



The potential of using *Cedrus atlantica* as a biomonitor in the concentrations of Cr and Mn

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Abstract

Air pollution is becoming increasingly dangerous which is quite a significant issue of today's world, especially air pollution from heavy metal, whose emission increases with industrial and traffic activities. This is of great importance in terms of environmental pollution and human health. Heavy metals do not deteriorate and disappear easily on earth. They are liable to bioaccumulate within cells in organisms. Most of them demonstrate harmful effects in addition as a result of advanced accumulation, and thus they emerge as toxic and carcinogenic. Therefore, it is of great importance to observe the changes in heavy metal concentrations in the air. One of the most effective techniques for monitoring the change of heavy metal concentrations in the atmosphere is the use of annual rings of trees as biomonitors. In this study, in the annual rings of the *Cedrus atlantica* Manetti tree cut at the Kastamonu province at the end of 2019, the variation of the concentrations of some of the heavy metals most associated with traffic density was tried to be determined. Within the scope of the study, Cr and Mn concentration in the outer bark and the inner bark was compared with the direction and wood for the variation of heavy metal concentrations. Also, variance analysis and Duncan test were applied and evaluated. As a result of the study, while the highest values in many heavy metals are generally obtained in the outer bark, the transfer of metals in the wood is limited, and some heavy metal concentrations change significantly depending on the direction, especially in the wood. This change is related to the traffic density, so *Cedrus atlantica* Manetti annual rings are very suitable as biomonitors for air pollution control.

Keywords Air pollution control · Annual ring · Biomonitor · *Cedrus atlantica* · Cr · Mn · Traffic density

Introduction

Heavy metals (HMs) are of particular significance among air pollution components. Notwithstanding HMs are found naturally on earth, increased levels of production that started with the industrial revolution resulted in the extraction of underground mineral resources and their use as a raw material in the industry; thus, the concentration of HMs in air, water, and soil is constantly increasing (Kumar and Khan 2021). This

increase poses a great danger to all living things, especially on human and ecosystem (Brázová et al. 2021). Because HMs do not decompose and disappear easily in nature (Farzin et al. 2017), they are prone to accumulate in organisms' cell, and some of them have carcinogenic or toxic effects, even if they exist at low concentrations (Isinkaralar et al. 2017; Sevik et al. 2018; Turkyilmaz et al. 2020; Dołęgowska et al. 2021; Kumar and Dwivedi 2021). HMs such as As, Ni, Zn, Cr, Mn, Pb, and Cd are mostly industrial based and carcinogenic although these wants and requests resulted in mining as well as underground mineral resources feed stock in manufacture and industry (Sultana et al. 2017; Bayraktar 2021). As some HMs are carcinogenic and toxic, they are elements that pose a great threat to living organisms (Sert et al. 2019; Sevik et al. 2019). Also, some of them (Ag, Al, As, Ba, Be, Cd, Co, Cr, Cu, Pb, Mn, Hg, Ni, Pd, Pu, Sb, Se, Sr, Tl, Th, U, V, and Zn) are included in the precursor pollutant list by the Agency for Toxic Substances and Disease Registry (ATSDR) due to their toxicity for human at high concentrations (Badea et al. 2018). In fact, HMs that are micronutrients for living beings can have

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toxicological effects for humans at high concentrations. Therefore, monitoring the heavy metal concentrations (HMC) in the air is of great importance (Turkyilmaz et al. 2018b; Alaqouri et al. 2020). Monitoring heavy metal pollution in the atmosphere can be carried out directly or indirectly. However, detecting the level of pollution directly is not preferred much due to its cost and the inability to identify the straight effect of the atmospheric pollution in terms of ecosystem (Al-Thani et al. 2018; Turkyilmaz et al. 2018c). Therefore, biomonitors are the most effective method used in monitoring heavy metal pollution (Kularatne and De Freitas 2013). Living things used as biomonitors can accumulate HMs in their several organs (Shahid et al. 2017). Also, measuring the heavy metal concentration in these organs provides important information about the concentration of HMs in the air (Demir and Yavuz 2020).

Biomonitoring can be defined as the most sensitive and accurate organisms that accumulate metals or pollutants in their bodies (Baroudi et al. 2020). The species to be used as a biomonitor should have the ability to accumulate HMs in their bodies but should not die due to the effect of the HMs. They should permanently live in the area where they will be sampled. They are abundant in the study area so, when desired, can be easily obtained. They have enough organs or tissues for metal analysis, and there should be a correlation between the heavy metal concentration in the organisms and the heavy metal concentration in the surrounding area (Çobanoğlu 2019; Ateya 2020). The plants have been used as biomonitors in many studies about HMC in the atmosphere to about (Turkyilmaz et al. 2018a; Aricak et al. 2020; Eid et al. 2020; Kumar et al. 2020).

However, there are various difficulties and uncertainties regarding the use of plants as biomonitors for monitoring HMs. First of all, it is not known how long algae and lichens, which have been used as biomonitors for many years, are liable to HM pollution in the air. The use of annual plant leaves that are not evergreen solves this trouble because these leaves can provide important information about HM pollution during the vegetation season (Ghosh et al. 2020; Soba et al. 2021). The problem in using these plants is that it is not known what this accumulation in the leaves means because they cannot supply information about the change in the amount of HMs accumulated in the organs of the plants from the past to the present (Turkyilmaz et al. 2018c; Cetin et al. 2020).

In light of these problems, it is stated that with the use of biomonitors, the most accurate information is obtained by using the needles of species such as fir, spruce, pine, and needles. They remain on the tree for many years which can be determined with certainty (Ateya 2020). However, with this method, information on the past 8–10 years can be obtained at most (Cetin et al. 2020). In order to overcome this problem, annual rings (ARs) of trees have been used in places with seasons like in our country, where there is a winter season during the year; the development of trees according to the

season is at different levels, and thus, ARs are formed in the trunk of trees. The HMs accumulated in the ARs of trees over a long period of time can give us important information about the history of air pollution (Khamesi et al. 2020; Cordova 2021). The ARs of the trees increase with the age of the tree due to they can live for so many years. The ARs of trees can be used as an indicator of air pollution besides these can provide important information on the distribution of air pollutants. Also, they can tell chronology of the elements that cause pollution where the tree grows (Yigit et al. 2019; Cesur 2019; Paluch 2021).

Studies on the utility of ARs of trees as biomonitors have been carried out for some time. However, information on the speciation of HMs in the plant and their passing between organs is still restricted (Cindoruk et al. 2020; Świsłowski et al. 2020; Uka et al. 2021).

In this study, the studies on the use of plants as biomonitors and the changes in the information obtained in light of these studies are evaluated, and the deficiencies in the literature are determined. Within the scope of the study, these HMC in the ARs of a *Cedrus atlantica* tree in Kastamonu were determined on the basis of organ, year, and direction. By interpreting the data obtained, how the accumulation of HMC in the air differs in the outer bark (OB), inner bark (IB), and wood of the tree, how this difference changes in different directions, how HMC in ARs of the tree change on a yearly basis (it is aimed to determine whether this change can be used effectively to monitor the change of HMC), and whether the change of different HMs is in parallel on a yearly basis have been tried to be determined.

Materials and methods

This study was carried out on samples of *Cedrus atlantica* Manetti specimens taken from the Kastamonu city center. Within the scope of the study, samples were taken from the log at the end of 2019. The place where the cedar tree of the samples grows is located next to the busiest street, which provides access to the city center, so there is a dense traffic around the location. To the east of the park is the main street with a high traffic density, and there is a main road with lower traffic density towards the north. The disc sample was taken from the cedar tree of 10 cm thickness and a height of 50 cm from the ground, also marking the north direction on the log. The top surface of the log was sanded and dulcified in the laboratory so that the ARs could be seen more clearly. The ARs of the cedar tree, which was determined to be 33 years old, are grouped range from 1 to 11 being 3 years old inside out, considering their width. At the end of the grouping, age ranges and the years in which wood was formed, corresponding to these intervals, are given in Table 1.

Later, the wood surface was apportioned groups, and the age ranges were determined; samples were taken from the OB,

Table 1 Range of age and years of ARs

Range of age	Years of ARs
1	1987–1989
2	1990–1992
3	1993–1995
4	1996–1998
5	1999–2001
6	2002–2004
7	2005–2007
8	2008–2010
9	2011–2013
10	2014–2016
11	2017–2019

IB, and wood of all age ranges with a steel-tipped drill and placed in glass petri dishes. The wood samples taken were cut and turned into sawdust. Meanwhile, care was taken not to use tools made of metals that were the subject of the study. The samples taken into glass containers were kept in the laboratory with their lids open for 15 days until they became room dry. A total of 15 days, the samples became room dry and dried at 45 °C for a week; 0.5 g of the dried samples was taken and added 6 ml of 65% HNO₃, and then 2 ml of 30% H₂O₂ was added. After this, the mixture was placed in a microwave oven. It was set to reach 200 °C in 15 min and remain at 200 °C for 15 min. After the samples were burned in the microwave oven, the samples that turned into solution were taken into a flask and filled to 50 ml with ultrapure water, and heavy metal analysis was performed with the ICP-OES (SPECTRO brand Spectroblue model) device. The results of the analysis were multiplied by 100 since the samples were taken 0.5 g specimen and completed to 50 g with water. Different calibration diagrams were prepared with parts per million (ppm) or parts per billion (ppb) levels according to the results out of the calibration diagram's range for Cr and Mn, respectively. Then, the reading was repeated using these diagrams, and all measurements in the study were carried out three times. The obtained was analyzed with variance analysis data with the SPSS 21.0 package program. As a result of the variance analysis, the Duncan test was performed for the determinant that was found to be statistically significant at a confidence level of at least 95% ($p < 0.05$).

Results

Changing concentration of the Cr element

The change in the concentration of the element Cr, which is one of the most harmful elements for human and

environmental health among the elements evaluated in the study, is given in Table 2 depending on the organ and the direction.

According to analysis of variance (ANOVA) results, it was understood that the change in the concentration of Cr is on the basis of direction. It is statistically significant at 99.9% in the OB and IB parts, and the change in the wood part is significant at the 99% confidence level. Considering the Duncan test results, it is seen that the OB and IB parts form four different homogeneous groups, and the wood part forms three different homogeneous groups. According to the values in the table, the lowest value in the OB is in the west direction (923.3 ppb), the highest value in the south direction (1588.4 ppb), the highest value in the IB part in the south direction (1158.5 ppb), the lowest value is in the west direction (673.4 ppb). In the wood part, the lowest value was obtained in the west direction (445.1 ppb), and the highest value was obtained in the south direction (765.8 ppb). The change in the Cr concentration in woods depending on the age range and direction is given in Table 3.

When the values showing the variation of the element Cr according to the age range were investigated, it was seen that the highest value in the south direction is in the 1st (1804.6 ppb), the lowest value is in the 5th (307.6 ppb) age range, the lowest value in the west direction is in the 1st (294.7 ppb), the highest value in the 11th (703.4 ppb), the highest value in the north direction in the 11th (1092.9 ppb), the lowest value in the 2nd (313.9 ppb), and the lowest value in the east direction in the 5th (439.4 ppb), and the highest value was obtained in the 11th (1711.4 ppb) age range. According to the variance analysis results, the directional variation of Cr concentration is not statistically significant in the 5th age range at the 95% confidence level, while it is statistically significant at the 99.9% confidence level in all other age ranges. According to Duncan test results, the 4th and 5th age ranges are gathered in two different homogeneous groups, the 6th, 9th, and 10th age ranges in three different homogeneous groups, and the other

Table 2 Change of Cr concentrations based on organ and direction

Organ	Location				F value
	South	West	North	East	
OB	1588.4 Ab	923.3 Dc	1187.2 c	1470.3 Bb	1378.7***
IB	1158.5 Bab	673.4 Ab	865.9 b	1072.3 Dab	2064.0***
Wood	765.8 Ca	445.1 Aa	572.4 ABa	708.9 BCa	5.8**
F value	4.271*	23.685***	13.693***	8.664**	

Uppercase letters show horizontal direction; however, lowercase letters indicate vertical directions

*Significant at 0.05 level; **significant at 0.01 level; ***significant at 0.001 level

ns not significant

Table 3 Age interval and directional change of Cr element in wood

Range of age	Location				F value
	South	West	North	East	
1	1804.6 Di	294.7 Aa	563.1 Bc	752.6 Cde	4100.5***
2	1566.9 Dh	658.0 Bf	313.9 Aa	703.6 Cd	1658.9***
3	733.0 Df	441.2 Bd	378.3 Aab	516.8 Cab	120.7***
4	675.0 Be	367.4 Ac	328.6 Aa	628.8 Bc	22.8***
5	307.6 Aa	319.8 ABb	428.1 Bb	439.4 Ba	3.8NS
6	346.2 Ab	349.1 Ac	545.2 Cc	446.6 Ba	44.3***
7	355.1 Ab	488.3 Ce	570.0 Dc	507.4 Cab	2120.7***
8	366.2 Ab	419.0 Bd	613.8 Dc	562.1 Cbc	60.9***
9	419.0 Ac	509.9 Be	690.8 Cd	741.7 Cde	83.9***
10	476.8 Bd	346.1 Ac	772.0 Ce	787.3 Ce	692.8***
11	1374.0 Cg	703.4 Ag	1092.9 Bf	1711.4 Df	1323.0***
F value	2321.7***	276.7***	82.0***	197.3***	

Uppercase letters show horizontal direction, whereas lowercase letters indicate vertical directions

*Significant at 0.05 level; **significant at 0.01 level; ***significant at 0.001 level

ns not significant

age ranges in four different homogeneous groups. When the concentration values of the element Cr are examined, it is seen that 3 of the highest values of the 11th age range are to the south and 2 are to the north. Five of the lowest values were found to be in the south direction and 3 in the west direction. In addition, it is noteworthy that there are no highest or lowest values in the east direction.

Changing concentration of the Mn element

Another element evaluated in the study is the Mn element, and it is one of the elements that are very harmful to health. The change in the concentration of the element Mn depending on the organ and the direction is given in Table 4.

Organ-dependent changes in the concentrations of the Mn element are statistically significant at the 99.9% confidence level in all directions according to the results of variance analysis. When the Duncan test results of the concentrations were

examined, it is observed that the west, north, and east directions formed three different homogeneous groups and the south side formed two different homogeneous groups. When looking at the values in the table, in general, it is noteworthy that the lowest values are obtained in the wood part in all four directions. Another point is that the highest value (29,531.7 ppm) is about 15 times higher than the lowest value (1929.0 ppm). According to the results of variance analysis, the variation of the values of the concentrations of the Mn element in the OB, IB, and wood parts, the values are statistically significant at the 99.9% confidence level except for the wood part. Looking at the Duncan test results, it is seen that the OB and IB parts form four different homogeneous groups. While the highest values were obtained in the north direction (29,531.7 ppm and 2668.8 ppm) in the IB and wood part, the highest value in the OB part is in the west direction (21,243.8 ppm), while the lowest values are in the east direction (1929.0 ppm) in the south direction (17,573.4 ppm) in the

Table 4 Change of Mn concentrations based on organ and direction

Organ	Location				F value
	South	West	North	Doğu	
OB	18,034.4 Cb	21,243.8 Dc	9372.6 Ab	11,138.8 Bb	12,577.0***
IB	17,573.4 Ab	18,000.0 Bb	29,531.7 Dc	19,686.6 Cc	48,916.6***
Wood	2041.3 ba	2039.2 ba	2668.8 a	1929.0 a	1.9 ns
F value	607.3***	744.2***	230.9***	1618.8***	

Uppercase letters show horizontal direction, whereas lowercase letters indicate vertical directions

*Significant at 0.05 level, **significant at 0.01 level, ***significant at 0.001 level

ns not significant

IB part and in the north direction (9372.6 ppm) in the OB part. The change in the Cr concentration in woods depending on the age range and direction is given in Table 5.

When the values showing the change in concentrations of the element Mn according to the age range are examined, the highest values in the south, west, north, and east directions were found in the 1st (5195.1 ppm, 5227.6 ppm, 8519.1 ppm, and 3189.0 ppm) age range, the lowest values in the south and west directions in the 5th (1121.4 ppm and 1293.2 ppm), in the north direction in the 4th (1224.7 ppm), and in the east direction in the 7th (1086.2 ppm) age ranges. When the variance analysis results regarding the variation depending on the direction are examined, it was found that the 4th age range differed significantly at the 99% confidence level, and all other age ranges at the 99.9% confidence level. According to Duncan test results, it is seen that 5th, 8th, and 11th age ranges form four different homogeneous groups, and all other age ranges form three different homogeneous groups. Three of the 11 age ranges in the north and east directions are in the lowest homogeneous groups. In addition, while the highest values were obtained in 2 age ranges in the north direction, the second highest value was obtained in 3 age groups.

Discussion and conclusion

As a result of the study, it was found that the changes in the organ base of the elements are statistically significant at the 95% confidence level. While the lowest values of Cr and Mn elements are obtained in wood, it is noteworthy that the concentrations in the east and north directions where the traffic is dense are quite high. In studies on HMs, it is stated

that the concentrations differ greatly on organ basis and depending on the traffic density. Akarsu (2019) evaluated the change in the elements Al, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Ni, Pb, and Zn and reported that the lowest concentrations of almost all elements were found in the wood, and the highest concentrations were found in the OB. Sevik et al. (2020) obtained the highest concentrations of Pb, Co, and Fe in the OB and the lowest concentrations in wood. In both studies, the concentrations of the elements in the OB facing the direction where there is no traffic were not at significant levels, while the highest concentrations were obtained in the OB in the part facing the traffic. Turkyilmaz et al. (2018b, 2019) stated in two separate studies that some HMC in the OB are much higher than those in other organs. Zhang (2019) suggested that the accumulation of Pb in the crust is extremely high, which is evidence that Pb concentrations are absorbed from the atmosphere rather than from the soil. Similarly, it is stated that the Hg in tree ARs is mostly of atmospheric origin (Chellman et al. 2020). The fact that HMC such as Pb, Cd, Cr, and Ni were found at a much higher level in barks than in wood in different studies supports this thesis (Akarsu 2019; Cesur 2019; Sevik et al. 2020). As a matter of fact, it has been stated in many studies that traffic is the most important source of many HMs together with industrial facilities (Shahid et al. 2017; Turkyilmaz et al. 2020).

The reason HMC in the OB is obtained t higher levels than other organs. This situation seen much more clearly in samples taken from the direction of heavy traffic is mostly due to the rough structure of the bark and the particulate materials contaminated with HMs adhering to this structure. In the studies conducted, it was determined that HMs in the air adhere to particulate materials and infect the particulate materials with

Table 5 Age interval and directional change of Mn element in wood

Range of age	Location				F value
	South	West	North	Doğu	
1	5195.1 Bk	5227.6 Bı	8519.1 Cg	3189.0 Ak	21,340.4***
2	2085.6 Bi	2721.8 Ch	1768.1 Acd	2725.8 Cj	1091.2***
3	1698.4 Ae	1882.6 Bg	1703.8 Acd	1964.4 Cg	683.2***
4	2459.2 Cj	1875.5 Bg	1224.7 Aa	2209.3 BCi	18.6**
5	1121.4 Aa	1293.2 Ba	1944.9 Dd	1838.4 Ce	1719.8***
6	1896.4 Bg	1450.7 Ac	2595.2 Ce	1907.4 Bf	153.4***
7	1824.1 Cf	1430.1 Bc	1436.0 Bab	1086.2 Aa	1570.0***
8	1565.6 Bd	1839.7 Cf	1385.3 Aab	2019.0 Dh	2568.7***
9	1463.0 Bc	1584.4 Cd	1568.0 Cbc	1396.8 Ac	120.3***
10	1188.0 Ab	1320.5 Bb	1590.5 Cbc	1308.5 Bb	111.9***
11	1957.5 Ch	1805.5 Be	5621.0 Df	1574.2 Ad	31,662.5***
F value	43,946.8***	25,316.2***	835.6***	3910.1***	

Uppercase letters show horizontal direction, whereas lowercase letters indicate vertical directions

*Significant at 0.05 level, **significant at 0.01 level, ***significant at 0.001 level

ns not significant

HMs and that the HMC in these organs increase with the settling of these particulate materials on the plant organs (Mossi, 2018; Sevik et al. 2019). The rough surface structure of the OB facilitates the attachment of particulate matter here, and the high concentration of HMs in the barks in the direction of heavy traffic is explained by the contamination of the particulate materials in this direction with HMs caused by traffic (Akarsu 2019) because traffic is one of the most important heavy metal resources (Shahid et al. 2017; Cetin et al. 2020). The potential of plants to capture absorbed particulate matter is directly related to the physiological characteristics of the plant species as well as the structure of the heavy metal (Nagajyoti et al. 2010). Therefore, the fact that the concentrations of some elements are higher in the direction where the traffic is intense. The directional change of some elements at an insignificant level can be explained by the change in the accumulation of elements depending on many factors because there are many factors that affect the penetration and accumulation of HMs in the plant. In addition to plant structure and environmental factors such as plant type, rainfall, and amount of moisture, plant habitus, organ structure, the type of heavy metal, and its interaction with the plant are also important factors that affect the accumulation of HMs in plant organs (Sevik et al. 2020; Aricak et al. 2020). In a study with *Cedrus atlantica* Manetti, it was given that the highest Ni concentrations in trees were inspected in the direction of high traffic volume, while the change in Co concentration was not related to traffic volume (Koç 2021).

As a result of the study, it was determined that the changes in the element concentrations in all directions on a yearly basis are statistically significant at a confidence level of at least 95%. However, the concentrations of the elements in different periods are at different levels. This situation arises due to the fact that there are many factors that affect the entry and deposition of HMs in the plant structure but also shows that the transfer of HMs within the plant, at least in the wood part, is limited. For this reason, the various concentrations of HMs in the atmosphere at the time wood was formed cause the HMC in the woods formed in different years to be at different levels. One of the main goals of the study has been to obtain information about the movement of HMs in the plant, in other words their displacement, from the moment they enter the plant. As a conclusion of the study, it was determined that there may be great differences in terms of element concentrations between the OB, IB, and woods that are adjacent to each other in the same direction, and between the woods formed in the same year but in different directions. This situation can be interpreted as the displacement of the elements between organs is very limited. The level of knowledge on the speciation and displacement of HMs starting from the time they enter the plant is very limited (Shahid et al. 2017). Zhang (2019) stated that the Zn and Pb concentrations in the ARs change to a certain degree, while the Cu concentration does not change at all.

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Declarations

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