# Metal accumulation in wild plants surrounding mining wastes

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Polygonum aviculare and Jatropha dioica accumulated Zn at concentrations near to the criteria for hyperaccumulator plants.

#### Abstract

Four sites were selected for collection of plants growing on polluted soil developed on tailings from Ag, Au, and Zn mines at the Zacatecas state in Mexico. Trace element concentrations varied between sites, the most polluted area was at El Bote mine near to Zacatecas city. The ranges of total concentration in soil were as follows: Cd 11–47, Ni 19–26, Pb 232–695, Mn 1132–2400, Cu 134–186 and Zn 116–827 mg kg<sup>-1</sup> air-dried soil weight. All soil samples had concentrations above typical values for non-polluted soils from the same soil types (Cd  $0.6 \pm 0.3$ , Ni  $52 \pm 4$ , Pb  $41 \pm 3$  mg kg<sup>-1</sup>). However, for the majority of samples the DTPA-extractable element concentrations were less than 10% of the total. Some of the wild plants are potentially metal tolerant, because they were able to grow in highly polluted substrates. Plant metal analysis revealed that most species did not translocate metals to their aerial parts, therefore they behave as excluder plants. *Polygonum aviculare* accumulated Zn (9236 mg kg<sup>-1</sup>) at concentrations near to the criteria for hyperaccumulator plants. *Jatropha dioica* also accumulated high Zn (6249 mg kg<sup>-1</sup>) concentrations.

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## 1. Introduction

There are a large number of sites worldwide polluted with trace elements as a result of human activities. The mining industry has produced a significant legacy of polluted and degraded soils. Historically, mining activities, in Mexico, started in the first half of the 16th century and continue to be an important component of the national economy. Currently, the volume of mineral production is in the order of thousand of tons per day. For example, the Cananea copper mine (Sonora State) produced approximately 6.552 million metric tons of waste (1926 data), and current waste production from the Colorada mine is around 2.36 millions per year

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(Ayala, 1999). Current Mexican legislation on waste disposal simply states that: "wastes should be isolated from people". Therefore, mining companies deposit residues and build the slag heaps on the ground in unpopulated areas. Following this procedure the companies save money. As a result, very significant volumes of wastes have been deposited on soil and wild plants and animals are exposed to elements contained in the residues. People living near these sites are also exposed through wind and soil erosion. In some wastes, trace element concentrations are very high. For instance it has been reported that As concentration reaches up to  $21,400 \text{ mg kg}^{-1}$  (Mendez and Armienta, 2003) and Pb up to 2300 mg kg<sup>-1</sup> (Mejía et al., 1999). In addition, contamination by Cd, Cu, Ni, and Zn will occur as these elements are secondary components of the ore minerals. This is not a minor problem, because in Mexico the area affected by mining activities is over 21.7 million hectares and 65% of the total residues come from these activities (CGM, 2001). However, there are no records of area of soil

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surface polluted and very few studies have been carried out on the concentration of pollutants and effects on plants and animals. Results of many of these limited numbers of studies are not in the public domain. In some towns and cities where people are exposed to trace elements from wastes, health problems have become apparent. For instance, high lead levels in the blood of children, arsenic in human hair (up to 20 mg kg<sup>-1</sup>), in groundwater (Armienta et al., 1997), arsenic in urine (70 µg g<sup>-1</sup>) from children (Mejía et al., 1999), and elevated lead in blood (45 µg L<sup>-1</sup>) (Cantú and Reyes, 2001) have all been reported. In addition Pb, Cd, As and Zn from mine wastes may be taken up by edible plants such as lettuce, radishes, beans, and tomatoes grown in the vicinity of mines (Cobb et al., 2000).

The treatment of polluted sites and reduction of trace metal exposure by conventional procedures is expensive and time consuming. For example, to remediate the area around the Cuale mine at Jalisco (covering with a layer of fertile soil and revegetate), the manager of Peñoles Company indicated a total cost of US \$200,000 and that it took eight years to sort out the problem (Lomelin, 2002). Taking in account the great number of mines in the country, the cost for remediation of polluted soils by such methods is prohibitively expensive.

Phytoremediation of soils is a plant-based technology that aims to either volatilize, stabilize, degrade, extract or inactivate the pollutants in soil. Phytoremediation of trace elements is the use of plants and soil amendments to reduce the hazard of pollutants by two strategies: phytostabilisation in which pollutant bioavailability and intrinsic hazard is reduced without removing it from the site; or phytoextraction which involves removing of potentially toxic substances from the soil (Huang et al., 1997; Lasat, 2002). One of its advantages is the low cost of implementation as compared to traditional engineering practices that rely on intensive soil manipulation. Another is the environmental benefits, because phytoremediation is considered a low impact technology.

Metallophytes are a group of plants that grow on mineralized areas and have developed mechanisms that allow them to resist metal concentrations which are toxic to most plants (Reeves and Baker, 2000). Some metallophytes are called hyperaccumulator plants, because they can accumulate very high concentrations of metallic or metalloid elements in their aerial tissues, far in excess of normal physiological requirements and of the levels found in most plant species (Baker and Brooks, 1989). There are also excluders which restrict uptake and transport of elements between root and shoot, maintaining low shoot levels over a wide range of external concentrations (Baker, 1981). More than 400 hyperaccumulator species have been identified (Brooks, 2000), most of them associated with metal rich soils. There are currently 172 hyperaccumulator species described in the literature for Latin America (Ginocchio and Baker, 2004), but there is a lack of knowledge of these plants in Mexico even though some endemic plants has been exposed to high concentration of trace elements for lengthy periods of time. Flores-Tavizón et al. (2003) reported that *Eleocharis* sp absorbed up to  $301 \text{ mg kg}^{-1}$  of As. It is apparently an accumulator species. The application of phytoremediation techniques, using hyperaccumulators, has raised some concerns related to invasiveness and disruption of indigenous ecosystems (Angle et al., 2001), because the introduction of alien plants may alter ecosystem function. Therefore, one alternate option is to find native hyperacumulator plants from polluted regions and use them for soil remediation in the same region. Because some plants have adapted to grow on polluted sites, it is possible to find and use them to revegetate degraded soils, either for extracting or stabilizing the elements. This research aimed to investigate polluted soils surrounding mining slag piles to identify endemic excluder, accumulator and hyperaccumulator plant species or ecotypes, and in the medium term to evaluate their capability to remove trace elements from the soil.

#### 2. Materials and methods

Mine wastes deposited on sites without any protection system, where wastes have been spread on the surrounding soils by natural agencies (wind, water rainfall), were investigated. Four sites were selected at Zacatecas, México. These were: 1) El Bote abandoned mine at Zacatecas 22° 47.085' north latitude and 102° 36.509' west longitude and 2369 m of altitude, 2) San Martin slag heaps at Sombrerete 23° 40.087' north latitude and 103° 44.868' west longitude and 2558 m of altitude, 3) Fresnillo slag piles; 23° 09.917' north latitude and 102° 51.683' west longitude and 2218 m of altitude, and 4) Noria de Angeles mining wastes; 22° 28.009' north latitude and 101° 54.305' west longitude and 2208 m of altitude. A total of 70 samples were collected from soils mixed with the slag from the areas surrounding the slag heaps. Plants were also collected here (Fig. 1), because no plants grew on the slopes and tops of the slag piles. Composite substrate samples were collected from the plant root zone (0-25 cm depth). Each plant sample represented a mixture of single samples of aerial parts taken from 3 to 5 plants. Plants samples were cleaned sequentially with a phosphate-free detergent (Extran 2%), rinsed once with tap water, once with distilled water and finally twice with deionized water, then dried at  $65 \pm 2$  °C for 48 h.

Analytical grade reagents were used throughout. Distilled-deionized water was prepared by passing distilled water through a Milli-Q Reagent grade Water System. Glassware and polyethylene containers were overnight soaked in 10% (v/v) laboratory reagent grade nitric acid, rinsed three times with distilled water, then three times with distilled-deionized water before use. Prior to chemical analysis, soils and waste samples were processed as follows: field-moist soil samples were air-dried in shade, ground, passed through a 2 mm sieve and stored in plastic bags.

Soil or slag pH was measured in a 1:2.5, soil to deionized water ratio, and soil to 10 mM CaCl<sub>2</sub> ratio using a 420A pH meter (Orion Research, Beverly, MA) (Peech, 1982). Moist slag color was determined in the laboratory on sieved samples using Munsell soil color charts (Munsell Color, 1998). Organic matter was determined by the Walkley and Black procedure (Nelson and Sommers, 1982). Particle distribution was determined according to Day (1965). Cation Exchange Capacity (CEC) was measured on duplicate samples following the standard procedure (Rowell, 1994). Triplicate waste and soil samples from the rhizosphere volume were analysed for metal content using aqua regia digestion (BS, 1995) and the DTPA-TEA-CaCl<sub>2</sub> procedure (Lindsay and Norvell, 1978). Dry samples of plant material were digested with HNO<sub>3</sub>-HClO<sub>4</sub>-H<sub>2</sub>SO<sub>4</sub> mixture (Walinga et al., 1995), with two replicates. Solutions from digested soil and plant samples were stored in 100 mL high density polyethylene samples bottles at 4 °C until analysis. Metal concentrations of the digests were determined using an flame atomic absorption spectrometer (FAAS-Perkin Elmer 2100) or inductively coupled plasma optical emission spectrometry ICP-OES (Varian). For quality control of the digestion procedures, blanks for digestion and analysis methods and internal reference sample were carried out in triplicate with each set of samples. The detection limit of the method (DL) was determined following the analysis of 10 blank replicates. The arithmetic mean and standard deviation were computed and DL was determined as three times the standard deviation. The DL for Cd,



Fig. 1. Map showing the location of the soil sampling sites: 1) El Bote mine at Zacatecas, 2) San Martin tailing mine at Sombrerete, 3) La Compania tailing mine at Fresnillo and 4) Noria de Angeles.

Cu, Pb and Zn were 0.01, 0.05, 0.07, and 0.01 mg kg<sup>-1</sup>. The average recovery rates for the spiked samples were from 94 to 98%. To identify the mineral composition, slag samples were analyzed by XRD from 3 to  $80^{\circ} 2\theta$  with a GBC 122D X-ray diffractometer and Traces v6 software (GBC Instrumentation). Samples were prepared for herbarium processing and identified at the University of Chapingo (UACh) and National University of Mexico (UNAM).

## 3. Results and discussion

Soil type at Site 1 and 3 are Kastanozems; Calcaric Regols and Calcaric Leptosols predominate at Site 2 with accumulation of iron oxides and at Site 4 the dominant soil types are Petric Calcisols and Calcaric Leptosols (according to the FAO-UNESCO classification scheme). Soil samples had different physicochemical properties and patterns of pollution. All the soil samples had neutral to alkaline pH values except for Site 1, where soils and brown slag had a slightly acid pH (Table 1). The low pH of the tailings may be due to the weathering of the sulphide minerals, and the alkaline values may be due the reaction with carbonates. The parental material of each

 Table 1

 Soil and slag pH in samples collected from abandoned mine sites in Zacatecas

Site <sup>a</sup>	1		2		3		4	
рН	$H_2O$	$CaCl_2$	H <sub>2</sub> O	$CaCl_2$	H <sub>2</sub> O	$CaCl_2$	$H_2O$	CaCl <sub>2</sub>
Topsoil (0-20 cm)	4.95	5.02	7.79	7.06	8.44	7.74	8.46	7.95
Layer 2 (20-40 cm)	4.61	4.39	-	-	7.85	7.41	-	_
Soil + slag	6.19	6.43	7.71	7.39	7.4	7.5	8.46	7.95
Brown slag	3.90	4.6	7.64	7.46	8.39	8.31	7.58	7.52
Yellow slag	7.06	7.54	7.7	7.41	-	_	7.62	7.57

<sup>a</sup> 1) El Bote mine at Zacatecas; 2) San Martin tailing mine at Sombrerete; 3) La Compania Tailing mine at Fresnillo and 4) Noria de Angeles, Zacatecas.

site has important influence on the pH of the soil-mine waste material, because the slag-soil mixtures have intermediate values between soil and slag reaction. At sites 2, 3 and 4, pH values of soil and slags were in the same range. The pH values can be explained if it is considered that tailings from ore minerals disposed at these sites are normally associated with calcite. It is expected that at high pH values low trace metal bioavailability should be found, whilst As will become more mobile. The CEC was low in these soils mixed with slags ranging from 5 to 17 cmol<sub>c</sub> kg<sup>-1</sup>, apparently due to the high proportion of sand present. The sand and clay distribution was as follows: in Site 1: 47% and 30%; site 2: 33% and 38%; site 3: 35% and 22%; and site 4: 49% and 22%.

The dominant mineral in the slags was quartz, followed by calcite, hematite and pyrite. According to the Munssel scale the colour of the residues varies from reddish yellow to red (5Y 6/6 to 2.5Y 5/6) at the Site 1, from black to light reddish brown (5Y 2.5/2 to 5Y 6/3) at Site 2; from light red to dusky red (2.5Y 6/6 to 10YR 3/4) at site 3 and from gray to dark gray to (7.5YR 5/0 to 7.5YR 4/0) at Site 4. A complete description of soil types is given by Sánchez-Guzmán (2005).

Metal concentrations in mine tailing were very variable, depending on the original mineral compositions. At Site 1 yellow residues had higher metal concentrations than the brown residues, possibly because the lower pH values have allowed leaching of metals from brown residues. At the El Bote mine, 14 ore minerals were extracted, therefore the residues have a heterogeneous composition. Mine wastes from Sites 2, 3 and 4 had lower Pb concentrations compared to those from Site 1 (Tables 2–5). The range of Zn concentrations at Site 2 was wider than at the other sites (Table 3). Two possible explanations are suggested: i) the heaps at site 2 were located on the slope of the hill, where water from rainfall flows very

Table 2 Total and DTPA extractable trace elements concentration in soil and slag residues from El Bote mine (Site 1)

Element	Cd	Ni	Pb	Mn	Cu	Zn
	mg kg <sup>-1</sup>					
Totals						
Soil + slag	22.6	17.5	1489.4	1197.1	197.5	947.7
Brown slag	7.7	9.2	1015.1	665.8	184.4	116.5
Yellow slag	30.0	18.9	2061.9	1499.0	12,313.1	1449.0
DTPA	Extractabl	e				
Soil + slag	0.12-1.9	Tz-0.7	56-188.6	7-68.4	3-12.6	6-51
Brown slag	1.04	Tz	307.6	22.6	9.9	18.4
Yellow slag	3.18	Tz	27.46	4.42	4.7	26.4

Tz = traces.

fast and has caused significant erosion from the tailing heaps; ii) residues dumped at this site come from different mines, where up to 17 different ore minerals are processed. Total metal concentrations in soil increased near to the slag heaps, and were greater in the upper soil layers. These also varied with the proportion of soil and wastes mixed. For example, Cd concentrations varied from 9 to 93 mg kg<sup>-1</sup> and Zn concentrations from 16 to 1776 mg  $kg^{-1}$  in the same area (Table 2). Metal concentration in the plant rhizosphere (soil + slag) also varied with the location in the field. Concentrations of DTPA extractable elements were less than 5% of the total element concentration. The element with the lowest concentration at Site 1 was Ni, followed by Cd; Pb had the highest concentration. At the Site 2, concentrations were higher, but the extractable levels were still low (less than 11% of the total) (Table 4). Element concentrations increased as follows: Ni < Cd < Pb  $\leq$  Mn  $\leq$  Cu  $\leq$  Zn. Total metal concentrations at Site 3 varied in the following order: Cd < Ni < Cu < Pb < Zn < Mn, and extractable concentrations were lower than 12%. Soils in the vicinity of the slag heap had lower Cd, Ni and Pb concentrations compared to those found in the waste. The main ore minerals extracted in this zone are pyrargyrite and acantite, but they have more than 12 secondary minerals associated with them.

At the Site 4 concentration of the elements increased in the following order:  $Cd < Ni < Pb \le Cu \le Zn \le Mn$ . Even the tailings, found in the same heap, have extremely variable

metal concentrations. This is apparently due to the origin of the wastes, because the residues disposed at this site come from 13 mines, where more than 17 ore minerals are extracted.

Wastes from the San Martin Mine at Sombrerete had different Cd, Pb, Mn and Zn concentrations which results in variable concentration in the associated soils. Here, the litter layer has higher metal concentrations compared with the A layer of the soil and with unpolluted soil. This may be due to direct deposition of particulate matter on litter from the eroding heaps. Trace element concentrations in soil and waste samples were higher than the values considered as frequent for uncontaminated soils (Table 6). Even in soil collected some distance from the slag heaps, Cd concentration was relatively high. This is almost certainly the result of re-entrainment of metal rich particulates from the slag heaps. This mechanism of exposure to trace elements has been documented by Mejía et al. (1999) in another region of Mexico.

More than 70 native and introduced plant species from 18 families were found growing in the polluted soils. Only 36 of them were identified, because of the lack of reproductive organs, and the results of their chemical analysis are presented here. Fifteen species of Compositae were identified as well as three species of Gramineae (Fig. 2; Table 7). Freitas et al. (2004) found a wide range of plant families growing on trace element-contaminated soils. These authors reported the occurrence of members of the genera Polygonum and Euphorbia, which were also found at these sites. Non-endemic tree species, such as: Eucalyptus sp., Casuarina cunninghamiana and Schinus molle were able to grow on these residues, but they do not produce a leafy crown and the trunks showed clear signs of poor growth. These plants had tiny leaves, which show chlorosis, necrotic brown spots and dried tips. In some cases they died after few years (5 to 10 years) exposure to the slag. Schinus molle is a native plant from Peru, but nowadays it is widely spread on arid Mexican soils. Not all analysed plants accumulated trace metals in shoots and leaves.

Native plants, e.g. *Teloxys graveolens* and *Jatropha dioica* accumulated 42.9 and 30.5 mg Cd kg<sup>-1</sup> DW and 37 and 28 mg Ni kg<sup>-1</sup> DW, respectively. Lead was accumulated in relatively high concentrations in *Polygonum aviculare* (124 mg kg<sup>-1</sup>) and *Teloxys graveolens* (125 mg kg<sup>-1</sup>), but Zn was accumulated at high concentrations by more species. The

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otal trace elements in the litter, surrounding soils and slag piles at the San Martin tailing mine at Sombrerete, Zacatecas (Site 2), compared to a non-polluted soil

	Cd	Ni	Pb	Mn	Cu	Zn
	mg kg <sup>-1</sup>					
Total						
Slag	83-110	22-38	319-1149	699-1397	771-1534	899-4107
Soil	9.3-93	27-58	126-702	999-1893	71-769	16-1776
Litter	80	28.1	856	866.4	1547	3616
Non-polluted soil	11	0.3	74.7	199.4	5.2	33.2
DTPA	Extractable					
Slag	5.6-11	0.02-0.42	<560	0.6-68	8-50	132-147
Soil	3.5-11	<1.0	6-71	0.2-4.2	4.5-26	20-58
Litter	11.5	0.58	2.3	1.8	13	155
Non-polluted soil	2.8	0.2	0.28	0.1	1.3	5.5

Table 4	
Total and DTPA extractable trace elements in surrounding soils-slag mixtures and slags of the La Compania tailing mine at Fresnillo, 2	Zacatecas (Site 3)

Element	Cd	Ni	Pb	Mn	Cu	Zn
	mg kg <sup>-1</sup>					
Total						
Soil-slag <sup>a</sup>	11-44	19-26	232-695	1132-2400	134-186	116-827
Slag	33-73	28-35	889-3388	2950-4189	280-344	1110-2776
Soil	3.0	23	16.3	599	15	283
DTPA	Extractable					
Soil-slag <sup>a</sup>	1-3.4	0.18-0.35	14-73	7.5-14.5	7.0-14.5	12-65
Slag	2.5-12.6	0.18	61-168	8-10	7.5-26	45-98
Soil	0.18	0.44	Tz	4.0	0.28	3.0
3011	0.10	0.44	12	4.0	0.20	3.0

<sup>a</sup> Soil-slag mixtures.

concentrations of Zn in *Brickellia veronicifolia*, *Jatropha dioica* and *Polygonum aviculare* were 6000, 6250, and 9230 mg kg<sup>-1</sup>, respectively (Fig. 2a). The concentration in *P. aviculare* was close to the criteria for considering a hyperaccumulator plant (10,000 mg kg<sup>-1</sup>). But, because the analysed samples come from the field condition there is always the possibility of foliar contamination from wind-blown particulates, therefore greenhouse experiments should be carried out to study the accumulation ability of this species. All other plants from Site 1 accumulated less than 1000 mg Zn kg<sup>-1</sup>. Although *P. aviculare* grows quickly during the rainy season, its biomass is approximately  $20 \pm 4$  g per adult plant.

The plants collected from Site 2 had lower Cd, Ni and Pb mean concentrations than in Site 1, and elevated Zn concentrations were only found in *Stachys coccinnea* and *Equisetum sp* (1025 and 1202 mg kg<sup>-1</sup> respectively). *Polygonum aviculare* had a high Zn concentration (925 mg kg<sup>-1</sup>), but lower than at Site 1. Zn concentration in other plant species ranged from 60 to 505 mg kg<sup>-1</sup>. *Stachys coccinnea* also had high Cu concentrations (112 mg kg<sup>-1</sup>), but all other species had low concentrations of trace elements (Fig. 2b).

Five plants species: *Teloxys graveolens*, *Bidens odorata*, *Cynodon* sp, *Xanthium strumarium* and *Haplopapus venetus*, from Site 3 had relatively low concentrations of trace elements. *T. graveolens* had lower Zn concentration than the specimen from Site 1. *Sanvitalia procumbens* accumulated 71 mg Pb kg<sup>-1</sup> and 400 mg Zn kg<sup>-1</sup>. *Solanum elaegnifolium* accumulated up to 75 mg Pb kg<sup>-1</sup> and 2299 mg Zn kg<sup>-1</sup> (Fig. 2c).

The concentrations of Cd, Ni, Pb and Cu in plants collected at Site 4 were relatively low. The highest Zn concentration was

Table 5

Total and DTPA extractable trace elements in surrounding soils and slags at Noria de los Ángeles, Zacatecas (Site 4)

Element	Cd	Ni	Pb	Mn	Cu	Zn		
	mg kg⁻	$mg kg^{-1}$						
Total								
Slag	20.8	36.8	665.9	1048.9	114.1	668.0		
Soil <sup>a</sup>	3.3	13.7	36.3	1032.3	18.0	782.6		
DTPA	Extract	Extractable						
Slag	1.1	0.5	84.7	6.5	2.3	14.1		
Soil <sup>a</sup>	0.3	0.5	2.5	0.3	0.4	3.0		

<sup>a</sup> Top soil.

found in *Asphodelus fistulosus* (430 mg kg<sup>-1</sup>). Trace element accumulation increased in the following order: Cd < Ni < Cu < Pb < Zn (Fig. 2d).

Three species, Bahia absinthifolia, Aster lanacetifolius and Andropogon barbinodis, accumulated low Cd, Cu, and Pb concentrations. Possibly the high soil pH had an important role in controlling plant metal absorption. Solanum elaeagnifolium was the species with most Pb accumulated (148 mg  $kg^{-1}$ ), but uptake of Cd was low  $(3.9 \text{ mg kg}^{-1})$ . This can be explained if we consider that some metals may interact competitively during uptake (Hossner et al., 1998). Therefore the ability of a plant to accumulate any metal may not infer the ability to accumulate other elements. In addition, although plants were carefully washed to remove surface deposits, is still possible that metal concentrations measured in shoots may have partially arisen from aerial deposition. However, most of the collected plants seem to be either metal tolerant or metal resistant species, because the soils in which they grew had concentrations of DPTA-extractable metals. Some of the species may be metal excluders, which actively prevent metal accumulation inside the cells (Baker, 1981). If we consider the bioconcentration factor (BCFs; Table 7), which is defined as the ratio of element concentration in plant tissue to that in soil or slag-mixture, just *Bourvardia ternifolia* (138) and Teloxys graveolens (69.4) from Site 1 had high BCFs for Zn, compared with the BCF (61) of Pityrogramma calomelanos the hyperaccumulator fern, which accumulated up to  $8350 \text{ mg kg}^{-1}$  grown in soil with  $135 \text{ mg kg}^{-1}$  of As (Francesconi et al., 2002). Polygonum aviculare (33.6) and Stevia salicifolia (24.2) from the same site, Haplopapus T-1-1- (

1	at	ne	0	

Normal range of trace element concentr	ations and permissible limits in soil
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Element	Cd	Ni	Pb	Mn	Cu	Zn
Normal	mg kg <sup>-1</sup> 0.06-1.1	<40	17-42	<100	2-100	10-300
Critical	>5	35-75	>100	80-5000	>300	>300
limits						
US EPA <sup>a</sup>	20	210	150	_	750	1400
Zacatecas <sup>b</sup>	$0.6\pm0.3$	$52\pm3$	$41\pm3$	$58.5\pm1$	$88\pm0.7$	$536\pm83$

Source: Alloway (1995), Visser (1994).

<sup>a</sup> Calculated from maximum cumulative pollutant loading limits into soil plow layer. Soil background concentration are not taken into account. USEPA (1993).

<sup>b</sup> Typical concentration in non-polluted soil at Zacatecas.



Fig. 2. Metal accumulation in native plants from four polluted sites at Zacatecas, Mexico. a) El Bote, b) Sombrerete, c) Fresnillo and d) Noria de los Angeles.

Table 7

Trace elements bioconcentration factor of wild plants growing on soil-slag mixtures surrounding slag heaps

Site	Plant species	Family	Zn	Cu	Pb	Cd
1	Tagetes lunulata Ort.	Compositae	2.7	4.3	0.6	6.1
	Polygonum aviculare L.	Polygonaceae	33.6	2.7	1.0	29.9
	Teloxys graveolens Willd.	Chenopodiaceae	69.4	3.3	Pb           0.6           1.0           2.0           1.7           1.2           1.3           0.8           1.4           0.4           0.3           0.3           0.3           2.5           6.8           2.7           2.0           6.8           5.2           2.1           2.6           2.6           2.1           2.6           2.1           2.6           2.1           3.0           0.4           1.3           0.4           1.0           1.6           7.3           3.4           0.9           2.7           0.7	27.9
	<i>Jatropha dioica</i> Sessé ex Cerv	Euphorbiaceae	195	6.5		18.8
	Bouvardia ternifolia (Cav.) Schlecht	Rubiaceae	13.8	5.2		8.2
	Brickellia veronicifolia (HBK)	Compositae	40	3.8		7.5
	Gnaphalium arizonicum Grav	Compositae	97	5.2	0.8	3.8
	Stevia salicifolia Cay	Compositae	24.2	2.3	1.4	9.5
	Salvia microphylla HBK	Labiatae	15	6.5	0.4	4.0
	Haplopappus venetus (HBK) Blake	venetus (HBK)Compositae7.92.3rLeguminosae5.83.6. exWilld	0.4	1.8		
	Dalea bicolour Humb&Bonpl. exWilld	Leguminosae	5.8	3.6	0.3	1.7
	Euphorbia sp.	Euphorbiaceae	1.3	5.1	0.3	3.5
	Asclepias linaria Cav.	Asclepiadaceae	5.6	2.0	0.3	2.3
2	Stachys coccinea Jacq	Compositae	3	0.9	2.5	0.1
	Aster gymnocephalus (DC) Gray	Polygonaceae	2.5	0.2	0.3 0.3 2.5 6.8 2.7 2.0 6.8 5.2 2.1 2.6	0.3
	<i>Viguiera linearis</i> (Cav.) Sch. Bip	Compositae	4.1	0.4	2.7	2.0
	Asphodelus fistulosus L.	Asphodelaceae	1.5	0.2	2.0	1.2
	Polygomun aviculare L.	Polygonaceae	6.0	7.6	6.8	1.2
	Equisetum sp.	Equisetaceae	9.2	1.5	5.2	0.6
	Schinus molle L.	Anacardaceae	2.2	0.9	2.1	0.5
	Juniperus sp.	Anacardaceae2.20.9Cupressaceae2.91.1	1.1	2.6	0.5	
	Erigeron pubescens HBK	Compositae	2.6	1.6	6.8 5.2 2.1 2.6 2.6 0.9	0.4
3	Heterospema pinnatum Cav.	Compositae	4.5	2.0	0.9	4.6
	Cyperus sp.	Polygonaceae	10.2	2.2	1.4	3.8
	Bidens odorata Cav.	Gramineae	3.1	1.6	1.3	2.2
	Cynodon sp.	Gramineae	3.9	1.1	0.6	4.0
	Xanthium strumarium L.	Compositae	10.7	2.5	1.1	1.5
	Solanum elaeagnifolium Cav.	Solanaceae	11.0	1.5	1.5	2.1
	<i>Haplopappus venetus</i> (HBK) Blake	Compositae	29.3	8.6	4.5	3.3
	Sanvitalia pronombens Lam.	Compositae	13.0	5.1	2.1	3.7
	<i>Aster tanacetifolius</i> (DC) Gray	Compositae	8.3	3.2	1.3	3.8
	Reseda luteola L.	Resedaceae	2.2	0.4	0.4	0.9
	Casuarina equisetifolia Mig.	Casuarinaceae	3.1	1.5	1.0	5.5
	Teloxys graveolens Willd.	Chenopodiaceae	4.1	1.4	1.0	1.9
4	Salsola kali L.	Chenopodiaceae	25.8	8.8	2.7 $2.0$ $6.8$ $5.2$ $2.1$ $2.6$ $2.6$ $0.9$ $1.4$ $1.3$ $0.6$ $1.1$ $1.5$ $4.5$ $2.1$ $1.3$ $0.4$ $1.0$ $1.0$ $1.6$ $7.3$	6.3
	Andropogon barbinodis Lag.	Gramineae	2.0	12.5	7.3	4.4
	Aster tanacetifolius H.B.R.	Compositae	34.7	12.7	1.3	1.9
	Bahia absinthifolia Benth	Compositae	2.3	37.5	3.4	5.8
	Asphodelus fistulosus L.	Asphodelaceae	29.0	3.0	0.9	9.8
	Solanum elaeagnifolium Cav.	Solanaceae	13.7	4.6	2.7	1.5
	<i>Dyssodia papposa</i> (Vent) Hitchc	Compositae	11.9	6.9	0.7	3.2

Bioconcentration factor (the ratio of metal concentration in plant tissue to those DTPA extracted from soil).

*venetus* (29.3) collected from Site 3, *Aster tanacetifolius* (34.7) and *Asphodelus fistulosus* (29) from Site 4 had medium BCFs values. All the other species had low BCFs, in some cases lower than 1.

Differences in element uptake were observed in the same species collected from different sites. Soil (metal concentration, speciation, pH) and plant (age and ecotype) factors may modify plant uptake and the ratio of concentration in the shoot to root (Florijn et al., 1993; Jiang and Singh, 1994; Tu et al., 2002). Soil pH at Site 1 was lower than at the other sites, potentially affecting metal bioavailability. Young plants of *Thlaspi caerulescens* accumulated lower amounts than old specimens with up to a 29-fold difference in BCF's (Küpper et al., 2004).

Mining activities have had a significant effect on the native vegetation with few species able to colonize the soil-slag mixtures, compared to the diversity frequently observed in adjacent, uncontaminated areas. Slags are usually set up in heaps or deposited on the side of hills, therefore vegetation is covered or eventually killed by the toxicity of the residues, and after period of time, adventive species have colonized the vicinity of the heaps, or some introduced tree species have survived. There is a lack of information of the effect of the wastes on wild herbivores.

## 4. Conclusions

- Trace element concentrations in soil-slag mixtures varied widely within and between sites. Soil characteristics and the minerals from which the tailings were derived determined trace element concentrations.
- Metal concentrations in wild plants were very variable. They are metal tolerant plants, because they were able to grow in highly polluted substrates. Some of them behave as excluder plants, because metal concentrations in their aerial tissues did not increase although concentrations in the soil-slag mixture were high.
- Most plants did not translocate metals to the shoot system even if metal concentrations in the soil-slag mixtures were high.
- *Polygonium aviculare* growing at Site 1 (with slightly acid soil) accumulated Zn at concentrations near to the criteria for hyperaccumulator plants, but accumulated lower concentrations at Site 2 where pH was higher.
- Greenhouse experiments are needed to confirm if species are accumulators or excluders.
- The bioconcentration factor for the same species collected from different sites showed site-dependant changes.

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