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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crossref http://dx.doi.org/10.5755/j01.erem.64.2.3866

(received in March, 2013, accepted in June, 2013)

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) 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,
cumulate metals, and 1 - 0.7% Fe, 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 SiO₂, 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. 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 Orдовicians to Carboniferous, organized into a series of anticlinorium and synclinorium, 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).

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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 transects (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
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 HNO₃ 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 HNO₃ 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 CaCl₂ 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 CaCl₂ 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 CaCl₂ soluble trace element concentrations were determined in 1/10 ratio, soil (0.01 M CaCl₂ 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 disturbances, active and abandoned mine areas). Differences were also found among sites with the highest concentration of metal measured in the region of El Arbi (0.52 mg/kg for Cd; 0.95 mg/kg for Cr; 1.05 mg/kg for Cu; 3.27 mg/kg for Zn; 0.17 mg/kg for Pb; and 0.02 mg/kg for Fe), as well as the lowest one in the region of El Oued. Statistical analyses indicated significant differences in metal concentration among sites (Table 3). Soil pH and conductivity were found to be significantly correlated with metal concentrations in shoots (Table 4). Soil pH and TKN were also significantly correlated with metal concentrations in shoots and roots. Soil pH and TKN were found to be significantly correlated with metal concentrations in shoots and roots. These results suggest that soil pH and TKN play a significant role in the accumulation of metals in plant tissues.
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).

### 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 | 1.73 | 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 | 0.0148 |
| 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 | 136.50 | 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 | 229030.00 | 199330.00 | 373790.00 | 31080.00 | 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 | - | 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 *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* (delleile) 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

| Family       | Species                        | Organs | Cd        | Cr         | Cu         | Fe         | Pb         | Zn         | P          |
|--------------|--------------------------------|--------|-----------|------------|------------|------------|------------|------------|------------|
| Asteraceae   | *Eryngium ilicifolium* Lam.    | Shoot  | 0.830*    | 1.090*     | 25.484**  | 565.225    | 0.727      | 63.789     | 2877.509   |
|              | *Eryngium triquetrum*          | Shoot  | 0.937     | 1.874      | 27.854     | 721.641    | -          | 54.458     | 823.527    |
|              | *Yalh.*                        | Shoot  | 0.837*    | 1.516*     | 18.771     | 336.144    | 0.366      | 61.592     | 1788.012   |
| Asteraceae   | *Carlineum acutatum subsp.*    | Shoot  | 0.923*    | 0.670*     | 18.704     | 204.816    | 0.311      | 71.724     | 1470.299   |
|              | *Carthamus lanatus* L.         | Shoot  | 1.182     | 2.456      | 2.456      | 2519.495   | 0.273      | 101.962    | 17.191     |
|              | *Cudranthus arboresis (L.)*    | Shoot  | 0.888*    | 0.940*     | 20.628**   | 892.077    | 1.044      | 72.956     | 1405.066   |
|              | *Cass.*                        | Shoot  | 0.887*    | 9.241*     | 17.244     | 636.567    | 2.478      | 90.400     | 3728.383   |
| Poaceae      | *Echinops spinosus L.*         | Root    | 1.152     | 5.341      | 45.657     | 2746.996   | 10.681     | 69.480     | 845.801    |
|              | *Leontodon hispidus* (Delile) Boiss. | Shoot  | 0.989*    | 0.728*     | 29.190*    | 297.778    | -          | 175.347**  | 2622.346   |
|              | *Scylomyrus hispanicus L.*     | Shoot  | 0.918     | 5.048      | 28.708     | 3113.491   | 17.286     | 79.189     | 2123.558   |
|              | *Bromus hordeaceus*            | Shoot  | 0.990     | 7.157      | 5.939      | 4391.650   | 47.817     | 123.350    | 31.218     |
|              | *Bromus rubens L.*             | Shoot  | 0.830*    | 4.514*     | 14.631     | 417.136    | 1.920      | 39.379     | 2074.059   |
|              | *Lamarckia aurea L.* (Moench).  | Shoot  | 1.271     | 10.064     | 36.799     | 3036.247   | 30.802     | 118.937    | 2451.017   |
|              | *Stipa capensis* Thum.          | Shoot  | 0.866*    | 4.583*     | 15.989     | 357.570    | 1.629      | 58.661     | 2251.899   |

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

*a, b, c, d, e* The values in the range of critical concentrations for plants (Kabata-Pendias and Pendias, 1992)

* Yearly results are higher of the normal range of Cd, 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 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 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 Lorentani 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 3). 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 excludes 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 is related to the increase in 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, Pb, Zn, 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. hispidulus (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. hispidulus (Delile) Bois 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 CaCl₂ 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 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 Pb | Plant Zn | Plant P |
|-------------|-------------|-------------|-------------|-------------|---------|---------|---------|---------|---------|---------|
| Available Cd | 1 | | | | | | | | | |
| Available Cu | -0.519 | | | | | | | | | |
| Available Fe | 0.369 | 0.454 | | | | | | | | |
| Available Zn | 0.419 | -0.895 | -0.204 | | | | | | | |
| Available P | -0.425 | 0.975* | 0.619 | -0.789 | | | | | | |
| Plant Cd | -0.340 | -0.340 | -0.972* | 0.018 | -0.534 | | | | | |
| Plant Cr | -0.954* | 0.331 | -0.622 | -0.349 | 0.189 | -0.015 | | | | |
| Plant Cu | -0.854 | 0.234 | -0.252 | 0.040 | 0.239 | 0.563 | -0.103 | 1 | | |
| Plant Pb | -0.455 | 0.282 | -0.610 | -0.626 | 0.061 | 0.265 | 0.545 | -0.101 | 1 | |
| Plant Zn | -0.980* | 0.517 | -0.461 | -0.506 | 0.386 | -0.197 | 0.716** | -0.314 | 0.458 | 1 |
| Plant P | 0.258 | -0.144 | -0.437 | -0.309 | -0.315 | 0.632* | 0.094 | 0.475 | 0.469 | -0.042 | 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 acaulis subsp caulescens; CL: Carthamus lanatus L.; CAC: Cladanthus arabicus (L.) Cass; ES: Echinops spinosus L.; LH: Leontodon hispidillus (Delile) Boiss; SH: Scolymus hispanicus L.; BH: Bromus hordeaceus; BR: Bromus rubens L.; LA: Lamarchia aurea L. (Moench).)

| Root | Shoot EI | Shoot ET | Root CAS | Shoot CL | Root CAC | Shoot ES | Root LH | Shoot SH | Root BH | Shoot BR | Root LA | Shoot SC |
|------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| EI   | 1        |          |          |          |          |          |          |          |          |          |          |          |
| Root | 0.017    | 1        |          |          |          |          |          |          |          |          |          |          |
| ET   | 0.557    | 0.818    | 1        |          |          |          |          |          |          |          |          |          |
| Shoot | 0.007 | 1.00** | 0.812** | 1        |          |          |          |          |          |          |          |          |
| CAS  | 0.934*  | 0.372    | 0.819*   | 0.361    | 1        |          |          |          |          |          |          |          |
| CL   |          |          |          |          | 1        |          |          |          |          |          |          |          |
| Shoot | -0.085 | 0.998*  | 0.779    | 0.998*   | 0.279    | 1        |          |          |          |          |          |          |
| Root | 1.00** | 0.024    | 0.563    | 0.013    | 0.936    | -0.078   | 1        |          |          |          |          |          |
| ET   | 0.419    | 0.915**  | 0.982**  | 0.911**  | 0.714    | 0.883**  | 0.424    | 1        |          |          |          |          |          |
| Shoot | 0.818* | 0.588    | 0.936    | 0.579    | 0.969    | 0.51     | 0.822    | 0.864    | 1        |          |          |          |          |
| CAS  | -0.009   | 1.00**   | 0.803    | 1.00**   | 0.347    | 0.999**  | -0.002   | 0.904*   | 0.567    | 1        |          |          |          |
| CL   | 0.693    | 0.733    | 0.987**  | 0.725    | 0.904*   | 0.672    | 0.698    | 0.945*   | 0.981**  | 0.498    | 0.484    | 0.972**  | 0.818**  | 1        |
| Root | 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        |
| ET   | 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 | -0.066 | 0.996*   | 0.767    | 0.997**  | -0.097   | 0.293    | 0.999**  | -0.06    | 0.876*   | 0.518    | 0.998**  | 0.242    | 0.999**  | 0.673    | 0.976**  | 0.555    | 1        |
| CL   | 0.099**  | 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    | 0.6  |
| Shoot | 0.022 | 1.00**   | 0.821*   | 1.00**   | 0.376    | 0.997**  | 0.029    | 0.917    | 0.592    | 0.999**  | 0.327    | 0.994*   | 0.736    | 0.991**  | 0.627    | 0.996*   | 0.029    | 1        |
| BR   | 0.731    | 0.694    | 0.977**  | 0.686    | 0.926**  | 0.628    | 0.736    | 0.928**  | 0.990**  | 0.675    | 0.905*   | 0.604    | 0.998*   | 0.785    | 0.995**  | 0.631    | 0.737   | 0.698    | 1        |
| Shoot | -0.022  | 0.999*   | 0.795**  | 1.00**   | 0.335    | 0.999**  | -0.015   | 0.899*   | 0.012    | 0.285    | 0.999**  | 0.706    | 0.985**  | 0.592    | 0.999**  | -0.015   | 0.999**  | 0.665   | 1        |
| 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 | 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**  | 0.848*   | 0.911**  | 0.356    | 0.944**  | 0.894*   | 0.929*  | 0.795**  | 1        |
| 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 | 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.
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. arabisus (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. spinosus 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).

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

Clustering 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).

| 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 |
|         | 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 |
| Asteraceae | 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 |

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

| Family | Species | Cd    | Cr    | Cu    | Fe    | Pb    | Zn    | P    |
|--------|---------|-------|-------|-------|-------|-------|-------|------|
| Poaceae | Bromus Rubens L | ++     |       |       |       |       |       |      |
|         | Lamarckia aurea L (Moench) | ++     | ++    |       |       |       |       |      |
|         | Eryngium ilicifolium Lam | ++     | ++    |       |       |       |       |      |
|         | Scolymus hispanicus L | ++     |       |       |       |       |       |      |
|         | Eryngium triquetrum Vahl | ++     |       |       |       |       |       |      |
|         | Carlina acaulia subsp caulescens | ++     |       |       |       |       |       |      |
|         | Carthamus lanatus L | ++     |       |       |       |       |       |      |
|         | 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.
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 BCF 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).

| Species            | Cd   | Cr   | Cu   | Fe   | Pb   | Zn   | P   |
|--------------------|------|------|------|------|------|------|-----|
| *E. ilicifolium* Lam | 1.230| 0.749| 3.744| 0.498| 6.993| 0.950| 537.720 |
| *E. spinosus* L.   | 0.893| 0.809| 0.674| 0.466| -    | 1.131| 2.171 |

Table 7 Metal transfer factors of the different study species

| Family     | Species                                    | TF |
|------------|--------------------------------------------|----|
| Apiaceae   | *E. ilicifolium* Lam                       | 1.230|
|            | *E. spinosus* L.                           | 0.893|
|            | CARLINA ACAULIA SUBSP. CAULESCENS           | 0.847|
|            | CARPATHUS LANTANUS L.                       | 0.751|
|            | CLADANTHUS ARABICUS (L.) CASS.              | 0.987|
|            | ECHINOPS SPINOSUS L.                        | 0.858|
|            | LEONTODON HISPIDULUS (Delile) Boiss.        | 0.842|
|            | SACOLYMS HISPANICUS L.                      | 0.901|
| Asteraceae | *Bromus hordeaceus*                        | 0.839|
|            | *Bromus rubens* L.                         | 0.681|
|            | LAMARCKIA AUREA L. (Moench)                | 0.696|
|            | STIPA CAPENSIS THUNB.                      | 1.245|
| Poaceae    |                                             |     |

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 metalloconcentrated populations over 1522 mg Fe kg⁻¹ and over 4612 mg P kg⁻¹ DW shoot (*L. hispidulus* (Delile) Boiss);
- Eleven potential metal excluders represent the candidates for phytostabilization; and
- Some plants can infect the human health through herbivore animals.

For Zn phytoextraction 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.

**Acknowledgements**

This work was carried out under a Project funded by the North Atlantic Treaty Organization (NATO), within the Program Science for Peace (Ref. SIP.983311). We thank Professor S. HAMMADA (University of Sultan Moulay Slimane, Faculty of Sciences and Techniques) for help in plants identification.

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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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(gauta 2012 m. kovo mėn., priimta spaudai 2013 m. birželio mėn.)

Straipsnyje analizuoti savaime augantys vietiniai augalai (atstovaujantys 12 rūšių, 10 genčių ir 3 šeimų), siekiant įvertinti Cd, Cr, Cu, Zn, Pb, Fe ir P akumuliaciją ūgliuose ir šaknyse. Ait Amar metalo rūdos kasykloje surinktos skirtingos augalų rūšys turėjo skirtingus metalų sankaupas ūgliuose ir šaknyse. Iš žolinių augalų (Apiaceae, Asteraceae ir Poaceae) didžiausius Cd, Cu, Zn stiebuose nustatė 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 nustatė 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 didžiausių Zn fitoekstrakcijos laipsnių, o kiti augalai gebėjo augti metalais užterštose teritorijose, pasisaviniai tik mažas metalų koncentracijas, todėl jie gali būti laikomi gerais fitostabilizatoriais.