

## The phytoremediation of manganese in Gumuskoy (Kutahya, Türkiye) mining soils by the native plants

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### ABSTRACT

Manganese (Mn) is one of the most critical elements in the environment and is expected to become an even more important metal in the future due to its widespread use. This study examined the Mn uptake and translocation in 11 different plant species growing in mining soils in Gümüşköy, Türkiye. Plants were washed, dried, and burned at 300 °C for 24 h in a drying oven. The Mn contents in plant samples and soil taken from the mining area were analyzed using an inductively coupled plasma mass spectrometer (ICP-MS). Average Mn concentrations in the shoots, roots, and soil of these plants were 1.037, 1.153 and 2.063 ppm, respectively. Based on their ECS and ECR values, *Anchusa arvensis*, *Verbascum thapsus*, *Silene compacta*, *Phlomis* sp. and *Glaucium flavum*, were the best accumulators (ECR and ECS > 1). *Onosma* sp. was a good accumulator (ECR and ECS are close to 1), and *Alyssum saxatile*, *Centaurea cyanus*, *Carduus nutans*, *Cynoglossum officinale*, and *Isatis* were less effective accumulators (ECR and ECS < 1). Those plants with ECR/ECS > 1 should be subjected to further studies involving the phytoremediation of Mn-polluted soils.

**Keywords:** mining area, accumulation, enrichment coefficient, ICP-MS.

### INTRODUCTION

Among trace elements in the continental crust, Mn is one of the most prevalent. The usual range found in rocks is between 350 and 2.000 ppm, with mafic rocks having the highest amounts (Kabata-Pendias, 2011). As a members of the iron family, Mn and other metals are intimately related to geochemical conditions (Sasmaz et al., 2020, 2021). Pyrolusite, manganite, hausmannite, and rhodochrosite are the most prevalent minerals containing Mn (Peng et al., 2008). Mn in superficial environments is oxidized by air during weathering, and the resulting Mn oxides are easily condensed into secondary Mn mineral formations, which frequently occur in the form of concretions and nodules. The redox states of Mn are changeable, ranging to +7 from +2, and is influenced by both biological and geochemical activities. The most prevalent cation is Mn<sup>2+</sup>, which easily takes the place of other divalent cations (such Fe<sup>2+</sup> and Mg<sup>2+</sup>). Numerous oxides and hydroxides with varying stability

and characteristics have been formed as a result of Mn's complicated chemical and mineralogical behavior, as well as its involvement in oxidation-reduction processes (Kabata-Pendias, 2011). Due to their persistent qualities and bioaccumulation in plants and animals, heavy metals are a significant environmental problems (Khan et al., 2014; Iqbal, 2016; Iqbal et al., 2016; Mani et al., 2016).

The list of heavy metals that can be eliminated by various plants includes: Mn, Sb, Tl, Hg, Th, Cd, U, As, Ni, Cu, Co, Cr, Zn, Pb, Ag, and Sr. These heavy metals contaminate surface soils and water in mining sites (USEPA, 2000; Wong, 2003). The maximum accumulation concentration value of Mn in agricultural soils is between 1.5 and 3.0 ppm (USEPA, 2000); however, it has not been deemed a polluting metal in soils. Sludge from sewage systems, metal smelting operations, and municipal wastewaters are the main sources of Mn. To properly nourish plants, growth media must include sufficient amounts of accessible Mn. According to Skinner et al. (2005), the metal is

transported in the reduced  $Mn^{2+}$  state across the soil- root interface, which is presumably comparable to the transport of other divalent cation species. However, Mn is also likely to be absorbed passively, particularly in high and hazardous quantities in the soil solution (Wei et al., 2023). Since Mn is generally known to be quickly absorbed and transported inside plants, it is unlikely that Mn is attaching to insoluble organic ligands in either the xylem fluid or root tissue (Kabata-Pendias, 2011). Among different plants growing on the similar soil, Mn varies widely, being found at levels over 500 ppm in *Lupinus albus* but reaching an average of only 30 ppm in *Medicago trunculata* (Kabata-Pendias, 2011). Globally, grasses contain 17–334 ppm of Mn, while clover contains 25–119 ppm. Significant changes can be seen in the Mn content between different plant species, growth stages, organ types, and habitats. The typical Mn concentration of cereal grains is between 18 to 48 ppm worldwide (Kabata-Pendias, 2011).

Phytoremediation is the cheapest heavy metal removal method for both water and soil compared to other technologic methods (Liu et al., 2008; Yoon et al., 2006; Sasmaz et al., 2008; Sasmaz et al., 2015; Ansari et al., 2015; Konakci et al., 2023; Sasmaz et al., 2024; Kilic et al., 2024). While numerous studies have been conducted on heavy metal uptake using terrestrial plants, there are limited studies on Mn accumulation. These plants were chosen because they are the most common plants growing naturally in the region. As a result, the main aim of this research was to study accumulation and uptake of Mn from the soil to the shoots and roots of 11 native plant species growing in Mn-polluted areas. The objective is to determine whether these plants, in the Gümüşköy mining area, can be used in rehabilitation of Mn-contaminated soils.

## MATERIALS AND METHODS

### The sampling area

The research region was situated approximately 25 km west of Kütahya, Türkiye, between 29° 48–29° 71 E longitude and 38° 96–39° 48 N latitude, where both continental and moderate climates can be found. The summer is hot and dry, whereas the winter is cold and rainy. Overall the area has an average temperature of 10.5 °C. Kütahya's forests cover a sizable portion of the city's

surroundings and are valuable economically due to the abundance of herbal plants and endemic trees. The Gümüşköy mine area is Türkiye's largest silver deposit (Yildirim and Sasmaz, 2017), and soil and plant samples were collected from this area (Fig. 1). Due to a lengthy mining history, Arik (2002a,b) and Arik and Yaldiz (2010) found that Gümüşköy and the surrounding regions have been heavily contaminated by both ancient and current mining operations involving Cu, Ag, Au, Pb, Zn, Sb and Ba (Yavuz et al., 2002; Kartalkanat 2008; Sasmaz et al. 2005; Ünal and Gokce, 2007; Kilic and Cakmak, 2021; Sasmaz et al., 2017; Azizi et al., 2017; Sinanoglu and Sasmaz, 2019; Konakci et al., 2023, Sasmaz, 2020; Konakci and Sasmaz, 2021). Samples were collected at random from the mining district between July and May of 2022 from 39 separate locations and depths between 0.10 and 0.40 meters below the surface because different plants have different root lengths (Table 1). In addition to these plant samples, a soil sample was also taken from around the root of each plant in Table 1. Therefore, in total, 39 soil, 39 root and 39 shoot samples were collected from the study area. A total of 11 native species that grew in and around the study area were examined for Mn concentrations: *Verbascum thapsus* (VR), *Carduus nutans* (CR), *Isatis* sp. (IS), *Anchusa arvensis* (AN), *Phlomis* sp. (PH), *Cynoglossum officinale* (CY), *Centaurea cyanus* (CE), *Silene compacta* (SL), *Onosma* sp. (ON), *Glaucium flavum* (GL) and *Alyssum saxatile* (AL). Plants in the study area are divided into groups according to their ECR and ECS values: the best (ECR and ECS > 1), good accumulator (ECR and ECS are close to 1) and less effective accumulator plants (ECR and ECS < 1).

### Plant and soilspecimens

Following an oven-dried process at 100 °C, the soil samples were placed in a solution of  $HNO_3$ ,  $H_2O$ , and HCl (Merck, Darmstadt, Germany) for one hour at 95 °C. The plant's root and shoot sections were properly cleaned in tap water, dried at 60 °C, and then ashed at 300 °C for a full day. The washed plants were combined with  $H_2O$ , HCl, and  $HNO_3$  (1:1:1, v/v; 6 ml per 1.0 g of sample) (Merck, Darmstadt, Germany) after being digested in  $HNO_3$  for an hour at 95 °C. The digest was analyzed by ICP-MS for Mn. Using an ICP-MS Perkin Elmer Elan 9000, Mn was measured using  $^{115}In$  and  $^{88}Mn$ . For the soils,

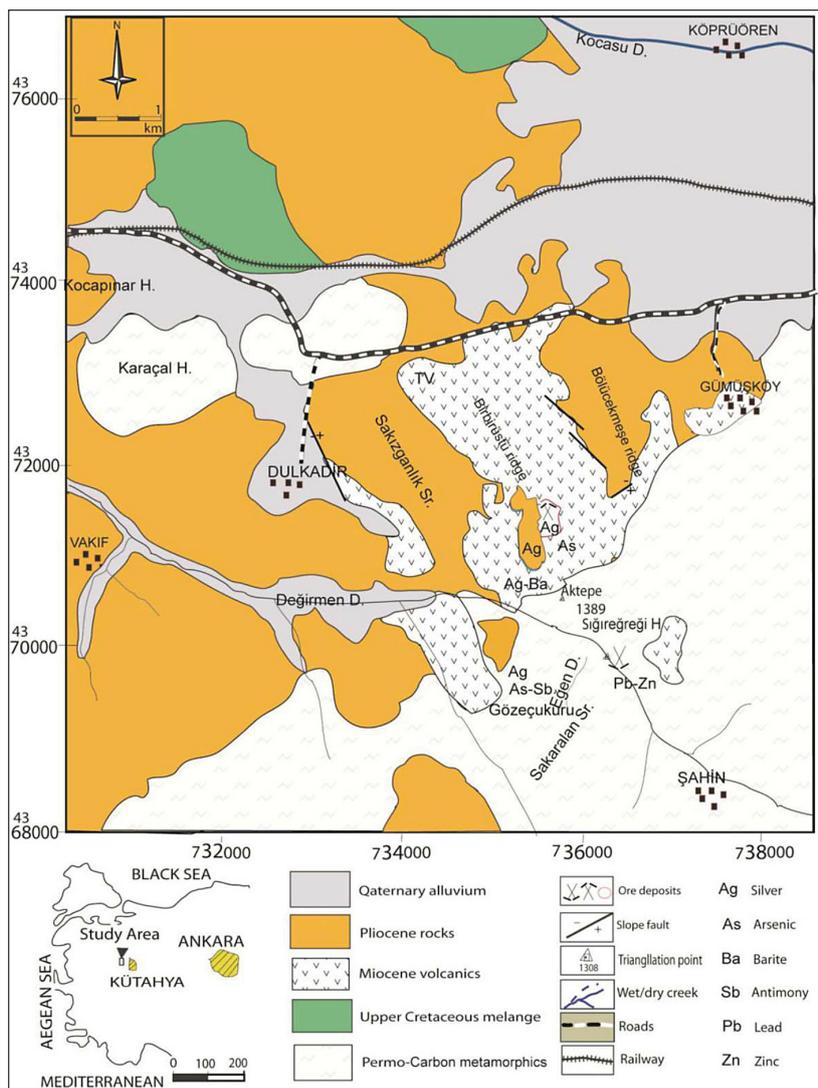


Figure 1. Location and geological map of the study area (Arik, 2002)

the laboratory used certified reference material CDV-1 and for plants V16.

### Enrichment coefficients for roots

The calculation of the enrichment coefficients for roots (ECR) involved dividing the soil concentration of the plant roots for every individual plant. According to Chen et al. (2005), this coefficient is a measure of the quantity of metal that has accumulated in plant roots from the soil. As reported by Wei et al. (2002), the ECR of metal excluder plants is  $< 1$ ; however, the ECR of hyperaccumulator plants is  $> 1$ .

### Enrichment coefficients for shoots

By dividing the soil values of the plant shoot values for each plant, the enrichment coefficients for

the shoots (ECS) were determined. Each plant's capacity for accumulation is represented by this coefficient (Zu et al. 2005). For similar investigations, this value is crucial since it illustrates the metal's capacity to accumulate in the shoot from the soil. Thus, a plant's capacity to absorb and store energy is defined by the ECS. Hyperaccumulator plants have an ECS larger than 1, whereas metal excluder plants have an ECS less than 1 (Wei et al., 2002; Sasmaz et al., 2021).

### Translocation factor

The metal ratio that is transferred from the plant roots to the shoot is known as the translocation factor (TLF). This variable shows the ability of the plant to move metal from its roots to its shoots (Zu et al., 2005). For investigations into phytoremediation, this value which indicates that

the metals can be transferred from the root to the shoot without accumulating is crucial (Sasmaz et al., 2021). The TLF is generally greater than 1 in hyperaccumulator plants.

### Analytical statistics

Using SAS (SAS Institute, Cary, NC), the data were connected to an ANOVA variance analysis with a p-value of 0.05 in every test. Using the Spearman rank correlation, the Mn levels in the Gümüşköy mining soils were associated with those of other metals. Also provided are the arithmetic means and median values for the Mn concentrations in the soil and plant sections.

## RESULTS AND DISCUSSION

### Manganese in soil

The Mn values in the studied soils were found between 110 and 10.868 ppm (mean:  $2.080 \pm 134$  ppm) (Table 1; Fig. 2). The results showed that the high Mn concentrations of these rocks were connected to hydrothermal mineralization (Ag, Pb, As, Zn and Sb) in this region due to high positive correlation values between the metals. Strong positive correlation relations were seen among Mn-Cu, Mn-Pb, Mn-Zn, Mn-Fe, Mn-Se and Mn-Cd, whereas weak negative relations were observed among Mn-P, Mn-U and Mn-Tl (Table 2).

### Manganese in plants

The average Mn values of the roots and shoots in the study area were  $1.153 \pm 44$  and  $1.037 \pm 52$  ppm, respectively. Therefore, the maximum and minimum levels of Mn in the studied plants were 85 and 4981 ppm in the shoots and, 101 and 11,244 ppm in the roots respectively.

The mean *A. saxatile* (AL) soil, root, and shoot values for Mn were, respectively, 5.813, 3.667, and 2.435 ppm (Table 1; Fig. 2). The Mn values in soils were higher than the shoot and root values, with the respective maximum and minimum. Mn values of AL ranging between 558 and 4,981 ppm for the shoots, and 938 and 11,244 ppm for the roots. As reported by Pais and Jones (2000), these values were much higher than the Mn levels of the reference plant (200 ppm). The ECR and ECS of Mn for AL were found to be 1.08 and 0.64, respectively. Their TLFs for Mn varied from 0.41

to 1.65 (mean: 0.82). These values show that AL's roots are good plant for the uptake of Mn, because the ECR was higher than 1. However, the average ECS (0.64) was lower than 1 and therefore it is not a good plant in terms of Mn accumulation.

The average Mn concentrations in soil, roots, and shoots of *A. arvensis* (AN) were 520, 911, and 620 ppm, respectively (Table 1; Fig. 2). The mean levels of ECR and ECS for Mn were 1.98 and 1.29, respectively. AN's TLF was between 0.73 and 0.65 (mean: 0.69) (Table 1; Fig. 2). These levels show that AN can very effectively accumulate Mn due to higher ECR and ECS values greater than 1.

The mean soil, root, and shoot concentrations of *C. cyanus* (CE) were 4.509, 928, and 1.616 ppm, respectively (Table 1; Fig. 2). The mean level of soils for Mn is higher than the means of root and shoot ( $p < 0.05$ ). The ECR and ECS values are lower than 1. These values show that *C. cyanus* cannot use in the rehabilitation studies of Mn due to lower ECS than 1 (Table 1; Fig. 3).

The mean *C. nutans* (CR)'s shoots, roots and soil levels for Mn are, respectively, 582, 379 and 1.535 ppm. The average Mn levels of CR's shoots and roots were lower than that in the soil. The average TLF, ECS, and ECR of CR for Mn were 1.79, 0.43, and 0.30, respectively (Table 1; Fig. 3). These data show that CR cannot be useful for Mn uptake because of an ECR and ECS lower than 1.

The average shoot, root and soil concentrations of *C. officinale* (CY) for Mn were 815, 195 and 1.094 ppm, respectively. The average Mn values of the soils were higher than those of CY's shoot and root. The average values of CY's ECR, ECS, and TLFs were 0.17, 0.65, and 3.57, respectively. These results show that shoot of CY cannot be considered good bioaccumulator of Mn due to an ECS and ECR lower than 1.

*G. flavum*'s (GL) mean soil, roots, and shoot values for Mn were 178, 222, and 247 ppm, respectively. The average ECR, ECS, and TLF values were respectively, 1.27, 1.40, and 1.11 (Fig. 3; Table 1). These values indicate that *G. flavum* is a good plant with respect to removing of Mn in polluted regions.

The mean concentrations of soil, root, and shoot of *Isatis* (IS) for Mn were 1.318, 214, and 159 ppm, respectively (Table 1; Fig. 2). The Mn concentrations in soil of IS were higher than those in the roots and shoots. The mean ECR, ECS, and TLFs of IS for Mn were 0.65, 0.38, and 0.83, respectively. These values show that *Isatis* is not an

**Table 1.** Mn concentrations (ppm) of soils, roots and shoots of 11 plant species and ECR, ECS and TLF values for Mn

Parameter	Root depth (m)	Mn in soil	Mn in root	Mn in shoot	ECR	ECS	TLF
AL-01	0.10-0.15	870±56	980±62	558±34	1.13	0.64	0.57
AL-02	0.10-0.15	775±45	2.159±122	1.180±98	2.79	1.52	0.55
AL-03	0.10-0.15	10.868±563	11.244±665	4.571±112	1.03	0.42	0.41
AL-04	0.10-0.15	5.886±220	938±44	885±35	0.16	0.15	0.94
AL-05	0.10-0.15	10.664±355	3.016±187	4.981±224	0.28	0.47	1.65
Average		5813	3667	2435	1.08	0.64	0.82
AN-01	0.10-0.12	467±28	684±36	500±45	1.46	1.07	0.73
AN-02	0.10-0.12	573±39	1.137±122	740±46	1.98	1.29	0.65
Average		520	911	620	1.72	1.18	0.69
CE-01	0.14-0.18	1.896±428	1.261±88	984±62	0.67	0.52	0.78
CE-02	0.14-0.18	977±54	178±15	165±11	0.18	0.17	0.93
CE-03	0.14-0.18	10.654±546	1.346±78	3.700±166	0.13	0.35	2.75
Average		4509	928	1616	0.32	0.35	1.49
CR-01	0.10-0.20	1.190±78	271±19	683±41	0.23	0.57	2.52
CR-02	0.10-0.20	1.085±42	595±28	532±26	0.55	0.49	0.89
CR-03	0.10-0.20	2.330±118	271±22	532±38	0.12	0.23	1.96
Average		1535	379	582	0.3	0.43	1.79
CY-01	0.10-0.14	1.386±98	268±16	1.390±82	0.19	1	5.19
CY-02	0.10-0.14	801±53	122±11	239±16	0.15	0.3	1.96
Average		1094	195	815	0.17	0.65	3.57
GL-01	0.10-0.12	141±12	194	206	1.38	1.46	1.06
GL-02	0.10-0.12	214±15	249±26	287±14	1.16	1.34	1.15
Average		178	222	247	1.27	1.4	1.11
IS- 01	0.15-0.20	865±52	193±16	147±12	0.22	0.17	0.76
IS 02	0.15-0.20	1.150±68	101±8	101±6	0.09	0.09	1
IS- 03	0.15-0.20	3.083±168	172±14	179±12	0.06	0.06	1.04
IS- 04	0.15-0.20	175±11	389±19	209±15	2.22	1.2	0.54
Average		1318	214	159	0.65	0.38	0.83
ON-01	0.12-0.22	1.135±58	1.514±66	1.290±92	1.33	1.14	0.85
ON-02	0.12-0.22	5.886±224	1.406±78	3.416±155	0.24	0.58	2.43
ON-03	0.12-0.22	1.870±142	1.893±143	2.266±166	1.01	1.21	1.2
Average		2964	1604	2324	0.86	0.98	1.49
PH-01	0.15-0.25	1.486±64	197±18	85±6	0.13	0.06	0.43
PH-02	0.15-0.25	665±42	794±38	755±65	1.19	1.14	0.95
PH-03	0.15-0.25	844±52	1.918±85	1.104±52	2.27	1.31	0.58
PH-04	0.15-0.25	970±88	1.131±46	1.156±76	1.17	1.19	1.02
Average		991	1010	775	1.19	0.92	0.75
SL-01	0.10-0.14	235±14	208±13	286±18	0.89	1.22	1.38
SL-02	0.10-0.14	315±17	294±19	353±22	0.93	1.12	1.2
SL-03	0.10-0.14	466±28	1.023±56	893±71	2.2	1.92	0.87
SL-04	0.10-0.14	209±15	224±12	288±17	1.07	1.38	1.29
SL-05	0.10-0.14	462±28	1.468±55	1.483±62	3.18	3.21	1.01
SL-06	0.10-0.14	312±14	611±42	530±41	1.96	1.7	0.87
Average		333	638	639	1.7	1.76	1.1
VR-01	0.25-0.40	954±56	1.158±64	1.869±138	1.21	1.96	1.61
VR-02	0.25-0.40	761±42	1.092±73	1.199±87	1.43	1.58	1.1
VR-03	0.25-0.40	110±8	376±23	332±26	3.42	3.02	0.88
VR-04	0.25-0.40	795±46	600±22	579±39	0.75	0.73	0.97
VR-05	0.25-0.40	120±11	275±16	234±15	2.29	1.95	0.85
Average		548	700	843	1.82	1.85	1.08

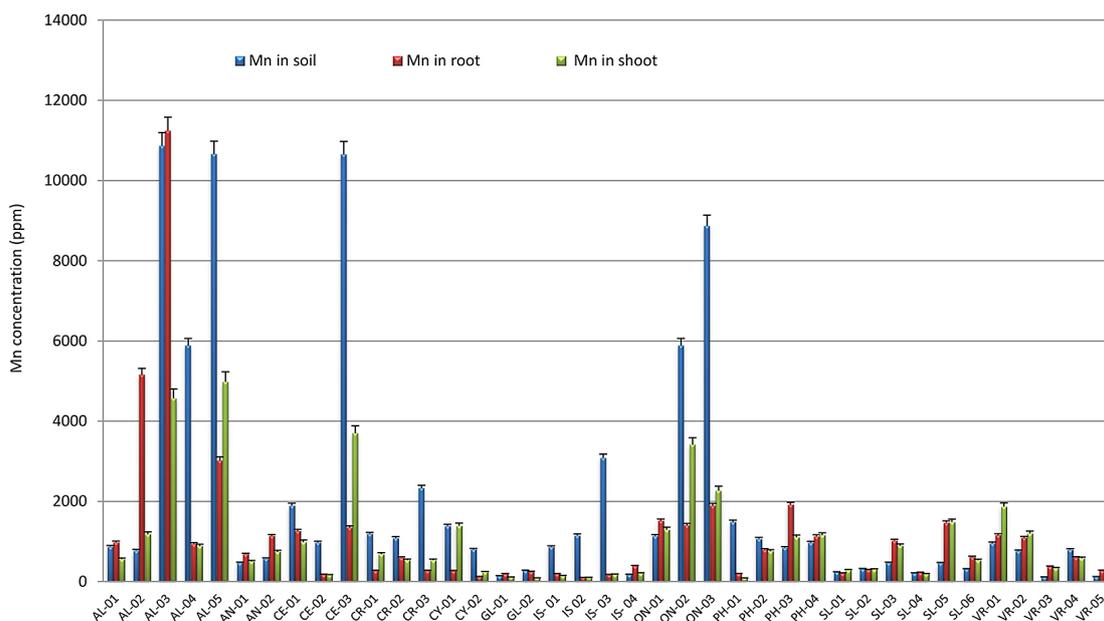


Figure 2. Mn concentrations for the shoots, roots and soils of eleven plants

Table 2. Spearman’s correlation relationships between Mn and other metals

Element	Cu	Pb	Zn	Ag	Fe	As	U	Sr	Sb	Ca
Mn	0.83	0.77	0.79	0.49	0.7	-0.01	-0.26	-0.35	-0.09	-0.03
Element	P	Ba	Hg	Na	K	Sc	Tl	Hg	Se	Cd
Mn	-0.30	0.28	0.06	-0.03	0.14	-0.22	-0.34	0.06	0.67	0.79

useful plant for phytoremediation studies of Mn (Table 1; Fig. 2). The average shoot, root and soil concentrations in *Onosma*'s (ON) were, respectively, 2.964, 1.604, and 2.324 ppm (Table 1; Fig. 2). The average Mn concentrations of ON soils were lower than those in ON's shoots and roots. The mean ECR and ECSs for Mn were 0.86 and 0.98, respectively. These levels indicate that the root of ON cannot accumulate Mn from the soil but that the shoot can very effectively accumulate Mn due to the ECS being close to 1.

The average soil, root and shoot concentrations in *Phlomis* (PH) for Mn were 991, 1010, and 775 ppm, respectively. PH's mean TLF, ECS and ECR were 0.75, 0.92 and 1.19, respectively for Mn (Table 1; Fig. 3). The ECR and ECS concentrations were greater than 1 or close to 1, that indicates that the PH shoot and root could be useful for rehabilitating or cleaning areas contaminated by Mn, as also seen for Se (Sasmaz 2009).

The average shoot, root and soil contents in *S.compacta* (SL) were, respectively, 639, 638, and 333, ppm (Table 1, Fig. 2). The average Mn concentrations in SL's soil were lower than in both SL

the roots and shoots, except for two samples. The mean ECR, ECS and TLF of SL were higher than 1 or close to 1 ( $p < 0.05$ ) (Fig. 3; Table 1). These levels show that SL can be used as a bioaccumulator plant for Mn.

Finally, the average soil, root and shoot concentrations in the average *V. thapsus* L. (VR) for Mn were 548, 700, and 843 ppm, respectively (Table 1). The soil levels of VR were lower than the Mn values in the roots and shoots ( $p < 0.05$ ) (Table 1). The mean ECR and ECS values were 1.82 and 1.85, respectively, and thus greater than 1 (Table 1; Fig. 3), which shows that *V. thapsus* would be a very effective plant for the uptake of soils polluted by Mn.

According to Kabata-Pendias (2011), the lithology of the wall rock is the primary indicator of the Mn level in the soil. The Mn concentrations of global soils ranged from 411 to 550 ppm across these soil samples. In calcareous and loamy soils, Mn is present in the highest quantities. The typical Mn content of soil varies globally, ranging from 525 ppm (in Cambisols) to 270 ppm (in Podzols). The mean for soils worldwide is 488 ppm, whereas

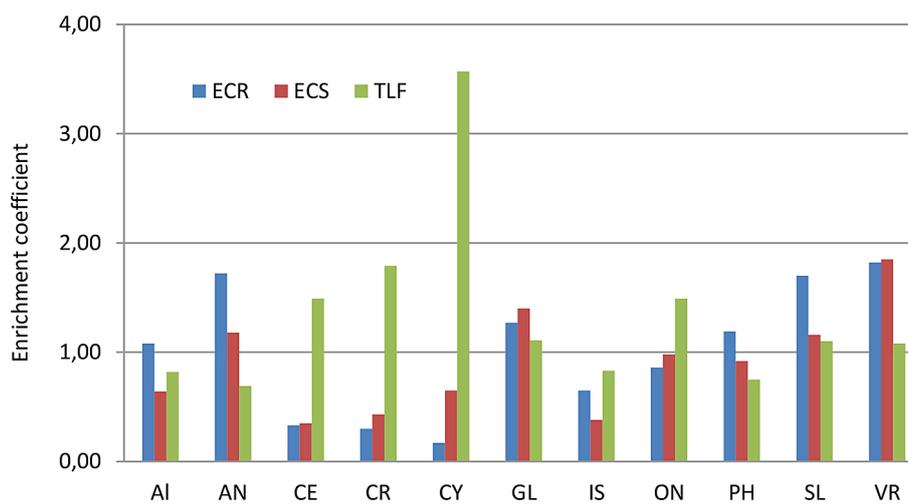


Figure 3. The average ECR, ECS and TLF values of the studied plants for Mn

the rate for soils in the United States alone is 495 ppm. In Finnish soils, the 90th percentile of the total Mn concentration is 600 ppm, whereas the level of acid-soluble Mn is 280 ppm. The median Mn values in Lithuanian soils depending on the kind of parent material range from 245 ppm in those transported from continental soils to 605 ppm in those derived obtained from loamy clay glacial deposits. Australia's soils generated from basalts and andesites have been found to have the greatest Mn content, reaching up to 9.200 ppm in some samples. In numerous additional soils from different nations, mostly belonging to the Cambisols group, the concentration of Mn can reach up to 4,000 ppm, with the average falling between 800 and 1.000 ppm. Certain top soils in the Slovak Republic have been observed to have high Mn concentrations, up to 8.510 ppm (Curlic and Sefcik, 1999). Although Mn has not been found to be a harmful element in soils, its maximal accumulation concentration in agricultural soils is thought to be between 1.500 and 3.000 ppm. Metal smelting operations, sewage sludge, municipal wastewaters and mining sites are the main human sources of Mn. The combustion of fuel additives' combustion is not as significant a source. Alluvial soils, however, can accumulate Mn from fuel consumption at rates up to > 1.000 ppm in some regions (such the Mississippi River Delta) (Mielke et al. 2002). Soils in polluted riparian regions can have as much as 2.700 ppm of Mn (Shanahan et al. 2007). Because of the reductive breakdown of Mn oxides, the soluble Mn fraction rises in soils that are irrigated with water impacted by acidic mine waters (Min et al. 2007).

Among plants growing on the same soil, Mn rates vary notably widely; in *Medicago truncatula*, the average is 30 ppm, while in *Lupinus albus*, it is almost 500 ppm. Similarly, reports from many nations indicate that a broad range of Mn has been found in forage plants. Most plants have critical Mn deficiency levels between 15 and 25 ppm, but the hazardous Mn concentration level for plants ranges depending on the soil and other plant variables. In general, Mn levels above 400 ppm in the soil cause some changes in most plants. However, for a number of more resistant species or genotypes, the accumulation exceeding 1.000 ppm has also frequently been recorded (Mielke et al., 2002; Shanahan et al., 2007; Green et al., 2003). According to Peng et al. (2008), hyperaccumulator plants such as *Phytoacca americana* accumulated over 13.400 ppm Mn in their shoot. This high accumulation value is understood to be very high when compared with the values of both Kabata-Pendias (2011) and Pais and Jones (2000). Krusne Bihanic et al. (2021) and Losfeld et al. (2015) have discussed success using *Grevillea meisneri* in the restoration of degraded mining sites in New Caledonia and in providing biomass for the synthesis of ecocatalysts. Transplanted seedlings from nurseries accumulate the same amount of Mn as plants do and store it in the same tissues to produce biomass that is high in Mn. It has been found that Mn can accumulate in the dried leaves of *Alyxia poyaensis* and *Denhamia* species at amounts of more than 1%, with these plants being referred to by van der Ent et al. (2013) as "Mn hyperaccumulators". In a similar vein, many species found in New Caledonia collect Mn at levels between 3.000 and 10.000 ppm.

Based on a field study conducted in Mn-rich soils, Min et al. (2007) identified *Phytolacca americana* as a new manganese hyperaccumulator plant. This species exhibits exceptional Mn absorption and accumulation capabilities, in addition to its amazing tolerance to the element. On the Mn tailings wastelands of Xiangtan, the greatest Mn level in the leaf dry matter was 8.000 ppm, with a mean of 6.490 ppm. A high TLF (>10.76) was found to be characteristic of the species. As external Mn levels grew in nutrient solution cultivation conditions, the concentrations of Mn in the shoots also increased. These species offer a novel plant resource for investigating the process underlying Mn hyperaccumulation and may prove useful in the phytoremediation of soils contaminated with Mn.

The level of Mn in the tissues above the ground is consistently higher than that in the roots, according to research by Yang et al. (2008). Mn levels in the stems and leaves all surpassed 10.000 ppm, the recommended threshold for Mn hyperaccumulation, when the external Mn supply was at high concentrations. A significant 86% of the Mn extracted from the substrates was deposited in the aboveground tissues. *Schima superba* is a Mn hyperaccumulator, as verified by these results.

The Krušné Hory Mountains (Ore Mountains) in Czech Republic, represent highly polluted area on a European scale. Branching and leaves of bilberry (*Vaccinium myrtillus*) grown on low-pH (2.77–3.62) soil with high Mn content (490–6.277 ppm) were gathered in the Krušné Hory Ore Mountains, Czech Republic. The range of Mn concentration in the leaves was 274–11.159 ppm, with a notable rise during the growth season when the leaves dried up early because of the lack of precipitation. The amounts of Mn in the branches of newly sprouted leaves were similar in the years of collection and in the growth seasons (2.062–3.885 ppm). It was established that Mn hyperaccumulation occurs in bilberries and that manganese levels rise steadily during the growing seasons. A favorable link was also found between soil moisture content and the Mn level of bilberry leaves (Kula et al., 2018).

## CONCLUSIONS

The plants collected from the Kütahya mining region were separated into three groups according to their ECS and ECR values: the best plants, good plants, and less effective plants regarding Mn accumulation. The best plants (higher ECS and ECR than

1) for Mn accumulation were *A. arvensis*, *G. flavum*, *Phlomis* sp., *S. compacta*, and *V. thapsus*. A good plant (ECR and ECS were close to 1) for Mn phytoremediation was *Onosma* sp. Therefore, these plants would be useful for the cleaning and/or rehabilitating of areas contaminated by Mn. Within the studied plants, *A. saxatile*, *C. cyanus*, *C. nutans*, *C. officinale* and *Isatis* can only be candidate plants, and not actual bioaccumulators, due to their ECS and ECR < 1. Plantings of these bioaccumulator groups can be used for the cleaning/rehabilitation of the areas polluted by Mn and the biomonitoring applications of environmental contamination. Finally, the TLF values indicate the ability to transfer Mn from roots to shoots, and in this regard, *C. officinale*, *G. flavum*, *Onosma* sp., *Phlomis* sp., *S. compacta* and *V. thapsus* plants were determined to be the most productive plants for Mn.

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## REFERENCES

1. Ansari AA, Gill SS, Gill R, Lanza GR, Newman L (2015) *Phytoremediation*. Management of Environmental Contaminants, Springer International Publishing Switzerland. 366.
2. Arik F (2002a) *Gümüşköy (Kütahya, Türkiye) gümüş yatağının jeokimyasal modellemesi*, Selçuk Üniv.Fen Bil. Enst. Doktora Tezi, 318.
3. Arik F (2002b) Genetic characteristics of the Gozecukuru As-Sb deposits near Kutahya, Turkey. *J. Geol.Soc. India* 2012, 80, 855–868.
4. Arik F, Yıldız T (2010) Heavy metal determination and pollution of the soil and plants of Southeast Tavşanlı (Kütahya, Turkey). *Clean Soil Air Water* 38, 1017–1030.
5. Azizi MR, Abedeni A, Alipour S, Niroomand S, Sasmaz A, Talaei B (2017) Rare earth element geochemistry and tetrad effect in fluorites: A case study from the Qahr-Abad deposit, Iran. *N.Jb. Palont. Abh* 283(3), 255–273.
6. Bihanic C, Petit E, Perrot R (2021) Manganese distribution in the Mn-hyperaccumulator *Grevillea meisneri* from New Caledonia. *Sci Rep* 11, 23780.
7. Chen SB, Zhu YG, Hu QH (2005) Soil to plant transfer of <sup>238</sup>U, <sup>226</sup>Ra and <sup>232</sup>Th on U mining-impacted soil from southeastern China. *J. Environ. Rad.* 82, 223–236.
8. Curlik J, Šefcik P (1999) *Geochemical atlas of the*

- Slovak Republic. *Soils*. Ministry of the Environ of the Slovak Republic.
9. Green CH, Heil DM, Cardon GE (2003) Solubility of manganese and trace metals in soils affected by acid mine runoff. *J. Environ. Qual.* 32, 1323–1334.
  10. Iqbal M (2016) Vicia faba bioassay for environmental toxicity monitoring: a review. *Chemosphere* 144, 785–802.
  11. Iqbal M, Iqbal N, Bhatti IA, Ahmad N, Zahid M (2016) Response surface methodology application in optimization of cadmium adsorption by shoe waste: a good option of waste mitigation by waste. *Ecol. Eng.* 88, 265–275.
  12. Kabata-Pendias A (2011) Trace Elements in soils and plants. *CRC Press, Boca Raton*.
  13. Khan K, Khan H, Lu Y, Ihsanullah I, Nawab J, Khan S, Shah NS, Shamshad I, Maryam A (2014) Evaluation of toxicological risk of foodstuffs contaminated with HMs in Swat. *Pakistan. Ecotox Environ Saf.* 108, 224–232.
  14. Kula E, Wildova E, Hrdlicka P (2018) Accumulation and dynamics of manganese content in bilberry (*Vaccinium myrtillus*). *Environ Monit Assess* 190, 224.
  15. Kartalkanat A (2008) Anadolu’da madenciligin tarihçesi, Kütahya-Gümüşköy’de 3500 Yıldır süren madencilik çalışmaları. *MTA Dergisi*, 137, 91–97.
  16. Kilic AD, Cakmak B (2021) Elemental analysis of ignimbirite by Raman spectroscopy methods and instrumental neutron activation analysis. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* 251, 119406.
  17. Kilic, A.D., Konakçı, N., Sasmaz, A. (2024) Garnet geochemistry of Pertek Skarns (Tunceli, Turkey) and U-Pb age findings. *Minerals*, 14, 539.
  18. Konakci N, Sasmaz Kislioglu M, Sasmaz A (2023) Ni, Cr and Co Phytoremediation by *Alyssum murale* grown in the serpentine soils around Guleman Cr Deposits, Elazig Turkey. *Bull Environ Contam Toxicol*, 110, 97.
  19. Konakci N, Sasmaz A (2021) Geochemical approach to the genesis of the Buyukkizilcik (Afsin) barite deposit, SE Turkey. *Italian Journal of Geosciences* 140 (3), 422–437
  20. Liu XH, Gao YT, Sardar K, Duan G, Chen AK, Ling L, Zao L, Zhonghan L, Xuecan W (2008) Accumulation of Pb, Cu, and Zn in terrestrial plants growing on contaminated sites and their potential accumulation capacity in Heqing, Yunnan. *J Environ Sci.* 20, 1469–1474.
  21. Losfeld G., L’Huillier, L., Fogliani, B. (2015) Leaf-age and soil-plant relationships: key factors for reporting trace-elements hyperaccumulation by plants and design applications. *Environ Sci Pollut Res* 22, 5620–5632
  22. Mani D, Kumar C, Patel NK (2016) Integrated micro-biochemical approach for phytoremediation of cadmium and lead contaminated soils using *Gladiolus grandiflorus* L cut flower. *Ecotox Env Saf.* 124, 435–446.
  23. Min Y, Tie B, Tang M, Aoyama I (2007) Accumulation and uptake of manganese in a hyperaccumulator *Phytolacca Americana*. *Miner Eng.* 20, 188–190.
  24. Mielke HW, Gonzales CR, Powell E (2002) Natural and anthropogenic processes that concentrate Mn in rural and urban environments of the Lower Mississippi River Delta. *Environ. Res. Sec.* A90, 157–168.
  25. Obek E, Sasmaz A (2011) Bioaccumulation of Aluminum by *Lemna gibba* from Secondary Treated Municipal Wastewater Effluents. *Bull Environ Contam Toxicol.* 86, 217–220.
  26. Pais I, Jones JB (2000) *The handbook of trace elements*. St. Lucie Press. Florida, 222.
  27. Peng KJ, Luo CL, You WX (2008) Manganese uptake and interactions with cadmium in the hyperaccumulator. *Phytolacca Americana* L. *J. Hazard. Mater.* 154, 674–681.
  28. Sasmaz A, Önal A, Sagioglu A, Önal M (2005) Origin and nature of the mineralizing fluids of thrust zone fluorites in Çelikhan (Adıyaman, Eastern Turkey): A geochemical approach. *Geochem. J.* 39(2), 131–139.
  29. Sasmaz A (2009) The distribution and accumulation of selenium in root and shoot of the plants naturally grown in the soils of Keban’s Pb-Zn-F mining area, Turkey. *Int. Journal of Phytorem* 11, 385–395
  30. Sasmaz M, Akgul B, Sasmaz A (2015) Distribution and accumulation of selenium in wild plants growing naturally in the Gumuskoy (Kutahya) Mining Area, Turkey. *Bull Environ Contam Toxicol* 94(5), 598–603.
  31. Sasmaz, A. (2008). Translocation and accumulation of boron in roots and shoots of plants grown in soils of low B concentration in Turkey’s Keban Pb-Zn mining area. *Int. Journal of Phytoremediation* 10, 302–310.
  32. Sasmaz A, Ozkan S, Gursu MF, Sasmaz M (2017) The hematological and biochemical changes in rats exposed to britholite mineral. *Applied Radiation and Isotopes* 129, 185–188.
  33. Sasmaz A (2020) The Atbara porphyry gold–copper systems in the Red Sea Hills, Neoproterozoic Arabian–Nubian Shield, NE Sudan. *J. Geochem. Exp.*, 214, 106539.
  34. Şaşmaz, A., Kılıç, A.D., Konakçı, N. (2024) Chemical and Thermal Changes in  $Mg_3Si_2O_5(OH)_4$  Polymorph Minerals and Importance as an Industrial Material. *Appl. Sci.* 14, 10298.
  35. Sasmaz A, Zagnitko VM, Sasmaz B (2020) Major, trace and rare earth element (REE) geochemistry of the Oligocene stratiform manganese oxide-hydroxide deposits in the Nikopol, Ukraine. *Ore Geol. Rev.* (126), 103772.
  36. Sasmaz A, Sasmaz B, Hein JR (2021) Geochemical approach to the genesis of the Oligocene-stratiform manganese-oxide deposit, Chiatura (Georgia). *Ore Geol. Rev.* (128), 103910.
  37. Sasmaz M, Uslu Senel G, Obek E (2021) Strontium

- accumulation by the terrestrial and aquatic plants affected by mining and municipal wastewaters (Elazığ, Turkey). *Environ Geochem Health* 43, 2257–2270
38. Sasmaz A, Kılıç AD, Akgül B, Sasmaz B (2023) A spectral approach on mineralogy and geochemistry of garnet skarns in Arc-Type granitoids. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* 286, 122037.
  39. Shanahan JO, Brummer JE, Leininger WC, Paschke MW (2007) Manganese and zinc toxicity thresholds for mountain and Greyer willow. *Int. J. Phytoremediat.* 9, 437–452.
  40. Sinanoglu D, Sasmaz A. (2019) Geochemical evidence on the depositional environment of Nummulites accumulations around Elazığ, Sivas, and Eskişehir (Turkey) in the middle Eocene sub-epoch. *Arabian J. Geosci.* 12, 759.
  41. Skinner WM, Martin RR, Naftel SJ (2005) Multi-technique studies of the distribution of metals between the soil, rhizosphere and roots of *Populus tremuloides* growing in forest soil. *ICOBTE, 8 Int. Conf. Book Abstr.* 488–489.
  42. Unal E, Gökçe A (2007) Geology and fluid inclusion characteristics of the Akgüney (Kabadüz-Ordu) copper–lead–zinc deposits. *Geological Bulletin of Turkey* 50(3), 158–175.
  43. US EPA (2000) Introduction to phytoremediation. National Risk Management Research Laboratory, Office of Research and Development, EPA/600/R-99/107
  44. van der Ent A, Baker AJM, Reeves RD, Pollard AJ, Schat H (2013) Hyperaccumulators of metal and metalloid trace elements: facts and fiction. *Plant Soil* 362, 319–334.
  45. Wei CY, Chen TB, Huang ZC (2002) Cretan bake (*Pteris cretica*): An arsenic-accumulating plant. *Acta Ecol. Sin.* 22, 777–782.
  46. Wei H, Tang M, Xu X. (2023) Mechanism of uptake, accumulation, transport, metabolism and phytotoxic effects of pharmaceuticals and personal care products within plants: A review. *Sci Total Environ.* 892, 164413.
  47. Wong MH (2003) Ecological restoration of mine degraded soils, with emphasis on metal contaminated soils. *Chemosphere* 50, 775–80
  48. Yang SX, Deng H, Li MS (2008) Manganese uptake and accumulation in a woody hyperaccumulator, *Schima superba*. *Plant Soil & Env.* 54(10), 441–446.
  49. Yavuz F., Gültekin AH, Örgün Y, Çelik N, Karakaya MÇ, Sasmaz A (2002) Mineral chemistry of barium- and titanium-bearing biotites in calc-alkaline volcanic rocks from the Mezitler area (Balıkesir-Dursunbey), Western Turkey. *Geochem. J.* 36, 563–580.
  50. Yildirim D., Sasmaz A. (2017) Phytoremediation of As, Ag, and Pb in contaminated soils using terrestrial plants grown on Gumuskoy mining area (Kütahya Turkey). *Journal of Geochemical Exploration* 182, 228–234.
  51. Yoon J, Cao X, Zhou Q, Ma LQ (2003) Accumulation of Pb, Cu, and Zn in terrestrial plants growing on a contaminated Florida site. *Plant Soil* 249, 37–43.
  52. Zhao FJ, Lombi E, McGrath SP (2014) Assessing the potential for zinc and cadmium phytoremediation with the hyperaccumulator *Thlaspi caerulescens*. *Plant & Soil* 249, 37–43.
  53. Zu YQ, Li Y, Chen JJ, Chen HY, Qin L, Schwartz C (2005) Hyperaccumulation of Pb, Zn and Cd in herbaceous grown on lead-zinc mining area in Yunnan, China. *Environ Int.* 31, 755–762.