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Translocation and Accumulation of Boron in Roots and Shoots of Plants Grown in Soils of Low Boron Concentration in Turkey's Keban Pb-Zn Mining Area

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TRANSLOCATION AND ACCUMULATION OF BORON IN ROOTS AND SHOOTS OF PLANTS GROWN IN SOILS OF LOW BORON CONCENTRATION IN TURKEY'S KEBAN PB-ZN MINING AREA

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Boron (B) concentrations were investigated in both shoots and roots of* Euphorbia macroclada, Verbascum cheiranthifolium, *and* Astragalus gummifer *grown in soil of the Keban, Turkey, Lead–zinc–copper–fluoride mining area, which has an arid climate. Soil B concentrations were also investigated. Plants and their associated soil samples were collected and analyzed by Inductively Coupled Plasma–Mass Spectrometry (ICP-MS). Total B concentrations of soils in the study area were very low (mean: 4.97 mg kg^{-1}) as compared with those in surface soils in other countries. Boron concentrations of plant organs were several times higher than those in their associated soils. The mean values of B concentrations in roots of* E. macroclada, V. cheiranthifolium, *and* A. gummifer *were 25, 70, and 69 mg kg^{-1}, respectively, while those in shoots were 75, 115, and 77 mg kg^{-1}, respectively. Results indicate that roots and shoots of plants grown in soils with low B concentrations can be used both as biomonitors for environmental contamination and biogeochemical indicators for B.

KEY WORDS: Boron (B) uptake, *Euphorbia*, *Verbascum*, *Astragalus*, soil, enrichment coefficient, translocation factor (TF)

INTRODUCTION

Elemental boron (B) is a member of Group IIIA of the periodic table (in the United States), along with aluminum, gallium, indium, and thallium. It has an atomic number of 5 and a relative atomic mass of 10.81. Boron is never found in the elemental form in nature (EHC, 1998); however, it is widely distributed in low concentrations throughout nature in the form of various inorganic borates. It constitutes approximately 11 mg kg^{-1} of the upper continental crust and 5 mg kg^{-1} of the lower continental crust (Wedepohl, 1995). Concentrations reported in sea water range from 0.5 to 9.6 mg kg^{-1}, with an average of 4.6 mg kg^{-1}. Fresh-water concentrations range from less than 0.01 to 1.5 mg kg^{-1}. Boron in the environment is always found chemically bound to oxygen, usually as alkali or alkaline earth borates, or as boric acid (IEHR, 1997; USEPA, 1987). Most B is found in oceans, at an average concentration of approximately 4.5 mg l^{-1} (Weast *et al.*, 1985). Borate deposits may often be important constituents of economic non-marine evaporites that are formed

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under arid climatic conditions in playa lakes. Borate minerals (such as colemanite, ulexite, and borax) are the major source of commercial B and are largely concentrated in continental Tertiary deposits in western Anatolia (Turkey) and the American continent (*e.g.*, western United States, central Andes) (Helvacı and Orti, 1998). In particular, the borate deposits of western Turkey are closely associated in space and time with Miocene tuffs and lavas (Helvacı, 1995; Helvacı and Orti, 1998).

Boron is adsorbed onto the surfaces of soil particles, the degree of adsorption depending on the soil type, pH and salinity, soil organic matter content, iron and aluminum oxide content, iron- and aluminium-hydroxy content, and clay content (Sprague, 1972). Boron is an essential micronutrient for higher plants; species differ in their requirements for optimum growth. Boron plays a role in carbohydrate metabolism, sugar translocation, pollen germination, hormone action, normal growth and functioning of the apical meristem, nucleic acid synthesis, and membrane structure and function (Lovatt and Dugger, 1984). Recent work has shown that B is important in cell wall cross-linking, which involves complexation with specific pectin components (Hu, Brown, and Labavitch, 1996).

The initial symptom of B toxicity in plants is chlorosis (yellowing) of the leaf tip, progressing along the leaf margin and into the blade. Necrosis of the chlorotic tissue occurs, followed by leaf abscission. Necrosis of the leaf tissue results in a loss of photosynthetic capacity, which reduces plant productivity (Lovatt and Dugger, 1984). Because more than 5 mg kg^{-1} of available soil B is toxic to most crop plants (Nable, Banuelos, and Paul, 1997), we would not have expected any plants to survive in the soil mining area, which had concentrations of available soil B of the 277 mg kg^{-1}. Boron at concentrations greater than 20 mg kg^{-1} in plant tissues appears to be toxic in grapevine (Gunes *et al*., 2006).

Concentrations of B have been shown to range between 26 and 382 mg kg^{-1} in submerged aquatic freshwater plants, from 11.3 to 57 mg kg^{-1} in freshwater emergent vegetation, and from 2.3 to 94.7 mg kg^{-1} dry weight in terrestrial plants (EHC, 1998).

The purpose of this study was to determine the translocation factors (TFs) and enrichment coefficients between soil and plant parts by studying the accumulation and distribution of B in roots and shoots of *Euphorbia macroclada* Boiss, *Verbascum cheiranthifolium* Boiss, and *Astragalus gummifer* grown in surface soils of the Keban, Turkey, mining area.

MATERIAL AND METHODS

Apparatus

A Perkin-Elmer ELAN 9000 (CT, USA) inductively coupled plasma mass spectrometer was used for the determination of B. The operating conditions recommended by the manufacturer were used.

Study Area

In this study, the plants and associated soil samples were collected from the area of the granite–syenites rocks in Keban mining district of Elazig province in Eastern Turkey (Figure 1). The plant samples together with their roots and soil samples were taken from 26 sites (nine *Euphorbia*, nine *Verbascum*, and eight *Astragalus* sites) of Keban mining areas in Elazig, Turkey. This district has a mining history of at least 6000 years and the area had been heavily enriched with metals caused by ancient and modern mining activities. ^{14}C absolute-age determinations were made by Seeliger *et al*. (1985) on wooden mining tools discovered in ancient mining cavities. Copper (Cu), zinc (Zn), lead (Pb), iron (Fe), and

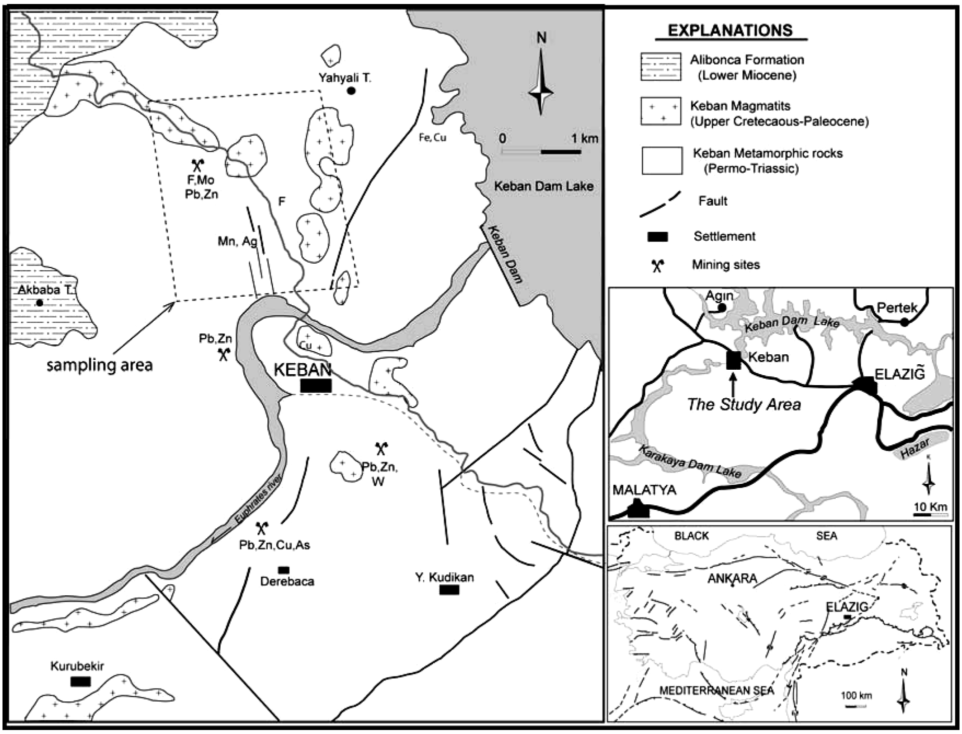

Figure 1 Geological and location map of the study area (simplified from Akgul, l987).

fluoride (F) ores were mined in this region, but only for short periods of time. The plant species in the Keban region have massive and deep-reaching root systems, which enable them to grow under severe climatic conditions and in soils that are deficient in organic matter. *E. macroclada* (local name: Sütlegen), *V. cheiranthifolium* (local name: Sigir Kuyrugu), and *A. gummifer* (local name: Keven) were examined for B content in this study.

Sample Preparation

Plant samples. Plant samples were randomly collected in the Keban mining area. Three samples of shoots and roots were taken from each of the sampling sites: the root samples were taken at a depth of 30–40 cm below the surface. The shoot and root samples of the studied plants were thoroughly washed with tap water followed by distilled water and then were oven dried at 100°C for 30 min and then at 60°C for 24 h. The dried plant samples (approximately 2.0–3.0 g) were ashed by heating at 250°C; the temperature was gradually increased to 500°C over 2 h. The ashed samples were digested in HNO_3 for 1 h, then in a mixture of HCl-HNO_3-H_2O for 1 h [6 mL of the mixture of 1:1:1 (vol:vol) was used for 1.0 g of the ashed sample] at 95°C. Lastly, all ashed plant samples were analyzed by ICP-MS.

Soil samples. Three soil samples (1.0 g) from soil surrounding the plant root samples were collected at 30- to 40-cm depths. It was considered that 30–40 cm was a suitable depth since two plant species (*Euphorbia* and *Verbascum*) used in this study have roots 30–40 cm long. However, *Astragalus* has a root length of about 5–10 m. After oven drying at 100°C for 4 h and removing the gravel, the soil samples were ground by hand using a mortar and pestle. Soil samples were digested in a mixture of HCl-HNO_3-H_2O [6 mL of the mixture of 1:1:1 (vol:vol) was used for 1.0 g] for 1 h at 95°C on a hot plate. Thus, all sample constituents except silicates were digested.

Enrichment Coefficients of Root and Shoot

Enrichment coefficients were found by calculating the ratios of specific activities in plant parts (ECR for root, ECL for leaves) and soil (concentration in mg kg^{-1} of plant organs divided by concentration in mg kg^{-1} of soil). This value was used as an index for the accumulation of trace elements in plant parts or the transfer of elements from soil to plant parts (Yanagisawa, Muramutsu, and Kamada, 1992; Whicker *et al*., 1999; Chen, Zhu, and Hu, 2005).

Translocation Factors

Translocation factors (TFs) were obtained by calculating the ratios of heavy metals or elements in plant shoot to that in plant root. In metal-accumulator species, TFs greater than 1 are common, whereas in metal-excluder species TFs are typically lower than 1 (Baker, l981; Shen and Liu, 1998; Zu *et al*., 2005).

Results and Discussion

Boron Concentrations in Soils

Total B contents of the soil samples in the study area were between 1.0 and 16 mg kg^{-1} (mean: 4.97 mg kg^{-1}; Figure 2). Among all 26 of the soil samples, B concentrations were lower than those (9–85 mg kg^{-1}) of surface soils in different countries (Kabata-Pendias and

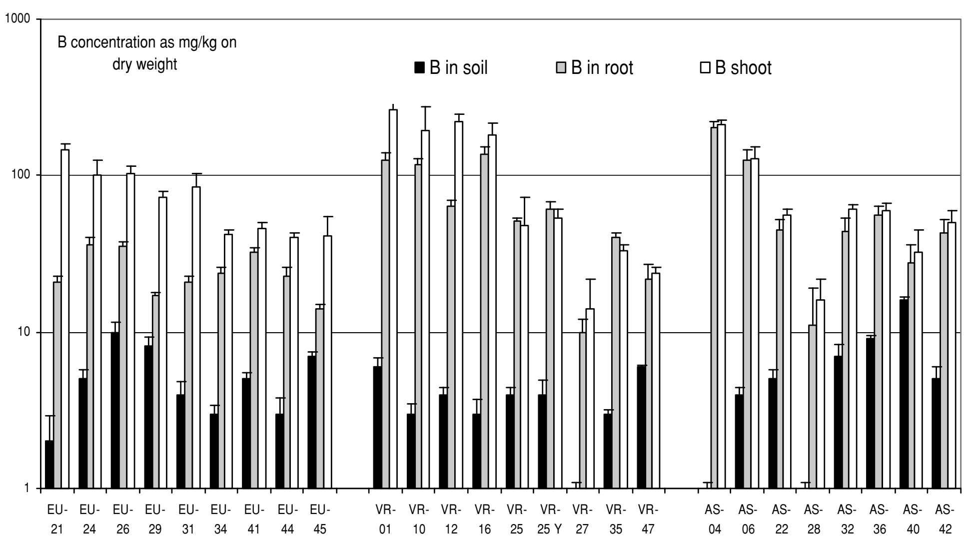

Figure 2 Mean B concentrations in roots and leaves of *E. macroclada,* VR, and AS together with soil concentrations.

Pendias 2001). Intermediate rocks (siyenite, diorite) are widespread in the Keban region and in the surrounding region. The B concentrations in these rocks range between 9 and 25 mg kg^{-1}, lower than those of the studied soils. The EU-26 and AS-40 soil samples have the highest B concentrations (10 and 16 mg kg^{-1}, respectively) of soils in the study area. Although the Keban region has an arid climate and is mined for Cu, Pb, Zn, and F, the B concentration of its soils is very low in comparison with the B concentrations of soils and rocks in other countries (Kabata-Pendias and Pendias, 2001; Bashkin, 2002). The regional arid soils have a relatively high B content and are characterized by a mosaic of very high B accumulation (Bashkin, 2002). No linear correlations ($r = 0.3$–0.4) were observed between B concentrations and other heavy metal concentrations in soils of the Keban region (Table 1). This result also shows that B and other metals are transported to together in soils of the study area.

B Concentrations in Plants

Assessing B uptake by plants from contaminated soils is very important for environmental studies because plants can possibly be used as biomonitors. The concentration of B in plant species is related to the spatial distribution of this element in soil and the major enrichment (mean: 145.8 mg kg^{-1} on the dried weight basis) was shown to be a characteristic of the plant species growing on the Solonchacks, Ozbekistan (Bashkin, 2002). On the Ustyurt plateau, the B concentration in *Salicornia herbacea* L. was 108 mg kg^{-1} on a dry weight basis. Some species, such as cruciferous and meadow species, are called "boron concentrators" because they accumulate B at higher amounts (Bashkin, 2002).

Boron concentrations (mg kg^{-1}) on a dry weight basis in plant parts are given in Figure 2, together with B concentrations of soils. The results are presented and discussed in detail later.

***E. macroclada* (EU).** Mean B values in shoot, root, and soil for *E. macroclada* were 5.24, 24.78, and 74.89 mg kg^{-1}, respectively. Boron values in soil around *E. macroclada* plants were significantly lower than the mean B values in shoot and root of *E. macroclada*. The B values of all *E. macroclada* ranged between 14 and 36 mg kg^{-1} for root, and between 40 and 145 mg kg^{-1} for shoot on a dry weight basis. Boron values in shoots of all *E. macroclada* samples were always higher than B values of their roots. These B concentrations in plant parts of *E. macroclada* in the study area are also higher than the normal B concentrations in different plants (Pais and Jones, 2000; Kabata-Pendias and Pendias, 2001).

The metal concentrations in shoots are invariably greater than those in soil with an enrichment coefficient greater than 1, showing the plant's special ability to absorb metals from soils and transport and store them in their aboveground parts (Baker, 1981; Brown *et al*., 1994; Wei, Chen, and Huang, 2002). The enrichment coefficients of root (ECRs) and shoots (ECSs) of *E. macroclada* for B are shown in Figure 3; mean enrichment coefficients for root and shoot are 5.86 and 19.9, respectively. The ECS is significantly higher than that for root of *E. macroclada*, which means that B uptake by *E. macroclada* from soil is significantly transferred to shoot and twig. The TF for B in *E. macroclada* is between 1.44 and 6.91 (Figure 4) and all TF values of *E. macroclada* are higher than 1. This also shows that *E. macroclada* is a good bioaccumulator plant of B for arid–semi-arid environments. In metal accumulator species, a TF greater than 1 is common, whereas for metal excluder species, TFs are typically lower than 1 (Baker, 1981; Zu *et al*., 2005). A TF higher than 1 indicates a high efficiency to transport metal from roots to leaves, probably due to efficient

Table 1 Correlation relationships between B and heavy metals in soils of the Keban mining area

	Mo	Cu	Pb	Zn	Ag	Ni	Co	Mn	Fe	As	Au	Cd	Sb	Bi	Cr	Ba	B
Mo	1.00																
Cu	0.89	1.00															
Pb	0.97	0.86	1.00														
Zn	0.89	1.00	0.87	1.00													
Ag	0, 96	0, 87	0, 95	0, 87	1, 00												
Ni	−0.05	−0.07	0.08	−0.08	0.01	1.00											
Co	0.88	0.95	0.87	0.94	0.86	0.20	1.00										
Mn	0.40	0.23	0.52	0.25	0.29	0.13	0.28	1.00									
Fe	0.91	0.91	0.90	0.91	0.91	0.19	0.97	0.28	1.00								
As	0.84	0.95	0.80	0.95	0.80	−0.06	0.94	0.25	0.89	1.00							
Au	0.88	0.93	0.87	0.93	0.85	−0.02	0.90	0.32	0.87	0.88	1.00						
Cd	0.90	1.00	0.87	1.00	0.88	−0.06	0.95	0.22	0.91	0.96	0.93	1.00					
Sb	0.23	0.12	0.36	0.15	0.13	0.10	0.15	0.85	0.11	0.19	0.30	0.13	1.00				
Bi	0.96	0.85	0.97	0.86	0.98	0.08	0.87	0.37	0.93	0.78	0.84	0.86	0.18	1.00			
Cr	0.19	0.10	0.25	0.10	0.19	0.74	0.39	0.15	0.40	0.22	0.20	0.11	0.18	0.24	1.00		
Ba	0.61	0.60	0.69	0.62	0.54	−0.08	0.55	0.74	0.49	0.58	0.69	0.60	0.77	0.57	0.01	1.00	
B	0.40	0.19	0.39	0.18	0.29	0.35	0.30	0.23	0.30	0.20	0.20	0.20	0.14	0.30	0.50	0.12	1.00

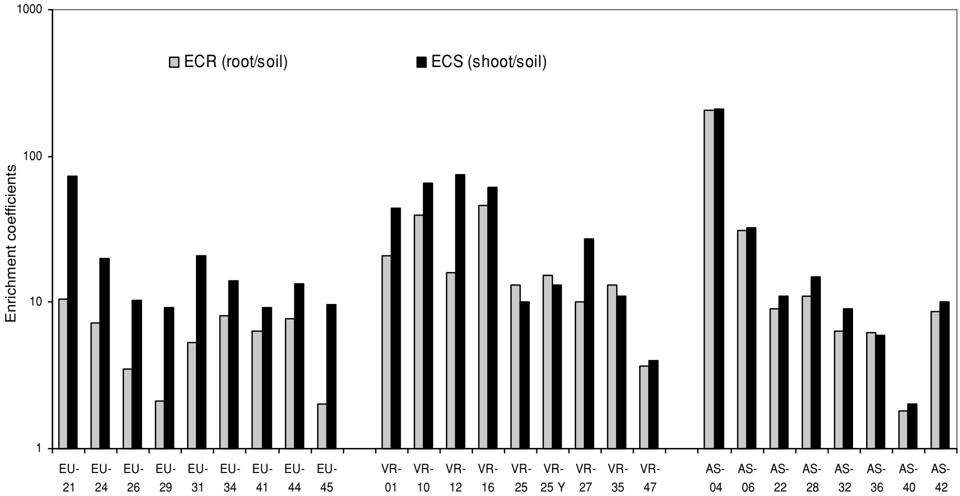

Figure 3 ECR and ECS of *E. macroclada,* VR, and AS.

metal transporter systems (Zhao, Lombi, and McGrath, 2003), and a probable sequestration of metals in leaf vacuoles and apoplast (Lasat *et al*., 2000). Some metals such as Zn have the highest transfer coefficients, which is a reflection of their relatively poor sorption in the soils. In contrast, metals such as Cu, Co, Cr, and Pd have low coefficients because they usually are strongly bound to sediment colloids (Moore and Romanorty, 1984).

V. cheiranthifolium. Boron concentrations in soil, root, and shoot of *V. cheiranthifolium* (VR) plants are given in Figure 2. Mean B values in the soil, root, and shoot for VR were 3.78, 69.78, and 115 mg kg^{-1}, respectively. Boron values of the soil around VR plants were significantly lower than the mean B values in shoot and root of VR and *E. macroclada*. The B values of all VR ranged between 10 and 138 mg kg^{-1} for root, and

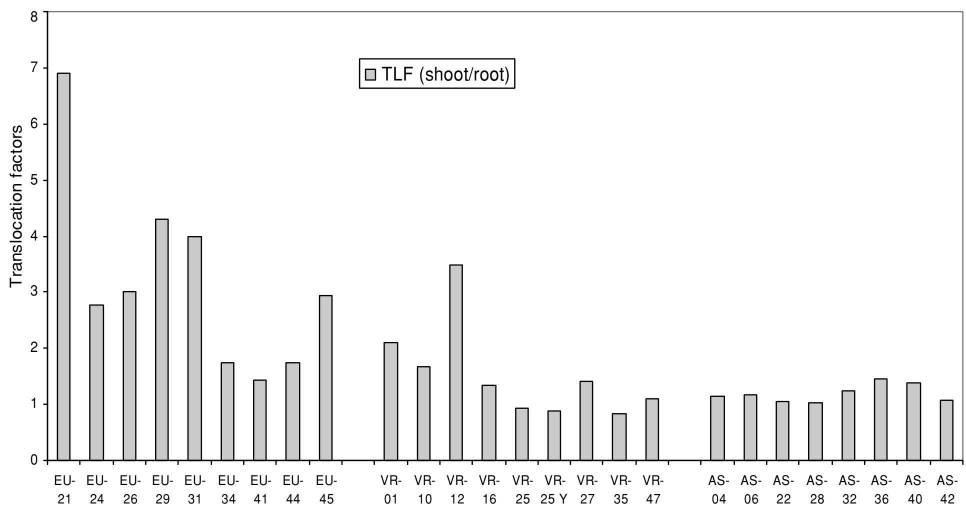

Figure 4 TFs for *E. macroclada,* VR, and AS.

between 14 and 264 mg kg^{-1} for shoot, on a dry weight basis. Boron values in shoots of all VR samples are higher than B values of their roots, except for three samples (Figure 2).

The ECR and ECS of VR for B are shown in Figure 3; mean enrichment coefficient values for root and shoot are 19.67 and 34.44, respectively. ECS is significantly higher than ECR and ECS valuesalso are significantly higher than that for the root. This indicates that B taken up by VR from soil is transferred significantly to shoot and twig, as in *E. macroclada*. The TFs for B in VR range between 0.83 and 3.49 (Figure 4) and all TF values of VR are higher than 1, except for three samples. This result indicates that VR can be a bioaccumulator plant for B in arid and semi-arid environments. Metals such as Zn have the highest transfer coefficients, which is a reflection of their relatively poor sorption in soils. Finally, high TFs of B in VR can display similar behaviors as relatively sorption by plant of Zn as *E. Macroclada*.

***A. gummifer*.** Boron concentrations in soil, root, and shoot of *Astragalus gummifer* were 6.0, 69.38, and 76.88 mg kg^{-1}, respectively (Figure 2). The B values of the soil around *A. gummifer* (AS) were significantly lower than the mean B values in shoot and root of AS, and in all other plants studied. The B values of all AS ranged between 11 and 204 mg kg^{-1} for root, and between 16 and 212 mg kg^{-1} for shoot on a dry weight basis. B values in shoots of all ASsamples were higher than B values of their roots.

The ECR and ECS of AS for B are shown in Figure 3; mean enrichment coefficient values for root and shoot were 34.74 and 37.13, respectively. The TFs for B ranged between 1.03 and 1.45 (Figure 4).

CONCLUSIONS

The B concentrations of roots and shoots of all studied plants were several times higher than B concentrations in their soils, although the mean B concentrations in soils in the study area were very low (mean: 4.97 mg kg^{-1}), This study has shown that for soils with low concentrations of B, *E. macroclada,* VR, and AS plants can be useful as both biomonitors of environmental pollution and biogeochemical indicators because of their high enrichment coefficients and TFs.

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