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Variation of Aluminum Concentrations in Annual Rings of Some Trees Growing in Ankara City Center Depending on Years and Species

***Emine Emel Yayla*[1]*, Hakan Şevik*[2]**

[1]*Kastamonu University, Graduate School of Natural and Applied Sciences, Department of Environmental Engineering, Kastamonu/TÜRKİYE*

[2]*Kastamonu University, Faculty of Engineering and Architecture, Kastamonu/TÜRKİYE*

***Correspondence**: hsevik@kastamonu.edu.tr*

Abstract: Heavy metal pollution is one of the most critical concerns threatening environmental and individual health worldwide in the last century. Heavy metals in the air have particular importance due to their effects on human health. Therefore, watching the difference in heavy metal pollution in the airborne is extremely important. Tree annual rings are the most efficient biomonitors used to define the differences in heavy metal concentration levels in the airborne during the years. However, the accumulation of each element in tree annual rings varies depending on the species. Therefore, it is necessary to determine the species that can be used as biomonitors separately in determining the difference in the concentration of each element in the air over the years. This study aimed to determine the variation of Aluminum (Al) concentration in the air in the last 30 years in Ankara city center by using the annual rings of *Platanus orientalis*, *Elaeagnus angustifolia* L., *Koelreuteria paniculata* Laxm, *Cedrus atlantica* (Endl.) Manetti ex Carr. *Ailanthus altissima* (Mill.) Swingle trees. As a result, the maximum aluminum concentrations were found in the outer bark of all species. The maximum concentrations were found in *Platanus orientalis* L. in the wood part.

Keywords: Aluminum, Ankara, Biomonitor, Heavy metal.

1. INTRODUCTION

Industrial movements have increased significantly in the last century due to industry developments worldwide. Mining activities carried out in order to provide the raw material resources required for increasing industrial activities have caused various elements to be extracted from the underground and released into nature (Ateya et al., 2023a, 2023b; Isinkaralar et al., 2022; Kuzmina et al., 2023). Population movement in parallel with the developments in the industry has caused population increases in urban areas (Dogan et al., 2023; Zeren Cetin et al., 2023); thus, urbanization has become one of the irreversible issues worldwide (Varol et al., 2022) along with global warming (Tekin et al., 2022; Cobanoglu et al., 2024). With the population density in urban areas, anthropogenic activities, especially traffic, have made air pollution the most critical threat to human health (Aricak et al., 2019; Elsunousi et al., 2021). Throughout these years, the concentrations of heavy metals in water (Ucun Ozel et al., 2020), soil (Elajail et al., 2022; Cetin et al., 2022a), and air (Koç, 2021; Istanbullu et al., 2023) have increased significantly.

Heavy metals are known as pollutants that do not break down easily in nature, bioaccumulate in living organisms, and some of them can be toxic, poisonous, carcinogenic, and fatal even at low concentrations (Key et al., 2022; Yayla et al., 2022). It is emphasized that heavy metals are much more harmful when inhaled into the body (Ghoma et al., 2022). It is stated that air pollution caused mass deaths in the past. Today, it causes serious health glitches such as stroke, lung cancer and heart disease, and the main reason for this effect is particles contaminated with heavy metals in the air (Turkyilmaz et al., 2020; Elajail et al., 2022). The WHO stated that more than 8 million individuals die yearly due to exceeding air pollution permissible limits (Isinkaralar et al., 2023a, 2023b; Sulhan et al., 2023).

Although heavy metals are dangerous, their concentrations in the air are constantly increasing. Therefore, monitoring changes in airborne heavy metal concentrations is essential, but airborne heavy metals are unstable, and their direct measurement is difficult and expensive. In addition, direct and instantaneous measurement of heavy metal concentrations in air does not provide information on the accumulation of heavy metals in the environment and their impacts on the environment. For these causes, biomonitors are used to monitor the variations in heavy metal concentrations in the airborne. Although different biomonitors are used for this purpose, tree annual rings are among the most suitable biomonitors that can be used to monitor the change of heavy metal contamination in airborne from past to present (Koç, 2021; Cesur et al., 2022; Key et al., 2022; Guney et al., 2023).

Aluminum (Al) is one of the most common and necessary nutrient elements for living things. Al is a soft and light metal and is found in some toothpaste, cigarette filters, food storage containers, aluminum foil, antacids used for the stomach, some cheeses and salts, sweat-protective deodorants, and is intensively emitted from industrial plants where it is used as raw material. In the body, Al accumulates mainly in the brain and liver tissue and can cause muscle aches, liver damage, psychosis, and loss of appetite. In addition, extra Al in the body can cause memory disorders (Kuzmina et al., 2023).

The present study aimed to determine the process- and species-dependent differences of aluminum (Al) concentrations, which is one of the heavy metals of great importance in terms of human and environmental health, in some trees growing in the capital city of Türkiye (Ankara), and one of the most densely populated provinces.

2. MATERIALS AND METHODS

The study was carried out on the annual rings of 5 tree species growing on the roadside in areas with heavy traffic in Ankara province. Ankara is Türkiye's capital and one of the provinces where anthropogenic heavy metal pollution, especially traffic density, is very high (Cetin et al., 2022a, 2022b). According to TUIK data, the population of Ankara is increasing rapidly, and the city's total population, which was 3.236.626 in 1990, reached 5.846.533 in 2023 (TUIK, 2023). For this reason, the study was carried out on plants collected from Ankara province. The species used in the study are given in Table 1.

Table 1. Tree species used in the study.

Latin Name	English Name	Species Abbreviation
Elaeagnus angustifolia L.	Silver berry	*El. an.*
Platanus orientalis L.	Oriental plane	*Pla. or.*
Koelreuteria paniculata Laxm	Golden rain tree	*Ko. pa.*
Ailanthus altissima (Mill.) Swingle	Tree of heaven	*Family. Alt.*
Cedrus atlantica (Endl.) Manetti ex Carr.	Atlas cedar	*Ced. at.*

The trees were cut in early December 2020 (end of the growing period) and transported to the laboratory. Stems were then cut into 1 cm thick discs in the laboratory, and the surface was sanded to make it smooth so that the annual rings could be seen clearly. Within the scope of the study, the annual rings of the trees were examined, and those suitable for the study purpose were divided into age categories according to their annual ring widths. Wood samples were taken from the determined sections with the help of a steel-tipped drill. The wood samples were crushed into sawdust. The samples were stored for 30 days until room dry and then dried in an oven at 50 ºC for one week.

0.5 g of the dried samples were taken, 6 ml of 65% HNO_3 and 2 ml of 30% H_2O_2 were added and placed in the microwave oven. The microwave program was set to rise up to 200 ºC in 15 minutes and stay at 200 ºC for 15 minutes. After the samples were burned in the Ethos one model microwave oven (Milostone brand), the samples in solution were taken into balloon tubes, filled to 50 ml with pure water, and made ready for elemental analysis with GBC Integra XL -SDS-270 ICP-OES device. Then, the plasma of the ICP-OES device was burned to analyze the samples, and pure water was circulated through the device system for 15 minutes to reach equilibrium.

Standard solutions were organized according to the Al (aluminum) element to be analyzed, and a calibration chart was formed. After, the samples were given to the system, and readings were taken. Since the sample was taken 0.5 g and completed to 50 g with water, the analysis results were multiplied by 100. According to the analysis results that did not fall into the calibration graph, different calibration graphs were created at ppm or ppb level and read again. This procedure is one of the most often used analysis methods in wood analysis in recent years (Erdem et al., 2023; Ghoma et al., 2023).

In the present study, all measurements were made in three repetitions, and the data obtained were evaluated with the help of the SPSS 21.0 package program. The study's data was evaluated by applying variance analysis with the help of the SPSS 22.0 package program, and the Duncan test was applied to the data with statistically significant differences at least at a 95% confidence level.

3. RESULTS

The organ-based differences in Al concentrations were evaluated separately according to the trees, and the mean values and statistical analysis results are shown in Table 2. The variation of Al concentration in all species organs was significant (*p<0.05*). The maximum values were found in *Platanus orientalis* L. 943226.0 ppb, *Elaeagnus angustifolia* L. 327260.0 ppb, *Koelreuteria paniculata* Laxm 309130.0 ppb, *Cedrus atlantica* (Endl.) Manetti ex Carr at 825988.6 ppb and *Ailanthus altissima* (Mill.) Swingle at 731598.0 ppb, and all these values were obtained in the outer bark. It is seen that the organ-wise variation of Al concentration is in the order of outer bark>inner bark>wood.

Table 2. Variation of Al concentration (ppb) by organs.

Organ	*El. an.*	*Pla. or.*	*Ko. pa.*	*Family. Alt.*	*Ced. at.*	F Value
Outer bark	327260.0Bb	943226.0 Eb	309130.0 Ac	731598.0 Cb	825988.6 Dc	53.482.5***
Inner bark	16937.0 Ba	47962.4 Da	63784.2 Eb	10130.8 Aa	43786.1 Cb	94.782.4***
Wood	21148.8 Aba	51267.8 Ca	15097.1 Aa	39778.3 BCa	13451.3 Aa	4.4**
F Value	500.0***	8840.2***	1196.3***	89.9***	76169.2***	

Note: Lower-case letter specifies to the vertical way within each row, whereas upper-case letter implies to the horizontal way within each column. ** means $p \leq 0.01$; *** means $p \leq 0.001$. This explanation also implies for Table 3.

The variation of Al concentrations in wood by species and period is shown in Table 3. As a result, the differences in Al concentration were significant (*p<0.001*) in all species by period and in all periods by species. When the values were analyzed, Al concentration varied between 7774.1 ppm and 310180.0 ppm. On a species basis, Al concentration varied between 8539.2 ppm and 67557.0 ppm in *Elaeagnus angustifolia* L., 34910.8 ppm and 78156.8 ppm in *Platanus orientalis* L., 4558.2 ppm and 42105.0 ppm in *Koelreuteria paniculata* Laxm. 105.0 ppm, 7774.1 ppm to 310180.0 ppm in *Ailanthus altissima* (Mill.) Swingle and 8986.1 ppm to 21483.0 ppm in *Cedrus atlantica* (Endl.) Manetti ex Carr. Notably, the Al concentration was higher in *Ailanthus altissima* (Mill.) Swingle in the 2012-2014 period. In addition, while there is only a 2.3-fold difference between the highest and lowest value in *Platanus orientalis* L., there is a 39.8-fold difference between the lowest and highest value in *Ailanthus altissima* (Mill.) Swingle. It can be interpreted that although Al transport in wood is relatively high in *Platanus orientalis* L., this transport is quite limited in *Ailanthus altissima* (Mill.) Swingle. The very high difference between Al concentrations in consecutive periods supports this result.

Table 3. Variation of Al concentration (ppm) by species and period.

Age	*El. an.*	*Pla. or.*	*Ko. pa.*	*Family. Alt.*	*Ced. at.*	F
2018-2020	19347.4 Cg	53489.3 Dg	LA	9680.5 Bd	8986.1 Aa	67197.3***
2015-2017	18412.4 Cf	40728.3 Eb	1869.3 Dh	9308.4 Acd	10649.0 Bc	74832.2***
2012-2014	15915.0 Bd	58872.5 Dh	1898.0 Cg	310180.0 Eg	15102.2 Ag	336512.9***
2009-2011	9319.7 Cb	34910.8 Ea	7974.7 Ab	8448.5 Bb	9788.2 Db	134918.8***
2006-2008	11326.3 Cc	45482.9 Ed	11472.3 De	9305.9 Acd	11171.3 Bd	150336.5***
2003-2005	8539.2 Aa	42371.4 Ec	11785.2 Cf	9521.8 Bd	14047.9 De	33739.8***
2000-2002	11305.6 Bc	59764.8 Ei	4558.2 Aa	14472.8 Cf	1671.0 Di	73006.0***
1997-1999	67557.0 Ei	51031.0 Df	9897.7 Bc	7774.1 Aa	13063.8 Cf	759038.3***
1994-1996	1849.6 Ce	47870.5 Ee	11313.6 Bd	10211.6 Ae	21483.0 Di	120208.8***
1991-1993	32915.7 Ch	78156.8 Ej	42105.0 Di	8879.4 Abc	16051.2 Bh	71408.8***
F	280114.1***	10847.8***	52643.2***	373519.1***	14292.4***	

4. DISCUSSION AND CONCLUSION

As a result, the change in Al concentration in the annual rings of 5 woody species growing in Ankara was determined based on species, organ, and period. Al is necessary for living things and is used in many areas. Exceeding Al limits for humans can cause some health disorders (Kuzmina et al., 2023). Therefore, it is vital to screen the difference of Al concentration in the air and reduce its concentration in polluted areas, such as urban sites and big towns.

Especially high-structured plants are essential tools in reducing heavy metal pollution in the atmosphere. However, studies show that each plant accumulates different heavy metals at different levels (Karacocuk et al., 2022; Sevik et al., 2023). Therefore, it is necessary to determine the species that can be used to reduce each heavy metal pollution separately. As a result, the highest Al values, especially in wood, were obtained in *Platanus orientalis* L. This result indicates that this species has a high potential to accumulate Al in the wood. Wood is the largest organ of plants in terms of mass. Therefore, *Platanus orientalis* L. is the most suitable species to reduce air pollution.

The most crucial feature sought in species that can be used as biomonitors in watching the difference of heavy metal contamination is the ability of the species to accumulate the elements subject to the study but limited transfer within the wood. As a result, although the uppermost Al concentrations in wood were obtained in *Platanus orientalis* L., it was determined that Al transport in wood was relatively high in this species, and it was not suitable for monitoring the change of Al contamination. The results of the study show that *Ailanthus altissima* (Mill.) Swingle is the most suitable species for monitoring the difference of Al concentration in the air. In plants, the element transfer in the wood section is primarily related to the cell wall and structure (Wani et al., 2018), and different elements in the wood differ in different species. In some studies to date, Cu in *Cedrus deodora* (Zhang, 2019), Ni, Cr, and Mn in *Cedrus atlantica* (Koç, 2021; Savas et al., 2022), Cd, Ni, Fe, and Zn in *Cupressus arizonica* (Cesur et al., 2021, 2022; Cobanoglu et al., 2023), Cd, Ni, Zn, Pb, Cr and Zn in *Corylus colurna* (Key et al., 2022; Key & Kulaç, 2022), which means that the displacement of these elements in the wood of these species is limited. However, in the same studies, it was reported that Pb and Zn in *Cedrus deodora* (Zhang, 2019), Co in *Cedrus atlantica* (Koç, 2021), Bi, Li and Cr in *Cupressus arizonica* could be displaced in wood (Zhang, 2019; Cesur et al., 2021, 2022; Cobanoglu et al., 2023). Therefore, suitable biomonitors should be determined separately to observe each element's process change. It was determined that *Ailanthus altissima* (Mill.) Swingle was the most appropriate species for watching the change in Al concentration among the species subjected to the current study.

As a result, all species obtained the maximum Al concentrations in the outer bark. Similar outcomes were acquired in different studies. For example, Savas (2021) determined that Al concentrations in *Cedrus atlantica* trunk were ordered as wood < inner bark< outer bark and Al concentrations in the outer bark could exceed 20000 ppm. Various studies have determined that heavy metal concentration levels in the outer bark are at high levels (Cesur et al., 2021; Ozel et al., 2021). This high concentration is generally due to the bark structure and the attachment of particulate matter polluted with heavy metals to the bark. First, particulate matter in the air is contaminated with heavy metals, and these particles can adhere to the bark surface due to the rough and cracked outer bark surface (Yayla et al., 2022). Al concentrations in the inner bark were greater than the concentrations determined in the wood in our study. This difference may be related to the entry of heavy metals into the tree. Heavy metals can enter the plant mainly through roots, leaves, and stem parts (Chen et al., 2022). It can be said that Al in the inner bark enters through the stem parts, and therefore, the concentrations in the inner bark, which is not in contact with air, are lower than in the outer bark but higher than in the wood.

The potential of plants to accumulate heavy metals is the product of a complicated mechanism shaped by the interaction of numerous factors. In this process, it is well known that many factors such as tree species, organ structure (surface area, texture, surface structure, etc.), the structure of the heavy metal, the interaction of the heavy metal with the plant and organ, the duration of exposure to heavy metals, atmospheric conditions (humidity, precipitation, wind, etc.) affect heavy metal entry into the plant body (Turkyilmaz et al., 2019; Aricak et al., 2020; Cesur et al., 2021). In addition, plant habitus and development also affect the uptake and accumulation of elements (Cesur et al., 2022). Therefore, all factors affecting plant habitus also affect the uptake and accumulation of elements into the plant, and plant habitus is shaped by the interaction of many interacting factors such as genetic structure (Ateya et al., 2023a; Kurz et al., 2023), environmental factors (Koç, 2022; Koç et al., 2022; Cetin et al., 2023), stress factors (Koç & Nzouko, 2022, 2023). Therefore, many of these factors, directly and indirectly, affect the uptake and accumulation of element potential in plants, and knowledge of this complex mechanism is still limited (Shahid et al., 2021; Isinkaralar et al., 2022).

In conclusion, the highest Al accumulation potential was in the 30-year-old *Platanus orientalis* tree. However, it has also been revealed that the Al element can be transferred within the wood in this species. Therefore, although *Platanus orientalis* is a suitable species for reducing Al pollution, it is not proper for monitoring pollution. The results also revealed that *Ailanthus altissima* (Mill.) Swingle is the most proper species for watching the difference of Al concentration in the airborne.

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