Change of Cr, Co, and V Concentrations in Forest Trees by Species, Organ, and Soil Depth

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Heavy metal pollution is one of the most important environmental problems threatening living organisms and environmental health. Thus, there is much research interest in monitoring and reducing heavy metal pollution. Plants' potential to accumulate heavy metals in various organs differs greatly. Therefore, it is necessary to determine the most suitable species and organs first and acquire knowledge of the subjects such as the transfer of heavy metals within plants and their particular intake into plants. This study investigated Cr, Co, and V, which are among the most important and dangerous heavy metals, and are listed in the primary pollutant list of the Agency for Toxic Substances and Disease Registry. Their concentrations were studied at different depths of soils where *Pinus nigra*, *Pinus sylvestris*, *Fagus orientalis*, and *Abies nordmanniana* subsp. *bornmüelleriana* species are grown, in the leaves, cones, wood, bark, and roots. The results showed that the intake of these elements into plant bodies generally occurs through the soil. Additionally, the highest concentrations in both leaves and roots were generally obtained in *Fagus orientalis* and *Abies nordmanniana* subsp. *bornmüelleriana* species. It can be stated that those species are the most suitable species to monitor and reduce heavy metal pollution.

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INTRODUCTION

Environmental pollution has become one of the most important problems worldwide due to anthropogenic activities in the last century (Elsunousi *et al.* 2021; Isinkaralar *et al.* 2022). It has directly and indirectly caused many problems for ecosystems and organisms such as global climate change, decrease in biodiversity, and many diseases and deaths among organisms (Tekin *et al.* 2022; Varol *et al.* 2022; Cobanoglu *et al.* 2023). Furthermore, it has been stated that environmental pollution is responsible for the deaths of more than 7 million people annually in the world (Key *et al.* 2022).

Among the components of environmental pollution, heavy metals are the most damaging to organisms and ecosystems (Ghoma *et al.* 2022). This is because heavy metals can be harmful to organisms even at low concentrations and they can remain undegraded in nature for a long time (Yayla *et al.* 2022). Among heavy metals, chromium (Cr), cobalt (Co), and vanadium (V), which were examined in this work, are the most harmful. Cr significantly affects the pollution, ecosystem, and natural sources, especially the water and soil (Prasad *et al.* 2021). Cr is as toxic for human health as it is for soil. In particular, Cr(VI) has no known biological function and is a strong carcinogen (Monga *et al.* 2022). Chronic exposure to and bioaccumulation of Cr cause many pathophysiological problems such as toxicity, allergic reaction, anemia, burns, wounds in stomach and small intestines, and damage in the male reproduction system and sperms (Hossini *et al.* 2022), as well as lung cancer, damages in liver, kidneys, and stomach, and epidermal damage and sensitivity (Kimbrough *et al.* 1999).

Co, another heavy metal, causes harmful effects on human health (Farjana *et al.* 2019). Potential leakage of Co ions might reduce the catalytic activity and threaten ecological safety and human health by causing secondary water pollution (Wang *et al.* 2022). Excessive Co^{2+} ion content might cause Co poisoning and cause negative effects on the human body such as vomiting, paralysis, diarrhea, and hypotension (Hu *et al.* 2000; Liao *et al.* 2018), as well as cancer (Farjana *et al.* 2019).

High concentrations of V might pose potential health risks for microbes, plants, animals, and humans (Hao *et al.* 2021). Exceeding the threshold level of V intake in humans causes problems including vasoconstriction, congestion, focal bleeding hemorrhage in lungs and adrenal cortex, fatty liver, diarrhea, dehydration, cardiac disorders, decreased food intake, and weight loss (Altaf *et al.* 2021). Moreover, long-term exposure to V has toxic effects on the human respiratory and digestive systems, kidneys, liver, skin, and immune system (Jayawardana *et al.* 2015; Hao *et al.* 2021), and it can cause pulmonary lesions, renal failure, and neurological disorders (Frank *et al.* 1996; Hao *et al.* 2021). The Agency for Toxic Substances and Disease Registry (ATSDR) included these three elements in the primary pollutant list because of their potential damage to humans and the environment (Savas *et al.* 2021).

Because of these effects, heavy metals pose a significant danger to organisms and the environment and, thus monitoring and reducing heavy metal pollution is one of the primary research subjects today (Karacocuk *et al.* 2022). It has been emphasized that the most useful instruments to be used in monitoring and reducing heavy metal pollution are plants (Turkyilmaz *et al.* 2020) because plants grown at locations with a high level of heavy metal pollution accumulate heavy metals from soil, water, and air in their bodies. Hence, they contribute to decreasing the heavy metal pollution in those environments (Erdem *et al.* 2023). Furthermore, each plant has its specific potential to accumulate heavy metals in its different organs (Yayla *et al.* 2022). For plants to be used in monitoring and reducing the heavy metal pollution, it is necessary to eliminate the knowledge deficiencies on this subject. It is important to determine which plants growing in the same environment accumulate more heavy metals in which organs, and reveal through which pathways the intake of heavy metals into plant body occurs, and then relate this knowledge to the soil (Erdem *et al.* 2023). The present study aimed to determine the accumulation of Cr, Co, and V, which are among the heavy metals that can be harmful to human and environmental health, in different organs of different plants and compare it to the changes in the concentrations in total.

EXPERIMENTAL

Materials

The change of the concentrations of Cr, Co, and V elements that are among the heavy metals widely used in many fields currently and concentrations of which increase in the air, soil and water. For this reason, locations and concentrations of these metals within plant organs and soils, where different plants grow, was investigated. For this purpose, leaf, bark, wood, cone, and root samples were collected from *Pinus nigra* Arnold, (Pni), *Pinus sylvestris* L. (Psi), *Fagus orientalis* Lipsky (Fo), and *Abies nordmanniana* subsp. *bornmüelleriana* Mattf. (Abo) species growing in a confined area that has similar soil and climate conditions, within the borders of Araç district of Kastamonu province (Türkiye). The region where the study was conducted is important in terms of growing different tree species in similar soil and climatic conditions. Due to this feature, the effect of other environmental conditions is minimized. Thus, it was thought that the accumulation of different heavy metals in the soil and plant organs could be evaluated more accurately.

Because it has no cone, *Fagus orientalis* Lipsky species was not involved in this study. Furthermore, by eliminating the dead cover on the soil under each tree, soil samples were taken from 0 to 5 cm depth (upper oil), 20 to 30 cm depth (intermediate soil), and 50 to 60 cm depth (lower soil). Soil samples taken to the laboratory were kept in a dry environment for 2 weeks under room conditions and then dried at 45 °C for 2 weeks after sieving. The same procedures (except for sieving) were applied to the plant samples.

Dried samples were analyzed for Cu, Mn, and Al elements using an inductively coupled plasma with optical emission spectrometry (ICP-OES) device (Spectroblue, Spectro GmbH, Kleve, Germany). Concentrations were determined at the level of ppb. This method is widely used in elemental analysis for soil (Cetin *et al.* 2022a,b) and different organs of plants (Aricak *et al.* 2020) in recent years. The data obtained were analyzed using SPSS 22.0 package software (IBM Corp., Armonk, NY, USA) and subjected to variance analysis and the Duncan test. The data obtained were interpreted after simplification and tabularization.

RESULTS AND DISCUSSION

Among the elements examined here, the changes in Cr concentrations in soil by species and soil depth are presented in Table 1.

Table 1. Change of Cr Concentration in Soils

Species	**Soil Depth**			**F Values**	**Average**
	Upper	**Medium**	**Lower**		
Abo	59.61	56.06 bc	72.89 c	2.86 ns	62.85 c
Pni	55.18	45.15 ab	46.50 ab	0.89 ns	48.94 ab
Psi	47.26	39.57 ba	36.64 a	2.75 ns	41.16 a
Fo	39.31	65.00 c	64.72 bc	2.84 ns	56.34 bc
F Values	1.84 ns	4.77**	6.78***		6.42***
Average	50.34	51.45	55.19	0.54 ns	

Upon examining the changes in Cr concentration in soils, it can be seen that the change between depth levels by species was statistically significant, except for upper soil. In general, the lowest Cr concentrations in soil were obtained with Psi, whereas the highest concentrations were obtained with Abo and Fo. In addition, the change in Cr concentration by soil depth was not statistically significant. The changes in Cr concentrations in plants are presented in Table 2.

Table 2. Change of Cr Concentration in Plants

Species	ORGAN					F-Values	Average
	Leaf	Bark	Cone	Wood	Root		
Abo	2599.53 Bb	1486.17 A	884.57 Aa	1105.28 A	3596.84 Bb	10.00***	1934.48 c
Pni	1039.24 Aa	1599.22 B	1979.62 Bb	767.06 A	1690.51 Ba	7.03***	1415.13 ab
Psi	1082.42 Aba	1382.11 B	740.20 Aa	895.15 A	2112.86 Ca	8.36***	1242.55 a
Fo	1425.46 Aa	1266.11 A	-	1402.37 A	2931.44 Bab	3.92*	1756.34 bc
F Val.	4.57*	0.53 ns	33.96***	1.58 ns	3.70*		3.64*
Average	1536.66 A	1433.40 A	1201.46 A	1042.47 A	2582.91 B	13.12***	

As a result of the variance analysis, it was determined that the change of Cr concentration by organs was statistically significant for all organs, with the exception of bark and wood, and the change in mean values by species was statistically significant. The highest concentrations in cones were obtained from Pni, whereas the lowest Cr concentrations in other organs and the lowest mean values were obtained from Psi, while the highest values were obtained from Abo. The changes in Cr concentrations by organs were statistically significant in all the species. In general, the lowest values were obtained from woods, whereas the highest values were found in roots.

The changes in concentrations of Co, another element examined here, in soils by species and soil depths are presented in Table 3.

Table 3. Change of Co Concentrations in Soils

Species	Soil Depth			F-Values	Average
	Upper	Medium	Lower		
Abo	7501.08 A	7359.30 A	9997.77 Bb	5.32*	8286.05
Pni	7780.55	6635.13	6117.38 a	1.04 ns	6844.36
Psi	8655.75	8134.52	8237.58 b	0.38 ns	8342.62
Fo	5889.02	8540.11	9675.77 b	2.77 ns	8034.97
F Values	1.88 ns	2.02 ns	3.32*		1.98 ns
Average	7456.60	7667.27	8507.13	1.63 ns	

As can be seen in Table 3, the results obtained from the variance analysis showed that the change of Co concentration between soil depths (except for lower soil) by species and the changes between species (except for Abo) by soil depths were not statistically significant ($p > 0.05$). Co concentration in lower soil was higher in Abo. The lowest Co concentration in lower soil was found in Pni species. The changes in Co concentration in plants are presented in Table 4.

Table 4. Change of Co Concentration in Plants

Species	ORGAN					F - Values	Average
	Leaf	Bark	Cone	Wood	Root		
Abo	396.26 Abab	462.95 Bb	407.11 Aba	340.22 A	759.51 Cb	24.91***	473.21
Pni	384.17 Ba	412.60 Bab	499.15 Cb	329.37 A	366.84 Aba	12.73***	398.43
Psi	381.22 Aa	365.86 Aa	366.35 Aa	341.15 A	590.06 Bb	16.98***	408.93
Fo	407.42 Ab	360.99 Aa	-	343.33 A	701.84 Bb	9.22***	453.40
F Val.	5.32**	6.26**	22.88***	1.42 ns	5.97**		2.39 ns
Average	392.27 AB	400.60 AB	424.20 B	338.52 A	604.56 C	23.86***	

The changes in Co concentration by organs were statistically significant in all species, and the changes by species were statistically significant in all organs (except for wood). Given the results, it can be seen that the lowest values were obtained from woods. Considering the species, the Duncan test determined that the values obtained from Abo were in the last groups in all organs, whereas the values obtained from Psi were in the first groups. The changes in the concentration of V, by species and soil depths are presented in Table 5.

Table 5. Change of V Concentration in Soils

Species	Soil Depth			F-Values	Average
	Upper	Medium	Lower		
Abo	74.74	73.50 ab	86.58	2.81 ns	78.27
Pni	79.46	62.84 a	72.97	0.92 ns	71.76
Psi	79.16	78.58 b	71.06	1.21 ns	76.27
Fo	49.26 A	82.64 Bb	81.08 B	8.63**	70.99
F Values	2.90 ns	4.75**	1.93 ns		0.83 ns
Average	70.65	74.39	77.92	1.19 ns	

As a result of the variance analysis, it was determined that the change by species was statistically insignificant in all soil depths (except for intermediate soil), whereas the change by soil depths was statistically insignificant in all species (except for Fo) ($p > 0.05$). In Fo, the concentration of V was at the lowest level in upper soils. The lowest V concentration in intermediate soils was found in Pni species. The changes in V concentrations in plants are presented in Table 6.

As a result of the variance analysis, the change of V concentration by organs was statistically significant in all species other than Fo. Given the values, it can be seen that the highest values were found in Abo and Fo among species and in roots among organs. However, the lowest values were obtained from wood, while the levels found in leaves were low in contrast to the other elements.

As a result of this study, the changes in concentrations of the elements examined here by species and soil depth were in general statistically insignificant. This finding suggests that plant species did not affect the concentrations of elements, which were examined here, in soil. Additionally, the highest concentrations were generally found in roots. Thus, it can be stated that the origin of Cr, Co, and V contents of plants is the soil. Previous studies showed that heavy metals enter into the plant body through absorption by roots from the soil, by leaves from the air, or directly into the stem (Chen *et al.* 2021).

Table 6. Change of V Concentration in Plants

Species	ORGAN					F-Values	Average
	Leaf	Bark	Cone	Wood	Root		
Abo	1757.73 Aa	2681.95 A	2347.43 A	1701.46 Aab	4400.60 B	7.19***	2738.41
Pni	1758.56 Aa	2447.35 A	2941.60 B	1864.66 Aab	2848.42 B	5.42**	2468.39
Psi	2231.24 Ab	1854.63 A	2461.66 A	1411.00 Aa	3440.11 B	6.85**	2364.27
Fo	2802.86 bc	2661.96	-	2200.63 b	4661.66	2.28 ns	3211.88
F Val.	11.67***	2.29 ns	3.19 ns	5.01*	1.31 ns		2.14 ns
Average	2213.49 AB	2442.11 AB	2607.94 B	1784.40 A	3837.69 C	11.31***	

The lowest values in Cr concentration were obtained in pines and the highest values in fir. In Co and V, there was no difference between the species according to the mean values. However, according to the mean values, the highest values in all elements were obtained in the roots.

The results can be reported by element as follows: For Cr the results indicated that the concentrations varied in Abo: root > leaf > bark > wood > cone, in Pni: cone > root > bark > leaf > wood, in Psi: root > bark > leaf > wood > cone, and in Fo: root > leaf > wood > bark. For Co the results indicated that the concentrations varied in Abo: root > bark > cone > leaf > wood, in Pni: cone > bark > leaf > root > wood, in Psi: root > leaf > cone > bark > wood, and in Fo: root > leaf > bark > wood. For V the results indicated that the concentrations varied in Abo: root > bark > cone > leaf > wood, in Pni: cone > root > bark > wood > leaf, in Psi: root > cone > leaf > bark > wood, and in Fo: root > leaf > bark > wood.

In plants, roots are the organs that have the least contact with air; however they are the organs through which most of the element intake from the soil occurs (Koç 2021). In plants, the organs with the highest contact with air are leaves and barks. Hence, heavy metal concentrations in these organs would be very high in environments with a high level of heavy metal pollution in the air (Cesur *et al.* 2022) because the particles in the air are contaminated by heavy metals and they can accumulate in barks, which have rough surfaces, by adhering to the surface (Isinkaralar *et al.* 2022). Similarly, heavy metal concentrations in leaves due to air pollution are at high levels (Karacocuk *et al.* 2022). At the end of this study, the finding that heavy metal concentrations in barks and leaves were very low suggests that Cr, Co, and V pollution in the air was at a minimal level. It suggests that the accumulation in roots originated from the soil.

Plants are among the most effective instruments to be used in reducing the heavy metal pollution, especially in the air. Considering the selection of plants contributing to reducing the heavy metal pollution in the air the most, although which heavy metals the plant accumulates in which organs more is important, the growth performance and total mass of those organs are also important. For instance, it was determined in many studies that heavy metal concentrations in tree barks were at high levels (Sevik *et al.* 2019). However, the bark is an organ that grows slowly and high levels of heavy metal concentration in bark mainly originate from the particles, which have been contaminated by heavy metals, on the surface of bark (Cesur *et al.* 2021). Thus, the bark is not an organ that can be used effectively in monitoring and reducing the heavy metal pollution. However, the plants that can accumulate heavy metal in their leaves, which actively operate and have a high mass, are suitable for this purpose because the leaf is an organ that has the most contact and interaction with the air.

Air intake occurs *via* stomas in leaves and heavy metals in the air can be taken into the leaf during this process (Karacocuk *et al.* 2022). As a result of this study, it was determined that heavy metal concentrations in leaves significantly differed by species and the highest concentrations in leaves were found in Abo for Cr, Fo and Abo for Co, and Fo for V. Previous studies revealed that one of the most important factors determining the change of heavy metal concentration in organs of plants was the plant species (Turkyilmaz *et al.* 2018). Upper limits of normal concentrations are 80 µg/g for Cr, 20 µg/g for Co, and 200 µg/g for V in non-polluted soils (Pais and Jones 1997). Studies have shown that Cr is harmful and carcinogenic in soils at concentrations above 12.2 mg/kg (Laszewski and Lehrke 1992).

The normal limits of Co contents in plants are stated as between 0.05 and 0.5 mg kg^{-1}. Plants can accumulate small amounts of Co from the soil. The uptake and distribution of Co in plants is species dependent and controlled by different mechanisms. Very little information is available regarding the phytotoxic effect of excess Co (Nagajyoti *et al.* 2010). Cr is toxic to most higher plants at 100 $\mu M \cdot kg^{-1}$ dry weight. Cr concentration was measured as 0.006 to 18 mg kg^{-1} in plants (Shanker *et al.* 2005). The growth of plants can be stimulated by trace quantities of V (1-10 µg L-1), but concentrations (100 µg L-1) were found to be toxic. V concentration above 2 ppm exerts toxic effects in plants by causing oxidative stress, growth inhibition, leaf chlorosis and necrosis, coralloid root structure and suppression in the uptake of different essential elements (Roychoudhury 2020).

The elements examined within the scope of this study are among those posing significant risks to human and environmental health, and thus, many studies have examined these elements (Sulhan *et al.* 2022). Those studies reported that these elements generally arise from anthropogenic sources such as urbanization, industry, and traffic (Kuzmina *et al.* 2023). Hence, heavy metal pollution in the air is high around industrial facilities, in urban areas, and in high-traffic areas (Sevik *et al.* 2020). The intake and bioaccumulation of heavy metals, which can penetrate the plants through soil or air in these regions, are shaped by complex mechanisms (Sulhan *et al.* 2022).

The factors playing role in the intake and accumulation of heavy metals in plant bodies include plant species, precipitation and air humidity, plant habitus, organ structure, heavy metal type, and heavy metal's interaction with the plant (Cesur *et al.* 2021). Furthermore, heavy metal absorption and accumulation potential of plants are closely related with plant metabolism and the conditions influencing the plant metabolism, such as stress level, genetic structure, and climate and soil conditions, also affect the heavy metal absorption and, consequently, heavy metal pollution (Key *et al.* 2022).

CONCLUSIONS

Previous studies showed that one of the most important factors determining the change of heavy metal pollution in plants' organs was the plant species. Therefore, accurately selecting the species to be used in monitoring and reducing the heavy metal pollution in the air is important. Given the results achieved in this study, it was determined that the most suitable species to be used in monitoring and reducing the concentrations of Cr, Co, and V in the air were Fo and Abo.

1. It was determined that Cr, Co, and V accumulating in different organs of plants originated mainly from the soil. In areas with a high level of heavy metal pollution in the air, the heavy metals accumulate in soil by sinking due to the gravity.
2. It was determined that Cr and Co accumulation in the roots of Fo and Abo species was high. These species can be used in reducing the heavy metal pollution in soil, as well as the heavy metal pollution in the air.
3. The present study aimed to determine the relationship between heavy metal concentrations in plant organs with the heavy metal concentrations in the soil.

Therefore, this provides important information about the pathway of heavy metal intake in plants and their accumulation in organs. Previous studies revealed that the most important knowledge deficiency in this subject was about pathways of heavy metal intake in plants and their speciation afterward. Because there still is a significant information deficiency in this subject, it is recommended to diversify and increase the studies examining this subject.

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