



Research Article

Monitoring of heavy metal pollution by using *populus nigra* and *cedrus libani*

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ABSTRACT

As metals and metal compounds have impact on human health, it is important to identify bio-monitor plants that can be used to monitor their levels in environmental and biological samples. In this study, two different plants (*Populus nigra* and *Cedrus libani*) were used as bioindicators. This was evaluated by monitoring heavy metal pollution in Kırşehir province with these plant samples collected from the vicinity of casting factory (Casting factory station) and the region where there is no casting factory (Boztepe station). Nickel (Ni), lead (Pb), and copper (Cu) levels were determined in the needle, leaves of plants, and soil samples where they grow using High Resolution-Continuum Source Flame Atomic Absorption Spectrometry (HR-CS FAAS). The levels of Ni, Pb, and Cu in *Populus nigra* were determined to be in the range of 0.87 to 2.59 µg/g, 0.40 to 0.75 µg/g, and 2.27 to 9.66 µg/g, respectively. In analysis of *Cedrus libani*, metal levels were found the range of 0.44 to 1.12 µg/g for Ni, 0.84 to 3.18 µg/g for Pb and 2.16 to 4.60 µg/g for Cu. The levels of Ni in *Populus nigra* samples collected from the Casting factory station (CFS) (2.49±0.09 µg/g) increased compared to the samples collected from the Boztepe station (1.16±0.24 µg/g) (p<0.05). Pb levels in *Populus nigra* were determined as 0.50±0.11 µg/g and 0.67±0.10 µg/g for samples collected from the CFS and Boztepe stations, respectively. Cu levels in *Populus nigra* were determined as 6.73±0.99 µg/g and 5.53±3.39 µg/g for the samples collected from the CFS and Boztepe stations, respectively. The levels of Pb and Cu in *Populus nigra* were not significant for both the stations (p>0.05). The levels of Ni in *Cedrus libani* samples collected from the Boztepe station (1.03±0.18 µg/g) were higher than that in the samples collected from the CFS (0.66±0.24 µg/g) (p<0.05). The levels of Pb in *Cedrus libani* were determined as 1.74±0.26 µg/g and 1.00±0.16 µg/g for the samples collected from the CFS and Boztepe stations, respectively (p<0.05). The levels of Cu in *Cedrus libani* were determined as 4.27±0.26 µg/g and 2.87±0.75 µg/g for the samples collected from the CFS and Boztepe stations, respectively (p<0.05). As a result, we suggest that *Cedrus libani* could be used as biomonitor plants for Pb and Cu and *Populus nigra* for Ni.

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INTRODUCTION

In recent years, heavy metals emanating from different anthropogenic sources have had a direct or indirect negative impact on the environment. As a result, atmospheric pollution has increased significantly [1, 2]. The prominent increase of heavy metals such as Cd, Ni, Cu, Cr, Zn, Pb, Al and Mn as principal air pollutants in the atmosphere causes significant dangers for the environment and human health in the long term [3–5]. Many heavy metals bind to sulfur, nitrogen, and other functional groups that are found in biomolecules and thereby, disrupt their functions [6]. Consequently, exposure of living things to these metals can result in DNA mutations, cell cycle malfunctions, neurological problems, liver and kidney damage, impairment of endocrine systems, cardiovascular dysfunction [7], tumor progression, or apoptosis with carcinogenic effects [8]. In many ecological systems, high levels of heavy metals can also degrade air and water quality, causing degradation of biodiversity and biota systems, thereby posing a severe threat to biodiversity [2, 9, 10]. Due to the effects of these pollutants on human health and the environment, it has become necessary to monitor and control them.

In recent years, the use of biomonitors, as an alternative analytical procedure to other conventional procedures, for air quality monitoring has increased [2, 11, 12]. “Biomonitoring is known as the methodology that takes into account the use of living organisms to monitor and evaluate the impact of different contaminants in a known area” [2, 13]. Thus, information about levels of toxic metals in soil, water, and air can be obtained by analyzing the parts of biomonitor plants, such as root, stem, shell, and leaf [14]. This type of monitoring is relatively inexpensive and easy to implement; it is a viable alternative in the absence of infrastructure/tools for conventional air quality monitoring. The aim of this study was investigate whether and *Cedrus libani* plants can serve as useful bioindicators in monitoring heavy metal pollution occurring in the casting factory. This was evaluated by monitoring heavy metal pollution in Kırşehir province with these plant samples collected from the vicinity of casting factory (Casting factory station) and the region where there is no casting factory (Boztepe station). The levels of Ni, Pb, and Cu in the needles and leaves of the plants as well as in the soil samples were determined by using High Resolution-Continuum Source Flame Atomic Absorption Spectrometer (HR-CS FAAS). This is the first study monitoring the pollution caused by the casting factory in the central Anatolian region in Turkey. The study will contribute to the literature from this aspect.

MATERIAL AND METHODS

Chemicals and Apparatus

Chemicals and reagents of analytical quality and high purity were used in all experiments in this study. The stan-

Table 1. The operating conditions for HR-CS AAS

Parameters	Pb	Ni	Cu
Wavelength, nm	217.0005	232.0030	324.754
Flow rate of C ₂ H ₂ -air, L/h	65	60	60
Burner height, mm	8	6	5
Evaluation Pixels, pm	3	3	3
Background correction	Simultaneous	Simultaneous	Simultaneous

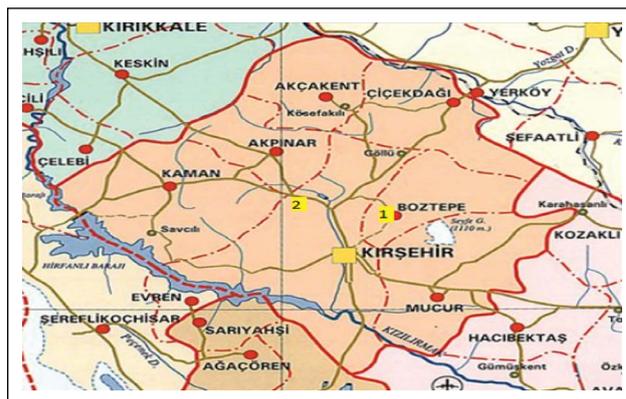


Figure 1. Geographical location of the study plant samples.

dard stock solutions of the metals (1000 mg/L) were obtained from Merck (Germany). Calibration standards and aqueous working standards were prepared by diluting these stock solutions. All aqueous solutions were prepared with ultrapure water that had been obtained by Milli-Qwater purification system (Millipore, Corporation, MA, USA). Analytik Jena ContraAA Model 300 series High Resolution-Continuum Source Flame Atomic Absorption Spectrometer (GLE, Berlin, Germany) was used for the analysis of metals. All absorption lines of an element in the spectral range of 185–900 nm can be analytically evaluated by using a xenon (Xe) short-arc lamp as a continuum lamp in the HR-CS FAAS [15]. The working conditions of HR-CS FAAS for the analysis of the metals are given in Table 1.

Samples and Analytical Procedure For Elemental Analyses

The leaves and needles of plant species poplar () and cedar (*Cedrus libani*) were collected from Kırşehir city of Turkey (1; Boztepe station: 39°15'05.8"N 34°15'40.4"E; 2; CFS: 39°14'55.1"N 34°07'27.3"E; Fig. 1) during June and July.

The identifications of plant species were performed by plant systematic expert at Kırşehir Ahi Evran University. The collected needle and leaf samples were taken from different parts of the trees and then the samples were mixed to ensure sample homogeneity. The samples were carried to the laboratory in plastic vessels and were thoroughly washed with tap water and ultrapure water to remove impurities. Thereafter, the samples were dried in an oven at 60°C (20–24 h) till a stable weight was attained.

Dried and homogenized samples weighing 0.50–1.50 g were transferred into a flask (Pyrex) and digested using the dry ashing method. For this, dried samples were heated in stages in an oven at 150°C for 15 min, 350°C for 15 min, 450°C for 10 min, and ashed at 500°C for 8 h, in sequence. A mixture of 2 mL of 65% concentrated nitric acid (HNO_3) and 1 mL of 30% hydrogen peroxide (H_2O_2) were added to the ashed samples and evaporated to near dryness. This procedure was repeated until a clean sample was obtained. Subsequently, samples were cooled, 6.0 mL of 0.2 mol/L HNO_3 was added and filtered (Fig. 2). Blank samples were also prepared using the same method [16].

Soil samples were taken from the places where these plant species were grown on the same date. Approximately 500 g soil samples were taken from the surface at a depth of 50–80 cm. These samples were brought to the laboratory in plastic nylon, dried in an oven at 75°C for 20–24 h, milled in a porcelain mortar, and passed through a 2-mm sieve (200 mesh). The acid extraction method as recommended by Environmental Protection Agency (EPA, Method 3050B) [17] for the decomposition of soil samples was used. 2.0 g of the powdered samples were weighed and transferred in 250 mL flask (Pyrex) for digestion. 10 mL of 50% HNO_3 was added and heated to 95°C. Thereafter, the samples were cooled and 65% HNO_3 was added until brown fumes disappeared. The solution was then evaporated to near dryness. Subsequently, 10 mL of 30% H_2O_2 and 10 mL of 37% HCl were added. This mixture was refluxed at 95°C for 15 min, cooled, filtered with a 0.45- μm membrane paper, and the total volume was maintained at 50 mL with ultrapure water (Fig. 3).

Statistical Analysis

The statistical analysis of the sample results were performed using the variance analysis by ANOVA (SPSS, v.13.0) for comparison between the groups. Least significant difference (LSD) test was performed to compare the results from the different-area groups. Statistical data processing was carried out at a level of reliability of 95%. p-value of less than 0.05 was considered to be meaningful.

RESULTS AND DISCUSSION

High heavy metal content in parts of plants taken from above ground tissues is considered as an indicator of air and soil pollution levels. The monitoring of atmospheric pollution by using leaves of trees has gained considerable attention in recent years. Due to the low cost of leaves, it has been suggested in the literature that leaves can be used for monitoring air pollution [14, 18–22].

The commonly investigated species among the wide variety of trees used as biomonitors of atmospheric pollution are some of the fast-growing trees belonging to the genera *Cedrus* and *Populus*. Many studies have shown that various species of *Populus* and *Cedrus* can tolerate

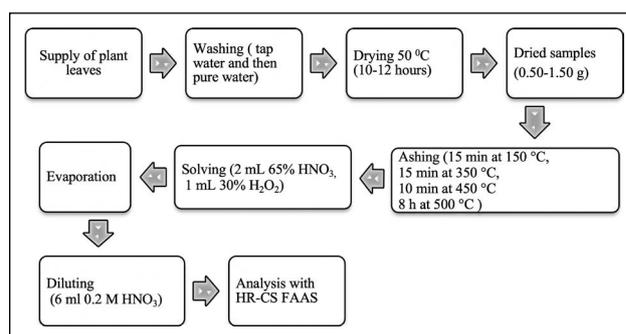


Figure 2. Analysis procedure of plant samples for HR-CS FAAS analyses.

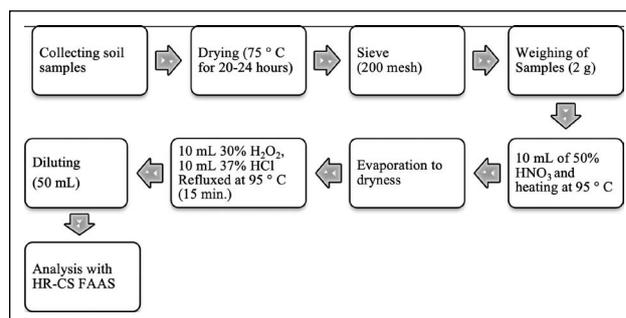


Figure 3. Analysis procedure of soil samples for HR-CS FAAS analyses.

and accumulate high concentrations of heavy metals in above ground tissues [23–28].

In this study, and *Cedrus libani* have been utilized because of they are the dominant tree species in Kırşehir. In addition, *Cedrus* species are also among the preferred biomonitors for atmospheric pollution, as they are evergreen trees [23]. Two stations were selected, one is the casting factory, which is a source of metal pollution, and the other is the Boztepe station, which has no factory and no urban area. The concentrations of Ni, Pb, and Cu in the samples of each station are shown in Table 2 and Table 3. The levels of heavy metals in the plant samples were evaluated statistically. The levels of Ni, Pb, and Cu in samples collected from the Boztepe station were determined to be in the range of 0.87 to 1.43 $\mu\text{g/g}$ (mean, 1.16 $\mu\text{g/g}$), 0.55 to 0.75 $\mu\text{g/g}$ (mean, 0.67 $\mu\text{g/g}$), and 2.27 to 9.66 $\mu\text{g/g}$ (mean, 5.53 $\mu\text{g/g}$), respectively.

On the other hand, the levels of Ni, Pb, and Cu in samples collected from the CFS were determined to be in the range of 2.40 to 2.59 $\mu\text{g/g}$ (mean, 2.49 $\mu\text{g/g}$), 0.40 to 0.66 $\mu\text{g/g}$ (mean, 0.50 $\mu\text{g/g}$), and 5.83 to 8.12 $\mu\text{g/g}$ (mean, 6.73 $\mu\text{g/g}$), respectively.

From the analysis, it was observed that the levels of Ni in the samples collected from the CFS were higher than that in the samples collected from the Boztepe station ($p < 0.05$). However, the levels of Pb and Cu in the samples collected from the CFS and Boztepe stations were not significant ($p > 0.05$).

Table 2. Concentrations of trace elements in the plant samples (N=4, µg/g)

Plant samples	Station	Element	Mean±SD	95% CI
<i>Populus nigra</i>	Boztepe	Ni	1.16±0.24	0.78–1.54
	CFS		2.49±0.09*	2.35–2.63
<i>Populus nigra</i>	Boztepe	Pb	0.67±0.10	0.51–0.83
	CFS		0.50±0.11	0.33–0.67
<i>Populus nigra</i>	Boztepe	Cu	5.53±3.39	0.14–10.92
	CFS		6.73±0.99	5.16–8.30
<i>Cedrus libani</i>	Boztepe	Ni	1.03±0.18	0.74–1.32
	CFS		0.66±0.24	0.28–1.04
<i>Cedrus libani</i>	Boztepe	Pb	1.00±0.16	0.75–1.25
	CFS		1.74±0.26*	1.33–2.15
<i>Cedrus libani</i>	Boztepe	Cu	2.87±0.75	1.68–4.06
	CFS		4.27±0.26*	3.86–4.68

*: The significant difference in metal content of plants in CFS according to Boztepe $p < 0.05$. SD: Standard deviation; CI: Confidence Intervals.

Table 3. Concentrations of trace elements in the soil samples (N=3, µg/g)

Station	Element	Mean±SD	95% CI
Boztepe	Ni	26.55±1.35	23.20–29.90
CFS		23.25±1.26	20.12–26.38
Boztepe	Pb	6.63±1.33	3.33–9.93
CFS		4.97±1.20	1.99–7.95
Boztepe	Cu	8.58±1.02	6.05–11.11
CFS		7.07±0.85	4.96–9.18

SD: Standard deviation; CI: Confidence Intervals.

The levels of Ni, Pb, and Cu in *Cedrus libani* samples collected from the Boztepe station were determined to be in the range of 0.93 to 1.12 µg/g (mean, 1.03 µg/g), 0.84 to 1.16 µg/g (mean, 1.00 µg/g), and 2.16 to 3.92 µg/g (mean, 2.87 µg/g), respectively. On the other hand, the levels of Ni, Pb, and Cu in *Cedrus libani* samples collected from the CFS were determined to be in the range of 0.44 to 0.86 µg/g (mean, 0.66 µg/g), 1.19 to 3.18 µg/g (mean, 1.74 µg/g), and 4.02 to 4.60 µg/g (mean, 4.27 µg/g), respectively.

From the analysis, it was observed that the levels of Pb and Cu in *Cedrus libani* samples collected from the CFS were higher than that in the samples collected from the Boztepe station ($p < 0.05$). We think that the main reason is the pollutants emitted from the casting factory.

Harmful waste generated by casting, melting, and manufacture are in fact associated with the use of additives and impurities in raw materials or fuels. The use of coal and other fuels for burning might lead to the accumulation of harmful matter in the environment. Various additives are used for the realization of the reaction. The presence of impurities in waste that blend by melting

may cause the formation of a product with incomplete combustion or recombination and dust. Dust metal and metal oxides may be generated from the process. During the melting process, compounds and elements evaporate. Afterward, the metal dust particles can be emitted from factory chimneys [29]. The levels of Ni, Pb and Cu were not significant in soil samples taken from different stations ($p > 0.05$). For this reason, we think that the changes in heavy metal levels observed in plants mostly effected by the parameters in the air for the studied elements.

The levels of Ni in *Cedrus libani* and soil samples from the Boztepe station were higher than that in the samples from the CFS. However, this increase was not significant ($p > 0.05$).

Rucandio et al. (2011) [19] investigated leaves of six different arboreal and bush species, which were collected from various parts of Madrid (Spain). The different investigated plant species (*Cedrus deodara*, *Cupressus sempervirens*, *Pinus pinea*, *Nerium oleander*, *Ligustrum ovalifolium*, and *Pittosporum tobira*) exhibited different capability for accumulation of specific elements. *Cedrus deodara* accumulated especially Ag, Hg, Mo, and V; *Cupressus sempervirens*, Zr; *Pinus pinea*, As and Sb; *Nerium oleander* Ni, Pb, Mo, and Se; *Ligustrum ovalifolium*, Sc and V; and *Pittosporum tobira*, Ag, Cd, Rb, and Sc. Madejón et al. (2004) [21] studied the elemental contents (As, Cd, Cu, Fe, Mn, Ni, Pb, and Zn) in leaves and stems of white poplar (*Populus alba*) trees. The levels of Cd, Zn, Pb, Cu, and as in white poplar (*Populus alba*) were determined as 1.25, 117, 63.3, 58.0, and 1.70 mg/kg respectively. They determined that poplar leaves could be used as biomonitors for soil pollution induced by Cd and Zn and moderately by as. In the study of Onder and Dursun (2006), the elemental contents (Pb, Cu, Zn, Co, Cr, Cd, and V) in the needles of cedar trees (*Cedrus libani*) were determined. They evaluated the heavy metal content accumulated by air pollution in cedar needles from the green area in Konya city center. The results of this study showed that heavy metal accumulation in the old trees is generally higher than in the young trees [23]. In another study that investigated the heavy metal content in black poplar leaves collected from Ust-Kamenogorsk cities of Kazakhstan. They determined the contents of some elements, such as Ag, As, Na, Sb, Sr, Ta, U, and Zn in this plant. They found the mean element contents (Ag, As, Na, Sb, Sr, Ta, U, and Zn) of 0.08, 0.38, 936, 0.32, 193, 0.01, 0.08, and 468 mg/kg, respectively. As a result, they determined that the main parameter affecting the change in the basic composition of poplar leaves is air pollution [30]. Kosheleva et al. (2016) [31] investigated changes in the trace element composition of poplar leaves in major cities and mining centers of Mongolia. They determined that the concentrations of many elements (Be, V, Pb, Cr, and Ni) in the background plants were lower than their worldwide values. Berlizov et al. (2007) [32] presented a comparative study of the bark of black poplar (*Populus nigra* L.) as a bioobserver of atmospheric heavy metal (As,

Table 4. Comparison of average elements concentrations ($\mu\text{g/g}$) in plant leaves with studies in the literature

Tree species*	Regions	Ni	Pb	Cu	References
<i>Aesculus hippocastanum</i>	Belgrade, Serbia	0.28–2.38	0.8–21.5	5.5–61.0	[14]
<i>Cedrus libani</i>	Konya, Turkey	–	0.58–3.99	1.14–6.89	[23]
<i>Populus tremula</i> L., <i>Salix alba</i> L., <i>Robinia pseudoacacia</i> L., <i>Quercus infectoria</i> L., <i>Pinus nigra</i> Arn. ssp. <i>pallasiana</i>	Kütahya, Turkey	–	0.1–55.0	2.1–59	[33]
<i>Pinus sylvestris</i> L.	Erzurum, Turkey	–	14.0–41.32	1.52–24.96	[34]
<i>Robinio pseudo-acacia</i> L.	Denizli, Turkey	–	11.5–53.0	5.64–20.81	[35]
<i>Acer platanoides</i>	Belgrade, Serbia	1.12–2.07	1.87–7.98	7.07–13.07	[36]
<i>Nerium oleander</i> L.	Rio de Janeiro City, Brazil	–	3.4–5.4	8.0–23.0	[37]
<i>Conocarpus erectus</i> , <i>Nerium oleander</i> , <i>Bougainvillea spectabilis</i> willd, and <i>Hibiscus rosa-sinensis</i>	Asaloyeh, Iran	0.55–5.15	1.50–15.34	–	[38]
<i>Platanus orientalis</i> L.	Isfahan, Iran	5.7–6.1	88.9–344.8 ($\mu\text{g/kg}$)	11.3–14.6	[39]
<i>Populus nigra</i>	Kırşehir, Turkey	1.16–2.49	0.50–0.67	5.53–6.73	This study
<i>Cedrus libani</i>		0.66–1.03	1.00–1.74	2.87–4.27	

–: Not available; *: Washed leaves (WL).

Au, Ce, Co, Cr, Cu, La, Mn, Mo, Ni, Sb, Sm, Ti, Th, U, V, W) pollution. The results of this study determined that black poplar bark yielded significant results compared to epiphytic lichen for monitoring heavy metal air pollution in urban and industrial areas.

Thus, the authors generally determined the metal concentrations in different plants gathered from different cities to appraise atmospheric pollution. When this study was compared to studies presented in the literature, it was found similar to the other studies (Table 4). However, in this study, the atmospheric quality and heavy metal distribution in the city of Kırşehir in Turkey was evaluated. Further, this study is the first study on the monitoring of the pollution caused by the casting factory in Central Anatolian region of Turkey. Hence, the study will contribute to the literature in this aspect.

CONCLUSIONS

We argued that if the levels of metals in the plants at the CFS are higher than the Boztepe stations and they exhibit statistically significant differences ($p < 0.05$), these plants may have biomonitoring potential. The levels of Ni, Pb and Cu were not significant in soil samples taken from different stations ($p > 0.05$). For this reason, we think that the changes in heavy metal levels observed in plants mostly effected by the parameters in the air for the studied elements. In this perspective, we suggest that *Cedrus libani* (for Pb and Cu) and *Populus nigra* plant (for Ni) have biomonitoring potential. Therefore, *Populus nigra* and *Cedrus libani* can be used as an economic tool for monitoring long-term pollution and accumulation of impurities. Other heavy metals can be studied in the tree species we work as a biomonitor. In addition, researches can be conducted on residential centers with high traffic and other centers.

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AUTHORSHIP CONTRIBUTIONS

Authors equally contributed to this work.

DATA AVAILABILITY STATEMENT

The published publication includes all graphics and data collected or developed during the study.

CONFLICT OF INTEREST

The author declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

ETHICS

There are no ethical issues with the publication of this manuscript.

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