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HEAVY METALS ACCUMULATION IN SILVER FIR NEEDLES IN SWIETOKRZYSKI NATIONAL PARK

Abstract: The article demonstrates the results of the research studies related to the air polluted with heavy metals in the area of Swietokrzyski National Park. The two-year-old needles of *Abies alba* (*Mill*) were used as the bioindicator with the intention of carrying out the research. The studies were conducted in the autumn of 2012. The results showed the spatial variability of concentrations in the range of the analysed metal deposition patterns in the needles of *Abies alba* (*Mill*). The average content of the analysed elements seemed to be the highest in the case of zinc (26.6 $mg \cdot kg^{-1}$ d.m.), strontium (6.5 $mg \cdot kg^{-1}$ d.m.) and nickel (1.6 $mg \cdot kg^{-1}$ d.m.). The research studies revealed that the significant role in determining the content of heavy metals in the two-year-old needles was played by the communication. The highest values were recorded at the research sites situated in the immediate neighbourhood of the voivodeship roads. It was also confirmed that the content of metals was influenced by the so-called low emission from the household and welfare sector together with the remote imission.

Keywords: bioindication, air pollution, *Abies alba*

Introduction

The research studies conducted in different regions of the world, associated with the circulation of heavy metals (TM) in the environment, focus on to their potential threat related to their toxicity and harmfulness to living organisms as well as their surroundings [1]. Consequently, in an attempt to estimate the degree of the environmental pollution, the living organisms, such as lichen thalli, needles or mosses, are employed more and more frequently as bioindicators [2-8]. The silver fir needles, i.e. of *Abies alba* (*Mill*) appear to be used most commonly as bioidicators. Undeniably, such organisms, due to their accumulation and bioindicator abilities, are often used to conduct the monitoring research studies. The needles of the silver fir trees, keeping the dusts on their surface (in epicuticular waxes) can play the role of the passive sampler, and in this sense, it can be treated as the accumulating bioindicator [9].

The research studies with the use of silver fir needles were conducted in the Swietokrzyskie Mountains. The Swietokrzyskie Mountains, elevated compared to the surrounding area, are influenced by both local and remote industrial and vehicle emissions, in particular from the prevailing western and south-western wind directions [10]. It allows the possibility of the regular and long-term direct impact of the atmospheric air masses saturated with industrial and communication emissions on the inhabitants and living

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organisms of this particular region [10, 11]. The research conducted by Kozlowski [11] by the use of an ED-XRF instrument for the microanalysis, indicated the existence of small vitreous balls known as spherule on the surface of silver fir needles. Spherules are considered to have the composition characteristic of aluminosilicates with the significant amount of iron in them. It is the product typical of coal combustion processes [12]. The size of the spherules ranges from a one to fifty μm [13]. In the combustion process, the iron contained in the coal (mainly in the form of sulphides) is converted into the magnetic iron oxides (mainly magnetite and maghemite). The photos taken to show the surface of the silver fir needles confirm the obvious influence of the energy industry on the natural environment in this particular area of Swietokrzyski National Park. The dominant wind directions and the size of the particles found there indicate that the Upper Silesian Industrial Region (Polish abbreviation: GOP) can be the potential source. As proven by Steinnes and Friedland [14] as well as Sarris et al. [15] heavy metals, including Cu, Pb and Zn, can be transferred over long distances in the atmosphere. Furthermore, forest stands under the influence of the pollution can increase the deposition of heavy metals [16], which, consequently, can lead to the increase of their content in the forest soils [17].

Analysing the chemical composition of the silver fir needles from the specific location, it is possible to gain information on the pollutants currently existing in the ecosystems as well as the attempt to evaluate the impact of anthropogenic emissions can be made. It allows to prepare the evaluation of such emissions considering the multi-year scale together with estimating the potential impact of anthropogenic emissions on plant organisms [18].

The aim of the research studies was to recognise the environmental pollution of the forest ecosystems in Swietokrzyski National Park in the range of heavy metals using two-year-old needles of *Abies alba* (*Mill*).

Research area

The part of Swietokrzyski National Park, which covers the area of 7,626.45 ha, constituted the area of the studies. Specifically, the research area involved the part of the park, which is located at the border of the buffer zone (the exact area of 20,786.07 ha). According to the regional division, this area is located in the Swietokrzyskie Mountains (342.34-35), in the 20th Western Malopolska climate region. The area is distinguished by the numerous days with freezing cold weather and the precipitation as well as by a very small number of chilly days without the precipitation [19].

Due to its location in the system similar to the latitudinal range together with its strong fragmentation, the park is extensively exposed to the local and regional anthropopressure, mainly low emissions of the atmospheric air pollution during the heating period.

Material and methods

The so-called bioindication studies were conducted in Swietokrzyski National Park in September 2020 (Fig. 1). The two-year-old needles of *Abies alba* (*Mill*), i.e. the European sliver fir were chosen for the laboratory research. The samples were collected from 30 research sites, and next, they were brought to the Laboratory of the Environmental Studies, where they were thoroughly examined. After drying them at the room temperature, the samples were then dried at 65 °C to get the constant weight. The dried samples were subsequently ground by the use of the IKA grinding mill and then mineralised employing the method of Wet Air Oxidation with the use of microwave energy by means of Anton Paar Multiwave 3000 - Microwave Digestion System. The evaluation of the air pollution was performed based on the concentration of heavy metals (i.e. Pb, Cd, Cu, Ni, Zn, Sr), which in the mineralised samples were assayed using the mass spectrometer, i.e. OptiMass 9500 ICP-MS-TOF from GBC Scientific Equipment.

The received results were statistically performed using the “Statistica 13.1 software”. To separate the spatial groups of the examined samples differentiated according to the concentration of heavy metals, Ward’s method considering the agglomerative hierarchical clustering procedure was used. Furthermore, Ward’s method was generalised to use with Manhattan distances as the similarity measure of unit clusters.

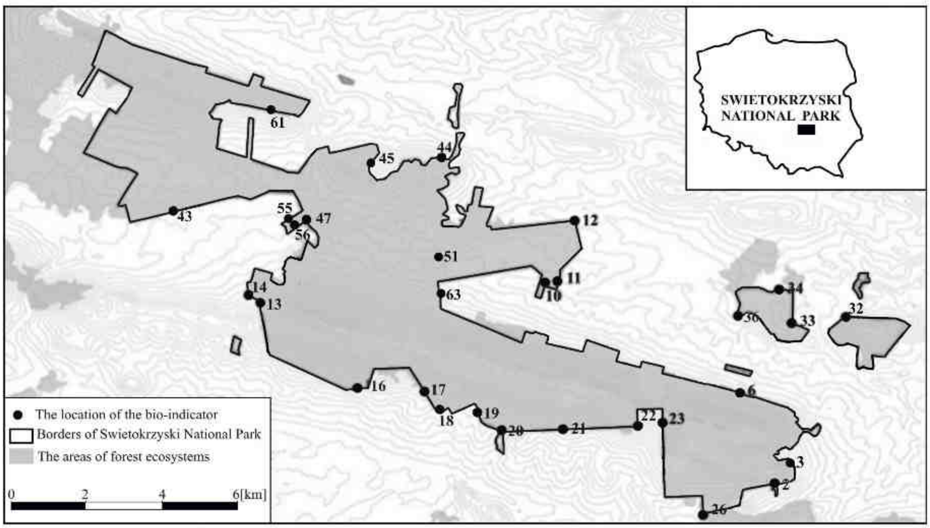

Fig. 1. Study area. In the text, the research sites are described as, e.g. the research site 2 - SPN02, the research site 3 - SPN03, the research site 4 - SPN04, etc.

Results and discussion

The performed analysis of the chemical composition of the two-year-old needles shown the varied content of heavy metals (Table 1, Fig. 2). The highest value of the concentration was recorded in the case of zinc with the average value of 26.6 $mg \cdot kg^{-1}$ d.m. and in the range from 14.1 to 47.4 $mg \cdot kg^{-1}$ d.m. as well as the coefficient of variation equal to 35.8. The next element was strontium with the average value of 6.5 $mg \cdot kg^{-1}$ d.m., than copper - 3.0 $mg \cdot kg^{-1}$ d.m., nickel - 1.6 $mg \cdot kg^{-1}$ d.m. and finally lead with 0.8 $mg \cdot kg^{-1}$ d.m. The lowest concentration was revealed in the case of cadmium with the average value of 0.1 $mg \cdot kg^{-1}$ d.m.

The conducted analysis of the agglomeration with the use of Ward’s method considering Manhattan distances revealed three spatial groups, which were similar in respect of heavy metal contents (Fig. 3). The first one was related to the sites characterised by the highest concentrations of Zn (average - 43.2 $mg \cdot kg^{-1}$ d.m.) and Pb (1.2 $mg \cdot kg^{-1}$ d.m.) among all analysed groups. They include six research sites (Polish abbreviations: SPN03, SPN13, SPN14, SPN19, SPN26 and SPN43), which were located in the neighbourhood of three voivodeship roads, i.e., DW752 (SPN13, SPN14 and SPN43), DW753 (SPN19 and SPN26) or DW756 (SPN03). The research studies conducted in the area of the Black Sea, which used a different bioindicator showed that, e.g. lichen samples contained the increased concentrations of titanium, chromium, manganese, iron, cobalt, nickel, copper, zinc, tin, barium and lead. The strong positive correlation between the concentration of lead in analysed bioindicator and the traffic intensity was recorded [20]. The Zn concentrations also indicated the highest concentrations in this spatial group. It happened due to the reduction of Pb content in petrol owing to the recommendations in the sphere of Zn being a good exhaust emission indicator [21].

Table 1

Accumulation of heavy metals in needle - results [$mg \cdot kg^{-1}$ d.m.]

Heavy metals	**Average**	**Minimum**	**Maximum**	***SD***	***CV***
Pb	0.8	0.3	2.0	0.4	52.3
Cd	0.1	0.0	0.4	0.1	139.7
Cr	0.8	0.4	1.5	0.2	29.5
Cu	3.0	0.6	6.2	1.6	52.4
Ni	1.6	0.3	4.2	0.9	54.2
Zn	26.6	14.1	47.4	9.5	35.8
Sr	6.5	2.3	17.4	4.2	64.4

SD - standard deviation, *CV* - coefficient of variation

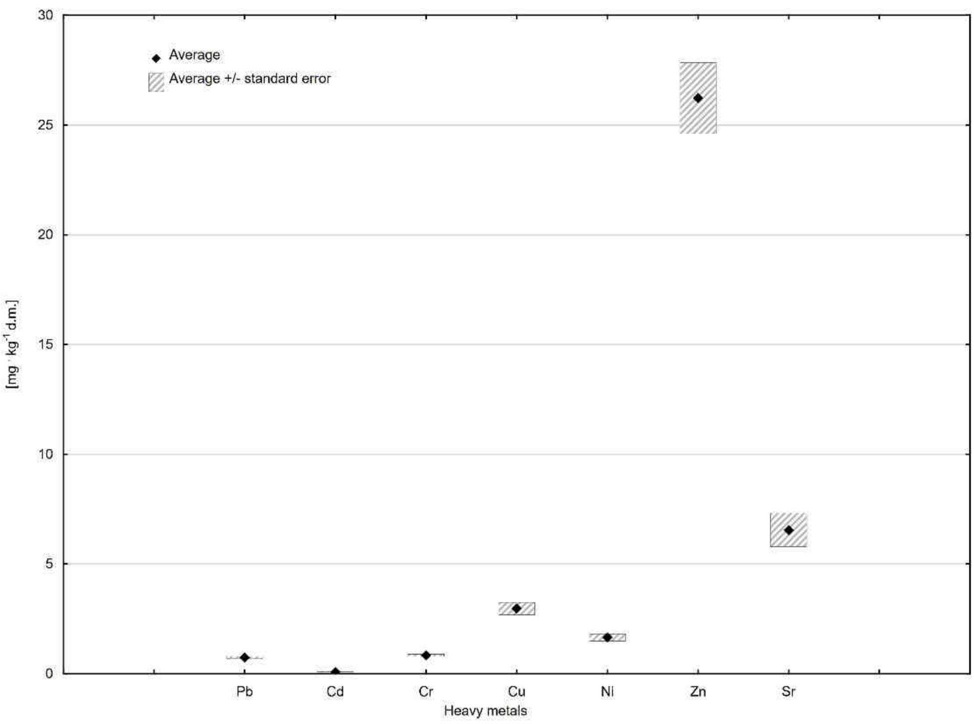

Fig. 2. Average values together with the standard error of the analysed heavy metal content in samples located in Swietokrzyski National Park

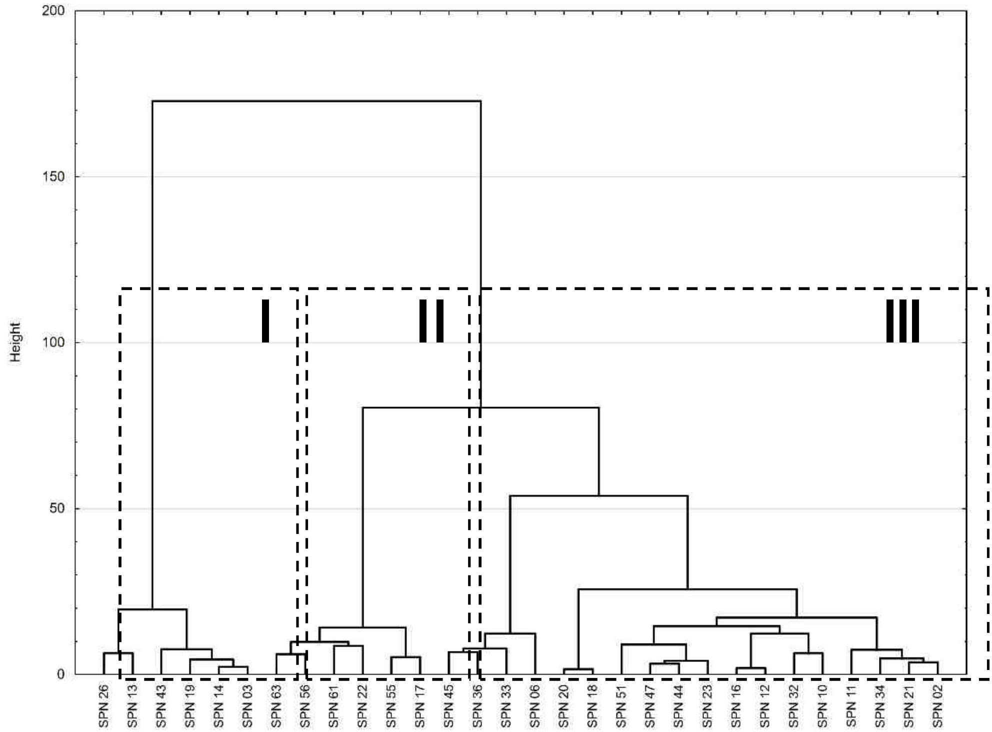

Fig. 3. Ward’s agglomeration results, Manhattan distance for the silver fir needle exposed in Swietokrzyski National Park

The second group was determined mainly by the following research sites SPN17, SPN22, SPN55, SPN56, SPN61, SPN63. They are located situated in the neighbourhood of local places of residence and local roads, moreover, they were characterised by relatively heavy traffic. At these sites, higher than average values of the concentrations of Pb, Cu, Sr were noticed, which could be caused by the emission sources characteristic of both the household and welfare sector as well as the communication-related pollution (remote emission sources).

The third group was primarily located along the southern borders of Swietokrzyski National Park as well as the places away from the local sources of emission (research sites: SPN02, SPN06, SPN10, SPN11, SPN12, SPN16, SPN18, SPN21, SPN23, SPN32, SPN33, SPN34, SPN36, SPN44, SPN 45, SPN47 and SPN51). The lowest concentrations of heavy metals were recorded at these sites, i.e., Zn - 21.0 $mg \cdot kg^{-1}$ d.m., Sr - 4.5 $mg \cdot kg^{-1}$ d.m., Cu - 2.3 $mg \cdot kg^{-1}$ d.m., Ni - 1.4 $mg \cdot kg^{-1}$ d.m. and Pb - 0.6 $mg \cdot kg^{-1}$ d.m. This particular area created the natural barrier to the transfer of pollutants from the western and south-western sectors. Together with the prevailing wind directions, the transfer of the pollutants, primarily connected with the so-called low emissions from the household and welfare sector and neighbouring towns, reached the area of the park. In this group, the essential role was also played by research sites located along the northern boarders of the park, where there was a lack of emission sources with the exception of the household and welfare sector.

Apart from the recognised factors influencing the content of heavy metals in the chosen bioindicators, the elevation could also have an significant impact on such content. The research studies carried out by Ciezka et al. [22] demonstrated that the highest concentrations of Zn, Pb and Cu were recorded for the samples located at the highest measuring sites, which signified the remote emission sources. Corresponding to the principal component analysis (PCA), these authors also indicated that the variability of metal concentrations in lichen thalli was influenced by the transport of pollutants from long distances as well as the local sources connected with the fuel combustion. The research outcomes conducted with the use of the thalli are confirmed by the research studies carried out with the help of the silver fir needles. In the research conducted by Gandois et al. [16] as well as Gandois and Probst [23], the dependence of the increase in the range of heavy metals accumulation (Cu, Cd and Ni) on elevations was confirmed The conducted research by Gandois and Probst [23] with the use of the needles of *Abies alba* (*Mill*) dealing with the content of heavy metals in the Pyrenees also verified that some metals, such as Cd, Cu, together with lead, to the great extent, are derived from the atmospheric deposition. In the case of lead, the content of this element in epicuticular waxes appeared to be ten times greater than in the interior part of the needles, which specified the anthropogenic origin of this element.

The comparison of the results of zinc concentration in Swietokrzyski National Park with other mountain areas, e.g. from the Choc Mountains (94 $mg \cdot kg^{-1}$ d.m. - research by Gresikova and Janiga [24]), the Trzebnickie Hills (30.9-35.0 $mg \cdot kg^{-1}$ d.m. - research by Szymura [25]) or the Pyrenees (43.8 $mg \cdot kg^{-1}$ d.m. - research by Gandoist and Probst [23]) indicates that the content of this metal is at a lower or similar level. The average value was within the lower value limits identified in the range of the realised research known as ICP-Forests, in which the zinc content ranged from 22 (percentile - 5 %) to 45 (percentile - 95 %) $mg \cdot kg^{-1}$ d.m. [26]. The contents of the remaining metals, i.e. Pb (0.8 $mg \cdot kg^{-1}$ d.m.) was lower than in the Choc Mountains [24] and significantly higher than in the Pyrenees (0.23 $mg \cdot kg^{-1}$ d.m.) and Wogez (0.33 $mg \cdot kg^{-1}$ d.m. - research by Gandois and Probst [23]).

Conclusion

The conducted research showed the various occurrence of heavy metals content in fir needles in Swietokrzyski National Park. The highest contents (inter alia, Zn and Pb) were recorded in the samples located in the immediate neighbourhood of roads, which indicated the communication sources of the emission of such metals. The spatial variability of the heavy metal contents demonstrated that in the examined area, the major role considering the emission of heavy metals to the environment was also played by the local emission sources (the combustion of fuels in the household and welfare sector), as well as the remote ones connected with the transport of pollutants from the prevailing wind directions, specifically the south-western and western sectors.

The increased heavy metal concentrations was noticed in the samples located along the southern border of the park, in particular at the point of the connection of voivodeship roads and the vicinity of places of residence, which signified the need for the systematic research to monitor the changes in the scope of the level of anthropopressure associated with its impact on the forest ecosystems of Swietokrzyski National Park.

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