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Monitoring the changes of germanium pollution in air and usability of *Cedrus atlantica* for pollution reduction

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Abstract

Heavy metal pollution is a serious threat to living organisms and ecosystems worldwide. Therefore, it is of great importance to identify suitable biomonitors that can be used to monitor the changes in heavy metal pollution and hyperaccumulator species that can be used to reduce pollution. In this study, the usability of *Cedrus atlantica* in monitoring the change in the concentration of germanium (Ge) in air and reducing pollution was evaluated. In addition, Ge pollution in the last 60 years in Düzce province, where air pollution is at a very high level, was evaluated and the source of pollution was tried to be determined. As a result of the study, it was determined that the species is a suitable species that can be used both to monitor the change of Ge pollution in the air and to reduce this pollution. It was determined that Ge pollution increased significantly in the study area after 2013. The results of the study reveal that this pollution is mostly caused by traffic and urban areas.

Keywords: Heavy metal; Germanium; *Cedrus atlantica;* Biomonitor; Phytoremediation

1. Introduction

In the last century, as a result of technological developments in the world and the reflection of these developments on industry, radical changes have been experienced in many areas, especially in population distribution, lifestyle, people's wishes and needs. As a result of these changes, the population has concentrated in certain areas and the problem of urbanization has occurred [1-9]. Urbanization has brought many problems and has become an irreversible problem that the world has to cope with today [10-17]. Another problem that is considered irreversible is global climate change [18-22].

The global problem that is linked to these two problems and considered by many researchers as the biggest problem worldwide is pollution [23-31]. In particular, air pollution is reported to cause approximately 6 million premature births, 3 million underweight babies and 7 million premature deaths worldwide every year [32,33]. World Health Organization (WHO) data show that almost the entire global population (99%) breathes air containing high levels of pollutants that exceed WHO-defined limits, with low- and middle-income countries suffering the highest exposure [34].

Among the components of air pollution, heavy metals are the most threatening and dangerous to human health [35-41]. Because many heavy metals can be toxic, carcinogenic and fatal for humans even at low concentrations. In addition, heavy metals can remain intact in nature for a long time and their concentrations in nature are constantly increasing [42-45]. Due to the importance of heavy metals for human health, many studies have been conducted on many heavy metals such as Pb, Ni, Zn, Cr, Cu, Mn, Cd and Al [46-48]. After the understanding of the possible damages of heavy metals

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on human health and ecosystem, studies on heavy metals such as Ba, Tl, Sr, Sb and V, which have not been emphasized much so far, have also intensified [49,50].

Germanium (Ge) is one of the elements that has not been the subject of many studies to date. Ge is a gray-white, brittle solid metalloid in elemental form. It shows both metallic and nonmetallic properties [51]. Excessive or prolonged exposure to Ge has been reported to have toxicological effects and damage to the kidneys, nervous system and lungs. Acute germanium poisoning can lead to depression, hypothermia, diarrhea, skin cyanosis, pulmonary edema, ascites, edema and changes in swelling of parenchymal cells of the liver, kidney or other organs. Some organogermanium compounds can cause nausea, vomiting, diarrhea and even liver and kidney damage and tremors [52]. When overexposure to Ge occurs, nephropathy, neuropathy and hepatotoxicity are often seen, and respiratory paralysis occurs at lethal doses [53]. Therefore, it is particularly important to monitor changes in Ge concentrations in the air and to reduce their concentrations because heavy metals pose much more serious health risks if they are inhaled [24]. Therefore, monitoring and mitigation of Ge pollution is of utmost importance. In this study, the accumulation levels of Ge in the trunk parts of cedar (*Cedrus atlantica*) trees growing in urban areas with high levels of heavy metal pollution were investigated and the potential of cedar trees in monitoring and mitigation of Ge pollution was tried to be revealed.

2. Material and methods

The study was carried out on cedar (*Cedrus atlantica*) growing in Düzce province. According to the World Air Pollution Report 2021, Düzce province is one of the 5 most polluted cities in Europe and it has been determined that heavy metal concentrations such as Cr [54], Bi [55], Sb [50], Pd [49] are quite high in the studies conducted in the region. Within the scope of the study, log samples taken by determining the north direction outside the vegetation season in 2022 were brought to the laboratory and the surface was leveled. It was determined that the tree subject to the study was 60 years old, and the wood was grouped into five-year groups. Then, sawdust samples were taken from each group of wood, inner bark and outer bark with the help of a steel drill. After standard drying procedures, the samples were analyzed with ICP-OES device and Ge concentrations were determined. This method is widely used for heavy metal analysis in previous studies in this field [56,57]. The data obtained were analyzed using the SPSS package program and analysis of variance was applied to the data. In addition, Duncan test was applied to the data with a margin of error below 5% ($p < 0.05$). The data were tabulated and interpreted by considering the results of Duncan test.

3. Results

Mean values and statistical analysis results for the variation of Ge concentration in *Cedrus atlantica* by organ and direction are given in Table 1.

Table 1 Variation of Ge concentration in *Cedrus atlantica* by organ and direction

Organ	North	East	South	West	F Value	Average
OB	3735.2 A	4205.4 B	5212.4 C	4156.7 B	29.5***	4327.4
IB	10468.2 B	4146.3 A	5030.5 A	3987.4 A	56.6***	5908.1
Wood	7650.6 B	4118.5 A	4715.7 A	3992.7 A	5.1**	5140.7
F Value	0.4 ns	0.0 ns	1.0 ns	0.0 ns		0.3 ns
Average	7572.2 B	4127.3 A	4773.7 A	4004.0 A	6.4***	

When the table values are examined, it is seen that the change in Ge concentration in *Cedrus atlantica* is statistically significant in all organs on the basis of direction. However, both in all directions and according to the mean values, the change in Ge concentration by organ is not statistically significant ($p>0.05$). When the values were analyzed, the highest value in the outer bark was obtained in the south direction, while the highest values in the inner bark and wood were obtained in the north direction. According to the mean values, two groups were formed as a result of the Duncan test, the north direction, where the highest value was obtained, was in the second group, while all other directions were in the first group. The variation of Ge concentration in *Cedrus atlantica* by period and direction is given in Table 2.

Table 2 The variation of Ge concentration in *Cedrus atlantica* by period and direction

Periods	North	East	South	West	F Value	Average
2018-2022	22853.6 bB	3389.0 A	3627.1 aA	4138.7 bcdA	9.4**	8502.1 bc
2013-2017	22670.5 b	Under Limit	4209.8 ab	4630.5 cd	2.2 ns	10503.6 c
2008-2012	5569.7 aB	4223.6 A	4184.1 abA	4045.6 bcA	7.2*	4505.7 ab
2003-2007	5172.7 a	4348.0	4448.5 bc	4268.2 cd	2.9 ns	4559.3 ab
1998-2002	4385.8 a	4365.0	4426.1 bc	4179.3 bcd	0.2 ns	4339.0 ab
1993-1997	4425.9 a	4157.2	4641.6 bcd	4566.0 cd	0.4 ns	4447.7 ab
1988-1992	4358.4 a	3825.8	4481.5 bc	4384.5 cd	1.0 ns	4262.5 ab
1983-1987	4716.0 aA	4532.6 A	5774.1 fB	5036.7 dAB	3.4 ns	5014.8 ab
1978-1982	4628.8 aA	3777.5A	5567.6 efB	4178.9 bcdA	9.2**	4538.2 ab
1973-1977	4235.6 aB	4394.5 B	4828.6 bcdB	2574.5 aA	13.8**	4008.3 a
1968-1972	4424.8 aB	4400.7 B	5305.4 defC	3324.9 abA	19.8***	4364.0 ab
1963-1967	4365.8 aBC	3889.5 B	5094.2 cdeC	2584.5 aA	12.7**	3983.5 a
F Value	3.2*	1.9 ns	8.7***	8.2***		2.0*
Average	7650.6 B	4118.5 A	4715.7 A	3992.7 A	5.1**	

When the values in the table are analyzed, it is seen that the directional change in Ge concentration in *Cedrus atlantica* was not statistically significant in the periods 1983-2007 and 2013-2017. The change on a period basis is statistically significant in all directions except east. According to the average values, the highest values were obtained in the north direction, while the highest values were obtained between 2013-2022 on a period basis. Apart from this, it is seen that there may be large differences between neighboring directions in the same period or between consecutive periods in the same direction. This result can be interpreted as a limited level of Ge transfer within the wood.

4. Discussion

As a result of the study, it was determined that *Cedrus atlantica* can accumulate a significant amount of Ge element in both wood and bark parts. As a result of the study, it was determined that the values obtained in the bark and wood parts did not differ statistically significantly. However, it is generally stated in the studies that the heavy metal concentrations obtained in the outer bark are at very high levels [57,58]. This is because in areas with high levels of heavy metal pollution, heavy particulate matter becomes a sink by being contaminated with heavy metals and easily adheres to the outer bark with a rough surface, significantly increasing the heavy metal concentration in the bark [27,28]. However, no statistically significant difference was found between bark and wood in this study.

As a result of the study, the highest Ge concentrations were obtained in the north direction according to the mean values. This result probably indicates that Ge originates from traffic or urban areas. Because there is a highway with heavy traffic in the north of the study area along with residential areas. Previous studies show that heavy metal pollution in the air is largely anthropogenic in origin such as industry, mining activities, traffic and urban areas [32,36,59]. Urban areas are also identified as a source of pollution in a very large amount and variety. In these areas, both construction and demolition activities, as well as human activities such as solid waste incineration and household waste, significantly increase the pollution level [60-66].

As a result of the study, it was determined that Ge concentration increased considerably in the periods after 2013 according to the average values. This is thought to be caused by vehicle traffic and human activities in urban areas. As a matter of fact, while the population of Düzce was 351,509 people in 2013, it increased continuously after this date and reached 405,131 people in 2022 when the study was conducted [67]. As it is known, a large number of houses have been built in recent years in order to meet the housing needs of the increasing population. In addition to this, activities such as the demolition of earthquake-resistant houses and the construction of new houses and the renovation of old buildings have led to a high amount of housing construction [68-72]. At the same time, the amount of vehicles used by the increasing population also increases, and in parallel with this increase, the amount of human activities and pollution also increases [54]. For this reason, the increase in Ge concentration in the air after 2013 in the study area is normal.

As a result of the study, it was determined that Ge concentrations in *Cedrus atlantica* wood were highly variable and there were large differences between Ge concentrations in different directions in the same period or in the same direction in different periods. For example, the Ge concentration determined in the north direction in the period 2013-2017 was 22670.5 ppb, while the Ge concentration measured in the same direction in the period 2008-2012 was 5569.7 ppb. In the same period, the Ge concentration in the neighboring eastern direction was below the determinable limits. These results indicate that there are large differences in Ge concentration between neighboring wood masses and therefore the transfer of Ge in wood is limited.

It is emphasized that the most important lack of information on the usability of biomonitors in monitoring heavy metal pollution is the transfer of elements in wood. In the studies, it is stated that the displacement potentials of different elements in the wood of different species are at different levels. In some studies on this subject, Zn and Pb are displaced in *Cedrus deodora* wood, Cu remains constant, Ni, Zn, Pb, Cr and Zn are limited in *Corylus colurna* wood, but Cd can be displaced, Sn is limited in *Pinus pinaster* and *Picea orientalis*, It has been reported that in *Cupressus arizonica* wood, Cd, Ni, Fe and Zn have limited translocation but Bi, Li and Cr can be translocated, and in *Cedrus atlantica* wood, Ni transfer is very limited but Co can be translocated [40,44,73]. If elements can be displaced in the wood, it is not possible to use that species as a biomonitor.

In plants, the transport of elements within the wood is largely related to cell structure and especially the cell wall (apoplastic pathway). Cell wall proteins are activated in various abiotic stresses [73]. Plants are frequently exposed to stress factors such as drought [74-77], frost [78], UV-B stress, radiation [79], and heavy metal pollution [44-46] during their life cycle. However, the stress factors to which plants are most exposed are climatic stress factors. Because plant development depends on the interaction between genetic structure [80-85] and environmental conditions [86-90]. Therefore, factors that cause significant and permanent changes in climatic parameters such as global climate change trigger stress mechanisms of plants [91,92].

The potential of plants to absorb and accumulate heavy metals is shaped by the interaction of many factors that affect each other. The most important of these factors are the structure of the heavy metal, its interaction with the plant organ and weather conditions [27,28,32]. Besides these, one of the most effective factors in this process is plant habitus [49]. Plant habitus is also shaped primarily by genetic structure [93,94] as well as edaphic [95] and climatic [96-99] factors and stress factors [69,76,93]. The entry and accumulation of heavy metals into the plant body is the result of a complex mechanism shaped under the influence of many factors and has not yet been completely solved [25,57,58].

5. Conclusion

Heavy metal pollution is a major problem for all living organisms and ecosystems around the world. Therefore, it is necessary to identify suitable biomonitors that can be used to monitor heavy metal pollution and hyperaccumulator species that can be used to reduce pollution. Although many studies have been conducted on the subject so far, these studies are mostly related to common heavy metals such as Pb, Ni, Cr, Cu. However, detailed studies should be carried out on other heavy metals that are less well known but highly harmful. In recent years, studies on heavy metals such as Pd, Sr, V, Tl and Sn have started to be carried out. However, many heavy metals are still not included in these studies. In this study, the usability of *Cedrus atlantica* in monitoring the change in air pollution of germanium, one of the neglected heavy metals, and reducing pollution was evaluated. As a result of the study, it was determined that *Cedrus atlantica* is a suitable species that can be used both for monitoring the change of Ge pollution in the air and for reducing this pollution. It is recommended that studies on the subject should be continued by diversifying and increasing.

Compliance with ethical standards

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Disclosure of conflict of interest

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

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