

Original Article

Arsenic Concentration in Wild Plants Growing on Two Mine Tailings

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ABSTRACT

Introduction: Plant metalloid contamination may represent an important pathway of Arsenic (As) intake by humans, wild herbivores and livestock. **Objective:** This study aimed at estimating Arsenic (As) exposition risks to wild plants naturally growing on the contaminated area of Zimapán, Hidalgo, Mexico. **Materials and Methods:** Arsenic concentrations in the rhizosphere, aerial and root parts, and deposition on leaves of wild plants from two mine tailings were analyzed. **Results:** The range of total and EDTA-extractable Arsenic (As) concentrations on the mine tailings were from 4016 to 17,178 mg kg⁻¹ and from 234 to 499 mg kg⁻¹, respectively. Eleven plant species were the dominant vegetation. Some of these are important in the folk Mexican medicine. Retention of Arsenic (As) in aerial part was between 49 to 7,521 mg kg⁻¹. The highest shoot As concentration, bioconcentration and translocation factors were observed in *Gnaphalium*. (2,939 mg kg⁻¹, 5.7, 10.3) and *Aster gymnocephalus* leaves (2,409 mg kg⁻¹, 8.6 and 9.6, respectively). *Juniperus* sp and *Ruta graveolens* behaved As excluders, while *Dalea bicolor* accumulated Arsenic (As) close to the maximum tolerate concentrations to animals. After a very drastic washing procedure, leaves still had structural high Arsenic (As) concentration (49-2,940 mg kg⁻¹). **Conclusion:** This study highlighted that plants are important organism for retaining Arsenic (As) not only on leaves surface but also structurally. Therefore, they strongly influence Arsenic (As) dispersion and risk from mine tailings. Phytoremediation using some of these plants is suggested taking into account control measures to deplete Arsenic (As) transfer to livestock or medicinal herb use.

Key words: Food web, Hyperaccumulation, Metalloid transfer, Native plants, Phytoremediation, Plant accumulation.

INTRODUCTION

Arsenic is a natural earth constituent and occurs in several chemical forms due to natural and anthropogenic sources.¹ Mining activity and the resultant huge amount of residues are one of the main via by which Arsenic (As) and other contaminants move in the environment.² When untreated

these residues may result in hazards to ecosystems due to dispersion and pose a potential risk to human health and animals³

Arsenic does not have any essential function to plants or humans. This has a very long soil residence time: from 1000 to 3000 years.¹ From a list of 275 of hazardous substances, the Agency for Toxic Substances and Disease Registry considers to Arsenic (As) the most harmful substance to human health.⁴ Some of the health problems due to high ingestion of Arsenic (As) are: dehydration, weakness and lethargy.⁵ It is involved in cardiovascular, gastrointestinal, hepatic and renal disease⁶ and is promoter of bladder, lung and skin cancer.⁷ Arsenic may enter to human body through consumption of contami-

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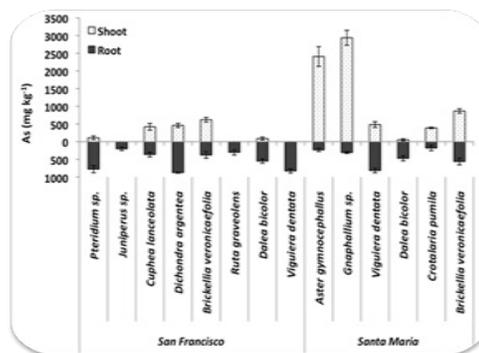
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As is dispersed from tailing heaps



We evaluated the risk of As exposure of medicinal plants around tailing heaps. As was detected on plant tissues

While some plants (*Juniperus* sp., *Ruta graveolens*, *Dalea bicolor*) behave as excluder or stabilizer of As, others (*Aster gymnocephalus*, *Gnaphalium* sp.) are As-hyperaccumulators. As-transfer to livestock or humans by forage or medicinal herb use is a concern.

Graphical Abstract

nated food plants.⁵ Herbal medicines are currently collected from wild fields by large sections of population and used with poor care, since these plants are not regulated Arsenic (As) medicines. Practices of indigenous herbal medicine include the use raw herbs, so toxic contaminants may come from environments where the medicine plants are grown or collected.

Under arid and semiarid conditions, the dispersion of the contaminants seems to respond in a greater degree to a physical dispersion of contaminants from mine tailings than their chemical mobility.⁸ Ramirez-Andreotta *et al.* (2013) mentioned that wind erosion disperse coarse particles which in minutes to hours settle out of the atmosphere with a wide distribution of metalloid concentrations.³ Hence, our hypothesis is that under these untreated abandoned and sky-open mine tailings at Zimapan, Hidalgo, Mexico there is a hazard to animals and humans due to Arsenic (As) contamination. Previous research in two mine tailings located at Zimapan, Hidalgo, in Mexico showed that native plants are an important phytoremediation alternative to decrease dispersion of several potential toxic elements such Arsenic (As) Cu, Pb, Ni, Cd and Zn.⁹ However, these authors did not consider the risk of Arsenic (As) in these mine tailings.

The objectives of this research were: 1) to assess the environmental risk of Arsenic (As) in wild plants naturally established in two mine tailings, 2) to analyze Arsenic (As) deposition in leaves of different wild plants, 3) to identify

wild plants useful for Arsenic (As) phytoremediation of two polluted mine tailings.

MATERIALS AND METHODS

Study Area

The study was developed in the municipality of Zimapan, Central Mexico in Hidalgo State. This is a semiarid area with 700 mm of annual rain. Mine tailings are mostly barren material mixed with the material rejected by mining activities. Two barren and uncover mine tailings heaps were selected for this study: San Francisco (SF) and Santa Maria (SM). The residues from SF mine have been deposited on nine tailing heaps since 1973 until the present days. These tailings range from fresh to oxidized and are located 10 km far from Zimapan town (20°49' 32.5" N and 99°22' 20.1" W) where house ship is in contact with these tailings, including around 30 families. In contrast, SM is an un oxidized mine tailing (20°44' 8.89" N and 99°23' 56.07" W). It is located next of the Zimapan town and the closer population settlement is within the 10 m next to the tailing; which implies a high health risk concern. The natural predominant vegetation was analyzed in these two sites.

Rhizospheric mine tailing and plant sampling

Mine tailing samples were collected from the top 15 cm in the rhizosphere (area of roots influence) of plants estab-

lished in the two mine tailings. Fresh plant tissues (shoots and roots) samples were collected for chemical analysis. Plant and mine tailing samples were stored in clean plastic bags until chemical analysis.

Physicochemical analysis

pH, Electrical Conductivity (EC), available P concentration, Organic Matter (OM) were analyzed in mine tailing samples. pH was determined in a 1:2.5 mine tailing: deionized water solution with a 420 A pH meter (Orion Research, Beverly, MA). In the same solution but after 24 h equilibrium, the EC was analyzed using a Fisher Brand 09-325-360 conductivity meter. Available P concentration

was determined by the Olsen method.¹⁰ Organic matter was analyzed by Walkley and Black procedure.¹¹ All parameters were analyzed in triplicate.

Arsenic analysis in plants and rhizospheric mine tailings

Prior to as analysis, mine tailing rhizospheric samples were air-dried at room temperature and then passed through a 2 mm stainless sieve. Total Arsenic (As) concentration in the mine tailings was analyzed in samples digested with concentrated HNO₃ following USEPA 3050 method¹² and using a flame atomic absorption spectrometer (FAAS-Perkin-Elmer Analyst 700). In addition,

Table 1: Total and EDTA-extractable Arsenic (As) concentrations, bioavailability index (BI), bioaccumulation (BAC) and translocation factors (TF) of wild plants growing on two mine tailings in Zimapan, Hgo.

Site/plant	pH	EC (d Sm ⁻¹)	P (mg kg ⁻¹)	OM (%)	Total Arsenic (As) (mg kg ⁻¹)	EDTA- Arsenic (As) (mg kg ⁻¹)	BI § (%)	BAF	TF
San Francisco									
<i>Pteridium</i> sp.	6.4 ± 0.4	2.8 ± 0.1	23.7 ± 2.2	0.82 ± 0.07	4016 ± 979	244 ± 13.4	6.1	0.5	0.1
<i>Juniperus</i> sp.	5.8 ± 0.2	1.8 ± 0.1	14.1 ± 1.1	2.94 ± 0.07	13413 ± 645	344 ± 7.7	2.6	0.0	0.0
<i>Cuphea lanceolata</i> Aiton (Lythraceae)	6.5 ± 0.2	1.8 ± 0.1	19.4 ± 1.1	8.1 ± 0.07	5066 ± 540	324 ± 11.2	6.4	1.3	1.2
<i>Dichondra argentea</i> Humb. & Bonpl. ex Willd (Convolvulaceae)	6.6 ± 0.2	2.4 ± 0.2	19.4 ± 1.1	2.5 ± 0.05	9488 ± 647	318 ± 9.6	3.4	1.4	0.5
<i>Brickellia veronicifolia</i> (Kunth) A. Gray (Asteraceae)	6.4 ± 0.2	1.9 ± 0.1	20.0 ± 2.2	2.5 ± 0.1	5879 ± 657	299 ± 16.2	5.1	2.1	1.6
<i>Ruta graveolens</i> L. (Rutaceae)	6.8 ± 0.1	1.8 ± 0.1	22.5 ± 0.0	3.5 ± 0.2	6367 ± 623	275 ± 14.6	4.3	0.0	0.0
<i>Dalea bicolor</i> Humb. & Bonpl. ex Willd (Fabaceae)	6.7 ± 0.1	1.7 ± 0.2	15.0 ± 0.0	4.4 ± 0.5	10309 ± 592	234 ± 9.7	2.3	0.4	0.2
<i>Viguiera dentata</i> (Cav.) Sprenguel (Asteraceae)	6.8 ± 0.1	1.6 ± 0.2	15.6 ± 1.1	6.7 ± 0.5	5586 ± 321	293 ± 13.7	5.2	0.0	0.0
Santa Maria									
<i>Aster gymnocephalus</i> A. Gray (Asteraceae)	6.4 ± 0.4	0.5 ± 0.1	3.8 ± 0.0	0.7 ± 0.2	17178 ± 1007	422 ± 4.9	2.5	5.7	10.3
<i>Gnaphalium</i> sp.	5.8 ± 0.2	0.5 ± 0.1	1.9 ± 0.0	0.1 ± 0.06	17021 ± 1000	343 ± 4.4	2.0	8.6	9.6
<i>Viguiera dentata</i> (Cav.) Sprenguel (Asteraceae)	6.5 ± 0.2	0.4 ± 0.1	7.5 ± 0.0	0.5 ± 0.05	15952 ± 344	499 ± 16.6	3.1	1.0	0.6
<i>Dalea bicolor</i> Humb. & Bonpl. ex Willd (Fabaceae)	6.6 ± 0.2	0.4 ± 0.1	7.5 ± 0.0	0.8 ± 0.10	15623 ± 816	457 ± 14.0	2.9	0.1	0.1
<i>Crotalaria pumila</i> Ortega (Fabaceae)	6.4 ± 0.2	0.4 ± 0.1	8.7 ± 1.0	0.8 ± 0.05	4760 ± 834	257 ± 8.9	5.4	1.5	2.2
<i>Brickellia veronicaefolia</i> (HBC) Similar to A. Gray (Asteraceae)	6.8 ± 0.1	0.4 ± 0.1	8.1 ± 1.0	0.1 ± 0.01	16660 ± 709	497 ± 30.9	3.0	1.7	1.5
Threshold Arsenic (As) limits	-	-	-	-	22† 260‡	-	-	-	-

§BI was calculated as ratio of EDTA-As/total-As*100; †NOM-147-SEMARNAT/SSA1-2004. Mexican regulation for soils for agricultural/residential/commercial use.⁴⁹; ‡NOM-147-SEMARNAT/SSA1-2004. Mexican regulation for soils for industrial use.⁴⁹; Mean ± standard deviation, n=3.

extractable Arsenic (As) was analyzed by using EDTA Arsenic (As) extractant in an extraction ratio 1:4 mine tailing: solution.¹³

Aerial plant parts were washed separately according to the next procedure to remove possible attached particles.¹⁴ Washing up with tap water for 10 min to remove mechanically soil particles was done. Then rinse with phosphate-free detergent Extran 2% for 10 min, rinse with distilled water for 10 min, wash with diluted HCl 10% for 15 min and three rinses with deionized water for 15 min. Root samples had the same washing protocol, but using twice the time in the first rinse with tap water and diluted HCl.

Air (Arsenic (As) dust) is an important via to disperse Arsenic (As) and other contaminants. It is recognized that plant surfaces act Arsenic (As) pollutant sinks; however, this pathway has not been quantified. Therefore, Arsenic (As) deposition in leaves was evaluated As follows: a set of aerial samples did not follow a washing treatment.

All samples (shoots and roots) were dried at 40°C during one week and then ground in a Stanley steel mill. About 500 mg of dry matter was acid-digested with 1 mL H₂O₂ and 4 mL H₂SO₄: HClO₄ (4:1 v/v). All extracts were analyzed for Arsenic (As) contents by hydride generation. Standard soil and plant reference materials were analyzed Arsenic (As) a part of the quality assurance–quality control protocol

(accuracies within 100 ± 10%). Analysis in all cases was followed in triplicate.

Bioaccumulation and translocation factors

Bioaccumulation (BAFs) and translocation factors (TFs) were calculated. The first one defined Arsenic (As) the ratio of shoot *vs* extractable soil concentration¹⁵ and the quotient of concentration in the aerial part to the roots,¹⁶ respectively. The BAF measures the efficiency of the plant in up taking Arsenic (As) from the soil; while TF in transporting Arsenic (As) from the root to the aerial part.

RESULTS AND DISCUSSION

Physicochemical analysis

pH in all rhizospheric samples was between 5.8 to 6.8 (Table 1). Apparently mineral oxidation does not deplete pH in the sampling points. At SF mine, EC varied in the range 1.6-2.8 dS m⁻¹. Variation in salt contents could be affected by the salts (such Arsenic (As) ZnSO₄) added to the minerals during ore minerals extraction. While OM content varied 0.82 to 8.1% and extracted P was very low (14-23.7 mg kg⁻¹; Table 1). Plant colonization increased OM incorporation to the soil and P availability. At SM mine EC and P were lower than in SF mine samples. EC

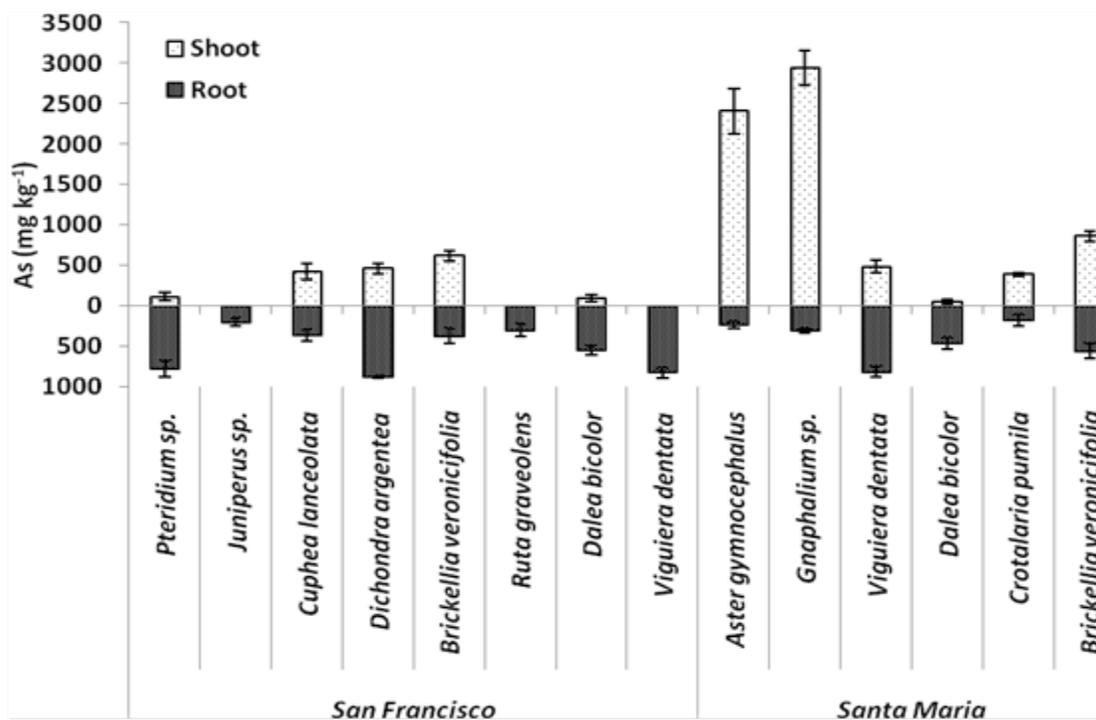


Figure 1: Concentration of arsenic in shoots and roots of wild plants growing on two mine tailings at Zimapan, Hgo
Bars represent mean (n=3) and standard deviation

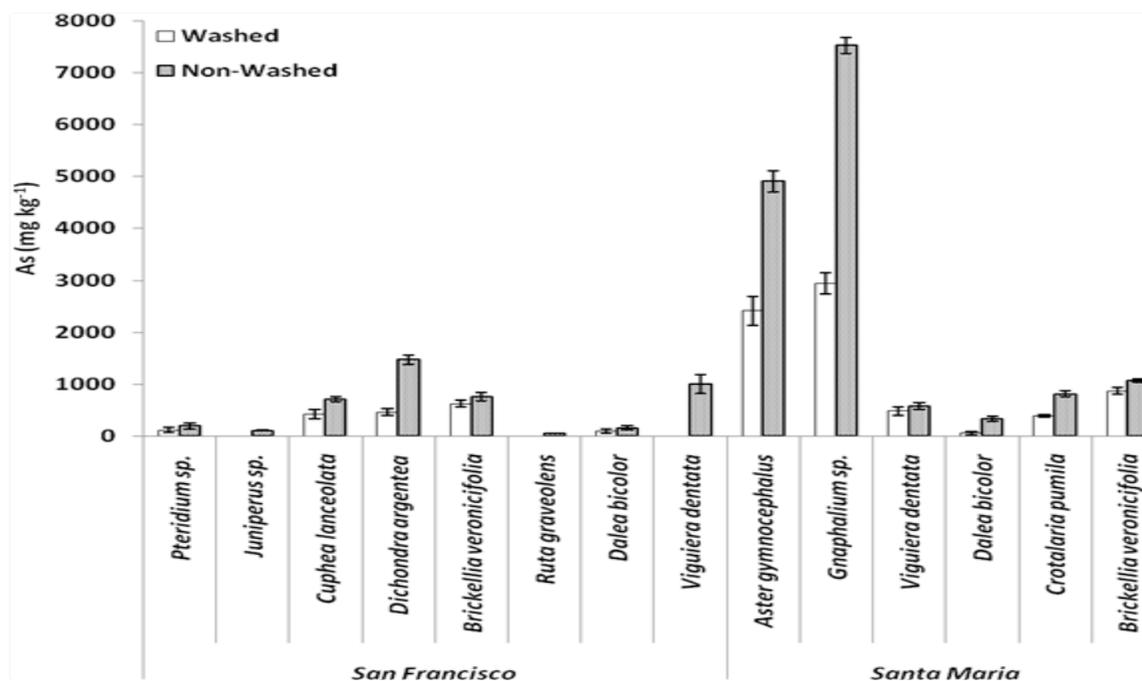


Figure 2: Arsenic concentration in washed and non-washed leaves of plants growing in mine tailings at Zimapan, Hgo. Bars represent mean (n=3) and standard deviation

was between 0.4 and 0.5 dS m⁻¹ and labile P was very poor (1.9 to 8.7 mg kg⁻¹). Low concentration of P in SM mine can be a restricted factor for plant growth.

Arsenic concentrations in the rhizosphere found on mine tailings

Arsenic natural soil concentration is around 1-20 mg kg⁻¹.¹⁷ and in rocks it reaches up to 900 mg kg⁻¹. The sites under study had very high total Arsenic (As) tailing concentrations and varied according to the sites and plant rhizosphere. The total Arsenic (As) concentrations in the mine tailings ranged from 4,016 to 13,413 mg kg⁻¹ DW for SF mine and 4,760 to 17,178 mg kg⁻¹ DW for SM mine (Table 1). The rhizosphere from *Pteridium sp.* and *Aster gymnocephalus* had the lowest and the highest values, respectively. In general, SM mine samples had higher Arsenic (As) total concentrations than these from SF mine tailings. Mining activity has been carried out in the area for long period; lots of tailing have been dispersed and mixed with soil through the history. Almost all rhizospheres of SM tailing had Arsenic (As) concentrations higher than 15,000 mg kg⁻¹, except this from *Crotalaria pumilla*. While, *Juniperus sp.* was the rhizosphere, from SF tailing, with the highest concentration of Arsenic (As) (13,413 mg kg⁻¹). Total Arsenic (As) concentrations were higher than those reported by Santos-Jallath *et al.* (2012) at three tailings impoundments from Queretaro, Mexico.¹⁸ These authors

found between 1,183-14,600 mg Arsenic (As) kg⁻¹. Affholder *et al.* (2013) observed Arsenic (As) concentrations of 1,127 mg kg⁻¹ on a former smelter site¹⁹ and Madejón *et al.* (2002) reported a sludge-covered soil affected by the Aznalcóllar mine spill in Spain containing Arsenic (As) in concentration of 929 mg kg⁻¹.²⁰ Baroni *et al.* (2004) reported total Arsenic (As) concentrations in the range from 5.3 to 2,035 mg kg⁻¹ in two former Sb-mining areas and on an old quarry once used for ochre extraction at the South of Italy.²¹ Juhasz *et al.* (2007) reported total Arsenic (As) concentration of 68 924 mg kg⁻¹ on Australian soils impacted by mining/smelting activities.²²

Extractable Arsenic (As) was very high in the rhizospheres from plants growing on the two mine tailings (Table 1). It was between the range from 230 to 499 mg kg⁻¹ DW. Rhizospheric samples from SF mine tailing presented lower extractable Arsenic (As) (maximum 344 mg kg⁻¹) than those from SM tailing (257 to 499 mg kg⁻¹). Available Arsenic (As) concentrations are not comparable with these reported by Madejón *et al.* (2002) on a polluted soil (2.05 mg kg⁻¹).²⁰ In the present research extractable Arsenic (As) concentrations are more than a hundred times.

Bioavailability Index (BI) on SF mine tailings was between 2.3% to 6.4% and the rhizosphere of *C. lanceolata* had the

highest BI. At SM, the range was between 2% and 5.4% and rhizosphere of *C. pumila* had the highest one.

Arsenic plant concentrations

Arsenic concentrations in shoots and roots

Plants collected for this study are natural colonizers of these sites and belong of the plant communities found in this region. They are ruderal and weed plants. Arsenic plant concentrations in the wild plants growing on the two mine tailings are presented in Figure 1. There is no relationship between Arsenic (As) concentration in roots and shoots. In general roots showed higher Arsenic (As) concentration than aerial parts, except for *A. gymnocephalus* and *Gnapallium* sp. growing in SM site. Several authors have reported higher Arsenic (As) concentrations in roots than in leaves and shoots.²¹

Root Arsenic (As) concentration ranged from 202 to 875 mg kg⁻¹ DW of plants established in SF tailing, while it was from 233 to 815 mg kg⁻¹ when these were developed on SM. Similar Arsenic (As) concentration of roots of *V. dentata* were observed on the two tailings; however roots from *D. bicolor* and *Brickellia veronicifolia* had different Arsenic (As) concentrations and it depended on the site where they were established.

In general, Arsenic (As) transfer rates from the soil to aerial plant parts are low in most species.²³ In this study, Arsenic (As) shoot concentrations ranged from 0 to 620 mg kg⁻¹ DW in plants from SF tailing and from 52 to 2,939 mg kg⁻¹ in plants from SM. These Arsenic (As) shoot concentrations are higher than those reported by several authors. Affholder *et al.* (2013) observed a concentration of Arsenic (As) in rosemary leaves of 0.35 mg kg⁻¹.¹⁹ Concentration of Arsenic (As) in aerial parts of some plants was 0.79 mg kg⁻¹.²⁴ Baroni *et al.* (2004) reported the highest concentration of Arsenic (As) in roots and leaves of *Mentha aquatica* (540 and 216 mg kg⁻¹, respectively).²¹ However, some plants may have higher Arsenic (As) shoot concentrations; such Arsenic (As) *Agrostiscanina* or *A. tenuis* which can accumulate 6,640 and 1,350 mg kg⁻¹, respectively.

Machado Estrada *et al.* (2006) reported that *V. dentata* can grow on soils containing Arsenic (As) concentrations up to 10,224 mg kg⁻¹ from which 85% (8,690 mg kg⁻¹) was accumulated in leaves.²⁵ Franco-Hernandez *et al.* (2010) reported that this plant was able to accumulate Arsenic (As), Cu, Pb and Zn and observed maximum Arsenic (As) shoot concentrations of 8,400 mg kg⁻¹.²⁶ In the present research we found Arsenic (As) aerial concentrations of

483 mg kg⁻¹ in this plant growing at SM tailing, but these were undetectable concentrations when grown in SF mine tailing. Baroni *et al.* (2004) also found different concentrations of Arsenic (As) in plants when grown on two or more sampling sites.²¹ Affholder *et al.* (2013) studied plant accumulation of several heavy metals on two sites and it depended from the total metal concentrations on the sites.¹⁹ For example, *Cynodon dactylon* (Bermuda grass) may tolerate 30,000 mg Arsenic (As) kg⁻¹ soil, stabilize spill-affected soils and accumulate up to 3,000 mg kg⁻¹.²⁷ In contrast, Madejón *et al.* (2002) reported in the same plant that accumulated 75 mg Arsenic (As) kg⁻¹ DW in their tissues when growing on a polluted soil containing 929 mg kg⁻¹ of Arsenic (As).²⁰

The normal Arsenic (As) concentration in plants is between 0.01 to 1 mg kg⁻¹ DW; while phytotoxic leaves concentrations are between 3 to 10 mg kg⁻¹ DW²⁸ or 20 mg kg⁻¹ DW taking into account the proposal of Vameralli *et al.* (2010).⁶ *Juniperus* sp. and *Ruta graveolens* may be considered Arsenic (As) plant excluders; while *Dalea bicolor* accumulated low Arsenic (As) concentrations, but still higher than normal and phytotoxic levels.

Tolerant plants restrict Arsenic (As) uptake from soil to plant and translocation from root to aerial parts.²⁹ In contrast, hyperaccumulator plants actively absorb and translocate this contaminant. *Aster gymnocephalus* and *Gnapallium* exceeded limits of accumulation (1000 mg kg⁻¹) and according to Van der Ent *et al.* (2013) may behave Arsenic (As) hyperaccumulator plants.³⁰ However, in order to corroborate the high Arsenic (As) shoot accumulation of these plants, they should be grown under greenhouse conditions on these mine tailings substrates, avoiding Arsenic (As) uptake from the leaves and stomata. These wild plants may be an important resource because they are adapted to very drastic adverse edaphic conditions; visually observed at the field some of them have large biomass allocation in the aerial plant part, fast growing of aerial biomass (during the rainfall season) and high field frequency. However, in order to have a successful and feasible phyto extraction alternative, it should be considered not only sufficiently high concentrations of Arsenic (As) in aerial parts, but also high biomass production. The combination of biomass production and efficiency of plants removing As from polluted substrates and it should be evaluated by net As removal.²

Although higher extractable Arsenic (As) concentrations were observed in SM rhizospheres, they were not related with high root nor shoot As concentrations in the plant species growing in this site. High concentration of Arsenic

(As) in the wild plants established in the mine tailings is an important health issue because many of them are edible plants for human or wild animals. The maximum level tolerated by cattle, sheep, chicken and swine is 50 mg kg⁻¹.²⁸ Therefore, high Arsenic (As) concentrations in leaves (accumulated or deposited) may represent an important pathway of Arsenic (As) intake by wild herbivores and livestock. *V. dentata* is one of the most important among the plants used in the folk medicine. It is edible, melliferous plant and used Arsenic (As) forage and for the treatment of baby rash because of its antibacterial and antifungal activities.³¹ Cattle consume this plant since early stages of development to the start of blossom time or just before it. This plant contains 17% of crude protein.³²

Similarly, it is known the hypoglycemic effect of *Brickellia veronicaefolia* extracts used in traditional medicine for diabetes treatment and this effect has been confirmed in mice.³³ It is also useful for rheumatism and intestinal infections.³⁴ *R. graveolens* one of the most versatile plants in terms of their uses. For example: stomachache, vomit, diarrhea, snakebite, wounds, cough, fever, headache, inflammation, nervousness, emmanagogue, abortifacient, anti-inflammatory, anti-spasmodic, anti-helminthic, flu, toothache, body pain, ear pain, etc.^{35,36} and more recently As strong antimicrobial.³⁷ Because of this, the use of plants collected from polluted sites could be a pathway of entrance to human body.

In the case of *D. argentea*, in Mexico it is used in the traditional medicine As remedy for intestinal disorders because of its antimicrobial activity and for inducing faster birth.³⁸⁻⁴⁰ *C. lanceolata* is a native Mexican plant used also in folk medicine. Infusion of the aerial part is recommended Arsenic (As) an anti-diarrheal agent⁴¹ and it contains also phenolic and flavonoids compounds with antioxidant properties.⁴² *D. bicolor* is a legume used to control fiber in human and animals. It is a weed plant that animals commonly consume.³⁴ *C. pumila* is a legume native species with potential for ecological restoration within the Neovolcanic Belt of Mexico.⁴⁵ *A. gymmocephalus* is another endemic plant with anti-inflammatory, antimicrobial, stomachache properties. In animals is useful in helping to expulse placenta.³⁴ *Gnaphalium* spp. Contain terpens, flavonoids, glycosides and polyacetylinic compounds acting in respiratory disorders.³⁴

In Mexico and other countries, medicinal plants are collected from the wild field sources or natural environments, rather than obtained from home gardens or cultivated area since they are not man domesticated plants and difficult to cultivate. These plants play an important role not only in remedial practices for more than one

illness, but also for magical-religious rituals. In most of the cases, aerial part and leaves are the most common plant part used.⁵⁵ Medicinal plants are commercialized under the category of food supplements. Like in other countries, there is insufficient regulation of the medicinal plant products. Future research with these medicinal plants from these mine tailings is necessary, which take into account phytochemical properties describing their active metabolites composition and toxicological studies. It is also necessary to determine bioaccessibility of elements contained in these plants, since Sánchez-López *et al.* (2015) in a risk assessment study for Cu, Pb, Ni Cd and Zn considered medium risk of exposition but for As it remains unknown.⁹

Arsenic deposition in aerial plant parts established in mine tailings

Air is an important via to Arsenic (As) and heavy metal containing particles dispersion. Ramirez-Andreotta *et al.* (2013) reported that the most elevated As concentrations were observed at 2.2 miles southeast and 1.1 mile away from The Iron Mine and Humboldt Smelter Superfund site in southern Arizona, UHA.³ Therefore, leaves of plants naturally growing on the two mine tailings may play an important role for Arsenic (As) retention or deposition (Figure 2), which could be used Arsenic (As) bio indicators.

The range of As retention in non-washed leaves was of 49 to 7,521 mg kg⁻¹ DW. Non-washed leaves of *D. bicolor* retained the lowest As concentration of plants from SF tailing (154 mg kg⁻¹), while *D. argentea* had the highest (1,470 mg kg⁻¹). *D. bicolor* and *Gnaphalium* sp. grown at SM tailing had the lowest and the highest Arsenic (As) concentrations retained in their leaves, respectively. Unwashed leaves reached Arsenic (As) concentrations up to 7,521 mg kg⁻¹ in *Gnaphalium* sp.

Although some authors have not found differences when comparing Arsenic (As) concentrations in washed and unwashed aerial plant parts, we observed significant changes in some plants. Madejon *et al.* (2002) reported no significantly difference in Arsenic (As) concentration in unwashed or washed leaves of two grasses: *C. dactylon* (0.78 vs 0.68 mg kg⁻¹, respectively) or sorghum plants (0.23 vs 0.20 mg kg⁻¹).²⁰ In the present research, leaves from *D. argentea* were the most relevant for As retention, because non-washed leaves accumulated three times more As than the washed leaves. Non-washed leaves of *A. gymmocephalus* and *Gnaphalium* sp. retained two and two and a half folds more Arsenic (As) in comparison to their washed leaves.

A well washing procedure significantly decreased as retained in leaves of some plants established in SF mine tailing, such Arsenic (As) *R. graveolens*, *V. dentata* and *Juniperus* sp. This showed that some of these plants do not accumulate a detectable Arsenic (As) concentration, but it also depends on plant superficial structures, site and environmental conditions.⁹ For example, leaves of *V. dentata* from SF did not accumulate As, but these from SM accumulated 483 mg of Arsenic (As) kg⁻¹ (Figure 2). After a well washing protocol some medicinal use may be allowed for *R. graveolens* without toxicological As risk; however, for *D. bicolor*, from the two sites, As shoot concentrations are close to the maximum tolerate by animals (50 mg kg⁻¹). In the cases of *A. gymnocephalus* and *Gnaphalium* sp. after well shoot washing procedure, they still showed extremely high As shoot concentrations (2409 and 2948 mg kg⁻¹, respectively).

In a previous research, it was reported that *A. gymnocephalus* behaved As highly accumulator plant of Zn, Cd, Pb and Cu, while *Gnaphalium* sp. of Cu.⁹ Therefore, besides As, other heavy metals may be a constrain for the possible use Arsenic (As) medicinal plants when established in the two mine tailings under study. Similarly, concentrations of Cd and Pb in leaves of *V. dentata*, *R. graveolens* and *D. bicolor* are higher than the maximum tolerable dietary intake by domestic animals (cattle, sheep, swine, chicken), but in the range for Zn and Cu; except for sheep.⁴⁴

Location of tailings and environmental conditions are relevant factors to determine accumulation and leaves As retention. Santa Maria mine tailing is 25 m tall and does not have trees or vegetation around it. This is very near to population and is strongly exposed to air events. In contrast, SF mine is in the middle of a forest area and less exposition is observed. Reduction of the dispersion of these tailings is required. For instance, phytostabilization through vegetal covering is an urgent necessity in SM mine tailing because of the risk of dissemination of contaminants. Restoration or forestation with a dense vegetation cover is the most useful and widespread alternative to physically stabilize uncover and open mine tailings and to reduce metal pollution effects. We recommend using autochthonous plant species for phytoremediation of these tailing heaps because they are well adapted to temperature and rainfall local conditions, there are natural pollinizers and dispersion agents, which could help to increase the populations. Most of them have developed tolerance to high concentrations of these elements. Sanchez-López et al. (2015) showed that especially *D. argentea* has long and very abundant trichomas; while *Gnaphalium* more over presents spikes along each trichome.⁹ Leaves of the three plant species also have abundant fungal myce-

lium; which are efficient microbial structures to sorption of metal (loids). All these plant and microbial structures may be relevant to retain Arsenic (As); however more studies should be followed in order to gain knowledge and better understanding on retention of contaminants from the air and avoid As dispersion.

Similar to castor bean naturally established in mine tailings,^{45,46} *Cuphea lanceolata* may be a worthy specie of domestication for agronomic or bioenergy purposes. *Cuphea* species have been targeted for cosmetic and personal care product manufacturing because of their seed oils. These species have genotypes rich in caprylic, lauric, myristic acids or various proportions of these fatty acids in their seed oil. They are a potential new oilseed crop rich in medium-chain fatty acids that may serve As a renewable, biodegradable source of oil for lubricants, motor oil, and aircraft fuel.^{47,48} The idea of growing plants in metalloids polluted sites should be addressed in future research in order to use marginal lands to produce crops with industrial interest.

Accumulation and translocation factors

Bioaccumulation factors were higher than 1 in three from the eight plant species growing at SF mine site (Table 1); where *B. veronicifolia* had the highest one (2.1). In SM mine tailing, *D. bicolor* had a BAF less than 1; while in *V. dentata* it was 1 and four species had a BAF higher than 1, being *Gnaphalium* sp. with the highest BAF (8.6). All the TF were lower in plants from SF than those from SM. *A. gymnocephalus* and *Gnaphalium* sp. had the highest TF of all plants growing in the two metal mine tailings. Affholder et al. (2013) reported BAF < 1 (0.0005); which is below international regulation limits concerning ingestion of medicinal herbs.¹⁹ Baroni et al (2004) reported in 91% of the plants studied BCF < 1; while TF for 76% were < 2.²¹ In a study regarding 25 plants growing in metal polluted sites, Vamerli et al. (2010) reported BAF in the range of 0.0-5.16 being the grass *Poa annua* with the highest value and TF in the range of 0.09-3.71 where the herb *Physalis minima* had the highest TF.⁶

CONCLUSION

This study aimed the estimation of As exposition to different naturally established wild plants. *Juniperus* sp., *R. graveolens* and *D. bicolor* are wild plants which appear to be are feasible vegetal species for functioning Arsenic (As) mine wastes stabilizers and reducing metalloids pollution effects. These plants with low As translocations rates

should be used as adequate planning revegetation program. This is possible due to their different plant attributes such as adaptation to the edaphic soil conditions in these mine tailings, tolerance to high concentration of Arsenic (As) and development of a strong root system. They are also important to reduce erosion and air dispersion, and decreasing the risk that As accumulating plants have to wild animals or humans.

Therefore they can be excellent prospects for soil remediation through phytostabilization. Phytoremediation actions in order to control As pollution and risk should be implemented using these plants. In contrast *A. gymnocephalus* and *Gnaphalium* may represent important hyperaccumulator plant species in the mine tailings for phytoextraction; high concentrations of As are deposited on their leaves, and also structurally accumulate excessive concentrations. Leaf-as deposition reduces the hazard to potential receptors by intercepting high concentrations of As dispersed by air. Their As hyperaccumulation should be confirmed taking into account their biomass allocation in the aerial plant part and growth speediness in order to recognize their importance and feasibility as hyperaccumulator plants. The data support our hypothesis, there is some risk

to transfer As to livestock or humans when consumed as forage or used as medicinal herbs, respectively.

CONFLICTS OF INTEREST

The authors have no conflicts of interest.

ABBREVIATION

As	: Arsenic
SF	: Saint Francisco
SM	: Saint Maria
EDTA	: Ethylenediaminetetraacetic acid
USEPA	: United States Environmental Protection Agency

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Highlights of Paper

- Arsenic (As) exposition to wild plants, with folk Mexican medicine importance, established on mine tailings was studied.
- Juniperus sp., Rutagraveolens and *Dalea bicolor* are prospects for As-phytostabilization.
- *Aster gymnocephalus* and *Gnaphalium* sp. behaved as As-hyperaccumulator plants.
- There is As-transference risk to livestock or humans when some plants may be consumed or used as medicinal herbs.

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