



Variations in Cu, Co, Cr, Cd, and Pb Concentrations Based on Soil Depth, Plant Species, and Plant Organs at Copper Mining Sites

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Variations in Cu, Co, Cr, Cd, and Pb concentrations were evaluated in soil and plant organs at a copper mining site. Soil and plant samples (leaf, bark, wood, and root) were taken from different soil depths in the spoil area, the rehabilitation area where *Pinus nigra* Arnold., *Pinus sylvestris* L., and *Robinia pseudoacacia* L. species were planted, and the forest area. It was found that Cr and Cd concentrations in soils and Cu concentration in spoil areas were largely below the detectable limits. However, the concentration of these elements in plants was quite high. The highest concentrations were generally obtained in *Pinus nigra*. Except for Cr, the highest mean values were obtained in *Pinus nigra*. The highest translocation factor (TF) values calculated in the same way were also obtained in *Pinus nigra* and it was determined that the TF value was up to 6.739. The study results also show that *Pinus nigra* is a suitable species that can be used to reduce the pollution of the heavy metals subject to the study.

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INTRODUCTION

The extraction of various minerals needed as raw materials in the industry from underground reserves and their release into the environment has made pollution a global problem (İstanbullu *et al.* 2023; Isinkaralar *et al.* 2024; Özel *et al.* 2024; Sevik *et al.* 2024a). Heavy metals are undoubtedly the most important factor in the globalization of the pollution problem. Heavy metals are elements that can be carcinogenic, toxic, and fatal to living beings, particularly humans, even at low concentrations (Canturk *et al.* 2024). These elements can remain in nature for many years without degrading, and their concentrations are constantly increasing due to anthropogenic factors (Ucun Ozel *et al.* 2019; Yayla *et al.* 2022).

Heavy metals are primarily extracted from reserves during mining activities and released into nature. However, it is known that there are still high concentrations of heavy metals in soils from which minerals were extracted. The high heavy metal content is among the biggest obstacles to rehabilitating and restoring these areas (Karatepe *et al.* 2020; Makineci 2021; Ergül and Kravkaz Kuşçu 2024).

Soils with high heavy metal contents cause a significant stress factor for plants. Therefore, in planting works to be carried out in these areas, plants that will not die due to

heavy metal content and will reduce heavy metal pollution by collecting heavy metals should be used. These features are also among the most basic features sought in plants to be used as biomonitors (Sulhan *et al.* 2023; Kuzmina *et al.* 2023).

The present study aimed to determine variations in the concentrations of Cu, Co, Cr, Cd, and Pb, which are among the most harmful heavy metals in terms of human and environmental health and, therefore, on the ATSDR (Agency for Toxic Substances and Disease Registry) substance priority list, in soils and plant organs at a mining site where copper (Cu) mining has been carried out for many years and rehabilitation works have been implemented.

Within the scope of the study, it was aimed to compare the concentrations of Cu, Co, Cr, Cd, and Pb heavy metals both in soils and in the organs of *Pinus nigra* Arnold., *Pinus sylvestris* L., and *Robinia pseudoacacia* trees in the Cu mine site, in the area where mining activities were carried out and in the forest area where the process has not yet been carried out. Thus, the objective was to determine the properties of these species that could be used as biomonitors for these heavy metals and their phytoremediation potentials. Both the species to be used as biomonitors and the plants to be used in phytoremediation studies should be able to absorb and accumulate heavy metals, but they should not die due to pollution (Ozturk Pulatoglu *et al.* 2025). In the species to be used for phytoremediation, it is desired that heavy metals accumulate as much as possible, especially in the wood, which is the largest organ of the tree in terms of mass (Sevik *et al.*, 2024a). Therefore, the hypotheses of the study were;

- a) *Pinus nigra* is a suitable biomonitor for monitoring Cu, Co, Cr, Cd, and Pb pollution.
- b) *Pinus sylvestris* is a suitable biomonitor for monitoring Cu, Co, Cr, Cd, and Pb pollution.
- c) *Robinia pseudoacacia* is a suitable biomonitor for monitoring Cu, Co, Cr, Cd, and Pb pollution.
- d) *Pinus nigra* is a suitable species for the mitigation of Cu, Co, Cr, Cd, and Pb pollution.
- e) *Pinus sylvestris* is a suitable species to be used to reduce Cu, Co, Cr, Cd, and Pb pollution.
- f) *Robinia pseudoacacia* is a suitable species for the reduction of Cu, Co, Cr, Cd, and Pb pollution.

EXPERIMENTAL

Materials and Methods

The current study was conducted in Küre district of Kastamonu, where copper mining has been carried out for many years and one of the largest copper mines in Türkiye is operated. Within the scope of the study, soil samples were taken from the topsoil (0 to 5 cm) and subsoil (30 to 35 cm) depths from the spoil area (the area where rehabilitation works have not been carried out yet), the rehabilitation area where planting was carried out and adult trees of at least 20 years old are located, and the forest area. Soil samples were taken from the regions where *Pinus nigra* Arnold. (Pn), *Pinus sylvestris* L. (Ps), and *Robinia pseudoacacia* L. (Rp) species grow in the rehabilitation and forest areas. Leaf, bark, wood, and root samples were also taken from trees in the same regions.

During sampling, samples were taken from 3 areas from each site (forest, rehabilitation area, and leach field) in 3 replicates. Thus, soil samples were taken from 9 areas: 3 forests, 3 rehabilitation areas, and 3 waste areas, from each of which 3 tree species grow (there are no trees in the waste area); thus, soil samples were taken from 21 areas. Since soil samples were taken from 2 depths, a total of 42 soil samples were taken. Since soil samples were analyzed in triplicate, a total of 126 soil samples were analyzed. Similarly, plant samples were taken from a total of 18 trees from the forest and rehabilitation area where 3 tree species grow. The branches taken from each tree were divided into wood, bark, and leaf samples, and root samples were also taken. Root samples were excavated from the closest possible point to the tree and taken as a whole from the section approximately 30 to 35 cm below the soil level. Thus, a total of 72 plant samples were analyzed in triplicate, resulting in a total of 216 plant samples.

Soil samples were air dried for a while, then sieved, and dried at 45 °C for two weeks. Plant samples were first crushed, dried for a while, dried at 45 °C for one week, then ground and dried at 45 °C for two weeks. In previous studies, it was stated that heavy metals can degrade at 50 °C and higher temperatures and drying at high temperatures can lead to erroneous results. For this reason, in many studies on heavy metals, drying was performed at 45 °C (Koç *et al.* 2025; Ozturk Pulatoglu *et al.* 2025).

Specimens of 0.5 g dried material were transferred into glass petri dishes, 65% HNO₃ (6 mL) and 30% H₂O₂ (2 mL) were added, then placed in the microwave oven (200 °C) for 15 min. Then, the solution was transferred into flasks and filled up to 50 mL of ultrapure water. This procedure has been frequently used in various studies (Erdem *et al.* 2023a; Sulhan *et al.* 2023).

The Cu, Co, Cr, Cd, and Pb concentrations were determined in the dried samples with the help of the ICP-OES device (Spectro, Kleve, Germany). The above-mentioned method has been frequently used in recent years to conduct elemental analyses in soils (Erdem *et al.* 2024) and various organs of plants (Key *et al.* 2022; Sevik *et al.* 2024b). The obtained data were evaluated with the help of the SPSS package (SPSS, IBM, v.20, Armonk, NY, USA), and analysis of variance and Duncan's test were applied to the data. The obtained data were tabulated and interpreted. In addition, the relationship of the elements subject to the study both with each other and with other elements included in the priority pollutant list of ATSDR was determined by correlation analysis in the forested area where the trees grow and in the soils in the spoil area.

In the study, the bioconcentration factor (BCF) and the translocation factor (TF) were also calculated, and the following formulas were used in the calculations (Takarina and Pin 2017).

$$BCF = \frac{\text{concentration in organ}}{\text{concentration in soil}} \quad (1)$$

$$TF = \frac{BCF \text{ of organ}}{BCF \text{ of root soil}} \quad (2)$$

RESULTS

Variation of Heavy Metal Concentrations in Plants

Table 1 shows variation in Co, one of the heavy metals evaluated within the scope of the study, on an organ basis in trees grown in different areas.

Table 1. Variation in Co (ppm) Concentration in Plants by Species and Organs

Location	Species	Root	Wood	Bark	Leaf	F	Average
Spoil Area	Pn	2.9 ^{cC}	1.1 ^{aC}	19.9 ^{aA}	8.2 ^{aB}	36.1 ^{***}	8.0 ^a
	Ps	4.6 ^{bcB}	0.6 ^{bC}	6.4 ^{cA}	3.2 ^{bB}	23.7 ^{***}	3.7 ^b
	Rp	3.6 ^{cB}	0.6 ^{bC}	6.8 ^{cA}	2.2 ^{bBC}	19.6 ^{***}	3.3 ^b
Forest	Pn	11.3 ^{aA}	0.5 ^{bcC}	14.4 ^{bA}	4.2 ^{bB}	30.9 ^{***}	7.6 ^a
	Ps	2.4 ^{cB}	0.5 ^{bcC}	4.6 ^{cA}	2.7 ^{bB}	99.9 ^{***}	2.5 ^b
	Rp	6.7 ^{bA}	0.4 ^{cD}	5.9 ^{cB}	2.9 ^{bC}	894.5 ^{***}	4.0 ^b
F-value		14.4 ^{***}	15.4 ^{***}	33.4 ^{***}	6.5 ^{***}		8.5 ^{***}
Average		5.2 ^B	0.6 ^C	9.7 ^A	3.9 ^B	45.4 ^{***}	

According to Duncan's test results, numbers followed by the same letters (A, B, or a, b) are not statistically different at $p > 0.05$. Lowercase letters illustrate vertical directions, while capital letters indicate horizontal directions. *** $p \leq 0.001$.

According to the values in the table, it was determined that variation in Co concentration in plants was statistically significant ($p < 0.05$) in all species on an organ basis and in all organs on a species basis. According to the average values, the highest values in species were obtained from Pn in the spoil area and Pn in the forest area. According to the average values regarding organs, the lowest value was observed in wood, whereas the highest value was observed in bark. Table 2 contains variations in Cu concentration in plants by species and organs.

Table 2. Variation in Cu (ppm) Concentration in Plants by Species and Organs

Location	Species	Root	Wood	Bark	Leaf	F	Average
Spoil Area	Pn	22.6 ^{cdBC}	3.7 ^{aC}	132.2 ^{aA}	58.4 ^{aB}	18.0 ^{***}	54.2 ^a
	Ps	42.0 ^{bcA}	1.30 ^{bC}	29.1 ^{cA}	10.6 ^{bB}	10.6 ^{***}	20.7 ^{bc}
	Rp	51.6 ^{abA}	2.1 ^{bC}	39.9 ^{cAB}	25.6 ^{bB}	8.5 ^{***}	29.8 ^b
Forest	Pn	70.0 ^{aB}	0.8 ^{cD}	90.3 ^{bA}	24.8 ^{bC}	53.7 ^{***}	46.5 ^a
	Ps	11.7 ^{dB}	1.0 ^{cC}	21.0 ^{cA}	11.8 ^{bB}	46.0 ^{***}	11.4 ^c
	Rp	40.2 ^{bcB}	0.9 ^{cD}	43.1 ^{cA}	23.9 ^{bC}	1918.4 ^{***}	27.0 ^{bc}
F-value		6.5 ^{***}	16.6 ^{***}	22.9 ^{***}	5.8 ^{***}		7.7 ^{***}
Average		39.7 ^B	1.6 ^D	59.3 ^A	25.9 ^C	33.3 ^{***}	

According to Duncan's test results, numbers followed by the same letters (A, B, or a, b) are not statistically different at $p > 0.05$. Lowercase letters illustrate vertical directions, while capital letters indicate horizontal directions. *** $p \leq 0.001$.

According to the analysis of variance results, variation in Cu concentration in plants was statistically significant in all species on an organ basis and in all organs on a species basis. According to the average values, the highest value in species was obtained in Pn in the spoil area and Pn in the forest area, while the lowest value was obtained in Ps in the forest area. It is seen that the highest values were in Pn. According to the average values regarding organs, the lowest value was observed in wood, whereas the highest value was obtained in bark. Table 3 shows variation in Pb concentration in plants by species and organs.

Table 3. Variation in Pb (ppm) Concentration in Plants by Species and Organs

Location	Species	Root	Wood	Bark	Leaf	F	Average
Spoil Area	Pn	9.6 ^{bA}	5.5 ^{aC}	6.5 ^{aC}	7.8 ^{aB}	18.0***	7.3 ^a
	Ps	8.3 ^{cA}	4.0 ^{bcC}	5.4 ^{bcB}	5.0 ^{dB}	89.1***	5.7 ^b
	Rp	8.9 ^{bcA}	4.3 ^{bcC}	5.7 ^{bB}	5.3 ^{cdB}	148.2***	6.0 ^b
Forest	Pn	11.8 ^{aA}	4.5 ^{bC}	6.6 ^{aB}	6.7 ^{bB}	61.1***	7.4 ^a
	Ps	8.0 ^{cA}	3.9 ^{cD}	5.0 ^{cC}	6.0 ^{bcB}	305.3***	5.7 ^b
	Rp	9.0 ^{bcA}	4.0 ^{bcD}	5.4 ^{bcC}	6.2 ^{bcB}	335.3***	6.2 ^b
F-value		14.1***	12.4***	9.7***	12.7***		5.3***
Average		9.3 ^A	4.4 ^C	5.8 ^B	6.2 ^B	171.3***	

According to Duncan's test results, numbers followed by the same letters (A, B, or a, b) are not statistically different at $p > 0.05$. Lowercase letters illustrate vertical directions, while capital letters indicate horizontal directions. *** $p \leq 0.001$.

According to the analysis of variance results, variation in Pb concentration in plants was statistically significant in all species on an organ basis and in all organs on a species basis. According to the average values, the highest value in species was obtained in Pn in the spoil area and Pn in the forest area. Again, it is remarkable that the highest concentrations were obtained in Pn. According to the average values regarding organs, the lowest value was obtained in wood, while the highest value was obtained in root. Table 4 presents variations in Cd concentration in plants by species and organs.

Table 4. Variation in Cd (ppm) Concentration in Plants by Species and Organs

Location	Species	Root	Wood	Bark	Leaf	F	Average
Spoil Area	Pn	0.6 ^{aB}	0.4 ^{aC}	0.7 ^{aA}	0.3 ^{aC}	46.5***	0.5 ^a
	Ps	0.4 ^{cA}	0.3 ^{cB}	0.4 ^{bA}	0.2 ^{cdC}	21.4***	0.3 ^b
	Rp	0.2 ^{dB}	0.2 ^{dB}	0.4 ^{bcA}	0.2 ^{cdB}	7.9***	0.3 ^b
Forest	Pn	0.4 ^{bB}	0.3 ^{bAB}	0.7 ^{aA}	0.3 ^{bC}	26.6***	0.5 ^a
	Ps	0.4 ^{cB}	0.3 ^{bcC}	0.4 ^{bA}	0.2 ^{cD}	75.5***	0.3 ^b
	Rp	0.3 ^{dA}	0.2 ^{dB}	0.3 ^{cA}	0.2 ^{dB}	97.4***	0.2 ^c
F-value		33.7***	18.6***	35.6***	14.7***		27.5***
Average		0.4 ^B	0.3 ^C	0.5 ^A	0.3 ^C	32.6***	

According to Duncan's test results, numbers followed by the same letters (A, B, or a, b) are not statistically different at $p > 0.05$. Lowercase letters illustrate vertical directions, while capital letters indicate horizontal directions. UL; Under detectable limits, ns = not significant; *** $p \leq 0.001$.

Considering the above-mentioned values, it was observed that variation in Cd concentration in plants was statistically significant in all species on an organ basis and in all organs on a species basis. According to the average values, the highest value in species was obtained in Pn in the spoil area, while the lowest value was obtained in Rp in the forest area. According to the average values regarding organs, the highest value was in bark, whereas the lowest value was in wood and leaves. Cd concentration in soils remained below detectable limits in all soil samples. Table 5 shows variations in Cr concentration in plants by species and organs.

Table 5. Variation in Cr (ppm) Concentration in Plants by Species and Organs

Location	Species	Root	Wood	Bark	Leaf	F	Average
Spoil Area	Pn	9.6 ^{bB}	6.8 ^{aB}	19.6 ^{aA}	21.6 ^{bcA}	15.6 ^{***}	14.4
	Ps	21.5 ^{aA}	5.6 ^{bC}	12.1 ^{bBC}	13.6 ^{cB}	7.7 ^{**}	13.2
	Rp	8.7 ^{bC}	5.3 ^{bcC}	14.2 ^{bC}	47.2 ^{aB}	8.4 ^{***}	18.9
Forest	Pn	17.3 ^{aA}	6.1 ^{abB}	20.3 ^{aA}	21.4 ^{bcA}	13.8 ^{***}	16.3
	Ps	10.1 ^{bB}	6.1 ^{abC}	12.6 ^{bB}	15.5 ^{cA}	16.5 ^{***}	11.1
	Rp	21.5 ^{aA}	4.6 ^{cD}	12.3 ^{bC}	35.3 ^{abB}	1063.5 ^{***}	18.4
F-value		6.7 ^{***}	6.1 ^{***}	4.9 ^{**}	5.5 ^{***}		1.9 ^{ns}
Average		14.8 ^B	5.7 ^C	15.2 ^B	25.8 ^A	28.9 ^{***}	

According to Duncan's test results, numbers followed by the same letters (A, B, or a, b) are not statistically different at $p > 0.05$. Lowercase letters illustrate vertical directions, while capital letters indicate horizontal directions. UL; Under detectable limits, n = not significant; *** $p \leq 0.001$.

Considering the analysis of variance results, it was determined that variation in Cd concentration in plants was statistically significant in all species on an organ basis and in all organs on a species basis. According to the average values regarding organs, the highest value in organs was observed in leaves, while the lowest value was observed in wood.

Variation of Heavy Metal Concentrations in Soils

Table 6 presents variation in Co concentration in soils by species and soil depth.

Table 6. Variation in Co (ppm) Concentration in Soils by Species and Soil Depth

Location	Species	Sub	Top	F	Average
Spoil	-	222.6 ^{aA}	184.8 ^{aB}	7.1 [*]	199.9 ^a
Spoil Area	Pn	133.2 ^b	124.4 ^b	0.4 ^{ns}	128.8 ^{bc}
	Ps	117.1 ^b	155.9 ^a	2.0 ^{ns}	136.5 ^b
	Rp	125.6 ^{bA}	88.2 ^{cB}	8.3 [*]	106.9 ^c
Forest	Pn	44.4 ^{cB}	65.7 ^{cdA}	21.8 ^{***}	55.0 ^d
	Ps	46.1 ^c	55.8 ^d	0.3 ^{ns}	51.0 ^d
	Rp	58.3 ^c	55.2 ^d	0.7 ^{ns}	56.8 ^d
F-value		27.8 ^{***}	24.9 ^{***}		44.3 ^{***}
Average		101.0	104.34	0.0 ^{ns}	

According to Duncan's test results, numbers followed by the same letters (A, B, or a, b) are not statistically different at $p > 0.05$. Lowercase letters illustrate vertical directions, while capital letters indicate horizontal directions. ns = not significant; * $p \leq 0.05$, *** $p \leq 0.001$.

According to the above-mentioned results, it was found that variation in Co concentration was statistically significant in the spoil, Rp in the spoil area, and Pn in the forest area on a soil depth basis and in all soils on a species basis. According to the average values, the highest value in species was observed in the spoil, while the lowest value was obtained in Pn in the forest area, Ps in the forest area, and Rp in the forest area. It is noteworthy that all Co concentrations in forest soils were in the first group as a result of Duncan's test. The highest Co concentration was also obtained in the spoil. Table 7 displays variation in Cu concentration in soils by species and soil depth.

Table 7. Variation in Cu (ppm) Concentration in Soils by Species and Soil Depth

Location	Species	Sub	Top	F	Average
Spoil	-	UL	UL	-	UL
Spoil Area	Pn	UL	UL	-	UL
	Ps	197.72 ^b	UL	-	197.72
	Rp	UL	UL	-	-
Forest	Pn	130.95 ^{cB}	248.95 ^{aA}	414.7 ^{***}	189.95
	Ps	UL	215.72 ^b	-	215.72
	Rp	232.38 ^a	UL	-	232.38
F-Value		344.8 ^{***}	1645.5 ^{***}		2.1 ^{ns}
Average		187.02	232.33	2.2 ^{ns}	

According to Duncan's test results, numbers followed by the same letters (A, B, or a, b) are not statistically different at $p > 0.05$. Lowercase letters illustrate vertical directions, while capital letters indicate horizontal directions. UL; Under detectable limits, ns = not significant; *** $p \leq 0.001$.

Table 7 reveals that Cu concentration in soils accumulated within detectable limits only in Ps in the spoil area, Pn in the forest area, and Rp in the forest area in subsoils and in Pn in the forest area and Ps in the forest area in topsoils. Because Cu concentration remained below detectable limits in rehabilitated spoil areas other than both the spoil and Ps indicates that Cu was largely removed from the soil during mining activities. Table 8 contains variations in Pb concentration in soils by species and soil depth.

Table 8. Variation in Pb (ppm) concentration in soils by species and soil depth

Location	Species	Sub	Top	F	Average
Spoil	-	52.2 ^{aA}	40.0 ^{bB}	9.4 ^{**}	46.1 ^{ab}
Spoil Area	Pn	42.5 ^b	40.0 ^b	0.5 ^{ns}	41.2 ^b
	Ps	48.4 ^{ab}	51.3 ^a	0.2 ^{ns}	49.8 ^a
	Rp	44.0 ^b	41.7 ^b	0.5 ^{ns}	42.9 ^b
Forest	Pn	29.9 ^{cB}	32.1 ^{cA}	7.0 [*]	31.0 ^c
	Ps	30.0 ^{cB}	35.7 ^{bcA}	30.0 ^{***}	32.8 ^c
	Rp	31.9 ^c	31.5 ^c	0.0 ^{ns}	31.7 ^c
F-value		12.5 ^{***}	9.2 ^{***}		17.9 ^{***}
Average		39.89	38.95	0.2 ^{ns}	

According to Duncan's test results, numbers followed by the same letters (A, B, or a, b) are not statistically different at $p > 0.05$. Lowercase letters illustrate vertical directions, while capital letters indicate horizontal directions; ns = not significant; *** $p \leq 0.001$.

Considering the results in the table, it was determined that variation in Pb concentration in soils was statistically significant in the spoil, Pn in the forest area, and Ps in the forest area on a soil depth basis, and in all soils on a species basis. According to the average values, the highest value in species was obtained in Ps in the spoil area, whereas the lowest value was obtained in Pn in the forest area, Ps in the forest area, and Rp in the forest area. The Cr and Cd concentration in soils also remained below detectable limits in all soil samples. The correlations of the elements subject to the study with each other and with other elements on ATSDR's priority pollutant list in forest soil and spoil area soils is given in Table 9.

Table 9. Correlations of the Elements

Elements	Forest			Spoil Area		
	Co	Cu	Pb	Co	Cu	Pb
Co	1	0.234	0.065	1	0.558	0.568**
Cu	0.234	1	0.291	0.558	1	0.949
Pb	0.065	0.291	1	0.568**	0.949	1
As	-0.533**	0.095	0.495**	0.473**	-0.902	0.397**
Ba	0.719**	0.326	0.050	0.021	0.966	0.544**
Be	0.822**	-0.173	-0.078	0.656**	0.896	0.845**
Ni	0.800**	0.100	0.081	0.258	-0.586	-0.402**
Se	0.481**	0.100	0.199	0.258	0.092	0.200
Ag	-0.171	-0.545*	0.389**	-0.118	0.989	0.382**
Sr	0.371**	0.064	0.011	-0.071	0.977	0.018
Tl	0.602**	-0.004	-0.057	0.616**	0.688	0.193
V	0.809**	-0.137	-0.130	0.494**	0.472	0.079
Zn	0.690**	0.127	0.117	0.200	-0.561	-0.295*
Pd	-0.320*	-0.230	0.464**	0.279*	-0.234	0.294*
Sb	0.641**	0.043	0.022	0.538**	0.596	0.166
Al	0.654**	0.072	-0.076	0.533**	0.958	0.139
Mn	0.500**	-0.195	-0.262	0.194	-0.901	0.501**

* $p \leq 0.05$; ** $p \leq 0.01$.

When Table 9 is examined, it is seen that only Co and Pb were in a statistically significant and strong relationship (0.568). However, it was determined that the elements subject to the study had statistically significant and strong relationships with many other harmful and hazardous elements. The strongest relationships were calculated between Cu and Ag (0.989), Sr (0.977) and Ba (0.958) in the spoil area, while the strongest negative relationships were calculated between Cu and As (-0.902), Mn (-0.901) and Ni (-0.586) in the spoil area.

BCF and TF Values

BCF values for the elements subject to the study are calculated and given in Table 10.

The concentrations of Cr and Cd in the soil were below the determinable limits. In addition, the Cu concentration in the soil in the spoil area was below the determinable limits in Pn and Rp species. Therefore, BCF values could not be calculated for these elements. Table 10 shows that BCF values ranged between 0.004 and 0.233 in the spoil area. The highest BCF value was obtained for Pb in Pn roots. In the forest area, the highest value was obtained in Pn bark for Cu with 0.475. TF values of the elements subject to the study are given in Table 11.

Table 10. BCF Values for the Elements Subject to the Study

Location	Element	Species	Root	Wood	Bark	Leaf
Spoil Area	Co	Pn	0.023	0.009	0.155	0.064
		Ps	0.034	0.004	0.047	0.023
		Rp	0.034	0.006	0.064	0.021
	Cu	Pn	-	-	-	-
		Ps	0.212	0.007	0.147	0.054
		Rp	-	-	-	-
	Pb	Pn	0.233	0.133	0.158	0.189
		Ps	0.167	0.080	0.108	0.100
		Rp	0.207	0.100	0.133	0.124
Forest	Co	Pn	0.205	0.009	0.262	0.076
		Ps	0.047	0.010	0.09	0.053
		Rp	0.118	0.007	0.104	0.051
	Cu	Pn	0.369	0.004	0.475	0.131
		Ps	0.054	0.005	0.097	0.055
		Rp	0.173	0.004	0.185	0.103
	Pb	Pn	0.381	0.145	0.213	0.216
		Ps	0.244	0.119	0.152	0.183
		Rp	0.284	0.126	0.17	0.196

Table 11. TF Values for the Elements Subject to the Study

Location	HM	Species	Wood	Bark	Leaf
Spoil Area	Co	Pn	0.391	6.739	2.783
		Ps	0.012	0.138	0.068
		Rp	0.176	1.882	0.618
	Cu	Pn	0.167	5.868	2.588
		Ps	0.033	0.693	0.255
		Rp	0.042	0.774	0.494
	Pb	Pn	0.571	0.678	0.811
		Ps	0.479	0.647	0.599
		Rp	0.483	0.643	0.599
Forest	Co	Pn	0.044	1.278	0.371
		Ps	0.213	1.915	1.128
		Rp	0.059	0.881	0.432
	Cu	Pn	0.011	1.287	0.355
		Ps	0.093	1.796	1.019
		Rp	0.023	1.069	0.595
	Pb	Pn	0.381	0.559	0.567
		Ps	0.488	0.623	0.75
		Rp	0.444	0.599	0.69

According to the calculations, the lowest TF values were obtained for Ps wood in Co with 0.012 in the spoil area and for Pn wood in Cu with 0.011 in the forested area. The highest values were obtained in Pn bark in Co with 6.739 in the spoil area and in Ps bark in Co with 1.915 in the forested area. In general, TF values in wood were much lower, while TF values in bark and leaves were much higher than in wood.

DISCUSSION

As a result of the study, it is remarkable that Cr and Cd concentrations in soils remained below detectable limits. Additionally, Cu concentrations in soils in the spoil area were also largely below the detectable limits. This result can be interpreted as the amount of Cd and Cr in the soil being at very low levels and Cu having been removed from the soil after mining activities. However, concentrations in plant organs in the same soils were quite high. The study calculated Cu concentrations to be 1.6 ppm in wood, 25.9 ppm in leaves, and 39.7 ppm in roots on average. These values are lower than the values obtained from other studies. For example, Turkyilmaz *et al.* (2018) stated that the average Cu concentrations in leaves in broad-leaved species ranged between 32.8 and 169.5 ppm. Cetin *et al.* (2020) determined that Cu concentration in *Picea pungens* ranged between 33.78 and 64.26 ppm in needles and between 15.39 and 96.76 ppm in bark. Mulenga *et al.* (2022) stated that the Cu concentration in *Brachystegia longifolia* leaves at copper mining sites was 296 mg/kg, while the Cu concentration in soils reached 1558 mg/kg. It is reported that Cu concentrations in plant leaves are in the range of 20 to 100 mg kg⁻¹ and the maximum allowable limit for plants used as animal feed is 40 mg kg⁻¹ (Milla-Moreno and Guy, 2021). In plants, Cu is phytotoxic at 200 mg kg⁻¹ dw (Filimon *et al.* 2021). However, in studies conducted in copper mines, Cu concentration was found to be 350 mg kg⁻¹ dw in Soapwort leaves and 630 mg kg⁻¹ dw in Orange mullein leaves (Antonijević *et al.* 2012). In another study conducted in another Cu mine, it was determined that the Cu concentration in plant shoots along the riverside ranged from 11.1 to 34.7 µg g⁻¹, while the Cu concentration in plant shoots in the waste sites ranged from 7.5 to 294.26 µg g⁻¹ (Alizadeh *et al.* 2022). In a study conducted in former Cu mining sites in Romania, the highest values in vegetables were found in parsley roots (6.88 mg kg⁻¹ fresh matter). In the same study, it was reported that the Cu concentration in parsley roots produced in the control plot was 1.22 mg kg⁻¹ fresh matter (Harmanescu *et al.* 2011).

The present study determined that Cd concentration in plant organs ranged between 0.2 ppm and 0.7 ppm. This result is consistent with similar studies. Isinkaralar *et al.* (2022) stated that Cd concentration in different species ranged between 0.094 ppm and 0.66 ppm in leaves and reached 0.23 ppm in branches and 0.35 ppm in wood but remained below detectable limits in branches and wood in some species. Cobanoglu *et al.* (2023) determined the Cd concentration in *Cedrus* wood to be 0.117 ppm in outer bark and 0.139 ppm in wood. Heredia *et al.* (2022) found that Cd concentration in *Larrea cuneifolia*, *Bulnesia retama*, *Plectrocarpa tetracantha*, and *Prosopis flexuosa* growing at the mining site ranged between 20.1 and 34.6 mg kg⁻¹. It is reported that Cd concentrations in plant leaves are at the level of 5 to 30 mg kg⁻¹ and the maximum allowable limit for plants used as animal feed is 10 mg kg⁻¹ (Milla-Moreno and Guy 2021). The permissible concentration of Cd in vegetables is 0.20 mg kg⁻¹ fresh matter, and in a study conducted in former Cu mine sites, it was determined that Cd did not exceed the limit values, unlike other heavy metals, and the maximum concentration of Cd was 0.20 mg kg⁻¹ fresh matter in plant roots

and 0.12 mg kg⁻¹ fresh matter in plant leaves (Harmanescu *et al.* 2011). In another study conducted at another former mining site, the highest Cd concentration was measured in cabbage leaves with 0.12 mg/kg fw. In the same study, Cd concentration in cucumber fruit was 0.13 mg/kg fw (Manea *et al.* 2020).

The study calculated that the average Cr concentration was 5.7 ppm in wood, 14.8 ppm in roots, 15.2 ppm in bark, and 25.8 ppm in leaves. Isinkaralar *et al.* (2022) stated that the Cr concentration in different species ranged between 1.175 and 2.960 ppm in leaves, between 0.87 and 4.23 ppm in branches, and between 0.85 and 1.48 ppm in wood. Savas *et al.* (2021) found that the Cr concentration in *Cedrus atlantica* ranged between 0.923 and 1.588 ppm in outer bark and between 0.44 and 0.76 ppm in wood. Koc *et al.* (2024a) revealed that Cr concentration in different species ranged between 1.11 and 3.02 ppm in outer bark and between 0.87 and 1.18 ppm in wood. It is reported that Cr concentrations in plant leaves are at the level of 5 to 30 mg kg⁻¹ and the maximum permissible limit for plants used as animal feed is 100 mg kg⁻¹ (Milla-Moreno and Guy 2021). In a study conducted in a Cu mine, it was determined that the Cr concentration in plant shoots near the river ranged between 0.475 and 1.50 µg g⁻¹. In the same study, it was determined that the Cr concentration in plant shoots in waste sites varied between 0.314 and 3.67 µg g⁻¹ (Alizadeh *et al.* 2022).

The study calculated that the average Pb concentration was 4.4 ppm in wood, 9.3 ppm in roots, 5.8 ppm in bark, and 6.2 ppm in leaves. Although Pb is essential as a nutrient for plants, it is toxic to plants at the level of 100 to 500 mg kg⁻¹ and its average level in plants is 0.2 to 20 mg kg⁻¹. However, studies have shown that Pb concentration can be quite high. For example, in Orange mullein, it was determined that it can reach 590 mg kg⁻¹ in the stem and 1400 mg kg⁻¹ in the leaves (Filimon *et al.* 2021). In other studies, conducted in Cu mine sites, the highest values were determined in parsley (15.78 mg kg⁻¹ fresh matter in roots and 1.97 kg⁻¹ fresh matter in leaves) and the highest permissible value in vegetables was 0.50 kg⁻¹ fresh matter (Harmanescu *et al.* 2011). In a study conducted away from mining sites but in an area with industrial pollution, Pb concentration was found to be as high as 4098.8 µg kg⁻¹ in *Picea* needles (Isinkaralar *et al.* 2025). It is reported that Pb concentrations are much higher in vegetables grown in urban areas, for example, up to 13240.4 µg kg⁻¹ in pepper leaves (Gültekin *et al.* 2025).

The concentration of heavy metals in plant tissues varied depending on many factors. Some of these factors include physical and chemical properties of metals, their forms, morphology of organs, surface area, plant habitus, surface texture, duration of exposure to metals, and environmental conditions (Koç *et al.* 2025). Among these factors, plant species is perhaps the most important. In fact, most of the other characteristics are related to the plant species. Therefore, in many studies, it has been determined that heavy metal concentrations in plants grown in the same environment are at different levels (Koc *et al.* 2024b; Yaşar Ismail *et al.* 2025). This result is quite natural because all phenotypic characteristics of living organisms are shaped under the interaction of genetic structure and environmental conditions (Çobanoğlu *et al.* 2023; Hrivnak *et al.* 2024; Özdikmenli *et al.* 2024). Plant species is the most important factor shaping the genetic structure and interaction of the plant with the environment. Therefore, it is natural that heavy metal concentrations in plants growing in the same environment vary depending on the plant species.

As a result of the study, because Cr and Cd concentrations in soils remained below the detectable limits but accumulated within detectable limits in plant organs indicates that these elements enter the plant body through different pathways. Heavy metals can enter the

plant body directly from the soil *via* roots, from the air *via* leaves, or from the stem sections (Key *et al.* 2023). The study results show that Cr and Cd probably enter the plant body directly from the air *via* leaves or from the stem sections. Because the concentrations of Cd in bark and the concentrations of Cr in leaves are higher than in roots can be interpreted as the entry of Cd into the plant body more from stem sections and the entry of Cr more from leaves.

The study found that Co concentration ranged between 44.4 and 222.6 ppm, and Pb concentration ranged between 29.9 and 52.2 ppm in soils. Cu concentration was below the determinable limits in most of the soil samples. The highest concentration was 248.95 ppm. The highest acceptable concentrations in agricultural soils were reported to be 63 mg kg⁻¹ for Cu and 70 mg kg⁻¹ for Pb (Milla-Moreno and Guy 2021). In a study conducted in a Cu mine, it was determined that Cu concentration in soils of the waste site was 34.4 µg g⁻¹, Cr concentration was 6.60 µg g⁻¹, Co concentration was 1.91 µg g⁻¹, and Pb concentration was up to 11.0 µg g⁻¹ (Alizadeh *et al.* 2022). In another study conducted in another copper mine, it was determined that Cu concentration reached a maximum of 122.01 mg kg⁻¹ dw and Pb concentration reached a maximum of 3.27 mg kg⁻¹ dw in areas outside the mine site, while Cu concentration reached 3800 mg kg⁻¹ dw and Pb concentration reached 1700 mg kg⁻¹ dw in soils in the pit area (Filimon *et al.* 2021).

Erdem (2023) determined that Co concentration ranged between 6.84 and 8.34 ppm in forest soils where different species grow. Co and Pb are elements that are particularly associated with traffic density. Sevik *et al.* (2019) determined that the Pb concentration in *Ailanthus altissima* leaves, which was 321 ppb in areas without traffic, increased to 8181 ppb in areas with heavy traffic. Many studies determined that Pb and Co were in high concentrations in both soils and plants, particularly in urban areas with heavy traffic (Yasin *et al.* 2021).

The study aimed to determine the most suitable phytoremediation species at mining sites. This issue is one of the most important environmental problems, and it is quite challenging to grow plants at mining sites because the soil structure is deteriorated (Makineci 2021). In these areas, herbaceous or short-lived species are usually used. However, these species are not sufficiently effective in reducing heavy metal pollution at mining sites. Cruzado-Tafur *et al.* (2021) stated that none of the plants *Pernettya prostrata*, *Gaultheria glomerata*, *Gaultheria glomerata*, *Festuca* sp., *Ageratina glechonophylla*, *Bejaria* sp., *Pernettya prostrata*, *Achyrocline alata*, *Ageratina fastigiata*, *Baccharis alnifolia*, *Calceolaria tetragona*, *Arenaria digyna*, *Hypericum laricifolium*, *Brachyotum radula*, and *Nicotiana thyrsoflora* were suitable phytoremediation plants for Cu and Pb. Yasin *et al.* (2021) stated that *Morus alba* was a suitable phytoremediation plant for Cd, Cu, and Pb at copper mining sites.

Within the scope of the study, the highest TF value in spoil area was obtained in Pn. The TF values obtained in Pn, especially in the shells, were considerably higher than the TF values obtained in other species. TF values in Pn shells were calculated as 6.739 for Co, 5.868 for Cu, and 0.678 for Pb. TF values in Pn leaves were also quite high and were 2.783 for Co, 2.588 for Cu, and 0.811 for Pb. TF value is an important criterion showing the suitability of a species for phytoremediation studies. Plants with larger TF are better in phytoremediation (Wang *et al.* 2019). Therefore, it has been the subject of numerous studies. In a study conducted in Cu mining sites in Yunnan, it was determined that TF values in vegetables were lower than 0.8 for Cu and Pb and lower than 0.5 for Cd (Liu *et al.* 2023). In a study conducted at a Cu mining site in Chile, it was reported that TF in *Prosopis tamarugo*, *Schinus molle* and *Atriplex nummularia* species ranged between 0.14

and 2.78 for Cu, between 0.004 and 2.74 for Pb and between 0.33 and 1.13 for Cd, and TF could not be calculated in *Schinus molle* species for Cd (Lam *et al.* 2017). In a study conducted in a Cu mine in Australia, TF could not be calculated for Cu and Pb in *Acacia pycnantha* and was calculated as 1.20 for Cd, while in *Eucalyptus camaldulensis* it could not be calculated for Cu, but was calculated as 1.04 for Cd and 3.9 for Pb (Nirola *et al.* 2015). In another study conducted in China, *P. yunnanensis* growing in Cu mine site in contaminated areas ranks as Mn, Cd, As, Zn, Pb, Cu (TF > 1.0) → Ag (0.5-1.0) → Cr, Ni, Mo (0.1-0.5), the translocation ability for heavy metals of *P. massoniana* in contaminated areas ranks as Mn, As, Cd, Cr, Cu, Pb, Zn (> 1.0) → Ni (0.5-1.0) → Ag (< 0.5). In the contaminated areas, the translocation factors of *P. yunnanensis* for Mn, Cd, As, Zn, Pb, Cu were all > 1, and the maximum was 5.60 (Wang *et al.*, 2019).

In general, TF values in wood were much lower, while TF values in bark and leaves were much higher compared to wood. The TF values in Pn wood were also considerably higher than the other species and were calculated as 0.391 for Co, 0.167 for Cu and 0.571 for Pb. As a result of the study, the highest values were generally obtained in *Pinus nigra*. It is remarkable that the elements subject to the study were found in high concentrations, especially in *Pinus nigra* wood. This shows that *Pinus nigra* is a good phytoremediation plant that can be used to reduce Cu, Cr, Co, Cd, and Pb pollution. The most basic features sought in plants that can be used to reduce heavy metal pollution are the ability to accumulate heavy metals in as high concentrations as possible and not to die due to the toxic effects of heavy metals (Koc *et al.* 2024a). Furthermore, in tall woody trees, the plant's largest organ in terms of mass is wood, and therefore plants that can accumulate high concentrations of heavy metals in the wood part reduce heavy metal pollution more effectively (Key *et al.* 2023). According to these results, hypotheses a and d were accepted.

Plants have been used as biomonitors for monitoring heavy metal pollution for many years. For example, *Acer platanoides*, *Fraxinus excelsior*, and *Tilia tomentosa* for Pb, Fe, Ni, Zn and Cu (Hrotkó *et al.* 2021), *Picea pungens* for Cr and Zn (Sulhan *et al.* 2023), *Azadirachta indica*, *Cassia fistula*, *Conocarpus erectus*, *Eucalyptus camaldulensis*, *Morus alba*, and *Populus deltoids* for Pb, Zn, Cd, and Cu (Rahman *et al.* 2022), *Picea orientalis* for Ni and Pb (Isinkaralar *et al.* 2025), *Solanum lycopersicum*, *Capsicum annuum*, *Phaseolus vulgaris*, and *Zea mays* (Gültekin *et al.* 2025) for Pb, Fe, and Al.

In determining the changes in heavy metal pollution over a long period of time and in reducing pollution, the wood of high structured plants is frequently used. In these plants, the wood part is of great importance because it forms new layers over the years and it is possible to determine which layer was formed in which year. In addition, since the wood has a much larger mass compared to other organs, species that can accumulate heavy metals in this organ are also valuable in phytoremediation studies (Key *et al.* 2022; Key and Kulaç, 2022; Koc *et al.* 2024a). The extent to which metal ions drawn up into the sapwood remain present in those tissues is likely to depend on the xylem's varying ion exchange capabilities in various tree species. The ion exchange capacity (IEC) controls the quantity of metal ions adsorbed onto biomaterials (Hubbe *et al.* 2011). For one mole of a divalent metal element absorbed, one mole of Ca element is relocated (Crist *et al.* 2003). In other words, depending on the valence of the metal species, each type of adsorbed metal ion is expected to displace many other ions, such as hydrogen or sodium (Hubbe 2013). Positively charged ions can relate to most cellulosic compounds (Hubbe *et al.* 2022).

In this study, it was determined that *Pinus nigra* is the most suitable species to be used for both biomonitoring and phytoremediation purposes. In the studies conducted so far, *Pinus nigra* has been evaluated for its potential to accumulate B, Na (Erdem *et al.*

2023a), As, Sr, Pd, V (Koç 2025), Cu, Mn, Al (Erdem *et al.* 2023b), Se, Ag, Tl, and Sb (Şevik *et al.* 2024c). Studies have shown that *Pinus nigra* is also suitable for reducing the pollution of heavy metals, which are toxic and harmful even at very low concentrations, including As, Sr, Pd, V (Koç 2025), Se, Ag, Tl, and Sb (Şevik *et al.* 2024c).

CONCLUSIONS

1. The study examined variations in Cu, Co, Cr, Cd, and Pb concentrations in soils and plant organs in areas where mining activities are currently carried out and not carried out at a copper mining site. As a result of the study, Cr and Cd concentrations in soils remained below detectable limits. Furthermore, Cu concentration also remained below detectable limits to a large extent in soils in the spoil area. However, the concentration of these elements in plants was quite high. This result shows that soil is not the only source of heavy metal pollution at mining sites. Heavy metal pollution sources during the mining process in these areas should be evaluated separately.
2. The study results reveal that *Pinus nigra* is a suitable species that can be used to reduce Cu, Co, Cr, Cd, and Pb pollution. These elements are also heavy metals found in quite high concentrations in urban areas. It is recommended that *Pinus nigra* be used in landscaping and afforestation studies in areas with high levels of Cu, Co, Cr, Cd, and Pb pollution.

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