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# Distribution and Accumulation of Selenium in Wild Plants Growing Naturally in the Gumuskoy (Kutahya) Mining Area, Turkey

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**Abstract** This study investigated selenium uptake and transport from the soil to 12 plant species in the mining area of Gumuskoy (Kutahya), Turkey. Plant samples and their associated soils were collected and analyzed for Se content by ICP-MS. Mean Se values in the soils, roots, and shoots of all plants were 0.9, 0.6, and 0.8 mg $kg^{-1}$, respectively. The mean enrichment coefficients for roots (ECR) and shoots (ECS) of these plants were 0.78 and 0.97. The mean translocation factors (TLF) were 1.33. These values indicate that all 12 plant species had the ability to transfer Se from the roots to the shoot, but that transfer was more efficient in plants with higher ECR and ECS. Therefore, these plants may be useful in phytoremediation in rehabilitating areas contaminated by Se because their ECR, ECS and TLFs are >1.

**Keywords** Selenium uptake · Wild plants · Phytoremediation · Mining area

Selenium is an essential nutrient in many biological systems, where it is present at low concentrations. However, high concentrations of Se are toxic to many organisms, including humans (Ellis and Salt 2003; Dhillon and Dhillon 2009; Pilon-Smits and LeDuc 2009). Although Se has not been demonstrated to be an essential element in vascular plants, a number of plants have the ability to accumulate Se and to transform it into bioactive compounds. Selenium uptake by plants therefore has important implications for human nutrition and health and for the environment (Ellis and Salt 2003). Based on samples taken at different locations, Se concentrations appear to differ by plant species and they also depend on the Se speciation, soil pH, Eh (oxidation potential), soil organic matter content, and Se concentration (Fordyce et al. 2000). Selenium enters the food chain through plants, which take it up from the soil. For environmental studies, plants are particularly useful as biomonitors or as hyperaccumulators for remediation of Se-contaminated soils (Zhu et al. 2008). Primary Se accumulators, such as *Astragalus bisulcatus* L., may contain higher Se concentrations on a dry weight basis, which is a toxic level for livestock (Lyons et al. 2005). In Turkey, many researchers have studied the distribution and speciation of Se and heavy metals in food, drinking and river waters, agricultural soils, and environmental samples (Tuzen et al. 2007; Yilmaz 2007; Somay et al. 2008; Sasmaz 2009). The aim of the present study was to investigate Se uptake and transport from soil to plants by studying the distribution and accumulation of Se in the roots and shoots of 12 wild plant species growing naturally in Se-contaminated surface soils of the Gumuskoy Ag–As mining area in Kütahya, Turkey).

## Materials and Methods

In the present study, the plants and the associated soil samples were collected from an area characterized by polymetallic ore deposits in the Gumuskoy mining district, Kutahya, Western Turkey. The study area is between

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38°96′–39°48′N latitude and 29°48′–29°71′E longitude with an altitude between 1100 and 1320 m above sea level. The chosen plants grow indigenously in the mining area and generally live for 1 or 2 years (annual). The plant species in the Gumuskoy region can grow under severe climate conditions due to their massive and deep-reaching root systems. These systems also give them the ability to live in areas deficient in organic matter. The Se content was measured in 12 plant species: *Alyssum saxatile* L. (AL), *Anchusa arvensis* L. (AN), *Centaurea cyanus* L. (CE), *Carduus nutans* (CR), *Cynoglossum officinale* (CY), *Glaucium flavum* (GL), *Isatis* L. (IS), *Onosma* sp. (ON), *Phlomis* sp. (PH), *Silene compacta* (SL), *Tripleurospermum maritimum* (TR) and *Verbascum thapsus* L. (VR). These plants were chosen because they are native and dominant species in the study area.

Soil depths in the study area vary between 0.3 and 6.0 m. The soils are generally light–dark brown and black in color, with a loamy and peaty clay texture (23.6 % sand, 51.4 % silt and 19.3 % clay). The soil pH varies between 6.4 and 7.2, and with an organic matter content of 2.32 %–6.48 %. An X-ray diffraction study on the clay minerals was not performed. Soil samples were collected from around the roots of the plants at a depth of 30–40 cm. After drying in an oven at 100°C for 4 h and removing rocks, the soil samples were ground using hand mortars. Soil samples were digested in a mixture of $HCl{:}HNO_3{:}H_2O$ (1:1:1, v/v; 6 mL per 1.0 g of soil) for 1 h at 95°C. This treatment dissolved all soil samples except for silicates, and the digests were analyzed using ICP/AES and MS techniques for Se at the ACME Analytic Laboratory, Vancouver, Canada (www.acmelab.com). A Perkin-Elmer ELAN 9000 (CT-USA) inductively coupled plasma mass spectrometer was used for the determination of Se, following the operating conditions recommended by the manufacturer.

Plant samples were randomly collected from sites that were chosen based on representative characteristics of the Gumuskoy mining area. Three samples of shoots and roots were taken from each sampling site. 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, rinsed with distilled water, and dried at 100°C in an oven for 30 min and then at 60°C for 24 h. A chelating EDTA wash was applied, and no differences were observed between the EDTA wash and without using an EDTA wash. The dried plant samples (approximately 2.0–3.0 g) were ashed by heating at 300°C for 24 h. The ashed samples were digested in $HNO_3$ for 1 h, followed by digestion in a mixture of $HCl{:}HNO_3{:}\ H_2O$ (1:1:1, v/v; 6 mL per 1.0 g of the ashed sample) for 1 h at 95°C. The digests were analyzed using ICP/AES and MS techniques for Se and the plant concentrations were calculated on a dry matter basis.

The enrichment coefficient 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). The enrichment coefficient was also calculated for shoots (ECS) (concentration in mg $kg^{-1}$ of the plant shoot divided by the concentration in mg $kg^{-1}$ of soil). The ECS is a very important factor, as it indicates the capacity of a given species for phytoremediation (Zhao et al. 2003) and this value is also used as an index to characterize the transfer of elements from the soil to the plant shoot (Baker et al. 1994; Brown et al. 1994; Wei et al. 2002). Translocation factors (TLF) are obtained by calculating the ratio of metal in the plant shoot to that in the plant roots (concentration in mg $kg^{-1}$ of the plant shoot divided by the concentration in mg $kg^{-1}$ of the root). In a metal accumulator species, a translocation factor >1 is common, whereas in metal excluder species, TLF are typically lower than 1 (Zu et al. 2005). Statistical analysis of data was carried out using Analysis of Variance (ANOVA) and Student Newman Keul's Procedure (SNK) (Sokal and Rohlf 1995) on a SPSS 15.0 software (IBM Corp., Armonk, NY, USA). The heavy metal results belong to soil samples of the study area were correlated with Se by using Spearman Rank correlation.

## Results and Discussion

The Se contents of the soil samples in the Gumuskoy study area were found to be between 0.2 and 2.3 mg $kg^{-1}$ (mean 0.90 mg $kg^{-1}$). Among all forty-one soil samples, Se concentrations were found to be 2.4 times higher than those reported for surface soils in different countries (mean 0.38 mg $kg^{-1}$; Kabata-Pendias and Pendias 2001). Kabata-Pendias and Pendias (2001) reported a range of Se concentrations for most soil analyses between 0.01 and 2 mg $kg^{-1}$. In England, total Se in soils ranged from 0.1 to 4 mg $kg^{-1}$ (Hawkesford and Zhao 2007). The total Se content in Se-contaminated soils of northwestern India varied from 0.023 to 4.91 mg $kg^{-1}$ (Dhillon and Dhillon 2014), whereas, in soils from the Keban Pb–Zn mining area, Turkey, Se content ranged between 0.1 and 6.5 mg $kg^{-1}$ (mean 1.35 mg $kg^{-1}$) (Sasmaz 2009).

In the Gumuskoy mining area and its surroundings, tufite and aglomerate of rhyolitic and dacitic composition are widespread. As these rocks are of acidic composition, they exhibit higher silica and much higher Se content than other rocks (Kabata-Pendias and Pendias 2001). The obtained results in this study showed that higher Se concentration in acidic rocks ($p < 0.5$) can also be related to the Ag, As, and Pb deposits of the Gumuskoy region, because the presence of Se showed a high linear Spearman's correlation coefficient with the occurrence of some heavy metals

(Table 1). Strong linear correlations (r = 0.40–0.76) were observed between Se and the heavy metals Cu, Pb, Zn, Mn, Cd and Ag, whereas weak linear correlations (r = 0.04–0.29) were observed between Se and the heavy metals As, Sb, Hg, Ba, Tl and U (Table 1).

The correlation (y = 0.728x) between the plant shoot and soil was higher than the correlation (y = 0.542x) between the plant roots and soil ($p < 0.5$). These correlations indicate that more soil Se was transported to the shoot than to the roots. The mechanisms for absorption and transport of Se differed among plants in the study area. The variations in Se content in different plants and plant tissue might be genetically controlled by the plant genotype (Li and Cao 2006). A similar linear relationship between Se concentrations of soils and plants from the Dukpyung area, Korea was suggested by Park et al. (2010). Correlation analysis for plant Se and soil properties have revealed a positive correlation between plant Se and clay phosphorus contents. Some soil characteristics may therefore possibly enhance or hinder plant Se uptake. Plants also differ in their ability to accumulate Se; selenium does not appear to be an essential element in all plants, except for Se accumulator species (Terry et al. 2000). The highest Se concentration in all analyzed soils was 2.3 mg kg$^{-1}$ in the AL-04 and ON-02 samples (Fig. 1), which were collected from a mineralized area.

In the soils of the Gumuskoy study area, the maximum concentration of Se was vertically accumulated at the surface or at depths close to surface. Similar values at the seleniferous sites are present in the soil profile up to 2 m depth; the surface layer is rich in Se containing 1.5–6.0 times more Se in comparison to the lower layers (Dhillon and Dhillon 2009). Soils with the maximum Se concentration were generally brown and dark in color containing more clay and organic matter. The Se content decreased sharply with increasing depth of soil profile, where the soils were generally light brown in color and contained more sand and rock, and less organic matter.

In the Gumuskoy mining area, 12 plant species were selected for determination of Se contents. The chosen plants grow indigenously in the mining area and generally live for 1 or 2 years (annual). The Se contents of plants in the study area varied considerably, but the average Se concentrations for plant roots and shoots were 0.6 and 0.7 mg kg$^{-1}$, respectively. However, Se concentrations of forty-one plant samples ranged from a minimum of 0.1 mg kg$^{-1}$ for both plant roots and shoots to a maximum of 1.8 and 4.7 mg kg$^{-1}$ for plant roots and shoots, respectively (see Fig. 1).

The mean Se values in the soil and roots and shoots of the *A. saxatile* (AL), were 1.12, 0.52, and 0.50 mg kg$^{-1}$, respectively. The Se levels in the soil around AL plants were significantly higher than the mean Se values in AL shoots and roots ($p < 0.5$). The Se levels for all AL samples ranged between 0.30 and 0.60 mg kg$^{-1}$ for roots, and between 0.40 and 0.60 mg kg$^{-1}$ for shoots on a dry weight basis (Fig. 1). These Se concentrations in AL plants were also higher than the Se concentrations previously reported for different plants (0.02 mg kg$^{-1}$; Pais and Jones 2000). The Se enrichment coefficients (ECR and ECS) for AL roots and shoots are shown in Fig. 2, with the mean ECR and ECS values 0.57 and 0.45 respectively. TLFs for Se in AL were between 0.67 and 1.33 (mean 1.00) in this study, which indicates that Se was only weakly transferred to the shoot following uptake from the soil to root.

Selenium concentrations in the soil and roots and shoots of the *A. arvensis* (AN) are given in Fig. 2. Mean Se values in the soil, roots, and shoots for AN were similar, at 0.40, 0.40, and 0.35 mg kg$^{-1}$, respectively, on a dry weight basis (Fig. 1). The enrichment coefficients (ECR and ECS) for Se in the roots and shoots gave mean values of 1.33 and 1.08, respectively (Fig. 2), indicating that Se taken up from the soil by AN was transferred to the root. The TLFs of AN ranged between 0.75 and 1.0 (mean 0.88) (Fig. 2); which meant that all AN TLF were lower than or equal to 1. This result indicates that AN could serve as a Se bioaccumulator plant in semi-arid environments or continental climates.

The mean Se concentrations in the soil and roots and shoots of the *Centaurea cyanus* (CE) were 1.07, 1.03 and 1.03 mg kg$^{-1}$, respectively (Fig. 1). The mean Se values in the shoots of two CE samples were higher than the mean Se values in the roots ($p < 0.5$), except for in one sample. However, the mean values for the soil and, roots, and shoots of all samples were similar to each other. Therefore, both the enrichment coefficients for roots and shoots and TLF were higher than 1 for two samples, except for one sample. The CE TLFs for Se ranged between 0.83 and 1.33 (mean 1.10) (Fig. 2). This value indicates that CE can be a

**Table 1** Spearman's correlation coefficients between Se and heavy metals in soils of the Gumuskoy mining area

| | Cu | Pb | Zn | Ag | Mn | As | U | Sr | Cd | Sb |
|---|---|---|---|---|---|---|---|---|---|---|
| Se | 0.73 | 0.72 | 0.76 | 0.40 | 0.67 | 0.29 | 0.08 | −0.02 | 0.76 | 0.25 |
| | Ca | P | Ba | Tl | Hg | Na | K | Sc | Tl | Fe |
| Se | 0.12 | 0.06 | 0.14 | 0.11 | 0.04 | 0.02 | 0.02 | −0.12 | 0.11 | 0.75 |

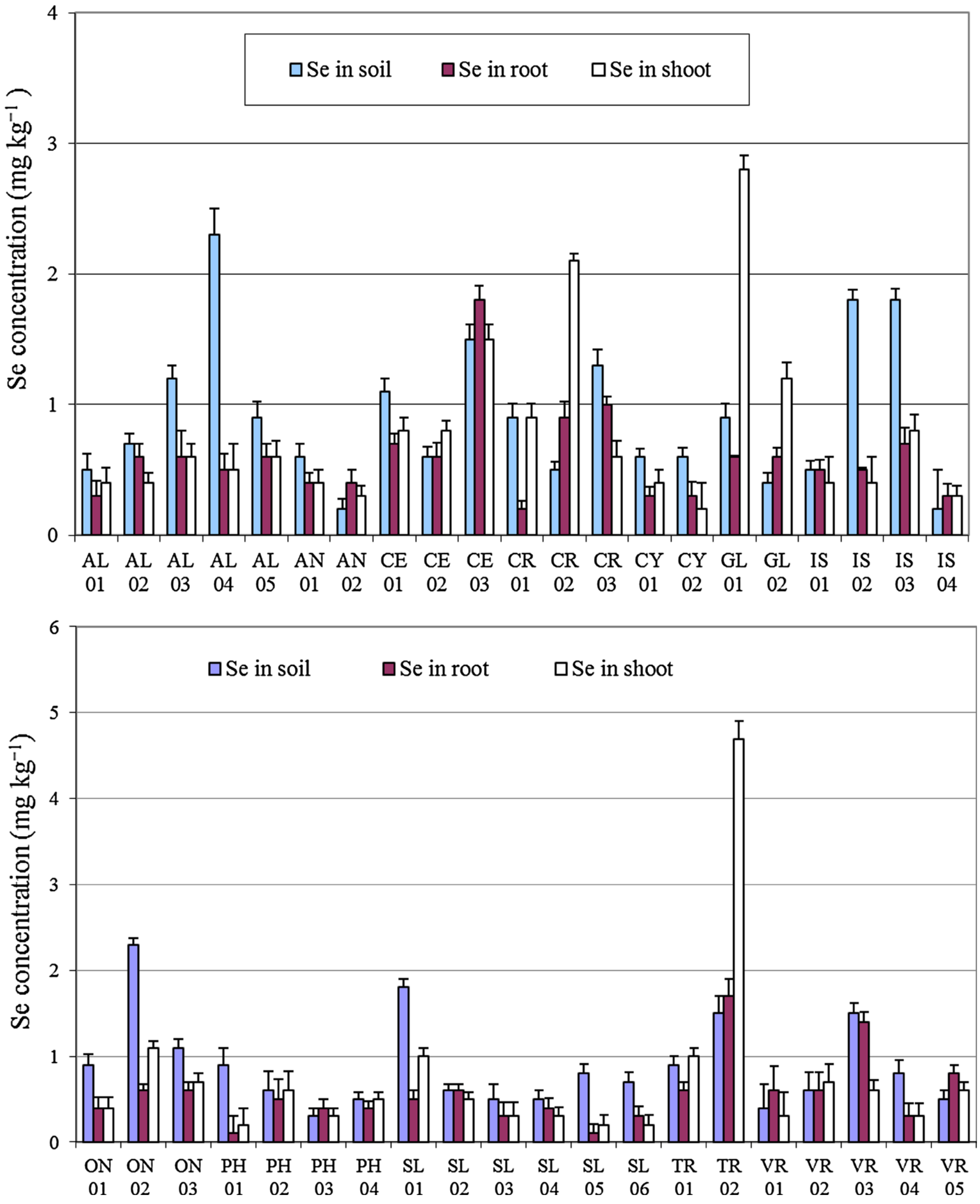

**Fig. 1** The Se concentrations of soils, roots and shoots of 12 plant species (AL, *Alyssum saxatile*; AN, *Anchusa arvensis*; CE, *Centaurea cyanus*; CR, *Carduus nutans*; CY, *Cynoglossum officinale*; GL, *Glaucium flavum*; IS, *Isatis* L.; ON, *Onosma* sp.; PH, *Phlomis* sp.; SL, *Silene compacta*; TR, *Tripleurospermum maritimum*; VR, *Verbascum thapsus* L.)

very good bioaccumulator plant for Se when growing in a similar environment and climate to our sampling site. It can be used to clean or rehabilitate soil and areas contaminated by Se.

The mean Se values of the *Carduus nutans* (CR) soil and, roots and shoots were 0.90, 0.70, and 1.20 mg kg$^{-1}$, respectively. The Se values in the soil surrounding CR plants were significantly higher than the mean Se values in the CR roots, but lower than the mean Se values in the CR shoots. The maximum Se concentration, at 2.1 mg kg$^{-1}$ (Fig. 1), was found in shoots of the *Carduss nutans* (sample CR-02). The mean ECR, ECS, and TLF for Se in CR plants were 0.93, 1.89, and 2.48, respectively (Fig. 2). The ECS and TLF of this plant were higher than 1 and ECR was close to 1. This indicates that Se is transferred to the shoot after CR takes up Se from the soil into root. The high ECS and TLF values indicate that CR could be a very good Se bioaccumulator plant.

The mean Se concentrations in the soil and, roots and shoots of the *Cynoglossum officinale* (CY) were 0.60, 0.30, and 0.30 mg kg$^{-1}$, respectively. The Se values in the soil were higher than in the CY roots and shoots. The ECR and ECS values for CY were lower than 1, but the mean TLF value was 1. Consequently, Se is weakly transferred from the soil to CY roots and shoots (Fig. 2).

The mean Se concentrations in the soil and, roots, and shoots of the *Glaucium flavum* (GL) were 0.65, 0.60, and 2.0 mg kg$^{-1}$, respectively (Fig. 1). The Se values for GL shoots were 2–3 times higher than the values for roots or soil ($p < 0.5$). The ECR, ECS, and TLF values for GL

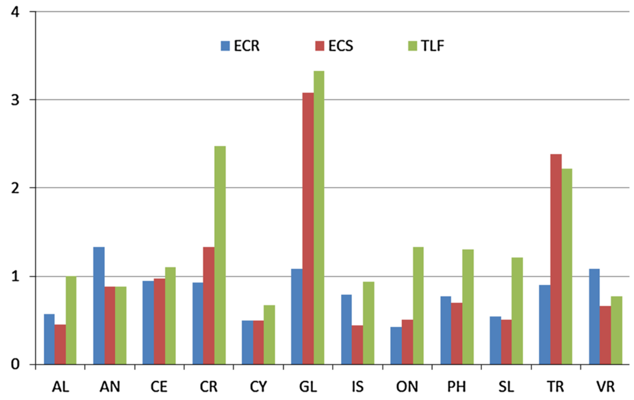

**Fig. 2** Mean translocation factors (TLF) and enrichment coefficients for roots (ECR) and shoots (ECS) of plant species in the study (AL, *Alyssum saxatile*; AN, *Anchusa arvensis*; CE, *Centaurea cyanus*; CR, *Carduus nutans*; CY, *Cynoglossum officinale*; GL, *Glaucium flavum*; IS, *Isatis* L.; ON, *Onosma* sp.; PH, *Phlomis* sp.; SL, *Silene compacta*; TR, *Tripleurospermum maritimum*; VR, *Verbascum thapsus* L.)

(mean = 1.08, 3.06, and 3.33 respectively) were higher than 1 (Fig. 2). The TLF of the GL-01 sample was very high (4.67), indicating that significant amounts of Se are transferred to the shoot after GL takes up Se from the soil into the root. The high ECS and TLF values indicate that GL could be a very good Se bioaccumulator/hyperaccumulator.

The Se content of the soil and, roots, and shoots were analyzed in four samples of the *Isatis* (IS), containing an average of 1.08, 0.50, and 0.48 mg Se kg$^{-1}$, respectively. The Se concentrations in IS shoots and roots were substantially lower than the Se concentrations in soil, except for the IS-04 sample. The mean ECR, ECS, and TLF values for IS were 0.79, 0.74 and 0.94, respectively (Fig. 2). The low ECR, ECS, and TLF values indicate that IS would not be a very good Se bioaccumulator.

The mean Se concentrations in the soil and, roots, and shoots of the *Onosma* (ON) were 1.43, 0.53, and 0.73 mg kg$^{-1}$, respectively (Fig. 2). The Se values in the shoots of three ON samples were higher than the Se values in the roots, but lower than the Se values in the soils. Therefore, the ECR and ECS values for ON are lower than 1, but the TLF values are higher than 1. These values indicate that the ON root does not accumulate Se from the soil, but it efficiently transfers SE to the shoot.

The Se contents of the soil and, roots, and shoots of the *Phlomis* (PH) were examined in four samples. The mean Se concentration of the soil, roots, and shoots were 0.58, 0.35, and 0.40 mg kg$^{-1}$, respectively. The Se concentrations in shoots and roots of PH were lower than the Se concentrations in the soil. The mean ECR, ECS, and TLF values for PH were 0.77, 0.81, and 1.30, respectively. The low ECR and ECS values indicate that PH would be ineffective at cleaning or rehabilitating the soils in areas contaminated by Se.

The mean Se concentrations in the soil and, roots, and shoots of the *Silene compacta* (SL) were 0.82, 0.37, and 0.42 mg kg$^{-1}$, respectively (Fig. 1). The Se values in the soil were higher than in SL roots and shoots. The mean ECR and ECS values for this plant were lower than 1. The TLF of SL was generally higher than 1 (mean 1.21), except for three samples. This means that Se was not transferred from the soil to the root or the shoot by this plant (Fig. 2). This indicates that SL cannot act as a Se bioaccumulator plant.

The Se contents of the soil and, roots, and shoots were investigated in two samples of *Tripleurospermum maritimum* (TM), containing an average of 1.20, 1.15, and 2.85 mg Se kg$^{-1}$, respectively. The Se concentrations in TM shoots were higher than those in the soil or the shoot. The Se values in the shoot of the TR-02 sample were three times higher than those found in the soil (Fig. 1). The mean ECR, ECS, and TLF values for TM were 0.90, 2.12, and 2.22, respectively (Fig. 2). These high ECR, ECS and TLF values indicate that TM could be a very good Se bioaccumulator/hyperaccumulator plant.

The Se contents of five samples of *Verbascum thapsus* (VR) were analyzed. The mean Se concentrations in the soil and, roots, and shoots of VR were 0.76, 0.74, and 0.50 mg kg$^{-1}$, respectively. The Se concentrations in VR shoots and roots were generally lower than the Se concentrations in soil, except for one root sample (VR-01) and one shoot sample (VR-05). Plant samples from VR-02 and VR-05 indicate an especially strong Se accumulation (Fig. 2). The mean ECR, ECS and TLF values for VR were 1.08, 0.78, and 0.77, respectively (Fig. 2). The ECS and TLF values close to 1 indicate that VR could be useful for cleaning or rehabilitating the soils and areas contaminated by Se.

Our study shows that the best bioaccumulator plant is GL, TR, CR, the mid-bioaccumulator plant is AN, CE, PH and VR, the worst plant for taking up Se is AL, CY, IS, ON, SL. Therefore the best plant from our study for cleaning and/or rehabilitating soils is GL, TR and CR. Plantings of this species could be used both rehabilitating or cleaning areas contaminated by Se and biomonitoring of environmental pollution.

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