



Variation in Some Macronutrients in Soil and Plant Organs at Copper Mining Sites

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ABSTRACT

The present study aimed to determine the variation in calcium (Ca), magnesium (Mg), and potassium (K), which are crucial macronutrients for plants, in soil and plant organs at a copper mining site. In the study, the soil was sampled from various soil depths in the spoil field, the rehabilitation site in which planting was carried out and adult trees were present, and the forest area. Furthermore, bark, leaf, root, and wood samples were taken from black pine (*Pinus nigra* Arnold.), scots (*Pinus silvestris* L.), and black locust (*Robinia pseudoacacia* L.) species growing in the rehabilitation and forest areas. The work determined general variation in the concentrations of elements in soils and organs according to the plant species, and variation in element concentrations depending on the soil depth was statistically significant only in Ca. However, the determined element concentrations were quite high. In line with the average values, the variation in Mg in plants was not statistically significant, while the highest Ca and K concentrations were obtained from *Robinia pseudoacacia* species.

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Introduction

Nowadays, environmental pollution constitutes one of the major problems on a global scale (Koç et al., 2024). Industrial activities are shown as the main cause of environmental pollution, which causes the death of millions of people every year, ecosystem disruption, loss of habitats for many living beings, and even global climate change (Şevik et al., 2024; Cantürk et al., 2024). In the last century, the extraction of underground mineral resources and their release into nature to meet the raw material needs in the industrial field is one of the activities increasing environmental pollution the most (Ghoma et al., 2022). Depending on the increase in the amount of raw materials required by the developing industry, mineral production and mining operations carried out for the extraction of underground mineral resources are rapidly increasing worldwide (Makineci et al., 2011; Gao et al., 2021; Kuzmina et al., 2023). As a result of these activities, some elements have been released into nature at levels well above normal. Accordingly, the concentrations of the said elements have increased significantly in the air (Key et al., 2022; Canturk et al., 2024), soil (Istanbullu et al., 2023), and water (Demir et al., 2021; Mutlu et al., 2023; Kutlu and Mutlu, 2024).

In the area where mining activities are carried out, the soil's chemical, physical, and biological characteristics are significantly affected, in addition to the effects of the elements extracted from underground reserves and released into nature. As a result of this process, organic matter in the soil is significantly lost, and a material that is very poor in plant nutrients is formed. This situation also substantially impacts the restoration of the area after the mining operation (Ribeiro et al., 2021; Ma et al., 2021; Ergül and Kravkaz Kuşçu, 2024).

The areas damaged after mining activities need to be restored quickly. Planting is the most commonly used method for the improvement of mining sites. However, soil that is physically, chemically, and biologically deformed restricts plant growth (Ahirwal and Pandey, 2021) because plant growth is mainly shaped under the influence of climatic factors such as precipitation and temperature (Erturk et al., 2024; Aricak et al., 2024) and edaphic factors, e.g. soil depth, organic matter content, pH, and nutrients (Kravkaz Kuscu et al., 2018b; Savas et al., 2021). Therefore, soil with changed chemical structure and nutrient content is among the most essential factors that influence planting success.

There are 16 absolute nutrients necessary for plant nutrition, nine of which are macronutrients (H, C, O, P, N, Ca, K, S, and Mg) and are absolutely necessary for plant development (Aygün et al., 2018). However, the amount and distribution of these elements in the soil change due to mining activities. In order to carry out successful rehabilitation work at mining sites, it is essential to determine the amount and distribution of these elements in the soil and the concentrations of these elements in plant organs growing in these areas. The objective of the current work was to determine the concentrations of macronutrients Mg, Ca, and K in soil and plant organs at a copper mining site.

Materials and Methods

The research was carried out in Küre district, in which one of the biggest copper mines in Türkiye is located. In the study, the soil was sampled from the topsoil (0-5 cm) and subsoil (30-35 cm) depths of the spoil field (the site at which rehabilitation work has not yet been performed), the rehabilitation site that afforested, mature and healthy trees, and the naturel forest area. The soil was sampled from the soils where *Pinus nigra* (Pn), *Pinus silvestris* (Ps), and *Robinia pseudoacacia* (Rp) species grow in the rehabilitation and forest areas. Furthermore, branch and root samples were obtained from trees growing in the area where soil samples were taken.

Preliminary preparations were made for the analysis of the samples brought to the laboratory after being labeled and put in bags. At this stage, soil samples were dried for a while and then sieved and dried at a temperature of 45°C for a period of two weeks. Plant samples were first disintegrated, and branches were separated into leaf, bark,

and wood parts. Samples were dried under room-dry conditions for a while, then dried at 45°C for one week, ground, and dried again at 45°C for two weeks. The Mg, Ca, and K concentrations in the dried samples were determined with the help of the ICP-OES device. Recently, the aforesaid method has frequently been utilized for elemental analysis in soils (Istanbullu et al., 2023) and various organs of plants (Erdem et al., 2023a,b). The acquired data were evaluated using the SPSS package, and the analysis of variance and Duncan's test were performed on the data. The researchers simplified, tabulated, and interpreted the data obtained.

Results

According to the variance analysis results given in Table 1, the variation in Mg concentration in plants was revealed to be statistically significant on an organ basis in all species and on a species basis in all organs. The average values in the plant organs showed that the highest value was obtained from leaves, while the lowest value was determined in wood. The highest Mg concentrations were found in wood and bark in Pn species and leaves in Rp species. Table 2 presents the variation in Mg concentration in soils by species and soil depth.

Considering the results in the table, the variation in Mg concentration in soils was identified to be statistically significant on a soil depth basis in Pn in the forest area and on a species basis in all soils. The highest value in subsoil and topsoil was acquired in the spoil and Pn in the spoil field. The maximum values according to average values were also obtained in the spoil and Pn in the spoil field. Table 3 shows the variation in Ca concentration in plants by species and organs.

Table 1. Variation in Mg (ppm) concentration in plants by species and organs

Area	Species	Root	Wood	Bark	Leaf	F	Average
Spoil	Pn	834.7 aA	502.2 cA	1817.7 bcB	2071.2 aB	14.1***	1306.4
	Ps	2157.4 bC	370.8 bA	1042.7 aAB	1229.5 aB	8.0***	1200.1
	Rp	701.2 aA	343.4 bA	1322.8 abA	4851.9 bB	8.4***	1804.8
Forest	Pn	1636.0 bB	417.7 bcA	1892.9 cB	2037.6 aB	15.0***	1496.0
	Ps	821.8 aB	429.3 bcA	1089.6 aC	1430.8 aD	21.9***	942.9
	Rp	2060.4 bC	246.2 aA	1066.3 aB	3872.3bD	2805.0***	1811.3
F-value		7.1***	6.9***	4.8**	6.0***		2.1 ns
Average		1368.6 B	384.9 A	1372.0 B	2582.2 C	29.6***	

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. ns=not significant; * $P\leq 0.05$; ** $P\leq 0.01$; *** $P\leq 0.001$.

Table 2. Variation in Mg (ppm) concentration in soils by species and soil depth

Area	Species	Sub	Top	F	Average
Spoil	-	37398.2 b	31920.7 b	3.3 ns	34659.5 b
	Pn	35240.9 b	39143.3 b	0.2 ns	37192.1 b
	Ps	14014.2 a	15176.0 a	0.1 ns	14595.1 a
	Rp	18242.7 a	14723.1 a	1.4 ns	16482.9 a
Forest	Pn	17441.5 aA	23190.5 aB	33.5***	20316.0 a
	Ps	12710.5 a	16731.0 a	0.4 ns	14720.8 a
	Rp	19417.9 a	19793.4 a	0.0 ns	19605.7 a
F-value		9.8***	9.5***		18.7***
Average		22066.6	22954.1	0.1 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; * $P\leq 0.05$; ** $P\leq 0.01$; *** $P\leq 0.001$.

Table 3. Variation in Ca (ppm) concentration in plants by species and organs

Area	Species	Root	Wood	Bark	Leaf	F	Average
Spoil	Pn	1087.7 aA	1746.9 bA	6296.3 bcC	3739.0 abB	89.6***	3217.5 a
	Ps	6604.9 cC	697.6 aA	4935.3 abBC	2750.5 aAB	8.4***	3747.0 a
	Rp	6253.2 cB	2515.1 cA	14389.6 cC	21191.2 cD	47.6***	11087.3 b
Forest	Pn	4393.8 bcB	890.2 aA	7668.3 cD	5378.3 bC	78.7***	4582.7 a
	Ps	3352.8 abB	894.6 aA	3777.2 aB	3350.0 aB	35.7***	2843.6 a
	Rp	12120.1 dB	2617.0 cA	15622.9 cC	30049.0 dD	423.8***	15102.2 c
F-value		15.1***	15.2***	56.3***	326.6***		29.0***
Average		5635.4 B	1560.2 A	8781.6 C	11076.3 C	22.3***	

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. ns=not significant; * $P\leq 0.05$; ** $P\leq 0.01$; *** $P\leq 0.001$.

Table 4. Variation in Ca (ppm) concentration in soils by species and soil depth

Area	Species	Sub	Top	F	Average
Spoil	-	3161.7 aB	1428.8 aA	13.9**	2295.3 ab
	Pn	882.4 aA	1161.3 aB	7.3*	1021.9 a
	Ps	15755.9 c	5124.1 b	8.3 ns	8313.6 c
	Rp	9059.4 bB	1802.8 aA	5.5*	4705.4 b
Forest	Pn	14138.2 c	13386.7c	0.4 ns	13762.4 d
	Ps	2535.8 a	2073.2 a	0.2 ns	2188.9 ab
	Rp	15847.5 c	15168.4 c	0.1 ns	15507.9 d
F-value		20.0***	51.7***		42.8***
Average		8656.3 B	5580.5 A	5.1*	

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; * $P\leq 0.05$; ** $P\leq 0.01$; *** $P\leq 0.001$.

Table 5. Variation in K (ppm) concentration in plants by species and organs

Area	Species	Root	Wood	Bark	Leaf	F	Average
Spoil	Pn	2094.8 bB	1589.9 cdA	3272.8 bC	5846.0 cD	118.3***	3200.9 b
	Ps	3615.6 cB	1194.5 bA	3793.7 cB	4187.7 bB	15.1***	3197.8 b
	Rp	4344.8 cB	1242.5 bcA	5125.8 dB	3881.1 bB	9.5***	3648.5 b
Forest	Pn	651.0 aA	770.4 aA	2173.2 aB	2529.6 aB	43.7***	1531.1 a
	Ps	611.1 aA	1874.2 dB	5480.9 dC	6800.1 cD	169.9***	3691.6 b
	Rp	11408.3 dD	1645.1 dA	5439.2 dC	4055.3 bB	230.0***	5637.0 c
F-value		84.7***	9.5***	56.3***	14.8***		11.7***
Average		3787.6 B	1386.1 A	4214.3 B	4550.0 B	21.4***	

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. ns=not significant; * $P\leq 0.05$; ** $P\leq 0.01$; *** $P\leq 0.001$.

Considering the values in the table, it is noteworthy that the variation in Ca concentration in plants was statistically significant on an organ basis in all species and on a species basis in all organs. Whereas the highest values in roots, bark, and leaves were obtained from Rp in the forest area, the highest value in wood was acquired from Rp in the spoil field and Rp in the forest area. Likewise, the average values demonstrated that the maximum value was acquired from Rp in the forest area. Table 4 contains the variation in Ca concentration in soils by species and soil depth.

Considering the analysis of variance results, the variation in Ca concentration in soils was determined to be statistically significant in the spoil, Pn in the spoil field, and Rp in the spoil field on a soil depth basis and in all soils on a species basis. Whereas the maximum value in subsoil was acquired from Ps in the spoil field, Pn in the forest area, and Rp in the forest area, the maximum values in topsoil were acquired from Pn in the forest area and Rp in the forest area. The average values showed that the highest value was obtained from Pn in the forest area and Rp in the forest area. The analysis of variance determined a statistically significant difference between the average

values, and the average Ca concentration was calculated as 5580.5 ppm in topsoils and 8656.3 ppm in subsoils. Table 5 presents the variation in K concentration in plants by species and organs.

The findings in the table demonstrated a statistically significant variation in K concentration in plants on an organ basis in all species and on a species basis in all organs. Upon examining the species according to the average values, the maximum value was acquired from Rp in the forest area, while the minimum value was acquired from Pn in the forest area. Likewise, the lowest value in accordance with average values was observed in wood. Table 6 shows the variation in K concentration in soils by species and soil depth.

Considering the values in the table, the variation in K concentration in soils was identified to be statistically significant in Pn in the forest area on a soil depth basis and in all soils on a species basis. The average values demonstrated that the maximum value in species was acquired in the spoil and Ps in the spoil field, while the minimum value was found in Ps in the forest area.

Table 6. Variation in K (ppm) concentration in soils by species and soil depth

Area	Species	Sub	Top	F	Average
Spoil	-	6985.2 c	6369.7 d	0.7 ns	6677.5 d
	Pn	2554.1 ab	3560.8 b	3.1 ns	3057.5 b
	Ps	7031.3 c	6259.5 d	0.2 ns	6645.4 d
	Rp	5645.0 c	4812.4 c	2.1 ns	5228.7 c
Forest	Pn	2482.6 abA	5085.0 cB	39.5***	3783.8 b
	Ps	1231.7 a	1706.0 a	4.1 ns	1468.9 a
	Rp	3533.0 b	2900.9 b	1.6 ns	3217.0 b
F-value		14.1***	19.5***		25.8***
Average		4209.1	4384.9	0.1 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; * $P\leq 0.05$; ** $P\leq 0.01$; *** $P\leq 0.001$.

Discussion and Conclusion

The study determined the variation in the concentrations of Mg, Ca, and K, which are the most important macronutrients for plant nutrition, in soil and plant organs. Of the studied elements, Mg is the 8th most abundant mineral on earth and is required for plant development and growth. A typical symptom of Mg deficiency leads to the formation of interveinal chlorosis in leaves, impacts various critical physiological and biochemical processes in higher plants, and prevents plant growth and development. Mg acts as the central atom in the chlorophyll molecule. It has a role in many enzyme activities and the structural stabilization of tissues. It is among the crucial macronutrients for plants and has a major role in numerous biochemical processes, particularly in photosynthesis as the central atom in chlorophyll (Wang et al., 2020; Erdem et al., 2024). The study found that the Mg concentration ranged from 14595.1 ppm to 37192.1 ppm on average in soils and from 942.9 ppm to 1811.3 ppm on average in plants. In wood, the Mg concentration was calculated to range from 246.2 ppm to 502.5 ppm. Erdem et al. (2024) determined that Mg concentrations in the wood of diverse plants varied between 157.8 ppm and 220.6 ppm.

Another element studied, K, is a vital macronutrient necessary for the development and growth of plants (Pramanik and Kalita, 2019). K plays essential roles in plants, such as membrane potential regulation, osmoregulation, co-transport of sugars, growth, and stress adaptation. It represents an essential fertilizer that plays a role in many physiological and biochemical processes crucial to plant growth, quality, yield, and stress tolerance. Its deficiency or excess causes many plant functions to deteriorate (Qi et al., 2019; Johnson et al., 2022). The study revealed that the K concentration in soils varied between 1468.9 ppm and 6677.5 ppm, and the K concentration in plants varied between 1531.1 ppm and 3691.6 ppm.

Another element subject to the study, Ca, plays a significant part in the growth and development of cells, the adjustment of membrane permeability, the stabilization of tissues, and the quality of plants. Furthermore, it has important effects on the chemical and physical characteristics of the soil. Therefore, it is indispensable for fauna, microflora, plants, and soil. In case of Ca deficiency, the quality and yield of plants generally decrease (Mossi, 2018). The study determined that the Ca concentration varied between 1021.9 ppm and 13762.4 ppm in soils and between 2843.6 ppm and 11087.3 ppm in plants. Erdem (2022) stated that the Ca concentration varied between 6473.47 ppm and 9470.12 ppm in soils and between 4374

ppm and 5473.2 ppm in plants, and the minimum average values were acquired in cones and wood.

The study results showed that the element concentrations in soils and plant organs were quite high. This situation significantly impacts plant development because the presence of these elements in high concentrations in the soil makes it difficult for plants to take water and creates drought-like stress. Plants are exposed to various stress factors that limit plant development throughout their lives, such as drought (Koc, 2021), heavy metals (Cobanoğlu et al., 2023), UV-B (Ozel et al., 2021a), nanoparticles (Isinkaralar et al., 2024; Özel et al., 2024) and radiation (Ozel et al., 2021b). The high levels of some nutrients in the soil are also a stress factor for plants, which increases osmotic pressure, prevents plants from taking water, and creates a drought-like effect. Drought is among the major stress factors that limit plant development (Koc, 2022).

The elements examined in the present study are also heavy metals. Whereas a number of heavy metals, e.g. Hg, Pb, V, As, and Cr, may be toxic and fatal to living beings even at low concentrations (Key et al., 2023; Isinkaralar et al., 2023; Sevik et al., 2024), it is reported that even heavy metals necessary as nutrients for plants harm them at high concentrations (Yayla et al., 2022; Sulhan et al., 2023). High concentrations of the elements, which have been studied, in soils also limit plant development in this respect.

As is known, plant development and all phenotypic characteristics are shaped due to the interaction between environmental conditions and genetic structure (Kurz et al., 2023; Özdikmenli et al., 2024; Hrivnak et al., 2024). Environmental factors are basically divided into two groups: climatic (Çobanoğlu et al., 2023; Ertürk et al., 2024) and edaphic (Kravkaz Kuşçu et al., 2018a). Plant nutrients are the most important factors affecting plant development among the edaphic factors. Mining activities not only disrupt the soil structure but also significantly impair its nutrient content.

Recommendations

The study determined that the Mg, Ca, and K concentrations in the soils and plants grown in the study area were quite high. The high levels of these elements are a factor limiting plant development. However, the plants examined in the study continue their normal development in the spoil field within this region. Hence it can be said

that the species, which have been researched, are resistant to high concentrations of these elements. It is recommended that the plants examined in the study be used in similar areas.

The study obtained the minimum element concentrations in the wood part. Wood represents the plant's largest organ, and the amount of elements stored in this organ is important. Both low and high concentrations of the elements subject to the study can lead to undesirable outcomes. Using the research results, species can be used in applications in line with the desired purpose. For example, the study found the lowest concentrations in wood in Ps species and the highest concentrations in Rp species. In locations with Ca deficiency in the soil, Ps should be preferred because it uses less Ca in the soil, and in locations with Ca pollution, Rp should be preferred to reduce the Ca concentration.

Declarations

Author Contribution Statement

H.A.E. and İ.S.K.K.: Data collection, investigation, formal analysis, writing the original draft, methodology, review and editing.

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Conflict of Interest

The authors declare no conflict of interest.

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