sampling, observations showed that the sites were altered substantially by visible leachate and surface runoff from mining waste. In addition, the water level of the creek fluctuated more than expected, due to higher-than-usual rainfall (over 700 mm/yr in the last two years; INEGI, 2014). People cut reeds and other plants, and constructed small dams for flood control, altering vegetation and water flow. Because of these modifications, new plant species were found on each sampling date and the shoreline varied considerably (Table 1).

Forty-nine species of herbaceous plants belonging to 20 families were identified in the sampled transects from the aquatic environment within the creek, to its banks and further inland (Table 1). Poaceae and Cactaceae families were not included in this study doubt to insufficient material to identification. The number of species per site varied from 16 to 25. It is noteworthy that there was more herbaceous vegetation on the northern bank (closest to the mining tails and runoff sediments) than southern bank (without herbs crowded out and shaded by trees). Among species of plant collected, 87% were native in a wider sense (originating from and widespread in the Americas) (Vibrans, 2009). In transects sampled, species of ruderal annuals represent 53% and perennials 47% of the herbaceous plants. Dominant presence of ruderals is a common phenomenon on mine tailings and PTE contaminated sites. Asteraceae family represents 25-50% of the total species. Hence, apparently occurrence of high concentrations of PTE was no problem to these species, in change it could be a factor associated with the presence of herbaceous

vegetation as perturbation is. Ninety three percent of the plant species were found on the flood plain or in the plain next to mine tailings, that is under influence of runoff as main source of PTE in an intermittent flooding area. Since none of the species is exclusive of metalliferous soil, the populations found in the study area can be considered as metal tolerant to EPT (Ernst, *et al.*, 2008).

Most of the found species had not been reported by other authors in soils associated with mine waste runoff, except *Dalea bicolor*, *Flaveria trinervia*, *Viguiera dentata* (Sánchez-López *et al.*, 2015), *Acmella repens*, *Bidens pilosa*, *Commelina diffusa*, *Lepidium virginicum*, *Mirabilis jalapa*, *Polygonum punctatum*, *Solanum americanum* and *Verbena litoralis* (Sánchez-Pinzón, 2010). Several species were found in all sites, including *Mirabilis violacea*, *M. jalapa*, *Plantago major*, *P. punctatum* and *R. nasturtium-aquaticum*, so these species are highly tolerant to contamination by PTE.

#### ***Characteristics of Rhizosphere and Non- rhizosphere Soil***

All sites had heavy silt clay soil (data not shown). Apparently, the particle distribution changed as minerals weathered. A negative correlation was observed between pH and pE values ( $r = -0.67$ );  $p < 0.001$ ); this means that oxidation of tail minerals increased the oxidizing conditions (pE values ranged from 443 to 581 mV and 53 to 306 mV).

Soils at sites I to III were strongly acidic (pH 2 to 3), neutral at site IV, and alkaline at sites V and VI (Table S4). The cause for these differences was the leachate and runoff from mine tailings affecting the soils. Preisser and Pal residues produced acid runoff (pH < 2.6) may be due to the oxidation of pyrite and arsenopyrite (González-Sandoval *et al.*, 2008). In contrast, the

leachates from sites V and VI originated from the San Antonio mine tailings were alkaline, due to their content of calcite and sphalerite (Moreno-Tovar *et al.*, 2009). Also, the soil of the region is alkaline to strongly alkaline (7.7 – 8.5). OM content in the non-rhizosphere soil ranged from 0.8% to 11.5%. Differences in pH were observed in rhizosphere soil as well. In sites I and II pH varied from 5.5 (*P. major*) to 5.7 (*P. punctatum*), while in site VI the pH was 8 (*Dalea minutifolia*), which shows the effect of the rhizosphere. In the rhizosphere soil, the highest OM content was observed around *C. diffusa* (12.6%) and *R. nasturtium-aquaticum* (11.1%). OM and pH were positively correlated ( $r= 0.99$ ;  $p<0.001$ ). PCA results showed that no group of factors analyzed had sufficient variability to be considered as principal component of the system or either had a directional behavior in the system studied.

#### ***Total and Available PTE Concentrations in Soils***

Total concentrations of PTE present in the soils were in the order Pb>Zn>Cu>Ni>Cd. All concentrations were higher than normal in agricultural soils (Kabata-Pendias, 2011) particularly total Pb (Tables S2 and S3). The highest concentrations of total PTE were found site II, directly exposed to the runoff from the Preisser and Pal mine tailings. The lowest total and extractable concentrations of PTE were detected at sites III and IV, located between the Preisser and San Antonio tailings (Figure 1; Table S2). Clearly, runoff from mining tailings have a direct influence on the soils adjacent to them.

Concentrations of extractable PTE for rhizosphere had the following order: Zn>Pb>Cu>Ni=Cd, the same trend as in water concentration of Santiago River. The bioavailability index (BI) (Tables S2 and S3) was very high, compared with the BI found by

Manab and Maiti (2008), in Cu mine tailings in India. These authors suggest that the terms of toxicity to plants BI are considerable high compared with other sites. Extractable PTE, particularly Cu and Ni, in soils of wetlands and aquatic environments was higher than in soils of terrestrial plants (Tables S2 and S3).

Most rhizosphere soil samples had total Cu concentrations considered phytotoxic (32-681 mg kg<sup>-1</sup>) by Kabata-Pendias (2011). These concentrations were slightly lower than those found by Bech *et al.* (1997) and Liu *et al.* (2008) on mine tailings in Peru and China (902, 5270 and 1020 mg kg<sup>-1</sup>, respectively). The highest extractable Cu concentrations were found at sites I and II (near Pal and Preisser tailings) with acid pH values, which may be directly related with the continuous oxidation of pirite (Manab and Maiti, 2008).

The total concentration of Zn in the rhizosphere varied from 638 to 29 190 mg kg<sup>-1</sup>. The lowest total Zn concentration was found at sites II to IV (638-5 110 mg kg<sup>-1</sup>) in contrast with highest concentrations of Pb in these stations. Total concentration of Zn increased in sites V and VI, where it reached the highest values (12 655 and 29 190 mg kg<sup>-1</sup>, respectively), but where extractable PTE were the lowest. These results are easily explained, as Zn tends to be adsorbed by soil at an alkaline pH; in addition, Zn ions are precipitated or form complexes with OM (Liu *et al.*, 2008). Total concentrations of Zn, Ni and Pb showed significant differences in total concentration per site (Pr<0.0001; Pr=0.0001; Pr=0.0004 respectively).

The total concentration of Ni in rhizosphere soil was within normal values proposed for non-polluted soils (Kabata-Pendias, 2011). This element showed a gradient from I (17-65 mg kg<sup>-1</sup>) to VI (79-106 mg kg<sup>-1</sup>), closely related to soil pH ( $r= 0.53$ ;  $p<0.001$ ) and OM content ( $r= 0.75$ ;

$p < 0.001$ ). Extractable Ni concentration was higher at sites I and II (4-12%) with low pH derived from the acidic Pal and Preisser residues) than sites V and VI due to the alkaline influence of San Antonio tailings. In these tailings alkalinity and high OM content diminished the availability of Ni, as concluded Chen, Huang and Liu (2009). These authors proposed that Ni is present as  $\text{Ni(OH)}_2$  under alkaline conditions and forms stable complexes with the OM, whereas under acidic conditions it takes the form of  $\text{Ni(H}_2\text{O)}_6^{2+}$  which is available to plants. This explanation agrees with the arguments of Kabata-Pendias (2011) and Van der Ent *et al.* (2013).

Total Cd concentrations exceeded normal values for agricultural soils (Kabata-Pendias, 2011). It was the least abundant element (3-49  $\text{mg kg}^{-1}$ ), but the most available (BI = 1-90; Tables S2 and S3). The concentration of Cd was slightly higher at site III (16-71  $\text{mg kg}^{-1}$ ). At sites V and VI, with higher OM content than other sites, extractable Cd concentration was from 1 to 4  $\text{mg kg}^{-1}$  due to its high solubility and limited tendency to form complexes with the OM. These concentrations are lower than those reported in Cu mines from Peru (8.9-499  $\text{mg kg}^{-1}$ ; Bech *et al.*, 1997). A negative correlation between available Cd and pH was found ( $r = -0.63$ ;  $p < 0.001$ ). As with the other PTE, Cd was more available under acid conditions than under alkaline conditions (Li *et al.*, 2012).

Sites I and II showed the highest total concentration of Pb (201-3991  $\text{mg kg}^{-1}$ ) as well as highest extractable concentration (6-552  $\text{mg kg}^{-1}$ ) compared with sites V and VI (1-96  $\text{mg kg}^{-1}$ ). Availability of Pb under acidic conditions is related to the oxidation of sulfide minerals present (Moreno-Tovar *et al.*, 2009), whereas in alkaline soils Pb is adsorbed onto the surfaces of clay particles, or precipitated (Chen *et al.*, 1996). Also, the higher content of OM in the soils of sites

V and VI (Table S4) may stimulate the formation of stable organic complexes and reactions with clays, phosphates, sulfates, carbonates and hydroxides (McLean and Bledsoe, 1992) which makes the metal unavailable to plants (Tables S2 and S3). As suggested Liu *et al.* (2008), the results confirmed that pH, pE, OM and clay content are the most important soil factors that control availability of PTE in soils.

### ***PTE Concentrations in Plants***

Remarkably, all of the 34 plant species analyzed for this research accumulated PTE in higher concentrations than those considered normal by Kabata and Pendias (2011). Almost all plants sampled translocated PTE to aboveground tissues. The order of accumulation was Zn > Pb or Cu > Ni > Cd. Thus, most of them were highly tolerant of Cd, Cu, Ni, Pb and Zn (Figure 2) and behaved as hypertolerant species (Ernst *et al.*, 2008).

According with results reported by Sánchez-Lopez *et al.* (2015) and González-Chávez *et al.* (2015), the concentration of PTE in the tissues varied among individuals of the same species and had different BCF and TF in different locations (Tables S5 and S6). We observed no relationship between the total concentration of PTE in rhizosphere soil and in the above ground plant tissues, although in most cases, accumulation in plants depended on the bioavailability of the PTE in the soil. Accumulation of PTE depends on the chemical form of the PTE in the soil, pH, age of the plants and, perhaps, their ecotypes (González and González-Chávez, 2006). Several species had a BCF >10 and a TF >1, which indicates considerable PTE accumulation (Tables S5 and S6). Some of them may have potential as phytoextractors under the criteria of Van der Ent *et al.*

(2013) and a few useful as stabilizers. They are discussed below, according the objectives of this study.

Local plant populations studied here showed an important adaptation of tolerance and accumulation and translocation of Cu. Root Cu concentrations ranged from 7 to 1669 mg kg<sup>-1</sup> and shoot concentrations ranged from 4 to 195 mg kg<sup>-1</sup> (Figure 2). These concentrations are higher than those reported by Liu *et al.* (2008) (36-1020 mg kg<sup>-1</sup>). Also, Cu concentration in aquatic plants and those growing in wet places near the creek was higher than in more terrestrial plants. All individuals of *R. nasturtium-aquaticum* had high BCF values for Cu and concentrations of 350 mg kg<sup>-1</sup> in stem, so the species may have potential as a phytoextractor of Cu and would be considered a hyperaccumulator of Cu under the criteria of Van der Ent *et al.* (2013) (300 mg kg<sup>-1</sup>). *A. repens* and *P. major* accumulated about 140 mg kg<sup>-1</sup> in both the roots and in the aerial parts. *C. diffusa* and *V. littoralis* accumulated more than 200 mg kg<sup>-1</sup> of Cu in roots. (Table S6; Figure 2). These species may serve as phytoextractors in wetlands.

The highest concentrations of Zn were found in *P. pensylvanica* (5 257 and 7 630 mg kg<sup>-1</sup> in the roots and stem respectively; Figure 2), *F. trinervia* (1 839 mg kg<sup>-1</sup> in the stem) and *C. diffusa* (5 086 mg kg<sup>-1</sup> in the leaves). These values were higher than those founded by Bech *et al.* (1997) (90-437 mg kg<sup>-1</sup>) but lower than those registred by Barrutia *et al.* (2011; >4 000 mg kg<sup>-1</sup>). According with results *P. pensylvanica* and *C. diffusa* can be considered hyperaccumulators of Zn according to the criteria of Van der Ent *et al.* (2013) (3 000 mg kg<sup>-1</sup>) (Tables S5 and S6).

Ni concentration was relatively similar between structures: 2.9-147 mg kg<sup>-1</sup> in roots, 2.8-117 mg kg<sup>-1</sup> in stems and 4.7-526 mg kg<sup>-1</sup> in leaves for all species (Figure 2), although none of the

plants in this study may be considered hyperaccumulator plant of Ni. The BCFs of Ni were between 20 to 100, particularly obvious in *Bacopa monnieri*, *Apium graveolens* and *C. diffusa* with a BCF > 300, *A. repens*, *L. virginicum* and *P. major* with a BCF > 100, and *B. monnieri*, *D. minutifolia*, *P. major*, *P. pensylvanica*, *R. nasturtium-aquaticum* and *V. littoralis* with BCF between 20 and 100 (Tables S5 and S6) .

The species with the highest BCF and TF corresponded to sites V and VI, where the available Ni concentration was very low and led to high quotients. BCF of Ni were related negatively to soil Ni extractable concentration in soil rhizosphere. However, tolerance to Ni could not be confirmed for any of the species due to the relatively low concentrations of this metal in the study area. The TF was generally below 2 (Table S6).

The highest concentrations of Cd in plants were found at sites IV to VI, whereas the plants at I and II with acid soils had the lowest concentrations (Figure 2). This was unexpected, as there is normally an inverse linear relationship between the pH and the Cd concentration in plants (Kabata Pendias, 2011). However, Zn concentrations were high at these sites, and apparently, the plants preferably absorb and accumulate Zn at expense of Cd. Also a direct relation among OM and Zn accumulated in roots, and shoots of plants was found ( $r=0.48$ ). The variability in the data can be explained by the degree of soil disturbance derived from the varying mechanisms of waste deposit, which are factors also reported in other mining areas (Barrutia *et al.*, 2011).

Concentration of Cd in above ground parts of plants was negatively related with total concentration of Zn in rhizosphere soil. Cd concentrations in roots, stems and leaves varied (1.17-20.7, 0.5-19.3 and 1.2-48.3 mg kg<sup>-1</sup> respectively). These values were two to four times



higher than the level considered phytotoxic (0.05-0.2 mg kg<sup>-1</sup>) (Figure 2). These concentrations were not enough to consider plants as hyperaccumulators (Van der Ent *et al.*, 2013). Nevertheless, several species show BCF>20 and TF>1 as *A. repens*, *A. graveolens*, *S. americanum* and *Sisymbrium irio*, so they may be promising as Cd phytoextractors.

The concentration of Pb, varied between 4-264, 2-162 and 1-204 mg kg<sup>-1</sup> for roots, stem and leaves, respectively. These fell within the concentrations of Pb registered on plants growing on mine-contaminated sites in the UK (63 - 230 mg kg<sup>-1</sup>; Kabata-Pendias, 2011). However, they were higher than the values reported by Bech *et al.* (1997; 1.41-2.13 mg kg<sup>-1</sup> in shoots). Roots had the highest Pb concentrations, with a BCF between 0 and 70 (Table S5). The plants at site II had the highest Pb concentrations in aboveground tissue overall, as well as the highest total and extractable concentrations of Pb in the rhizosphere soil. In the same way, plants of sites V and VI showed low Pb concentration in tissue, related with the lowest Pb extractable concentrations in soil.

*R. nasturtium-aquaticum* at VI had the highest BCF (70, 31 and 46 mg kg<sup>-1</sup> in roots, stem and leaves, respectively), and TF <1, and so the species can be considered as stabilizers of Pb. Other species with a high BCF for Pb were *P. punctatum*, *B. monnieri*, *Ludwigia peploides*, *A. repens* and *F. trinervia*.

Concentration of PTE in roots had a positive relationship with soil OM ( $r= 0.81$ ;  $p<0.001$ ). Also, concentrations of Cu, Zn and Pb in roots had a high correlation with total concentrations of Zn and Cu in soil ( $r>0.94$ ). The results confirm that species such as *A. repens*, *P. major*, *B. monnieri* and *F. trinervia* are accumulators and can be useful in phytoremediation in wetlands, as

reported by Kosobrukhov, Knyazeva and Mudrik (2004), Shukla, Dubey and Rai (2007) and Sánchez-López *et al.* (2015).

### Conclusions

The leachate and runoff from mine tailings had a direct influence on pH and total concentration of PTE in soils next to mine tailings. The acidic leaching and runoff from the oxidized mine tailing was neutralized in the water stream. Plants had a direct effect on rhizosphere soil modifying pH and increasing OM content, which had a direct and strong correlation with each other. Factors that controlled availability of PTE in soils were pH, pE, OM and clay content. Wetlands functioned as a sink of PTE where availability of PTE is higher than in terrestrial soils. Consequently, the absorption and accumulation of PTE by aquatic plant species and wetlands were higher than by terrestrial plants. The occurrence of high concentrations of PTE and perturbation in the flood plain next to mine tailings were the principal factors associated with the presence of ruderal herbaceous plant species. Riparian populations of ruderal plant species act as accumulators of PTE in soil with runoff from mines.

Accumulation was the most frequent plant strategy for dealing with high concentrations of Zn, Cu, Ni, Cd and Pb and depends mainly of bioavailability of PTE in soil and pH. None of the species found were exclusive of metalliferous soil, but the local populations of vegetal species can be considered metal tolerant particularly to Cu, Cd and Pb. Several species have potential as phytoextractors of Cu and Zn.

For species as *R. nasturtium-aquaticum* (a possible hyperaccumulator of Cu), *P. pensylvanica* and *C. diffusa* (possible hyperaccumulators of Zn) is suitable to evaluate these

species under controlled conditions to prove their tolerance strategy. Several species were promising for Cd extraction, among them *S. irio*, *P. major*, *P. punctatum*, *F. trinervia*, *D. minutifolia*, *R. nasturtium-aquaticum* and *C. diffusa*. Other species as *P. punctatum*, *B. monnieri*, *L. peploides*, *A. repens* and *F. trinervia*, must be probed as stabilizers of Pb. A relatively large number of tolerant species could be employed for revegetation. An exhaustive research is recommended to probe the usefulness for phytoremediation of other species presents in Santiago stream not analyzed in this study.

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## **Supplemental Material**

Supplemental data for this article can be accessed on the publisher's website.

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Table 1. Species of plants collected in Santiago River, Zimapan, Hidalgo.

Species	Family	Id	Life form	Life cycle	Habitat	Status	Presence by site						
							I	II	III	IV	V	VI	
Analyzed													
<i>Acnema repens</i> (Walter) Rich.	Asteraceae	Ar	2	P	B	N		X		X	X	X	
<i>Apium graveolens</i> L.	Apiaceae	Apg	2	P	A, B	I		X		X	X	X	
<i>Argemone grandiflora</i> Sweet	Papaveraceae	Argr	1	AN	A, B, C	N		X	X	X			X
<i>Aster subulatus</i> Michx.	Asteraceae	Ass	2	AN	A	N		X					
<i>Bacopa monnieri</i> (L.) Pennell	Scrophulariaceae	Bm	3	P	A	N	X	X				X	X
<i>Bidens pilosa</i> L.	Asteraceae	Bp	1	AN/P	A, B, C	N	X	X	X			X	
<i>Calyptocarpus vialis</i> Less.	Asteraceae	Cv	2	P	A, B	N				X	X	X	
<i>Chenopodium ambrosoides</i> L.	Chenopodiaceae	Cha	1	AN	A	N						X	X
<i>Commelina diffusa</i> Burm. f.	Commelinaceae	Cod	1	P	A, B	N						X	X
<i>Dalea bicolor</i> Humb. & Bonpl. ex Willd.	Fabaceae	Dab	5	P	B, C	N			X				
<i>Dalea foliolosa</i> var. <i>foliolosa</i> (Ait.) Barneby	Fabaceae	Df	1	AN	C	N			X				
<i>Dalea minutifolia</i> (Rydb.) Harms	Fabaceae	Dm	5	P	C	N			X				X
<i>Flaveria trinervia</i> (Spreng.) C. Mohr	Asteraceae	Ft	1	AN	B, C	N	X	X	X	X			
<i>Lepidium virginicum</i> L.	Brassicaceae	Lv	1	AN	C, D	N			X	X	X	X	
<i>Ludwigia peploides</i> (Kunth) P.H. Raven	Onagraceae	Lp	3	P	A	N		X					
<i>Lycopersicon esculentum</i> P. Mill.	Solanaceae	Le	1	AN	A, B	N		X					X
<i>Mentzelia hispida</i> Willd.	Loasaceae	Mh	1	P	D	N						X	
<i>Mirabilis violacea</i> (L.) Hemerl	Nyctaginaceae	Mv	1	P	C, D	N	X	X	X	X	X	X	X
<i>Oxalis corniculata</i> L.	Oxalidaceae	Oc	1	AN/P	D	N						X	
<i>Parietaria pensylvanica</i> Muhl. ex Willd.	Urticaceae	Pp	1	AN	C, D	N						X	X
<i>Petroselinum crispum</i> (Miller) A. W. Hill	Apiaceae	Pc	2	AN	B	I							X
<i>Petunia parviflora</i> Juss.	Solanaceae	Pe p	2	AN	A	N	X						
<i>Phyla fruticosa</i> (Mill.) K. Kenn. ex Wunderlin & B.F. Hansen	Verbenaceae	Pf	2	P	B	N	X		X	X	X		
<i>Piqueria pilosa</i> Kunth	Asteraceae	Pip	1	P	C	N			X				

<i>Plantago major</i> L.	Plantaginaceae	P m	2	P	A, B, C	I	X	X	X	X	X	X
<i>Polygonum punctatum</i> Elliot var. <i>eciliatum</i> Small	Polygonaceae	Po p	3	P	A	N	X	X	X	X	X	X
<i>Rorippa nasturtium-aquaticum</i> (L.) Schinz & Thell.	Brassicaceae	Ron	3	P	A	I	X	X	X	X	X	X
<i>Sisymbrium irio</i> L.	Brassicaceae	Sis	1	AN	A, B	I			X			
<i>Solanum americanum</i> Mill.	Solanaceae	S a	1	AN/P	A, B, C	N	X				X	X
<i>Spirodela polyrrhiza</i> (L.) Schleid.	Lemnaceae	S po	4	AN	A	N		X				
<i>Verbena litoralis</i> Kunth	Verbenaceae	V l	2	P	A, B	N		X	X	X	X	X
<i>Verbesina encelioides</i> (Cav.) Benth. & Hook. ex A. Gray	Asteraceae	V e	1	AN	B	N	X		X			
<i>Viguiera dentata</i> (Cav.) Spreng.	Asteraceae	V d	1	P	C	N	X	X	X	X		
<i>Xanthium strumarium</i> L.	Asteraceae	X s	2	AN	B	N	X			X		
Not Analyzed												
<i>Berula erecta</i> (Huds.) Coville	Apiaceae	Ver	3	P	A	N		X			X	X
<i>Brickellia veronicifolia</i> (Kunth) A. Gray	Asteraceae	B v	1	AN	C,D	N				X		
<i>Cardiospermum halicacabum</i> L.	Sapindaceae	C h	1	P	B	N			X		X	
<i>Cirsium vulgare</i> (Savi) Tenore	Asteraceae	C v	1	AN	B	I			X	X	X	X
<i>Conyza canadensis</i> (L.) Cronquist	Asteraceae	C c	1	P	A, B,C,D	N		X	X	X	X	X
<i>Datura innoxia</i> P. Mill.	Solanaceae	D i	1	P	C,D	N				X		
<i>Dyssodia papposa</i> (Vent.) A. S. Hitchc.	Asteraceae	D p	1	AN	C	N				X		
<i>Lantana camara</i> L.	Verbenaceae	L c	1	AN	B, C	N			X	X		
<i>Maurandya scandens</i> (Cav.) Pers.	Scrophulariaceae	M s	1	AN	B	N					X	
<i>Mirabilis jalapa</i> L.	Nyctaginaceae	M j	1	AN	C,D	N	X	X	X	X	X	X
<i>Nicotiana glauca</i> Graham	Solanaceae	N g	1	AN	C	N	X		X			
<i>Oenothera rosea</i> L'Her. ex Ait.	Onagraceae	O r	1	AN	C	N		X				
<i>Sanvitalia procumbens</i> Lam.	Asteraceae	S p	1	P	C,D	N	X			X		
<i>Vinca major</i> L.	Apocynaceae	V m	1	P	B	I				X		
<i>Zinnia peruviana</i> (L.) L.	Asteraceae	Z p	1	AN	C	N				X		
Total of species present by site							16	20	23	24	25	21

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Life form: 1= Terrestrial Herb; 2 =Terrestrial herb of wet land; 3= Rooted emergent aquatic plant; 4= Free floating aquatic herb; 5= Terrestrial shrub. Habitat:

A= Riverside; B= Floodplain; C= Plain next to mine tailings; D= On mine tailings; Life cycle: AN= Annual, P= Perennial; Status: N= Native; I= Introduced. Id: abbreviations used in the tables and figures.

Figures legends

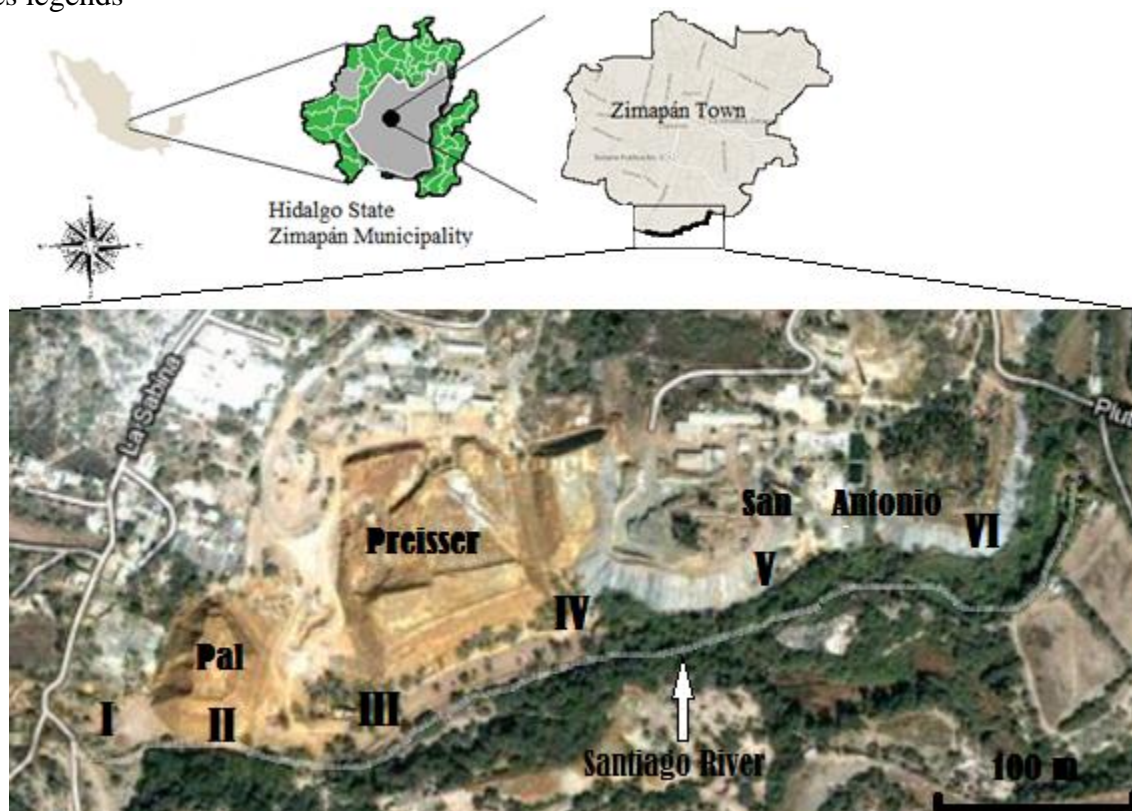


Figure 1. Mine tailings next to the Santiago River and sampling sites.

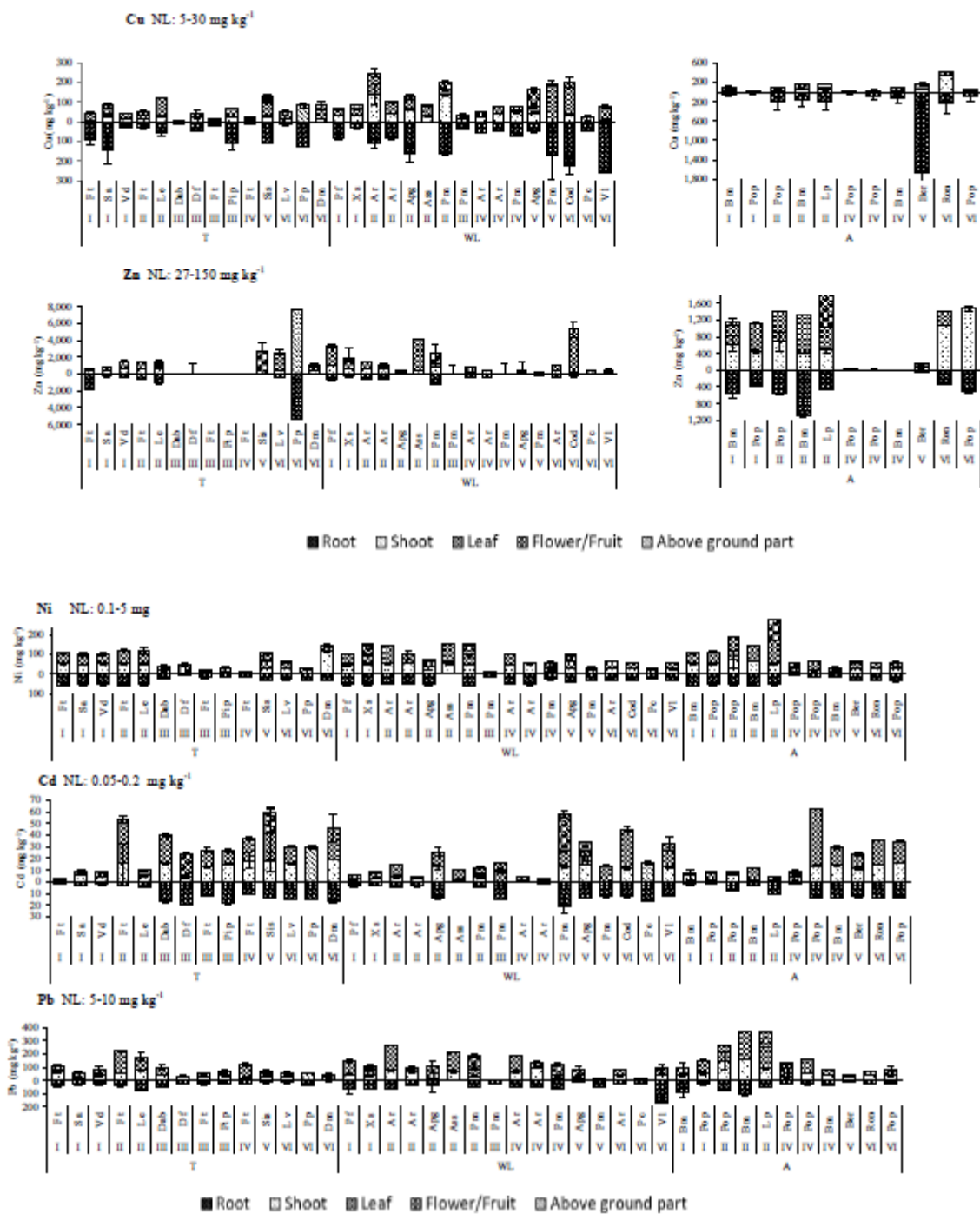


Figure 2. Concentration of potentially toxic elements in plant tissues established along to the Santiago River, Zimapan, Hidalgo. T = terrestrial species; WL= wet land species; A = aquatic species. NL= normal level (Kabata-Pendias, 2011).