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Phytoextraction of Cu, Cd, Zn and As in four shrubs and trees growing on soil contaminated with mining waste

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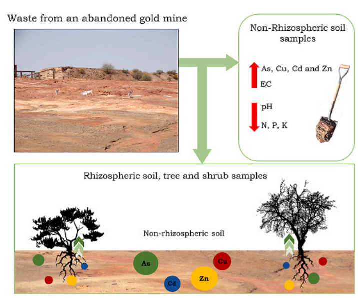
HIGHLIGHTS

- Mining waste caused acidification and high accumulation of metal(loid)s in soil.
- The presence of vegetation decreases the available fractions of metal(loid)s.
- *P. tetracantha* is a potential hyper-accumulator of Cd.
- Roots and cortex of *P. flexuosa* presented the highest concentration of Zn and As.
- The four native species could be used in remediation plans for contaminated soil.

GRAPHICAL ABSTRACT



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ABSTRACT

Mining activity has degraded large extensions of soil and its waste is composed of metals, anthropogenic chemicals, and sterile rocks. The use of native species in the recovery of polluted soils improves the conditions for the emergence of other species, tending to a process of ecosystem restoration. The objective of this study was to evaluate the bioaccumulation of metal(loid)s in four species of native plants and the effect of their distribution and bioavailability in soil with waste from an abandoned gold mine. Soil samples were taken from two sites in La Planta, San Juan, Argentina: Site 1 and Site 2 (mining waste and reference soil, respectively). In Site 1, vegetative organ samples were taken from *Larrea cuneifolia*, *Bulnesia retama*, *Plectrocarpa tetracantha*, and *Prosopis flexuosa*. The concentration of metal(loid)s in soil from Site 1 were Zn > As > Cu > Cd, reaching values of 7123, 6516, 240 and 76 mg kg^{-1}, respectively. The contamination indices were among the highest categories of contamination for all four metal(loid)s. The spatial interpolation analysis showed the effect of the vegetation as the lowest concentration of metal(loid)s were found in rhizospheric soil. The maximum concentrations of As, Cu, Cd and Zn found in vegetative organs were 371, 461, 28, and 1331 mg kg^{-1}, respectively. *L. cuneifolia* and *B. retama*

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presented high concentrations of Cu and Zn. The most concentrated metal(loid)s in *P. tetracantha* and *P. flexuosa* were Zn, As and Cu. Cd was the least concentrated metal in all four species. The values of BAF and TF were greater than one for all four species. In conclusion, the different phytoextraction capacities and the adaptations to arid environments of these four species are an advantage for future phytoremediation strategies. Their application contributes to the ecological restoration and risk reduction, allowing the recovery of ecosystem services.

1. Introduction

Mining has degraded large areas of land on a global level, as consequence of environmentally unsustainable mining model (Keesstra et al., 2017). In particular, abandoned metal mines leave behind waste compose of anthropogenic chemicals, metals and sterile rocks (Golui et al., 2019). Metals are non-biodegradable elements with enduring persistence in the environment (Bader et al., 2019). Metals can be bioaccumulated in living organisms and, therefore, be transferred to different trophic levels (Modabberi et al., 2018; O'Connor et al., 2020; Raj and Maiti, 2019). This causes an imbalance in the functionality of the ecosystem, producing losses to ecosystem services and risks to human health (Sivarajasekar et al., 2018).

In recent years, phytoremediation technologies have been implemented with the aim of recovering polluted soils. Phytoremediation consists of employing plants in soil decontamination and its effectiveness depends on the plants ability to absorb, transfer, stabilize, concentrate and/or degrade contaminants (Favas et al., 2018; Lam et al., 2017). Plants called metallophytes are used for the remediation of soils contaminated with metal(loid)s. These plants can be either indicator, excluding or hyperaccumulator species (Kataweteetham et al., 2020; Zalewska and Danowska, 2017). Indicator plants concentrate metals in aerial organs indicating their presence in soil, and excluders restrict the entry of metals into different tissues. Whereas hyperaccumulator plants have the ability to grow in soil with high concentrations of metals and accumulate them in their tissues (Baker and Walker, 1990).

The phytoremediation abilities derive from the anatomic, structural, physiological and biochemical adaptations that different species have developed to survive in extreme environments (Muszyńska et al., 2019). In comparison with conventional methods, such as vitrification, electrokinetics and soil washing technique, among others, phytoremediation is less costly, environmentally sustainable, socially acceptable, and can be applied to several organic and inorganic contaminants (Jiang et al., 2018; Ramezani et al., 2021; Yan et al., 2020). Many plants growing in contaminated sites have the ability to accumulate heavy metals cannot withstand environmental conditions, such as high temperatures, low rainfall and salinity (Wei et al., 2021). Therefore, the evaluation of phytoremediation techniques should not only consider the plant accumulation capacity, but also its adaptation to local climate conditions (Arreghini et al., 2017). Trees with rapid growth, woody deep root systems, and resistance to extreme conditions (e.g., metals in soil, drought) are generally preferred for soil restoration in mining areas (Tozser et al., 2017). Several species of trees and shrubs have been used in drendroremediation processes, such as Eucalyptus, Populus and Acer (Bandyopadhyay and Maiti, 2019; Kataweteetham et al., 2020). However, drendroremediation primarily considers the economical aspects of phytoremediation without contemplating some ecological aspects. In this sense, dendroecology includes both the economical and ecological aspects, such as the introduction of exotic species (Hartman and McCarthy, 2007).

The use of native woody species in phytoremediation processes generates advantages due to the growth of their root system and greater biomass production. Particularly, native species of arid zones have developed several adaptations that allow them to resist stress factors. Their implementation for the recovery of polluted soils generates better conditions for the emergence of other species by natural succession, tending to a process of ecosystem restoration (Villagra et al., 2021).

Mining is the main economic activity in the province of San Juan, Argentina. In particular, soil pollution in the town of Planta was caused by an abandoned gold mine, characterized by an inappropriate waste management and lack of implementation of mitigation measures (Calabró et al., 2022). The area is inhabited by a human population, who carry out subsistence economic activities, mainly goat raising. Therefore, the presence of mining waste and their potential dispersion by different erosive agents presents a great risk to human health. Native species of trees and shrubs that grow in this contaminated soil were identified. Given the need to study the soil pollution level to evaluate future phytoremediation strategies in this arid region, the aims of the present study were to evaluate a) the metal(loid)s bioaccumulation capacity of *Larrea cuneifolia*, *Bulnesia retama*, *Plectrocarpa tetracantha*, and *Prosopis flexuosa*, and b) the effect of spatial distribution patterns and the bioavailability of metal(loid)s in soil with (rhizospheric) and without (non-rhizospheric) vegetation.

2. Materials and methods

2.1. Area of study and sampling

The area of study is located in La Planta town, department of Caucete, southeastern of San Juan province, Argentina. It is located between the parallels 31°10′24.38″ S, 67°52′57.26″ W and 31°10′55.83″ S, 67°24′38.04″ W, bordered on the east by the Valle Fértil and La Huerta mountains, and on the west by the Pie de Palo mountain chain (Fig. 1). The Papagayos River, a seasonal river, runs near the abandoned mining infrastructure in La Planta. Environmentally the region is considered part of the Monte phytogeographic province that spans almost the entirety of the arid belt of Argentina (Villagra et al., 2004). The climate is characteristically hot and dry, with rainfall varying between 80 and 200 mm annually, and temperatures up to 46 °C (Magliano et al., 2015). The soil is of alluvial origin, poorly developed, and saline with high electrical conductivity values due to shallow groundwater depths and high evaporation rates (Villagra et al., 2021). The vegetation in this area is uniform, in both its physiognomy and richness, composed by xerophytic woody vegetation. The area is composed of a shrub steppe of *Larrea cuneifolia*, *Larrea divaricata*, *Tricomaria usillo*, *Atriplex lampa* and *Suaeda divaricata*, and open forests predominated by species such as *Prosopis flexuosa* and *Bulnesia retama* (Dalmasso and Anconetani, 1993; Villagra et al., 2011). Approximately 60 years ago, a gold extraction plant operated in La Planta. Rocks from different mines were transported to this town. The extractions were first carried out with mercury and later with cyanide. The site belonged to different private companies which left the infrastructure in a state of abandonment and to date no mitigation measures have been implemented. In preliminary studies, an analysis of the different chemical elements found high concentrations of As, Cu, Cd and Zn in this mining waste (Table Suppl. 1).

Two sampling sites were selected: abandoned mining waste site (Site 1) and a reference site (Site 2) used as a control. The site defined as a reference is located approximately 1 km from the contaminated site on the opposite side of the Papagayos River. The reference site was selected considering the slope and the direction of the prevailing winds. Samples were taken from the rhizospheric and non-rhizospheric soils at depths of 0–20 cm. The non-rhizospheric soil samples were taken randomly in both sites to determine the distribution of the metal(loid)s in soil without vegetation ($n = 10$ per sampling site). Rhizospheric soil samples were taken only from Site 1 to understand the effects of vegetation on the concentration and bioavailability of metal(loid)s in soil with mining waste. Each rhizospheric soil sample was composed of four soil subsamples taken from each of the studied species (n = 12 samples).

Samples of the vegetative organs from four native species were taken to determine their metal(loid)s bioaccumulation capacity (Table Suppl. 2). The sampling species included three shrubs belonging to the Zygophyllaceae family: 1) *Larrea cuneifolia*, a resinous xerophilous shrub with perennial leaves and a woody stem that grows up to 2 m; 2) *Bulnesia retama* that reaches up to 3 m, with striated growth patterns (sharpened stems) and branches and young stems with a white waxy covering; and 3) *Plectrocarpa tetracantha*, a poorly studied woody species, grows up to 2 m, with propagative roots, perennial leaves and clustered thorns. Also, the sampling included a tree belonging to the Fabaceae family: *Prosopis flexuosa* reaches up to 10 m, with deciduous leaves and thorns that can access the groundwater table in extremely dry environments. Three samples for each species were taken from adult plants (n = 12), including leaves, branches, stems, cortex and roots. Adult plants were considered to be those capable of completing their phenological cycle, similar height and stem with a basal diameter greater than 7 cm. The leaf and branch samples were cut with pruning shears, while the trunk and root samples were obtained from a v-cut made with a saw. The cortex was extracted by gently peeling it off by hand. The samples were placed in paper bags for transfer to the laboratory.

2.2. Soil and vegetation analysis

Physicochemical variables measured in soil included pH (paste), electrical conductivity (EC; saturation extract), organic matter (OM; Walkley-Black method), total Kjeldahl nitrogen (N), available phosphorous (carbon extraction method, 1:50 ratio w:v), exchangeable potassium (ammonium acetate method), cations (Ca^{+2}, Mg^{+2}, Na^{+}) and anions (HCO_3^-, Cl^-, SO_4^{-2}) (saturation extract). Soil samples were dried at room temperature, sifted through a 2 mm mesh, and treated using three extraction agents to measure the total, mobilizable and soluble concentrations of Cu, Cd, Zn and As. The treatments were performed according to the following procedures: 1) Microwave digestion: A microwave digester Milestone Start-D (Sorisole, Italy) was used to digest the soil sample to obtain the total fraction of metal(loid)s. The digestion consisted of 0.25 g sample, 4 mL of HNO_3 at 65%, 1 mL of H_2O_2 at 30%, and 3 mL of HF at 40% mixed in a polytetrafluoroethylene (PTFE) reactor. Dissolution was then carried out by steadily increasing the temperature in 10 min up to 200 °C and maintaining it constant for a further 20 min. The microwave potential reached up to 1000 W (Martínez et al., 2018); 2) Diethylenetriaminepentaacetic acid (DTPA, metal chelating agent): The mobilizable fraction was determined by mixing a soil sample with a DTPA extracting solution (0.005 M DTPA, 0.01 M $CaCl_2$ and 0.1 M triethanolamine (TEA)) in a 1:2 ratio w:v, and filtering the supernatant after 2 h of agitation (Lindsay and Norvell, 1969; Maiz et al., 1997); and 3) Deionized water (aqueous extract): A soil sample was mixed with deionized water in a 1:4 ratio w:v for 30 min and the supernatant was filtered after a further 60 min (USEPA, 1998). The extract obtained was used to determine the soluble fraction of metal (loid)s, pH and EC.

Previous to preparation, the vegetation samples were rinsed with tap water and subsequently with deionized water to assure that no soil particles remained on the organs (Poschenrieder et al., 2001). Samples were dried in a stove at 70 °C for 48 h until reaching constant weight, and then they were pulverized in a FW100 high-speed universal disintegrator. A 0.05 g sample of the pulverized material was digested with 1 mL of HNO_3 and 0.5 mL of H_2O_2, then placed in a thermal bath at 60 °C for 90 min and 100 μL de HF were added. After that, Milli Q quality water was added to the digested samples until they reached a total volume of 6 mL, which was centrifuged at 1250 rpm for 5 min. Finally,

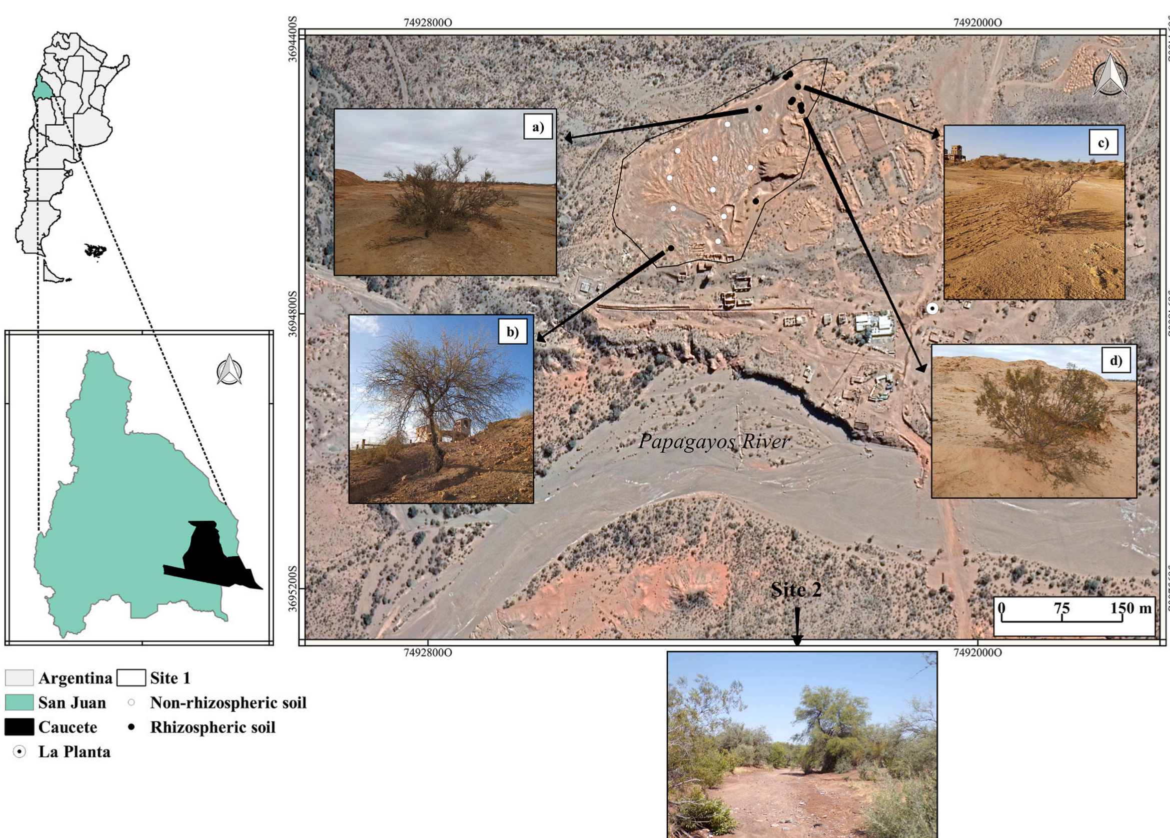

Fig. 1. Study area located in La Planta, San Juan, Argentina. Site 1: soil with mining waste, and Site 2: reference soil. a) *Bulnesia retama*, b) *Prosopis flexuosa*, c) *Plectrocarpa tetracantha*, d) *Larrea cuneifolia*.

the supernatant was extracted to determine the metal(loid)s content. The digestion method was validated by comparison with microwave acid digestion using quantitative recoveries.

The concentration of Cu, Cd, Zn and As in soil fractions and vegetation extracts were measured using a mass spectrometer (ICP-MS) with a detection limit of 0.001 mg kg^{-1}. The methodology was validated by analyzing 3 certified reference materials: NIST SRM 2709 San Joaquín soil; NIST SRM 2711 Montana soil and NIST SRM 1570a Trace Elements in Spinach leaves. The recoveries for the analyzed elements ranged from 95.9 to 102.4%.

The soil contamination generated by mining waste was determined by calculating the Geoaccumulation Index (I_{geo}) (Muller, 1969), the Contamination Factor (CF) for each metal(loid)s and the overall Contamination Degree (Cdeg) (Hakanson, 1980).

$$I_{geo} = log_2(MC / (1.5 * RC)) \tag{1}$$

$$CF = MC/RC \tag{2}$$

Where MC is the concentration of a particular metal(loid) in soil with mining waste (Site 1), and RC is the concentration of this metal(loid) in soil from the reference site (Site 2). The factor 1.5 is added to minimize the possible variations in the base levels attributable to lithogenic effects.

$$Cdeg = \sum CF \tag{3}$$

where Cdeg is the sum of the measured CF.

Bioaccumulation Factor (BAF) and Translocation Factor (TF) were calculated for each organ of the studied species to evaluate their phytoremediation potential. BAF relates the concentration of a specific metal(loid) in each organ with the total concentration of this metal(loid) in rhizospheric soil (Yoon et al., 2006). TF is the relation of the concentration of a specific metal(loid) in different aerial organs and the concentration of that metal(loid) at the root (Cui et al., 2007).

2.3. Data analysis

The data of the concentration of metal(loid)s in the soil fractions and vegetative organs were compared using one-way ANOVA followed by the Tukey post-hoc test. If the assumption of normality and the homogeneity of variance were not met, the data were transformed logarithmically or non-parametric statistics were applied (Kruskal Wallis test). Multivariate analyses were conducted using the total, soluble and mobilizable concentrations of metal(loid)s, contamination indices, pH and EC, which included Principal Component Analysis (PCA) and Spearman correlation analysis. A spatial interpolation was conducted using the data of the total concentration of metal(loid)s in rhizospheric and non-rhizospheric soil of Site 1 (Qgis software version 3.16.4). Data analyses were carried out using R version 2.1.

3. Results

3.1. Physicochemical soil characterization

The non-rhizospheric and rhizospheric soil of Site 1 showed an acidic pH that varied between 2 and 4.4 (Table 1). A neutral pH similar to those obtained in Site 2 was recorded in the rhizospheric soil of *L. cuneifolia*. The highest EC values were found in the non-rhizospheric soil (41.2 and 5.9 mS cm^{-1}), whereas the lowest ones were found in the rhizospheric soil of *L. cuneifolia* and the reference soil. The macronutrients (N, P and K) showed highest values in the rhizospheric and reference soil. The OM content was low in all the soil samples, and the texture was loamy sand and sandy loam.

Table 1
Physicochemical parameters of rhizospheric and non-rhizospheric soil samples from the contaminated (Site 1) and reference site (Site 2).

Site 1						Site 2
	Non-rhizospheric soil	Rhizospheric soil				
		Lc	*Br*	*Pt*	*Pf*	
EC (mS cm^{-1})	41.2	5.9	28.9	14.6	27.9	5.4
pH	2.6	7.2	3.7	4.4	2.0	7.5
Ca^{+2} [mg kg^{-1}]	nd	418.8	124.3	186.4	nd	1787.6
Mg^{+2} [mg kg^{-1}]	nd	383.0	3167.7	681.0	1095.3	73.0
Na^{+} [mg kg^{-1}]	128.8	662.4	430.1	1078.7	719.9	4046.8
HCO_3^- [mg kg^{-1}]	13538.1	176.9	73.2	54.9	nd	12226.4
Cl^- [mg kg^{-1}]	18981.7	719.8	4531.8	2563.8	2624.0	2801.3
SO_4^{-2} [mg kg^{-1}]	nd	2780.9	8525.3	1873.2	2305.4	96.1
N [mg kg^{-1}]	256.0	268.8	355	297.0	361.8	241.0
P [mg kg^{-1}]	6.0	20.0	13.3	16.7	12.3	46.0
K [mg kg^{-1}]	34.0	90.7	65.7	71.3	21.0	160.0
OM [%]	1.0	0.7	1.2	0.8	1.0	0.2
C/N	22.0	15.8	13.1	15.6	16.2	4.0
Texture	sandy loam	loam sandy	loam sandy	loam sandy	loam sandy	sandy loam

Lc: *Larrea cuneifolia*, *Br*: *Bulnesia retama*, *Pt*: *Plectrocarpa tetracantha*, *Pf*: *Prosopis flexuosa, EC: Electrical conductivity, OM: Organic matter.*

3.2. Concentration of Metal(loid)s in soil

The concentrations of Cu, Cd, Zn and As measured in the soil are shown in Table 2. These results were contrasted with the established guidelines for residential and agricultural use in Argentina (Federal Law 24,051) and with the Canadian soil quality guidelines for environmental health-SQGE (Canadian Council of Ministers of the Environment, 2007). The concentration of the four metal(loid)s in Site 2 were below the established guideline values for Argentina and Canada with the exception of As. It was 1.7 times above the recommended values for agricultural use in Argentina and residential use in Canada. The concentrations of all four metal(loid)s found in the non-rhizospheric soil in Site 1 were higher than the recommended levels for agricultural and residential use for both countries. The concentrations of Cu and Zn in the rhizospheric soil were lower than the established levels for Argentina, but the concentrations of all four metal(loid)s were higher than the Canadian guidelines.

The highest concentrations of As and Zn were found in the non-rhizospheric soil of Site 1 (6516.3 and 7122.6 mg kg^{-1}, respectively), followed by the rhizospheric soil of *P. flexuosa*, *B. retama* and *P. tetracantha*. By contrast, the lowest concentrations of As and Zn were found in the reference site (20.3 mg kg^{-1} and 78.19 mg kg^{-1}, respectively), followed by the rhizospheric soil of *L. cuneifolia*. The highest concentrations of Cu were recorded in the non-rhizospheric and rhizospheric soil of *B. retama* and *L. cuneifolia* ($p < 0.001$), while the lowest concentration was found in the rhizospheric soil of *P. flexuosa*. Significant differences were only found between the concentrations of Cd in Site 1 and 2 ($p < 0.001$; Table 2).

The mobilizable and soluble concentrations of all four metal(loid)s were significantly higher in the non-rhizospheric soil than the rhizospheric soil ($p < 0.001$), and they were lower than 1% in the rhizospheric soil. Mobilizable fractions represented between 7% and 38% of the total concentration of metal(loid)s recorded in the non-rhizospheric

Table 2
Mean (±SD) total, mobilizable and soluble concentration of metal(loid)s in soil (mg kg^{-1}).

	Site 1					Site 2	Guideline Values			
	non-rhizospheric soil	Rhizospheric soil					Residential use		Agricultural use	
		L. cuneifolia	*B. retama*	*P. tetracantha*	*P. flexuosa*					
Total metal(loid)										
As	6516.3 ± 3136.4^{a}	23.5 ± 7.2^{cd}	188.9 ± 173.7^{bc}	164.6 ± 196.9^{bc}	344.7 ± 174.1^{b}	20.3 ± 14.02^{d}	30$^{(1)}$	12$^{(2)}$	20$^{(1)}$	12$^{(2)}$
Cu	239.5 ± 137.7^{a}	71.2 ± 18.3^{ab}	82.3 ± 48.6^{ab}	36.2 ± 48.2^{bc}	12.2 ±7^{c}	17.7 ± 6.0^{bc}	100$^{(1)}$	63$^{(2)}$	150$^{(1)}$	63$^{(2)}$
Cd	75.9 ± 61.8^{a}	20.1 ± 16.4^{a}	34.6 ± 13^{a}	21.0 ± 16.5^{a}	26.6 ± 18.7^{a}	0.8 ± 0.7^{b}	5$^{(1)}$	10$^{(2)}$	3$^{(1)}$	1.4$^{(2)}$
Zn	7122.6 ± 6102.3^{a}	337.3 ± 184.2^{b}	450.6 ± 92.6^{b}	278.3 ± 214.8^{bc}	323.5 ± 295.6^{c}	78.2 ± 84.9^{c}	500$^{(1)}$	200$^{(2)}$	600$^{(1)}$	200$^{(2)}$
Mobilizable metal(loid)										
As	464.4 ± 467.6^{a}	nd	0.03 ± 0.04^{c}	nd	0.01 ± 0.01^{c}	2.4 ± 1.8^{b}				
Cu	91.2 ± 85.2^{a}	0.010 ± 0.003^{c}	0.04 ± 0.06^{c}	0.01 ± 0.01^{c}	0.02 ± 0.01^{c}	2.4 ± 2.1^{b}				
Cd	28.9 ± 25.7^{a}	0.002 ± 0.002^{c}	0.012 ± 0.004^{c}	0.002 ± 0.001^{c}	0.02 ± 0.01^{c}	0.3 ± 0.3^{b}				
Zn	1511.7 ± 966.0^{a}	0.1 ± 0.1^{c}	1.1 ± 0.9^{bc}	0.3 ± 0.1^{c}	1.9 ± 1.7^{c}	28.3 ± 11.7^{b}				
Soluble metal(loid)										
As	16.1 ± 8.3^{a}	0.003 ± 0.003^{b}	0.02 ± 0.02^{b}	0.010 ± 0.002^{b}	0.01 ± 0.01^{b}	nd				
Cu	83.8 ± 84.1^{a}	0.001 ± 0.001^{c}	0.04 ± 0.06^{b}	0.01 ± 0.01^{bc}	0.02 ± 0.02^{b}	nd				
Cd	34.9 ± 26.3^{a}	0.001 ± 0.001^{b}	0.070 ± 0.003^{b}	0.004 ± 0.004^{b}	0.02 ± 0.02^{b}	nd				
Zn	2152.5 ± 940.0^{a}	0.01 ± 0.01^{d}	0.8 ± 0.8^{bc}	0.3 ± 0.5^{cd}	2.1 ± 2.8^{bc}	3.1 ± 2.4^{b}				

Different letters indicate significant differences ($p < 0.001$) between soil samples. References used as guide values: 1) Argentine Law 24,051, 2) SQGE: Soil quality guideline for environmental health established by the Canadian Council of Ministers of the Environment (CCME). nd = not detected.

and reference soil. Values higher than 1% in the soluble fractions were found for Cu, Cd and Zn in the non-rhizospheric soil (up to 46%), and only for Zn in the reference soil.

3.3. Soil contamination indices

Results of the Igeo values showed that the rhizospheric soil was categorized in the lowest contamination level (Table 3). The exception was the Cd value that corresponded to the categories 5 ("strongly polluted") and 6 ("strongly to very strongly polluted"). In the non-rhizospheric soil, the Igeo values for As, Cd, and Zn were higher than 5, which corresponds to the highest category of contamination ("very strongly polluted"), according to Förstner et al. (1990). Only the level of Cu corresponded to the lowest categories ("unpolluted to moderately polluted").

Analysis of the Contamination Factor (CF) showed that the level of Cd present in the rhizospheric soil of all four species corresponded to the category 6 ("very strong contamination"), while the rest of the metal (loid)s had values that varied between category 1 ("moderate contamination") and category 6 (Table 4). The CF values for the non-rhizospheric soil corresponded to the category 6 for all four metal (loid)s. The Cdeg values for all the soil samples in Site 1 indicated a high grade of contamination (highest category).

The Principal Component1 (87%) and 2 (11%) of the PCA explained 98% of the total data variability (Fig. 2). The total, soluble and mobilizable concentrations of metal(loid)s, Igeo, CF and EC were all associated with the non-rhizospheric soil (nr). The correlation analysis showed a positive correlation between the three fractions of the metal(loid)s ($R > 0.7$; $p < 0.001$; Table Suppl. 3). The values of EC showed a positive correlation with the majority of the specified variables ($R > 0.7$; $p < 0.001$). On the other hand, a negative correlation of pH was observed with the total As, mobilizable As and Zn, and Igeo and CF of As ($R > -0.7$; $p < 0.001$).

Table 3
Mean (±SD) of the Geoaccumulation Index in samples of rhizospheric and non-rhizospheric soil.

Soil	I_{geo}			
	As	Cd	Cu	Zn
Rhizospheric				
L. cuneifolia	−0.4 ± 0.5	3.6 ± 1.5	1.4 ± 0.4	1.3 ± 0.9
B. retama	2.0 ± 1.7	4.8 ± 0.6	1.1 ± 1.7	1.9 ± 0.3
P. tetracanta	1.6 ± 2.0	3.7 ± 1.6	−0.6 ± 2.1	0.9 ± 01.2
P. flexuosa	3.3 ± 0.9	4.2 ± 1.0	−1.3 ± 0.9	0.9 ± 1.2
Non-rhizospheric	7.6 ± 0.7	5.7 ± 0.9	3.0 ± 0.7	5.5 ± 1.1

$I_{geo} \leq 0$: class 1, "practically unpolluted"; $0 < I_{geo} < 1$: class 2, "unpolluted to moderately polluted"; $1 < I_{geo} < 2$: class 3, "moderately polluted"; $2 < I_{geo} < 3$: class 4, "moderately to strongly polluted"; $3 < I_{geo} < 4$: class 5, "strongly polluted"; $4 < I_{geo} < 5$: class 6, "strongly to very strongly polluted"; $I_{geo} > 5$: class 7, "very strongly polluted", according to Förstner et al. (1990).

Table 4
Mean (±SD) of Contamination Factor (CF) per metal(loid) for rhizospheric soil of the four species and non-rhizospheric soil , and the Degree of Contamination (Cdeg).

Soil	Contamination Factor				Degree of Contamination
	As	Cd	Cu	Zn	
Rhizospheric soil					
L. cuneifolia	1.2 ± 0.4	25.2 ± 20.6	4.0 ± 1.0	4.3 ± 2.4	34.7 ± 11.1
B. retama	9.3 ± 8.6	43.4 ± 16.3	4.7 ± 2.8	5.8 ± 1.2	63.1 ± 18.5
P. tetracantha	8.1 ± 9.7	26.3 ± 20.7	2.0 ± 2.7	3.6 ± 2.8	40.0 ± 11.2
P. flexuosa	17.0 ± 8.6	33.4 ± 23.6	0.7 ± 0.4	4.1 ± 3.8	55.2 ± 14.8
Non-rhizospheric	321.1 ± 154.6	95.3 ± 77.5	13.5 ± 7.8	91.1 ± 78.0	521.0 ± 132.7

$CF < 1$: low contamination factor; $1 \leq CF < 3$: moderate contamination factor, $3 \leq CF < 6$ high contamination factor, $CF \geq 6$ very high contamination factor, according to Hakanson (1980). $Cdeg < 6$ low degree of contamination, $6 \leq Cdeg < 12$ moderate degree of contamination, $12 \leq Cdeg < 24$ high degree of contamination, $Cdeg \geq 24$ very high degree of contamination, according to Hakanson (1980).

3.4. Spatial interpolation

The spatial interpolation analysis displays the distribution of the total concentration of all four metal(loid)s in the rhizospheric and non-rhizospheric soil (Fig. 3). It shows how the concentration of the metal (loid)s decreases around the vegetation. The highest values for the four elements were found in the non-rhizospheric soil that also coincided with the lowest pH values. It can be observed that the soil associated

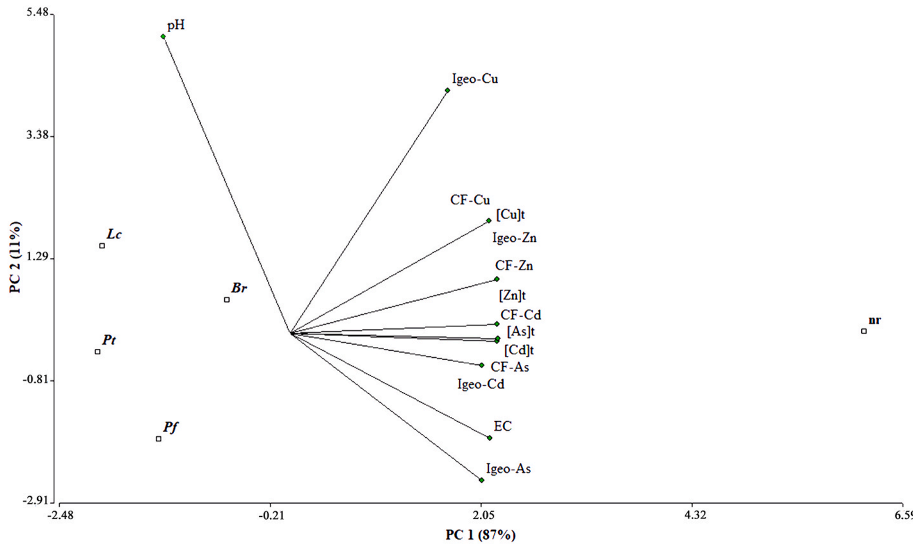

Fig. 2. Principal Component Analysis of the variables measured in soil (Site 1). PC: Principal Component, Nr: Non-rhizospheric, *Lc*: *Larrea cuneifolia*, *Br*: *Bulnesia retama*, *Pt*: *Plectrocarpa tetracantha*, *Pf*: *Prosopis flexuosa*, Igeo: Geoaccumulation Index, CF: Contamination Factor, [As]t: total concentration of As, [Cu]t: total concentration of Cu, [Cd]t: total concentration of Cd, [Zn]t: total concentration of Zn.

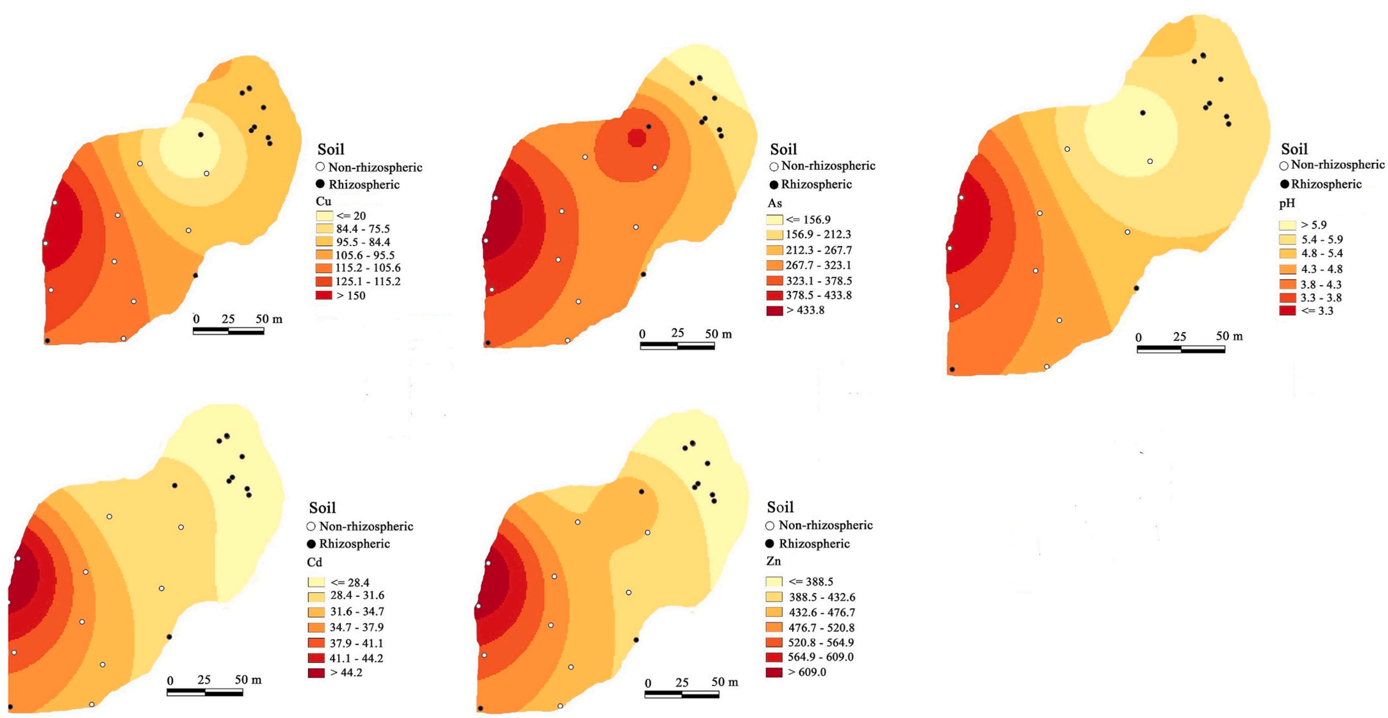

Fig. 3. Spatial interpolation of the metal(loid)s concentration in rhizospheric and non-rhizospheric soil at Site 1.

with vegetation growth presented a pH higher than that in non-rhizospheric soil.

3.5. Concentration of Metal(loid)s in vegetative organs

The metal(loid)s were most concentrated in the leaves of *L. cuneifolia*, the branches and roots of *B. retama*, the leaves and stems of *P. tetracantha*, and the stems of *P. flexuosa*. For example, in this vegetative organs were found 123–461 mg kg^{-1} of Cu and 82–1331 mg kg^{-1} of Zn (Fig. 4). Additionally, the cortex of *P. flexuosa* accumulated up to 371 mg kg^{-1} of As ($p < 0.001$). In all four species Cd was the least concentrated metal(loid).

3.6. Bioaccumulation and Translocation Factors

All four studied species presented BAF and TF values greater than one, with variations depending on the vegetative organ (Table 5). Significant differences in the BAF values between metal(loid)s ($p < 0.001$) were observed in *L. cuneifolia* reaching a value of up to 6.7 for Cu in the leaves. For the same species, significant differences were observed between the TF values of the metal(loid)s ($p < 0.001$), reaching the highest value for Zn (6.3). For *B. retama*, Cu was the only metal that had BAF values lower than one in the photosynthetic branches and stem, with statistically significant differences between metal(loid)s ($p < 0.001$). The TF was greater than one for As, Cu and Zn in both organs, without

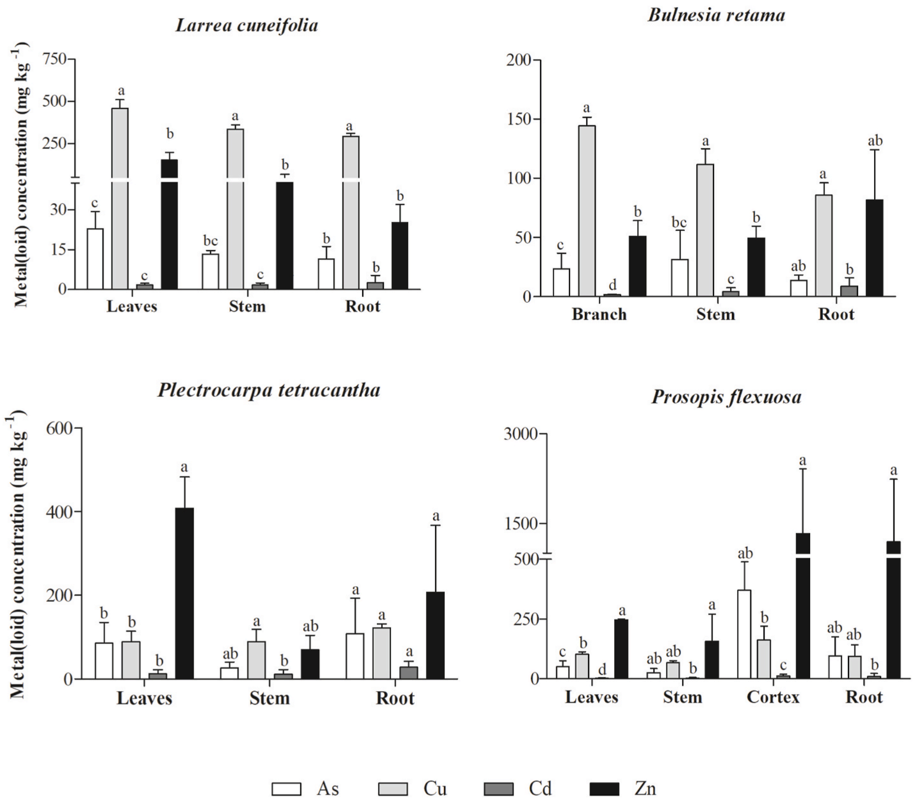

Fig. 4. Mean concentration (±SD) of metal(loid)s in vegetative organs. Different letters indicate significant differences ($p < 0.001$) between the concentration of metal(loid)s for each vegetative organ. Bars represent standard deviation.

Table 5
Mean (±SD) of Bioaccumulation Factor (BAF) and Translocation Factor (TF), obtained for the different vegetative organs of the four species studied.

Species	Organ	As		Cu		Cd		Zn	
		BAF	TF	BAF	TF	BAF	TF	BAF	TF
L. cuneifolia	Leaves	1.1 ± 0.7^b	2.4 ± 1.6^b	6.7 ± 1.6^a	1.6 ± 0.2^b	0.2 ± 0.2^b	1.4 ± 1.0^b	0.7 ± 0.6^b	6.3 ± 2.0^a
	Stem	0.6 ± 0.4^b	1.4 ± 0.7^a	4.9 ± 1.1^a	1.1 ± 0.1^a	0.1 ± 0.1^b	1.3 ± 1.1^a	0.2 ± 0.1^b	1.8 ± 0.7^a
	Root	0.4 ± 0.2^b		4.3 ± 1.2^a		0.2 ± 0.2^b		0.1 ± 0.1^b	
B. retama	Branch	0.3 ± 0.2^b	1.2 ± 0.3^a	1.4 ± 0.1^a	1.6 ± 0.2^a	0.04 ± 0.01^b	0.4 ± 0.3^a	0.1 ± 0.04^b	2.1 ± 2.9^a
	Stem	0.3 ± 0.2^b	1.5 ± 0.2^a	1.1 ± 0.2^a	1.1 ± 0.3^a	0.2 ± 0.2^b	0.6 ± 0.4^a	0.1 ± 0.05^b	2.2 ± 3.0^a
	Root	0.2 ± 0.2^b		0.8 ± 0.1^a		0.2 ± 0.2^b		0.2 ± 0.1^b	
P. tetracantha	Leaves	1.2 ± 1.1^a	1.5 ± 1.0^a	7.0 ± 5.4^a	0.7 ± 0.2^a	2.4 ± 4.0^a	0.8 ± 0.6^a	2.4 ± 2.2^a	4.7 ± 5.8^a
	Stem	0.4 ± 0.3^a	0.5 ± 0.4^a	8.2 ± 9.0^a	0.7 ± 0.3^a	2.4 ± 4.0^a	0.6 ± 0.5^a	0.5 ± 0.6^a	0.6 ± 0.6^a
	Root	1.4 ± 1.9^a		11.6 ± 10.1^a		3.1 ± 3.5^a		1.6 ± 1.9^a	
P. flexuosa	Leaves	0.2 ± 0.1^b	0.7 ± 0.7^a	10.6 ± 6.1^a	1.2 ± 0.5^a	0.2 ± 0.2^b	1.1 ± 1.2^a	1.4 ± 1.3^b	1.3 ± 1.3^a
	Stem	0.1 ± 0.1^b	0.5 ± 0.3^a	6.7 ± 3.2^a	0.8 ± 0.4^a	0.2 ± 0.1^b	1.7 ± 2.5^a	0.9 ± 0.7^b	1.2 ± 1.6^a
	Cortex	1.2 ± 0.4^c	4.3 ± 3.8^a	14.6 ± 3.7^a	2.0 ± 1.2^a	0.5 ± 0.1^d	2.8 ± 2.7^a	4.4 ± 0.6^b	4.6 ± 5.3^a
	Root	0.6 ± 0.7^b		8.8 ± 4.6^a		0.3 ± 0.2^b		2.5 ± 2.3^{ab}	

Different letters indicate significant differences ($p < 0.001$) between BAF or TF values of each metal(loid) determined at each vegetative organ.

statistically significant differences ($p > 0.05$). The values of BAF in *P. tetracantha* did not show statistically significant differences between metal(loid)s, reaching values greater than one for Cu and Cd in all vegetative organs and for As and Zn only in the leaves and roots. For this species, TF values greater than one were only found for As and Zn in the leaves, but no statistically significant differences were observed between metal(loid)s ($p > 0.05$). *P. flexuosa* showed BAF values greater than one for Cu, Cd and Zn ($p < 0.001$), while TF showed values greater than one for all four metal(loid)s in the leaves and cortex ($p > 0.05$).

4. Discussion

Based on the results obtained in our study, the town of La Planta is contaminated with at least Cu, Cd, Zn and As as a by-product of waste from an abandoned gold mine. The presence of these metal(loid)s is considered a health liability because they are hazardous to humans and persist in the environment (Lee et al., 2006; Li et al., 2014; Ozden et al., 2018). The concentrations of metal(loid)s reported in our study not only exceed the established guideline levels for residential and agricultural use in Argentina, but also those set for other countries, such as Canada. The values of the Igeo, CF and Cdeg obtained for the four metal(loid)s in the non-rhizospheric soil samples from Site 1 correspond to the highest contamination categories. The Igeo values in the rhizospheric soil, however, vary between the moderately to strongly polluted categories. These results are similar to, and in some cases higher than, those reported in other studies such as those found in an abandoned As mine in China (Ran et al., 2021) and an Ag mine in Peru (Cruzado-Tafur et al., 2021). Even when the values of CF and Cdeg for the rhizospheric soil corresponded to the highest contamination categories, they are still lower than those reported in the non-rhizospheric soil. Nevertheless, the values obtained in our study indicate a very high grade of contamination in the soil of La Planta with and without vegetation.

The accumulation of mining waste has acidified the soil and reduced the nutrient content in the contaminated site. Similar results were found in other mining areas worldwide, such as those reported for Ag ore deposits in Argentina (Kirschbaum et al., 2012) and Peru (Cruzado-Tafur et al., 2021), and Cu mines in China (Wang et al., 2019) and Brazil (Afonso et al., 2020). Soil polluted by environmental mining liabilities causes toxicity to plants, giving origin to large extensions of bare soil. In La Planta we found higher total concentrations of metal(loid)s than those reported in similar cases. For instance, the maximum values of Zn and Cd recorded in a small-scale gold mine in Nigeria were 286 and 3 mg kg^{-1}, respectively, in comparison with 7122.6 mg kg^{-1} of Zn and 75.9 mg kg^{-1} of Cd, found in the non-rhizospheric soil in our study (Okonkwo et al., 2021). However, the concentration of Cu in the rhizospheric and non-rhizospheric soil was similar to those reported in studies conducted in Cu mines (Afonso et al., 2020; Wang et al., 2021; Wu et al., 2021).

Soil acidity triggers the release of metal(loid)s from soil particles, which result in a negative correlation between their availability and the pH value (Rosselli et al., 2003). However, we only found a negative correlation between the pH and the mobilizable fractions of As and Zn. Availability depends on certain soil characteristics, such as the OM content and the presence of salts like calcium carbonate, that increase adsorption and diminish availability (Wenzel, 2012). Even though As was the second most concentrated element in both the rhizospheric and non-rhizospheric soil, the mobilizable and soluble fractions were less than 10% of the total fraction. Authors demonstrated the time-dependent metal availability in soil, which is higher in recently contaminated soil (Wijayawardena et al., 2015). This process, called aging, is the result of the decrease in the available fraction of metal causing stronger adsorption to the soil particles. On the other hand, it has been shown that the availability of As is limited with the presence of Fe (Wenzel, 2012). In a preliminary study carried out in the town of La Planta, we recorded 3,740 mg kg^{-1} of Fe. This could explain the low availability of As due to the adsorption by this element to Fe.

Despite the extreme conditions present in the studied site, some plant species are adapted to this hostile environment and successfully completed their life cycle. Although several species have been previously identified as capable of remediating soils contaminated by mining waste (Afonso et al., 2020), native plants growing in contaminated sites are strong potential candidates for phytoremediation (Cruzado-Tafur et al., 2021; Marchiol et al., 2013). Native species have an advantage for survival, growth and reproduction due to their adaptation to local climate conditions (Gajić et al., 2018). Authors have reported the use of Argentine native species from the Monte phytogeographic region for the restoration of environments impacted by mining activity (Dalmasso, 2010), who used *Prosopis flexuosa* for reforestation of an area contaminated by hydrocarbons and reported a survival rate higher than 75%. The adaptations of native species to stressful conditions, such as salinity, water deficit, among others, allow them to face the challenges presented by the environments to be remediated, beyond the presence of metal (loid)s. Their extensive roots allow them to reach a greater exploration of the soil and accumulate metal(loid)s in their different organs.

The highest concentrations of metal(loid)s were found in leaves and roots. Chandra and Kumar (2017) also reported that the leaves and roots of shrub species are the principal accumulating organs. High concentrations of Zn and Cu were found in the vegetative organs for all four species. These metals are essential micronutrients for plants that contribute to their development and metabolism, and form part of many regulatory enzymes and proteins (Ghori et al., 2019; Mengel and Kirkby, 1987). However, high concentrations of Zn and Cu can alter the metabolism in plants (Guo et al., 2020). The species evaluated in our study achieved reproduction despite the high concentrations of metal(loid)s. Therefore, future studies could investigate the physiological and epigenetic mechanisms underlying adaptation to this polluted environment.

The concentrations of Cu found in all four species were more than three times those concentrations accumulated in two species of trees that grow in soil contaminated with mining waste, e.g. *Pinnus massoniana* and *Pinus yunnanensis* (Wang et al., 2019). These authors reported higher Cu concentrations in the aerial organs of the pine species than in the roots, and were similar to those found in the tree and shrub species studied here. In contrast, *Baccharis dracunculifolia* used for phytoremediation accumulate Cu only in the roots (Afonso et al., 2020). In comparison with this species, the plants used in our study translocated Cu highlighting their capacity for phytoextraction.

Zn was the most concentrated metal in the soil and vegetative organs for all four species studied. Shrub species like *Baccharis amdatensis* that grow in soil with concentrations of Zn between 58 and 18,610 mg kg^{-1} can accumulate more than 2000 mg kg^{-1} in the leaves (Bech et al., 2017), a value close to what we found in the cortex and roots of *P. flexuosa*.

After Zn, As was the most concentrated metal(loid) in the soil but the second least accumulated in the plants. Although no function of As has been identified in plants, some tree species may accumulate up to 43.1 mg kg^{-1}, such as *Azadirachta indica* and *Tectona grandis* (Patel et al., 2015). We found concentrations of As up to 370.5 mg kg^{-1} in plants, which are higher than those reported for other species used in phytoremediation.

Cd also does not seem to have any biological function in plants. In our study, Cd was the least concentrated metal(loid) in the soil and plants. The low bioaccumulation of this metal could be attributable to the limited absorption of Cd by high concentrations of Zn, according to Zhou et al. (2019). Furthermore, it was observed that the presence of Zn coincided with a decrease in the toxicity of Cd in wheat crops as these elements compete for membrane transports (Hart et al., 2002; Zhou et al., 2019).

BAF and TF are used to determine the bioaccumulation capacity of plants, which indicate the phytoremediation efficiency (Cioica et al., 2019). Several authors propose that species with BAF and TF values greater than one could be used for phytoextraction and those with BAF $>$ 1 and TF $<$ 1 can be used for phytostabilization (Buscaroli, 2017; Yang et al., 2015). The species evaluated in our study showed BAF and TF values greater than one for all four metal(loid)s, although low concentrations of Cd and As were found in some of the vegetative organs. Plants can use several mechanisms to reduce toxicity triggered by metal(loid)s such as amino acids, glutathione, phytochelatins and metallothioneins, and involve enzymes such as superoxide dismutase and peroxide (Ghori et al., 2019; Shang et al., 2020). These physiological mechanisms are involved in the survival of plants that grow in environments with high concentrations of metal(loid)s (Pandey et al., 2016; Wu et al., 2021).

In summary, the acidic pH and the high concentrations of metal(loid) s found in the mining waste of La Planta demonstrate as need to implement remediation strategies. Future actions could be taken to improve the soil quality by increasing the pH and decreasing the availability of metal(loid)s, creating conditions that encourage microbial diversity and plant growth. Additionally, we specifically recommend the use of *P. flexuosa*, *B. retama*, *L. cuneifolia* and *P. tetracantha* for phytoremediation due to their metal(loid)s bioaccumulation capacity. The bioaccumulation potential shown by the species evaluated in the present study allows us to think about the application of remediation strategies aimed at environmental restoration. The capabilities of each species could act synergistically allowing not only the effective soil decontamination, but also improving the environmental conditions that promote the settlement of new species. Further studies should focus on the physiological, biochemical and epigenetics mechanisms underlying the phytoextraction of metal(loid)s in this highly polluted environment.

5. Conclusions

A small scale gold mine, as a consequence of the lack of implementation of mitigation measures, has polluted the soil in La Planta town with mining waste, characterized by low pH values, high concentrations of Cu, Cd, Zn and As, and salinity. The highest categories of the contamination indices were found in the non-rhizospheric soil in the following order: As > Cd > Zn > Cu and to a lesser extent in the rhizospheric soil. The concentration of metal(loid)s in the soil exceed the guideline levels for residential and agricultural areas in different countries (e.g., Argentina and Canada).

We identify *P. tetracantha*, *L. cuneifolia* and *P. flexuosa* as bioaccumulators of As; all four species as bioaccumulators of Cu; *P. tetracantha* as the only bioaccumulator of Cd; and *P. flexuosa*, *P. tetracantha* and *L. cuneifolia* as bioaccumulators of Zn. The adaptations of these tree and shrub species allow them to survive the adverse environmental conditions of the arid and semi-arid ecosystems, such as limited rainfall, high temperatures, and poorly developed soils. These characteristics and the different phytoextraction capacities presented by the four species should be taken as advantages in phytoremediation strategies, as they contribute to ecological restoration. The presence of vegetation would prevent the spread of pollutants by different erosive agents. These plants also provide ecosystem services and improve soil quality, promoting the growth of new species. Considering that the main subsistence productive activity in La Planta is extensive goat farming, a complete remediation of the contaminated site would provide an enlarged area available for livestock feed.

CRediT author statement

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2022.136146.

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