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Original Article

Variations in Barium Concentrations Over Time in Regions with Elevated Air Pollution

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What is already known on this topic?

- Barium (Ba) is a toxic pollutant that poses significant threats to both environmental and human health, with atmospheric deposition being a major pathway for contamination in urban areas.
- Trees can serve as biomonitors for tracking historical changes in atmospheric metal pollution by analyzing the metal concentrations in their annual growth rings.
- The suitability of a tree species for biomonitoring a specific metal element depends on its physiological capacity to limit the translocation of that metal between adjacent annual rings after initial uptake and fixation.

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ABSTRACT

Heavy metals are one of the most important pollution factors threatening the environment and people's health today. Barium, one of the most widely used heavy metals, is among the most dangerous regarding the environment and human health; all its compounds are poisonous. Therefore, monitoring and decreasing barium pollution are among the priority research topics. This study aimed to evaluate barium sources in Düzce, identify suitable biomonitor species for monitoring changes in barium pollution, determine the parts of tree stems where barium accumulates most, and assess changes in barium levels over 60 years. Within the scope of the study, samples taken from *Tilia tomentosa*, *Robinia pseudoacacia*, *Cedrus atlantica*, *Pseudotsuga menziesii*, and *Fraxinus excelsior* species growing in Düzce, which is among the five most polluted cities in Europe according to the World Air Pollution Report, were examined. Changes in barium concentrations over the past 60 years were assessed based on species, direction, organs, and range of age. As a result, barium concentrations in *R. pseudoacacia, P. menziesii*, and *C. atlantica* species were below detectable boundaries. It was determined that the primary sources of barium pollution are traffic and urban areas. It was also determined that *F. excelsior* is the only species suitable as a biomonitor among the species studied, that barium accumulates most in the outer bark of tree stems, and that there has been a significant increase in barium concentration in recent years.

Keywords: Heavy metal, barium, hyperaccumulator, phytoremediation

Introduction

The last century's industrial revolution and technological developments have caused significant changes worldwide (Bayraktar et al., 2024; Özel et al., 2024). In this process, air pollution has also become one of the most important problems on a global scale. The World Health Organization (WHO) reported that almost the entire global population (99%) inhales air containing elevated levels of pollutants exceeding the limits set by the WHO, with low- and middle-income countries suffering the highest exposure (WHO, 2024). Air pollution is associated with 9–12 million deaths annually worldwide (Kulac et al., 2025). It is also stated that air pollution causes permanent destruction to the ecosystem, affects the composition of the atmosphere, and causes climate change globally (Isinkaralar et al., 2024; Yaşar Ismail et al., 2025).

The most harmful factors of air pollution are heavy metals (HMs). Heavy metals, which tend to bioaccumulate in living organisms, and some of which can be toxic, cancer-causing, and fatal even at small concentrations, are of particular importance because they can endure in nature for a long period without deteriorating (Sevik et al., 2025a). Studies show HM pollution is exceptionally high in urban areas (Gültekin et al., 2025). Since the number of people living per unit area is higher in urban areas, pollution in these areas is much more dangerous.

Barium (Ba), one of the most harmful HMs in terms of public health, plays a key role in producing many goods in the industry. In addition to the production of Ag, Zn, Pb, Ba, and its isotopes, compounds, and alloys are used in paint, rubber, medicine, brake pad base, ink, machine oil, glue, candles, photo paper, optical glass, detergents, batteries, oil paint production, drilling applications, plastic and textile products, in the petroleum industry, paper coatings, unique glass production, fireworks, ceramic glazes, and many other areas. However, all Ba compounds are poisonous (Koç et al., 2024a). Moreover, HMs can be much more dangerous and even fatal when inhaled into the human body (Ghoma et al., 2023).

What this study adds on this topic?

- This study demonstrates that *Fraxinus excelsior* (European ash tree) is a suitable biomonitor for monitoring changes in Ba pollution throughout the process. At the same time, *Tilia tomentosa* (Silver linden tree) is not a suitable biomonitor due to the transport of Ba between tissues in its wood (WD) after it enters the WD.
- It demonstrates that in a highly polluted urban environment, Ba accumulates most heavily in the outer bark of trees and that the primary sources of this pollution are linked to traffic and urban activities.
- The analysis of tree rings reveals a significant recent increase in Ba concentrations in the study region (Düzce, Türkiye) over the past decades, providing direct evidence of escalating pollution trends.

Therefore, tracking and reducing the change in Ba concentrations in the atmosphere is crucial. Studies have shown that the woody parts of trees are suitable biomonitors for monitoring changes in HM pollution over time. In regions like our country, Türkiye, which experiences different seasons, color changes in the woody parts of trees can be used to determine which part was formed in which year. Thus, reliable information about HM concentrations in different years can be obtained through analyses, "if the transport of HMs within the wood is limited." This procedure has been used in numerous studies in recent years aiming to define the shifts in HM pollution over time (Koç et al., 2024b; Kulac et al., 2025; Ozturk Pulatoglu et al., 2025). However, since the number of studies on this subject in the region is limited, there is a lack of information on Ba accumulation in different tree species. In addition, there is insufficient information on long-term Ba pollution in Düzce province, Türkiye, and there is uncertainty about which species can be used as reliable biomonitors in tracking shifts in Ba pollution. In fact, a recent study on the subject determined that *Pseudotsuga menziesii*, *Cupressus arizonica*, *Cedrus atlantica*, *Pinus pinaster*, and *Picea orientalis* species frequently used in landscape studies in the region, are suitable for tracking changes in atmospheric Ba concentration over time (Sevik et al., 2025a).

However, no studies have been conducted on the usability of *Tilia tomentosa*, *C. atlantica*, *Robinia pseudoacacia*, and *Fraxinus excelsior*. These species have grown abundantly in the region, in determining changes in Ba concentration. Furthermore, the inclusion of different species in studies is crucial for determining the most suitable biomonitor and hyperaccumulator species. In this study, the aims in Düzce were a) to identify Ba sources, b) to identify suitable biomonitor species, c) to determine in which parts of tree stems Ba accumulates more, and d) to evaluate the changes in Ba over 60 years.

Material and Methods

The city center of Düzce provided the study samples. The World Air Pollution Report 2021 states that Düzce city, within European towns, has the 5th-highest pollution level (Koç et al., 2024b). In Düzce, domestic fuel usage, vehicle traffic, and industrial establishments are typically the primary sources of air contamination (Key et al., 2023). For this research, log samples were collected from several tree (*P. menziesii, T. tomentosa, C. atlantica, R. pseudoacacia,* and *F. excelsior*) trunks that are commonly used in landscaping in the province. Sample trees were selected from healthy trees of similar age and height, growing under similar conditions, located equidistant from the pollution source, and close to each other but without interfering with each other's growth. Before the trees were cut down, their north orientation was marked. This determined their location relative to the pollution source. In the late vegetative season of 2022, trees were cut down from 50 cm above the ground, and 10 cm thick log samples (north direction marked on it) were obtained. In the lab, the surface of the logs was sanded, the annual tree rings were counted, and all trees were determined to be 60 years old. Samples collected from the trunk stumps were categorized based on the age of the tree, which is 60 years old, and the annual ring widths. Because of their age and the width of the annual rings, they were separated into age groups of five years. Samples were taken from the logs used in the study from the outside to the inside, separately from all four directions (south, north, east, west). Sampling of the bark was done from two parts: the part in direct contact with the external environment (outer bark (OB)) and the part immediately after the cambium that is not in direct contact with the external environment (inner bark (IB)). For both bark and wood (WD), samples were taken from the main direction (south, north, east, west) to a maximum depth of 0.5 cm, extending 1 cm to the side of the line leading to the center. For the analysis, five tree species × four directions × five log samples × 14 (12-year age group + OB + IB) × three replicates = 4200 samples were used.

A stainless steel drill is used to extract sawdust samples from the IB, OB, and WD of each age range, place them in glass Petri dishes, and let them air dry in the lab. After being pre-dried for 15 days in the lab, the samples were dried in an oven (45°C) for a week. It has been noted that some HMs can degrade at high temperatures. Therefore, in recent years, drying processes at temperatures of 45–50°C have been carried out on WD and bark (Sevik et al., 2024; Kulac et al., 2025). Six milliliters of 65% nitric acid (HNO_3) and two milliliters of 30% hydrogen peroxide (H_2O_2) were added to 0.5 grams of the dried samples, which were then put in a microwave oven. Microwave-assisted (Ethos One, Milestone GmbH, Germany) strong acid digestion method was used on the US Environmental Protection Agency (USEPA, method 3052) mixture, which was heated to 150°C for 3 hours until a transparent solution at 280 PSI and 180°C during 20 minutes. Following the burning process, the samples were moved into graduated vials; ultrapure water was added to complete 50 milliliters of the final volume. An ICP-OES instrument was used to analyze the liquid solutions, and the results were multiplied by the dilution factor to acquire the Ba amounts. Prior research in this region has considerably used this approach (Erdem et al., 2023a,b; Sevik et al., 2024; Isinkaralar et al., 2025).

The SPSS 22.0 statistical software assessed the data through variance analysis. Prior to statistical analysis, the normality of the data was tested; since the data showed a normal distribution, no transformation parameters were applied. The Duncan test was also assessed for factors that showed statistically notable differences at a minimum 95% confidence level ($p < .05$).

Table 1.
Variations in *T. tomentosa*'s Ba concentration (ppb) According to Organs and Directions

Organ	North	East	South	West	F value	Mean
OB	41764.0^{cD}	38531.6^{cC}	34164.2^{cB}	32565.1^{cA}	666.5***	36756.2^{C}
IB	23880.4^{bB}	25522.9^{bC}	20926.9^{bA}	24031.3^{bB}	514.0***	23590.4^{B}
WD	2494.9^{aA}	2470.8^{aA}	2869.9^{aB}	2605.5^{aA}	4.7**	2610.3^{A}
F value	18305.7***	15861.8***	8498.5***	6536.3***		5959.6***
Mean	6827.4	6693.1	6395.0	6275.9	0.0ns	

The letters are groups formed as a result of the Duncan test. Capital letters are values in rows, lower case letters are groups of values in columns. ns = $p > .05$, * = significant at 0.05 level ($p < .05$), ** = significant at 0.01 level ($p < .01$), *** = significant at 0.001 level ($p < .001$). These explanations are valid for each table.

Results

As a result, a statistical evaluation could not be made since Ba concentrations in *R. pseudoacacia*, *C. atlantica*, and *P. menziesii* were below detectable limits. Table 1 shows the variations in Ba concentration in *T. tomentosa* according to organs and directions.

The OB in all directions has the greatest values when the variations in Ba concentration in *T. tomentosa* according to organs and directions are analyzed, and the Ba concentration is ranked as OB > IB > WD. It has also been determined that the Ba concentrations in WD are much lower than in bark. Especially in the north cardinal direction, Ba concentration in the OB is approximately 16.7 times that in WD. According to the average values, this difference is approximately 14 times. Regarding direction, Ba concentration is ranked north > east > south > west in the OB, and the highest values are obtained in the east in the IB and the south in the WD. The alterations in Ba concentration in *T. tomentosa* WD based on periods and directions are given in Table 2.

When the table values are examined, the change in Ba concentration is generally irregular on a period basis, and there are differences between neighboring cell groups that do not reach several times. While the highest concentrations are obtained in the south direction according to the average values, it is noteworthy that the values obtained in recent years are quite low on a period basis. The alteration in Ba concentration in *F. excelsior* by organ and direction is given in Table 3.

When the variations in Ba concentration in *F. excelsior* based on organ and direction are examined, the maximum concentration is found in the OB in all directions, and the Ba concentration is ranked as OB < IB < WD. Furthermore, Ba concentrations in the WD are much lower than in the bark, and the Ba in the OB is approximately 11.2 times that in the WD, according to the average value. In terms of direction, Ba concentration is ranked as east<west<south<north in the OB, and this order is south>east>north>west in the IB. The difference between the directions in WD was statistically insignificant ($p > .05$). The alterations in Ba concentration in *F. excelsior* WDs based on period and direction are given in Table 4.

Although Ba concentration change in *F. excelsior* by period is generally irregular, it is remarkable that the concentrations in all directions are much higher in the recent period. Apart from this, it has been determined that there may be a significant difference between neighboring cell groups, although in limited numbers. For example, the Ba concentration in the north direction was 2642.7 ppb in 2003–2007, 10522.1 ppb in the previous period (1998–2002), and 3419.2 ppb in the period

Table 2.
Variations in Ba Concentration (ppb) in *T. tomentosa* Wood Based on Periods and Directions

Age Group	North	East	South	West	F value	Mean
2018–2022	2875.4^{jD}	1912.8^{aB}	2514.9^{bC}	1753.8^{bA}	6883.5***	2264.2^{a}
2013–2017	2831.5^{iC}	2451.5^{fB}	2826.7^{eC}	1735.3^{aA}	5706.0***	2461.3^{ab}
2008–2012	2005.4^{aA}	2390.1^{eB}	2501.6^{bC}	1995.9^{dA}	1430.5***	2223.2^{a}
2003–2007	2407.9^{eC}	2480.0^{gD}	2234.0^{aB}	1976.3^{cA}	704.2***	2274.6^{a}
1998–2002	2541.7^{gB}	2229.6^{dA}	2958.2^{fC}	2212.5^{fA}	2318.3***	2485.5^{ab}
1993–1997	2060.7^{bA}	2193.8^{cB}	2634.1^{dC}	2898.7^{hD}	2525.8***	2446.8^{ab}
1988–1992	2373.7^{dA}	2858.0^{iB}	3476.5^{iD}	3256.2^{iC}	4742.1***	2991.1^{c}
1983–1987	2322.5^{cA}	2940.5^{jC}	3297.9^{hD}	2763.1^{gB}	2663.3***	2831.0^{c}
1978–1982	2045.5^{bA}	2202.3^{cB}	3061.4^{gC}	3486.1^{kD}	12510.0***	2698.8^{bc}
1973–1977	2461.3^{fC}	2058.8^{bA}	2514.1^{bD}	2155.3^{eB}	771.1***	2297.4^{a}
1968–1972	2639.5^{hB}	2560.6^{hA}	2549.4^{cA}	3328.2^{jC}	2457.0***	2769.4^{bc}
1963-1967	3374.3^{kA}	3370.9^{kA}	3870.3^{jC}	3704.7^{lB}	636.0***	3580.0^{d}
F value	3425.6***	2026.0***	4826.4***	2125.3***		13.3***
Mean	2494.9^{aA}	2470.8^{aA}	2869.9^{aB}	2605.5^{aA}	4.7**	

Table 3.
Change in Ba Concentration (ppb) in *F. excelsior* by Organ and Direction

Organ	North	East	South	West	F value	Mean
OB	58053.2^{cD}	46279.2^{cA}	51948.7^{cC}	47979.3^{bB}	1003.1***	51065.1^{C}
IB	19058.8^{bB}	25246.1^{bC}	28401.8^{bD}	1895.9^{aA}	45464.5***	18650.6^{B}
WD	4829.3^{a}	3412.7^{a}	5814.9^{a}	4043.4^{a}	2.8ns	4525.1^{A}
F value	441.2***	6286.7***	123.8***	231.6***		587.5***
Mean	9647.4	8034.1	10723.5	7028.3	0.6ns	

before that (1993–1997). According to the average values, the change in direction is statistically significant.

Discussion

Ba concentrations remained below detectable limits in *R. pseudoacacia, C. atlantica, P. menziesii* evaluated within the scope of the study; very high values, such as 2610.3 ppb in WD and 36756.2 ppb in OB, were obtained in *T.* tomentosa, and 4525.1 ppb in WD and 51065.1 ppb in OB were obtained in *F. excelsior*. Similar results have been obtained in many studies on the subject. Sevik et al. (2024) determined in the same region that the Pd concentration varied between 3248.8 ppb and 13163.9 ppb in different types of OB and between 4768.7 ppb and 11065.1 ppb in WD. Another study in the same region showed that the arsenic concentration was 55295.6 ppb in *R. pseudoacacia* WDs and 27106.0 ppb in *C. atlantica* WDs (Yaşar Ismail et al., 2025). Many studies conducted in different regions showed that HM concentrations in plants growing in similar environments varied significantly based on species (Canturk et al., 2024; Koç et al., 2025; Ozturk Pulatoglu et al., 2025). As a result of the study, Ba concentration in the OB was much higher than in the WDs, and this difference could exceed 15 times.

The HMs can enter the plant body directly from the roots, soil, and air through the leaves or stem sections (Cobanoglu et al., 2023). Since the OB interacts with the external environment, the HM concentrations determined in the OB are generally much higher than in the IB. Because HMs in the air in the external environment adhere to particulate matter, particulate matter contaminated with HMs adheres to the OBs of plants. It increases the HM concentrations in the OB (Key et al., 2023). However, the WD part is an organ without a direct connection with the external environment. The accumulation of metal ions in WD depends on the changing ion exchange capabilities of the xylem in several plant species. Ion exchange capacity regulates the quantity of metal ions adsorbed to biomaterials. For one mole of divalent metal element absorbed, one mole of Ca element is displaced. The plant cell wall is a complex and multifunctional system, part of the apoplast. Due to the existence of ion exchange groups, the plant cell wall controls the movement of metabolites and the composition of the periplasmic media and ions across the plasma membrane (Ozturk Pulatoglu et al., 2025).

HM concentrations in WD are much lower than in the OB, which has been emphasized in many studies (Cobanoglu et al., 2023; Canturk et al., 2024; Koç et al., 2024b). However, the WD component is an enormous plant organ in terms of biomass. HMs in the WD part are trapped for extended periods (tens or even hundreds of years), which ensures that the HMs accumulated in the plant WD part are kept away from the receiving environments. Thus, species that can accumulate HMs in the WD portion at elevated levels are also significant (Koç et al., 2024b; Şevik et al., 2024). Plant species that can accumulate HMs at high concentrations (more than 1000 $\mu g\ g^{-1}$ dry mass, i.e., 1 mg/g = 1000 mg kg^{-1}) are called "hyperaccumulator" plants (Çobanoğlu & Kulaç, 2025).

Table 4.
Variations in Ba Concentration (ppb) in *F. excelsior* Woods Based on Period and Direction

Age Group	North	East	South	West	F value	Mean
2018–2022	12914.8^{jB}	2714.7^{bA}	22604.6^{iC}	13041.5^{iB}	12590.6***	12818.9^{c}
2013–2017	2838.2^{bC}	2822.4^{cC}	2762.7^{aB}	1945.5^{bA}	4091.4***	2592.2^{a}
2008–2012	3120.7^{cD}	2513.8^{aB}	2883.4^{abC}	2078.1^{dA}	4626.9***	2649.0^{a}
2003–2007	2642.7^{aB}	3247.7^{eD}	2926.3^{bC}	1998.1^{cA}	6675.1***	2703.7^{a}
1998–2002	10522.1^{iD}	3261.7^{eB}	3800.0^{eC}	1877.8^{aA}	62919.7***	4865.4^{a}
1993–1997	3419.2^{eC}	3307.7^{fB}	4499.6^{gD}	2073.7^{dA}	8731.3***	3325.1^{a}
1988–1992	3321.9^{dC}	2865.4^{dB}	4023.4^{fD}	1945.0^{bA}	21440.0***	3038.9^{a}
1983–1987	4268.8^{hD}	3395.0^{gB}	3901.9^{efC}	2189.4^{eA}	20946.6***	3438.8^{a}
1978–1982	3503.3^{fC}	4018.7^{iD}	3220.7^{cB}	1920.8^{bA}	26202.1***	3165.9^{a}
1973–1977	3117.8^{cA}	3459.3^{hB}	3608.1^{dC}	4596.9^{fD}	3046.7***	3695.5^{a}
1968–1972	4011.6^{gA}	4105.5^{jB}	4451.5^{gC}	4711.1^{gD}	658.6***	4319.9^{a}
1963–1967	4270.0^{hA}	5240.6^{kB}	11096.9^{hD}	10142.6^{hC}	15703.4***	7687.5^{b}
F value	42591.7***	9369.1***	18624.5***	67384.4***		15.9***
Mean	4829.3	3412.7	5814.9	4043.4	2.8ns	

According to the research results, there was no significant difference between the Ba concentrations in adjacent cell groups in the WDs of *T. tomentosa*. On the contrary, there was a notable difference between adjacent cell groups in *F. excelsior* WDs. These results can be interpreted as the Ba element can be translocated between WD tissues in *T. tomentosa* WDs, while this translocation is more restricted in *F. excelsior* WDs. The possibility for translocation of HMs within WD tissues is the most critical factor determining the usability of species' WDs as biomonitors in HM changes during the process. Studies have shown that diverse species can be used as biomonitors for different HMs. For example, it has been determined that WDs of *Corylus colurna* are appropriate biomonitors for Ni, Cd, Co, and Mn (Key et al., 2022; 2023), *Cedrus deodora* for Cu (Zhang, 2019), *C. arizonica* for Tl (Canturk et al., 2024).

In contrast, *Pinus nigra* WDs are not suitable biomonitors for Se, Ag, Tl, and Sb (Şevik et al., 2024). According to the current study results, *T. tomentosa* WDs are not suitable as biomonitors of the Ba element, but *F. excelsior* WDs are suitable. As a current study result, Ba concentration in *F. excelsior* WDs has reached very high concentrations recently. In addition, both species obtained the highest values in the OB in the north direction. As explained above, the HM concentration in the OB is primarily related to particulate matter adhering to the bark and contaminated with HMs. Therefore, the concentration of HMs in the OB delivers important knowledge about the source of pollution. In the northern side of the study site, one of the busiest freeways in Türkiye and residential areas are located. Therefore, it can be said that Ba pollution largely results from traffic and urban areas. Studies reveal that the primary sources of HM pollution are industry (Istanbullu et al., 2023), traffic (Gültekin et al., 2025), mining actions (Kuzmina et al., 2023), and agricultural activities (Sevik et al., 2025b). Ba is used extensively in paint, petroleum, brake pad bases, optical glass, machine oil, and the plastic industry (Koç et al., 2024a). Similarly, Ba is also found in the structure of textiles and plastic products frequently found in urban areas, oil paint production, paper coatings, special glass production, inks, paints, and lamps, glues, candles, and detergents (Sevik et al., 2025a). This explains the increase in Ba due to traffic and urban areas. Therefore, it is a rational conclusion that Ba is caused by traffic and urban areas. Therefore, it is a rational conclusion that Ba is caused by traffic and urban areas. However, there is a distance of hundreds of meters between the pollution source and the trees that are the subject of this study. Studies have shown that HMs can be transported hundreds of kilometers by wind (Key et al., 2022). In addition, HMs can enter the plant body through the above-ground organs by attaching to plant organs, as well as by contaminating the soil and entering the plant body through the roots (Erdem et al., 2024). Thus, HMs can accumulate in the bodies of plants that are not very close to the pollution source.

In line with the study objectives, the results indicate that: a) traffic and urban areas are the main sources of Ba pollution; b) *F. excelsior* is the only species suitable as a biomonitor among the species studied; c) Ba accumulates most in the OB of tree trunks; and d) there has been a significant increase in Ba concentration in recent years.

Conclusion and Recommendations

In conclusion, Ba accumulated at elevated levels in the WDs of *T. tomentosa* and *F. excelsior*, and this accumulation in both species far exceeded the limit value in plants that can be used for phytoremediation. These results indicate that these two species can effectively reduce Ba pollution. Cultivating these species in areas with high levels of Ba pollution can help reduce contamination.

Based on the results, Ba element can be displaced between WD tissues in *T. tomentosa*, while this displacement is more limited in *F. excelsior*. So, *T. tomentosa* WDs are not suitable as biomonitors of Ba element, while *F. excelsior* WDs are suitable. *F. excelsior* WDs can provide important details about the Ba pollution change in a place over a long period.

According to the outcomes obtained in *F. excelsior* WDs, Ba pollution has increased significantly in recent years. Furthermore, it was determined that Ba concentrations in the OBs accumulated more particularly in the north and west directions. Therefore, it was concluded that Ba pollution originates from traffic and urban areas. In this case, barriers should be placed around highway edges or dense urban areas to prevent Ba pollution from affecting other areas. Tree species, such as *T. tomentosa* or *F. excelsior*, can be used as barriers to help prevent the spread of pollution while mitigating the pollutants from nature.

Data Availability Statement: The data that support the findings of this study are available on request from the corresponding author.

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