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Distribution of Chromium, Nickel, and Cobalt in Different Parts of Plant Species and Soil in Mining Area of Keban, Turkey

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Abstract: The distribution of chromium, nickel, and cobalt in the plant species and soil of the Zn-Pb-Ag sulfide deposits of the Keban area in Turkey have been studied to determine both biogeochemical indicators and biomonitoring of environmental pollution. Plants, including *Euphorbia, Verbascum*, and *Astragalus*, and their associated soil samples were collected, and the roots and shoots of these plants together with soils were analyzed by inductively coupled plasma-mass spectrometry (ICP-MS). The three metal concentrations in the shoots of *Euphorbia* samples were found to be lower than in their roots, whereas the metal concentrations in shoots of *Verbascum* are higher than in their roots. Although the metal concentrations in soils were found to be lower than the permissible limits for agricultural purposes, the concentrations of these metals in different parts of some plants were observed at excessive/toxic levels. As a result, the roots of *Euphorbia* and the shoots of *Verbascum* and *Astragalus* can be used to biomonitor environmental contamination and as biogeochemical indicators.

Keywords: Antagonistic effect, biomonitoring, chromium, cobalt, nickel, plant and soil contamination

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INTRODUCTION

Chromium (Cr) in trivalent form, nickel (Ni), and cobalt (Co) have been considered as essential elements when present at trace levels, whereas the same metals are contaminants for soil, surface water, and groundwater when present in excess levels (Kabata-Pendias and Pendias 2001). The necessity of Cr(III) was given in detail in the literature (Anderson 1999): chromium(III) is essential for normal carbohydrate and lipid metabolism and improves insulin function. Chromium in hexavalent form is potentially cancerous for humans (WHO 1988). As a result, the recommended daily allowance (RDA) for Cr is 50–200 microgram/day for adults in the USA (Noel, Leblanc, and Guerin 2003). Furthermore, Cr levels higher than 5.0 mg kg^{-1} in plant species are considered excessive or toxic on a dry-weight basis (Kabata-Pendias and Pendias 2001). Maximum allowable levels of Cr in agricultural soils were suggested as 50–100 mg kg^{-1} according to different countries (Jones 1997).

Nickel is the metal component of the enzyme urease and, therefore, is considered to be essential to the living. The essentiality, toxicity, and carsinogenicity of Ni were reviewed by Denkhaus and Salnikow (2002) in recent times. More attention has been focused on the toxicity of nickel because it can cause allergic reactions and certain nickel compounds have carcinogenic effects (Nriago 1980; McKenzie and Smythe 1988; WHO l991; Taljaard and van Staden 1998; Kasprzak, Sunderman, and Salnikow 2003). Hence, the studies of the uptake and chemical behavior of Ni in plants are related mainly to its toxicity to animals and humans. Maximum nickel concentrations in plants have been suggested in ranges of 0.1 to 5 mg kg^{-1}, on a dry-weight basis (Kabata-Pendias and Pendias 2001). Maximum allowable Ni levels in agricultural soils were described in the range of 20–100 mg kg^{-1} according to different countries (Jones l997).

The distributions of Ni and Co in the Earth's crust are similar. Cobalt is essential for plants that fix atmospheric nitrogen. Co concentrations in uncontaminated areas have been found in ranges of 2.0 to 27.0 mg kg^{-1} for soil and 0.03 to 1.0 mg kg^{-1} for plants on a dry-weight basis (Kabata-Pendias and Pendias 2001). Maximum Co levels in agricultural soils were suggested in the range of 20–50 mg kg^{-1} (Jones 1997).

The metals are commonly determined to monitor the pollution levels in both environmental and biological matrices such as plants, foods, vegetables, fruit, and other similar samples (Zayed et al. 1998; Yaman and Gucer 1995; Yaman and Gucer 1998; Yaman 2000; Divrikli et al. 2003). As a result, raised Cr, Ni, and Co levels have been found in some plant species grown in contaminated areas (Shallari et al. 1998; Reimann et al. 2001; Kfayatullah, Shah, and Arfan 2001; Shah, Kfayatullah, and Arfan 2003). Very high metal levels have been found in the vicinity of some metallic ore deposits and metal industries (Dinelli and Lombini l996; Shallari et al. 1998; Arne, Stott, and Weldron 1999; Kfayatullah, Shah, and Arfan 2001; Shah, Kfayatullah, and Arfan 2003; Deo 2004; Baroni et al. 2004).

In the current study, Cr, Ni, and Co concentrations were determined using ICP-MS in the soil samples and the roots and shoots of plant samples including *Euphorbia macroclada, Verbascum cheiranthifolium Boiss*, and *Astragalus gummifer* growing in these soils. The results were compared with each other to investigate the correlation among the soil and roots and shoots of the plants. The antagonistic effects of the various metals on uptake of the studied metals by plants were evaluated.

MATERIALS AND METHODS

The Study Area

In this study, the plants and the associated soil samples were collected in Keban mining district of the Elazig province in eastern Turkey (Figure 1). This district has a mining history as long as 6000 years, and the area had been heavily charged with metals by ancient and modern mining activities. ^{14}C absolute age determinations on wooden mining tools discovered in ancient mining cavities were conducted by Seeliger et al. (1985). Copper, iron (Fe), and fluorine (F) ores were mined only in short periods.

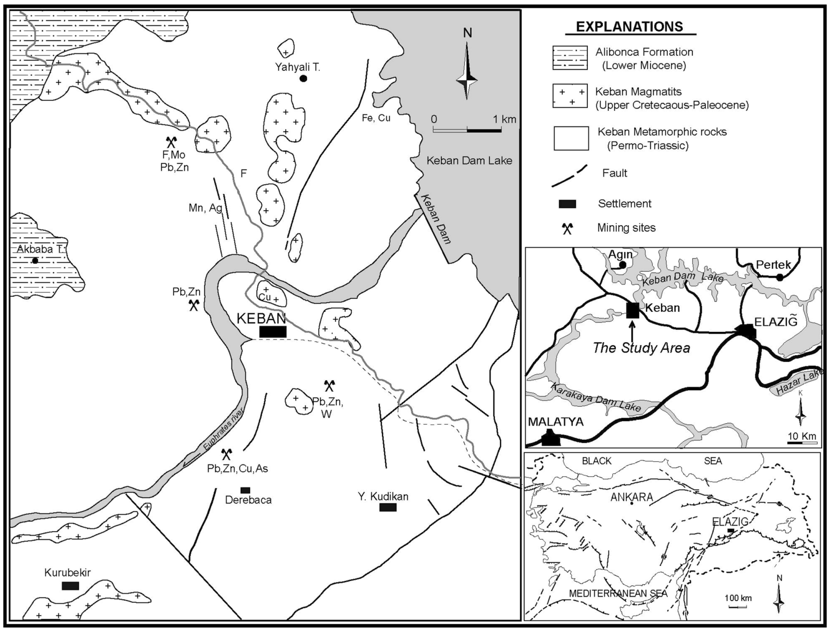

Figure 1. Geology of the study area (simplified from Akgul l987).

The plant species in the Keban region are among the plants grown in severe climate conditions because of their massive and deep-reaching root systems and ability to live in the areas not rich in organic matters. Briefly, *Euphorbia macroclada Boiss*. (local name: Sütlegen), *Verbascum cheiranthifolium Boiss* (local name: Sigir Kuyrugu), and *Astragalus gummifer* (local name: Keven) were examined for this study. Q1

Preparation of Samples

Plant Samples

Plant samples were collected randomly, and the collection sites were determined in accordance with a pattern that represents the whole of the Keban mining area. Triplet shoot and root samples were taken from each plant sampling site. The root samples were taken from the depth of 30–40 cm from the surface. The ashed plant matters were used for metal analysis. The ratio of ashing samples to dry samples were found as follows: *Euphorbia* 42%, *Verbascum* 44%, and *Astragalus* 44%. Thus, the metal concentrations on a dried-weight basis have been calculated from the concentrations on the ashed-weight basis.

Shoot and root samples of the studied plants were carefully washed with deionized water and oven-dried at 100°C for 30 min and then at 60°C for 24 h. Plant samples were ashed by heating at 250°C and gradually increased to 500°C for 2 h. These ashed samples were ground using hand mortars, labeled, and then analyzed with the ICP/MS technique at ACME Analytical Labs, Canada. HNO_3 for 1 h and a mixture of HCl-HNO_3-H_2O for 1 h at 95°Cwere used.

Soil Samples

Triplet soil samples were collected at 30–40 cm depths and from the surrounding of the roots of the sampled plants. For digestion of the soil samples, the mixture of HCl-HNO_3-H_2O was used for 1 h at 95°C.

RESULTS AND DISCUSSION

The obtained results for all studied soil samples were found in the range of 2.1–34.4 mg kg^{-1} for Cr, 2.6–49.3 mg kg^{-1} for Ni, and 2.2–39.2 mg kg^{-1} for Co. As can be seen from Table 1, the observed metal levels in soil samples are lower than the maximum permissible values of 100, 50, and 100 mg kg^{-1} for Cr, Ni, and Co, respectively (Kabata-Pendias and Pendias 2001). These results can be attributed to the fact that Cr, Ni, and Co behaviors are identical. The obtained results are similar to the values

Table 1. Chromium, Ni, and Co concentrations in soil and the roots and shoots of *Euphorbia*, *Verbascum*, and *Astragalus* ($mg\,kg^{-1}$)

	In plant						In soil		
Sample no.	Cr in root	Cr in shoot	Ni in root	Ni in shoot	Co in root	Co in shoot	Cr (ppm)	Ni (ppm)	Co (ppm)
EU-21	0.86	0.47	2.73	1.22	1.57	0.5	2.1	4.6	3.9
EU-24	2.98	0.5	4.22	1.39	1.2	0.36	26	16.2	7.4
EU-26	6.51	0.45	13.1	2.23	2.77	1.13	31.2	14.4	10
EU-29	4.85	0.42	4.2	1.09	6.65	0.49	23.3	12.9	39.2
EU-31	2.44	0.85	4.03	1.89	1.07	0.4	22.7	18	8.3
EU-34	2.08	1.01	3.7	1.72	1.29	0.37	8.8	7.3	4
EU-41	5.96	0.75	7.35	0.97	2.1	0.26	26.2	16.4	8.6
EU-44	8.88	0.96	6.13	1.38	1.85	0.28	19.6	13.9	8.2
EU-45	6.83	0.66	11.7	1.85	2.62	0.4	34.4	49.3	12.7
Mean	4.60	0.67	6.35	1.53	2.35	0.47	21.6	17	11.4
SD	2.66	0.23	3.71	0.42	1.72	0.26	10.3	12.9	10.8
Min	0.86	0.42	2.73	0.97	1.07	0.26	2.1	4.6	3.9
Max	8.88	1.01	13.1	2.23	6.65	1.13	34.4	49.3	39.2
VR-25	0.45	8.1	0.21	6.51	0.18	2.12	27.8	17.9	8.7
VR-27	1.32	2.43	1.97	3.61	0.89	1.11	2.1	2.6	2.2
VR-35	2.35	5.1	18.9	6.68	0.84	1.72	17.3	16.4	6.4
VR-47	6.65	7.52	9.03	10.5	1.68	1.73	23	22	6.2
Mean	2.58	5.49	6.4	6.4	0.88	1.58	19.6	15.4	6.4
SD	2.40	2.34	7.8	2.6	0.53	0.42	10.7	7.4	2.7
Min	0.45	2.43	0.2	3.6	0.18	1.11	2.1	2.6	2.2

(*continued*)

Table 1. Continued

Sample no.	In plant						In soil		
	Cr in root	Cr in shoot	Ni in root	Ni in shoot	Co in root	Co in shoot	Cr (ppm)	Ni (ppm)	Co (ppm)
Max	6.65	8.1	18.9	10.5	1.68	2.12	27.8	22	8.7
AS-22		4.43		4.58		1.09	27.5	22.4	8.7
AS-28		2.08		3.99		1.12	2.9	10.7	4.1
AS-32		6.26		7.35		1.77	23.8	17	8.6
AS-36		6.13		6.59		1.69	26.3	20.7	9.9
AS-40		7.61		8.44		1.86	17.7	16	5.6
AS-42		8.78		10.4		2.24	18.3	15.5	6.4
Mean		5.88		6.89		1.63	19.4	17.1	7.2
SD		2.37		2.40		0.45	9	4.1	2.2
Min		2.08		3.99		1.09	2.9	10.7	4.1
Max		8.78		10.40		2.24	27.5	22.4	9.9

observed in the mining area of Pb-Zn-Ag deposits of Besham in northern Pakistan. Mulligan, Yong, and Gibbs reported that phytoremediation could be a good method for rehabilitation among the remediation technologies (2001). To determine both plant and biomonitoring of environmental contamination and also biogeochemical indicator abilities, the studied plants were separately evaluated as follows.

Euphorbia

As can be seen from Table 1 and Figures 2–4, Cr concentrations in both shoots and roots of all studied *Euphorbia* plants except three shoot samples are higher than normal accepted levels ($0.5\,mg\,kg^{-1}$) for dried plant tissue. Although Cr concentrations of the studied soils are in the ranges of normally accepted levels, the high levels of chromium in plants can be attributed to the Cr uptake of this plant. However, the obtained Cr levels in all shoot and root samples except four roots are not higher than the excessive/toxic concentration ($5.0\,mg\,kg^{-1}$). Cr concentrations in the root samples were found to be higher than in those shoot samples of *Euphorbia* ($p = 0.002$).

In the literature, Ni concentrations as high as $357.9\,mg\,kg^{-1}$ in *Empetrum nigrum* grown in contaminated soil and $12625\,mg\,kg^{-1}$ in *Alyssum markgrafii* in serpentine soil were reported (Shallari et al. 1998; Reimann et al. 2001). Nickel concentrations in both shoots and roots of all studied *Euphorbia* plants except four root samples were found to be lower than the levels of normally accepted values ($5.0\,mg\,kg^{-1}$) on a dried-weight basis. Furthermore, the observed high Ni levels in two root samples were higher than the excessive/toxic concentration ($10\,mg\,kg^{-1}$).

Cobalt concentrations in all roots and one shoot sample of *Euphorbia* plants are higher than in the normal level ($1.0\,mg\,kg^{-1}$) on a dried-weight basis, but these high Co levels are not higher in the excessive/toxic concentration ($15\,mg\,kg^{-1}$). Similar Cr, Ni, and Co levels of the *Euphorbia* root samples were also found higher than those in the shoot samples ($p = 0.002$ for Ni and $p = 0.005$ for Co). As a result, *Euphorbia* roots can be used as a biomonitor of environmental pollution and biogeochemical indicator. However, *Euphorbia* is not useful for phytoremediation.

Verbascum

As can be seen from Table 1 and Figures 2–4, Cr concentrations in both shoots and roots of all studied *Verbascum* plants except one root sample were found to be higher than in the levels of normally accepted values. Furthermore, Cr levels in one root and three shoot samples were found to be higher than the excessive/toxic concentration. In contrast to *Euphorbia*, Cr concentration of the *Verbascum* shoot samples were higher than the root samples of *Verbascum* ($p < 0.1$).

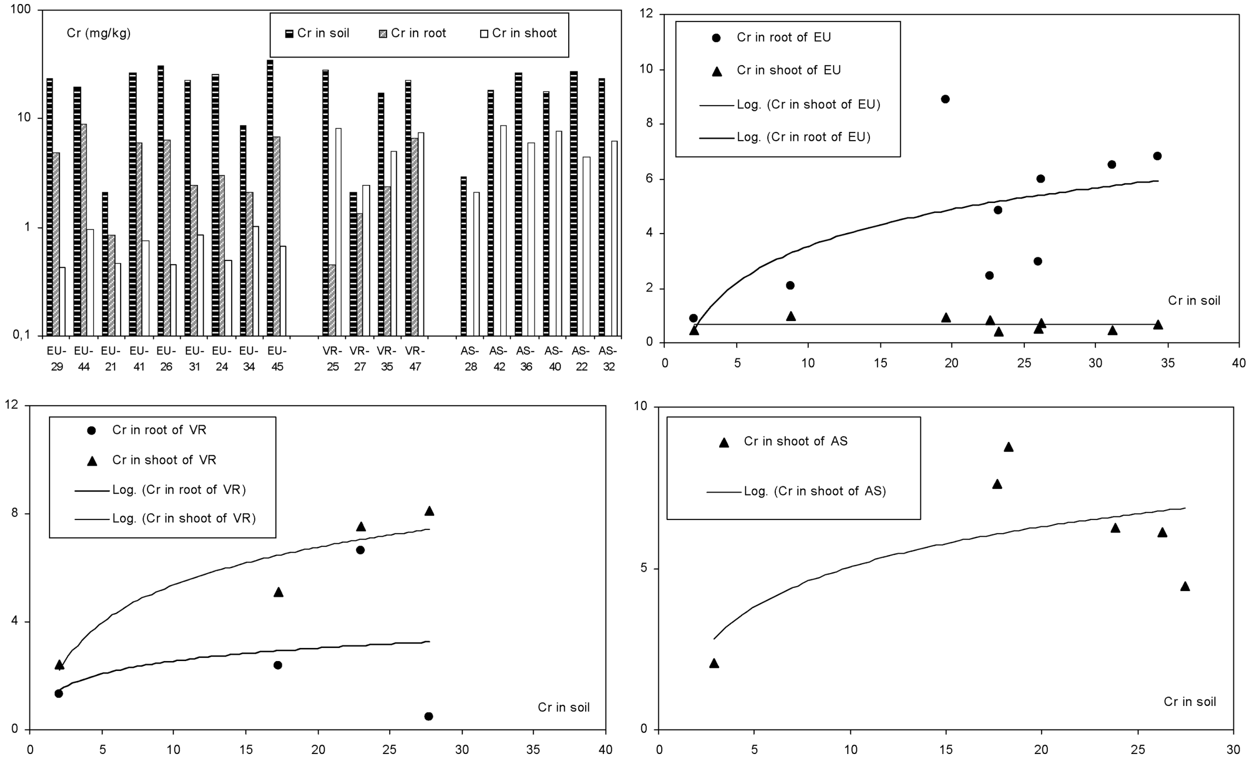

Figure 2. Histogram and correlation relationships for Cr contents of soil, root, and shoot samples (EU: *Euphorbia*, VR: *Verbascum*, AG: *Astragalus*) in Keban mining area (the units are mg per kg of dried sample).

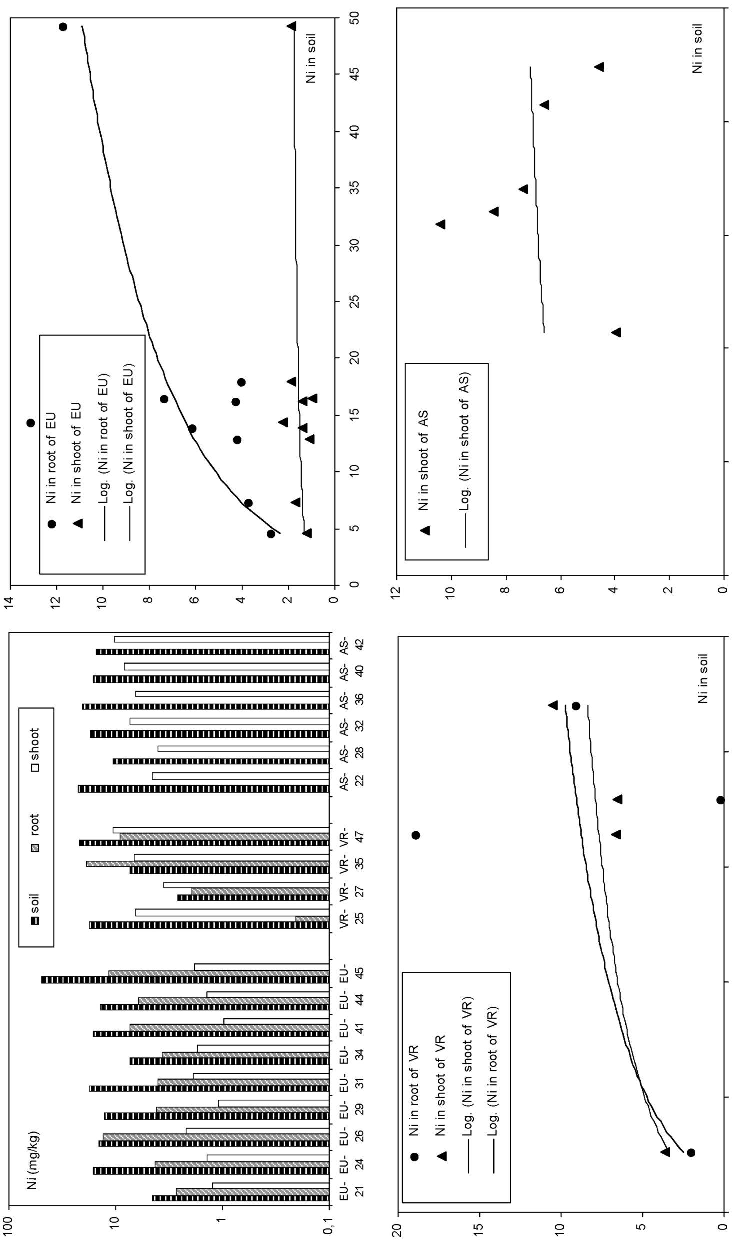

Figure 3. Histogram and correlation relationships for Ni contents of soil, root, and shoot samples (EU: *Euphorbia*, VR: *Verbascum*, AG: *Astragalus*) in Keban mining area (the units are mg per kg of dried sample).

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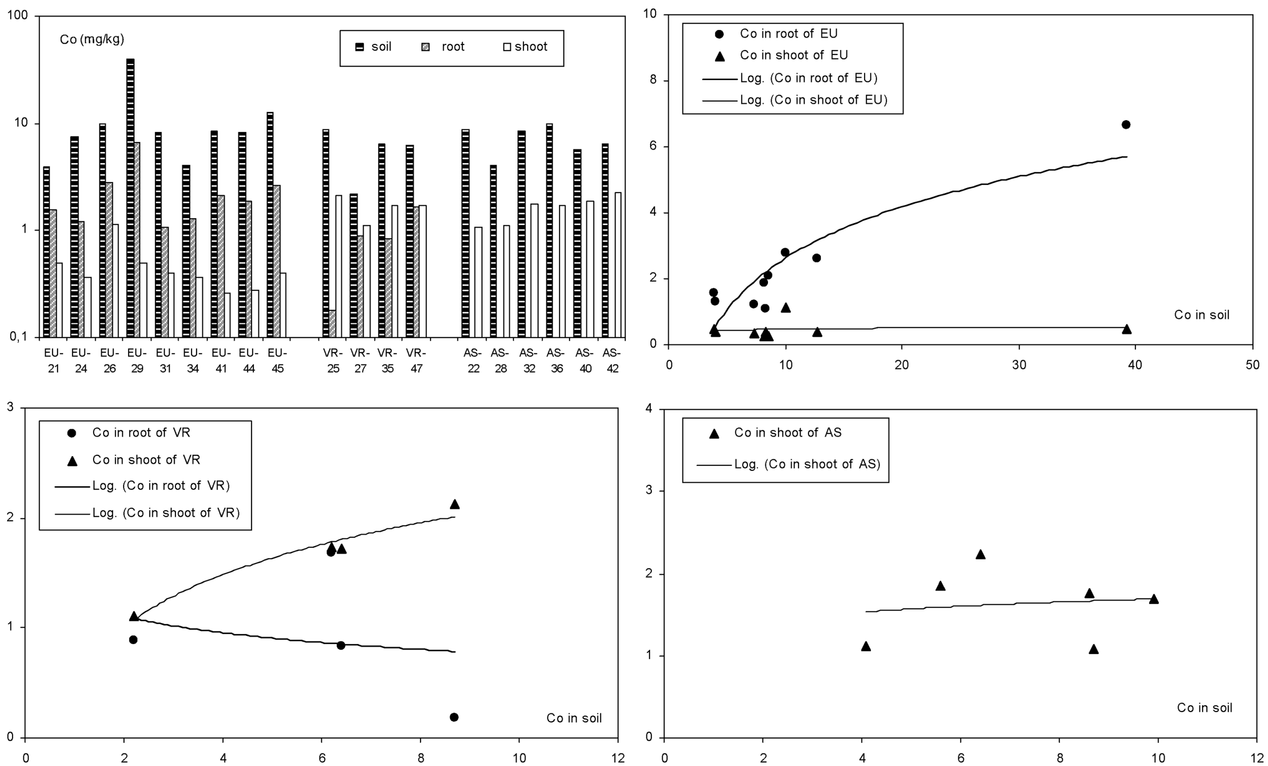

Figure 4. Histogram and correlation relationships for Co contents of soil, root, and shoot samples (EU: *Euphorbia*, VR: *Verbascum*, AG: *Astragalus*) in Keban mining area (the units are mg per kg of dried sample).

Nickel concentrations in three shoot and two root samples of *Verbascum* were found to be higher than the normally accepted level (5.0 mg kg^{-1}), and Ni concentrations of one root and one shoot sample are higher than the excessive/toxic level (10 mg kg^{-1}).

On the contrary of *Euphorbia*, cobalt concentrations in all shoot samples and one root sample of *Verbascum* were found to be higher than normal (1.0 mg kg^{-1}), but these levels are not higher than the excessive/toxic concentration of 15 mg kg^{-1}. As a result, unlike in *Euphorbia*, Cr, Ni, and Co concentrations in the root of *Verbascum* were lower than those shoot samples of *Verbascum* ($p < 0.5$ for Ni and $p = 0.05$ for Co).

Although Cr concentration in the soil of VR-25 was found to be 10 times higher than in the soil of VR-27, the Cr level in the root of VR-25 was found to be three times lower than in the root of VR-27. Similar results were also observed for Ni and Co. These results can be attributed to the antagonistic effect sourced from the other metals such as molybdenum (Mo), copper (Cu), zinc (Zn), and silver (Ag) because the concentration of these metals in both soil and plant roots of VR-25 were significantly higher than in both soil and plant roots of VR-27. In addition, Cr levels of both root and shoots of VR-35 and VR-47 are higher than the root and shoots of VR-27. This can be attributed to the Cr concentrations in soils of VR-35 and VR-47, which are higher than in the soil of VR-27. As a result, *Verbascum* shoots can be used as a biomonitor of environmental pollution and biogeochemical indicator.

Astragalus

As can be seen from Table 1 and Figures 2–4, Cr concentrations in shoots of all studied *Astragalus*, except two samples, were found to be higher than the levels of excessive/toxic concentration. Furthermore, chromium levels of all *Astragalus* shoot samples were higher than the normal concentration. Similar to Cr values, Ni concentrations of all *Astragalus* shoot samples were higher than the normal concentration, but these levels are not higher than the excessive/toxic concentration except one sample. Similar to those in *Euphorbia* and *Verbascum*, Co concentrations in all shoot samples of *Astragalus* are higher than the normal value of 1.0 mg kg^{-1}, but these levels are not higher than the excessive/toxic concentration of 15 mg kg^{-1}. As a result, it can be suggested that *Astragalus* shoots can be used as a monitor of environmental pollution and biogeochemical indicator similar to *Verbascum*.

CONCLUSIONS

The concentrations of Cr, Ni, and Co in shoot and root parts of plants vary on the plant species. Although the studied metal concentrations in soils were lower than the permissible limits for agricultural purposes, the concentrations of these metals in different parts of some plants were observed at excessive/toxic levels. Therefore, the root of *Euphorbia* and the shoots of *Verbascum* and *Astragalus* are useful as biomonitors of environmental contamination and biogeochemical indicators. The observed results agree with the values found in the similar mining area of zinc–lead deposits of Besham in northern Pakistan (Kfayatullah, Shan, and Arfan 2001; Shah, Kfayatullah, and Arfan 2003). In addition, the studied plant samples, particularly *Verbascum*, can have an environmental risk for the living animals in surroundings of mineralized area, if they are eaten.

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