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Heavy metals distribution in soils surrounding an abandoned mine in NW Madrid (Spain) and their transference to wild flora

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ABSTRACT

The present work concerns the distribution and mobility of heavy metals (Fe, Mn, Cu, Zn and Cd) in the surrounding soils of a mine site and their transfer to wild flora. Thus, soils and plants were sampled from a mining valley in NW Madrid (Spain), and total and extractable heavy metals were analysed. Soils affected by mining activities presented total Cd, Cu and Zn concentrations above toxic thresholds. The percentage of extractable element was highest for Cd and lowest for Cu. A highly significant correlation was observed between the total and extractable concentrations of metals in soils, indicating that, among the factors studied, total metals concentration is the most relevant for heavy metals extractability in these soils. $(NH_4)_2SO_4$-extractable metal concentrations in soils are correlated better with metal concentrations in several plant species than total metals in soils, and thus can be used as a suitable and robust method for the estimation of the phytoavailable fraction present in soils. Twenty-five vascular plant species (3 ferns and 22 flowering plants) were analysed, in order to identify exceptional characteristics that would be interesting for soil phytoremediation and/or reclamation. High Cd and Zn concentrations have been found in the aerial parts of *Hypericum perforatum* (Cd), *Salix atrocinerea* (Cd, Zn) and *Digitalis thapsi* (Cd, Zn). The present paper is, to the best of our knowledge, the first report of the metal accumulation ability of the two latter plant species. The phytoremediation ability of *S. atrocinerea* for Cd and Zn was estimated, obtaining intervals of time that could be considered suitable for the phytoextraction of polluted soils.

1. Introduction

The potential risk for the environment and population due to soil heavy metals arising from metallic mining has been well described [1,2]. Several studies have reported a high degree of metal pollution in soils affected by the oxidation of pyritic materials [3–5], a type of frequent waste in metallic mines. After the accumulation of metallic elements in the soil, several physico-chemical factors condition the transfer of each heavy metal from the solid to the liquid soil phase, causing differences in the availability and, finally, the toxicity of elements such as Cd, Cu, Mn or Zn. The estimation of metals availability for plants using unbuffered salt solutions has been described as suitable [6], but less information is available about the correlation between extractable element and phytoavailability, especially when wild plants are involved. Heavy metals can induce toxicity in wildlife if the soil level reaches critical values; also, plant accumulation in above-ground tissues can result in an increase of metal accumulation in top-soil, via leaf deposition, or can create an exposure pathway for metal introduction into the food chain [7,8]. On the other hand, plants living in metalliferous soils can have exceptional properties which make them interesting for phytoremediation [9]. Thus, many authors have reported plant screening in sites enriched with metals and have identified interesting plants for further studies [8,10,11], aiming to find self-sustainable plants that could clean polluted environments [12]. Moreover, other studies focus on the possibilities of revegetation and phytostabilisation of mine tailings with Iberian tolerant plants [13–15].

In our study site, the Mónica pyrite mine, mining activities were carried out from 1427 until 1980 [16], and a group of galleries and pyritic dumps remain, close to the village of Bustarviejo, across the La Mina stream gorge (Sierra de Guadarrama, NW Madrid, Spain). Many plants species inhabit in this valley and some of them could show properties useful in phytotechnolgies. These plants present the advantage of being adapted to the edaphoclimatic conditions of this area.

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Table 1
pH, dichromate-oxidable organic matter and metal concentrations in soils surrounding Mónica mine (Bustarviejo, Spain)

	Soils close to mining dumps			Soils affected by mine drainage			Unaffected soils		
	Mean (S.E.)	Median	Range	Mean (S.E.)	Median	Range	Mean (S.E.)	Median	Range
pH	4.87 (0.25)	4.17	3.89–5.99	5.27 (0.13)	5.20	4.24–6.09	5.08 (0.11)	5.16	4.01–5.90
% OM	4.33 (1.00)	3.19	0.69–8.61	5.91 (0.94)	5.41	1.83–13.04	6.28 (0.70)	6.62	2.11–11.66
Total Fe (%)	2.02 (0.01)	1.86	1.32–3.38	2.16 (0.02)	2.03	1.01–3.45	1.36 (0.01)	1.42	0.94–1.65
Total metal concentration (mg kg^{-1})									
Cd	16.35 (3.15)	13.72	1.78–34.98	8.68 (1.37)	9.75	2.44–15.29	2.91 (0.50)	2.89	n.d.–6.15
Cu	308.7 (56.4)	301.7	17.3–605.3	182.2 (38.9)	186.7	15.5–444.3	16.6 (2.3)	13.3	6.2–32.5
Mn	353.6 (47.8)	298.9	184.7–658.4	432.6 (62.2)	405.3	158.9–1002.0	427.8 (49.7)	517.3	76.9–647.8
Zn	845.7 (186.2)	604.2	92.4–2243.6	571.1 (111.4)	566.4	75.2–1437.5	96.7 (14.0)	92.9	30.8–200.3
Extractable metal concentration (mg kg^{-1})									
Fe	4.49 (0.99)	3.57	1.07–12.48	3.64 (0.29)	3.35	2.22–5.52	2.67 (0.21)	2.67	2.15–4.73
Cd	2.01 (0.72)	1.32	0.06–7.23	1.36 (0.26)	1.38	0.10–2.66	0.19 (0.06)	0.11	n.d.–1.00
Cu	2.68 (0.59)	2.21	0.46–6.32	2.08 (0.58)	1.35	0.30–4.30	0.34 (0.04)	0.33	0.05–0.71
Mn	18.2 (3.9)	17.2	1.4–46.6	34.3 (7.1)	34.2	3.7–73.7	48.7 (15.8)	28.1	3.21–255.9
Zn	51.0 (15.9)	42.8	1.24–149.4	38.6 (8.5)	36.5	4.95–84.5	1.9 (0.7)	0.8	0.1–13.1
Relative extractable metal concentration (%)									
Fe	0.023 (0.004)	0.017	0.005–0.049	0.020 (0.003)	0.015	0.009–0.036	0.022 (0.002)	0.022	0.013–0.040
Cd	9.7 (2.27)	7.9	3.7–25.1	14.9 (1.41)	14.2	3.6–22.4	6.0 (1.33)	4.0	0–17.9
Cu	1.4 (0.25)	1.5	0.4–2.7	1.3 (0.21)	0.9	0.7–3.1	2.3 (0.29)	2.0	0.3–4.3
Mn	6.2 (1.42)	6.0	0.8–15.6	7.2 (0.89)	6.8	2.3–10.5	10.5 (2.68)	7.1	1.5–21.8
Zn	6.5 (1.65)	3.9	1.3–14.6	6.4 (0.80)	6.9	1.9–12.3	2.9 (0.54)	3.2	0.4–8.1

Mean, standard error (S.E.), median and range (n = 12–16).

Our study focuses on the dispersion of heavy metals in soils in the vicinity of the Mónica mine and the availability of these metals for the plant community at this site. Metal accumulation and transfer to natural flora was also studied, in order to evaluate the phytoremediation ability of these plant species.

2. Materials and methods

2.1. Site description

Soils and plants were sampled in the surroundings of the Mónica mine, close to the village of Bustarviejo (Madrid) (Fig. S1). The studied site extends across 200 000 m^2 within the La Mina stream valley, between the following UTM coordinates: 30 T—X = 0438606, Y = 4524302; X = 0437797, Y = 4523518. Sampling was carried out between May and June 2006. Shoots of 25 vascular plant species were collected (Table S1), as well as the soil below the plants (top 0–30 cm soil layer). Moreover, water from the La Mina and La Barranca streams was sampled. All sampling points were georeferenced by GPS. Fig. S1 shows the sampling points within the site, dividing soils into three groups: (1) soils close to mining dumps, (2) soils affected by mine drainage and (3) potentially unaffected soils.

The mining area shows three types of vegetation: in the upper zones, a dense scrub dominated by *Genista cinerascens* Lange and *Cytisus oromediterraneus* Rivas Mart. et al. (Genisto-Cytisetum oromediterranei); in the lower zones, an open forest of *Quercus pyrenaica* Willd. with a grass pasture (Luzulo-Quercetum pyrenaicae); along the stream, a riparian community (Rubo-Salicetum atrocinereae) with *Salix atrocinerea* Brot., *Athyrium filix-femina* (L.) Roth and *Frangula alnus* Miller.

2.2. Analytical procedures

Soils were dried at 50 °C for 7 days, sieved to 2 mm and homogenised. Dichromate-oxidable organic matter (OM) and the pH of a 1:2.5 (soil:water) suspension were measured following the protocols of the Spanish Ministry of Agriculture [17]. Pseudo-total concentrations of elements were assayed after HNO_3:H_2O_2 digestion in an autoclave [18]. The extractable metals content of the soils was extracted by shaking 2 g of soil with 20 mL of 0.1 M $(NH_4)_2SO_4$ for 4 h; the suspension was filtered and the filtrate analysed [19].

Surface waters were sampled in plastic flasks and 1 mL of HNO_3 was added to 40 mL of water. Samples were stored at 4 °C and analysed as soon as possible.

Plant material was washed thoroughly in tap and distilled water and dried at 50 °C for 7 days. For acid mineralisation of plant tissues, 10 mL of mili-Q water, 3 mL of HNO_3 and 2 mL of H_2O_2 were added to 0.5 g dry weight (DW) of tissue and digestion was performed at 1500 Pa and 125 °C [20], in an autoclave. The extract was filtered and diluted to 25 mL.

The metals (Cd, Cu, Fe, Mn and Zn) in the surface water and the soil and plant extracts were analysed by atomic absorption spectrometry (PerkinElmer AAnalyst 800). Three analytical replicates were measured for each sample.

2.3. Statistical analysis

The data were analysed statistically using SPSS 14.0® for Windows. Statistical differences among soil groups were analysed using the non-parametric Kruskal–Wallis or Wilcoxon tests. Linear regression, simple and bivariate correlations and principal components analysis (PCA) were performed for the soil and plant analysis data.

3. Results and discussion

3.1. Metal distribution and mobility in soils

Both pH and dichromate-oxidable organic matter (Table 1) were in the same range as values reported as normal in soils from the northwestern mountains of Madrid [21]. Both affected and unaffected soils were acid and contained high levels of organic matter, and no significant differences were observed among soil groups.

Levels of Cd, Cu and Zn in soils close to mining dumps and soils affected by mine drainage were much higher than those from unaffected soils (P < 0.001), but Mn levels were in the same range in the

Table 2
Results of the principal component analysis (factor loadings) of the total metal concentration and other properties in soils, and of the metals in the shoots of all plant species

	Soils		Plants		
	Comp. 1 (47%)	Comp. 2 (27%)	Comp. 1 (34%)	Comp. 2 (31%)	Comp. 3 (17%)
Cd	0.88		0.89		
Zn	0.95		0.84		
Cu	0.91			0.76	
Mn		0.77			0.82
Fe	0.70	0.07		0.77	
OM		0.84	–	–	–
pH		0.62	–	–	–

Factor loadings smaller than 0.5 were omitted.

entire valley (Table 1). The Cd, Cu and Zn levels in unaffected soils and the Mn in all soils were quite similar to the geochemical background of the soils from this orophilous region of Madrid (Table S2) [21]. More than 80% of the soils close to the mining dumps and 50% of the soils affected by mine drainage exceeded the toxic concentration in soils (Table S2) [3,22,23] for at least one metal (Zn, Cu and Cd), posing an important environmental risk.

$(NH_4)_2SO_4$-extractable Cd, Cu and Zn concentrations were much higher in affected soils than in unaffected ones ($P < 0.001$), while the extractable Mn and Fe concentrations were similar in all soils (Table 1). Although the total metal concentrations are usually used as the primary pollution reference in legislation, the occurrence of toxic elements in soils, especially in disused mining areas, needs further analysis [24]. The extractable heavy metals show a better correlation with the metal concentration in plant tissues [6], so it appears to be a better indicator of the environmental risk caused by the presence of metals in soils [2].

The percentages of extractable metals, in relation to total soil metals, show that Cd and Mn were significantly more easily extractable than the other metals ($P < 0.001$), while Cu showed low extractability and Fe was strongly retained in soils (Table 1). The relative proportions of extractable Cd, Cu, Mn and Zn (10, 1.5, 6.5 and 4%, respectively in average) were in the range reported as normal [25], Cd and Zn usually being more mobile in soils than Cu [26]. Total Fe concentrations in the soils are similar to those for other soils close to pyritic mines [3,27]. The relative abundance of total heavy metals at the polluted sites was Fe > Zn ≈ Mn > Cu ≫ Cd, while for the extractable metal concentrations it was Zn ≈ Mn ≫ Fe > Cu ≈ Cd. The degree of mobility of the metals, given as the percentage of extractable metal with respect to the total, was: Cd ≈ Mn ≫ Zn > Cu ≫ Fe, showing the higher environmental risk posed by Cd, despite its lower total concentration in the soil.

After a bivariate correlation analysis, extractable and total Cd, Cu and Zn were strongly associated (Pearson's coefficients from 0.65 to 0.99; $P < 0.001$), indicating their simultaneous presence in the mine wastes. Total Fe was moderately correlated with total Cu and Zn ($P < 0.01$). Total and available Mn were not correlated with the other heavy metals, but showed moderate correlation with organic matter ($P < 0.01$) and low correlation with pH ($P < 0.05$). Metal availability in soils is generally controlled by total metal concentration, pH and organic matter [2], but in our study only total metal significantly explained metal extractability after linear regression analysis, so that organic matter and pH were omitted from the model.

The first PCA component for soils (Table 2) explained 47% of the total variance, and the factor loadings of Cd (0.88), Zn (0.95), Cu (0.91) and Fe (0.70) showed the highest values for this component. This fact, together with the high correlation among all these elements, supports the hypothesis that metal pollution is mainly due

Table 3
Metal concentrations in shoots of plants growing in the areas surrounding the Mónica mine (Madrid, Spain)

Plant species	Cd ($\mu g\,g^{-1}$ shoot DW)	Zn ($\mu g\,g^{-1}$ shoot DW)	Cu ($\mu g\,g^{-1}$ shoot DW)	Mn ($\mu g\,g^{-1}$ shoot DW)	Fe ($\mu g\,g^{-1}$ shoot DW)
Seedless vascular plants					
Equisetum ramosissimum	1.53 (1.24–1.83)	172.9 (172.7–173.1)	8.22 (7.8–8.6)	49.2 (47.5–50.9)	55.0 (53.4–56.6)
Pteridium aquilinum	0.81 (n.d.–1.74)	91.3 (9.5–191.1)	11.2 (5.5–22.9)	85.3 (23.8–196.1)	100.0 (119.2–232.4)
Athyrium filix-femina	1.83 (1.13–2.34)	204.9 (126–247)	12.0 (10.3–13.4)	19.8 (14.9–22.2)	117.2 (76.5–141.8)
Annual and perennial herbs					
Centaurea nigra	1.28 (0.24–2.92)	150.6 (19.0–277.9)	13.4 (9.9–17.0)	86.9 (42.6–108.5)	89.9 (72.7–109.6)
Hypericum perforatum	10.22 (6.29–20.32)	59.18 (24.09–102.73)	16.11 (5.21–26.50)	230.2 (134.4–344.5)	108.11 (92.8–119.2)
Digitalis thapsi	13.28 (0.85–22.04)	245.3 (107–351)	23.5 (3.3–70.2)	182.7 (83.4–362.4)	422.1 (107.1–831.6)
Aira caryophyllea	2.16 (1.64–2.37)	65.8 (62.7–68.8)	2.77 (2.68–2.86)	163.9 (138.2–189.5)	140.9 (120.7–161.2)
Glyceria fluitans	5.64 (1.16–11.02)	364.9 (77.4–663.0)	18.6 (9.2–35.2)	55.5 (22.3–69.2)	200.1 (46.6–448.9)
Diplotaxis erucoides	14.51 (1.90–19.04)	581.1 (101.3–1048.0)	15.24 (10.87–22.98)	46.5 (30.1–60.1)	367.8 (256.4–540.1)
Daucus carota	4.06 (3.01–5.11)	91.2 (79.6–102.9)	7.11 (4.45–9.77)	66.7 (49.1–84.3)	39.5 (39.4–39.7)
Silene latifolia	6.91 (0.48–13.59)	228.1 (21.3–440.0)	6.42 (4.36–9.66)	95.0 (27.0–155.9)	160.8 (52.6–399.8)
Woody plants					
Cytisus scoparius	0.87 (n.d.–2.48)	200.1 (15.2–902.9)	19.1 (4.9–57.6)	104.7 (26.5–215.6)	57.5 (28.5–140.1)
Cytisus oromediterraneus	0.98 (n.d.–3.90)	158.9 (13.1–509.1)	4.59 (3.6–5.7)	85.0 (48.2–201.4)	94.9 (24.5–226.6)
Genista cinerascens	1.07 (n.d.–2.74)	108.5 (26.1–425.8)	6.16 (4.52–8.69)	90.8 (15.8–212.0)	85.8 (39.6–128.9)
Adenocarpus complicatus	2.86 (1.56–3.98)	299.3 (246–358)	4.55 (2.52–6.03)	86.9 (43.9–170.1)	98.9 (88.2–136.8)
Thymus mastichina	1.82 (0.35–3.70)	30.3 (8.3–58.3)	9.9 (7.3–12.3)	77.3 (52.3–109.8)	344.4 (229.2–430.0)
Santolina rosmarinifolia	19.43 (18.5–20.4)	349.8 (345.9–353.6)	12.89 (12.7–13.0)	44.6 (39.5–49.7)	50.7 (49.6–51.7)
Frangula alnus	0.56 (0.31–0.72)	129.8 (30.5–235.6)	7.81 (6.25–9.68)	199.6 (104–171)	62.4 (57.2–69.2)
Betula pendula	4.75 (3.23–6.27)	708.5 (629–787)	6.17 (6.03–6.31)	102.4 (83.6–121.3)	35.5 (34.5–36.5)
Erica arborea	0.20 (n.d.–0.37)	35.2 (20.4–70.7)	7.92 (4.65–10.76)	125.7 (60.9–306.9)	108.7 (40.9–223.2)
Salix atrocinerea	33.26 (13.1–53.1)	667.7 (310–936)	7.13 (4.71–11.86)	163.2 (61.8–400.6)	53.9 (21.0–95.9)

Means (range), $n = 2$–12.

Table 4
Correlations between metal concentrations in plants and soils (total and available) for the dominant plant species (n = 6–12; $^{*}P < 0.05$; $^{**}P < 0.01$; $^{***}P < 0.001$)

	Total				Available			
	Cd	Zn	Cu	Mn	Cd	Zn	Cu	Mn
S. atrocinerea	0.68*	0.81*	0.10	0.06	0.75*	0.88**	0.31	0.22
Cytisus scoparius	0.70*	0.36	0.24	0.02	0.75**	0.59*	0.56*	0.15
G. cinerascens	0.70	0.76*	0.82*	0.32	0.83**	0.99***	0.82*	0.49
E. arborea	0.17	0.44	0.06	0.56	0.45	0.71*	0.40	0.94***
P. aquilinum	0.51	0.11	0.15	0.50	0.68*	0.45	0.28	0.38

to dispersion of mining wastes in these soils. The second component (27%), associated mainly with Mn (0.77), organic matter (0.84) and pH (0.62), was not correlated directly with mining pollution. The proximity to mining dumps or to mine drainage seemed to enrich the soils in metals, probably due to an enrichment in pyritic particles via transfer from the dumps and/or retention of metals mobilised by waters.

Stream water was also sampled along the site (Fig. S1). In both streams (La Mina and La Barranca), heavy metals ranged across the following concentrations: n.d.–0.024 mg Cd L^{-1}; 0.078–0.196 mg Zn L^{-1}; 0.073–0.131 mg Cu L^{-1}; 0.024–0.042 mg Mn L^{-1}; 0.125–0.487 mg Fe L^{-1}. The concentrations of Cd, Zn and Cu were higher than the Spanish indicative values for surface waters [28].

3.2. Metal concentrations in plants. Screening for phytoremediation

Three seedless vascular plants and 22 flowering plants (3 of them monocots) were collected and analysed (Table 3; Table S3). Many of these species (11 for Cd and 3 for Zn) showed Cd and Zn concentrations much higher than the normal levels for plants (Table S2) [3,22,23], but none of the plants analysed could be classified as hyperaccumulators [29]. When possible, metal concentrations in woody plants were also evaluated, separating leaves and stems (i.e. *S. atrocinerea*, *Betula pendula* and *F. alnus*): in all cases, the metal concentrations were higher or much higher in leaves than in stems (30% higher for Cd, 200% for Mn and 36% for Zn on average), in agreement with previous observations in the literature [3,8]. Despite the high levels of Cu in the soils, no plant species exceeded the normal tissue levels, the highest values being found in *Digitalis thapsi*. Similar effects were observed for Fe and Mn. Some of the studied species have stood out in previous reports for their ability to accumulate certain metals: for example, high Cd accumulation in *Hypericum perforatum* [22] or high Mn and Zn concentration in *S. atrocinerea* [3]. Thus, many *Salix* taxa have been described as metal accumulators, although there were considerable variations among species, ecotypes and clones [8,30,31].

In order to study metal phytoavailability, total and available metal concentrations were correlated with metal concentrations in the shoots of the dominant plant species (Table 4). Higher positive correlations were obtained for plant metal concentrations and their extractable fraction in soils than for the total metal concentration, indicating that phytoavailability is better predicted by the extractable fraction than by the total metal concentrations. These data, from various plant species under field conditions, are in agreement with the results obtained by Vázquez et al. [19] for lupin plants grown under controlled conditions in slightly multi-contaminated soils, corroborating the use of $(NH_4)_2SO_4$ extraction as a suitable and robust method for the estimation of the phytoavailable fraction of metals present in soils.

To evaluate metal transference from the soil to the plants, a transfer factor was calculated by dividing the shoot metal concentration of each species by the total metal concentration in the soil surrounding the plant [32] (Fig. 1). *S. atrocinerea* showed the highest TF for Cd (4.3) and Zn (1.5), but not for Cu. *H. perforatum* and *D. thapsi* had higher transfer factors than the other herbaceous species for most metals, although *Silene latifolia* also showed a high TF for Zn and Cd. All the seedless vascular plants showed low transfer of metals to the aerial parts. Moreover, *Erica arborea* and *F. alnus* showed lower transfer factors (except for Mn) than the other woody plants, while *Centaurea nigra* and *Aira caryophyllea* had lower Cd and Zn transfer factors than the other herbaceous species.

Although the shoot metal concentrations clearly differed among species, the data were studied by a factorial analysis. The first PCA component (Table 2) explained 34% of the variance, and the factor loadings of Cd (0.89) and Zn (0.84) showed the highest values. Both elements showed a high availability in soils after mine pollution (Table 1) and the highest differences in metal transfer to plants among the species (Fig. 1), i.e. between *S. atrocinerea* (4.3 for Cd and 1.4 for Zn) and *E. arborea* (0.03 for Cd and 0.09 for Zn). Both elements, Cd and Zn, are usually taken up by plants as divalent cations [33,34], and there is evidence that they are absorbed, at least in part, by the same transporter in plant cells [35]. The factor loadings of Cu (0.76) and Fe (0.77) were the highest for component 2 (31%). Both are present in the mine dumps, but their transfer factors to plants were lower and more homogeneous among species than for Cd or Zn. Thus, as expected, the plant species is a primary factor for interpreting metal accumulation in flora. Finally, the third component, which explained 17% of the variance, showed the highest factor loading for Mn (0.82), the presence of which in soils seemed to be independent of the pollution after mining activities.

Some of the studied species showed high levels of metals in their aerial parts or high transfer factors. Among them, *H. perfora-*

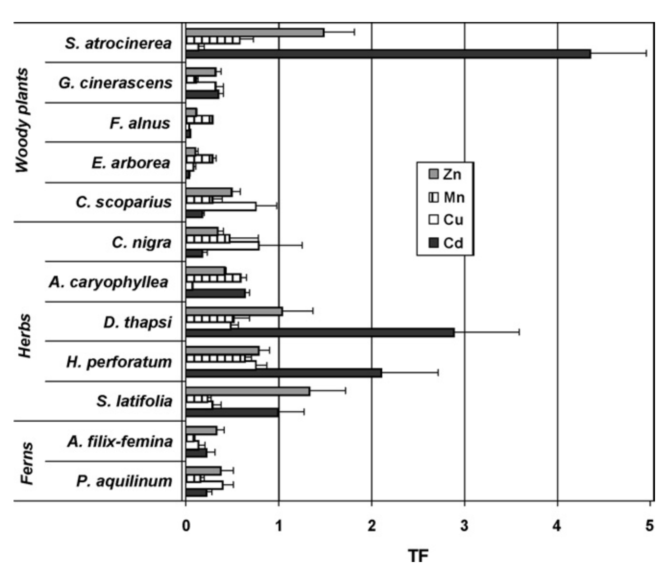

Fig. 1. Transfer factor (TF = $[\text{metal}]_{\text{shoot}}/[\text{metal}]_{\text{soil}}$) for Cd, Cu, Mn and Zn in different plant species (ferns, herbaceous and woody plants) growing in soils surrounding the Mónica mine (Bustarviejo, Spain). Mean ± S.E. (n = 4–12).

tum reached 10 μg g^{-1} Cd and a transfer factor of more than 2 for Cd, and has been reported previously as a Cd-accumulator [22]. *D. thapsi* showed higher shoot Cd concentrations (13.3 μg g^{-1} Cd) and a higher TF (2.9) than *H. perforatum*, but has not been described previously in the literature as a Cd-accumulator species, to the best of our knowledge. Only *H. perforatum*, *C. nigra* and *Cytisus scoparius* reached TF values close to 1 for Cu; the other species showed values below 1. Several *Salix* spp. have been reported as metal-accumulators and, specifically, *S. atrocinerea* in Galicia (Spain) accumulated high concentrations of Zn and Mn [3]. Despite this, the ability of *S. atrocinerea* to accumulate Cd has not been reported previously. As *S. atrocinerea* showed interesting transfer factors for Zn and Cd, its ability to phytoextract Cd- and Zn-polluted soils was estimated as Zhao et al. [32] described, using a transfer factor of 4.3 for Cd and 1.5 for Zn. Assuming a dry biomass production of 1 kg m^{-2} year^{-1}, which is on the low side for *Salix* spp. [36,37], *S. atrocinerea* could decrease the Cd and Zn concentrations in soils by a half after 41 and 120 years, respectively. These time intervals, especially for Cd, could be considered as suitable for applying phytoextraction in polluted soils [38]. Although time intervals could be considered long, *S. atrocinerea* can be used as a sustainable alternative in sites of high-ecological value, where it is more important to avoid the dispersion of the contaminants than the time involved in the restoration process, like the one used in this study.

4. Conclusions

Heavy metal pollution has spread along the studied valley, both from the mining dumps and from the surface mine drainage. In these soils, total heavy metals are the main factor conditioning heavy metal extractability, while the $(NH_4)_2SO_4$-extractable fraction appears to be a better index of phytoavailability. The metal levels observed in the soils, streams and plants reflect the potential risk still remaining due to the past mining activities at this site.

A description of the flora growing in this area is reported. Many of these plants survive in contact with relatively high levels of heavy metals in the soils. Among them, *S. atrocinerea* and *D. thapsi* have not been, to the best of our knowledge, previously reported as Cd- or Zn-accumulators. *S. atrocinerea* stands out as a good candidate for Cd- and Zn-phytoextraction.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2008.05.109.

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