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Metal and Phosphorus Uptake by Spontaneous Vegetation in an abandoned iron mine from a Semiarid Area in Center Morocco: Implications for Phytoextraction

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Spontaneously growing native plants (belonging to 12 species, 10 genera, and 3 families) were analyzed to study the accumulation of Cd, Cr, Cu, Zn, Pb, Fe and P in shoots and roots. The different plant species collected in Ait Amar iron mining site exhibited large differences in shoot and root accumulation of metals. Among the grass species (*Apiaceae*, *Asteraceae* and *Poaceae*), the highest shoot Cd, Cu, Zn concentrations were found in *Echinops spinosus L* (0.989, 29.190 and 175.347 mg Kg^{-1} respectively), Cr in *Cladanthus arabicus (L) Class* (9.241 mg Kg^{-1}) and Pb, Fe and P in *Leontodon hispidilus (Delile) Boiss* (5.952, 1522.839 and 4612.795 mg Kg^{-1}). The highest bioconcentration factors (BCF) were recorded for *E. spinosus L* and Zn (1.68). The highest soil-plant transfer factor (TF) of Cd was 1.24 (*Stipa Capensis thumb*), of Cr was 2.01 (*C. arabicus (L) Class*), of Cu was 8.40 (*Carthamus lanatus L*), of Zn was 2.52 (*E. spinosus L*), of Pb was 7.00 (*Eryngium ilicifolium Lam*), of P was 537.72 (*E. ilicifolium Lam*) and of Fe was 0.52 (*L. hispidilus (Delile) Boiss*). *E. spinosus L* showed the highest Zn phytoextraction capacity and other plant species demonstrated to grow well in metal contaminated soil taking up only low concentrations of metals, and, therefore they are good candidates for phytostabilization.

Keywords: *mining site, bioaccumulation, native plants, BCF, TF.*

1. Introduction

Heavy metals are significant environmental pollutants, and their toxicity is a problem of increasing significance for ecological, evolutionary, nutritional and environmental reasons (Nagajyoti et al. 2010). Mining is known to being one of the primary sources of metal pollution (Wei and Zhou, 2008) and generate a large amount of tailings that are generally deposited upon the ground surface. Tailings usually provide an unfavorable substrate for plant growth because of their low pH, high concentrations of toxic metals and low nutrient content (Ha et al. 2011).

Various physicochemical methods for remediation of heavy metals from the terrestrial and aquatic environment are not feasible due to energy intensive and cost expensive (Horsfall and Abia, 2003). Hence, there is an urgent need of some biological treatment system, which could replace these traditional treatment systems. Phytoremediation techniques are now considered to be promising alternatives to conventional techniques for the remediation of diffused or moderately contaminated soils (Díez Lázaro et al. 2006; Chehregani et al. 2009). Plants have the ability to accumulate metals such as Fe, Zn and Cu, that are essential for their growth and development, but only certain plants encompass the ability to gather heavy metals (Lasat 2002). It is important to use native plants for phytoremediation because such plants respond better to the stress conditions at the site than would plants introduced from other environments (Yoon et al. 2006).

In the past few years, an increased awareness of the importance of metallophyte biodiversity has emerged in the scientific community (Barrutia et al. 2011). Natural variation occurs in the uptake and distribution of essential and nonessential trace elements among crop species and among cultivars within species (Grant et al. 2008). Plants growing on contaminated soils respond to elevated concentrations of heavy metals in the soil to varying extents, depending on the total soil metal concentrations, soil physicochemical conditions (especially pH) and the cultivars of plant (Wu and Zhang, 2002; Alexander et al. 2006). The spontaneous plant colonization in mine tailings is usually slow since the physicochemical characteristics of these sites are not suitable for most of the plant species (Conesa and Faz 2011). Nevertheless, some of the tolerant plant species can spread easily in these environments due to the lack of competitors (Conesa and Faz 2011).

The identification of plant species able to accumulate metals in their tissues represents an important strategy for the remediation of heavy-metal polluted sites, demonstrates that plants have the genetic potential to clean up contaminated soil. Phytoremediation is a subject of public and scientific interest and a topic of many researches (Raskin et al. 1997; Horsfall and Spiff, 2005; Igwe and Abia, 2006; Chehregani et al. 2009). An efficient approach to identify tolerant plants is the isolation of species growing in those contaminated soils or water bodies.

Phytoremediation is a cost-effective technology for environmental cleaning, if native plants were applied in each polluted areas. We need new and variable accumulator plants for phytoremediation in different climates, thus new studies are still necessary to find new accumulator plants for being used in different conditions. In this study, we investigated the concentrations, translocation and bioconcentration factors of toxic metals (Cd, Cr, Cu, Zn and Pb), Fe (the mine of iron) and P (the region rich with natural phosphate) of 12 plant species that were grown in the abandoned polluted sites of an iron mine (Oued Zem, Morocco) with the objective (1) to get a better knowledge of the accumulating capacity of 12 plant species, of Cd, Cr, Cu, Zn, Pb, Fe and P, and (2) to evaluate the potential use of these plant species for phytoremediation (phytoextraction, hytostabilization).

2. Materials and Methods

2.1. The studied area

The iron deposit of Ait Amar (33° 04’ N; 6° 38’ W), as part of the anticlinorium khouribga-Oulmes, is in the Hercynian Central Massif. The latter is the vast plateau, which occupies the northern part of the western Moroccan Meseta. The Hercynian Central Massif consists mainly of Paleozoic terrain ranging from Ordovician to Carboniferous, organized into a series of anticlinoria and synclinoria, general orientation NE-SW, and Hercynian granitic intrusions intersected.

The iron mineralization occurs as two lenticular layers of iron Oolitic intersperse throughout this set sandstone, whose capacity is estimated (1000 to 1500 m). The mineralized layer starts with a black chloritic schist. This deposit, operated between 1937 and 1962 by the Moroccan society Mining and Chemicals (SMMPC), produced about 6 million tons of ore. This operation, done in its career and partly underground, has ceased, firstly by lack of opportunity, low Fe content (between 43 and 47%) and high silica (12 to 17%) and Alumina (8 %), secondly, due to high operating costs (passing from the extraction in discovery to underground extraction in 1957).

Inside the perimeter containing an exploitable potential (226 ha), resources are estimated at 86 million tons of ore at 43% of Fe, 16% of SiO_2 and 0.7% of P with an average capacity of the mineralized layer of 10.5 m. However, as with other Oolitic iron deposits of Morocco, the high silica content restricts the marketing of their ores. It is worth noting that the company operated under very adverse consequences: a lack of mechanization (crushing, loading and slaughter), many and unstable worker staff and high transport price. The combination of these factors led to the closure of the mine in 1963-1964 (Department of Energy and Mining, Regional Directorate Beni Mellal).

2.2. Soil Physicochemical Characterization

Because polluted sites are often of a highly heterogeneous composition, a systematic sampling was designed. The studied area was divided into four transepts (T.1.1, T.2.1, T.3.1 and T.4.1) (Table 1). Soil samples (0 - 20 cm depth) were collected on 19 July, 2010. The samples were sieved to 2 mm and subjected to chemical characterization. Soil pH (KCl) values were measured in a 1/5 extraction ratio (sample/1 M KCl) after shaking for 15 minutes and left to settle for 30 minutes. Total organic carbon (TOC) was analyzed by dichromate oxidation and titration with ferrous ammonium sulphate (Walkley and Black, 1934). TKN was determined by the

Kjeldahl procedure. Soil pH (H_2O) and conductivity were measured in a soil-water suspension (1:5, w/v extraction ratio) according to the method described in FAOUN (1984). Soil moisture was determined by oven drying at 105 °C for 24 hours.

Table 1 Description of the study site in the Oued Zem region of center Morocco

Sample code	UMT coordinates
T.1.1	29S 720066 3661172
T.2.1	29S 720014 3661211
T.3.1	29S 719983 3661228
T.4.1	29S 719992 3661144

2.3. Total and bioavailable metal concentrations

Concentrations of total metals were determined by inductively coupled plasma atomic emission spectrometry ICP-AES after digestion of the samples. 2 mL of concentrated HNO_3 were added to 150 mg of soil samples, and mixed. The samples were then heated on a hot plate at 100 °C until dryness. After this, 3 mL of concentrated HF were added to the Teflon vessels and heated at 140 °C for 15 hours at the minimum (vessels closed). After cooling the vessels were opened and heated until dryness at 110 °C. 2 mL of concentrated HNO_3 were added and heated (110 °C) until dryness, this step was repeated, and the fifth time of dryness was got with 2 mL of concentrated HCl and 120 °C. 25 mL of 2M HCl were added and heated for 2 hours at 100 °C and the vessels were closed. After cooling and filtration, all samples were analyzed for Cd, Cr, Cu, Pb, Zn, Fe and P by ICP-AES using a Jobin Yvon ULTIMA 2 apparatus (the National Centre for Scientific and Technical Research (NCSTR), Rabat, Morocco).

Metal bioavailable (mobile) fraction determined using the 0.01 M $CaCl_2$ extraction procedure (Gupta et al. 1996) and sometimes this method referred as the ‘‘effective bioavailable metal fraction” (Alvarenga et al. 2009). From the experience obtained by Pueyo et al. 2004, the 0.01 M $CaCl_2$ extraction procedure seems to be a suitable method for the determination of Cd, Cu, Pb, and Zn mobility in soils, since this procedure presents an appropriate extraction capacity for this type of studies and also uses the lowest salt concentration. This fact simplifies the matrix of the extracts and facilitates the metal determination with analytical techniques, such as ICP–AES. Soil 0.01 M $CaCl_2$ soluble trace element concentrations were determined in 1/10 ratio, soil /0.01 M $CaCl_2$ extracts, (Houba et al. 1990; NEN 5704, 1996). After shaking for 2 h on a tabletop shaker, extracts were decanted and 60 mL were centrifuged (2000 xg), and metal concentrations were measured by ICP-AES (NCSTR, Rabat, Morocco).

The plants reflecting most of plant biodiversity of herbaceous and shrub species present in the studied area were selected (07 May 2010). Plant samples were gently uprooted, taken to the laboratory, thoroughly washed with tap water in order to remove any surface soil or dust deposit, and then rinsed twice with distilled water and then separated into roots and shoots. Shoot and root dry biomass of each species was obtained after oven drying plant samples at 80 °C for 24 hours. Subsequently, plant samples were ground into fine powder. For total metal concentrations in the plant components, 1 g of plant samples were digested using nitric and hydrochloric acids. The sample was diluted to 100 mL and analyzed for total (Cd, Cr, Cu, Zn, Pb and Fe) and P by ICP-AES using (USEPA Method 3050) (NCSTR, Rabat, Morocco).

A bioconcentration factor for soil (BCF) is defined as the metal concentration in dry shoot plant tissue / metal concentration in soil quotient (Mattina et al. 2003, Ha et al. 2011). A transfer factor (TF), or also called translocation factor (Mattina et al. 2003, Ha et al. 2011), is the ratio between the concentration of metals in shoots and roots and defines the effectiveness of the plant to translocate the metals to the shoots.

Statistical analyses of experimental data were performed using the SPSS 17.0 package for Windows. Kruskal-Wallis and Pearson correlation tests were used to detect significant differences in plant concentrations of heavy metals and between plant roots and shoots. Statistical significance in this analysis was defined at $P<0.05$ and $P<0.01$.

3. Results and discussion

3.1. Characterization of the soils

As expected, soil properties and chemical composition depended upon the geological material from which the soil was derived (Table 2). Substrate pH affects plant growth mainly through its effect on the solubility of chemicals, including toxic metals and nutrients. It is commonly recognized that at pH = 6.5, nutrient availability to plants is at a maximum and toxicity is at a minimum (Harris et al. 1996; Wong, 2003; Freitas et al. 2004). Soil pH was around of this value. Organic matter (OM) concentration of soils ranged between 0.77 and 2.69, with a mean of 1.8%. Total nitrogen showed percentage below 0.091%, resulting in high C/N ratios (17.17 – 45.04), this could suggest poor humification of organic matter, which might be due to low or disturbed soil microbial activity (Remon et al. 2005). Furthermore, in this soil samples the pH, conductivity, OM and TKN were the lowest, as well as found by Ma and Dong (2004), Remon et al. (2005), Barrutia et al. (2011). It is known that polluted mining soils are characterized by low nutrient content and adverse conditions for plant growing (Wong 2003; Freitas et al. 2004). Under these conditions, the competition for main nutrients such as nitrogen or phosphorus represents a limiting factor for plants and soil microorganisms (Unterbrunner et al. 2007).

Soil metal concentrations were highly heterogeneous among sites, probably due to the nature of mining operations (mineral extraction, storage, mechanical dispersion, presence of overburden materials, degree of mineral weathering, etc.) (Barrutia et al. 2011). The concentration of different metals in soil around all selected plant species are shown in Table 2.

Iron showed the highest concentrations in soil (mean value = 278557.50 mg kg^{-1}), followed by P (mean value = 5372.50 mg kg^{-1}), but Cr and Zn were also detected at relatively high levels (130.39 mg kg^{-1} and 104.25 mg kg^{-1}, respectively, for mean values). Concentrations of other associated non-target metals, such as Cd (mean value = 1.47 mg kg^{-1}), Cu (mean value = 44.90 mg kg^{-1}), and Pb (mean value = 7.24 mg kg^{-1}), were lower. These metal concentrations are lower than Maximum Allowable Concentrations of metals in agricultural soils proposed by the European common (1986). The Maximum total concentrations of Cr, Cu and Pb were found in the T.4.1 soil (up to 156, 62 and 14 mg kg^{-1}, respectively) and of Cd, Zn, Fe and P in T.3.1 soil (up or equal to 3, 145, 373790 and 8240 mg kg^{-1}, respectively).

Bioavailability of metals to plants and biota including fauna and microorganisms is controlled by their total concentration in the soil and their chemical forms (Freitas et al. 2004). Metal bioavailability is estimated using the 0.01 M $CaCl_2$ extractions (Table 2) a relatively high percentage of the $CaCl_2$ extracted metal content in soil samples especially for Cd (25.69% in T.4.1), Pb (9.77% in T.2.1), Cu (1.48 % in T.1.1) and Zn (1.07 % in T.2.1).

On the other hand, this percentage is low for P and very low for Fe, while Cr was almost insoluble (<0.002 %), as well as found by Remon et al. (2005). Venditti et al. (2000) also showed that heavy metals were poorly soluble in water when pH was kept between 6.6 and 7.6. Nonetheless, demonstration of Remon et al. (2005) heavy metals are neither leachable nor phytoavailable does not mean that pollutants are immobilized and pose no hazard for the environment and human health.

Table 2 Some physicochemical properties of the Ait Amar iron mining area

Samples	**T.1.1**	**T.2.1**	**T.3.1**	**T.4.1**	**Average**
pH (KCl)	6.13 ± 0.06	5.60 ± 0.05	5,44 ± 0,01	5.06 ± 0.06	5.56
pH (water)	7.20 ± 0.10	6.94 ± 0.14	7.11 ± 0.06	6.84 ± 0.09	7.02
Conductivity	151.77 ± 6.2	75.57 ± 4.40	55.37 ± 2.30	70.10 ± 2.00	88.20
OM Content (%)	2.69	2.68	1.07	0.77	1.80
Water content (%)	2.11	1.51	1.75	2.18	1.89
TOC (%)	1.5593	1.5565	0.6216	0.4447	1.0455
NTK (%)	0.0908 ± 0.0003	0.0489 ± 0.0000	0.0138 ± 0.0002	0.0140 ± 0.0000	0.0418
C/N Ratio	17.17	31.83	45.04	31.76	31.45
Total metal concentration (mg kg^{-1})					
Cd	1.37	0.91	3.06	0.55	1.47
Cr	108.38	119.74	136.97	156.50	130.39
Cu	28.78	36.19	51.97	62.67	44.90
Zn	76.24	65.56	145.32	129.90	104.25
Pb	12.46	0.91	0.82	14.76	7.24
Fe	228030.00	199330.00	373790.00	313080.00	278557.50
P	5530.00	1540.00	8240.00	6180.00	5372.50
$CaCl_2$ extractable metal concentration (mg kg^{-1})					
Cd	0.14	0.14	0.13	0.14	0.1375
Cr	-	-	-	-	-
Cu	0.43	0.23	0.41	0.26	0.3325
Zn	0.38	0.70	0.37	0.49	0.485
Pb	-	0.09	-	-	0.09
Fe	0.20	0.08	0.03	0.03	0.085
P	0.78	0.12	0.60	0.09	0.3975

-, below detection limit (Pb: 0.004 mg L^{-1}, Cr and Cu: 0.002 mg L^{-1})

Actually, the possibility of horizontal spreading of metal-rich particles due to mechanical erosion and human activities remains. In the case, when the remediation is technically and economically unrealistic, erosion control could be efficiently achieved by phytostabilization (Wong, 2003), i.e. establishing an overall and self-sustainable vegetation cover.

3.2. Plant accumulation and transport of metals

Plants that were more popular at the mine were collected and identified for their scientific name and family name. Analyses of metals in the shoots and roots of plants are summarized in Table 3 and show that shoot contents vary between 0.827 and 0.989 mg Cd kg^{-1}, 0.67 and 9.241 mg Cr kg^{-1}, 12.421 and 29.19 mg Cu kg^{-1}, 204.816 and 1522.839 mg Fe kg^{-1}, 0.366 and 5.952 mg Pb kg^{-1}, 33.521 and 175.347 mg Zn kg^{-1} and 1405.066 and 4612.795 mg P kg^{-1}. Cadmium concentrations in shoots and roots are in the same range for the twelve plant species studied (~ 0.93 mg kg^{-1}).

Normal and toxic concentrations of heavy metals (mg kg^{-1}) are respectively considered to be 0.1–0.5 and 5–30 for Cr, 5–30 and 20–100 for Cu, 27–150 and 100–400 for Zn, 0.05–0.2 and 5–30 for Cd, and 5–10 and 30-300 for Pb (Kabata-Pendias and Pendias, 1992). All of the collected plant species show the concentrations higher than these normal levels for Cd and Cr.

By comparing the values obtained with the critical concentrations above which toxicity effects are possible, we have found that the levels critical in this range are: Cr for *C. arabicus (L) Cass*, Cu for *E. ilicifolium Lam. C. lanatus L. E. spinosus L.* and Zn for *E. spinosus L.*. For Zn, it is shown that the concentration of 100 mg kg^{-1} in feed is considered to be chronically toxic for animals (Dudka et al. 1995). In relation to Pb, *L. hispidilus (delile) boiss* shows higher concentrations, more of the normal range. And this shows that these plants had a strong ability to tolerate heavy metals.

Yoon et al. (2006) reported concentrations (mg kg^{-1}) varying from undetectable to 1183, 6–460 and 17–598 for Pb, Cu and Zn, respectively, in native plants growing on a contaminated site. Moreno-Jimenez et al. (2009) reported concentrations (mg kg^{-1}) varying of Cu, Zn, and Cd of 2.68–70.2, 9.5–1048, and undetectable to 22.04, respectively, in shoots of plants growing in an area surrounding a mine site. Stoltz and Greger (2002) reported concentrations of Cu, Zn, Cd, and Pb of 6.4–160, 68–1630, 0.1–12.5, and 3.4–920 mg kg^{-1}, respectively in wetland plant species growing on submerged mine tailings.

Table 3 Concentrations (mg kg^{-1} dry weight (DW) material) of Cd, Cr, Cu, Fe, Pb, Zn and P in the shoot and root tissues of different study species

Family	Species	Organs	Cd	Cr	Cu	Fe	Pb	Zn	P
Apiaceae	***Eryngium ilicifolium Lam.***	Root	0.675	1.455	6.806	1134.062	0.104	67.177	5.351
		Shoot	0.830^{a}	1.090^{b}	25.484*^{c}	565.225	0.727	63.789	2877.509
	Eryngium triquetrum Vahl.	Root	0.937	1.874	27.854	721.641	-	54.458	823.527
		Shoot	0.837^{a}	1.516^{b}	18.771	336.144	0.366	61.592	1788.012
Asteraceae	***Carlina acaulia subsp caulescens***	Root	1.095	6.256	37.694	3002.823	43.481	64.856	1084.044
		Shoot	0.927^{a}	0.670^{b}	18.704	204.816	-	71.724	1470.299
	Carthamus lanatus L.	Root	1.182	2.456	2.456	2159.485	0.273	101.962	17.191
		Shoot	0.888^{a}	0.940^{b}	20.628*^{c}	892.077	1.044	72.956	1405.066
	Cladanthus arabicus (L.) Cass.	Root	0.889	4.601	29.960	2516.769	8.366	70.272	1584.098
		Shoot	0.878^{a}	9.241*^{b}	17.244	636.567	2.478	90.400	3728.383
	Echinops spinosus L.	Root	1.152	5.341	45.657	2746.996	10.681	69.480	845.801
		Shoot	0.989^{a}	0.728^{b}	29.190*^{c}	297.778	-	175.347*^{e}	2622.346
	Leontodon hispidilus (Delile) Boiss.	Root	0.993	4.755	29.625	2877.625	13.115	135.796	2551.120
		Shoot	0.835^{a}	2.506^{b}	19.005	1522.839	5.952^{d}	85.525	4612.795
	Scolymus hispanicus L.	Root	0.918	5.048	28.708	3113.491	17.286	79.189	2123.558
		Shoot	0.827^{a}	2.531^{b}	15.601	346.005	1.085	58.322	3058.514
Poaceae	***Bromus hordeaceus***	Root	0.990	7.157	5.939	4391.650	47.817	123.350	31.218
		Shoot	0.830^{a}	4.514^{b}	14.631	417.136	1.920	39.379	2074.059
	Bromus rubens L.	Root	1.271	10.064	36.799	3036.247	30.802	118.937	2451.017
		Shoot	0.866^{a}	4.583^{b}	15.989	357.570	1.629	58.661	2251.899
	Lamarckia aurea L. (Moench).	Root	1.206	7.917	31.983	3003.610	55.945	215.338	1732.296
		Shoot	0.839^{a}	4.037^{b}	17.145	930.875	1.573	66.851	1697.638
	Stipa capensis Thunb.	Root	0.668	11.659	8.320	2928.177	104.825	77.245	26.707
		Shoot	0.832^{a}	3.950^{b}	12.421	371.065	-	33.521	1596.464

-, Below detection limit (Pb: 0.004 mg/L).

**, The values in the range of critical concentrations for plants (Kabata-Pendias and Pendias, 1992)*

a, b, c, d, e, The values are higher of the normal range of Cd, Cr, Cu, Pb and Zn in plant respectively (Kabata-Pendias and Pendias, 1992).

Rio et al. (2002) reported concentrations (mg kg^{-1}) of Pb, Zn, Cu and Cd varying from of undetectable to 450, 13–1138, 1.2–152 and from undetectable to 9.7, respectively, in wild vegetation in a river area after a toxic spill at a mine site. In an analysis of wetland plant species collected from mine tailings, Deng et al. (2008) reported concentrations of up to 11116, 1249, and 1090 mg kg^{-1} for Zn, Pb, and Cd, respectively, in *Sedum alfredii* growing on tailings at a Pb–Zn mine. Chehregani et al. (2009) reported concentrations (mg kg^{-1}) varying from of undetectable to 14.6, 9.60–84.0, 4.00–1485, and 20.0–1987 for Cd, Cu, Pb, and Zn, respectively, in shoots and leaves of plants collected in a waste pool at a Pb–Zn mine.

In the present study, the concentrations of Pb, Cu, Zn and Cd are in agreement with those of previous studies reported by Yoon et al. (2006), Moreno-Jimenez et al. (2009), Stoltz and Greger (2002), Rio et al. (2002) and Chehregani et al. (2009). But lower than the concentrations of Zn, Pb and Cd in the plants assessed by Deng et al. (2008), and higher than the concentrations of Zn, Cu, Pb and Cr determined by Remon et al. (2005). The concentrations of Fe conform to the concentrations reported by Lorestani et al. (2011) (mg kg^{-1}) 349.6–22645.3 in roots and 309.6–10604.9 in shoots.

Metals accumulation by the site's vegetation was checked by measuring metal concentrations in shoots and roots from the dominant species taken (Table). In shoots, the average metal contents were 0.86 mg kg^{-1} for Cd, 3.02 mg kg^{-1} for Cr, 18.73 mg kg^{-1} for Cu, 573.17 mg kg^{-1} for Fe, 1.86 mg kg^{-1} for Pb, 73.13 mg kg^{-1} for Zn and 2431.91 mg kg-1 for P. As a general trend, root metal concentrations were slightly higher for all metals, with a mean of 0.99 mg kg-1 for Cd, 5.71 mg kg-1 for Cr, 24.31 mg kg-1 for Cu, 2636.05 mg kg-1 for Fe, 30.24 mg kg-1 for Pb and 98.17 mg kg-1 for Zn, except P with 1106.33 mg kg-1 as a mean. Remon et al. (2005) also noticed the same trend for Zn, Cu, Pb and Cr. Metal excluders accumulate metals from substrate into their roots but restrict their transport and entry into their aerial parts (Malik and Biswas, 2012). Such plants have a low potential for metal extraction but may be efficient for phytostabilization purposes (Lasat, 2002). Although the reason for such a higher P content in shoots than in roots, that could be due to the distribution and dynamics of P in soil, rhizosphere and plant processes associated with soil P transformation, P mobilization and P acquisition, also could suggest root morphology, root architecture and root physiology, Pi transporters localized in the plasma membranes of roots, mycorrhizal and microbial activity (Schachtman et al. 1998; Raghothama and Karthikeyan 2005; Shen et al. 2011). The decreasing uptake of Cd by roots supplied with increasing Zn concentration found in Cd/Zn hyperaccumulator A. halleri and in most ecotypes of T. caerulescens clearly demonstrates that Cd influx is largely due to Zn transporters, with a strong preference for Zn over Cd (Zhao et al. 2002).

Accumulation of metals in organ plants arranged in the order, for roots: Fe, P, Zn, Pb, Cu, Cr, Cd and for shoots: P, Fe, Zn, Cu, Cr, Pb, Cd. Kisku et al. (2011) found plants (e.g. Wheat, Anise, Datura) absorbed larger proportion of Zn than Cu and Pb. *E. ilicifolium Lam, E. triquetrum Vahl. C. lanatus L. C. arabicus (L.) Cass. E. spinosus L. L. hispidilus (Delile) Bois, S. hispanicus L. B. rubens L.* and contained higher quantities of Fe, Zn and Cu, which are micronutrients in plants, compared to Pb and Cd, the elements toxic (Lasat 2000).

However, differences between the metal content of roots and shoots were significant (Pearson correlation test, $p<0.05$ regardless of the metal) unless for *E. triquetrum Vahl, L. hispidilus (Delile) Boiss* and *L. aurea L. (Moench)* (Table 5). This indicates that, in this plant community, metal concentrations were not in high equilibrium between roots and shoots. Consequently, each metal was accumulated with a good content in roots (Cd, Cr, Cu, Pb, Zn and Fe) or in shoots (P). Metals (Cd, Cr, Cu, Pb, Zn and Fe) and P concentrations extracted with a 0.01 M $CaCl_2$ solution, which represent the soluble and easily exchangeable metal fraction in the soil (Houba et al. 1996; Pueyo et al. 2004; Walker et al. 2003; Pérez-de-Mora et al. 2006), were not correlated with their contents in the plants (Table 4). This fact is confirming that metals and P concentrations in the plants could not be considered as a good ‘‘indicator” of metals and P availability in the soil (Baker, 1981). Similar results were obtained by Alvarenga et al. 2009, for Cu, Pb and Zn using *Lolium perenne L.*

However, our results also suggest that, independently of the soil metal content, the different plant species present on the site had the same abilities to take up and accumulate metals (Kruskal-Wallis test $p < 0.05$, using shoots and roots data ($r = 1$ and 0.86 respectively)). Our statistic results e differ from those of Remon et al. (2005) for Cu, Cr, Pb and Zn, reported that the different plant species present on the site had varying abilities to take up and accumulate metals. This may be due, first to the contamination origin of soil (natural or anthropogenic), second to the vegetable species used.

None of the plants studied exceed the contents proposed by Baker and Brooks (1989) to be accepted as hyperaccumulators. Furthermore, on only one occasion the BCF reaches a value higher than 1 and this is with Zn in *E. spinosus L.* (Table 6).

Table 4 Correlation between available metals and their contents in the plants

	Available Cd	Available Cu	Available Fe	Available Zn	Available P	Plant Cd	Plant Cr	Plant Cu	Plant Fe	Plant Pb	Plant Zn	Plant P
Available Cd	1											
Available Cu	-0,519	1										
Available Fe	0,369	0,454	1									
Available Zn	0,419	-0,895	-0,204	1								
Available P	-0,425	0,975*	0,619	-0,789	1							
Plant Cd	-0,340	-0,340	-0,972*	0,018	-0,534	1						
Plant Cr	-0,954*	0,331	-0,622	-0,349	0,189	-0,015	1					
Plant Cu	-0,854	0,234	-0,252	0,040	0,239	0,563	-0,103	1				
Plant Fe	-0,455	0,282	-0,610	-0,626	0,061	0,265	0,545	-0,101	1			
Plant Pb	-0,980*	0,517	-0,461	-0,506	0,386	-0,197	0,716**	-0,314	0,458	1		
Plant Zn	0,258	-0,144	-0,437	-0,309	-0,315	0,632*	0,094	0,475	0,469	-0,042	1	
Plant P	-0,347	0,533	0,640	-0,101	0,681	0,063	0,150	0,473	0,289	-0,288	0,326	1

**. Correlation is significant at the 0.01 level.
*. Correlation is significant at the 0.05 level.

Table 5 Correlation between shoot and root plant species (EI: Eryngium ilicifolium Lam.; ET: Eryngium triquetrum Vahl; CAS: Carlina acaulia subsp caulescens; CL: Carthamus lanatus L.; CAC: Cladanthus arabicus (L.) Cass; ES: Echinops spinosus L.; LH: Leontodon hispidilus (Delile) Boiss; SH: Scolymus hispanicus L.; BH: Bromus hordeaceus; BR: Bromus rubens L.; LA: Lamarckia aurea L. (Moench).and SC: Stipa capensis Thunb.)

	Root EI	Shoot EI	Root ET	Shoot ET	Root CAS	Shoot CAS	Root CL	Shoot CL	Root CAC	Shoot CAC	Root ES	Shoot ES	Root LH	Shoot LH	Root SH	Shoot SH	Root BH	Shoot BH	Root BR	Shoot BR	Root LA	Shoot LA	Root SC	Shoot SC
Root EI	1																							
Shoot EI	0,017	1																						
Root ET	0,557	0,818*	1																					
Shoot ET	0,007	1,00**	**0,812***	1																				
Root CAS	0,934**	0,372	0,819*	0,361	1																			
Shoot CAS	-0,085	0,998**	0,779	0,998**	0,279	1																		
Root CL	1,00**	0,024	0,563	0,013	0,936**	-0,078	1																	
Shoot CL	0,419	0,915**	0,982**	0,911**	0,714	0,883*	0,424	1																
Root CAC	0,818*	0,588	0,936**	0,579	0,969**	0,51	0,822*	0,864*	1															
Shoot CAC	-0,009	1,00**	0,803	1,00**	0,347	0,999**	-0,002	0,904**	0,567	1														
Root ES	0,951**	0,322	0,786	0,312	0,999**	0,226	0,953**	0,676	0,955**	0,297	1													
Shoot ES	-0,114	0,994**	0,76	0,996**	0,25	0,999**	-0,107	0,869*	0,484	0,997**	0,197	1												
Root LH	0,693	0,733	0,987**	0,725	0,904**	0,672	0,698	0,945**	0,981**	0,715	0,880**	0,649	1											
Shoot LH	0,152	0,991**	0,889*	0,989**	0,494	0,979**	0,159	0,961**	0,692	0,987**	0,448	0,972**	**0,818***	1										
Root SH	0,792*	0,623	0,951**	0,614	0,958**	0,549	0,797*	0,885**	0,999**	0,602	0,941**	0,523	0,989**	0,723	1									
Shoot SH	-0,066	0,996**	0,767	0,997**	0,293	0,999**	-0,06	0,878**	0,518	0,998**	0,242	0,999**	0,673	0,976**	0,555	1								
Root BH	0,999**	0,024	0,566	0,013	0,937**	-0,075	1,00**	0,424	0,823*	-0,002	0,954**	-0,105	0,698	0,159	0,797*	-0,06	1							
Shoot BH	0,022	1,00**	0,821*	1,00**	0,376	0,997**	0,029	,917**	0,592	0,999**	0,327	0,994**	0,736	0,991**	0,627	0,996**	0,029	1						
Root BR	0,731	0,694	0,977**	0,686	0,926**	0,628	0,736	0,925**	0,990**	0,675	0,905**	0,604	0,998**	0,785*	0,995**	0,631	0,737	0,698	1					
Shoot BR	-0,022	0,999**	0,795	1,00**	0,335	0,999**	-0,015	0,899**	0,556	1,00**	0,285	0,998**	0,706	0,985**	0,592	0,999**	-0,015	0,999**	0,665	1				
Root LA	0,846*	0,547	0,918**	0,538	0,979**	0,467	0,850*	0,838*	0,998**	0,525	0,968**	0,441	0,970**	0,655	0,995**	0,475	0,850*	0,551	0,982**	0,514	1			
Shoot LA	0,35	0,943**	0,965**	0,939**	0,66	0,916*	0,356	0,997**	0,824*	0,934**	0,62	0,904*	0,918**	0,979**	0,848*	0,911**	0,356	0,944**	0,894**	0,929**	**0,795***	1		
Root SC	0,999**	0,02	0,567	0,01	0,936**	-0,074	0,999**	0,421	0,820*	-0,006	0,952**	-0,103	0,695	0,156	0,795*	-0,063	1,00**	0,026	0,734	-0,019	0,847*	0,353	1	
Shoot SC	0,016	0,999**	0,839*	0,999**	0,376	0,994**	0,023	0,926**	0,596	0,998**	0,324	0,990**	0,743	0,995**	0,631	0,993**	0,027	1,00**	0,704	0,997**	0,554	0,952**	0,028	1

***. Correlation is significant at the 0.01 level.*

**. Correlation is significant at the 0.05 level*

Table 6 Bioncentration factors of Cd, Cr, Cu, Fe, Pb, Zn and P of the different study species

		BCF						
Family	**Species**	**Cd**	**Cr**	**Cu**	**Fe**	**Pb**	**Zn**	**P**
Apiaceae	***Eryngium ilicifolium Lam.***	0.564	0.008	0.568	0.002	0.100	0.612	0.536
	Eryngium triquetrum Vahl.	0.569	0.012	0.418	0.001	0.051	0.591	0.333
Asteraceae	***Carlina acaulia subsp caulescens***	0.630	0.005	0.417	0.001	-	0.688	0.274
	Carthamus lanatus L.	0.603	0.007	0.459	0.003	0.144	0.700	0.262
	Cladanthus arabicus (L.) Cass.	0.597	0.071	0.384	0.002	0.343	0.867	0.694
	Echinops spinosus L.	0.672	0.006	0.650	0.001	-	**1.682**	0.488
	Leontodon hispidilus (Delile) Boiss.	0.568	0.019	0.423	0.005	0.823	0.820	0.859
	Scolymus hispanicus L.	0.562	0.019	0.347	0.001	0.150	0.559	0.569
Poaceae	***Bromus hordeaceus***	0.564	0.035	0.326	0.001	0.265	0.378	0.386
	Bromus rubens L.	0.588	0.035	0.356	0.001	0.225	0.563	0.419
	Lamarckia aurea L. (Moench).	0.570	0.031	0.382	0.003	0.217	0.641	0.316
	Stipa capensis Thunb.	0.565	0.030	0.277	0.001	-	0.322	0.297

Plant metal accumulation is often expressed as a BCF. McGrath and Zhao (2003) considered that BCF < 0.2 as normal for plants growing on polluted materials. The data presented in this study indicate that hyperaccumulation levels were obtained only for *Echinops spinosus L.* for Zn (1.68), and this reflected the ability of this plant species to accumulate this metal from the soil and to transport it from the roots to shoots, and all other plant species had a BCF less than one (Table 6).

Cluster analysis according to the BCF revealed that the three plant species (*B. Rubens L, L. aurea L (Moench)*, and *B. hordeaceus*) presented metal accumulation strictly linked together at a low Squared Euclidean distance of 2 and they linked together with *E. ilicifolium Lam, S. hispanicus L, E. triquetrum Vahl, C. acaulia subsp caulescens, C. lanatus L* and *S. capensis Thunb* at Squared Euclidean distance of 4 and with *C. arabicus (L) Cass* and *L. hispidilus (Delile) Boiss* at Squared Euclidean distance of 16. However, *E. spinosus L* was distinctly different, having accumulation capacity at a considerably higher Squared Euclidean distance (Figure 1).

Tolerant plants have TF values << 1 and hyperaccumulators >> 1(Conesa and Faz, 2011). In our case, *E. ilicifolium Lam* had four TF values > 1: 1.23, 3.74, 6.99 and 537.72 for Cd, Cu, Pb and P, respectively, and one close to 1 (0.95) for Zn, *C. lanatus L. C. arabicus (L.) Cass* and *S. capensis Thunb* had three TF values > 1, *E. triquetrum Vahl, C. acaulia subsp caulescens*, *E. spinosis* and *B. hordeaceus* had two TF values > 1, *L. hispidilus (Delile) Boiss* and *S. hispanicus L.* had only one TF value > 1 and for other plants all TF values are < 1 (Table 7).

```
                                                 Rescaled Distance Cluster Combine
                                          0         5        10        15        20        25
                                          +---------+---------+---------+---------+---------+

  Bromus Rubens L                          -+
  Lamarckia aurea L (Moench)               -+-+
  Bromus hordeaceus                        -+ +-+
  Eryngium ilicifolium Lam                 -+-+ |
  Scolymus hispanicus L                    -+   |
  Eryngium triquetrum Vahl                 -+   |
  Carlina acaulia subsp caulescens         -+---+-------------------------+
  Carthamus lanatus L                      -+   |                         +-----------------+
  Stipa capensis Thunb                     -----+                         |                 |
  Cladanthus arabicus (L) Cass             -----+-------------------------+                 |
  Leontodon hispidilus (Delile) Boiss      -----+                                           |
  Echinops spinosus L                      -------------------------------------------------+
```

Fig. 1. Hierarchical dendrogram of plants on the basis of BCF obtained by the Ward's hierarchical clustering method

This showed that *E. ilicifolium Lam* was the most efficient in translocating metals in shoots between these 12 species (Figure 2).

Cluster analysis of plant effectiveness to translocate the metals to the shoots indicated that all vegetable species were closely aligned (at Squared Euclidean distance of 3) and dissimilar from *E. ilicifolium Lam*, having a considerably higher ability to translocate the metals from the roots to the shoots (Figure 3). Better translocation is advantageous to phytoextraction; as it can reduce metal concentrations and thus reduce toxicity potential to the root, and translocation to the shoot is one of the mechanisms of resistance to high metal concentrations (Ghosh and Singh, 2005a, b). The *C. lanatus L* species showed a highest level to translocate metals (Cu, TF=8.400).

Table 7 Metal transfer factors of the different study species

		TF						
Family	**Species**	**Cd**	**Cr**	**Cu**	**Fe**	**Pb**	**Zn**	**P**
Apiaceae	***Eryngium ilicifolium Lam.***	1.230	0.749	3.744	0.498	6.993	0.950	537.720
	Eryngium triquetrum Vahl.	0.893	0.809	0.674	0.466	-	1.131	2.171
Asteraceae	***Carlina acaulia subsp caulescens***	0.847	0.107	0.496	0.068	-	1.106	1.356
	Carthamus lanatus L.	0.751	0.383	8.400	0.413	3.828	0.716	81.734
	Cladanthus arabicus (L.) Cass.	0.987	2.008	0.576	0.253	0.296	1.286	2.354
	Echinops spinosus L.	0.858	0.136	0.639	0.108	-	2.524	3.100
	Leontodon hispidilus (Delile) Boiss.	0.842	0.527	0.642	0.529	0.454	0.630	1.808
	Scolymus hispanicus L.	0.901	0.501	0.543	0.111	0.063	0.736	1.440
Poaceae	***Bromus hordeaceus***	0.839	0.631	2.463	0.095	0.040	0.319	66.437
	Bromus rubens L.	0.681	0.455	0.435	0.118	0.053	0.493	0.919
	Lamarckia aurea L. (Moench).	0.696	0.510	0.536	0.310	0.028	0.310	0.980
	Stipa capensis Thunb.	1.245	0.339	1.493	0.127	-	0.434	59.777

Among the 12 plant species collected in the study area, *E. spinosus L.* appears to be the phytoextractor of Zn. This plant accumulated concentration of Zn as did the other species analyzed in the present study. The other BCFs values of *E. spinosus L.* were 0.67 (Cd) and 0.65 (Cu) (Table 6). But *E. ilicifolium Lam* appears as a useful species in translocating heavy metals from the roots to shoots. TF values exceeding 1 were obtained for this plant for Cd, Cu, Pb, P, and one value close to 1 was obtained for Zn (Table 7).

```
                                                Rescaled Distance Cluster Combine
                                       0         5        10        15        20        25
                                       +---------+---------+---------+---------+---------+

  Bromus Rubens L                       -+
  Lamarckia aurea L (Moench)            -+
  Carlina acaulia subsp caulescens      -+
  Scolymus hispanicus L                 -+
  Eryngium triquetrum Vahl              -+-+
  Leontodon hispidilus (Delile) Boiss   -+ |
  Cladanthus arabicus (L) Cass          -+ +---------------------------------------------+
  Echinops spinosus L                   -+ |                                             |
  Bromus hordeaceus                     -+ |                                             |
  Stipa capensis Thunb                  -+-+                                             |
  Carthamus lanatus L                   -+                                               |
  Eryngium ilicifolium Lam              -------------------------------------------------+
```

Fig. 2. Groupings of plants on the basis of TF by the Ward's hierarchical clustering method

Finally, phytoextraction process was evaluated according to the metals removal efficiency from soil. Our findings illustrate that Zn is the highest metals bioavailable, this allowed an enhancement for *E. spinosus L.* to accumulate this metal and, consequently, a higher phytoextraction of this metal from contaminated soil. Thus, this can be considered as successful biotechnological tools for the remediation of polluted soils. On the other hand, the plants with BCF values lower than one indicate that these species can be suitable for phytostabilization.

4. Conclusions

Based on the findings of this experimental work, it is identified:

- Metal and phosphorus accumulation depended on the plant species;
- Of the twelve study species, a population was recognized as Zn phytoextractor (*E. spinosus L.*), since (i) it accumulated the metal in plant tissues, and (ii) the translocation factor was higher than one;
- Some metallicolous populations concentrated over 1522 mg Fe kg^{-1} and over 4612 mg P kg^{-1} DW shoot (*L. hispidilus (Delile) Boiss*);
- Eleven potential metal excluders represent the candidates for phytostabilization; and
- Some plants can infect the human health through herbivore animals.

For Zn phytorextraction We propose native accumulator plant, *E. spinosus L.* because of its efficiency to remove Zn. However, there is a need to better understand the precise mechanisms by which *E. spinosus L.* extract Zinc from soil. Further work could be performed to validate the impact of metal on growth and metabolism of cereal crops growing around the mine and to study the entry of metals in the food chain. Thus, it has to be pointed out the interest in the potential exploitation of hyperaccumulators (plants or bacteria) as a rich genetic resource to develop engineered phytoextractor plants with high biomass (e.g. eucalyptus) (underway results). Furthermore, it is necessary to further investigate other methods for phytoremediation of metal-contaminated soils.

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Savaiminis metalų ir fosforo sunaudojimas vegetacijos metu apleistose centrinio Maroko metalo rūdos *Semiarid* kasyklose: vertinimas taikant fitoekstarkcijos metodą

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Straipsnyje analizuoti savaime augantys vietiniai augalai (atstovaujantys 12 rūšių, 10 genčių ir 3 šeimas), siekiant įvertinti Cd, Cr, Cu, Zn, Pb, Fe ir P akumuliaciją ūgliuose ir šaknyse. *Ait Amar* metalo rūdos kasykloje surinktos skirtingos augalų rūšys turėjo skirtingas metalų sankaupas ūgliuose ir šaknyse. Iš žolinių augalų (*Apiaceae*, *Asteraceae* ir *Poaceae*) didžiausios Cd, Cu, Zn stiebuose nustatytos *Echinops spinosus L* (0,989 29,190 ir 175,347 mg Kg^{-1}), Cr *Cladanthus arabicus (L) Class* (9,241 mg Kg^{-1}), o Pb, Fe ir P – *Leontodon hispidilus (Delile) Boiss* (5,952, 1522,839 ir 4612,795 mg Kg^{-1}) augaluose. Didžiausias Zn biokoncentracijos veiksnys nustatytas *E. spinosus L* (1,68). Didžiausias pasisavinimo iš dirvos veiksnys: Cd – *Stipa Capensis thumb* (1,24), Cr – *C. arabicus (L) Class* (2,01), Cu – *Carthamus lanatus L* (8,40), Zn – *E. spinosus L* (2,52), Pb – *Eryngium ilicifolium Lam* (7,00), P – *E. ilicifolium Lam* (537,72), Fe – *L. hispidilus (Delile) Boiss* (0,52). *E. spinosus L* pasižymėjo didžiausiu Zn fitoekstrakcijos laipsniu, o kiti augalai gebėjo gerai augti metalais užterštose teritorijose, pasisavindami tik mažas metalų koncentracijas, todėl jie gali būti laikomi gerais fitostabilizatoriais.