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Phytoremediation of Cadmium by Native Plants Grown on Mining Soil

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Abstract
The Gümüsköy mining area is located about 25 km west of Kutahya and is the largest silver deposit in Turkey. The present study investigated translocation and accumulation of cadmium (Cd) from the soil into 11 native plants. Plant and soil samples were collected from the field, and Cd concentrations were analyzed by inductively coupled plasma mass spectroscopy. Mean Cd values in the soil, root, and shoot of native plants in the study area were 82.8 ± 5, 55.4 ± 6, and 43.5 ± 4 mg kg^{-1}, respectively. Plants were separated into several groups according to the enrichment coefficients for shoot and root values of plants. These groups showed *Carduus nutans* and *Phlomis* could be potentially bioaccumulator plants useful for phytoremediation of mining soils contaminated by Cd.

Keywords Bioaccumulation · Mining area · Pollution

Average Cd content in the Earth's crust and in world soils is estimated to be 0.1 and 0.41 mg kg^{-1}, respectively (Kabata-Pendias 2011). Cd generally occurs together with Pb and Zn ore deposits and within sphalerite, smithsonite, biotite, and amphibole minerals. Cd is mainly used in battery and plastic production because of its unique chemical and physical characteristics (Kabata-Pendias 2011). The average Cd contents in uncontaminated soils range from 0.01 to 0.03 mg kg^{-1} in sandy, 0.2 to 0.8 mg kg^{-1} in loamy, and 0.2 to 2.5 mg kg^{-1} in organic soils (Kabata-Pendias 2011). Curlic and Forgac (1996) found up to 222 mg kg^{-1} Cd from altered pyritized quartz and andesine in Slovakia. Mining area Cd concentrations were reported to vary between 2 and 336 mg kg^{-1} in Great Britain and 0.5 and 8 mg kg^{-1} in Pakistan (Nawab et al. 2015). The highest levels of Cd contamination compared to surface and agricultural soils were detected around Pb–Zn mining areas and smelting operations in the U.S., Poland, and Belgium (Kabata-Pendias 2011). The toxicity of metals is a significant environmental problem because of their persistence, non-biodegradable characteristic, and bioaccumulation in the body of living animals and plants (Khan et al. 2014; Mani et al. 2016). Metals (Cd, As, Cu, Ag, Zn, Cr, Pb, Co, Ni, Hg, and Sb) in mining areas contaminate surface soils and water (US EPA 2000; Wong 2003), but they can be removed through the use of phytoremediation with different plants. Phytoremediation is based on the metal accumulation capacities of each plant according to their different characteristics such as the morphologic, physiologic, genetic, and anatomic (Yoon et al. 2006; Liu et al. 2008). Although Cd is nonessential for metabolic processes in plants, it is absorbed into both shoots and roots from the soil. Kabata-Pendias (2011) suggested Cd in plant material had a linear correlation with its concentration during the growth of the plant. Different species of plants have been reported as metal accumulators for Cd: *Carthamus oxyacantha, Brassica napus; Rorippa globosa, Solanum sürattense, Xanthoxylem armatum, Sacharum griffthi* and *Arabidopsis thaliana* (Selwam and Wong 2008; Saraswat and Rai 2009; Sun et al. 2010; Nawab et al. 2015). The main objective of this study was to research Cd transport and accumulation from the soil to the shoot and root parts of different native plants in Cd contaminated soils.

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Materials and Methods

Plant and soils were collected from the Gümüsköy mining area situated among the Dulkadir, Sahin and Gümüsköy villages. Arik (2002, 2012) and Arik and Yaldiz (2010) detected that Gümüsköy and its surrounding area have been intensely contaminated by both modern and ancient mining activities of different metals (Kartalkanat 2008). All samples were randomly (not systematically) taken in July and May of 2013 from 39 different points in the mining district between 0.1 and 0.4 m depth.

Cd concentrations were investigated in 11 dominant, native species growing around and in the study area: *Alyssum saxatile* (AL), *Cynoglossum officinale* (CY), *Anchusa arvensis* (AN), *Onosma* sp. (ON), *Glaucium flavum* (GL), *Phlomis* sp. (PH), *Carduus nutans* (CR), *Silene compacta* (SL), *Verbascum thapsus* (VR), *Isatis* (IS), and *Centaurea cyanus* (CE). After soil samples were oven dried at 100°C, they were digested in a mixture of HNO_3, H_2O and HCl (1:1:1, v/v; 6 mL per 1.0 g of soil) for 1 h at 95°C. The samples were then analyzed with inductively coupled plasma mass spectroscopy (ICP-MS) (Perkin-Elmer ELAN 9000) in Acme Laboratory, Vancouver, BC Canada (http://www.acmelab.com) for Cd (detection limit 0.01 mg kg^{-1}). In tap water, the plant roots and shoots were thoroughly washed and dried at 60°C, and after that, ashed at 300°C for 24 h. Ashed plants were digested in HNO_3 for 1 h, then mixed with H_2O, HCl and HNO_3 (1:1:1, v/v; 6 mL per 1.0 g of the ashed sample). The digest was analyzed for Cd using ICP-MS. Enrichment coefficients for plant roots (ECR) were found by calculating the ratios of specific activities in plant roots and soils (concentration in mg kg^{-1} of the plant root divided by the concentration in mg kg^{-1} of soil). This coefficient is an indicator of metal accumulated in plant root (Chen et al. 2005). Enrichment coefficients for shoot (ECS) were found by dividing the plant shoot concentration by the soil concentration. This coefficient shows the accumulation ability for shoots from the soil (Zhao et al. 2003). The translocation factor (TLF) was the metal ratio transfer capacity from root to shoots (Zu et al. 2005). Hyperaccumulator plants have translocation factors > 1.

Data were exposed to ANOVA variance analyses with a critical p value of 0.05 in all tests by using SAS (SAS Institute, Cary, NC). Both the median values and the arithmetic means in Cd concentrations of both soils and plant parts were reported.

Results and Discussion

Cd concentrations in sampled soils were between 6.04 and 343 mg kg^{-1} (mean: 82.8 mg kg^{-1}; median: 55.8 mg kg^{-1}). Cd values of urban soils observed in different countries include Great Britain (2–336 mg kg^{-1}), Belgium (2–144 mg kg^{-1}), Canada (2–36 mg kg^{-1}), Netherlands (9–33 mg kg^{-1}), Japan (1.88–270 mg kg^{-1}), Spain (3.76 mg kg^{-1}), France (0.53 mg kg^{-1}), Iran (1.53 mg kg^{-1}), Hong Kong (0.62 mg kg^{-1}), Norway (0.06–3.10 mg kg^{-1}), and Finland (0.22 mg kg^{-1}) (Tijhuis et al. 2002; Hernandez et al. 2003; Li et al. 2004; Salonen and Korkka-Niemi 2007; Rodriguez et al. 2009; Kabata-Pendias 2011; Sayadi and Rezaei 2014, Su et al. 2014). Soil Cd levels in agricultural areas include USA (13.5 mg kg^{-1}), India (0.82 mg kg^{-1}), Iran (0.34 mg kg^{-1}), Spain (4.69 mg kg^{-1}), Korea (0.30 mg kg^{-1}), Finland (0.74 mg kg^{-1}), and Hong Kong (2.09 mg kg^{-1}) (Kim and Kim 1999; Jean-Philippe et al. 2012; Sayyed and Sayadi 2011, Su et al. 2014).

Mean Cd levels of roots and shoots of the studied plants were 55.4 and 43.5 mg kg^{-1}, respectively. However, the maximum and minimum values of Cd in the studied plants were 166 and 8.60 mg kg^{-1} in the roots and 135 and 2.65 mg kg^{-1} in the shoots, respectively. Mean *Alyssum saxatile* (AL) soil, root, and shoot concentrations were 160, 88.4, and 67.7 mg kg^{-1} (medians: 174, 88 and 63 mg kg^{-1}), respectively. Cd level in AL soils was greater than the shoot and root values. These levels are much higher than limits of Cd (0.3 mg kg^{-1}) reported by WHO (2007) and the reference plant (0.05 mg kg^{-1}) suggested by Pais and Jones (2000). The ECS and ECR of Cd for AL shoots and roots were 0.65 and 0.92, respectively, and were lower than their soil values, except for the ECR of AL-02 and AL-01. The AL TLFs for Cd were between 0.46 and 0.99 (mean: 0.77). This indicates AL is not a promising plant for Cd bioaccumulation due to lower ECRs and ECSs.

Mean Cd levels in *Anchusa arvensis* (AN) soil, roots, and shoots were 44.4, 26.9, and 15.7 mg kg^{-1}, respectively. Average ECS and ECR for AN Cd were 0.40 and 0.72, respectively. An TLF was between 0.47 and 0.91 (mean: 0.69), indicating it is not an appropriate candidate to bioaccumulate Cd.

Average *Centaurea cyanus* (CE) soil, root, and shoot Cd values were 122, 86.7, and 61.4 mg kg^{-1}, respectively. The average Cd concentration in soil was higher than the average shoot and root concentrations ($p < 0.05$). Both ECS and ECR were lower than one, indicating *C. cyanus* cannot be used in phytoremediation of Cd (Table 1).

Mean soil, root, and shoot Cd concentrations of Cd in *Carduus nutans* L. (CR) were, 48.1, 81.8, and 83.1 mg kg^{-1}, respectively. Mean Cd concentrations of CR roots and shoots were greater than the surrounding soil. The mean ECR, ECS, and TLF for Cd in CR were 2.01, 1.67, and 1.07, respectively. Therefore, CR can be useful in phytoremediation of Cd.

Mean soil, root, and shoot Cd values of *Cynoglossum officinale* (CY) were 27.1, 18.6, and 26.6 mg kg^{-1}, respectively. The average concentration of Cd in soils was higher

Table 1 The Cd concentrations of soils, roots and shoots of 11 plant species and translocation factors (TLF) and enrichment coefficients for the roots (ECR) and shoots (ECS) for Cd

Sample no.	Cd in soil (mg kg^{-1})	Cd in root (mg kg^{-1})	Cd in shoot (mg kg^{-1})	ECR	ECS	TLF
AL-01	28.8 ± 3	48.1 ± 4	39.5 ± 3	1.67	1.37	0.82
AL-02	54.4 ± 6	88.3 ± 6	40.4 ± 5	1.62	0.74	0.46
AL-03	292 ± 21	124 ± 14	92.7 ± 7	0.43	0.32	0.75
AL-04	252 ± 18	77.4 ± 5	62.5 ± 7	0.31	0.25	0.81
AL-05	174 ± 14	104 ± 11	103 ± 9	0.60	0.59	0.99
AN-01	55.8 ± 5	14.4 ± 9	13.1 ± 2	0.26	0.24	0.91
AN-02	33.0 ± 2	39.3 ± 5	18.3 ± 2	1.19	0.56	0.47
CE-01	107 ± 8	74.0 ± 9	58.4 ± 5	0.69	0.55	0.79
CE-02	51.1 ± 5	46.9 ± 4	46.7 ± 5	0.92	0.91	1.00
CE-03	207 ± 17	139 ± 12	79.1 ± 7	0.67	0.38	0.57
CR-01	55.2 ± 4	62.4 ± 6	102 ± 9	1.13	1.85	1.63
CR-02	25.7 ± 3	86.5 ± 9	36.9 ± 4	3.36	1.43	0.43
CR-03	63.3 ± 6	96.5 ± 11	110 ± 13	1.52	1.74	1.14
CY-01	39.7 ± 2	28.5 ± 3	42.2 ± 4	0.72	1.06	1.48
CY-02	14.4 ± 2	8.60 ± 1	11.0 ± 1	0.60	0.76	1.28
GL-01	81.4 ± 7	40.8 ± 4	4.70 ± 4	0.50	0.06	0.12
GL-02	82.3 ± 9	43.8 ± 4	13.7 ± 2	0.53	0.17	0.31
IS-01	26.0 ± 3	90.5 ± 8	49.9 ± 4	3.47	1.92	0.55
IS 02	343 ± 37	101 ± 12	57.1 ± 7	0.30	0.17	0.56
IS-03	232 ± 19	60.9 ± 5	31.4 ± 3	0.26	0.14	0.51
IS-04	85.6 ± 7	21.0 ± 3	3.44 ± 1	0.25	0.04	0.16
ON-01	75.9 ± 6	70.3 ± 8	53.3 ± 4	0.93	0.70	0.76
ON-02	152 ± 12	138 ± 10	135 ± 14	0.90	0.88	0.98
ON-03	116 ± 10	166 ± 14	132 ± 11	1.43	1.14	0.79
PH-01	74.7 ± 5	9.82 ± 1	4.00 ± 1	0.13	0.05	0.41
PH-02	28.5 ± 4	24.4 ± 2	29.1 ± 3	0.86	1.02	1.19
PH-03	28.0 ± 3	45.3 ± 4	38.2 ± 4	1.62	1.36	0.84
PH-04	26.0 ± 2	36.5 ± 3	46.9 ± 5	1.40	1.80	1.29
SL-01	33.2 ± 3	20.4 ± 3	13.7 ± 2	0.61	0.41	0.67
SL-02	9.64 ± 1	9.07 ± 1	2.65 ± 1	0.94	0.27	0.29
SL-03	6.04 ± 1	10.2 ± 1	2.77 ± 1	1.68	0.46	0.27
SL-04	10.8 ± 2	20.5 ± 2	9.52 ± 1	1.91	0.88	0.46
SL-05	11.4 ± 1	19.7 ± 1	6.35 ± 2	1.72	0.56	0.32
SL-06	11.4 ± 1	11.7 ± 1	14.0 ± 1	1.03	1.23	1.19
VR-01	15.2 ± 2	18.4 ± 3	32.9 ± 4	1.21	2.17	1.79
VR-02	56.2 ± 6	51.0 ± 4	89.7 ± 9	0.91	1.60	1.76
VR-03	129 ± 15	68.2 ± 8	21.9 ± 3	0.53	0.17	0.32
VR-04	78.5 ± 7	27.4 ± 4	19.3 ± 3	0.35	0.25	0.71
VR-05	60.1 ± 6	18.4 ± 3	29.7 ± 3	0.31	0.49	1.61

than that in CY shoot and root, with one site exception. Average values of CY ECR, ECS, and TLFs were 0.66, 0.91 and 1.38, respectively. These parameters indicate that CY shoot may be used as a biomonitor for Cd due to the mean CY ECS being higher than one or close to one.

Mean *Glaucium flavum* (GL) soil, root, and shoot Cd concentrations were 81.9, 42.3, and 9.2 mg kg^{-1}, respectively. Mean GL ECR, ECS, and TLF were 0.52, 0.11, and 0.21, respectively for Cd. As with AL, AN and CE, these results show that GL is not a promising candidate for Cd phytoremediation in mining areas.

Average *Isatis* (IS) soil, root, and shoot Cd concentrations were 172, 68.5, and 35.4 mg kg^{-1}, respectively (medians: 159, 75.7, and 40.6 mg kg^{-1}). Cd values in IS soil were higher than those in shoots and roots, except for IS-01. The mean ECR, ECS, and TLFs of IS for Cd were 1.07, 0.56, and 0.45, respectively. The IS ECS, ECR, and TLFs for Cd show that *Isatis* is not useful for phytoremediation of Cd.

Mean *Onosma* (ON) soil, root, and shoot concentrations were 115, 125, and 107 mg kg^{-1}, respectively. Mean Cd levels of ON soils were higher than in ON shoot and root, except for ON-03. Mean ECR and ECS values for Cd were 1.09 and 0.91, respectively, indicating the root and shoot of ON accumulate Cd from the soil.

Mean *Phlomis* (PH) soil, root and shoot Cd concentrations were 39.3, 29.0, and 29.5 mg kg^{-1}, respectively (medians: 28.2, 30.4 and 33.6 mg kg^{-1}). Mean PH ECR, ECS, and TLF for Cd were 1.00, 1.06, and 0.93, respectively, with ECR and ECS values > 1. *Phlomis* root and shoot could be useful for cleaning soils polluted by Cd.

Mean *Silene compacta* L. (SL) soil, root, and shoot Cd concentrations were 13.7, 15.3, and 8.2 mg kg^{-1}, respectively (medians: 11.1, 15.7 and 7.9 mg kg^{-1}). Mean TLF of SL is > 1 ($p < 0.05$). These parameters indicate SL root can be a bioaccumulator plant for Cd. The mean Cd values of SL root were higher than in both SL shoots and soils, except for SL-06.

The mean *Verbascum thapsus* L. (VR) soil, root, and shoot Cd concentrations were 67.9, 36.7, and 38.7 mg kg^{-1}, respectively (medians: 60.1, 27.4, and 29.7 mg kg^{-1}). Mean soil values of VR were higher than mean Cd concentrations in shoots and roots ($p < 0.05$), except for VR-01 (Table 1). Mean ECR and ECS were < 1, indicating *V. thapsus* is not well suited for phytoremediation of soils contaminated by Cd.

Some plants (*Azolla pinnata, Eleocharis acicularis, Rorippa globosa, Solanum photeinocarpum, Thlaspi caerulescens*) have been reported to be natural hyperaccumulators for Cd (Lombi et al. 2001; Vogel-Mikus et al. 2005; Rai 2008; Wei et al. 2008; Sakakibara et al. 2011; Zhang et al. 2011). These plants showed Cd accumulations between 100 and 740 mg kg^{-1}. Sewalem et al. (2014) suggested sunflower *(Helianthus)* remediated Cd in polluted soils, because it accumulated 89% of Cd in the root and 11% of Cd in shoot. Similarly, Andrade et al. (2008) suggested Cd is mainly accumulated in the roots and shoots of sunflower.

Athyrium wardii was defined as a Cd hyperaccumulator by Zhang et al. (2012) because Cd values in the root were higher than in the root of other plants. The highest levels of Cd were found to be > 250 mg kg^{-1} during the growth period of *A. wardii*. The bioconcentration factor (BCF) was > 1, while the TLF was < 1, indicating a large portion of Cd was absorbed into the roots, and only a small portion was transported from the roots to the shoots. The root biomass of *A. wardii* was also highest among tested species over the entire growth period (Zou et al. 2012). In the field survey, *A. wardii* exhibited a high BCF, low TLF values, high biomass, and was thus a potential candidate for phytostabilization of mine tailings to minimize the migration of Cd into groundwater while reducing the risk of entry into the food chain.

Kabata-Pendias (2011) indicated that the highest Cd levels in wheat grains and brown rice were 14.2 and 5.2 mg kg^{-1}, respectively, and the accumulation of metal concentrations in the root and shoots of these plants was lower. Alvarenga et al. (2008) pointed out that candidate plants for phytostabilization should have a large amount of biomass and an extensive root system to accumulate metals in high amounts.

Our study showed the best bioaccumulator plants for Cd among the studied plants were *Carduus nutans* (CR) and *Phlomis* (PH). Plantings of these bioaccumulator plants can be use for biomonitoring studies of environmental pollution and the cleaning/rehabilitation of areas polluted by Cd.

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