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HEAVY METALS ACCCUMULATION IN LICHENS IN SWIETOKRZYSKI NATIONAL PARK

AKUMULACJA METALI CIĘŻKICH W PLECHACH EKSPONOWANYCH NA TERENIE ŚWIĘTOKRZYSKIEGO PARKU NARODOWEGO

Abstract: The article reveals the outcomes of the research studies related to air polluted with heavy metals in Swiętokrzyski National Park. The thalli of *Hypogymnia physodes L.* were used as the bioindicator in order to conduct the research. The samples of monk's-hood lichen were transplanted from the unpolluted area of north-eastern Poland to the area of Swietokrzyski National Park. The research studies were carried out in the warmer half of 2019. The received outcomes indicated the spatial variability of concentrations in the range of analysed metal deposition patterns in the lichen thalli. The average content of the analysed elements tended to be the highest in the case of iron (1,111 mg · kg^{-1} d.m.), zinc (87.7 mg · kg^{-1} d.m.) and strontium (27.7 mg · kg^{-1} d.m.). The research revealed that the important role in determining the content of heavy metals in the lichen thalli was played by the communication. The highest values were recorded at the sites located in the immediate neighbourhood of the voivodeship roads. It was verified that the content of metals was also influenced by the so-called low emission from the household and welfare sector as well as remote immission.

Keywords: bioindication, air pollution, *Hypogymnia physodes*

Introduction

The research studies carried out in various regions of the world, related to the circulation of heavy metals in the environment, pay attention to their potential threat connected with their toxicity and harmfulness to living organisms as well as their surroundings [1]. For that reason, the living organisms, such as lichen thalli, needles or mosses, are being used more and more frequently as bioindicators so as to estimate the degree of the environmental pollution [2–7]. Definitely, lichens are the most commonly used bioidicators. The research studies dealing with their use have been conducted in various regions of the world for many years [8–15]. These organisms, as a result of their accumulation and bioindicator abilities, are regularly used in monitoring studies [7]. One of the methods of employing lichens in

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this type of research studies refers to the transplantation of indigenous (autochthonous) species from the areas characterised by low pollution levels to the areas where lichens do not occur naturally or their populations are significantly limited due to the pollution caused by human activities [16].

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 [17]. It creates the possibility of the frequent and long-term direct impact of the atmospheric air masses saturated with industrial and communication emissions on the inhabitants and living organisms of this particular region [17]. Furthermore, as revealed by Steinnes and Friedland [18] as well as Sarris et al. [19] heavy metals, including Cu, Pb and Zn, can be transferred over long distances in the atmosphere.

The aim of the research studies was to evaluate the environmental pollution of the forest ecosystems in Swiętokrzyski National Park in the range of heavy metals using *Hypogymnia physodes* (L.).

Material and methods

The so-called bioindication studies with the use of lichens were carried out in Swietokrzyski National Park (Fig. 1). *Hypogymnia physodes* (L.) and epiphytic lichen, i.e. common species in Europe were chosen for the research studies [20]. The area of the Borecka Forest, located in the Warmian-Masurian Voivodeship, in the Kruklanki Administrative District (Gizycko County), was specified for the lichen collection. The lack of the local sources of the pollution along with the low level of anthropopressure are confirmed by the national and international research programmes. These pro-

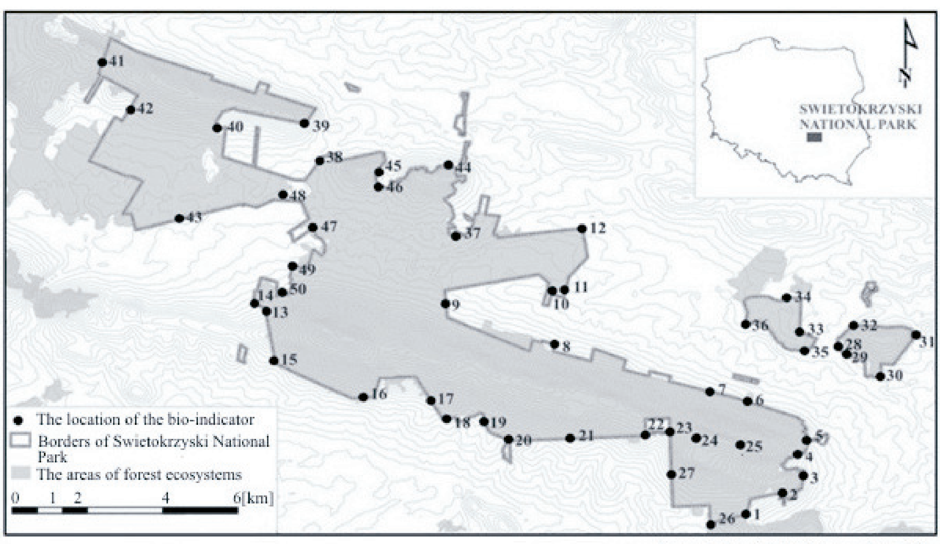

Fig. 1. Research area

grammes included the area of the Borecka Forest in the functioning network within the framework of the State Environmental Monitoring Program [21]. Lichens of the *Hypogymnia physodes* kind, placed on the approximately 30-cm twigs from the Borecka Forest were brought, and then, located at 50 measuring sites as high as approximately 2 m above soil level, by using self-locking plastic ties. The time of the lichen exposure reached up to 6 months (the season of summer) from 1 April, 2019 to 30 September, 2019. After the transplantation time, the samples were transported to the Environmental Research Laboratory, where they were subjected to further laboratory examinations**.** The lichen thalli, which were first debarked and dried at 60 °C, were then mineralized employing the method of Anton Paar Multiwave 3000 – Microwave Digestion System. The assessment of the air pollution was performed based on the concentration of heavy metals (i.e. Pb, Cd, Cu, Sr, Pb, Zn), which in the mineralized samples were assayed using the mass spectrometer, i.e. OptiMass 9500 ICP-MS-TOF from GBC Scientific Equipment.

The outcomes 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.

Results and discussion

The performed analysis of the chemical composition of the transplanted lichen samples after 6 months of their exposure demonstrated the differentiated content of heavy metals (Table 1, Fig. 2). The highest value in the sphere of the concentration was indicated in the case of iron, with the average value of 1,111 mg $\cdot$ kg^{-1} d.m. and its fluctuations from 334.9 to 2.083 mg $\cdot$ kg^{-1} d.m. as well as the lowest coefficient of variation (*CV*) among the examined metals. The next, in terms of its value, appeared zinc with the average value of 87.7 mg $\cdot$ kg^{-1} d.m., followed by strontium – 27.7 mg $\cdot$ kg^{-1} d.m., then, copper – 8.07 mg $\cdot$ kg^{-1} d.m. and lead with 4.64 mg $\cdot$ kg^{-1} d.m. occurred as the last one. The lowest concentrations were recorded in the case of cadmium with the average value of 0.09 mg $\cdot$ kg^{-1} d.m.

Table 1

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

Heavy metals	Av	Min.	Max.	*SD*	*CV*
Pb	4.64	1.23	11.8	2.25	48.4
Cu	8.07	0.63	31.9	6.82	84.5
Zn	87.7	25.6	163.6	32.34	36.9
Fe	1,111	334.9	2,083	379.6	34.2
Cd	0.09	0.00	2.73	0.42	458.3
Sr	27.7	8.46	67.3	14.2	51.1

Av – average, Min. – minimum, Max. – maximum, *SD* – standard deviation*, CV* – coefficient of variation.

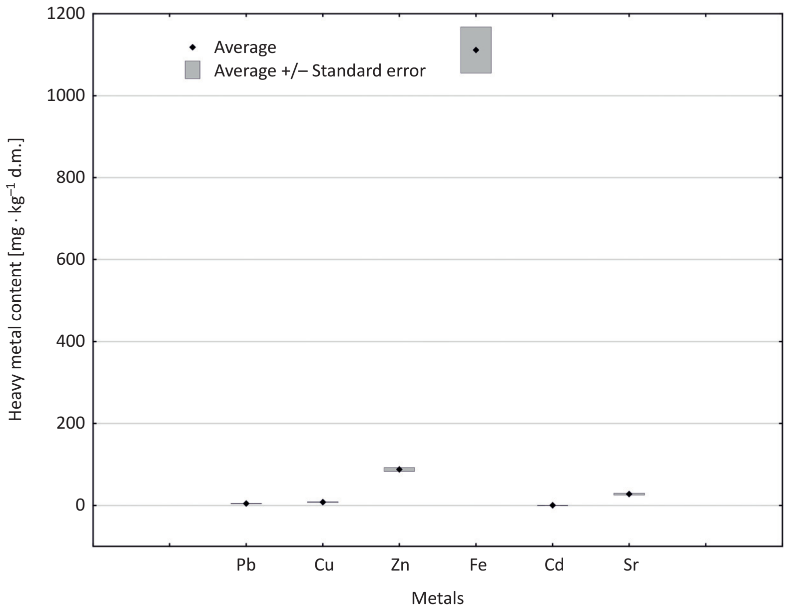

Fig. 2. Average values together with the standard error (*SE*) of the analysed heavy metal content in samples located in Swietokrzyski National Park

The analysis of the agglomeration with the use of Ward's method considering Manhattan distances specified four spatial groups, which were similar in respect of heavy metal contents (Fig. 3). The first one referred to the sites characterised by the highest concentrations of Zn (average 123.9 mg · kg^{-1} d.m.), Fe (1.815 mg · kg^{-1} d.m.), Cu (12.9 mg · kg^{-1} d.m.) as well as Pb (8.6 mg · kg^{-1} d.m.) among all analysed groups. They involve four research sites (Polish abbreviations: SPN01, SPN13, SPN19 and SPN46), which were located in the neighbourhood of two voivodeship roads, namely nr 752 (SPN13 and SPN46) and nr 753 (SPN01 and SPN19). The research studies carried out in the region of the Black Sea constituted that 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 lichens and the traffic intensity was recorded [22]. The Zn concentrations also indicated the highest concentrations in this spatial group. It occurred due to the reduction of Pb content in petrol as the consequence of the recommendations in the range of Zn being a good exhaust emission indicator [23].

The second spatial group is constituted mainly by the sites located along the southern border of Swietokrzyski National Park (measuring sites of SPN 2, 4, 5, 9, 14, 15, 16, 17, 21, 26, 31, 41 and 47). Higher values of the concentrations of heavy metals than the average ones were recorded there. Nevertheless, it must be stated that they were still lower than those revealed in the neighbourhood of roads (Zn 109.1 mg · kg^{-1} d.m., Fe 1399 mg · kg^{-1} d.m., Cu 7.8 mg · kg^{-1} d.m. and Pb 5.5 mg · kg^{-1} d.m. respectively). This particular area creates the natural barrier to the transfer of pollutants from the western

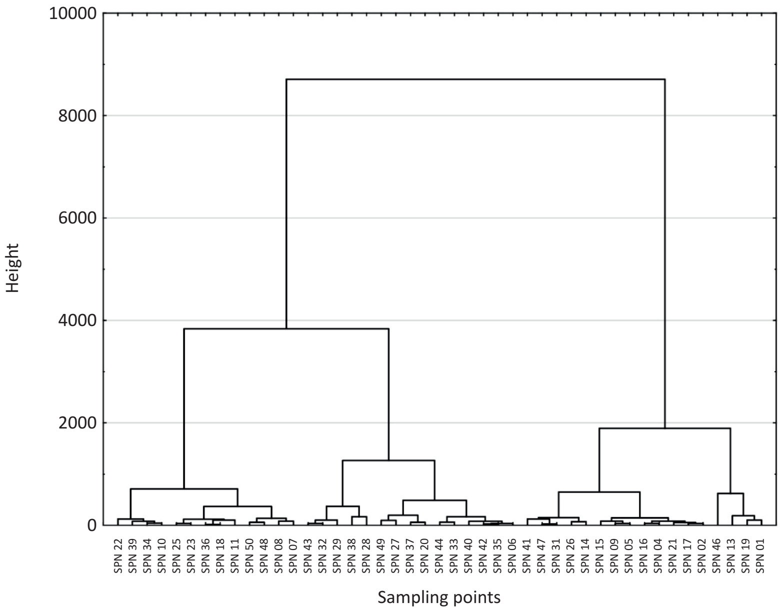

Fig. 3. Results of Ward's Method, i.e. agglomerative hierarchical clustering procedure considering Manhattan distances for the lichen samples exposed in Swietokrzyski National Park

and south-western sectors. Together with the prevailing wind directions, the pollutants, mainly linked to the so-called low emissions from the household and welfare sector and neighbouring towns, reach the area of the park. The important role is also played by the communication-related pollution in this range.

The lowest concentrations of heavy metals were recorded at the sites primarily located along the northern boarders of the park, where the significant emission sources, except for the household and welfare sector, can be spotted. The average concentrations of metals in the lichen thalli of this spatial group could be identified respectively – 59.7 mg · kg^{-1} d.m. for Zn, 691.8 mg · kg^{-1} d.m. for Fe, 5.5 mg · kg^{-1} d.m. for Cu, and 2.8 mg · kg^{-1} d.m. for Pb.

Apart from the recognised factors influencing the content of heavy metals in the lichen thalli, the elevation can also have an impact on such content. The research conducted by Ciężek et al. [14] identified that the highest concentrations of Zn, Pb and Cu were found at the highest measuring sites, which signifies the remote emission sources. In line with the principal component analysis (*PCA*), these authors also constitute that the variability of metal concentrations in lichen thalli is influenced by the transport of pollutants from long distances along with the local sources associated with the fuel combustion. Baranowska-Bosiacka et al. [24] indicated that the thalli of *Hypogymnia* kind accumulated Cu, Pb and Zn in the preferable way. Moreover, Parzych et al. [25] shows that *Hypogymnia physodes*, among all the examined lichens, contained the highest concentrations of Pb. It can result from the undulated thalli which can increase the contact area [26].

It should also be emphasised that the lichen thalli from sites located in the immediate neighbourhood of the roads after the exposure period demonstrated the significant macroscopic changes revealed by their discoloration and turning brown. Jozwiak [27] argues that the anthropogenic stress caused by the automotive pollution tends to be the source of such process.

Conclusion

Derived from the conducted research studies, the diversified content of heavy metals in the transplanted lichen samples in Swietokrzyski National Park was indicated. The highest contents (inter alia, Zn and Pb) were registered in the samples located in the immediate neighbourhood of roads, which can constitute the communication sources of emissions of such metals. The spatial variability of the heavy metal contents indicated that in the analysed area, the significant role in view of the emission of heavy metals to the environment is also played by the local emission sources (the combustion of fuels in the household and welfare sector), as well as the remote ones related to the transport of pollutants from the prevailing wind directions concerning the south-western sector as well as western sector.

The increased heavy metal concentrations, found in the samples located along the southern border of the park, indicate the need for the systematic research so as to monitor the changes in the range of the level of anthropopressure considering the forest ecosystems of Swietokrzyski National Park.

Acknowledgement

The research studies were conducted thanks to co-financing from the Forest Improvement Fund provided by the State Forests – National Forest Holding in 2019. (Final research report on: "Assessment and forecasting the impact of anthropopression on forest ecosystems Swiętokrzyski National Park").

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