



Evaluation of Environmental Barium Concentration Biomonitoring in Tree Rings

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ABSTRACT

The effect of barium element that can be extremely harmful heavy metal to human and environmental health in urban centers. The barium can cause various environmental pollution due to its anthropogenic accumulation in the environment. Also, it has negative effects on plants, animals, and humans through atmospheric deposition. All Barium (Ba) compounds are harmful heavy metals and they show a poisonous effect on the environment. Thus, it is crucial to determine the Ba concentration in plants grown in areas with high pollution in the landscape, park, and roadside. Biomonitoring with the tree species can be determined which is the best passive biomonitoring method with the tree rings formed by the effect of seasonal differences. The barium has been accumulated in the tree rings for a long time that can provide critical knowledge about the atmospheric barium deposition. The temporal and spatial variations of Ba concentration were analyzed with organs of *Ailanthus altissima* (Mill.) as biomonitors. This study results show that the outer bark of *Ailanthus altissima* (Mill.) is a convenient biomonitor for Ba deposition.

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Introduction

Environmental heavy metal pollution monitoring and identifying risky are essential procedures in terms of human and environmental health (Isinkaralar et al., 2017; Jacob et al., 2018; Işınkaralar and Varol, 2021). Heavy metal concentrations in urban air are likely to increase over time due to continued improper urbanization and atmospheric heavy metal deposition (Kurnaz et al., 2016; Yilmaz and Isinkaralar, 2021a, b). In these periods of rapid urbanization, the emission resulting from the fuels used in industry, vehicles, and residences has accelerated by anthropogenic sources (Isinkaralar et al., 2021; Önaç and Sütçüoğlu, 2021). With the increase in environmental pollution, new methods for the removal of environmental pollutants have come to the fore (Şutan et al., 2020; Isinkaralar et al., 2022). Especially, Heavy metal pollution in the air, water, or soil has been one of the vital subjects for many years (Yalçın and Çimrin, 2019; Isinkaralar, 2020; Tokatli et al., 2021; Mutlu, 2021; Wei et al., 2021). Especially pollutants in soil and water are much easier than air pollutants because they can be determined by direct measurements (Sevik et al., 2018; Abacioglu et al., 2019; Manisalidis et al., 2020). They tend to accumulate in the environment due to their non-biodegradable properties. Although it is not easy to monitor environmental pollutants monitoring them and evaluating their status is very important (Turkyilmaz et al., 2020; Yang et al., 2021).

Among these pollutants, Barium (Ba) an abundant alkaline earth metal, belongs to Group 2A, a can be found more than zinc (Madejón, 2013). Ba is not found in nature in its form because it is an extremely active element (Pena et al., 2021). Therefore, it is generally seen as a form of barite ($BaSO_4$) and with rite ($BaCO_3$) (Böttcher et al., 2018). They have commonly used substance in drilling operations, which is generally applied in oil extraction operations. Ba^{+2} or its composites, used in many fields, are used in plastic and adhesive, ceramics and protection, hair dyes and cosmetics, medical engineering, white colorant, and fireworks (Aziz et al., 2017). Although the solubility of barium sulfate and barium salts can increase in reduced environments, their solubility varies such as barite due to easily oxidized by oxygen in air and water (Rye 2005). In some cases, (acidic, oxygen ninety, and when microbial activities are fast), their solubility may increase the possibility of environmental contamination (Landreau et al., 2021). Ba precipitates as a carbonate salt and/or sulfate at neutral or basic pH conditions (Cravotta 2008). Hence, Ba has negligible mobility under the same conditions, thus decreasing the adverse health effects and the risk of leaching. However, when it is not worked under appropriate conditions, Ba^{+2} can cause toxic effects by sulfate and sulfur residues. The Ba emission resulting from

various industrial and industrial activities can easily mix with air, soil, and water (Boev and Lepitkova, 2021).

As a result of high concentration, it causes various health problems. It was observed that both acute poisoning and chronic exposure increased as the solubility of barium increased. The usage of Ba for industrial goals steadily increases, the importance of assessing the risks associated with barium exposure or poisoning is increasing (Jing et al., 2011). Here we want to provide a synopsis of the distinct exposure pathways for humans and their effects on health. Although it is seen as a bio-essential substance for human nutrition, it is absorbed by people in different ways such as ingestion, inhalation, and through the skin. In particular, it gets more through eating and drinking, that is, food depending on the barium level in food products and drinking water, the amount of intake may increase. While this value is less than 2.0 µg/g for edible products, it is 200 µg/day for drinking water (Kravchenko et al., 2014). More than these amounts accumulate in humans' skeletal systems, teeth, and bones. It threatens organs that perform other vital (such as liver, kidney, heart) and gastrointestinal activities. It induces destructive cell processes such as hypokalemic paralysis, resulting in cardiac and respiratory arrest. Also, it can be seen in different tissues (such as the aorta, brain, pancreas, blood-urine-stool, placenta, muscles) although there is no accumulation there (Schroeder et al., 1972). approximately 90% of Ba taken into the body in various ways is excreted in the first two weeks in urine and feces. However, if insoluble compounds are inhaled, their levels can build up in the lungs causing a benign condition known as "Baritosis" (Peana et al., 2021). Tests that can measure the extent of barium exposure are still being studied. Ba has a toxic effect on humans and affects other living things, especially plants. Ba toxicity has been demonstrated in studies on plants from anthropogenic pollutants. Studies have revealed the accumulation of Ba in various species (Nagaraju and Karimulla, 2002). While there is 49 ppm in apple leaves, it has been determined that there is 63 ppm in tomatoes due to the continental crust being predicted to hold 425 ppm of Ba (Padilla and Anderson, 2002). Like other elements in the plant, they can accumulate with the root and the transfer system between each other (Usman et al., 2019).

Trees can be used as biomonitors that should be capable of accumulating heavy metals in their bodies, but should not die from the effects of heavy metals (Sevik et al., 2019; Maresca et al., 2020; Savas et al., 2021). In addition, they should live in the sample area, have enough samples, organs, or tissue for metal analysis, be easy to sample whenever desired, and there should be a correlation between organisms and the environment in terms of the heavy metal concentration (Koç, 2021; Rakib et al., 2021). In addition, it is known that the heavy metals accumulating in this tree are transmitted to humans, since people are trying to consume this tree in various ways, believing that this tree is beneficial (Turkyilmaz et al., 2019). Therefore, it is stated that the most suitable biomonitors are plants to trace heavy metal pollution changes (Barandovski et al., 2021; Jeddi et al., 2021). The primary problem with using plants as biomonitors is to determine which plant and its organs are more suitable for monitoring which metal (Karacocuk et al., 2021). Because plants accumulate different elements in different organs and at different

levels. Although the annual tree rings are used effectively as biomonitors, the amount of information about the speciation of heavy metals in the plant and their transition between organs is quite limited, starting from their entry into the plant. The study aimed to evaluate the accumulation of Ba concentration in organs and its potential to use tree rings of *Ailanthus altissima* (Mill.) as a biomonitor.

Material and Method

Study Area and Sampling

Ailanthus altissima (Mill.) was used barks-wood and 69 years old. It was collected from the city center of Ankara province, Turkey. It is a malodorous tree from the *Simaroubaceae* family that blooms with greenish-yellow flowers between May and June. It is believed among the locals that it is healing various diseases when it is extracted. It has an antipyretic and emetic effect. It helps to reduce intestinal worms. Considering that it is beneficial in diarrhea and dysentery, it is either brewed or consumed like tea. It was aimed to determine atmospheric barium deposition by rings of the *Ailanthus altissima* (Mill.). Samples taken from the tree main trunk at a height of approximately 1.5 meters from the ground were kept in a controlled oven for 2 weeks to be dried at 45°C. The samples were not washed in some cases because it causes the elements to change.

Chemical Analysis

The dried samples were weighed as 0.5 g blended with 6 mL and 2 mL (65% HNO₃ and 30% H₂O₂), and inserted into the microwave for the digestion system (Milestone Ethos). The machine was programmed to raise the temperature to 200°C for 15 minutes and then replenish with 25 mL of deionized water, the GBC Integra XL-SDS-270 ICP-OES device was used in analyzing for Ba concentration.

Data Analysis

The data were analyzed by analysis of variance (ANOVA) using the SPSS 22.0 package software program. Also, Duncan's test was used for the factors that showed statistically significant differences (P<0.05). The obtained homogeneous groups were simplified, represented in tables, and interpreted. The data obtained were interpreted after simplification and tabularization. All the measurements were triplicated and the coefficient of variation was found to be within 11% for Ba.

Results and Discussion

The accumulation of Ba element in *Ailanthus altissima* (Mill.) species was determined to be highest in the outer bark (37784.4 ppb), slightly less in the inner bark (26088.4 ppb), and least in wood (2936.9 ppb). According to the ANOVA test applied to the obtained data, it was determined that the change in all of the metals subject to the study on an organ basis was statistically significant at the 99.9% confidence level (P<0.001). When the groups formed as a result of the Duncan test are examined, it is seen that the values obtained in the outer bark are in the last group in Figure 1.

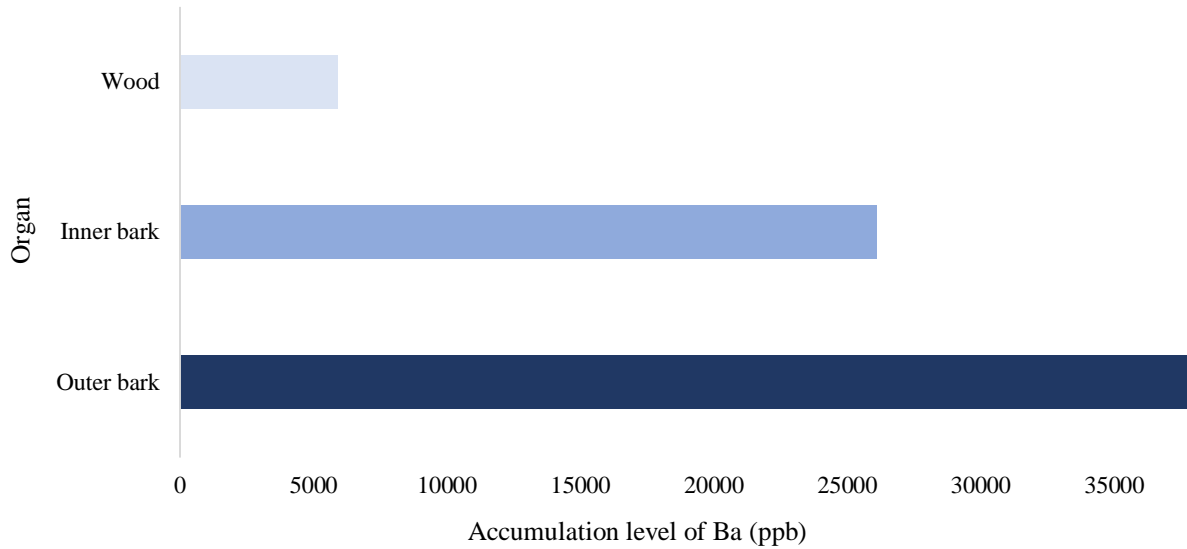


Figure 1. Ba concentrations (ppb) based on organ

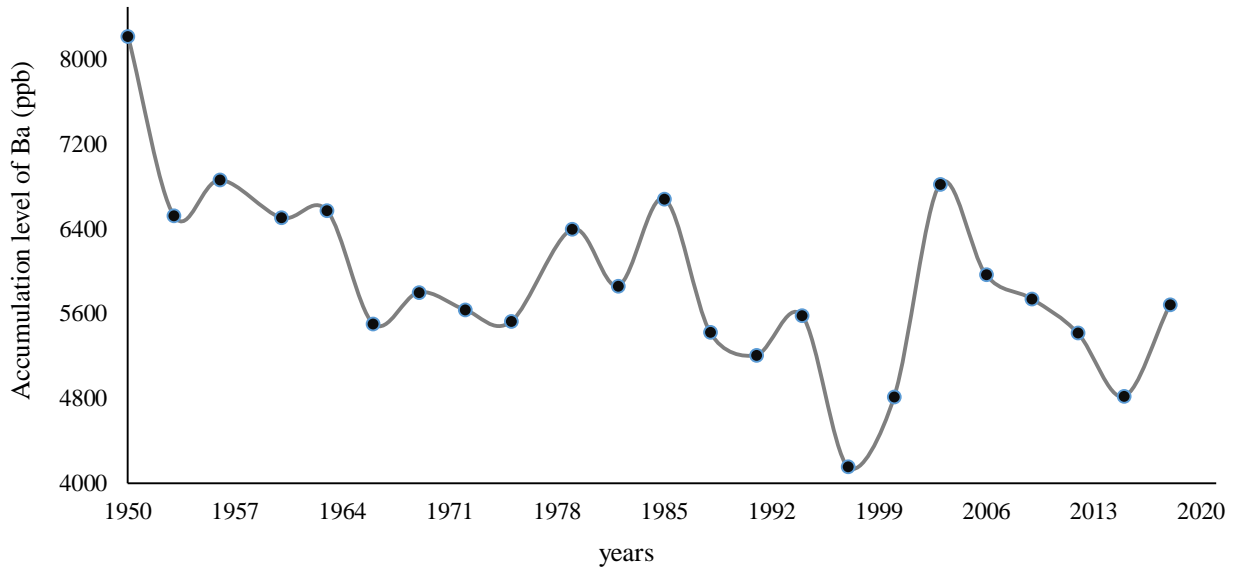


Figure 2. Ba concentrations (ppb) of tree rings in the plots

When the Ba concentration accumulation in the annual rings of *Ailanthus altissima* (Mill.) is examined, the highest Ba concentration was found in 1950 with 8219.7 ppb. Although the Ba level in its body decreased with a fluctuating course with the development of the plant species until 1995, it experienced a jump after 1995 and reached 6825.2 ppb in 2003. Although there were decreases afterward, there was no increase with the accumulation of Ba level approximately 30 years apart in Figure 2.

Discussion

There are many studies in which tree rings are used as a biomonitor for trace, nutrient, and toxic elements, especially heavy metals although studies following the change in barium accumulation and level of plants are very

limited (Turkyilmaz et al., 2018; Goddard et al., 2019; Şevik, 2021). Kirchner et al. (2008) was determined using tree rings of 350 years old *Pinus jeffreyi* as a biomonitoring trace metal in Nevada, USA. Sr^{+2} , Ba^{+2} , and Ca^{+2} were showed similar results due to having the greatest affinity. Balouet et al., (2009) were searched environmental contamination with dendrochronological methods for anthropogenic effect on species. Padilla and Anderson (2002) were examined tree rings of 350+ years old *Pinus ponderosa* as trace elements including Ba. It has a positive correlation for relatively constant from the mid-1600s to the early 1800s. Bardule et al., (2020) were studied stem disc samples of six-year-old hybrid aspen (*Populus tremuloides* Michx. × *P. tremula* L.) in the spring of 2011. They were analyzed major elements and toxic heavy metal content in the disc of species. They found a correlation between the accumulation of various elements in soil and

tree species. Perone et al., (2018) were evaluated atmospheric pollution from several sources. They hypothesized that tree-rings of *Quercus pubescens* could accumulate heavy metal from anthropogenic activities in the period 1958–2009. The type used was useful in describing the types of welds of each heavy metal and other elements, as well as the types of welds. Cetin et al., (2021) was assessed Ba concentration in fir organs of some species and were found Ba concentration varies considerably in organs and age. Cetin and Jawed (2022) were determined the variation of Ba concentrations in leaves and branches of *Ficus bengalensis*, *Ziziphus mauritiana*, *Conocarpus erectus*, and *Azadrechtia indica* species depending on traffic density. They were found the most suitable organs were *Azadrechtia indica* leaves. Heavy metals released into the atmosphere because of traffic and industrial activities accumulate in different plant species (Monaci et al., 1997; Frati et al., 2005; Jabłońska et al., 2016). About the Ba and Sb elements show that they are released from non-exhaust vehicle emissions and have a positive association of their levels (Gietl et al., 2010). It has been discovered that plant and tree species can adsorb heavy metals and toxic metals according to their environment. The recent studies have been carried out that several species of plants have been used as a very successful environmental biomonitoring tool for passive sampling of atmospheric heavy metal deposition in urban areas (Oliva and Rautio, 2004; Vergel et al., 2019; Isınkaralar and Erdem, 2021). There have been studies that used passive sampling, not only an urban scale, but also in indoor air (Ghoma et al., 2022). In particular, plants and tree species in areas close to traffic accumulate in their bodies through adsorption. At the same time, it has been revealed in studies that trees and plants in areas close to industrial areas commonly contain heavy metals.

Conclusion

Heavy metals are highly hazardous that can be extremely harmful to both living things and ecosystems, especially humans. Therefore, it is crucial to monitor the change in heavy metal concentrations in the air. However, an effective, easy, inexpensive, and effective method has not been developed yet to trace the change of heavy metals concentrations in the air. The environmental pollutant is Ba, which mixes with the water, is filtered, and accumulates in the atmosphere deposition from the soil into the ants. It is released into the atmosphere that releases non-exhaust vehicle emissions by forming compounds with radicals. Accordingly, the *Ailanthus altissima* (Mill.) usability as a biomonitor was investigated for Ba concentration with tree bark and trunk wood. As a result, the effect of Ba on soil-grown plant Ba-containing still needs to be investigated further. However, it was hard to say that Ba, which has a high variability rate according to years, can be a very good biomonitor. It is foreseen that, if possible, a clearer conclusion can be reached with the analysis of the soil data of the analyzed years. Despite this, it is thought that the increase in specific years is the precipitation of pollutants by atmospheric deposition. However, detailed scientific data on how elements are physiologically incorporated into tree rings are still needed to draw precise conclusions from temporal trends in tree ring element content.

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