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Determination of Some Exotic Landscape Species As Biomonitors That Can Be Used for Monitoring and Reducing Pd Pollution in the Air

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Abstract Heavy metal levels have steadily risen over the past century due to the presence of human activity and are hazardous to human health and the environment. Regarding the health of humans and the environment, palladium (Pd) is among the most hazardous and toxic heavy metals. It is listed as a priority contaminant by the Agency for Toxic Substances and Disease Registry (ATSDR). As a result, eliminating pollution and tracking changes in Pd contamination in the air are the top research priorities. This study will be conducted on trees grown in Düzce, the fifth dirtiest city on the European continent, to identify appropriate species that may be utilized for tracking and mitigating Pd pollution in the air. Samples from *Cupressus arizonica*, *Pinus pinaster*, *Cedrus atlantica*, *Pseudotsuga menziesii*, and *Picea orientalis* will all be analyzed as part of the study, and the variations in Pd content according to species, organ, and direction will be assessed. The goal is to ascertain which biomonitors are best suited for tracking and mitigating lead contamination in the atmosphere. The study consistently found Pd contents in woods with different directions that developed within the same period. However, when the species were compared, notable differences were detected between the Pd levels formed in different directions in the same period for each species and the wood formed in the same direction in other periods. This variation suggests that Pd transfer in wood is restricted in all tested species. Consequently, every species performs as a reliable biomonitor for tracking Pd contamination.

Keywords Biomonitoring · Düzce · Heavy metal · Palladium · Pollution · Trace element

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1 Introduction

Air pollution seriously threatens the ecosystem, humans, and other living things globally (AlOmar et al., 2023; Asril et al., 2023; Durmanov, 2023). Heavy metal (HM) pollution is shown to be the most harmful among air pollution (Canturk, 2023; Key et al., 2023). HM levels in soil, air, and water are gradually rising due to anthropogenic reasons such as automobiles, solid fuel burning, mining, and industrial actions, particularly in densely populated urban regions (Ali et al., 2021; Canturk, 2023; Cetin et al., 2022). HMs are among the most unsafe environmental pollutants that threaten the health of other living things, especially human bodies and ecosystems (Sulhan et al., 2023; Key et al., 2023; Koc et al., 2024a). Especially HMs in the air becomes much more detrimental when taken into the human body through breathing. HMs are the most perilous elements of air contamination, which causes the death of roughly 7 million individuals yearly (Ghoma et al., 2022).

Palladium (Pd), critical and common HM, is among numerous noble metal catalysts. In recent years, its constantly increasing concentrations in the environment have attracted attention due to its excellent catalytic properties applied in many important chemical transformations and its three-way catalyst that oxidizes exhaust gas pollutants resulting from automobile emissions and fuel cell technology (Wu et al., 2019). It is known that Pd group elements accumulate in city air, road surfaces, roadside soil, and plants, and they pollute aquatic surroundings. Bioavailability, possible uptake into the biosphere, carries potential risks to human bodies and nature (Wang & Li, 2012).

The increasing release of Pd nanoparticles into the community and occupational environments due to increased technological applications raises public health concerns regarding potentially unfavorable consequences for exposed individuals, especially for highly and chronically exposed workers to these materials (Leso & Iavicoli, 2018). The individuals may be exposed to Pd by inhaling ambient respirable particles from Pd-containing vehicle catalytic converters. However, information and research on these situations are scarce in the literature. The oral toxicity of Pd is thought to be low, though it depends on the water solubility of Pd compounds. Observed symptoms include dizziness, itching, asthma, stomatitis, swelling of the cheeks and lips, chronic urticaria, and oral lichen planus. Lately, Pd has been used for radioactive sources implanted straight into a malignant tumor; no complications associated with Pd have been informed (Laprise-Pelletier et al., 2017). Although respiratory sensitization (e.g., bronchial asthma) may occur in workers exposed to Pd and its compounds, its occurrence is low. However, it has been reported that the rate of contact sensitivity to Pd increases in humans (Umemura et al., 2022a, 2022b). Due to its effects on human health, Pd is listed as one of the ATSDR's priority contaminants (Savas et al., 2021). Therefore, monitoring and reducing the changes in Pd concentrations in the environment, especially in the air, are priority research topics.

In this study, determining the shift in Pd concentration in the air in Düzce, the 5th most air-polluted municipality in Europe, over the four decades, factors that may be effective in this alteration and possibilities of reducing Pd pollution in the air were investigated. Unlike environments such as water and soil, it is challenging to determine the shift in HM concentrations in the airborne (Erdem et al., 2023; Kuzmina et al., 2023). Because direct measurement of HM pollution in the air is costly and very difficult, and it cannot give a clue about the change in HM concentrations during the process and their effects on the ecosystem (Cesur et al., 2021; Guney et al., 2023). For this reason, biomonitors are often used to observe the differences in HM concentrations in the airborne (Key et al., 2022). Annual tree rings are known as the most convenient biomonitors that can be used for this determination due to less damage to plant species (Canturk, 2023; Cobanoglu et al., 2023; Yayla et al., 2022). However, in addition to the potential of species to accumulate different HMs, the potential to accumulate the same HM in different organs of the same species is also at different levels (Karacocuk et al., 2022). Therefore, the type of biomonitor that can be used to screen the shift of each HM must be determined separately.

In this study, the changes in Pd concentration of *Pinus pinaster* (Maritime pine), *Cupressus arizonica* (Arizona cypress), *Picea orientalis* (Oriental spruce), *Cedrus atlantica* (Atlas cedar), and *Pseudotsuga menziesii* (Douglas fir) species growing in Düzce province with polluted air were evaluated based on species, organ, and direction. This study aims to determine the most proper biomonitors that can be used to monitor and diminish the Pd concentration in the atmosphere.

2 Materials and Method

In the study, log samples taken from *P. pinaster* (PS1), *C. arizonica* (PS2), *P. orientalis* (PS3), *C. atlantica* (PS4), and *P. menziesii* (PS5) trees, which are species frequently grown throughout Europe and preferred in urban areas in landscape studies, were used. Studies have determined that many heavy metal concentrations are strongly related to each other (Şevik et al., 2024). The area where the study was conducted is an area where the level of heavy metal pollution is relatively high. The tree species used in the study have been the subject of studies conducted to monitor the changes in Cr (Koc et al., 2024a), Sn (Cetin et al., 2023), Tl (Canturk, 2023), and Bi (Isinkaralar et al., 2023) pollution in this area, and this heavy. It has been determined that they have the potential to accumulate metals at high levels. In these studies, the average concentrations in wood in different directions were increased up to 1369.6 ppb in Cr (Koc et al., 2024a), 2695.1 ppb in Sn (Cetin et al., 2023), 5384.0 ppb in Tl (Canturk, 2023), and 6232.0 ppb (Isinkaralar et al., 2023) in Bi. For this reason, it was decided to use these tree species in the study. Studies have determined that heavy metals generally show a high correlation with each other (Şevik et al., 2024). For this reason, the study was conducted in Düzce, Türkiye, since Pd pollution was estimated to be at high levels in the study area.

Log samples of the species (directions marked on the logs) were taken in February 2022 after their coordinates were noted and cut (one single tree from each tree species). Samples were taken from each species' bark [inner (IB) and outer (OB)], as well as wood (WD) and brought to the laboratory in three replicates. Wood samples (5 discs for each species) were age-classified by considering the width of the annual rings of the logs (10 cm thickness) of the species and the groupings made in previous studies. After the age classification of the species was determined to be 5 years, wood samples in each age cluster were acquired with using a steel-tipped drill and located in glass petri dishes. The samples were shredded and turned into sawdust. During this preparation, the precaution was taken not to use instruments made of the metals. Soil samples were also taken in the study. After sieving soil samples (2 mm sieve mesh), they were labeled and subjected to pretreatment like wood.

The petri dishes were kept open in the laboratory until the samples became room dry. Then, the samples were moved to the oven and dried (45 °C) for two weeks. After weighing out 0.5 g of the oven-dried samples, they were placed into closed ceramic vessels. Then, 6 ml of 65% HNO_3 (Merck, Germany) and 2 ml of 30% H_2O_2 (Merck, Germany) were added, and the microwave oven (Ethos One, Milestone GmbH, Germany) was then used for burning. The microwave's program was designed to increase the temperature to 200 °C for 15 min and then hold it there for another 15 min.

After the sample burning process, the solution samples were placed into 50 ml flasks and diluted with ultrapure water to a volume of 50 ml. The ICP-OES (Inductively Coupled Plasma-Optic Emission Spectrometer, GBC Scientific Equipment Pty Ltd., Melbourne, Australia) instrument was then used to perform elemental analysis on the samples. For the element analysis of the samples, the plasma of the ICP-OES device was burned, and ultrapure water was passed through the system for 15 min to equilibrate. A calibration chart was created by preparing standard solutions according to the elements to be analyzed. After creating the calibration chart, the samples were placed in the system, and concentration values were obtained. According to the analysis results that did not fall into the calibration chart, different charts were created at the ppm or ppb level and read again. Since the device could not read values below 1 ppb and the samples were diluted 100-fold, values below 100 ppb in the samples remained below detectable limits. The analytical data were multiplied by 100 because the samples were obtained at 0.5 g and were then diluted to 50 g with water. The analysis results that did not fit into the calibration chart were used to create different calibration charts at the ppb level, and the readings were repeated. During the process, a blank sample was used for the Pd element for quality assurance/quality control (QA/QC). Five standards for the accuracy of the Pd assessment process were used to plot the calibration curve simultaneously. The Pd metal concentration detection limit was measured at 118 ppb. The main expense item in the project is the procurement of services for HM analysis using the ICP-OES device. A total of 3 thousand samples (5 species × 5 log samples × 4 directions × 10 (8 age cluster + inner bark + outer bark) × 3 replications) were taken for Pd analysis. Pd metal analyses were carried out in an accredited central research laboratory.

Variance analysis was applied using the SPSS 21.0 package program to the obtained data. As a result of the variance analysis (ANOVA), the Duncan test was applied for the parameter that were determined to have statistically momentous differences at alpha = 0.05 (95% confidence interval). ANOVA is a collection of statistical models used in statistics to analyze group averages and their related processes (Campbell, 1989). In short, ANOVA is a parametric inferential method used to test whether there is a difference between population means. Duncan's test, used to determine the groupings of variables, was developed by Duncan in 1951. In this method, each process average is compared with all other averages and test values separately (Quinn & Keough, 2002). In similar studies conducted to date, these analysis methods have been frequently used in the evaluation of data (Key et al., 2023; Koc et al., 2024a). Since Pd concentrations in the soil samples taken in the study were below the detectable limits (100 ppb), the soil samples were not included in the statistical analysis.

3 Results

The Pd concentration change in all directions is statistically significant ($P < 0.05$). In the north aspect, the uppermost Pd was detected in PS4, while the lowest was achieved in PS3 and PS5. The highest Pd in the east direction is seen in PS1 and PS2; in the south direction, the maximum Pd is seen in PS2. Considering the averages, the lowest value among the species was obtained in PS3 and PS5 (Table 1).

The difference of Pd concentration (ppb) by species and organ is illustrated in Table 2. It is seen that the variation of Pd concentration on a species basis is statistically substantial in all organs. While the smallest value in the outer bark was detected in PS2 and PS4, the uppermost Pd in the inner bark was found in PS1. Notably, the most elevated Pd value in wood is seen in PS2. According to the mean values, the minimum Pd among the species was in the PS3 species.

When the difference in Pd concentration on a period and direction basis (Table 3) is examined, the change is statistically remarkable on a direction basis in all periods except the 2003–2007 period. The change on a period basis in all routes except the west is not statistically significant. The periods have no statistically significant difference based on the Pd averages. The uppermost value in the western aspect was detected between 1988–1992 and 2018–2022.

According to the values of the difference in Pd concentration based on direction and plants organ (Table 4), the alteration in Pd concentration based on aspect in all organs is notable ($P < 0.05$). The change in Pd concentration on an organ basis in all directions

Table 1 Pd concentration (ppb) differences based on direction and plant species

Plant species	North	East	South	West	Mean
PS1	11,544.1 ± 5489.8^{b}	13,080.4 ± 7663.5^{b}	1596.7 ± 1069.8^{a}	434.7 ± 298.6^{a}	8402.3^{b}
PS2	13,685.8 ± 7663.5^{bc}	12,806.0 ± 7842.1^{b}	4413.3 ± 3036.1^{c}	< 100 ppb	10,122.8^{b}
PS3	6964.5 ± 4596.2^{a}	6269.2 ± 5781.3^{a}	2684.5 ± 1973.7^{ab}	< 100 ppb	5199.1^{a}
PS4	15,025.3 ± 3887.1^{c}	6203.9 ± 6376.6^{a}	3714.1 ± 2933.3^{bc}	9210.1 ± 7758.8^{c}	8542.2^{b}
PS5	7576.1 ± 6446.3^{a}	8087.0 ± 5830.7^{a}	4066.5 ± 2703.7^{bc}	7002.9 ± 5079.2^{b}	6476.6^{a}
F value	13.9***	6.2***	5.6***	5.3*	7.9***

Average concentrations followed by different letter means they are statistically different. Capital letters (A, B, and C) indicate horizontal course, whereas lowercase letters (a, b, and c) demonstrate vertical courses. < 100 ppb = Below-detectable-limit. $^{*} = p \leq 0.05$; $^{**} = p \leq 0.01$; $^{***} = p \leq 0.001$; ns = not significant. These explanations are valid for all tables

Table 2 Pd concentration (ppb) differences by species and organ

Plant species	OB	IB	Wood	Mean
PS1	12,949.7 ± 8886.1^{b}	12,499.0 ± 7494.8^{b}	7223.6 ± 6991.5^{bc}	8402.3^{b}
PS2	3248.8 ± 1732.3^{a}	5690.0 ± 3756.4^{a}	11,065.1 ± 7098.0^{d}	10,122.8^{b}
PS3	7478.0 ± 5081.8^{ab}	6835.9 ± 6368.6^{a}	4768.7 ± 4261.1^{a}	5199.1^{a}
PS4	4949.2 ± 2203.5^{a}	6523.6 ± 5122.2^{a}	9129.1 ± 7130.4^{cd}	8542.2^{b}
PS5	13,163.9 ± 7162.4^{b}	4175.3 ± 2401.6^{a}	6006.6 ± 4683.7^{ab}	6476.6^{a}
F value	3.8*	3.0*	11.8***	7.9***
Mean	9141.1 ^{C}	7200.3 ^{A}	7663.4 ^{B}	

is insignificant ($P > 0.05$). According to the means, the smallest Pd is in the south aspect, and the uppermost is in the west aspect.

The change of Pd level in PS1 based on direction and plants organ is displayed in Table 5. According to the outcomes of ANOVA, the variation in Pd concentration based on organ is substantial in all aspects except the eastern direction, and the change on a direction basis is significant in all organs ($P < 0.05$). When looking at the average Pd concentrations, the lowermost Pd values are in the south and west directions, while the highest are in the north and east routes. In the western way, the Pd concentration change in the outer and inner barks remained below detectable limits.

The change of Pd level in PS1 by direction and measurement period (Table 6) is statistically momentous in wood in all age periods on a direction basis and in all orientations except the west on a period basis. According to the mean concentrations, the directions are divided into two groups. While the south and west directions are in the group with the lowest values, the north and east are in the group with the highest values. The 2003–2007 period in the north direction, the 1988–1992 period in the east direction, and the 2003–2007 and 2008–2012 periods in the south direction remained below the detectable limits regarding Pd concentration change. The western direction remained below

Table 3 Pd concentration differences (ppb) based on aspect and age period

Age	North	East	South	West	*F* value	Mean
2018–2022	11,521.6 ± 6097.5^{B}	5398.4 ± 3808.6^{A}	4580.1 ± 2121.9^{A}	18,013.3 ± 1168.7^{Cb}	13.0***	8194.1^{a}
2013–2017	10,904.8 ± 7157.1^{B}	6722.1 ± 3279.9^{AB}	3642.8 ± 3598.2^{A}	2444.8 ± 831.4^{Aa}	5.9**	6810.6^{a}
2008–2012	8986.3 ± 5912.0^{B}	11,504.5 ± 6729.4^{B}	2096.9 ± 787.7^{A}	1010.0 ± 181.5^{Aa}	9.0***	7456.8^{a}
2003–2007	10,110.7 ± 7649.6	6671.3 ± 8578.7	3317.5 ± 920.2	4415.9 ± 4177.2^{a}	2.3 ns	6393.4^{a}
1998–2002	12,250.5 ± 7016.1^{B}	13,500.7 ± 7136.6^{B}	2146.2 ± 1172.5^{A}	4329.9 ± 4469.9^{Aa}	13.3***	8714.5^{a}
1993–1997	9780.7 ± 4685.9^{B}	10,077.4 ± 8377.9^{B}	3514.7 ± 3335.0^{A}	6172.2 ± 257.4^{ABa}	4.4*	7530.6^{a}
1988–1992	10,712.1 ± 8377.9^{B}	10,303.1 ± 8376.5^{B}	3562.4 ± 2526.4^{A}	13,702.3 ± 5992.9^{Bb}	6.0**	8749.3^{a}
1983–1987	10,675.3 ± 5122.6^{B}	10,108.2 ± 7233.7^{B}	3360.8 ± 3847.5^{A}	2703.6 ± 1175.7^{Aa}	7.9***	7251.3^{a}
F value	0.3 ns	1.8 ns	1.3 ns	10.4***		0.8 ns

Table 4 Difference of Pd levels (ppb) based on direction and plant organ

Organ	North	East	South	West	*F* value
OB	12,071.7 ± 6384.7^{Ca}	10,623.0 ± 9069.2^{Ba}	4366.3 ± 3886.6^{Aa}	< 100.0	4.9*
IB	12,291.3 ± 6209.1^{Ba}	5987.7 ± 6243.4^{Aa}	2937.4 ± 613.8^{Aa}	6949.2^{A} ± 743.0	10.7***
Wood	10,630.8 ± 6112.8^{Ca}	9596.9 ± 7392.4^{Ca}	3307.7 ± 2656.5^{Aa}	6495.3 ^{B} ± 6251.2	36.7***
F value	0.7 ns	1.1 ns	1.0 ns	0.0 ns	
Mean	10,947.2^{C}	9398.2 ^{C}	3358.4 ^{A}	6560.1 ^{B}	47.4***

Table 5 Pd concentration (ppb) differences in PS1 based on direction and organ

Organ	North	East	South	West	*F* value	Mean
OB	14,162.2 ± 196.9^{ab}	22,548.0 ± 219.3^{b}	2139.0 ± 243.0^{ab}	< 100.0	6491.0***	12,949.7^{a}
IB	20,077.9 ± 871.3^{b}	14,293.3 ± 675.2^{ab}	3125.7 ± 838.4^{b}	< 100.0	348.4***	12,499.0^{a}
Wood	9951.0 ± 4947.9^{Ba}	11,554.7 ± 7758.1^{Ba}	1251.5 ± 931.8^{Aa}	434.7 ± 298.6^{A}	17.7***	7223.6^{a}
F value	7.1**	3.2 ns	6.4**	-		4.0*
Mean	11,544.1^{B}	13,080.4^{B}	1596.7^{A}	434.7^{A}	26.8***	

the detectable limits regarding Pd concentration change in all periods except 1998–2002.

When the alteration of Pd concentration in PS2 based on aspect and plant organ (Table 7) is examined, the change in Pd level in PS2 is statistically remarkable based on organ in all aspects except the south and based on aspect in all organs. According to the mean Pd concentrations, the lowest Pd concentration was detected in the outer bark, whereas the uppermost values were detected in the wood. Pd concentration differs in the outer and inner bark in the east direction, and in the wood, the outer and inner bark remained < 100 ppb in the west direction.

The change of Pd concentration in PS2 woods based on period and direction (Table 8) is statistically significant on a direction basis in all age clusters and on a period basis in all orientations. The lowest Pd concentration in the north direction is seen in the 1993–1997

Table 6 Change of Pd concentration (ppb) in PS1 woods based on period and aspect

Age	North	East	South	West	*F* value	Mean
2018–2022	12,286.8 ± 206.5[c]	1699.4 ± 330.5[a]	2330.5 ± 543.7[b]	< 100.0	709.3***	5438.9[a]
2013–2017	3170.9 ± 214.8[a]	10,909.4 ± 224.2[d]	733.8 ± 417.9[a]	< 100.0	937.2***	4938.0[a]
2008–2012	2513.3 ± 160.0[a]	22,168.2 ± 514.2[e]	< 100.0	< 100.0	3996.8***	12,340.8[a]
2003–2007	< 100.0	23,087.5 ± 1070.3 eV	< 100.0	< 100.0	1191.0***	11,850.8[a]
1998–2002	15,643.0 ± 719.9[e]	8867.3 ± 454.2[Bc]	325.2 ± 122.9[Aa]	255.5 ± 7.7[A]	898.2***	6272.7[a]
1993–1997	11,833.1 ± 589.3[c]	9106.8 ± 980.2[c]	1882.1 ± 772.2[b]	< 100.0	124.9***	7607.3[a]
1988–1992	14,367.7 ± 668.5[d]	< 100.0	1960.2 ± 302[b]	< 100.0	858.2***	8163.9[a]
1983–1987	9842.0 ± 304.5[b]	5044.3 ± 980.8[b]	277.5 ± 4.3[a]	< 100.0	195.1***	5054.6[a]
F value	373.6***	377.4***	12.7***	3.0 ns		1.2 ns
Mean	9951.0[B]	11,554.7[B]	1251.5[A]	434.7[A]	17.7***	

Table 7 Pd concentration (ppb) differences in PS2 based on direction and plant organ

Organ	North	East	South	West	*F* value	Mean
OB	4781.0 ± 659.3[a]	< 100.0	1716.6 ± 158.3	< 100.0	61.2**	3248.8[a]
IB	9112.1 ± 374.8[ab]	< 100.0	2267.9 ± 71.1	< 100.0	965.5***	5690.0[ab]
OD	15,370.6 ± 4858.7[Bb]	12,806.0 ± 7842.1[B]	5018.6 ± 3125.0[A]	< 100.0	22.0***	11,065.1[b]
F value	9.1**	-	2.6 ns	-		5.1**
Mean	13,685.8[B]	12,806.0[B]	4413.3[A]	< 100.0	23.8***	

Table 8 Change of Pd concentration in wood at PS2 based on age cluster and aspect

Age	North	East	South	West	*F* value	Mean
2018–2022	21,723.6 ± 943.0[Ce]	10,225.1 ± 452.0[Bd]	6465.1 ± 575.4[Cb]	< 100.0	399.2***	12,804.6[b]
2013–2017	21,035.0 ± 925.6[Cde]	5703.6 ± 177.6[Ab]	10,040.0 ± 527.6[Bc]	< 100.0	481.8***	12,259.5[ab]
2008–2012	13,367.2 ± 289.8[Cbc]	7678.6 ± 271.6[Bc]	3081.2 ± 377.3[Aa]	< 100.0	796.1***	8042.3[ab]
2003–2007	12,705.5 ± 661.0[Cb]	719.0 ± 93.3[Aa]	2485.6 ± 153.9[Ba]	< 100.0	803.2***	5303.4[a]
1998–2002	19,717.1 ± 713.1[Bd]	22,761.3 ± 1312.3[Cg]	2413.1 ± 346.5[Aa]	< 100.0	461.1***	14,963.8[b]
1993–1997	7216.5 ± 1224.5[Aa]	23,389.4 ± 137.4[Cg]	9644.2 ± 786.5[Bc]	< 100.0	320.3***	13,416.7[b]
1988–1992	12,519.8 ± 698.3[Bb]	18,074.6 ± 209.3[Cf]	2795.7 ± 184.6[Aa]	< 100.0	951.8***	11,130.0[ab]
1983–1987	14,680.6 ± 637.6[Bc]	13,896.1 ± 899.6[Be]	3224.2 ± 167.3[Aa]	< 100.0	296.3***	10,600.3[ab]
F value	117.7***	552.7***	160.5***	-		1.8 ns
Mean	15,370.6[Bb]	12,806.0[B]	5018.6[A]	< 100.0	22.0***	

period, the lowest Pd level in the east direction is in the 2003–2007 period, and the highest Pd level in the south course is seen in the 1993–1997 and 2013–2017 periods. Pd concentration changes in the west direction remained below detectable limits in all periods.

The change of Pd level in PS3 based on organ and direction (Table 9) is statistically noteworthy in all organs based on orientation and in the north direction on an organ basis. While the lowest Pd concentration is detected in the wood in the north, the uppermost concentrations are seen in the inner and outer bark. In the east direction and all organs in the west direction, the Pd level remained below detectable limits. According to the average concentration, there is no substantial alteration between organs ($P > 0.05$).

The change of Pd concentration in PS3 woods on a period and direction basis (Table 10) is statistically momentous on a direction basis in all periods except the 2003–2007, 2013–2017, and 2018–2022 periods. In all aspects, it is statistically significant based on age cluster. The uppermost Pd concentration in the north direction was seen in the 1998–2002 and 2018–2022 periods, in the east direction in the 1988–1992 period, and in the south direction in the 2003–2007 and 2013–2017 periods. In the eastern direction, the 2013–2017 and 2018–2022 periods remained below the detectable limits regarding Pd concentration change. In the western route, the Pd concentration level remained below detectable limits in all periods.

The change of Pd level in PS4 by direction and plant organ (Table 11) is statistically momentous in all studied organs by orientation and in the north direction by species organ. In the north direction, the top value is seen in the inner bark and wood, while the lowest is in the outer bark. When looking at the orientations according to the mean concentration, the lowest Pd concentration is detected in the south direction, while the uppermost is acquired in the north. The Pd concentration change in the outer bark in the southern and western directions remained below detectable limits. According to the average concentrations, there is no statistically substantial alteration between organs.

The change of Pd level in PS4 woods on an age period and orientation basis (Table 12) is statistically significant based on the direction in all periods and based on the period in all directions. When looking at the average Pd concentration, the lowest value is found in the south orientation, while

Table 9 Pd concentration (ppb) differences in PS3 based on direction and plant organ

Organ	North	East	South	West	*F* value	Mean
OB	12,107.7 ± 499.4^{b}	< 100.0	2848.2 ± 94.2	< 100.0	996.1***	7478.0^{a}
IB	15,241.0 ± 241.9^{Cb}	1649.6 ± 339.1^{A}	3617.2 ± 458.3^{B}	< 100.0	1265.8***	6835.9^{a}
Wood	5287.1 ± 3359.8^{Ba}	7039.1 ± 5908.9^{B}	2547.5 ± 2180.8^{A}	< 100.0	7.1**	4768.7^{a}
F value	18.2***	2.3 ns	0.3 ns	-		1.6 ns
Mean	6964.5^{a}	6269.2^{a}	2684.5^{ab}	< 100.0	8.5***	

Table 10 Change of Pd concentration (ppb) in wood in PS3 based on age cluster and aspect

Age	North	East	South	West	*F* value	Mean
2018–2022	7117.5 ± 392.6^{c}	< 100.0	7146.7 ± 871.1^{d}	< 100.0	0.0 ns	7132.2^{b}
2013–2017	3325.5 ± 170.6^{ab}	< 100.0	3571.4 ± 449.9^{c}	< 100.0	0.7 ns	3448.5^{ab}
2008–2012	3009.0 ± 26.7^{Aab}	9886.8 ± 686.2^{Bd}	2211.4 ± 379.3^{Ab}	< 100.0	260.4***	5035.7^{ab}
2003–2007	3915.4 ± 179.6^{Ab}	3560.3 ± 950.5^{Ab}	3461.9 ± 225.0^{Ac}	< 100.0	0.5 ns	3645.9^{ab}
1998–2002	6282.4 ± 1077.6^{Bc}	3140.2 ± 379.5^{Ab}	2401.3 ± 596.1^{Ab}	< 100.0	23.0**	3941.3^{ab}
1993–1997	12,896.5 ± 436.8^{Cd}	4966.2 ± 413.3^{Bc}	512.0 ± 85.1^{Aa}	< 100.0	960.2***	6124.9^{ab}
1988–1992	3302.4 ± 476.3^{Bab}	18,561.6 ± 99.7^{Ce}	463.4 ± 183.1^{Aa}	< 100.0	3154.4***	7442.5^{b}
1983–1987	2447.8 ± 527.9^{Ba}	2119.8 ± 261.7^{Ba}	611.7 ± 191.0^{Aa}	< 100.0	22.4**	1726.4^{a}
F value	140.8***	400.5***	76.4***			1.9 ns
Mean	5287.1^{Ba}	7039.1^{B}	2547.5^{A}	< 100.0	7.1**	

the uppermost value is detected in the north. Pd concentration changes in the western direction remained below detectable limits in all periods except 1983–1987 and 1988–1992.

The shift of Pd level in PS5 based on organ and direction (Table 13) is statistically substantial in all studied organs based on route. The Pd concentration change in other orientations except north and south is statistically significant. While the highest Pd concentration in the north and south orientations were seen in the outer bark, the lowermost concentration were seen in the wood and inner bark. The Pd concentration change in the outer bark in the western direction remained below detectable limits.

The shift of Pd level in PS5 woods based on direction and age period (Table 14) is statistically significant on a direction basis in all periods and on a period basis in all orientations. The uppermost Pd concentration in the north orientation was seen in the 2013–2017, while the maximum Pd in the south was seen in 1988–1992. The lowest concentration in the western orientation was achieved in the 2008–2012 period, and the lowest value in the eastern was obtained in the 1988–1992 and 2003–2007 periods. In addition, the Pd concentration change in the east direction between 1983–1987, 1993–1997, 2013–2017, and 2018–2022 remained below the detectable limits.

Table 11 Change of Pd concentration (ppb) in PS4 based on direction and plant organ

Organ	North	East	South	West	*F* value	Mean
OB	6944.6 ± 183.8[a]	2953.7 ± 399.0[a]	< 100.0	< 100.0	247.6***	4949.2[a]
IB	14,465.6 ± 709[Db]	2020.1 ± 188.1[Aa]	3029.6 ± 374.6[B]	6579.2 ± 574.7[C]	400.8***	6523.6[a]
Wood	16,105.4 ± 3038.0[Cb]	7133.2 ± 6833.0[Aba]	3799.7 ± 3105.7[A]	10,525.6 ± 9485.7[B]	24.6***	9129.1[a]
F value	14.2***	1.3 ns	0.1 ns	0.4 ns		1.6 ns
Mean	15,025.3[C]	6203.9[AB]	3714.1[A]	9210.1[B]	27.1***	

Table 12 Change of Pd concentration (ppb) in PS4 woods based on direction and age period

Age	North	East	South	West	*F* value	Mean
2018–2022	11,884.2 ± 504.4[Ba]	4270.5 ± 576.6[Ab]	4394.4 ± 923.6[Ad]	< 100.0	118.8***	6849.7[a]
2013–2017	11,912.9 ± 376.9[Ca]	3553.3 ± 180.6[Bab]	397.8 ± 3.7[Aa]	< 100.0	1824.4***	5288.0[a]
2008–2012	17,109.6 ± 415.9[Cc]	3148.7 ± 190.4[Ba]	1058.5 ± 159.7[Aab]	< 100.0	2919.7***	7105.6[a]
2003–2007	20,918.5 ± 737.9[Ce]	3429.0 ± 81.7[Aab]	4637.0 ± 377.6[Bde]	< 100.0	1237.7***	9661.5[a]
1998–2002	17,316.6 ± 929.7[Bcd]	17,916.0 ± 735.7 [Bc]	1864.3 ± 89.0[Abc]	< 100.0	527.1***	12,365.6 [a]
1993–1997	14,680.9 ± 643.1[Bb]	2847.1 ± 244.7[Aa]	2276.4 ± 461.7[Ac]	< 100.0	642.7***	6601.5[a]
1988–1992	18,340.5 ± 683.4[Cd]	2528.5 ± 219.8[Aa]	5316.9 ± 74.6[Be]	19,152.1 ± 701.6[C]	884.2***	11,334.5[a]
1983–1987	16,679.9 ± 832.4[Cc]	19,372.6 ± 1227.2[Dd]	10,452.0 ± 729.8[Bf]	1899.2 ± 1099.2[A]	183.4***	12,100.9[a]
F value	66.0***	476.4***	140.1***	525.1***		1.5 ns
Mean	15,025.3[C]	6203.9[AB]	3714.1[A]	9210.1[B]	27.1***	

Table 13 Pd concentration (ppb) differences in PS5 based on direction and plant organ

Organ	North	East	South	West	*F* value	Mean
OB	22,362.9 ± 136.5[b]	< 100.0	10,761.6 ± 456.7[b]	< 100.0	1922.4***	13,163.9[b]
IB	2559.9 ± 331.8[a]	< 100.0	2646.7 ± 146.5[a]	< 100.0	80.7***	4175.3[a]
Wood	6354.8 ± 4362.0[Ba]	8517.0 [B] ± 6499.6	3407.1 ± 1622.8[Aa]	7002.9 ± 5079.2[B]	4.5**	6006.6[a]
F value	23.6***	0.3 ns	33.3***	0.0 ns		10.1***
Mean	7576.1[BC]	8087.0[C]	4066.5[A]	7002.9[B]	17.5***	

Table 14 Change of Pd concentration (ppb) in PS5 in woods based on direction and age period

Age	North	East	South	West	*F* value	**Mean**
2018–2022	4595.8 ± 837.1^{b}	< 100.0	2563.9 ± 571.7^{ab}	18,013.3 ± 1168.8^{f}	266.8***	8391.0^{a}
2013–2017	15,079.7 ± 86.9^{Cd}	< 100.0	3470.8 ± 222.8^{Bd}	2444.8 ± 831.4^{Ab}	592.1***	6998.5^{a}
2008–2012	8932.3 ± 410.3^{Cc}	14,640.4 ± 468.6^{Db}	2036.5 ± 73.8^{Ba}	1010.0 ± 181.6^{Aa}	1145.8***	6654.8^{a}
2003–2007	2903.5 ± 178.6^{Aa}	2560.9 ± 305.2^{Aa}	2685.6 ± 400.8^{Abc}	8217.8 ± 366.8^{Be}	216.6***	4092.0^{a}
1998–2002	2293.5 ± 65.3^{Aa}	14,818.9 ± 457.0^{Db}	3726.8 ± 283.7^{Bd}	8404.2 ± 386.2^{Ce}	863.5***	7310.8^{a}
1993–1997	2276.7 ± 167.3^{Aa}	< 100.0	3258.8 ± 382.6^{Bcd}	6172.2 ± 257.5^{Cd}	153.4***	3902.6^{a}
1988–1992	5030.2 ± 1311.0^{Bb}	2047.7 ± 149.3^{Aa}	7275.9 ± 277.0^{Ce}	8252.5 ± 441.8^{Ce}	45.2***	5651.6^{a}
1983–1987	9726.4 ± 376.9^{Cc}	< 100.0	2238.8 ± 292.7^{Aab}	3508.0 ± 553.6^{Bc}	270.5***	5157.7^{a}
F value	177.3***	1136.4***	72.0***	228.2***		1.1 ns
Mean	6354.8^{Ba}	8517.0^{B}	3407.1 A^{a}	7002.9^{B}	4.5**	

4 Discussion and Conclusion

The study showed that Pd concentration varied considerably between species, with PS3 and PS5 species exhibiting the lowest and others exhibiting the highest concentrations. Other research has also shown similar results, and other investigations have reported significant species-specific differences in HM concentrations (Karacocuk et al., 2022; Canturk, 2023; Koç et al., 2024b).

It was also determined that Pd concentration did not differ significantly between organs according to the average values. However, when examined based on a species, the concentrations obtained in the outer barks of many species, especially in the northern side, are at very elevated levels. Similar outcomes were seen in related research. Several studies have found significantly larger quantities of HM in the outer bark. For example, Koc et al., (2024a) determined in their study that, on average, the Cr concentration in the wood varies between 646.1 ppb and 1369.6 ppb in different directions, while the Cr concentration in the outer bark varies between 1491.7 ppb and 1965.5 ppb. Similarly, Canturk, (2023) determined that the Tl concentration in woods reached a maximum level of 5384.0 ppb on average, while it exceeded 8000 ppb in barks. Many studies obtained similar results (Cesur et al., 2022; Cobanoglu et al., 2023; Key et al., 2023). This issue is believed to be mostly due to airborne particles. Research shows that particle matter is polluted with HMs, and particulate matter sticks to HMs in the air. When this particulate matter settles on plant organs, the concentration of HMs in those organs rises (Cesur et al., 2022; Sevik et al., 2020; Turkyilmaz et al., 2019). Particulate matter is easily trapped by the outer bark due to its rough structure (Yayla et al., 2022; Koc et al., 2024a). The study determined that the species with the highest Pd concentration in the outer bark compared to the Pd concentration in the wood were *P. pinaster* (PS1), *P. orientalis* (PS3), *and P. menziesii* (PS5). In the study's area, these species have more cracked barks than others. This situation is compatible with the literature data.

As a result, while the values obtained in the western direction generally remain below the limit (< 100 ppb), the values obtained in the northern and eastern directions are quite high. This situation is thought to be caused by traffic. A highway passes north and east of where the samples were taken. Studies reveal that many HMs originate from traffic (Aricak et al., 2019; Cesur et al., 2021; Sulhan et al., 2023). Pd is generally dispersed as small particles in the exhaust gas stream from automotive catalytic converters. Therefore, Pd concentration is expected to be high in areas near highways (Tilch et al., 2000). For example, it was determined that the Pd concentration in dust samples collected in the "Mittlerer Ring" tunnels in Munich, Germany, increased from 21.8 ± 3.5 ng/g in 1994 to 100.5 ± 15.1 ng/g in 1997/98. The increase has been associated with increased traffic density over the same period (Zereini & Alt, 2012). A study conducted in Germany determined that Pd concentration remained below detectable limits in some measurements but increased up to 221.0 ng/g in dust and 14.6 pg/m^3 in air (Tilch et al., 2000). In their study in Zagreb, Rinkovec et al., (2018) determined that the Pd concentration remained below detectable limits in some samples, reaching up to 15.31 pg/m^3, and that the Pd concentration in road dust also varied seasonally. A study conducted in Salzburg determined that the monthly average Pd concentration varied between 7.1 and 31.2 pg/m^3 (Limbeck et al., 2004). The average natural Pd concentration in the earth's crust is estimated to be 15 pg/g (Tilch et al., 2000).

Data on Pd toxicity is quite limited, underscoring the importance of our research. Similar intravenous LD50 values have been notified for several Pd compounds: from 3 to 6.4 mg/kg body weight. From a four-week toxicity analysis of tetraammine palladium hydrogen carbonate in rats conducted through gavage, the no-observed-adverse-effect level was 1.5 mg/kg body weight/day (Umemura et al., 2022a, 2022b). These findings emphasize the possible health risks associated with Pd exposure, making our research crucial in understanding and mitigating these risks.

HMs can penetrate the tree body from the soil via the roots, the air across the leaves, or the trunk (Cobanoglu et al., 2023). In the current study, Pd concentrations in soil samples remained below detectable limits. Therefore, it can be said that Pd in plants accumulates in plant bodies due to airborne sources.

The highest Pd concentrations in the wood part were obtained in PS4 and PS2 species. The wood part is the enormous part of the trees in terms of volume, that is, biomass, and the amount of HM that can be stored in this part determines the plant's potential to clean the air. Therefore, among the species subject to the study, these are the most proper species that can be used to diminish Pd pollution. In numerous studies conducted to date, the species with the highest heavy metal accumulation potential in the wood part have been determined as the most proper species for decreasing the pollution of that heavy metal in the air (Key et al., 2023; Koc et al., 2024a; Şevik et al., 2024). In our study, since the highest Pd concentrations in wood among the species subject to study were obtained in PS4 and PS2 species, these species were described as the most suitable species that can be used to reduce Pd pollution.

In the current study, although average values between the years did not alter, it was determined that the Pd concentrations between adjacent woods in all species were quite different. This difference shows that Pd does not transfer between the woods of the species in this study. In order to use annual tree rings to monitor the change of HM pollution over time, the displacement of the Pd element to be monitored in the wood must be limited. As a consequence of the current research, it was noted that there was no statistically substantial difference between the Pd concentrations between the directions in almost all periods, according to the average values. It has been determined that the proper species for screening HMs in various studies, such as Atlas cedar is for Mn, Cr, and Ni (Koç, 2021; Savas et al., 2021), Himalayan cedar is for Cu, Arizona cypress is for Ni, Cd, Ni, Zn, and Fe (Cesur et al., 2021, 2022; Cobanoglu et al., 2023), Turkish Hazel is for Zn, Cd, Cr, Fe, Pb, and Al (Key & Kulaç, 2022; Key et al., 2022). In other words, it has been determined that these elements' displacement in the specified species' wood is limited. Nevertheless, according to the same investigations, Co in Atlas cedar (Koç, 2021), Pb and Zn in Himalayan cedar (Zhang, 2019), and Li, Cr, and Bi in Arizona cypress (Cesur et al., 2021, 2022; Cobanoglu et al., 2023; Zhang, 2019) could have been replaced in the wood.

This study determined no substantial alteration between the Pd concentrations determined in woods of different orientations formed in the same period, according to the average values. However, when examined based on a species, there is a significant difference between woods formed in different orientations in similar period and dissimilar age periods in the same way in all species. The outcome shows that the transport of Pd in wood is limited in all species subject to the current study. Therefore, all species are suitable biomonitors that can be used to screen Pd pollution.

In conclusion, first, the transfer of Pd in wood is limited to all species subject to study. Therefore, all of these species can be used as biomonitors to monitor the change in Pd pollution. Second, Pd pollution can be largely related to traffic density. In other words, the main source of Pd pollution in the air is traffic, that is, vehicles. Last, the highest Pd concentrations were obtained in *C. arizonica* (PS2) and *C. atlantica* (PS4) species. These are the most suitable species that can be used to reduce Pd pollution in the air.

Authors' Contributions Hakan Sevik: designed the study, analyzed the data, and wrote and reviewed the original manuscript. İsmail Koç: designed the study, raw material collection and edited the original manuscript. Hatice Cobanoglu: sample preparation, analyzed the data and edited the original manuscript. All authors read and approved the final manuscript.

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Data Availability The data that support the findings of this study are available from the corresponding author, upon reasonable request.

Declarations

Conflicts of Interest The authors declare that they have no conflict of interests.

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