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Usability of *Cedrus atlantica* in monitoring changes and reducing airborne palladium pollution

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Abstract

Heavy metal pollution has become a global problem threatening the health of humans and other living things. It is crucial to monitor the changes in air concentrations and reduce pollution, mainly due to the potential harm of heavy metals taken into the body by inhalation. For these purposes, plants have begun to be used extensively as biomonitors or accumulators. However, since each heavy metal accumulates in different plants at different levels, the appropriate biomonitor or accumulator species for each heavy metal must be determined separately. This study aimed to assess the usability of *Cedrus atlantica*, grown in Düzce, where heavy metal pollution is at high levels, for monitoring and reducing the change in palladium (Pd) pollution in the air. Within the scope of the study, changes in Pd concentration in *Cedrus atlantica* stem sections grown in Düzce, which is among the five most polluted cities in Europe, depending on organ, direction, and age range in the last 60 years, were evaluated. As a result, it was determined that Pd pollution in the region has increased significantly in recent years, and traffic density is thought to be effective in this increase. It was also determined that *Cedrus atlantica* is a highly suitable species for monitoring the changes in Pd pollution and reducing pollution.

Keywords: Heavy metal; *Cedrus atlantica*; Palladium; Pollution

1. Introduction

Today, air pollution is one of the most important global problems, causing more than 4 million premature births and the death of approximately 7 million people annually worldwide. This problem has reached such serious levels that it is stated that approximately 2.5 million living spaces across Europe are polluted, 90 percent of the world's population breathes polluted air, and one in every eight deaths is related to air pollution [1,2]. Global climate change and urbanization are irreversible problems [3-6]. Pollution has become one of the most important problems worldwide with these problems [7]. Among the components of air pollution, heavy metals pose the most serious threat to human and environmental health. It is stated that heavy metals, some of which can be harmful, toxic, and fatal to humans even at low concentrations, can be harmful at high concentrations, even those that are necessary as nutrients for living things [8].

Heavy metals have been rapidly released into nature as a result of industrial and technological developments in the last century, and in this process, water [9], soil [10], and air [11,12] have been significantly polluted by heavy metals. Heavy metal pollution released into nature, largely due to mining [13], industry [14], and traffic [15], is at much higher levels in urban areas [14].

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Monitoring the change in heavy metal pollution and reducing pollution in areas with high levels are among the priority study subjects [16]. Although many studies have been conducted on this subject, the studies generally focus on more common and known elements such as Pb, Ni, Cr, Cu, and Mn [17-19]. However, due to the significant increase in its industrial use in the last 20 years, Pd has reached high levels in receiving environments. Pd is widely used in many industrial sectors, such as the chemical and petroleum industries, as well as the production of automobile catalysts, electronic devices, dental applications, and fine jewelry. Exposure to Pd may cause respiratory symptoms, urticaria, contact dermatitis, and acute toxicity or hypersensitivity in humans. Epidemiological studies have shown that Pd ions are one of the most frequently reacted sensitizers among metals. This effect on the immune system shows that Pd is a very risky and harmful element for humans [20]. Therefore, monitoring and reducing Pd pollution is extremely important. This study investigated the accumulation levels of Pd element in the trunk sections of cedar (*Cedrus atlantica*) trees growing in urban areas where heavy metal pollution is high.

2. Material and methods

The study was conducted on cedar (*Cedrus atlantica*) growing in Düzce province. According to the World Air Pollution Report 2021, Düzce province is one of the five most polluted cities in Europe [21]. In 2022, log samples taken outside the vegetation season by determining the north direction were brought to the laboratory, and their surfaces were leveled. The examination determined that the tree was 60 years old; the wood (WD) was grouped into five-year groups, and sawdust samples were taken from each group of wood, as well as from the inner bark (IB) and outer bark (OB), with the help of a steel drill. The samples dried in an oven at 45 °C were subjected to pre-burning in a specially designed microwave oven. The samples whose pre-combustion process was completed were analyzed with the ICP-OES device, and Pd concentrations were determined. This method has been used in previous studies in this field, including wood and bark samples [22], as well as other plant organs such as leaves and fruits, as in this study. It is also widely used for heavy metal analysis of soil samples [23].

The data obtained was analyzed using the SPSS package program, and variance analysis was applied. Additionally, the Duncan test was applied to data with a margin of error below 5% ($p < 0.05$). The data were tabulated and interpreted, considering the Duncan test results.

3. Results

Average values and statistical analysis results regarding the change of Pd concentration in cedar based on organ and direction are given in Table 1. When the above results were examined, it was determined that the Pd concentration change in cedar was statistically significant on a directional basis in all organs and on an organ basis in the south and north directions. When we look at the organs according to the average values, the highest value was obtained in the inner bark (IB). Likewise, the highest value was obtained in the north direction when looking at the directions according to the average values.

Table 1 Change of Pd concentration in Cedar based on organ and direction

Organ	North	East	South	West	F	Average
OB	47587.3 aB	45771.4 A	50180.3 bC	44530.7 A	23.7***	47017.4 a
IB	107552.1 bC	43771.1 A	46651.2 aB	46118.0 B	2163.3***	61023.1 b
WD	59022.6 aB	43925.1 A	48638.7 abA	45395.9 A	13.1***	49358.8 a
F	8.6**	1.1 ns	3.3*	0.1 ns		4.2*
Average	61672.2 B	44055.3 A	48606.9 A	45385.6 A	17.8***	

The change of Pd concentration based on period and direction is given in Table 2. When the values in the table were examined, it was determined that the change in Pd concentration in cedar was statistically significant on a direction basis in all periods and on a period basis in all directions. When looking at the average values according to the periods, the highest value was obtained in the 2013-2017 and 2018-2022 periods. Again, when we look at the directions according to the average values, we see that the highest value is in the north direction. Pd concentration change in the east direction during the 2013-2017 period remained below detectable limits.

Table 2 Change of Pd concentration in Cedar wood based on period and direction

Age category	North	East	South	West	F value	Average
2018-2022	1826.8^{Ca}	1586.8^{Bb}	920.1^{Ab}	UDL	76.5***	1444.6^{a}
2013-2017	1949.4^{a}	1418.1^{ab}	UDL	UDL	14.5*	1683.7^{a}
2008-2012	5191.9^{Bcd}	1369.0^{Aa}	UDL	UDL	384.3***	3280.4^{abc}
2003-2007	5996.8^{Ce}	1431.7^{Bab}	832.8^{Aa}	UDL	3169.1***	2753.7^{abc}
1998-2002	5083.7^{Bc}	5162.2^{Bc}	925.8^{Ab}	UDL	345.7***	3723.9^{bc}
1993-1997	2608.0^{b}	1307.5^{a}	UDL	UDL	105.0**	1957.8^{ab}
1988-1992	5526.0^{Cd}	1260.1^{Ba}	765.3^{Aa}	5581.2^{C}	787.9***	3283.1^{abc}
1983-1987	4941.9^{Bc}	5284.0^{Cc}	3126.2^{Ac}	UDL	219.6***	4450.7^{c}
F value	159.9***	803.8***	1438.9***	-		2.9*
Average	4140.5^{B}	2352.4^{A}	1314.0^{A}	5581.2^{B}	15.1***	

4. Discussion

As a result of the study, it was determined that the cedar tree can accumulate significant amounts of Pd elements in both its wood and bark parts. It was determined that the values obtained in the barks and wood parts were very close to each other, and although there was a statistically momentous difference, the values were proportionally close, and there was a difference of around 20%. However, studies generally indicate that the heavy metal concentrations obtained in the outer bark are very high [24]. The reason for this is that in areas where heavy metal pollution is at high levels, the heavy particulate matter becomes a sink by being contaminated with heavy metals, and it easily adheres to the rough outer bark, significantly increasing the heavy metal concentration in the bark [25]. Increasing the heavy metal concentration in the bark also increases the heavy metal concentration in the wood because heavy metals can enter the plant body from the soil through the roots, from the air through the leaves, and from the stem parts by direct adsorption [26,27].

The current study obtained the highest Pd concentrations in the northern direction. It is thought that the highway located in the northeast of the study area caused this situation. Studies show that traffic is one of the most important reasons for heavy metal pollution in the air [28]. The sector where Pd is most commonly used is automobile catalysts [29]. Therefore, it is expected for Pd pollution to be high in the direction of heavy traffic.

It was also determined that the Pd concentration increased significantly both in the northern direction and during the periods after 2013 compared to the average values. This situation may be related to the increase in vehicle traffic. In fact, Cesur et al. [30] stated that the increase in heavy metal concentrations in recent years is due to the increase in the number of vehicles and traffic density.

As a result of the study, it was determined that Pd concentrations in cedar wood were highly variable and that there were large differences between Pd concentrations in different directions in the same period or different periods in the same direction. For example, while the Pd concentration determined in the northern direction in the 2013-2017 period was 106533.8 ppb, the Pd concentration measured in the same direction in the 2008-2012 period was 55787.3 ppb. During the same period, the Pd concentration in the adjacent eastern direction remained below detectable limits. These results show large differences in Pd concentration between adjacent wood masses; therefore, the transfer of Pd within the wood is limited.

It is emphasized that the most important lack of information about the usability of biomonitors in monitoring heavy metal pollution is about the transfer of elements in wood [31]. Studies have shown that plants are the most effective arguments in monitoring the changes in heavy metal pollution in the air and reducing pollution [32]. Plants that can accumulate heavy metals, especially in the wood part, are the most suitable plants for this purpose. Because the wood part is the largest organ of the tree, heavy metals trapped in the wood part are not released into nature for tens or even hundreds of years [33]. However, suitable biomonitor or accumulator species must be determined separately for each heavy metal [34]. Studies have shown that different elements' displacement potential in different species' wood is at different levels. In studies on this subject, it has been shown that Zn and Pb are replaced in *Cedrus deodora* woods, while the Cu element remains constant [35] and that the displacement of Ni, Zn, Pb, Cr, and Zn elements is limited in *Corylus colurna* woods, but Cd is displaced [36,37]. In *Pinus pinaster* and *Picea orientalis*, the displacement of Sn is limited [31]; in *Cupressus arizonica* wood, the displacement of Cd, Ni, Fe, and Zn elements is limited, but Bi, Li, and Cr are displaced [27,30]. In *Cedrus atlantica* wood, the transfer of the Ni element is quite limited, but the Co element can be replaced [38].

The transport of elements within the wood part of plants is largely related to the cell structure and especially the cell wall (apoplastic pathway). Apoplast, located between the cell wall and plasma membrane (CWPM) in plants, is a flexible structure that detects and produces signals in metal/metalloid stress. Cell wall proteins (CWPs) are activated in various abiotic stresses [31]. Plants frequently face abiotic stress factors throughout their life cycle. The most common stresses that plants encounter are stress factors related to climatic parameters such as drought [39-45] and frost [46,47]. Because plant development depends on the interaction of genetic structure [48-51] and environmental conditions [52-62]. Therefore, factors that cause significant and permanent changes in climatic parameters, such as global climate change, trigger the stress mechanisms of plants [63-71]. In addition, increasing UV-B stress due to climate change [72], anthropogenic radiation [73], and heavy metal pollution [71,75] are also important stressors for plants. CWPs activated in various abiotic stresses have been extensively identified and characterized among different types of plants. Since the CWPM interface accumulates the majority of heavy metals, this region is believed to be the potential region responsible for HM tolerance [76].

The potential of plants to absorb and accumulate heavy metals depends on many factors, such as organ structure, weather conditions, and plant habitus, as well as the structure of the heavy metal and its interaction with the plant [77-78]. Therefore, plants absorb and accumulate heavy metals through the interaction of many influencing factors originating from plants, heavy metals, or environmental conditions. Therefore, many of these factors directly and indirectly affect plants' heavy metal accumulation potential, and information about this complex mechanism is still limited [15,25,79].

5. Conclusion

Heavy metal pollution is a big problem for all living things and the environment, and it is necessary to determine appropriate biomonitors that can be used to monitor pollution and accumulator types that can be used to reduce pollution. Although many studies have been carried out on the subject to date, the studies are mostly related to common heavy metals such as Pb, Ni, Cr, and Cu. However, detailed studies need to be carried out on other heavy metals, which are less known but quite harmful. This study evaluated the usability of *Cedrus atlantica* in monitoring the changes in air pollution of Pd, one of the neglected heavy metals, and in reducing pollution. In conclusion, it was determined that *Cedrus atlantica*, the subject of the study, is a suitable species that can be used both for monitoring the changes in Pd pollution in the air and reducing this pollution.

Compliance with ethical standards

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Disclosure of conflict of interest

The authors declare that they no conflict of interest. The none of the authors have any competing interests in the manuscript.

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