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Phytoremediation of As, Ag, and Pb in contaminated soils using terrestrial plants grown on Gumuskoy mining area (Kutahya Turkey)



Derya Yildirim, Ahmet Sasmaz*

Department of Geological Engineering, Firat University, Elazig 23119, Turkey

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ABSTRACT

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Keywords: Accumulation Heavy metal uptake Terrestrial plants Phytoremediation Mining area Gumuskoy Ag (As, Zn and Pb) deposits are located about 25 km west of Kutahya, Turkey and one of the largest silver deposits in the country. This study investigated the accumulation and transport of As, Ag, and Pb from the soil into 11 terrestrial plants. Plant and soil samples were collected from the field and As, Ag, and Pb content was measured with inductively coupled plasma mass spectroscopy. The mean values in the soil, roots, and shoots of the studied plants were, respectively, 4771, 2320, and 1340 mg kg⁻¹ for As; 35.93, 10.19, and 11.51 mg kg⁻¹ for Ag; and 4180, 1424, and 1050 mg kg⁻¹ for Pb. The plants collected from the study area were separated into different groups based on the As, Ag and Pb concentrations in plants and their soils. The results showed that *Glaucium* root, *Phlomis* root and shoot for Pb could be good a bioaccumulator because of their higher ECRs and ECSs. Therefore, these plants can be useful for cleaning or rehabilitating the soils polluted by Ag, As and Pb.

1. Introduction

Heavy metal pollution in both terrestrial and aquatic environments has emerged as a global problem. The toxic metals (As, Ag, Cd, Cr, Tl, Ni, Pb, and Zn) are the main problem because they are persistent in nature, are non-biodegradable, and they bioaccumulate in living animals and plants. These metals enter the environment mainly through various anthropogenic sources, such as smelting processes, mining, fuel production, and industrial effluents (Soylak and Turkoglu, 1999; OECD, 2003; Shah et al., 2010; Muhammad et al., 2011, 2013; Unsal et al., 2013; Agnieszka et al., 2014: Sungur et al., 2014), and they occur in aquatic systems as a result of the weathering of rocks and soils, volcanic eruptions, and various human activities. The most common heavy metal contaminants are As, Ag, Cd, Cr, Cu, Ni, Pb, Zn, and Hg, which enter the surface soils and then the freshwater in mining areas (US EPA, 2000). The removal of heavy metals from cultivated lands is possible through the use of certain plants (Vetiveria zizanioides, Commelina communis, Paspalum notatum, and Imperata cyclindrica). The restoration of these lands is very important for a clean environment (Wong, 2003). Among the different techniques used for the removal of heavy metals, such as ion exchange, solvent extraction, oxidation reduction, reverse osmosis, phytoremediation, membrane separation, and precipitationfiltration, phytoremediation is the cheapest and involves green technology that uses only living plants for the removal of heavy metals from

* Corresponding author. *E-mail addresses*: asasmaz@firat.edu.tr, asasmaz@gmail.com (A. Sasmaz). water and soil (Dabrowski et al., 2004; Goswami et al., 2014). Phytoremediation depends on the ion uptake mechanism of each species according to its genetic, physiologic, anatomic, and morphologic characteristics (Yoon et al., 2006; Liu et al., 2008; Rahman and Hasegawa, 2011). There are several known methods for removing heavy metals and toxins from contaminated soil and water, including phytoextraction. In this method, metals are taken up into shoots, which are then harvested so that the metals are removed from the polluted area. Phytostabilization is another method of phytoremediation. using plants to remove or reduce the mobility of metals in contaminated soils (Ma et al., 2001). Phytoextraction refers in particular to the ability to accumulate metals from the soil and transport them to the aboveground parts of the plant, accumulating them in greater values than in non-accumulator plants (Baker et al., 2000). Heavy metal hyperaccumulator plants have been observed in tropical regions, but there are limited endemic plants growing in the soil of mining areas. Several plant species are reported as different metal-accumulators: Alyssum wulfenianum for Ni (Baker and Brooks, 1989); Azolla pinnata and Lemna minor for Cu and Cr (Jain et al., 1990); Brassica juncea for Cu and Ni (Ebbs and Kochian, 1998); Pteris vitata for Cu, Ni, and Zn; Brassica napus for Cd (Selvam and Wong, 2008); Arabidopsis thaliana for Zn and Cd (Saraswat and Rai, 2009); Rorippa globosa for Cd (Sun et al., 2010); Epilobium fragilis for As; Carthamus oxyacantha for Cd; Verbascum speciosum for Cu; and Carthamus oxyacantha for Fe (Malayeri et al., 2013).

The aim of this study is to investigate As, Ag, and Pb accumulation and transport from the soil to the roots and shoots of 11 terrestrial plants grown in the As, Ag, and Pb contaminated soils of the Gümüsköy mining area.

2. Material and method

2.1. The study area

The study area is located in the west of Kütahya, Turkey (between 38° 96′–39° 48′ N latitude and 29° 48′–29° 71′ E longitude) about 25 km (Fig. 1) and observed both the continental climate and the mild climate. The summers are dry and hot, while winters are rainy and cold. The average temperature of the region is about 10.5 °C. The forests of Kütahya are spread over a large area surrounding the city and have high economic value because they contain many endemic trees and herbal plants. Both soil and plant samples were collected from the Gümüsköy mining district and its surrounding. The sedimentary volcanic and metamorphic rocks in different ages from Permian to present day are formed in the study area. Gümüsköy ore deposits represented by As, Ag, Pb, Zn, Tl and Sb occur among the Sahin, Gümüsköy and

Dulkadir villages (Fig. 1). Soil and plants are contaminated by the heavy metals as a result of both naturally and mining works. Kartalkanat (2008) specified that Gümüsköy had a long mining history of about 3500 years, according to ¹⁴C absolute age determinations. As a result, Gümüsköy and its surrounding with both ancient and modern mining studies have been charged by these metals (Arik, 2002, 2012; Arik and Yaldiz, 2010).

2.2. Plant and soil samples

All plant and soil samples were randomly collected from sites on the Gümüsköy mining area between May and July 2013. Three samples of shoots and roots were taken from each sampling site in the study area. The samples were taken from 39 sites in and surrounding the mining area. The plant species have deep-reaching root systems and the ability to grow under different climate systems and conditions, and all of them grow wild in nature and generally die within one or two years (annuals). As, Ag, and Pb content was studied in 11 native and dominant plant species growing in and around Gümüsköy: *Anchusa*



Fig. 1. Geological and location map of the study area (simplified from Arik, 2002).

arvensis (AN), Alyssum saxatile (AL), Onosma sp. (ON), Cynoglossum officinale (CY), Phlomis sp. (PH), Carduus nutans (CR), Glaucium flavum (GL), Centaurea cyanus (CE), Isatis (IS), Verbascum thapsus (VR), and Silene compacta (SL).

2.3. Sample preparation

Soil samples were collected from different depths ranging between 0.10 and 0.40 m. and near the root of the plant. The soil colors vary from light brown to dark brown. These soils have 51.4% silt, 23.6% sand, 2.32-6.48% organic matter content and 19.3% clay, pH between 6.4 and 7.2. After it is dried at 100 °C in an oven during for 4 h, the soil samples were ground using hand mortars. Soil samples were digested in a mixture of HNO₃ (Merck, Darmstadt, Germany); HCl; H₂O (1:1:1, v/v; 6 mL per 1.0 g of soil) for one hour at 95 °C. This treatment dissolved all soil samples, and the digest was measured by using ICP-MS for As, Ag and Pb. Plant samples were randomly collected from the sites of the Gümüsköy mining area and taken at a depth of 30-40 cm below the surface. The root and shoot samples were thoroughly washed with tap water and dried at 60 °C in an oven for 24 h. The dried plant samples were ashed at 300 °C for 24 h. The ashed samples were digested in HNO3 for one hour, followed by digestion in a mixture of HNO3 (Merck, Darmstadt, Germany). HCl; H₂O (1:1:1, v/v; 6 mL per 1.0 g of the ashed sample) for one hour at 95 °C. The digests were measured by using ICP-MS for As, Ag and Pb.

2.4. Enrichment coefficients of roots (ECR)

The ECR was calculated by dividing metal concentration in soil of that in plant root (ECR: Plant root concentration/Soil concentration). This value is an index to be used in calculating accumulation of metals in upper part of plant or to realize the element transfers to plant root from soil (Chen et al., 2005; Sasmaz et al., 2015a, 2016).

2.5. Enrichment coefficient for shoots (ECS)

The ECS was also calculated by dividing metal value in soil of that in plant shoot (ECS: Plant shoot concentration/Soil concentration). The ECS indicates the accumulation capacity for phytoremediation studies (Zhao et al., 2002; Sasmaz et al., 2015a). This value shows the transfer ability of the metals to the shoot from the soil and this is very important for similar studies. Therefore, The ECS defines the absorbing and storing ability of a plant (Wei et al., 2002; Sasmaz et al., 2015a,b, 2016).

2.6. Translocation factors (TLF)

The TLF was the metal rate transported from the plant roots to that of shoot (TLF: Plant shoot concentration/plant root concentration). Translocation factor in hyperaccumulator plants is >1. This value shows the transfer ability (not accumulating) of the metals to the shoot from the root and this is very important for phytoremediation studies (Zu et al., 2005).

2.7. Apparatus

As, Ag and Pb values of both soil and plant samples were measured by using ICP-MS (Perkin-Elmer ELAN 9000) technique. The operation conditions of ICP-MS are given in Sasmaz and Yaman (2008).

3. Results and Discussion

3.1. As, Ag, and Pb in soil

Soil samples were collected from Gümüsköy, Gözeçukuru, Bölücekmeşe Hill, and Aktepe (Fig. 1). The levels of As, Ag, and Pb in the samples were detected to be between 411 and 14.66 mg kg⁻¹

 $(\text{mean: } 4771 \text{ mg kg}^{-1})$ for As, between 0.37 and 127 mg kg⁻¹ (mean: 37.78 mg kg⁻¹) for Ag, and between 168 and 13,556 mg kg⁻¹ for Pb $(mean: 4320 \text{ mg kg}^{-1})$ (Table 1). Boyle and Jonasson (1984) reported a total As value in soil of between 0.1 and 55 mg kg $^{-1}$. The As content of surface soils in different countries varies, with values of 5.6 mg kg⁻¹ in Bulgaria, 5.8 mg kg⁻¹ in Canada (Kabata-Pendias, 2011), up to 660 mg kg⁻¹ in Turkey (Gunduz et al., 2010), 22.1 mg kg⁻¹ in Bangladesh (Mandal and Suzuki, 2002), 14 mg kg⁻¹ in Mexico (Mandal and Suzuki, 2002), 3.5 mg kg⁻¹ in Germany (Mandal and Suzuki, 2002), 16–417 mg kg^{-1} in India (Singh et al., 2015), 23 mg kg⁻¹ in Spain (Gómez et al., 2006), up to 18.000 mg kg⁻¹ in Poland (Karczewska et al., 2007), 41 mg kg⁻¹ in Italy (Mandal and Suzuki, 2002), 11 mg kg⁻¹ in Japan (Mandal and Suzuki, 2002), 16.3 mg kg⁻¹ in Great Britain, 200–860 mg kg⁻¹ in Brazil, up to 489 mg kg⁻¹ in Chile, and 2.5 mg kg⁻¹ in Norway (Kabata-Pendias, 2011; Bundschuh et al., 2011; Das et al., 2013). While total As concentration in soil from Salamanca, Spain, was 5.5-150 mg kg $^{-1}$, the As content of mining areas in Salamanca were observed to be much higher than 1500 mg kg $^{-1}$ (Garcia-Sanchez et al., 2010). Otones et al. (2011) reported that As contamination in the Barruecopardo mining area was detected at higher levels (70-5330 mg kg $^{-1}$) in the upper most soil layers, but the concentration decreased moderately at greater depths. The level of As in similar contaminated areas ranges from 90 to 900 mg kg $^{-1}$ in non ferric metal mining, 33 to 2000 mg kg⁻¹ in metal-processing industries, 10 to 2000 mg kg⁻¹ in chemical works, and 800 to 1500 mg kg⁻¹ in coal combustion (Kabata-Pendias, 2011). Moore et al. (2016) demonstrated that Ag values in the soils in the epithermal gold mining area, West Iran were found up to 10.2 mg kg $^{-1}$. The Ag content in soils of different countries detected the values between 0.03 and 0.4 mg kg^{-1} in Finland, 0.2 and 3.2 mg kg⁻¹ in Canada and up to 9 mg kg⁻¹ in Wales (Mukherjee, 1997; Kabata-Pendias, 2011). Montagne et al. (2007) indicated that the major sources of Pb contamination in agricultural soils were the smelting minerals, waste treatment (such as landfill, etc.), sewage sludge, automobile exhaust, fertilizers and pesticides, etc. Pb contents in different countries were reported to be 17 mg kg^{-1} in Finland, 47 mg kg⁻¹ in Iran, 1505 mg kg⁻¹ in Spain, 139 mg kg⁻¹ in Slovakia, 55 mg kg⁻¹ in USA, 43 mg kg⁻¹ in France, 17 mg kg⁻¹ in Syria, 25,380 mg kg⁻¹ in Baoji-China and 94 mg kg⁻¹ in Hong Kong (Su et al., 2014).

Tufitic and aglomeratic rocks with rhyolitic and dacitic compositions were observed in the study area. As these rocks have an acidic composition, they exhibit higher silica levels and much higher metal content than other rocks (Kabata-Pendias, 2011). The results obtained in this study showed that higher metal concentrations in acidic rocks can also be related to polymetallic deposits in the study area because of a high linear Spearman's correlation coefficient among some metals (Table 2). Strong positive correlations (r = 0.51-0.95) were seen in Pb-Zn, Pb-Cu, Pb-Fe, Pb-Cd, Pb-Se, As-Sb, As-Sr, As-U, As-P, As-Hg, As-Tl, Ag-Cu, and Ag-Zn, whereas negative correlations were detected in As-K, Ag-Sr and Ag-Tl (Table 2). The correlations between plant shoots and soil were stronger than between the roots and soil, indicating that more soil As, Ag, and Pb was transported to the shoot than accumulated in the roots. The absorption and transport mechanism of As, Ag, and Pb differed among the studied plants. Changes in As, Ag, and Pb content in different plants and plant tissues can depend on plant genotype, according to Li and Cao (2006).

3.2. As, Ag, and Pb in plants

The mean values in the roots and shoots of the studied plants were, respectively, 2320 and 1340 mg kg⁻¹ for As, 34.6 and 79.6 mg kg⁻¹ for Ag, and 5450 and 9328 mg kg⁻¹ for Pb. However, the minimum concentrations of As, Ag, and Pb in the studied samples were, respectively, 52, 0.05, and 15 mg kg⁻¹ in the roots and 42, 0.22, and 7 mg kg⁻¹ in the shoots, while the maximum respective values were 20,100, 34.60, and

 Table 1

 The As, Ag and Pb concentrations in soils and roots and shoots of 11 plant species and ECR, ECS and TLF for As, Ag and Pb.

	As in soil	As in root	As in shoot	ECR	ECS	TLF	Ag in soil	Ag in root	Ag in shoot	ECR	ECS	TLF	Pb in soil	Pb in root	Pb in shoot	ECR	ECS	TLF
AL-01	544 ± 28	287 ± 18	300 ± 14	0.53	0.55	1.05	16.2 ±	5.6 ±	$6.6 \pm$	0.35	0.41	1.18	955 ± 55	682 ±	531 ± 32	0.71	0.56	0.78
AL-02	1073 ± 58	1487 ±	400 ± 32	1.39	0.37	0.27	41.6 ±	16.5 ±	11.1 ±	0.40	0.27	0.67	2126 ±	3971 ±	885 ± 55	1.87	0.42	0.22
AL-03	4356 ±	124 1696 ±	1014 ±	0.39	0.23	0.60	3.2 68.8 ±	1.1 19.6 ±	0.8 15.8 ±	0.28	0.23	0.81	112 7819 ±	137 4586 ±	1,792,152	0.59	0.23	0.39
AL-04	7052 ±	998 ± 76	896 ± 45	0.14	0.13	0.90	120.5 ±	1.4 23.9 ±	26.7 ±	0.20	0.22	1.12	12,322 ±	$3740 \pm$	$2121~\pm$	0.30	0.17	0.57
AL-05	129 3199 ±	470 ± 38	1220 ±	0.15	0.38	2.60	9.2 50.4 ±	1.5 13.0 ±	2.2 16.9 ±	0.26	0.33	1.30	1142 7745 ±	236 1058 ±	143 2400 ±	0.14	0.31	2.27
AN-01	230 8306 ± 468	$3634 \pm$	68 3553 ± 242	0.44	0.43	0.98	4.4 37.7 ±	0.9 10.6 ± 1.2	1.5 6.8 ± 6.1	0.28	0.18	0.64	1442 ± 87	88 905 ± 72	$\frac{175}{826 \pm 56}$	0.63	0.57	0.91
AN-02	1541 ±	783 ± 28	$\frac{242}{405 \pm 29}$	0.51	0.26	0.52	0.5 ±	0.4 ±	0.5 ±	0.95	1.07	1.13	3454 ±	2041 ±	666 ± 24	0.59	0.19	0.33
CE-01	230 2387 ± 187	858 ± 24	1025 ±	0.36	0.43	1.20	0.1 71.8 ± 5.2	0.1 16.5 ± 1 3	0.1 19.2 ± 1.2	0.23	0.27	1.16	166 4656 ± 328	144 1446 ± 42	1500 ±	0.31	0.32	1.04
CE-02	1093 ± 80	122 ± 9	149 ± 11	0.11	0.14	1.22	36.9 ±	2.5 ±	3.3 ±	0.07	0.09	1.31	2277 ±	200 ±	181 ± 15	0.09	0.08	0.91
CE-03	4622 ± 162	505 ± 42	1633 ± 187	0.11	0.35	3.24	2.5 127 ± 10 3	0.9 34.6 ± 3 1	0.2 73.3 ± 6.8	0.27	0.58	2.12	198 10,653 ± 1204	15 1029 ± 56	3273 ± 148	0.10	0.31	3.18
CR-01	1107 ± 98	1077 ± 98	612 ± 34	0.97	0.55	0.57	51.3 ± 3.5	24.8 ± 1.6	14 ± 1.1	0.48	0.27	0.56	2278 ± 153	877 ± 52	833 ± 57	0.38	0.37	0.95
CR-02	629 ± 42	52 ± 4	433 ± 48	0.08	0.69	8.33	12.6 ± 0.8	0.3 ± 0.1	5.1 ± 0.4	0.02	0.41	18.61	1022 ± 85	2749 ± 158	481 ± 44	2.69	0.47	0.17
CR-03	4929 ± 230	749 ± 66	967 ± 62	0.15	0.20	1.29	117 ± 12	26.8 ± 3.2	16.1 ± 1.8	0.23	0.14	0.60	8652 ± 321	1149 ± 96	1267 ± 98	0.13	0.15	1.10
CY-01	843 ± 46	209 ± 21	338 ± 22	0.25	0.40	1.62	19.1 ± 2.2	3.5 ± 0.4	4.4 ± 0.6	0.19	0.23	1.24	1449 ± 48	220 ± 14	693 ± 62	0.15	0.48	3.15
CY-02	4798 ± 364	147 ± 12	42 ± 3	0.03	0.01	0.28	0.4 ± 0.1	0.2 ± 0.1	0.3 ± 0.1	0.62	0.76	1.21	173 ± 22	15 ± 2	7 ± 1	0.09	0.04	0.46
GL-01	$12,325 \pm 1052$	$15,110 \pm 1452$	980 ± 84	1.23	0.08	0.06	1.7 ± 0.1	1.7 ± 0.2	0.9 ± 0.1	1.03	0.55	0.53	7986 ± 543	5451 ± 331	361 ± 35	0.68	0.05	0.07
GL-02	$10,542 \pm 885$	10,822 ± 886	4615 ± 220	1.03	0.44	0.43	1.1 ± 0 1	1.5 ± 0 1	0.8 ± 0.1	1.38	0.78	0.57	5982 ± 454	3380 ± 276	856 ± 65	0.56	0.14	0.25
IS-01	543 ± 28	378 ± 22	$\frac{223}{345}\pm26$	0.70	0.63	0.91	10.5 ±	7.6 ±	4.6 ±	0.73	0.44	0.60	1413 ± 78	823 ±	359 ± 30	0.58	0.25	0.44
IS-02	$\begin{array}{c} 7263 \pm \\ 652 \end{array}$	1124 ± 54	263 ± 14	0.15	0.04	0.23	68.5 ± 7.2	12.3 ± 1.4	3.5 ± 0.3	0.18	0.05	0.29	11,469 ± 886	2192 ± 137	251 ± 22	0.19	0.02	0.11
IS-03	4048 ± 335	555 ± 65	192 ± 16	0.14	0.05	0.34	64.7 ± 5.3	25.9 ± 2.2	3.7 ± 0.5	0.40	0.06	0.14	13,556 ± 752	1350 ± 94	302 ± 14	0.10	0.02	0.22
IS-04	$14,662 \pm 1114$	7277 ±	801 ± 52	0.50	0.05	0.11	$^{1.3}\pm$	0.7 ± 0 1	0.2 ± 0.03	0.50	0.17	0.34	7634 ± 468	2147 ± 112	204 ± 15	0.28	0.03	0.09
ON-01	1732 ±	375 ± 32	764 ± 28	0.22	0.44	2.04	72.3 ±	12.9 ±	19.4 ± 1.5	0.18	0.27	1.51	3442 ± 284	826 ±	1478 ± 102	0.24	0.43	1.79
ON-02	7052 ± 473	956 ± 78	2895 ± 220	0.14	0.41	3.03	119 ±	30.6 ±	79.6 ±	0.26	0.67	2.60	10,353 ±	2979 ±	9328 ±	0.29	0.90	3.13
ON-03	2594 ±	477 ± 42	829 ± 65	0.18	0.32	1.74	76.2 ±	10.2 ±	17.5 ±	0.13	0.23	1.71	5656 ±	1284 ±	1364 ±	0.23	0.24	1.06
PH-01	8492 ± 823	808 ± 59	578 ± 47	0.10	0.07	0.72	2.0 ±	0.5 ±	0.6 ±	0.26	0.33	1.24	1972 ± 96	201 ±	107 ± 13	0.10	0.05	0.53
PH-02	729 ± 48	486 ± 28	855 ± 52	0.67	1.17	1.76	18.4 ±	6.9 ± 0.8	10.1 ±	0.38	0.55	1.47	1186 ± 61	628 ±	872 ± 71	0.53	0.74	1.39
PH-03	609 ± 52	710 ± 61	896 ± 63	1.16	1.47	1.26	12.0 ± 1.4	13.1 ± 1.2	9.1 ± 0.8	1.09	0.76	0.70	1193 ± 57	$\begin{array}{c} 1440 \pm \\ 82 \end{array}$	1151 ± 124	1.21	0.97	0.80
PH-04	630 ± 35	631 ± 66	889 ± 38	1.00	1.41	1.41	15.3 ± 1.2	7.8 ± 0.9	9.5 ± 0.7	0.51	0.62	1.22	1179 ± 69	967 ± 68	1118 ± 93	0.82	0.95	1.16
SL-01	11,028 ± 735	5015 ± 412	15,942 ± 778	0.45	1.45	3.18	0.7 ± 0.1	0.1 ± 0.01	1.1 ± 0.1	0.08	1.57	20.91	2653 ± 188	140 ± 11	599 ± 53	0.05	0.23	4.28
SL-02	$\begin{array}{r} 4223 \pm \\ 415 \end{array}$	704 ± 48	167 ± 12	0.17	0.04	0.24	0.5 ± 0.04	0.6 ± 0.07	0.2 ± 0.03	1.42	0.52	0.36	168 ± 22	34 ± 2	10 ± 1	0.20	0.06	0.29
SL-03	5207 ± 360	1102 ± 114	317 ± 24	0.21	0.06	0.29	0.4 ± 0.03	0.8 ± 0.04	0.4 ± 0.03	1.82	0.84	0.46	181 ± 13	41 ± 3	11 ± 1	0.23	0.06	0.27
SL-04	6995 ±	1808 ±	775 ± 58	0.26	0.11	0.43	0.6 ±	1.2 ±	0.8 ± 0.07	1.94	1.22	0.63	369 ± 26	101 ± 7	42 ± 3	0.27	0.11	0.42
SL-05	8757 ±	678 ± 50	712 ± 69	0.08	0.08	1.05	0.5 ±	$0.4 \pm$	0.6 ±	0.81	1.33	1.64	400 ± 23	43 ± 3	39 ± 2	0.11	0.10	0.93
SL-06	7202 ± 356	424 ± 25	405 ± 32	0.06	0.06	0.95	0.05 0.8 ± 0.07	0.03 0.8 ± 0.07	0.04 0.9 ± 0.06	1.06	1.18	1.11	322 ± 28	122 ± 4	63 ± 4	0.38	0.20	0.52

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Table 1 (continued)

	As in soil	As in root	As in shoot	ECR	ECS	TLF	Ag in soil	Ag in root	Ag in shoot	ECR	ECS	TLF	Pb in soil	Pb in root	Pb in shoot	ECR	ECS	TLF
VR-01	411 ± 23	276 ± 19	695 ± 15	0.67	1.69	2.52	45.1 ± 3.5	20 ± 1.5	18.9 ± 2.2	0.44	0.42	0.95	1237 ± 122	751 ± 44	1235 ± 88	0.61	1.00	1.65
VR-02	1265 ± 487	805 ± 74	1451 ± 96	0.64	1.15	1.80	50.6 ± 5.2	23.7 ± 1.4	28.3 ± 1.8	0.47	0.56	1.19	2715 ± 115	1888 ± 156	2056 ± 125	0.70	0.76	1.09
VR-03	12,330 ± 1308	20,100 ± 677	2045 ± 152	1.63	0.17	0.10	0.8 ± 0.1	0.5 ± 0.1	4.6 ± 0.3	0.59	5.71	9.63	$\begin{array}{c} 6124 \pm \\ 432 \end{array}$	2471 ± 171	411 ± 38	0.40	0.07	0.17
VR-04	2058 ± 268	568 ± 61	540 ± 44	0.28	0.26	0.95	65.9 ± 6.6	18.1 ± 2.2	7 ± 0.5	0.28	0.11	0.39	3601 ± 184	956 ± 74	735 ± 52	0.27	0.20	0.77
VR-05	12,685 ± 995	10,400 ± 884	3551 ± 188	0.82	0.28	0.34	$\begin{array}{c} 0.6 \ \pm \\ 0.04 \end{array}$	0.6 ± 0.05	$\begin{array}{c} \textbf{6.4} \pm \\ \textbf{0.7} \end{array}$	1.05	10.41	9.90	$\begin{array}{c} 5213 \pm \\ 306 \end{array}$	$\begin{array}{c} 643 \pm \\ 43 \end{array}$	537 ± 32	0.12	0.10	0.84

5450 mg kg $^{-1}$ in the roots and 15,942, 79.59, and 9328 mg kg $^{-1}$ in the shoots.

The mean As values in the soil. roots. and shoots of Alvssum saxatile (AL) were 3245, 988, and 766 mg kg $^{-1}$, respectively. The As concentration in the soil of AL was higher than in its roots and shoots, with the respective minimum and maximum As concentrations of AL ranging between 287 and 1696 mg kg⁻¹ for the roots and between 300 and 1220 mg kg $^{-1}$ for the shoots (Table 1). These were higher than the As concentrations previously reported for different plants (0.1 mg kg⁻¹) by Pais and Jones (2000). The ECR and ECS of As for AL's roots and shoots are given in Table 1. The TLFs for As in AL were between 0.27 and 2.60 (mean: 1.08) in this study, indicating that As was weakly transferred to the shoot from the root. The mean values of AL's soil, roots, and shoots were, respectively, 59.49, 10.64, and 15.42 mg kg $^{-1}$ for Ag and 6193, 2808, and 1546 mg kg⁻¹ for Pb. The ECR, ECS, and TLFs of AL for Ag and Pb were observed to follow similar trends with As. These results show that AL is not a very good bioaccumulator plant for As, Ag, and Pb because of lower ECR and ECS.

The mean As levels in the soil, roots, and shoots of *Anchusa arvensis* L. (AN) had close values at 4923, 2208, and 1979 mg kg⁻¹, respectively (Table 1). ECR and ECS for As had mean values of 0.47 and 0.35, respectively (Table 1), indicating that As was taken up from the soil and passed into the roots of AN. The TLF values of AN ranged between 0.52 and 0.98 (mean: 0.75) (Table 1), which meant that all AN translocation factors were \leq 1. The mean values in the soil, roots, and shoots of AN were, respectively, 19.06, 5.54, and 3.64 mg kg⁻¹ for Ag and 2449, 1473, and 746 mg kg⁻¹ for Pb. The mean ECR, ECS, and TLF of AN for Ag and Pb had values of <1. However, one AN sample (AN-02) had ECS values of >1 for Ag and of ECR for Pb. This result indicates that AN could serve as an As, Ag, and Pb bioaccumulator plant.

The mean As values in *Centaurea cyanus* L. (CE)'s soils, roots, and shoots were 2700, 495, and 936 mg kg⁻¹, respectively (Table 1). CE's shoot values for As were higher than the root values but lower than in the soil. Therefore, both ECS and ECR were <1. The TLF value of CE for As ranged between 1.20 and 3.24 (mean: 1.88) (Table 1). The mean values of CE's soil, roots, and shoots, respectively, were 78.59, 17.88, and 31.94 mg kg⁻¹ for Ag and 5862, 892, and 1652 mg kg⁻¹ for Pb. The mean ECR and ECS values of CE for Ag and Pb were observed to be <1. These values show that CE is not a good plant for the phytoremediation of As, Ag, and Pb due to lower ECR and ECS.

The mean As values of the *Carduus nutans* L. (CR) soil, roots, and shoots were 2222, 626, and 671 mg kg⁻¹, respectively (Table 1). The

soil As values surrounding CR's shoots were higher than in the CR root, with a maximum As concentration of 967 mg kg⁻¹ (Table 1) found in the shoots (sample CR-03). The mean ECR, ECS, and TLF for As in CR were 0.40, 0.48, and 3.40, respectively (Table 1). The TLF of this plant was >1 and the ECR and ECS values were <1. The mean values in the soil, roots, and shoots of CR were, respectively, 60.30, 17.30, and 11.74 mg kg⁻¹ for Ag and 3984, 1591, and 860 mg kg⁻¹ for Pb (Table 1). The mean ECR, ECS, and TLF for Ag and Pb in CR were <1, but the ECR for sample CR-02 was >1. These results indicate that As is very well transferred to the shoot of CR after being taken up from the soil into the root. As was seen in sample CR-02, Pb was generally observed to accumulate more in the root than the soil of CR. All samples of CR showed very low accumulation ability for Ag.

The mean As values in *Cynoglossum officinale* (CY)'s soil, roots, and shoots were 2821, 178, and 190 mg kg⁻¹, respectively (Table 1). The soil As values were higher than in the CY roots and shoots. The mean ECR and ECS were <1, but the mean TLF was close to 1. The mean values of CY's soils, roots, and shoots, respectively, were 9718, 1889, and 2342 mg kg⁻¹ for Ag and 811, 118, and 350 mg kg⁻¹ for Pb. Consequently, As, Ag, and Pb metals were weakly transported to CY roots and shoots from the soil (Table 1), with the shoots accumulating more of these metals compared to the roots.

The mean As values in the soil, roots, and shoots of *Glaucium flavum* L. (GL) were 11,434, 12,961, and 2798 mg kg⁻¹, respectively (Table 1). The As values for GL roots were higher than those for the shoots or soil. The ECR, ECS, and TLF values of As for GL were 1368, 1599, and 877, respectively. The mean values in the soil, roots, and shoots of GL were, respectively, 1.37, 1.60, and 0.88 mg kg⁻¹ for Ag and 6984, 4415, and 609 mg kg⁻¹ for Pb. These results show that As, Ag, and Pb were very well accumulated from the soil by the root of GL, but were not transferred through to the shoots. The high ECR value indicates that GL could be a very good As, Ag, and Pb bioaccumulator plant.

The As content of *Isatis* (IS)'s soil, roots, and shoots was analyzed in four samples, with averages of 6629, 2334, and 400 mg As kg⁻¹, respectively. The As values in IS shoots and roots were substantially lower than those in soil. The mean values in the soil, roots, and shoots of IS were, respectively, 36.24, 11.62, and 3.01 mg kg⁻¹ for Ag and 8518, 1628, and 279 mg kg⁻¹ for Pb. The mean ECR, ECS, and TLFs for IS were, respectively, 0.37, 0.19, and 0.40 for As; 0.45, 0.18, and 0.34 for Ag; and 0.29, 0.08, and 0.22 for Pb (Table 1). The low ECR, ECS, and TLFs of As, Ag, and Pb indicate that IS would not be a very good As, Ag, and Pb bioaccumulator.

Table 2
Spearman's correlation coefficients between some metals and As. Ag and Pb in soils (All values were taken from Sasmaz, 2011

	Cu	Zn	Mn	Fe	U	Th	Sr	Cd	Sb	Ca	Р	Ba	Tl	Hg	Se	Na	К	As	Ag	Pb
As	-0,07	-0,08	-0,01	0,42	0,79	0,14	0,81	0,22	0,92	0,30	0,76	0,37	0,80	0,51	0,29	-0,09	-0,75	1.00		
Ag	0,55	0,63	0,49	0,14	-0,44	-0,16	-0,55	0,34	-0,37	-0,15	-0,43	-0,07	-0,48	-0,12	0,40	-0,27	0,41	-0,42	1.00	
Pb	0,76	0,71	0,77	0,65	0,12	-0,11	-0,01	0,82	0,31	0,06	-0,03	0,42	0,11	0,48	0,72	-0,18	-0,03	0,31	0,31	1,00

The mean As values in the soil, roots, and shoots of Onosma (ON) were 3793, 603, and 1496 mg kg⁻¹, respectively (Table 1). The mean As values in three ON shoots were two times higher than in ON roots, but lower than in the soil. The mean values in the soil, roots, and shoots of ON were, respectively, 89.16, 17.89, and 38.83 mg kg⁻¹ for Ag and 6483, 1696, and 4057 mg kg $^{-1}$ for Pb. The ECR and ECS values for As, Ag, and Pb of ON were <1 and close to each other, but the TLF values were >1 (Table 1). The values higher than 1 indicated that the ON root does not accumulate As, Ag, and Pb from the soil, but it efficiently transfers As, Ag, and Pb to the shoot.

The As, Ag, and Pb content of the soil, roots, and shoots of the Phlomis (PH) plant were examined in four samples. The mean concentrations in the soil, roots, and shoots, respectively, were 2615, 659, and 805 mg kg^{-1} for As; 11.93, 7.07, and 7.34 mg kg $^{-1}$ for Ag; and 1382, 809, and 812 mg kg⁻¹ for Pb (Table 1). The As values in PH shoots were higher than in both the soil and the roots, except for one sample. PH's mean ECR, ECS, and TLF values, respectively, were 0.73, 1.03, and 1.29 for As; 0.56, 0.56, and 1.16 for Ag; and 0.67, 0.68, and 0.97 for Pb (Table 1). The ECR and ECS of PH for Ag and Pb were <1, except for the PH-03 sample. The ECR and ECS values of ≥1 indicate that PH could be useful for rehabilitating or cleaning soils contaminated by As, Ag, and Pb.

The mean values in the soil, roots, and shoots of Silene compacta L. (SL) were, respectively, 7235, 1622, and 3053 mg kg $^{-1}$ for As; 0.58, 0.65, and 0.68 mg kg⁻¹ for Ag; and 682, 80, and 127 mg kg⁻¹ for Pb (Table 1). The soil As levels were higher than in both SL roots and shoots, except for the SL-01 shoot. The mean ECR, ECS, and TLF values for Ag of this plant were >1, but the ECR and ECS values for both As and Pb in S. compacta L. were <1. The TLF of SL was >1 (mean 1.02), demonstrating that As and Pb were not very well carried to the roots or shoots from the soil (Table 1). The high ECR, ECS, and TLF indicate that SL could be a very good Ag bioaccumulator plant.

The As, Ag, and Pb contents of four Verbascum thapsus L. (VR) samples were analyzed. The mean values in the soil, roots, and shoots, respectively, were 4016, 5437, and 1183 mg kg⁻¹ for As; 38.26, 10.56, and 11.20 mg kg⁻¹ for Ag; and 3778, 1342, and 995 mg kg⁻¹ for Pb (Table 1). The As values in VR shoots and roots were generally lower than in soil, except for one root sample (VR-03) and two shoot samples (VR-01 and VR-02). VR-01 and VR-02 indicated especially strong As accumulation in their shoots. VR-03 had a strong As accumulation in its root and shoot. The ECR and ECS of VR-05 and the ECS of VR-03 for Ag were >1 (Table 1). The ECR of VR-03 and the ECS of VR-01 and VR-02 for As were all >1 (Table 1). The ECR, ECS, and TLF values close to 1 and >1 indicate that VR could be useful for cleaning or rehabilitating soils and areas contaminated by As and Ag.

Chaney et al. (1999) indicated that Alyssum sp. easily accumulated Ni from soils, such as those of hyperaccumulator plants. Ghaderian et al. (2007) reported that Alyssum sp. in serpentine soils in Turkey, Iraq and Iran were the best hyperaccumulator plants for Ni among these species. Li et al. (2003) detected that Alyssum sp. hyperaccumulated high amounts of both Ni and Co under certain conditions. Among Alyssum sp., A. murale and A. serpyllifolium have been found to accumulate much higher Ni than the non-accumulator A. saxatile (Baklanov, 2011), whereas there was no information about other heavy metal accumulations in A. saxatile. Recently, Ma et al. (2001) suggested the first arsenic hyperaccumulator in terrestrial plants: the brake fern, Pteris *vittata*. This plant can accumulate up to 22,000 mg kg⁻¹ of As in the frond's dry weight, although phytotoxicity occurs when shoot As is more than about 10,000 mg kg⁻¹ (Wang et al., 2002). When grown in pots with soil containing 98 mg kg⁻¹ of As for 20 weeks under greenhouse conditions, P. vittata's bioconcentration factor reached 87 and the fronds removed 26% of the soil's initial As (Tu et al., 2002). More recently, several other fern species, including Pityrogramma calomelanos (Wang et al., 2002), Pteris cretica, Pteris longifolia, and Pteris umbrosa (Francesconi et al., 2002), have been identified as arsenic hyperaccumulators. With >10,000 fern species not yet screened, it is likely that more As-hyperaccumulating ferns will be discovered. All five hyperaccumulating ferns identified so far are in the Pteridales order (Zhao et al., 2002).

4. Conclusions

Our study shows that the best bioaccumulator plants are AN, PH, GL, and VR for As; SL, VR, and GL for Ag; and CR and PH for Pb. Therefore, these plants can be also useful for cleaning and/or rehabilitating soils. The mid-bioaccumulator plants are AL and CR for As; AN, CY, and PH for Ag; and AL, AN, GL, ON, and VR for Pb. They can also be considered as potential candidates for the biomonitoring studies. Finally, the worst plants for heavy metal uptake are CE, CY, IS, ON, and SL for As; AL, CR, CE, ON, and IS for Ag; and CE, CY, IS, and SL for Pb. Plantings of the best bioaccumulator plants could be used for both rehabilitating and cleaning soils contaminated by As, Ag, and Pb and also to biomonitor environmental pollution.

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