3rd INTERNATIONAL CONGRESS ON ENGINEERING AND LIFE SCIENCE
ICELIS 20-22 SEPTEMBER 2023 TRABZON-TURKIYE

ORAL PRESENTATION https://doi.org/10.61326/icelis.2023.24

Determination of 180-Year Variation of Li Concentration in the Atmosphere using *Corylus colurna* L. Annual Rings

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Abstract: Environmental pollution has increased significantly in the current century due to various anthropogenic effects, especially industrial activities, mining, urbanization, and traffic. Significantly increasing air pollution has become a global problem that causes millions of people to die yearly. Heavy metals, the most dangerous and harmful components of air pollution, do not easily deteriorate and disappear in nature. They can be carried far from their source, tend to bioaccumulate in living organisms, and some can be toxic, carcinogenic, and fatal even at low concentrations for humans and animals. Therefore, monitoring the change of heavy metal concentrations in the air is critical. One of the most effective methods in determining the heavy metal concentration changes in the atmosphere from past to present is using annual rings of trees as biomonitors. In this study, the variation of Li concentrations, which is one of the most harmful heavy metals in terms of human and environmental health, in the last 180 years, was tried to be determined by using *Corylus colurna* L. annual tree rings, which was cut at the end of 2020 in Kastamonu province, Türkiye. Within the scope, the heavy metal concentrations in the bark and inner bark were also compared with the heavy metal concentrations in the woods, and the directional variation of the heavy metal concentrations was also evaluated. As a result, there was a significant difference between wood and bark ($p<0.05$) except for the north direction of Li element, and the concentrations obtained in the woods were much higher than those in the bark. In the annual rings, the variation of the Li concentration in all directions, except for the west direction, is significant ($p<0.05$). However, Li concentration generally varies in a narrow range, and this can be interpreted as the Li element being transferred between woods in *C. colurna*.

Keywords: Oak seedling, Biomass, Carbon sequestration, Basic density, Root collar diameter.

1. INTRODUCTION

Environmental and especially air pollution has become one of the most critical issues worldwide in the last century, increasing rapidly due to anthropogenic factors, especially industrial activities (Ateya et al., 2023a, 2023b; Cobanoglu. et al., 2023a; Isinkaralar et al., 2023). It is stated that approximately 2.5 million living spaces across Europe are polluted, and 90 percent of the world's population now breathes polluted air (Cesur et al., 2022). It is emphasized that air pollution causes more than 4 million premature births and approximately 7 million deaths worldwide every year (Ghoma et al., 2022). Air pollution is one of the most critical global problems associated with urbanization, and global climate change is considered an irreversible problem worldwide (Varol et al., 2022; Canturk et al., 2023a; Cetin et al., 2023).

Amongst the ingredients of air contamination, heavy metals are significant for human and environmental health. Heavy metals do not degrade quickly in nature. Many are toxic and lethal to living organisms, even at low concentrations. Even those necessary as nutrients for living organisms are harmful at high concentrations, and their inhalation into the living body is a significant threat to living health. Therefore, monitoring the alterations in heavy metal levels in the air is crucial. However, studies on observing the difference in heavy metal contamination in the air mostly focus on heavy metals such as Co, Cr, Pb, Ni, Cu, and Mn, while many other elements are neglected. One of the neglected elements in these studies is Lithium (Li).

Li is widely preferred in the innovative industry of recent times. It is used in organic synthesis, glass, plastic and aluminum production, radio engineering, computers, cameras, telephone batteries, electronics, and laser devices. With the increase in these uses, the amount of Li in the biosphere is also increasing (Kashin, 2019). Li has no known biological usage and does not appear to be a crucial element for life. The Australian Inventory of Chemical Substances has categorized metallic lithium as a health, ecotoxicological, and/or physiochemical hazard according to the National Occupational Health and Safety Commission (NOHSC) approved criteria for categorizing hazardous substances. Li, lithium aluminum hydride, and lithium methanolate are dangerous substances on the Danish list (Aral & Vecchio-Sadus, 2008).

Therefore, monitoring the difference of Li concentration in the airborne is crucial. Tree annual rings are the most frequently used biomonitors for observing the variations in heavy metal concentrations in the air. This study aimed to determine the variation in Li concentration over time by analyzing the annual tree rings of a 180 years old Turkish hazelnut (*Corylus colurna* L.) tree.

2. MATERIALS AND METHODS

The present research was conducted on the specimens obtained from the stem of Turkish hazelnut (*Corylus colurna* L) grown in a site (41°38ˈ14″N-33°29ˈ58″E) near Ağlı region (Müsellimler Village) of Kastamonu city. The stem was taken after the growing period at the end of 2020. The direction of the stem was marked before cutting. The tree is surrounded by pasture, agriculture, and a forest stand. Except for small-abandoned settlements, no industrial plants and heavy metal contamination sources exist at 5 km of air space.

Ten cm thick wood sample cut roughly 50cm above the soil level. It was taken to the laboratory, and it was polished by a planner to see tree rings nicely. The plant was found to be 180 years old by calculating the annual tree rings. Considering the annual ring widths, they were grouped into 10-year age clusters. It was documented which stage occurs in which years. Then, samples were taken from each age group's wood, inner bark, and outer bark using a steel drill. These specimens were placed into the petri dishes, and metal instruments were not used during the analysis.

All these procedures were described as follows (Koç, 2021a; Key & Kulac, 2022; Yayla et al., 2022; Kuzmina et al., 2023). Wood samples were crushed into chips, and after marking, they were moved into glass petri dishes. In order to get air-dried specimens, they were held in petri dishes with open lids for 14 days. Then, the specimens were dried (45 °C) in an oven for a week. After that, 0.5g dried samples were taken; they were added with 2 ml 30% H_2O_2 and 6 ml 65% HNO_3 and moved into a microwave developed for this element analyses. The microwave program was set to rise to 200 °C for 15 minutes and then remain at this temperature for 15 minutes. After burning the samples, the solution specimens were placed to flasks and filled to 50 mL using ultrapure water. The ICP-OES device was used for this heavy metal analysis. The analyses were triplicated.

Analysis of Variance (ANOVA) and Duncan tests were used to evaluate the data using SPSS 21.0 software. Homogeneous groups are presented in the tables by applying Duncan tests for the factors with significant differences ($p<0.05$) in the ANOVA test.

3. RESULTS AND DISCUSSION

3.1. Results

The mean values, Duncan test results and P-values obtained from the ANOVA regarding Li concentration difference in terms of direction and organ are given in Table 1. As a result of the ANOVA, Li concentrations differed based on organs in all directions except north, and in all organs based on directions, statistically significant at least at 95% confidence level. When the values are evaluated, the highest value was obtained in the wood in the west direction with 2079.9 ppb. The lowest value was obtained in the outer bark in the south with 519.8 ppb.

Table 1. Variation in Li (ppb) concentration levels by direction and organ.

Organ	East	West	South	North	P - value
Outer Bark	570.2^{Aa}	1700.1^{Bb}	519.8^{Aa}	1667.0^{B}	***
Inner Bark	640.5^{Aa}	1306.0^{Ba}	880.4^{Aa}	1646.0^{B}	**
Wood	1422.7^{Ab}	2079.9^{Cc}	1769.5^{Bb}	1467.3^{A}	***
P – value	*	***	***	ns	

Note: Lower-case letter indicates to the vertical way within each row, whereas upper-case letter suggests to the horizontal way within each column. ns: not significant. * = P≤0.05; ** = P≤0.01; *** = P≤0.001. This explanation is also valid for Table 2.

The Li concentration variations in wood by periods and directions is given in Table 2. As a result of the ANOVA, it was determined that Li concentrations differed statistically at a 99.9% confidence level in all periods in all directions except the west. When the change of the values on a period basis is analyzed, it is seen that the values obtained in the western direction are generally higher than the other directions. In contrast, the values obtained in the eastern direction are quite variable.

Table 2. Variations in Li (ppb) concentration level in *Corylus colurna* wood by period and direction.

Periods	East	West	South	North	P- value
1841-1850	1100.2^{Bcd}	1993.7^{C}	1786.6^{Ccde}	520.4^{Aa}	***
1851-1860	989.9^{Aabc}	2142.0^{C}	1831.0^{Cdef}	1337.4^{Bdef}	***
1861-1870	2093.2^{Be}	2124.9^{B}	1483.0^{Aabc}	1273.1^{Acdef}	**
1871-1880	2284.0^{Bef}	2049.0^{B}	1563.2^{Aabcd}	1319.2^{Adef}	***
1881-1890	2236.1^{Cef}	1911.9^{B}	1565.6^{Aabcd}	1362.2^{Aef}	***
1891-1900	2390.4^{Cfg}	1870.0^{B}	1611.2^{Aabcde}	1444.2^{Af}	***
1901-1910	2546.8^{Cgh}	1932.0^{B}	$1607.4^{ABabcde}$	1343.9^{Adef}	***
1911-1920	2634.2^{Ch}	2121.3^{B}	1915.6^{Befg}	1155.6^{Abcde}	***
1921-1930	935.0^{Aabc}	2127.0^{C}	1750.1^{Bbcde}	1072.5^{Abc}	***
1931-1940	904.3^{Aabc}	2181.1^{D}	1850.0^{Cdef}	1131.5^{Bbcd}	***
1941-1950	1043.3^{Abcd}	2083.3^{B}	1850.0^{Bdef}	1063.0^{Abc}	***
1951-1960	862.2^{Aabc}	2142.7^{B}	2162.0^{Bfgh}	1066.7^{Abc}	***
1961-1970	745.1^{Aa}	2213.4^{B}	2190.7^{Bgh}	987.5^{Ab}	***
1971-1980	1255.5^{Ad}	2149.7^{B}	2376.5^{Bh}	2129.4^{Bgh}	***
1981-1990	933.1^{Aabc}	2196.3^{BC}	1943.0^{Befg}	2325.7^{Chi}	***
1991-2000	957.4^{Aabc}	2049.8^{C}	1556.7^{Babcd}	2002.9^{Cg}	***
2001-2010	910.5^{Aabc}	2160.6^{C}	1387.0^{Ba}	2359.8^{Ci}	***
2011-2020	787.8^{Aab}	1989.8^{C}	1421.0^{Bab}	2517.2^{Di}	***
P - value	***	ns	***	***	

3.2. Discussion

In this study, the directional variation of the concentration of Li in the outer bark, inner bark, and 180-year-old annual rings in *Corylus colurna* was evaluated. As a result, Li accumulated in all directions of all organs within determinable limits. This result indicates that the species subject to the study has a high Li accumulation potential. The most critical feature sought in species that can be used in determining heavy metal contamination is the ability of the species to accumulate the elements subject to the study. In many studies, it has been determined that some species have different levels of potential to absorb some elements (Karacocuk et al., 2022; Guney et al., 2023).

Another feature that determines the usability of annual rings as biomonitors is the limited movement of the element in the wood. According to the results, the transfer of Li in the wood is restricted. Indeed, when the values are evaluated, for example, Li concentration in the north direction was 987.5 ppb in 1961-1970. However, in the same direction, the Li concentration was 2129.4 ppb in the next period. Similarly, the Li concentration in the neighboring west direction was 2213.4 ppb in the same period. These results show that the transfer of Li in wood is limited. In studies conducted on this topic, it has been determined that the transfer of elements in wood differs according to the species. For instance, Pb and Zn element concentrations changed slightly, while the Cu element concentration did not alter in the annual tree rings of *Cedrus deodara* (Zhang, 2019). It was reported that Co, Mn, and Ni transfer in *Corylus colurna* woods is quite restricted (Key et al., 2022). It was also pointed out that Ni, Cd, and Fe transfer was restricted in *Cupressus arizonica* woods, but Li, Cr, and Bi transfer was more remarkable in its wood (Cesur et al., 2021, 2022). Therefore, proper plant species should be determined individually for each heavy metal contamination determination.

In plants, the transfer of elements within the wood section is primarily related to the structure of the cell and cell wall (apoplastic pathway). In plants, the apoplast between the cell wall and the plasma membrane is an apoplastic obstacle and a flexible structure that senses and signals metal/metalloid stress. Cell wall proteins (CWPs) that are activated under numerous abiotic strains have been considerably identified and categorized among diverse types of plants (Wani et al., 2018).

Plants frequently face various stress factors throughout their life cycle. Plants' most common stresses are related to climatic parameters such as drought (Koç, 2021b; Koç & Nzokou, 2022, 2023) and frost (Sevik & Karaca, 2016). Because plant development is shaped by the interaction of genetic structure (Kurz et al., 2023; Koç et al., 2023) and environmental conditions (Tandoğan et al., 2023; Sulhan et al., 2023; Yigit et al., 2023; Zeren Cetin et al., 2023). Therefore, changes in genetic structure and environmental conditions affect the heavy metal uptake of plants. For example, Lorenc-Plucińska et al. (2013) determined that Pb concentration in *Alnus incana* leaves of different origins grown in the same environment varied between 279-430 ppb and Zn concentration between 21000-30000 ppb, while Pb concentration in *Alnus glutinosa* leaves varied between 630-920 ppb and Zn concentration between 19200-27000. This outcome shows that heavy metal accumulation potential varies significantly depending on the origin, even in the same environment and in plants belonging to the same species.

The potential of plants to accumulate heavy metals also varies depending on environmental conditions. Therefore, factors that cause significant and permanent changes in climatic parameters, such as global climate change, trigger the stress mechanisms of plants (Koç, 2021c, 2022; Varol et al., 2021; Tekin et al., 2022; Dogan et al., 2023). In addition to these, stress factors such as UV-B stress (Ozel et al., 2021a; Çobanoğlu et al., 2023), anthropogenic radiation (Ozel et al., 2021b; Cobanoglu et al., 2023b), and heavy metal pollution (Cesur et al., 2022; Isinkaralar et al., 2022; Key et al., 2023; Erdem et al., 2023; Ghoma et al., 2023), which increase due to climate change, also affect plant metabolism and thus the potential of plants to accumulate heavy metals.

4. CONCLUSION AND RECOMMENDATIONS

One of today's most critical global problems is air pollution. Heavy metals are among the most studied subjects among the components of air pollution due to their potential hazards. The significance of heavy metals for people’s health is known, and numerous studies have been conducted on this topic. However, the studies primarily focus on Co, Pb, Cd, Ni, and Cr. Still, it is essential to increase studies on elements such as Li, B, Tl, Ag, Sr, Sr, Ga, and As, which can be tremendously detrimental to environmental and human health but have not been given much prominence and have not been studied much until today, and to determine the risky areas.

In conclusion, in the current study, there was a significant difference between wood and bark in terms of Li concentration except for the north direction, and the concentrations obtained in the woods were much higher than those in the bark. In the annual rings, the variation of the Li concentration in all directions, except for the west direction, is noteworthy. However, Li concentration commonly varies in a limited range, and this can be interpreted as the Li element being transferred between woods in *Corylus colurna*.

Although many tree species have been the topic of studies to date, there needs to be more information about the accumulation potential of heavy metals in many tree species. However, as in the current study, it has been concluded that there are significant alterations between tree species' heavy metal accumulation potentials in various studies. Therefore, research on the topic should be expanded and continued.

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