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Usability of *Robinia pseudoacacia* in monitoring changes and reducing airborne palladium pollution

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Abstract

Palladium (Pd), whose use has been increasing in recent years, is one of the heavy metals that pose a danger to the environment and human health, and it is known that heavy metals can be extremely harmful when inhaled from the air and taken into the human body. Therefore, monitoring and reducing the change of Pd pollution in the air is very important. This study aimed to determine the usability of *Robinia pseudoacacia*, which is grown intensively in urban areas where heavy metal pollution may be high, to monitor and reduce the change in Pd pollution in the air. Within the scope of the study, changes in Pd concentration in *Robinia pseudoacacia* stem sections grown in Düzce, among the 5 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 may have been released into nature through agricultural activities or transported from much more distant sources. It was also determined that the species is not a suitable biomonitor that can be used to monitor the change in Pd pollution. Still, it is an accumulator species that is extremely suitable for reducing Pd pollution.

Keywords: Heavy metal; Palladium; Biomonitor; Accumulator; *Robinia pseudoacacia*

1. Introduction

The industrial revolution in the last century has caused significant changes worldwide. The most important of these changes are global climate change [1-2], which is now considered irreversible globally, and urbanization [3-8]. Another factor that is stated to be largely due to industrial activities and affects all living things and ecosystems on a global scale is pollution [9-12]. As a result of the extraction of various elements from mineral deposits to be used as raw materials in industrial activities and their release into nature, water [13], soil [14], and air [15-17] have become significantly polluted and started to threaten living life. The extent of air pollution is especially frightening. It was reported that 99% of the global population is subjected to low air quality; outdoor air pollution is estimated to have caused 4.2 million premature deaths and 6.7 million premature deaths annually [18-20].

Among air pollution components, heavy metals are the most dangerous and harmful. While some of them can be toxic, carcinogenic, and fatal to humans, even at low concentrations, it is stated that even those necessary for life can be harmful at high concentrations [21-23]. Moreover, if inhalation takes them from the air, their effects are much greater and harmful [24-26]. Therefore, it is critical to monitor changes and reduce the heavy metal pollution in the air [27-30].

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Due to the potential harms of heavy metal pollution, many studies have been conducted on the subject. Studies have shown that plants are the most effective arguments in monitoring the changes in heavy metal pollution in the air and reducing pollution [31,32]. 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]. This study examined the accumulation levels of Pd elements in the trunk parts of Acacia (*Robinia pseudoacacia*) trees growing in urban areas with high heavy metal pollution.

2. Material and methods

The study was carried out on Acacia (*Robinia pseudoacacia*) growing in Düzce, one of Europe's 5 most polluted cities, according to the World Air Pollution Report 2021 [24]. The samples were taken in late 2022, off the growth period, by determining the north direction. It was determined that the log sample, whose surface was smoothed after being brought to the laboratory, was 60 years old, and samples were taken from the wood (WD) part, grouped into five-yearly groups, and from the inner bark (IB) and outer bark (OB), with the help of a steel drill. The samples were then dried in a 45 °C oven and pre-burned in a microwave oven specially designed for this process. The samples whose pre-combustion process was completed were analyzed with the ICP-OES device, and Pd concentrations were determined. This method has been widely used in previous studies in this field [35-38].

The data obtained was analyzed using the SPSS package program, and variance analysis was applied to the data. The Duncan test was also applied for factors showing statistically significant differences at the minimum 95% confidence level ($p < 0.05$). Considering the Duncan test results, the data were presented in tables, and interpretations were made.

3. Results

Average values and statistical analysis results regarding the change of Pd concentration in Acacia based on organ and direction are given in Table 1. It can be seen that the Pd concentration change in Acacia is statistically significant in all organs on a directional basis and in the east direction on an organ basis (Table 1). The highest value in the east direction was obtained in the inner crust. When we look at the directions according to the average values, the highest value is seen in the south direction, while the lowest is in the west direction. Pd concentration changes in all organs towards the north remained below detectable limits.

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

Organ	East	South	West	F-value	Average
OB	99648.8 aC	104396.8 B	93600.4 A	7.4*	99215.3
IB	106381.9 bC	101797.9 B	97202.2 A	5.4*	101794.0
WD	99065.3 aB	102803.3 C	95262.0 A	44.9***	99043.5
F-value	6.7**	0.5 ns	0.7 ns		1.4 ns
Average	99629.6 B	102845.3 C	95281.9 A	49.2***	

The change of Pd concentration in Acacia based on period and direction is given in Table 2. Pd concentration in Acacia remained below detectable limits in all samples in the northern direction. According to the results of variance analysis, it was determined that the change in Pd concentration in Acacia was statistically meaningful on a direction basis and a western direction basis in all periods except the 1983-1987, 2003-2007, 2008-2012, 2013-2017, 2018-2022 periods. The highest value in the western direction was obtained in 2003-2007, 2013-2017 and 2018-2022. According to the average values, the highest value was obtained in the south direction and the lowest in the west direction. Therefore, when the north direction is included in the evaluation, it can be said that the Pd concentration is south>east>west>north.

Table 2 Change of Pd concentration in the wood of *Acacia* tree based on period and direction

Age group	East	South	West	F-value	Average
2018-2022	101839.2	103179.5	99386.1 c	1.1 ns	101468.2
2013-2017	97179.9	102780.0	100464.9 c	1.8 ns	100141.6
2008-2012	98548.2	102860.8	97637.8 bc	1.8 ns	99682.3
2003-2007	99123.4	104504.0	100363.8 c	4.1 ns	101330.4
1998-2002	97569.7 B	103213.7 C	93892.8 abA	6.9*	98225.4
1993-1997	100770.7 B	103866.3 C	93251.1 abA	9.5*	99296.0
1988-1992	96213.9B	101845.5 C	93420.8 abA	8.9*	97160.1
1983-1987	98893.2	101785.2	94021.3 ab	3.8 ns	98233.2
1978-1982	98893.6 B	103396.9 C	94425.6 abA	5.7*	98905.4
1973-1977	98807.7 B	102153.2 C	93264.7 abA	6.6*	98075.2
1968-1972	99708.2 B	100446.4 C	91256.5 a A	5.4*	97137.0
1963-1967	101235.6 B	103607.7 C	91758.5 aA	19.4**	98867.3
F-value	0.6 ns	0.3 ns	5.3***		0.8 ns
Average	99065.3 B	102803.3 C	95262.0 A	44.9***	

4. Discussion

In the study, it was determined that the acacia tree can accumulate significant amounts of the Pd element in its wood and bark parts. Since the importance of heavy metals for human health has been understood, many studies have been carried out on monitoring changes and reducing heavy metal pollution. However, these studies generally focus on more common and known elements such as Pb, Ni, Cr, Cu, and Mn [38-40]. However, due to its unique chemical and physical properties, Pd is widely used in many industrial sectors, such as the chemical and petroleum industries, automobile catalysts, electronic devices, dental applications, fine jewelry production, etc. The significant increase in the industrial use of Pd over the last 20 years has resulted in high levels of this metal in air, water, and soil. Exposure to Pd may cause acute toxicity or hypersensitivity with respiratory symptoms, urticaria, and contact dermatitis. 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 [41]. Therefore, monitoring and reducing Pd pollution is extremely important.

The study determined that there was no statistically significant difference in Pd accumulation between bark and wood. In studies conducted to date, generally, high heavy metal concentrations have been obtained in the outer [30,38,41]. However, some studies also obtained the opposite results [42]. It is stated that the heavy metal concentration in the barks is largely related to the heavy metal content of the particulate matter adhering to the barks [26,40].

The current study determined that the highest Pd concentrations were obtained in the southern direction, while Pd concentrations in the northern direction remained below the detectable limits. This can be interpreted as Pd not accumulating in the study area due to traffic. Studies show that heavy metals are intensively released into nature because of mining [17], industry [21], traffic [28], and agricultural activities [22,41]. The study results also show that Pd may have been released into nature through agricultural activities or transported from much more distant sources. As a matter of fact, studies show that heavy metals can adhere to particulate matter and be transported far from their source with the help of wind [26,38].

In the current study, there was a statistically noteworthy difference between the periods only in the western direction, and there was no statistically meaningful difference between the periods in terms of other directions and average values. This result can be explained as Pd pollution in the study area has not changed remarkably from past to present or Pd can be transferred between tissues. The fact that the Pd concentration in the northern direction remains below

the detectable limits but is high in the other directions and remains in a narrow range can be interpreted as Pd being transported in the vertical direction but not in the horizontal direction. Studies show that some elements can be transferred within different types of wood tissue, while some elements are limited [24,30,39].

The study results show that *Acacia* accumulates Pd intensively in its bark and wood, which can exceed 100 ppm. As it is known, the phenotypic characters of all living things are shaped under the mutual interaction of genetic structure [43-49] and environmental factors [50-63]. Therefore, all factors affecting plant physiology also affect the entry and accumulation of heavy metals into the plant, which is shaped under the mutual interaction of many factors affecting each other, such as edaphic [64], climatic factors [65-70], and stress factors [71-78], in addition to genetic structure. Therefore, many of these factors, directly and indirectly, affect plants' heavy metal accumulation potential, and information about this complex mechanism is still limited [35,41].

5. Conclusion

In conclusion, while the study results show that *Acacia* is an extremely suitable species for reducing Pd pollution, satisfactory results have not been achieved regarding whether the species can be used to monitor the change in Pd pollution. The study results show that Pd can be transferred between the bark and wood of *Acacia* and within the wood. The study results can be interpreted as Pd can be transported in the vertical direction but cannot be transferred in the horizontal direction. However, there are almost no studies on the vertical or horizontal transport of heavy metals in wood. It is recommended that detailed studies be conducted on this subject.

Compliance with ethical standards

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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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