World Journal of Advanced Research and Reviews
eISSN: 2581-9615 CODEN (USA): WJARAI
Cross Ref DOI: 10.30574/wjarr
Journal homepage: https://wjarr.com/

(Research Article)

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Change of Lithium concentration in *Cedrus atlantica* and *Pseudotsuga menziesii* tissues in the higher air-polluted areas

Halil Baris OZEL [1], Hakan SEVIK [2,*] and Vedat KARACAN [3]

[1] *Department of Forest Engineering, Faculty of Forestry, Bartin University, Turkey.*
[2] *Department of Environmental Engineering, Faculty of Engineering and Architecture, Kastamonu University, Turkey.*
[3] *Department of Forest Engineering, Graduate School, Bartin University, Turkey.*

World Journal of Advanced Research and Reviews, 2023, 20(03), 028–036

Publication history: Received on 18 October 2023; revised on 27 November 2023; accepted on 30 November 2023

Article DOI: https://doi.org/10.30574/wjarr.2023.20.3.2436

Abstract

Heavy metal pollution is today's most critical pollution element, threatening the atmosphere and health. Lithium (Li), a heavy metal, has recently been extensively used in various industrial areas and poses a risk to environmental health, including human health. It is well-known that heavy metals can be much more harmful when taken into the human tissues via inhalation. Therefore, tracking and decreasing the alteration in Li contamination in the airborne is essential. The current study aimed to define whether *Pseudotsuga menziesii* and *Cedrus atlantica* are suitable for monitoring and reducing Li pollution in the air. Within the scope of the study, variations in Li concentration depending on organ, direction, and age range in the last 40 years were evaluated in *Pseudotsuga menziesii* and *Cedrus atlantica* species growing in Düzce, Türkiye, which is amongst the 5 most contaminated provinces in Europe. As a result, it was determined that Li pollution in the region was of anthropogenic origin and that both species were suitable for monitoring Li pollution but were not suitable for use in reducing it.

Keywords: Biomonitoring; contamination; Düzce; Heavy metal; Toxicity

1. Introduction

Environmental contamination has rapidly expanded in the last century due to the influence of anthropogenic reasons, especially industrial actions, and evolved into one of the most crucial glitches worldwide [1,2]. In particular, air pollution is one of the most critical sources of respiratory disorders and one of the most severe threats to human health [3,4]. This problem has reached such serious levels that it is stated that 90 % of the population worldwide nowadays inhales contaminated air [5]. It is underlined that air contamination causes roughly 4 million premature births and the death of about 7 million people around the world each year [6]. Air contamination is shown to be one of the most serious universal glitches related to global climate change and urbanization, which are considered irreversible problems worldwide [7-10].

Heavy metals, one of the most dangerous components of air smog, are particularly vital for environmental and human health. Heavy metals do not break down easily in the environment [11, 12]. Many are noxious and fatal to living things, even at low amounts [13]. Even those that are essential as nutrients for living beings are toxic in high amounts, and their breath into the living tissue is a noteworthy hazard to the health of living beings [14]. Therefore, it is critical to track the changes in heavy metal concentrations in the air.

Many studies have been conducted to monitor and reduce the alteration in heavy metal pollution in the airborne [15]. However, these studies mainly focus on heavy metals such as Pb, Cr, Co, Ni, Mn, and Cu, and various other elements are

* Corresponding author: Hakan SEVIK

ignored. One of the elements ignored in studies on this subject is Lithium (Li). Li has been commonly selected in the modern industry of the latest eras. Organic synthesis is used in producing plastic, glass, and aluminum, cameras, computers, radio engineering, phone batteries, laser devices, and electronics. With these usages, the concentrations of Li in the biosphere also increase [16].

Lithium has no recognized biological use and does not seem to be a fundamental element for existence. The Australian Inventory of Chemical Substances has sorted metallic lithium as a health, ecotoxicological and/or physiochemical threat according to the National Occupational Health and Safety Commission (NOHSC) permitted standards for classifying perilous materials. Lithium, lithium methanolate, and lithium aluminum hydride are found on the Danish list of hazardous substances [17]. Therefore, it is crucial to observe the variation in Li concentration in the air. In this study, we tried to define the usability of *Pseudotsuga menziesii* and *Cedrus atlantica* species in determining the change of Li amount in the airborne from past to present-day in Düzce, Türkiye, one of the provinces with the uppermost air contamination in Europe.

2. Material and methods

The current study was conducted in Düzce region, located in the Western Black Sea territory of Türkiye. Based on the 2021 World Air Pollution Report, Düzce is among the 5 most contaminated towns in Europe [18]. Within the scope of the research, the main stems of *Cedrus atlantica* and *Pseudotsuga menziesii* trees were cut down by marking the northern directions at the end of the 2022 growing period, and ten cm thick log samples were obtained from a height of roughly 50 cm from the soil level. In the log samples, the annual tree rings were made visible, and the annual ring widths were clustered into five-year groups. Then, samples were taken from the inner bark, outer bark, and wood of all ages with the assistance of a steel drill. Samples taken as sawdust were positioned in glass petri dishes and left to air dry for 15 days, then dried at 45 °C for a week. 0.5 g of 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 designed for the element analysis. The samples that became solution were taken into volumetric flasks and filled to 50 ml with ultrapure water. The prepared samples were analyzed with the ICP-OES gadget, and the Li concentrations were calculated by multiplying the obtained values by the dilution factor. The method used in the study is a method frequently used in studies conducted on this subject in recent years [19-21]. The obtained data were evaluated with the help of the SPSS package program.

3. Results

The change of Li concentration in *Cedrus atlantica* based on direction and organ is presented in Table 1.

Table 1 Alteration of Li concentration based on direction and organ in *Cedrus atlantica*

ORGAN	North	East	South	West	F value	Average
Outer bark	1038.2^{a}	1319.9	UDL	UDL	1.4^{ns}	1179.1
Inner bark	4455.4^{Cb}	1050.1^{A}	1181.0^{A}	2202.0^{Ba}	506.4^{***}	2222.1
Wood	4140.5^{Bb}	2352.4^{A}	1314.0^{A}	5581.2^{Bb}	15.1^{***}	2913.4
F value	5.7^{**}	1.3^{ns}	0.0^{ns}	600.1^{***}		2.9^{ns}
Average	3861.8^{B}	2118.9^{A}	1291.8^{A}	3891.6B	13.1^{***}	

Different letters following each other represent the statistical difference at $p \leq 0.05$. Lowercase letters represent from top to bottom while uppercase letters left to right direction. UDL= Under Detection Limit. ***≤0.001. **≤0.01. *≤0.05. ns=not significant.

As a result of the variance analysis, the highest Li amounts in *Cedrus atlantica* were obtained in the inner bark and wood. In contrast, the values found in the outer bark in the south and west directions remained below the detectable limits. Directionally, the minimum concentrations were obtained in the east and south and the uppermost in the north and west. However, when Table 2 was examined, it was determined that the Li concentration in wood remained largely below detectable limits in the western direction. Therefore, the maximum amounts were obtained in the northern direction. The change of Li concentration in *Cedrus atlantica* based on period and direction is presented in Table 2.

Table 2 Alteration of Li concentration in *Cedrus atlantica* wood based on period and direction

Age category	North	East	South	West	F value	Average
2018-2022	1826.8^{Ca}	1586.8^{Bb}	920.1^{Ab}	UDL	76.5***	1444.6^{a}
2013-2017	1949.4^{a}	1418.1^{ab}	UDL	UDL	14.5*	1683.7^{a}
2008-2012	5191.9^{Bcd}	1369.0^{Aa}	UDL	UDL	384.3***	3280.4^{abc}
2003-2007	5996.8^{Ce}	1431.7^{Bab}	832.8^{Aa}	UDL	3169.1***	2753.7^{abc}
1998-2002	5083.7^{Bc}	5162.2^{Bc}	925.8^{Ab}	UDL	345.7***	3723.9^{bc}
1993-1997	2608.0^{b}	1307.5^{a}	UDL	UDL	105.0**	1957.8^{ab}
1988-1992	5526.0^{Cd}	1260.1^{Ba}	765.3^{Aa}	5581.2^{C}	787.9***	3283.1^{abc}
1983-1987	4941.9^{Bc}	5284.0^{Cc}	3126.2^{Ac}	UDL	219.6***	4450.7^{c}
F value	159.9***	803.8***	1438.9***	-		2.9*
Average	4140.5^{B}	2352.4^{A}	1314.0^{A}	5581.2^{B}	15.1***	

Different letters following each other represent the statistical difference at p≤0.05. Lowercase letters represent from top to bottom while uppercase letters left to right direction. UDL= Under Detection Limit. ***≤0.001. **≤0.01. *≤0.05.

As a result of the variance analysis, the alteration in Li concentration in *Cedrus atlantica* wood remained below detectable limits in the western direction. Apart from this, it was determined that there was a statistically significant change in all directions on a period-by-period basis. The uppermost value in the north was seen in the 2003-2007 period, and the maximum value in the east was seen in the 1983-1987 and 1998-2002 periods. While the minimum value in the south direction was obtained in the 1988-1992 and 2003-2007 periods when looking at the average values, the highest value was generally seen in 1983-1987. The Li concentration change remained below detectable limits in all periods except the 2008-2012 and 2013-2017 periods in the south direction and the 1988-1992 period in the west. According to the average values, the minimum value was observed in the east and south directions, while the uppermost value was obtained in the north direction. The variation of Li concentration in *Pseudotsuga menziesii* based on direction and organ is presented in Table 3.

Table 3 Alteration of Li concentration based on direction and organ in *Pseudotsuga menziesii*

ORGAN	North	East	South	West	F value	Average
Outer bark	5904.6^{Bb}	UDL	2942.0^{Ab}	UDL	1296.0***	3387.7^{b}
Inner bark	1130.1^{Ba}	UDL	960.7^{Aa}	UDL	27.4**	1465.3^{a}
Wood	1810.4^{Aba}	2815.7^{C}	1356.4^{Aa}	2439.7^{BC}	5.8**	2036.4^{a}
F value	44.0***	-	22.2***	-		5.8**
Average	2189.7^{B}	2815.9^{D}	1488.6^{A}	2439.7^{C}	1298.7***	

Different letters following each other represent the statistical difference at p≤0.05. Lowercase letters represent from top to bottom while uppercase letters left to right direction. UDL= Under Detection Limit. **≤0.01. *≤0.05.

According to the results of variance analysis, Li concentration in *Pseudotsuga menziesii* is below the detectable limits in the eastern and western barks. It is statistically significant in the north and west directions. While the maximum values in the north and south directions were obtained from the outer bark, the values achieved from the wood and inner bark were in the same groups because of the Duncan test. The alteration of Li concentration in the wood of *Pseudotsuga menziesii* based on period and direction is presented in Table 4.

When the values in the table are examined, it is seen that the Li concentration change is statistically significant on a direction basis in all periods and on a period basis in all routes. The peak value in the north direction was obtained in the 1983-1987 period, the uppermost concentration in the east direction was obtained in the 1998-2002 period, the maximum value in the south direction was found in the 1988-1992 period, and the highest value in the west direction was obtained after 2018. It is quite remarkable that the highest value compared to average values was seen after 2018. In addition, the Li concentration change remained beneath the detectable limits in the north direction in the 2018-2022 period, in the east direction in the 1983-1987, 1993-1997, 2013-2017, 2018-2022 periods, and the south direction in the 2018-2022 period.

Table 4 Change of Li concentration in *Pseudotsuga menziesii* woods based on period and direction

Age category	North	East	South	West	F value	Average
2018-2022	UDL	UDL	UDL	5312.3^{e}		5312.3^{b}
2013-2017	2726.9^{Bc}	UDL	1281.2^{Aa}	1352.6^{Ab}	114.1***	1786.9^{a}
2008-2012	1267.3^{Ba}	4463.7^{Cb}	1079.7^{Aba}	846.6^{Aa}	323.2***	1914.3^{a}
2003-2007	1288.5^{Aa}	1055.1^{Aa}	1095.8^{Aa}	2493.8^{Bd}	90.8***	1483.3^{a}
1998-2002	1089.3^{Aa}	4692.3^{Db}	1298.5^{Ba}	2677.2^{Cd}	836.6***	2439.3^{a}
1993-1997	1244.3^{Aa}	UDL	1215.3^{Aa}	2341.8^{Bd}	57.0***	1600.5^{a}
1988-1992	1832.1^{Bb}	1052.0^{Aa}	2378.7^{Cb}	2615.3^{Cd}	57.8***	1969.5^{a}
1983-1987	3224.1^{Cd}	UDL	1145.5^{Aa}	1877.7^{Bc}	72.6***	2082.4^{a}
F value	130.3***	660.0***	35.5***	105.6***		5.4***
Average	1810.4^{Aba}	2815.7^{C}	1356.4^{Aa}	2439.7^{BC}	5.8**	

Different letters following each other represent the statistical difference at p≤0.05. Lowercase letters represent from top to bottom while uppercase letters left to right direction. UDL= Under Detection Limit. ***≤0.001. **≤0.01.

4. Discussion

In the study, the seasonal alterations in Li concentration in organs, directions, and wood in *Pseudotsuga menziesii* and *Cedrus atlantica* trees growing in Düzce's city center were evaluated. Li has been widely selected in the modern industry of the latest times. Organic synthesis is used in producing plastic, glass, and aluminum, computers, radio engineering, cameras, phone batteries, laser devices, and electronics. With these usages, the quantity of Li in the airborne also increases [16].

As a result, the Li concentration in the outer barks in the west and south routes of *Cedrus atlantica* and in the east and west directions of *Pseudotsuga menziesii* remained below the detectable limits. The uppermost Li amount in the outer barks was generally obtained in the northern direction. There are residential areas and areas with heavy traffic in the north of the area where the samples were taken. Therefore, Li concentration is of anthropogenic origin. Studies have determined that heavy metal concentrations are high in many species, especially in the outer barks [24]. This is due to the structure of the outer bark and its interaction with heavy metals and contaminated particles. First, particulate matter in the airborne is polluted with heavy metals, and since the outer bark surface is rough and cracked, these particles can stick to the bark surface [25]. Thus, in areas where heavy metal contamination in the air is elevated, heavy metal amounts in the outer barks are at high levels [26].

As an outcome of the analysis, Li concentration accumulated within determinable limits in the inner bark and wood in all routes in *Cedrus atlantica* and the wood in all directions in *Pseudotsuga menziesii*. In *Pseudotsuga menziesii*, the Li concentration in the inner barks, as well as in the outer barks in the east and west routes, remained below detectable limits. Studies have revealed that heavy metal amounts in diverse tissues of the same trees can differ significantly [27, 28]. Heavy metal concentrations in diverse tissues of trees grown in a similar environment differ depending on features such as the morphology, structure, surface texture, surface area, and mass of the tree organ [29]. Heavy metal concentrations, especially in the inner barks, are primarily related to entering heavy metals into the tree tissue. Heavy metals enter the tree tissue mainly through stem parts, leaves, and roots [30].

As an outcome of the analysis, it was found that the Li amount in the wood of both species was highly variable, and the concentrations obtained in neighboring wood samples differed significantly. For example, while the Li concentration in *Cedrus atlantica* in the western direction remained below the detectable limits in all periods, one of the highest values obtained in the study was obtained in the period 1988-1992. Similar results were obtained in *Pseudotsuga menziesii*. This result shows that the allocation of Li into the wood is constrained in both species. It is stated that a need for more information in studies on monitoring the alteration in heavy metal contamination in the airborne is the transfer of heavy metals entering the wood between organs [31,32]. Some studies on this subject reveal that the movement of elements within wood may vary depending on the plant species. For example [33], found that the allocation of Ni, Cd, and Zn elements within the wood of cedar trees was limited, [34] stated that the allocation of Mn, Ni, and Co concentrations in *Corylus colurna* wood was quite restricted, [35-36] stated that the transfer of Ni, Fe and Cd concentrations in *Cupressus arizonica* wood was limited, but the transfer of Cr, Li, and Bi concentration was higher in wood. Thus, the plant species appropriate for defining each heavy metal contamination must be determined individually.

As an outcome of the study, the uppermost values were generally found in the north direction. The north of the study area is a region where residential areas are located, and the influence of urban and traffic is high. Studies display that the most important sources of heavy metals are anthropogenic factors, especially traffic and urban areas [37-39].

As a result of the study, it was decided that the Li concentration in the species subject to study varied significantly both on a species and organ basis. Similar results have been expressed in many studies on heavy metals, and heavy metal accumulation is important both based on species [40] and organs of the same species [41]. It has been emphasized that it has changed considerably. This change is because many factors are effective in the entry and accumulation of heavy metals into the tree tissue. Namely, the entry of heavy metals into the tree is shaped by many factors, such as tree species, tissue structure, surface area, heavy metal and plant interaction, and weather conditions [42].

In addition, plant habitus and development also affect the plant's heavy metal uptake and accumulation [43]. Therefore, all factors affecting plant habitus also affect the entry and accumulation of heavy metals into the tree, which is shaped under the mutual interaction of many factors affecting each other, such as genetic structure [44-49], edaphic [50-53], climatic factors [54-63] and environmental stress [64-66] factors. Therefore, many of these factors directly and indirectly affect the heavy metal accumulation potential of plants, and information about this complex mechanism is still limited [67,68].

5. Conclusion

Heavy metals can be tremendously hazardous and destructive to environmental and human health, and one of them, Li, is an element that has a wide range of usages and is detrimental to human and environmental health in high concentrations. Therefore, it is crucial to watch and reduce the change of Li concentration in the airborne during the process. The study results reveal that the concentration of Li in the air increases due to anthropogenic origin, and its transfer into the wood is limited in *Cedrus atlantica* and *Pseudotsuga menziesii* woods. Therefore, these two types are suitable biomonitors that can be used to track the alteration of Li concentration in air. However, in conclusion, it was found that the Li concentration in the wood of these species remained below detectable limits for many periods. This result reveals that *Cedrus atlantica* and *Pseudotsuga menziesii* cannot be used effectively to decrease Li contamination in the airborne.

Compliance with ethical standards

Acknowledgments

We thanks to Bartin University, Faculty of Forestry and Kastamonu University, Faculty of Architecture and Engineering.

Disclosure of conflict of interest

The authors declare that they no conflict of interest. The none of the authors have any competing interests in the manuscript.

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