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Usage of *Robinia pseudoacacia* and *Cedrus atlantica* in Monitoring and Reduction of Change of Niobium Pollution in Air

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Abstract: In this study, it was aimed to monitor the change in niobium (Nb) pollution, one of the heavy metals that can be harmful and toxic for human and environmental health, and to determine the usability of *Robinia pseudoacacia* and *Cedrus atlantica* species, which were determined to be biomonitors, in reducing Nb pollution.Within the scope of the study, samples were taken from the main stem of Robinia pseudoacacia and Cedrus atlantica, which grow under similar growing conditions in Düzce province, which is among the 5 most polluted cities in Europe according to the 2021 World Air Pollution report, and Nb concentrations were determined. As a result of the study, it was determined that *Cedrus atlantica* is suitable for monitoring the change in Nb concentration and *Robinia pseudoacacia* is suitable for reducing Nb pollution.

Keywords: Heavy metal, niobium, Atlas cedar, Black locust

Öz: Bu çalışmada, insan ve çevre sağlığı için zararlı ve toksik olabilen ağır metallerden biri olan niyobyum (Nb) kirliliğindeki değişimin izlenmesi ve *Robinia pseudoacacia* ve *Cedrus atlantica*'nın kirliliğin azaltılmasında kullanılabilirliğinin belirlenmesi amaçlanmıştır. Çalışma kapsamında 2021 Dünya Hava Kirliliği raporuna göre Avrupa'da havası en kirli 5 şehir arasında yer alan Düzce ilinde benzer yetişme koşullarında yetişen *Robinia pseudoacacia* ve *Cedrus atlantica*'nın ana gövdesinden örnekler alınarak Nb konsantrasyonları belirlendi. Çalışma sonucunda *Cedrus atlantica*'nın Nb konsantrasyonundaki değişimi izlemek için uygun olduğu, *Robinia pseudoacacia*'nın ise Nb kirliliğini azaltmak için uygun olduğu tespit edilmiştir.

Anahtar Kelimeler: Ağır metal, niyobyum, Atlas sediri, Yalancı akasya

1. Introduction

Air pollution, which has increased in the last century due to anthropogenic sources, especially industrial activities, is one of the most important global problems. It is stated that air pollution causes the death of approximately 7 million people every year [1], 6 million premature births, and 3 million low-weight babies [2]. It is stated that 92 percent of the world's population breathes polluted air, one in every 8 deaths is related to air pollution [3, 4], and air pollution is also one of the most important causes of global climate change [5]. Anthropogenic sources mainly cause air pollution and seriously threaten human health, especially in urban areas with high population density.

Studies conducted in recent years have shown that urbanization, like global climate change, is now an irreversible problem [6, 7]. The fact that more people live per unit area in urban areas and that pollution factors such as traffic, fuel burning, and garbage are very common in these areas causes the environment and especially air pollution, to affect human health more [8, 9].

Heavy metals are the most important and threatening components of air pollution [10]. Moreover, the concentrations of heavy metals in the air, which can be toxic and fatal to living things even at low concentrations, are constantly increasing due to anthropogenic sources [11]. Therefore, monitoring the change in heavy metal pollution in the air and studies on reducing pollution are among the priority research topics [12]. Therefore, many studies have been conducted on known and widely used heavy metals such as Cr [12], Co, Ni [13], and Cd [1]. However, in recent years, in addition to heavy metals such as Ba [4], Pd [14], and Sb [15], which are extremely harmful even at low concentrations, many studies have been conducted on heavy metals such as Fe [8], Mg [16] and Zn [17], which are necessary as nutrients for living things but can be harmful at high concentrations.

However, many elements are still neglected in these studies. One element neglected in heavy metal studies is niobium (Nb). Nb and its compounds can be toxic [18].

Moreover, it is known that heavy metals can be much more harmful when inhaled [19]. Indeed, when Nb is inhaled, it primarily adheres to the lungs and secondarily to the bones and interferes with calcium as an activator of enzyme systems. In laboratory animals, it has been determined that inhalation of niobium nitride and/or pentoxide causes lung scarring at exposure levels of 40 mg/m^3 [18]. Therefore, reducing Nb pollution in the air is of great importance. In this study, the wood of *Robinia pseudoacacia* and *Cedrus atlantica* species, which are frequently grown in urban areas, were examined to determine whether Nb accumulation occurs. In addition, it was aimed to determine the changes in Nb pollution levels until 2022, taking into account the pollution rates in the past years. As a result of the study, it is estimated that these data will increase towards 2022 and will differ according to the directions.

2. Material and Method

The study was carried out on trees growing in the city center of Düzce, among Europe's 5 most polluted cities [20, 21]. Materials taken from the main trunks of *Robinia pseudoacacia* (Black locust) and *Cedrus atlantica* (Atlas cedar) species were used in the study. These species are frequently used in landscape studies in Türkiye and Europe. Log samples were taken at the end of the vegetation season in 2022 by determining the north direction and brought to the laboratory, and the surface was smoothed. When the annual rings were examined, it was determined that the trees were 60 years old.

The annual rings were grouped over five years, and sawdust samples were taken from each group of wood (WD), inner bark (IB), and outer bark (OB) with the help of a steel drill. The study was conducted in 3 replications. Thus, 12 wood and bark samples from each species (12 wood, 1 outer bark, 1 inner bark) * 4 directions * 3 replicates, 144 samples were analyzed. Since there were 2 species in the study, a total of 288 samples were analyzed. The samples were dried in an oven at 45 °C, sorted and pre-burned. After pre-treatment, 65% HNO_3 and 30% H_2O_2 were added to the 0.5 g weighed samples. The chemically treated samples were incinerated at 200 °C. Then pure water was added to the burned samples and after reaching the desired level for measurement, they were analyzed with ICP-OES device and Nb concentrations were determined. This method is one of the most frequently used methods in previous studies in this field [2-21]. Variance analysis was applied to the obtained data with the help of the SPSS package program, and the data was evaluated using the Duncan test, simplified, tabulated, and interpreted.

3. Result

According to the average values and statistical analysis results regarding the change of Nb concentration in *Robinia pseudoacacia* based on organ and direction are given in Table 1.

Table 1. Change of Nb concentration (ppb) in *Robinia pseudoacacia* based on organ and direction

Organ	East	South	West	F	Mean
Ob	54278.1 a	56027.2	53004.4	3.9 ns	54436.6
Ib	56758.8 b	54709.5	52613.6	5.0 ns	54694.0
Wd	53448.7 a	55112.5	52750.8	3.7	53770.6
F	9.5***	0.5 ns	0.0 ns		1.7 ns
Mean	53744.3	55149.0	52759.1	0.2 ns	

*Different letters following each other represent the statistical difference at p≤0.05. Uppercase letters represent from right to left direction while lowercase letters from top to bottom. ns=not significant. *<0.05. **<0.01. ***<0.001. This explanation is valid for all tables.*

As a result of the analyses, all samples' Nb concentrations in the north direction remained below the detectable limits. When the table results are examined, it is seen that the change in Nb concentration in all directions on an organ basis and in all organs on a direction basis is statistically insignificant (p>0.05). The average values and statistical analysis results regarding the change in Nb concentration in *Robinia pseudoacacia* on a period and direction basis are given in Table 2.

Table 2. Change in Nb concentration (ppb) in *Robinia pseudoacacia* on a period and direction basis

Period	East	South	West	F	Mean
2018-2022	54903.7	55044.0	53881.4 cde	0.7 ns	54609.7
2013-2017	52776.9	55440.2	54604.9 e	2.3 ns	54274.0
2008-2012	53829.9	55119.6	52560.7 abc	1.8 ns	53836.7
2003-2007	53481.5	55707.6	54128.1 de	4.6 ns	54439.0
1998-2002	52128.4	54802.6	52065.5 ab	3.2 ns	52998.8
1993-1997	53680.3	55151.2	52926.3 bcd	3.3 ns	53919.3
1988-1992	52484.7 A	55148.3 B	52506.1 abcA	7.3*	53379.7
1983-1987	53279.2	54388.6	52414.4 abc	1.5 ns	53360.7
1978-1982	53639.8	55937.3	52848.0 abcd	4.5 ns	54141.7
1973-1977	53282.6 AB	54805.6 B	52032.2 abA	5.3*	53373.4
1968-1972	53964.8	54063.0	51250.1 a	3.6 ns	53092.6
1963-1967	53932.5 B	55741.5 C	51791.7 abA	5.4*	53821.9
F	1.1 ns	0.3 ns	4.2**		0.9 ns

The change in Nb concentration in *Cedrus atlantica* on an organ and direction basis is given in Table 3. When result is examined, it is seen that the change in Nb concentration in *Robinia pseudoacacia* woods is statistically significant only in the west direction on a period basis and only in the periods 1963-1967, 1973-1977, and 1988-1992 on a direction basis. Therefore, it can be said that the change in Nb concentration in *Robinia pseudoacacia* woods in terms of direction and period is statistically insignificant ($p>0.05$).

Table 3. The change in Nb concentration (ppb) in *Cedrus atlantica* on an organ and direction basis

Organ	North	East	South	West	F	Mean
OB	26418.8 aBC	25960.5 B	26808.4 C	25158.1 A	24.5***	26086.4 A
IB	56873.5 bC	24909.3 A	26191.1 B	25630.4 AB	2234.2***	33401.1 B
WD	31792.7 aB	24857.5 A	26292.0 A	25112.6 A	11.1***	27059.6 A
F	8.3**	1.5 ns	1.0 ns	0.1 ns		4.7*
Mean	33200.3 B	24946.4 A	26321.6 A	25152.8 A	15.7***	

According to Table 3, the change in Nb concentration in *Cedrus atlantica* based on organs is statistically significant only in the north direction. In terms of direction, the change in Nb concentration in all organs is statistically significant, and the highest values in all organs are obtained in the north direction. According to the average values, the data were collected in two groups; all directions were in the first group, while the value obtained in the north direction was in the second group. The change in Nb concentration in *Cedrus atlantica* based on period and direction is given in Table 4.

Table 4. Change in Nb concentration (ppb) in *Cedrus atlantica* based on period and direction

Period	North	East	South	West	F	Mean
2018-2022	56408.6 eB	25208.6 deA	25033.7 aA	25416.9 cA	1241.5***	33017.0 B
2013-2017	56384.6 eB	25119.3 deA	26383.9 bcdA	25845.4 cA	6182.5***	36204.6 B
2008-2012	29895.2 dC	21838.8 aA	26775.5 cdB	26079.1 cB	82.2***	26147.2 A
2003-2007	27173.8 bcC	24453.8 bA	25757.1 bB	26222.4 cB	38.7***	25901.8 A
1998-2002	27290.2 cC	24559.7 bcA	25865.2 bB	26231.2 cB	42.4***	25986.6 A
1993-1997	26727.9 abcB	24536.3 bcA	26099.1 bcB	26346.2 cB	16.8**	25927.4 A
1988-1992	26447.7 abcB	25017.0 cdA	26047.1 bcB	26007.8 cB	8.9**	25879.9 A
1983-1987	26763.4 abcC	25423.4 deA	26441.6 bcdBC	26226.7 cB	17.8**	26213.8 A
1978-1982	25925.5 aB	25255.3 deA	26930.9 dC	26525.8 cBC	15.1**	26159.4 A
1973-1977	26089.8 abB	25465.8 deB	26355.3 bcdB	20188.1 aA	36.4***	24524.7 A
1968-1972	26199.8 abcB	25632.3 efB	26749.0 cdB	23058.3 bA	16.4**	25409.9 A
1963-1967	26205.9 abcB	26042.0 fB	27065.2 dC	23203.1 bA	89.2***	25629.1 A
F	1070.6***	42.7***	6.6***	28.1***		3.8***

The change in Nb concentration in *Cedrus atlantica* is statistically significant in all periods in terms of direction and period. When the periods are examined according to the average values, it is striking that there has been a significant increase in the last 10-year period. Regarding direction, the highest values were generally obtained in the north direction.

4. Discussion

When the results obtained from the current study were evaluated, it was determined that there was a significant difference in Nb concentration among the species included. It was determined that the average Nb concentration, which was 53770.6 ppb in *Robinia pseudoacacia* woods, was 27059.6 ppb in *Cedrus atlantica* woods. This result shows that species' potential for Nb accumulation in woods varies significantly. This result has also been obtained in studies conducted to date, and it has been frequently emphasized that the potential for heavy metal accumulation varies significantly by species [22]. Because the potential of plants to absorb and accumulate heavy metals depends on many factors, such as the structure of the heavy metal and its interaction with the plant, as well as organ structure, weather conditions, and plant habitus [14].

These factors are also linked to other factors and to each other. For example, plant physiology is shaped by genetic structure [23-24] and environmental conditions [25]. Therefore, all factors affecting plant physiology also affect the entry and accumulation of heavy metals into the plant. Plant physiology is also shaped by the interaction of many factors affecting each other, such as genetic structure [26], edaphic [27], climatic [28] factors, stress factors [29]. Each of these factors primarily depends on the plant species and the responses of the plant species to environmental conditions.

As a result of the study, it was determined that there was no significant difference between the Nb concentrations in neighboring cell groups in *Robinia pseudoacacia* woods. At the same time, there was a significant difference between the Nb concentrations in neighboring cell groups in *Cedrus atlantica* woods. This situation can be interpreted as the Nb element can be displaced in *Robinia pseudoacacia* woods, but its displacement is limited in *Cedrus atlantica* woods. After heavy metals enter the plant body, their transport within the wood part is largely related to the cell structure, especially the cell wall (apoplastic pathway). Cell wall proteins (CWP) in plants come into play in various abiotic stresses [4].

Plants frequently face stress factors in their lives. The most common stress factors that plants encounter are high or low temperatures [29] and climatic factors [7]. Drought, in particular, is the factor that stresses plants the most [9, 30]. It is stated that the effects of drought will be felt more intensely with the impact of global climate change [6, 31]. The presence of stress factors changes the environmental conditions where plants grow, thus affecting plant development in many ways. This change directly affects the process of plants absorbing and accumulating heavy metals. These results are consistent with the literature. Studies show that the most important heavy metal sources are mining [3], traffic [17], industrial activities [13], agricultural activities [15] and urbanization [21]. Additionally, many studies are showing that air pollution has increased significantly in recent years [11].

5. Conclusion

As a result of the study, it was determined that there has been a significant increase in Nb concentration in *Cedrus atlantica* woods in the last decade. In addition, the highest Nb values in this species were obtained in the north direction. In the north of the area where the study was conducted, one of the busiest highways in Türkiye has a heavy traffic flow. These results show that the Nb concentration in the air increases due to traffic, and this increase has reached more serious levels in the last decade.

Conflict of Interest

All authors certify that they have no affiliations with or involvement in any organization or entity with any financial interest or non-financial interest in the subject matter or materials discussed in this manuscript.

Ethics Committee Approval

Ethics committee approval is not required.

Author Contribution

Conceptization: HÇ, RE, ŞK; methodology and laboratory analyzes: RE, ŞK; writing draft: HÇ, RE, ŞK; proof reading and editing: All authors have read and agreed to the published version of manuscript.

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