

Directionality in Tree Ring Accumulation of Tin (Sn) in Three Tree Species

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The objective of this study was to determine suitable tree species to monitor and reduce Sn concentrations in the environment of Düzce province in Türkiye. A further goal was to test the hypothesis that, possibly due to air transport, the uptake of Sn in tree rings would show a significant and consistent dependency on compass direction. The timber samples were from the trunks of *Tilia tomentosa* (linden), *Robinia pseudoacacia* (black locust), *Cedrus atlantica* (cedar), *Pseudotsuga menziesii* (Douglas fir), and *Fraxinus excelsior* (European ash), which are commonly used in landscaping in Düzce province. Levels of Sn concentrations in annual rings were determined. *Cedrus atlantica* and *F. excelsior* were found to be suitable biomonitors that can be used to monitor changes in annual amounts of Sn contamination. Among the studied tree species, *R. pseudoacacia* had the highest average values and *C. atlantica* had the second-highest levels of Sn uptake. However, no consistent dependency on compass direction was found. It follows that rather than depending on the direction of prevailing winds, the uptake of metals to the xylem of trees must be due to direction-independent processes, such as transport *via* roots and xylem or absorption into leaves and subsequent transport *via* the phloem.

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INTRODUCTION

Air pollution is considered one of the most significant environmental issues. Air pollution and its effects are at a higher level in urban areas because of industrial activities and traffic density. These factors increase the heavy metal concentrations. Elements that are considered as heavy metals have relatively high density, usually higher than 5 g/cm³, and are indestructible or non-degradable; even low levels of heavy metals can be toxic or poisonous (Sulhan *et al.* 2023). In addition to their ecological effect on natural environments, heavy metals are also a major concern for global public health (Cetin *et al.* 2022; Isinkaralar *et al.* 2023). Inhaling high amounts of heavy metal particles in the course of time can increase the metal load in the human body, and it poses a health risk (Gray *et al.* 2003). Heavy metal pollutants can affect people living near the source through suspended dust or direct contact (Chen *et al.* 2010). In agricultural lands, these pollutants can also enter the human food chain through edible plants and cause people to be exposed to heavy metals (Sevik *et al.* 2020). Heavy metals accumulate in the atmosphere and pose harm to ecosystems and organisms. Plant leaves and stems can also absorb heavy metals from atmospheric particles (Karacocuk *et al.* 2022). Heavy metals can be transported to the

soil through atmospheric deposition (Nabuloa *et al.* 2006). Plant roots uptake heavy metals from soil (Erdem *et al.* 2023). Some changes are observed in physiological and biochemical processes in plants grown in heavy metal-contaminated soils such as DNA damage, disruptions in biosynthetic pathways, and reduced growth (Taofeek and Tolulope 2012).

Tin (Sn) is one of the most concerning heavy elements. Its tendency to biologically accumulate increases the severity of its toxic effects. It is known that inorganic tin compounds have mutagenic, carcinogenic, and teratogenic potential and that they can damage the cardiovascular system. In addition to symptoms, such as shortness of breath, coughing, and wheezing, inhaling tin can lead to dizziness, balance disorders, headaches, diarrhea, vomiting, abdominal pain, muscle weakness, paralysis, anemia, and severe liver and kidney damage (Cima 2011; Sharma and Kumar 2020). Inhalation, oral intake, or dermal contact with specific Sn compounds was observed to be associated with skin and eye irritation, respiratory distress, gastrointestinal disorders, and neurological problems (Nakanishi 2008). Poisoning related with certain tin compounds can result in permanent neurological problems, and even death (ATSDR 2015).

For a sustainable environment, it is important to assess the risk levels associated with heavy metals that can persist in nature for extended periods without degradation, identify high-risk areas, and monitor the heavy metal levels. Trees in urban areas contribute to the filtration of the surrounding air and the reduction of pollution levels by absorbing heavy metals (Dzierżanowski *et al.* 2011). By capturing pollutants and reducing the amounts in the air or soil, there is potential to improve urban air or soil quality (Freer-Smith *et al.* 2005; Tomašević *et al.* 2005; Chakre 2006; Peachey *et al.* 2009; Warczyk *et al.* 2024; Zhao *et al.* 2024). However, plant capacity for heavy metal translocation and accumulation is highly variable, depending on genotypic and environmental traits (Pietrini *et al.* 2010; Di Baccio *et al.* 2014). Popek *et al.* (2017) investigated the accumulation of particulate matter (PM), including heavy metals and polycyclic aromatic hydrocarbons, on the foliage of small-leaved lime (*Tilia cordata* Mill.) in five Polish cities. The study showed that there were significantly different PM amounts found in the trees between the cities which related to the different quantities of PM in the atmosphere at these cities. The results of the study suggested that *T. cordata* improves the air quality in cities. A similar phenomenon was observed in another study, in which the root systems of *Salix integra* accumulated relatively high concentrations of Zn and Cd in the root and above ground tissues and in *Quercus* spp. and *Salix matsudana*, the highest absolute concentrations of Pb, Zn, and Cd were retained in roots. (Shi *et al.* 2017). Another study states that *Lolium multiflorum* is suitable for phytoestabilization since it is able to uptake heavy metals such as Pb and Zn and improve the soil properties (Mugica-Alvarez *et al.* 2015).

The use of urban trees as bioindicators is a sustainable ecological approach to preserve urban living spaces. Therefore, trees can be used as bioindicators to obtain time-dependent information on pollutant levels in cities (Gupta *et al.* 2011; Ghoma *et al.* 2023). The use of annual rings as indicators of heavy metal pollution can yield valuable data on the chronology and distribution of elements contributing to pollution (Chen *et al.* 2021; Savas *et al.* 2021; Key *et al.* 2023; Cobanoglu *et al.* 2023). Previous studies documented the usability of tree rings in monitoring heavy metal pollution (Edusei 2021; Isinkaralar 2022, 2024; Cuciurean *et al.* 2024). It was reported in many studies that there is a relationship between elemental concentrations in annual rings and environmental pollution (Key *et al.* 2022; Erdem *et al.* 2024; Ozturk Pulatoglu 2024; Şevik *et al.* 2024). However, the transfer of elements within wood varies between the plant species. Further studies are necessary to analyze the concentration and long-term level of Sn in the air-soil-plant system

for realistic risk assessments. Monitoring urban air quality is important to determine the atmospheric pollution and potential damage. Therefore, it is important to identify tree species suitable for detecting heavy metal pollution separately for each heavy metal. The objective of this study is to determine the most suitable species to monitor and accumulate Sn concentrations, with an assumption that the primary route of contamination is through the air. The main hypothesis of the study is that, because of prevailing winds, the Sn accumulation in the tree rings of the species under study will depend on the compass direction.

MATERIALS AND METHODS

As reported in the 2021 World Air Pollution Report, Düzce province has the fifth-highest pollution level in Europe (IQAir Staff Writers 2021). The topography and meteorological characteristics of Düzce province located in the Western Black Sea region of Türkiye can intensify some air pollution effects. The main pollutants causing air pollution in Düzce province generally originate from industrial facilities, residential fuel use, and vehicular traffic.

The timber samples used in this study were obtained from the trunks of *Tilia tomentosa* Moench (linden), *Robinia pseudoacacia* L. (black locust), *Cedrus atlantica* (Endl.) G. Manetti ex Carrière (Cedar), *Pseudotsuga menziesii* (Mirb.) Franco (Douglas fir), and *Fraxinus excelsior* L. (European ash), which are commonly used in landscaping in Düzce province. Trees of similar ages were preferred for this work. The timber samples were collected in the year 2022 and were approximately 10 cm thick, taken from an aboveground height of approximately 50 cm during the non-vegetation season. Because the trees are close to each other, it is thought that they are exposed to similar amounts of soil and airborne pollutants. To date, this method has been used in studies on the accumulation and transmission of elements in wood depending on the pollution source (Sevik *et al.* 2020; Cesur *et al.* 2021; Isinkaralar *et al.* 2022). The area where the trees were taken is on the edge of the city and there is a highway on one side and an agricultural area on the other. To interpret the pollutant source correctly, during the collection of timber samples, directions (east, west, north, and south) were labeled on the logs. Sections taken from the trunk logs were sanded in the laboratory to flatten the upper surface for clearer visibility of annual rings.

Because the annual rings are narrow, samples cannot be taken from the rings formed each year. Rather, the annual rings were grouped by considering their width and the age of the tree. In the studies, it was determined that 20-year-old trees were grouped for two years of annual rings (Turkyilmaz *et al.* 2019), 55-year-old trees were grouped for 5 years (Ozturk Pulatoglu 2024), 30-year-old trees were grouped for 3 years (Isinkaralar *et al.* 2022), and 33-year-old trees were grouped for 3 years (Koc 2021; Savas *et al.* 2021). Annual rings were clustered considering the ring width and the age of the trees. Therefore, trees that were approximately 40 years old were divided into 5-year age groups. Then, the outer bark, inner bark, and wood samples were collected from each age group using stainless steel drills and then placed in glass Petri dishes. These samples were processed into sawdust without using any tools made of the metals examined in this study and they were left in the laboratory, uncovered, for 15 days until completely dry to achieve air-dried specimens. Then, these samples were subjected to one week of drying in an oven set at 45 °C. Following this process, 0.5 g of the dried samples were mixed with 6 mL of 65% HNO₃

and 2 mL of 30% H₂O₂ before placing them in a microwave oven (Key *et al.* 2023; Erdem *et al.* 2024; Şevik *et al.* 2024).

After the combustion, the samples were transferred to measuring bottles, and the final volume was completed to 50 mL by using ultra-pure water. The samples were analyzed by using an ICP-OES (Inductively Coupled Plasma-Optic Emission Spectrometer, GBC Scientific Equipment Pty Ltd., Melbourne, Australia) device, and Sn concentrations were determined by multiplying the results with the corresponding dilution factor. This method has been commonly used in literature (Işınkaralar *et al.* 2022; Key *et al.* 2023).

Variance analysis was conducted by using the SPSS package program. Moreover, the Duncan test was conducted for factors showing statistically significant differences at a minimum of 95% confidence level ($P < 0.05$). Considering the results achieved from the Duncan test, analyses and interpretations were conducted after tabularizing the results. In each organ (outer bark, inner bark, wood) on a tree basis, in each tree on an organ basis, in each tree's annual rings on a direction basis, in each tree's annual rings on an age range basis, and in the process, the changes in heavy metal concentrations in the air were analyzed separately.

RESULTS

The annual variations of Sn concentrations in annual rings were determined in this study. Additionally, changes in Sn concentration by years and directions were calculated by comparing Sn concentrations in the inner bark (IB) and outer bark (OB) to the wood (WD). The statistical analysis results, average values, and the Sn concentration changes by species and directions are shown in Table 1.

Table 1. Sn Concentrations (ppb) by Species and Direction

Species	North	East	South	West	F	Average
<i>Tilia tomentosa</i>	560.9 ^{aB}	351.5 ^{aA}	494.1 ^{bB}	516.0 ^{aB}	7.5 ^{***}	480.6 a
<i>Robinia pseudoacacia</i>	UL	15331.9 ^{cB}	15925.4 ^{dC}	14544.1 ^{cA}	50.8 ^{***}	15267.2 c
<i>Cedrus atlantica</i>	9489.6 ^{bB}	6671.3 ^{bA}	7460.9 ^{cA}	6888.5 ^{bA}	18.6 ^{***}	7645.0 b
<i>Pseudotsuga menziesii</i>	646.6 ^{aC}	235.9 ^{aAB}	172.9 ^{aA}	399.7 ^{aB}	9.9 ^{***}	255.2 a
<i>Fraxinus excelsior</i>	876.7 ^a	372.3 ^a	306.6 ^a	560.0 ^a	1.7 ns	423.2 a
F-value	95.1 ^{***}	13212.6 ^{***}	16237.8 ^{***}	2926.9 ^{***}		3959.6 ^{***}
Average	4616.4	4562.5	5080.4	5464.0	0.865 ns	

According to statistical analysis, values followed by the different letters mean they are different at $P \leq 0.05$. Lowercase letters (a, b) show vertical directions, while uppercase letters (A, B) show horizontal directions; * = $P \leq 0.05$; ** = $P \leq 0.01$; *** = $P \leq 0.001$; ns = not significant; UL: under limit

Changes in Sn concentration were statistically significant in all directions (Table 1), though the trends were not consistent among different species. The changes by direction were found to be statistically significant in all species other than *F. excelsior*. Tin concentrations in the wood were found to change and there were differences between different directions and periods. In *R. pseudoacacia*, the change in Sn concentration in the

north remained lower than the measurable limits. The highest concentration found in the north (9490 ppb) was measured in *C. atlantica*, whereas the highest concentrations in the east (15300 ppb), west (14500 ppb), and south (15900 ppb) were measured in *R. pseudoacacia*. Considering the average values, *R. pseudoacacia* was found to yield the highest concentration (15300 ppb).

Table 2. Sn Concentrations (ppb) by Periods and Directions

Age	North	East	South	West	F	Average
2018-2022	8400	4620	5920	5430	0.4 ns	5670
2013-2017	8440	3850	7950	5050	0.9 ns	5830
2008-2012	4560	4350	4780	570	0.1 ns	4850
2003-2007	4190	4520	4830	7690	0.6 ns	5210
1998-2002	4120	4440	4810	5530	0.1 ns	4790
1993-1997	4070	4540	4820	7450	0.5 ns	5150
1988-1992	3850	4450	4820	5550	0.1 ns	4760
1983-1987	4030	4600	4820	5560	0.1 ns	4840
1978-1982	4020	4590	4950	4520	0.0 ns	4610
1973-1977	3920	4540	4820	4964	0.0 ns	4660
1968-1972	3930	4560	4780	5130	0.0 ns	4690
1963-1967	3830	4700	4910	5080	0.0 ns	4750
F	0.6 ns	0.0 ns	0.2 ns	0.2 ns		0.2 ns
Average	4780	4490	5074	5524	0.8 ns	

Given the results obtained from variance analysis, the changes in Sn concentration by periods and directions were not determined to be statistically significant (Table 2). Similarly, no significant changes were determined in the average values. Tin concentrations by organs and directions are presented in Table 3.

Table 3. Sn Concentrations (ppb) by Organs and Directions

Organ	North	East	South	West	F	Average
OB	2730	5050	5330	4590	0.6 ns	4510
IB	5810	4910	4910	5820	0.0 ns	5280
WD	4780	4490	5070	5520	0.8 ns	4970
F	1.1 ns	0.0 ns	0.0 ns	0.1 ns		0.239 ns
Average	4620	4560	5080	5460	0.865 ns	

OD: Outer bark, IB: Inner bark, WD: Wood

The changes in Sn concentration by directions and organs were not statistically significant (Table 3). Examining the average values, the results also confirmed that there was no significant difference by organ and direction. The changes in Sn concentration by periods and species are presented in Table 4.

Table 4. Sn Concentrations (ppb) by Periods and Species

Age	<i>Tilia tomentosa</i>	<i>Robinia pseudoacacia</i>	<i>Cedrus atlantica</i>	<i>Pseudotsuga menziesii</i>	<i>Fraxinus excelsior</i>	F
2018-2022	416 ^A	15700 ^C	9220 ^{bB}	231 ^A	1570 ^{bA}	79.5 ^{***}
2013-2017	336 ^A	15400 ^C	10400 ^{bB}	204 ^A	280 ^{aA}	91.0 ^{***}
2008-2012	370 ^A	15400 ^C	7260 ^{aB}	96.9 ^A	282 ^{aA}	912.0 ^{***}
2003-2007	424 ^A	15600 ^C	7240 ^{aB}	145 ^A	202 ^{aA}	2455.0 ^{***}
1998-2002	431 ^A	15000 ^C	7260 ^{aB}	124 ^A	160 ^{aA}	1614.2 ^{***}
1993-1997	399 ^A	15300 ^C	7270 ^{aB}	154 ^A	219 ^{aA}	1979.4 ^{***}
1988-1992	448 ^A	14900 ^C	7220 ^{aB}	126 ^A	189 ^{aA}	2238.3 ^{***}
1983-1987	521 ^A	15100 ^C	7280 ^{aB}	135 ^A	246 ^{aA}	2416.6 ^{***}
1978-1982	483 ^A	15400 ^C	7290 ^{aB}	161 ^A	213 ^{aA}	2415.7 ^{***}
1973-1977	410 ^A	15100 ^C	6690 ^{aB}	177 ^A	175 ^{aA}	857.4 ^{***}
1968-1972	450 ^A	14800 ^C	7020 ^{aB}	159 ^A	130 ^{aA}	1175.4 ^{***}
1963-1967	374 ^A	15100 ^C	7000 ^{aB}	158 ^A	267 ^{aA}	1227.6 ^{***}
F	1.6 ns	0.9 ns	3.6 ^{***}	1.8 ns	4.0 ^{***}	
Average	422 ^A	15200 ^C	7540 ^B	154 ^A	339 ^A	4022.3 ^{***}

Variance analysis results showed that the changes in Sn concentrations were statistically significant by period in all species (except for *C. atlantica* and *F. excelsior*) and by species in all periods. When the changes in Sn concentration on a period basis were examined, it was determined that it ranged between 336 to 521 ppb in *T. tomentosa*, 14800 to 15700 ppb in *R. pseudoacacia*, 6690 to 10400 ppb in *C. atlantica*, 96.9 to 231.3 ppb in *P. menziesii*, and 130 to 1570 ppb in *F. excelsior*. The highest value in *C. atlantica* was obtained in the periods 2013-2017 and 2018-2022. In *F. excelsior*, however, the highest concentration was obtained in the period 2018-2022. Moreover, the highest average concentration was found in *R. pseudoacacia* (15238.3 ppb), whereas the lowest ones were found in *T. tomentosa* (421.8 ppb), *P. menziesii* (153.8 ppb), and *F. excelsior* (338.7 ppb).

Table 5. Sn Concentrations (ppb) by Organs and Species

Organ	<i>Tilia tomentosa</i>	<i>Robinia pseudoacacia</i>	<i>Cedrus atlantica</i>	<i>Pseudotsuga menziesii</i>	<i>Fraxinus excelsior</i>	F
OB	1020 ^{Ac}	15300 ^C	7160 ^{aB}	719 ^{cA}	1110 ^{bA}	1642.8 ^{***}
IB	650 ^{Ab}	15600 ^C	9390 ^{bB}	516 ^{bA}	406 ^{aA}	98.7 ^{***}
WD	422 ^{Aa}	15200 ^C	7540 ^{cB}	154 ^{aA}	339 ^{aA}	4022.3 ^{***}
F	83.6 ^{***}	0.887 ns	4.415 [*]	320.2 ^{***}	7.6 ^{**}	
Average	481 ^A	15300.2 ^C	7640 ^B	255 ^A	423 ^A	3959.6 ^{***}

Changes in Sn concentration were statistically significant by species in all organs (except for *R. pseudoacacia*) and by organ in all species. The lowest concentration was found in wood, followed by inner bark and outer bark, respectively, in *T. tomentosa* and *P. menziesii*. In *C. atlantica*, however, the ranking is outer bark < inner bark < wood. Given the average values, the highest average concentration was found in *R. pseudoacacia* (15267.2 ppb), followed by *C. atlantica* (7645.0 ppb).

Table 6. Sn Concentrations (ppb) in *Tilia tomentosa* by Organs and Directions

Organ	North	East	South	West	F	Average
OB	1450 ^{cC}	900 ^{bB}	925 ^{bB}	788 ^{bA}	225.7 ^{***}	1020 ^C
IB	699 ^{bB}	287 ^{aA}	931 ^{bC}	686 ^{bB}	162.7 ^{***}	651 ^B
WD	475 ^{aB}	311 ^{aA}	422 ^{aB}	479 ^{aB}	14.6 ^{***}	422 ^A
F	127.4 ^{***}	39.2 ^{***}	66.5 ^{***}	8.1 ^{**}		83.6 ^{***}
Average	561 ^b	352 ^a	494 ^b	516 ^b	7.5 ^{***}	

The changes in Sn concentration by organs and directions were determined to be statistically significant in *T. tomentosa* (Table 6). The lowest level of Sn in the north was found in wood (475 ppb), followed by inner bark (699 ppb) and outer bark (1450 ppb). The highest levels in the south and west were found in the outer and inner bark, whereas the highest value in the east was obtained in the outer bark. Further, the highest average Sn levels were observed in the north (560 ppb), south (494 ppb), and west (516 ppb), whereas the ranking by organs is wood (422 ppb) < inner bark (651 ppb) < outer bark (1020 ppb).

Table 7. Sn Concentrations (ppb) in *Tilia tomentosa* by Periods and Directions

Age	North	East	South	West	F	Average
2018-2022	536 ^{fC}	91.1 ^{aA}	650 ^{gD}	388 ^{cB}	215.3 ^{***}	416
2013-2017	420 ^{bcC}	140 ^{aA}	470 ^{efC}	313 ^{bB}	32.3 ^{***}	336
2008-2012	327 ^{aA}	304 ^{aA}	504 ^{fB}	345 ^{bcA}	56.8 ^{***}	370
2003-2007	386 ^{bB}	321 ^{cdA}	459 ^{efC}	531 ^{dD}	51.4 ^{***}	424
1998-2002	470 ^{cdeB}	278 ^{aA}	342 ^{bA}	636 ^{eC}	62.3 ^{***}	431
1993-1997	442 ^{bcdB}	224 ^{bA}	416 ^{cdeB}	515 ^{dC}	45.8 ^{***}	399
1988-1992	285 ^{aA}	470 ^{gC}	388 ^{bcdB}	648 ^{eD}	195.4 ^{***}	448
1983-1987	624 ^{gB}	376 ^{aA}	443 ^{defA}	640 ^{eB}	33.1 ^{***}	521
1978-1982	594 ^{gB}	369 ^{deA}	420 ^{cdeA}	551 ^{dB}	27.0 ^{***}	483
1973-1977	600 ^{gD}	286 ^{cB}	222 ^{aA}	533 ^{dC}	87.5 ^{***}	410
1968-1972	495 ^{defC}	415 ^{efB}	356 ^{bcA}	530 ^{dC}	19.8 ^{***}	449
1963-1967	521 ^{efD}	459 ^{fgC}	393 ^{bcdB}	121 ^{aA}	112.8 ^{***}	374
F	32.6 ^{***}	43.5 ^{***}	26.9 ^{***}	93.5 ^{***}		1.6 ns
Average	475 ^{aB}	311 ^{aA}	422 ^{aB}	479 ^B	14.6 ^{***}	

The variance analysis results revealed that there were significant changes in Sn concentration in *T. tomentosa* by directions and periods. The highest values in the south were found in the period 2018-2022 (650 ppb), whereas the highest values were found in the period 1983-1987 (624 ppb) in the north and in the periods 1988-1992 (648 ppb) in the west. Examining the average Sn concentrations, the highest average levels were found in the west (479 ppb), north (475 ppb), and south (422 ppb).

Table 8. Sn Concentrations (ppb) in *Robinia pseudoacacia* by Organs and Directions

Organ	North	East	South	West	F	Average
OB	UL	15400 ^a	16100	14300	7.2*	15250
IB	UL	16300 ^b	15700	14800	3.8 ns	15630
WD	UL	15200 ^a	15900	14500	45.1***	15240
F		4.6*	.3 ns	.5 ns		0.8 ns
Average	UL	15300 ^c	15900 ^d	14500 ^c	50.8***	

As shown in Table 8, the changes in Sn concentrations in *R. pseudoacacia* were statistically significant by direction were significant in organs other than the inner bark. The change in Sn concentration in the north was determined to be lower than the detectable limits in all organs. However, the changes by organs were not statistically significant in directions other than the east. The highest Sn level in the east was measured in the inner bark (14810.4 ppb) and the lowest one in the outer bark (14250.9 ppb) and wood (14546.4 ppb). Considering the average values, the highest average value was measured in the south (15925.4 ppb).

Table 9. Changes in Sn Concentration (ppb) in *Robinia pseudoacacia* by Periods and Directions

Age	North	East	South	West	F	Average
2018-2022	UL	15800	16000	15200 ^{cd}	1.8 ns	15700
2013-2017	UL	14800	16000	15500 ^d	3.6 ns	15400
2008-2012	UL	15300	16000	15000 ^{bcd}	1.9 ns	15400
2003-2007	UL	15300	16100	15000 ^d	2.2 ns	15600
1998-2002	UL	15000	16100	14100 ^{ab}	10.4*	15000
1993-1997	UL	15500	15900	14500 ^{abc}	7.0*	15300
1988-1992	UL	14800	15900	14100 ^{ab}	16.9**	14900
1983-1987	UL	15200	15690	14300 ^{abc}	3.4 ns	15100
1978-1982	UL	15400	16100	14600 ^{abcd}	5.1 ns	15400
1973-1977	UL	15200	15900	14100 ^{ab}	8.2*	15100
1968-1972	UL	15200	15440	13800 ^a	3.6 ns	14800
1963-1967	UL	15600	15900	14000 ^a	9.1*	15100
F		0.7 ns	0.3 ns	3.9**		0.9 ns
Average	UL	15200 ^a	15900	14500	45.1***	

Given the variance analysis results, the changes in Sn concentration in *R. pseudoacacia* by directions were found to not be statistically significant in periods other than 1963-1967, 1973-1977, 1988-1992, 1993-1997, and 1988-2002. The concentration changes in the north direction remained lower than detectable limits for all periods. Moreover, the only significant change in concentration was found to be in the west. The highest value in this direction was obtained in the periods 2003-2007 (15400 ppb) and 2013-2017 (15500 ppb).

Table 10. Sn Concentrations (ppb) in *Cedrus atlantica* by Organs and Directions

Organ	North	East	South	West	F	Average
OB	7240 ^{aB}	6990 ^{AB}	7720 ^C	6710 ^A	16.1 ^{**}	7160 ^A
IB	16600 ^{bC}	6740 ^A	7110 ^B	7150 ^B	2010 ^{***}	9390 ^B
WD	9090 ^{aB}	6640 ^A	7470 ^A	6880 ^A	14.0 ^{***}	7540 ^A
F	8.6 ^{**}	1.4 ns	2.6 ns	0.2 ns		4.4 [*]
Average	9490 ^b	6670 ^a	7460 ^a	6890 ^a	18.6 ^{***}	

The changes in Sn concentration in *C. atlantica* by direction were found to be statistically significant in all organs (Table 10). However, the changes by organs were not statistically significant in directions other than the north. Considering the average values by organs, the highest level was measured in the inner bark (9390 ppb) and the lowest ones in the wood (7540 ppb) and outer bark (7160 ppb). Similarly, regarding the averages by directions, the highest value was found in the north (9490 ppb).

Table 11. Sn Concentrations (ppb) in *Cedrus atlantica* by Periods and Directions

Age	North	East	South	West	F	Average
2018-2022	16300 ^{fB}	6760 ^{cdeA}	6650 ^{aA}	7220 ^{cA}	460.5 ^{***}	9220 ^B
2013-2017	16500 ^{fB}	UL	7340 ^{bcA}	7370 ^{cA}	3955.1 ^{***}	10400 ^B
2008-2012	8790 ^{ec}	5650 ^{aA}	7280 ^{bb}	7340 ^{cB}	155.1 ^{***}	7260 ^A
2003-2007	7990 ^{dd}	6500 ^{bA}	7370 ^{bcdC}	7100 ^{cB}	69.7 ^{***}	7240 ^A
1998-2002	7760 ^{cdC}	6570 ^{bcA}	7380 ^{bcdB}	7330 ^{cB}	21.8 ^{***}	7260 ^A
1993-1997	7710 ^{bcdB}	6530 ^{bcA}	7440 ^{bcdB}	7380 ^{cB}	20.7 ^{***}	7260 ^A
1988-1992	7410 ^{abcB}	6640 ^{bcdA}	7500 ^{bcdB}	7320 ^{cB}	11.5 ^{**}	7220 ^A
1983-1987	7440 ^{abcBC}	6900 ^{deA}	7610 ^{cdeC}	7180 ^{cAB}	10.9 ^{**}	7280 ^A
1978-1982	7450 ^{abcC}	6700 ^{bcdA}	7810 ^{ed}	7180 ^{cB}	40.3 ^{***}	7290 ^A
1973-1977	7250 ^{abBC}	6840 ^{deB}	7650 ^{deC}	5040 ^{aA}	47.9 ^{***}	6690 ^A
1968-1972	7360 ^{abcC}	6870 ^{deB}	7800 ^{ed}	6050 ^{bA}	39.3 ^{***}	7020 ^A
1963-1967	7150 ^{aB}	7000 ^{eb}	7800 ^{ec}	6070 ^{bA}	76.5 ^{***}	7000 ^A
F	513.8 ^{***}	21.2 ^{***}	12.6 ^{***}	28.7 ^{***}		3.6 ^{***}
Average	9090 ^{aB}	6640 ^A	7470 ^A	6880 ^A		

Considering the results achieved, it was determined that the changes in Sn concentration in *C. atlantica* by periods and directions were statistically significant. The highest level in the north was measured for the periods 2013-2017 (16465.6 ppb) and 2018-2022 (16260.5 ppb) and the highest one in the east was measured for the period 1963-1967 (7004.2 ppb). The concentration changes in the east were found to be lower than the detectable limits for the period 2013-2017. Given the average values by periods, the highest value was measured for the periods 2013-2017 (10392.6 ppb) and 2018-2022 (9222.6 ppb).

Table 12. Sn Concentrations (ppb) in *Pseudotsuga menziesii* by Organs and Directions

Organ	North	East	South	West	F	Average
OB	646.6 ^A	823 ^{cB}	627 ^{cA}	241 ^{aB}	25.6 ^{***}	719 ^C
IB	UL	457 ^b	436 ^b	656 ^b	24.8 ^{**}	516 ^B
WD	UL	168 ^a	101 ^a	778 ^b	30.4 ^{***}	154 ^A
F		239.4 ^{***}	499.1 ^{***}	69 ^{***}		320.2 ^{***}
Average	646.6	236 ^a	173 ^a	400 ^a	9.9 ^{***}	

The changes in Sn concentration in *P. menziesii* by direction were determined to be statistically significant in all organs (Table 12). The changes in Sn concentration by organs were also statistically significant in the east, west, and south. In the north direction, however, the changes in Sn concentration in both inner bark and wood remained lower than the detectable limits. The values can be ranked as wood (154 ppb) < inner bark (516 ppb) < outer bark (719 ppb) for the east and south directions. The changes in Sn concentration in *P. menziesii* by period and direction are presented in Table 13.

Table 13. Sn Concentration (ppb) in *Pseudotsuga menziesii* by Periods and Directions

Age	North	East	South	West	F	Average
2018-2022	UL	133 ^b	UL	330 ^b	45.9 ^{**}	230
2013-2017	UL	88 ^a	UL	319 ^b	149.7 ^{***}	204
2008-2012	UL	82 ^a	76 ^a	133 ^a	21.0 ^{**}	97
2003-2007	UL	214 ^{ef}	76 ^a	UL	2563.7 ^{***}	145
1998-2002	UL	168 ^{bcd}	80 ^a	UL	10.9 [*]	124
1993-1997	UL	183 ^{cde}	125 ^c	UL	11.4 [*]	154
1988-1992	UL	140 ^{bc}	113 ^{bc}	UL	4.7 ns	126
1983-1987	UL	192 ^{de}	78 ^a	UL	110.6 ^{***}	135
1978-1982	UL	212 ^{ef}	88 ^{ab}	182 ^a	12.3 ^{**}	161
1973-1977	UL	238 ^f	115 ^{bc}	UL	40.5 ^{**}	177
1968-1972	UL	151 ^{bcd}	167 ^d	UL	.9 ns	159
1963-1967	UL	222 ^{ef}	94 ^{ab}	UL	78.8 ^{**}	158
F		13.8 ^{***}	9.3 ^{***}	30 ^{***}		1.8 ns
Average	646.6 ^c	236 ^{ab}	173 ^a	400 ^b	9.9 ^{***}	

It was determined that the changes in Sn concentration in *P. menziesii* by direction were statistically significant in periods other than 1968-1972 and 1988-1992 (Table 13). The changes in Sn concentration were also determined to be statistically significant in all directions other than the north. The changes in Sn concentration in the north remained lower than the detectable limits in all periods. Moreover, the changes in Sn levels were found to be lower than the detectable limits in the south for the periods 2013-2017 and 2018-2022 and in the west direction for the periods other than 1978-1982, 2008-2012,

2013-2017, and 2018-2022. The highest level was measured for the period 1973-1977 in the east (238 ppb), for the period 1968-1972 (167 ppb) in the south, and for the periods 2013-2017 (319 ppb) and 2018-2022 (330 ppb) in the west. Considering the average values, the highest average level was measured in the north (647).

Table 14. Sn Concentrations (ppb) in *Fraxinus excelsior* by Organs and Directions

ORGAN	North	East	South	West	F	Average
OB	1600 ^D	1140 ^{cB}	1260 ^{bC}	423 ^A	508 ^{***}	1110 ^B
IB	153	734 ^b	329 ^a	UL	1230 ^{***}	406 ^A
WD	UL	278 ^a	218 ^a	576	2.2 ns	339 ^A
F	1657.9 ^{***}	149.9 ^{***}	213.6 ^{***}	0.0 ns		7.6 ^{**}
Average	877	372	307	560	1.7 ns	

Changes in Sn concentration in *F. excelsior* by directions and organs were found to be statistically significant in both inner and outer bark and in all directions other than the west, respectively. In the north, the changes in Sn levels were found to be lower than the detectable limits in wood for the north and in inner barks for the west. Considering the average values by organs, the highest value was measured in the outer bark (1105.8 ppb). The changes in Sn concentrations in *F. excelsior* by periods and directions are presented in Table 15.

Table 15. Sn Concentrations (ppb) in *Fraxinus excelsior* by Periods and Directions

Age	North	East	South	West	F	Average
2018-2022	UL	304 ^c	352 ^g	4050 ^c	2560 ^{***}	1570 ^B
2013-2017	UL	367 ^d	UL	149 ^{ab}	47 ^{**}	280 ^A
2008-2012	UL	476 ^e	87 ^a	UL	298 ^{***}	282 ^A
2003-2007	UL	270 ^{bc}	135 ^{ab}	UL	140 ^{***}	202 ^A
1998-2002	UL	240 ^b	171 ^{bcd}	69 ^a	55 ^{***}	160 ^A
1993-1997	UL	274 ^{bc}	164 ^{bc}	UL	13 [*]	219 ^A
1988-1992	UL	242 ^b	224 ^{de}	101 ^a	83 ^{***}	189 ^A
1983-1987	UL	381 ^d	258 ^{ef}	101 ^a	222 ^{***}	246 ^A
1978-1982	UL	238 ^b	289 ^f	112 ^{ab}	38 ^{***}	213 ^A
1973-1977	UL	157 ^a	218 ^{cde}	148 ^{ab}	3.2 ns	175 ^A
1968-1972	UL	129 ^a	147 ^b	115 ^{ab}	1.4 ns	130 ^A
1963-1967	UL	261 ^{bc}	349 ^g	192 ^b	20 ^{**}	267
F		34.9 ^{***}	21.3 ^{***}	2942.3 ^{***}		4.0 ^{***}
Average	876.7	372	307	560	1.7 ns	

Given the results shown in Table 15, the changes in Sn concentrations in *F. excelsior* by directions were found to be statistically significant in all periods other than 1968-1972 and 1973-1977. The changes in Sn levels in the north were determined to be

lower than detectable limits for all periods. Moreover, the changes in Sn concentration were found to be lower than the detectable limits for the period 2013-2017 in the south and for the periods 1993-1997, 2003-2007, and 2008-2012 in the west. The highest value was obtained for the period 2008-2012 (476.1 ppb) for the east, for the period 2018-2022 (4054.0 ppb) for the west, and for the periods 1963-1967 (348.7 ppb) and 2018-2022 (352.2 ppb) for the south.

When the changes in wood based on period and direction are examined, it is seen that there was no significant difference between neighboring wood groups in *T. tomentosa*, *R. pseudoacacia*, *P. menziesii*, and the values were relatively close to each other. However, there were big differences between neighboring woods in *C. atlantica* and *F. excelsior*. For example, in *C. atlantica*, while it was 16300 ppb in the north direction in the 2018-2022 period, it was determined as 6650 ppb in the south direction in the same period. Again, in *C. atlantica*, 16500 ppb in the north direction and 7340 ppb in the south direction were determined in the period 2013-2017. In the *F. excelsior* species, it was determined as 304.3 ppb in the east direction and 4050 ppb in the west direction in the period 2018-2022. According to these results, it can be said that Sn can be transported in the wood of *T. tomentosa*, *R. pseudoacacia*, and *P. menziesii*. The study results indicate that *T. tomentosa* are not suitable bio-monitors for monitoring the changes in the Sn concentrations and cannot be recommended for the purposes of phytoremediation of Sn-contaminated sites.

DISCUSSION

The main hypothesis of the study is that Sn accumulation in the organs of the species under study varies depending on the compass direction. Although the study results revealed differences between the directions, it can be said that the data on compass directions did not show a consistent trend as a result of the study. Since the data did not match the hypothesis, this situation shows that the entry of metals into tree rings varies depending on other factors. For example, it is well known that water is transmitted from the roots of a tree upwards through the xylem of the last year. Another possible path may be downwards, if the metal is able to pass into the leaves, from which it would be conducted through the phloem tissue and then to some parts of the xylem *via* ray cells. The mechanism involving passage into leaves does not match the originally proposed hypothesis, because a leaf on the side away from the wind is still expected to be affected by the wind. There is no mechanism that would allow the metal falling on the trunk of a tree to enter the lower xylem on that side of the tree (Shahid *et al.* 2017; Wani *et al.* 2018). Based on the present findings, any mechanism that would be expected to have contributed to a consistent directionality does not have empirical support. According to these results, the hypothesis of the study can be rejected.

Heavy metals in the air enter the plant directly by respiration or by adhering to plant organs with the help of particulate matter. Some of them mix into the soil and water due to the effects of rain and gravity. Phytoremediation of soil contaminated with heavy metals involves various steps and processes, which include heavy-metal uptake (phytoextraction), accumulation and translocation of heavy metals (phytoaccumulation), emission to atmosphere (phytovolatilization), and their stabilization in the root zone (phyto-stabilization) (Shah and Daverey 2020). Heavy metals can be taken up by root cells from soil, with subsequent storage in root tissues, long-distance transport upwards *via* xylem and downwards *via* phloem (Luo *et al.* 2016; Cao *et al.* 2020; Rosa *et al.* 2022). Heavy

Metals are primarily taken up by the plants along with water and nutrients (Shah and Daverey 2020). The roots receive metal either by symplastic transport (*via* plasma membrane of endodermal cells of roots) or by apoplastic transport (movement *via* free space between cell wall) (Ling *et al.* 2017; Thakur *et al.* 2016). Heavy metals enter through intercellular spaces (apoplast) in apoplastic transport and through specific ion channels or carriers in symplastic transport (Chaudhary *et al.* 2018). Metals are stored in vacuoles by the non-hyperaccumulator plant, while they are translocated very efficiently from root-to-shoot *via* xylem in the hyperaccumulator plant. Heavy metals are primarily transported to the aboveground tissues *via* xylem (Wu *et al.* 2010). For xylem loading, metal ions have to cross a water impervious barrier Casparian band. As a result, it blocks the apoplastic efflux of metal ions from the root cortex to stele and metals start moving through symplastic transport to pass this barrier and to reach the xylem (Mahmood 2010). The heavy metal is then absorbed, precipitated and accumulated in the aerial parts of the plant (*i.e.*, shoot, leaves, *etc.*) by the process called phytoaccumulation (Shah and Daverey 2020). According to studies, heavy metals can be efficiently moved through the root symplast and loaded into xylem vessels, where subsequent transport to the above-ground tissues is driven by transpiration stream (Deng *et al.* 2016; Zeng *et al.* 2013). Thus, plants contribute to cleaning the environment by absorbing heavy metals from the air, water, and soil in their organs (Shahid *et al.* 2017; Türkyılmaz *et al.* 2020; Ghoma *et al.* 2022; Hlihor *et al.* 2022).

Many studies have been conducted on the use of plants as biomonitors and to decrease heavy metal pollution (Tufail *et al.* 2022; Yaashikaa *et al.* 2022; Kuzmina *et al.* 2023). Several studies reported the level of heavy metal accumulation to vary depending on the species (Türkyılmaz *et al.* 2019; Karacocuk *et al.* 2022). The most critical feature sought in species that can be used to determine heavy metal pollution is the ability of the species to accumulate heavy metals in their bodies (Savas *et al.*, 2021). Çetin *et al.* (2023) suggested *Pinus pinaster* and *Picea orientalis* as suitable species for monitoring Sn pollution, whereas *Cupressus arizonica*, *Cedrus atlantica*, and *Pseudotsuga menziesii* were reported to have the potential to mitigate Sn pollution. However, it was found in the present study that *Robinia pseudoacacia* and *Cedrus atlantica* trees yielded the highest average Sn concentrations, which indicates that *Robinia pseudoacacia* and *Cedrus atlantica* are the most suitable species for reducing Sn pollution among those studied.

The anatomical and genetic structure of plants plays a critical role in the interaction between plants and heavy metals. Previous studies reported that heavy metal concentrations might exhibit significant variation between different organs of the same plant (Sevik *et al.* 2019a,b; Sulhan *et al.* 2023). For instance, Cetin and Jawed (2022) determined that there were traffic density-related changes in Ba concentration in the leaves and branches of *Ficus bengalensis*, *Ziziphus mauritiana*, *Conocarpus erectus*, and *Azadirachta indica*. *Azadirachta indica* leaves were found to be the most suitable organ. Plants growing in the same environment have different heavy metal concentrations in different organs depending on factors such as organ structure, morphology, surface area, surface texture, and size (Isinkaralar *et al.* 2022). Therefore, it is important to identify specific species for each heavy metal to effectively reduce heavy metal pollution (Yayla *et al.* 2022).

Wood is the largest part of a plant in terms of mass and, therefore, it has the highest heavy metal accumulation capacity. Differing from many other parts, wood remains integrated with the tree for a long period. Thus, plants that can accumulate heavy metals in their wood are of particular importance to prevent air-borne heavy metal pollution (Koc 2021; Key *et al.* 2023). Considering the average values of species in this study, the lowest

average Sn concentration was found in *Pseudotsuga menziesii* (255 ppb), whereas *Robinia pseudoacacia* (15300 ppb) was determined to have the highest average concentration, followed by *Cedrus atlantica* (7640 ppb). Therefore, the most suitable species to reduce Sn pollution was determined to be *Robinia pseudoacacia*, which has the highest Sn concentration in wood.

Previous studies revealed that heavy metal concentrations were high in many species, especially in the outer bark (Koç 2021; Çobanoğlu *et al.* 2023). Gueguen *et al.* (2012) observed V, Ni, Cr, Sb, Sn, and Pb pollutions in the outer bark of plants taken from areas near traffic axes Strasbourg and Kehl in the Rhine Valley, whereas Cr, Mo, and Cd pollutions were found in samples taken from industrial areas. This is because of the structure of the outer bark and its interaction with metal-contaminated particles. In this study, the highest Sn concentrations were found in the outer bark of *Tilia tomentosa*, *Pseudotsuga menziesii*, and *Fraxinus excelsior* species. This result can be explained by the outer surface serving as the source of pollutant material and the presence of Sn-contaminated particles.

The complex transfer of elements within the wood is an important uncertainty in understanding the applicability of biomonitors in examining heavy metal pollution. Although the internal conductivity and transport of substances vary among species, other studies have shown that all of them have more/less transport and accumulation (Turkyilmaz *et al.* 2020). However, it has been reported that some of them have become widely preferred in mitigation of environmental pollution due to their higher absorption capacity compared to others. Previous studies reported remarkable variations in the transfer of different elements within the wood of different tree species. Çobanoğlu *et al.* (2023) emphasized that the transfer of Cd, Ni, and Zn in cedar wood is limited, whereas Zhang (2019) reported variations in Zn and Pb concentrations in the annual rings of *Cedrus deodara* but no change in Cu concentration. Key *et al.* (2022) determined that the transfer of Ni, Co, and Mn in the wood of *Corylus colurna* was very limited. Cesur *et al.* (2021, 2022) reported limited transfers of Fe, Cd, and Ni elements in the wood of *Cupressus arizonica* but higher levels of transfer for Bi, Li, and Cr. Moreover, it was found that the transfer of Ni in the wood of *Cedrus atlantica* is quite restricted, whereas Co has more mobility (Koç 2021).

The transfer of various elements within wood varies between species and it is related to cell structure and cell wall. The cell wall-plasma membrane represents a flexible structure involved in the perception and signaling of metal/metalloid stress (Wani *et al.* 2018). The interface between the cell wall and plasma membrane is considered the potential region for heavy metal tolerance because it accumulates large heavy metal fractions (Wu *et al.* 2010).

Concentrations obtained in the outer bark and on the sides of the tree where pollution is present are expected to be much higher. Studies show that heavy metals in the air adhere to particulate matter in areas close to the pollution source and contaminate particulate matter with heavy metals, and these particulate matter settles in plant organs and increases heavy metal concentrations in these organs (Sevik *et al.* 2020; Yayla *et al.* 2022; Kuzmina *et al.* 2023). Airborne metals (as ions) can enter a tree by means of rainfall, which allows the ions to be taken up by the tree's roots and then be distributed to the leaves and other parts of the plant. Elements uptake by plants is highly dependent on the concentration, amount, and activity of element in the soil solution (Erdem *et al.* 2024).

In urban-industrial areas exposed to anthropogenic pressures and with high traffic density, proper plantations might contribute to environmental improvements and air pollution reduction. This study showed that selected plants can accumulate heavy metals

while growing in polluted environments without compromising their physiological vitality. Thanks to their tolerance to heavy metal pollution, it is recommended to use these species for biological monitoring of air quality in urban environments. These plants can provide a valuable ecosystem service by removing heavy metals from the air. Expanding such studies can provide insights into pollution levels in environments contaminated with heavy metals. Air quality maps can be created in urban areas to obtain information about the effects of air pollution on ecosystems and organisms.

CONCLUSIONS

1. To use annual rings to monitor the change of heavy metal pollution in the process, the displacement of the element to be monitored in the wood must be limited. When the changes in wood based on period and direction were examined, it was seen that there was no significant difference between neighboring wood groups in *T. tomentosa*, *R. pseudoacacia*, *P. menziesii*, and the values were relatively close to each other. According to these results, *T. tomentosa*, *R. pseudoacacia*, *P. menziesii* were not suitable biomonitors for monitoring the change of Sn pollution.
2. However, there were big differences between neighboring woods in *C. atlantica* and *F. excelsior*. Therefore, *C. atlantica* and *F. excelsior* were judged to be suitable biomonitors that can be used to monitor the change in air concentrations of Sn.
3. The present study revealed that the species examined here have different capacities regarding Sn accumulation. *R. pseudoacacia* and *C. atlantica* were found to be the most suitable species for mitigating Sn pollution. Examining the average values by species, *P. menziesii* was determined to have the lowest average Sn concentration in all organs, whereas *R. pseudoacacia* had the highest average values and *C. atlantica* had the second-highest ones. Therefore, *R. pseudoacacia*, which has the highest wood concentration, was determined to be the most effective species for reducing Sn pollution. Therefore, it is appropriate to use *R. pseudoacacia* and *C. atlantica* species to reduce Sn pollution in urban areas where Sn pollution is high.
4. Extensive measurements were analyzed in this work to examine a hypothesis regarding the compass orientation of metal uptake – especially with respect to the annual rings of trees. Though the data included various statistically significant differences, when considering individual tree species and specific year spans, none of these correlations showed consistency across different tree species and different time periods, as would have been expected for a mechanism influenced by prevailing winds. On this basis, the hypothesis was rejected. Instead, the present results suggest that metal uptake into the xylem of trees involves mechanisms that are unrelated to prevailing wind directions, sunlight directions, or other such factors that would be expected to have a consistent relationship to compass orientation.

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Declaration of Interest Statement

No potential conflict of interest was reported by the author(s).

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