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**BIOMONITORING OF HEAVY METALS
IN THE BIESZCZADY NATIONAL PARK USING SOIL
AND *Fagus sylvatica* L. LEAVES**

**BIOMONITORING METALI CIĘŻKICH
W BIESZCZADZKIM PARKU NARODOWYM
PRZY UŻYCIU GLEBY I LIŚCI *Fagus sylvatica* L.**

Abstract: The investigation of zinc, cadmium, lead and copper content was carried out in the soil (from the level 0–10 cm) and in the leaves of European beech (*Fagus sylvatica* L.) in the Bieszczady National Park.

Samples of soil and plants material were collected in 2007 from 63 selected sites. The level of Zn, Cd and Cu in the plants leaves and soil was below the values considered as toxic levels for the protected area. The lowest and the average (4,4 µg/g d.m.) concentrations of copper in the leaves of *Fagus sylvatica* L. were definitely lower than the normal level, which indicated a deficiency of that element. In the analyzed soil samples it was noted that the concentration of Pb (mean 31 µg/g d.m.) which as higher than the normal level for the protected area.

Keywords: heavy metals, *Fagus sylvatica* L., Bieszczady National Park

National parks usually include well-preserved and unspoiled parts of nature, shaped by the specificity of particular environment and adapted to it in the long process of evolution [1].

Forest ecosystems, including protected reserves, are subject to different dangers whose scale increases all the time [2]. Nowadays some disadvantageous changes can be observed in the protected parts [3]. They are caused by various factors. The most important is the industrial pollution, above all heavy metals and sulfur, which affect the ecosystems over a long period of time.

75 % of Polish parks are situated in the threatened areas, ie where the environment contamination by the toxic metals and gases repeatedly exceeds the standards for the protected areas [4]. One of them is the Bieszczady National Park, which protects the nature of the Eastern Carpathians.

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European beech (*Fagus sylvatica* L.) in the Bieszczady National Park is the most frequent and common species. Next to oaks, it is the most important deciduous species which contributes to the forest expansion. The chemical analysis of the assimilation apparatus and the bark of European beech (*Fagus sylvatica* L.) is often used in the biomonitoring of the environment [1, 5, 6].

The objective of this elaboration was to determine a load factor of the chosen heavy metal (Zn, Cu, Pb, Cd) in the Bieszczady National Park on the basis of a chemical analysis of the upper layer of the soil as well as the assimilation apparatus of European beech (*Fagus sylvatica* L.)

Material and method

The investigation was carried out in the soil and leaves of European beech (*Fagus sylvatica* L.) in the Bieszczady National Park. Samples of soil (from the level 0–10 cm) and leaves of European beech (*Fagus sylvatica* L.) were collected from 63 previously set stands in the whole area of the park in the vegetation season of 2007. On the map of the Bieszczady National Park (Fig. 1) marked location research points in the Bieszczady National Park. In order to determine the heavy metals concentration, plant material was dried in 105 °C to a constant weight, ground to powder, then mineralized and dissolved in 10 % HNO₃. After filtration Cd, Pb, Zn, Cu and Fe content was determined using flame Atomic Absorption Spectrometry (AAS) [7]. Soil was air dried and extracted with 10 % HNO₃ then measured using the conventional Atomic Absorption Spectrometry (AAS) [7].



Fig. 1. Location of research points in the Bieszczady National Park

The quality of the analytical procedures was controlled using the reference material (Certified Reference Material CTA – OTL – 1 Oriental Tobacco Leaves). Figures 2–7 were drawn with the use of Surfer 8 program.

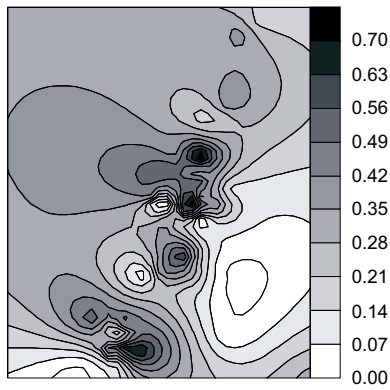


Fig. 2. Distribution of Pb concentrations in beech leaves from BdnP [$\mu\text{g/g}$]

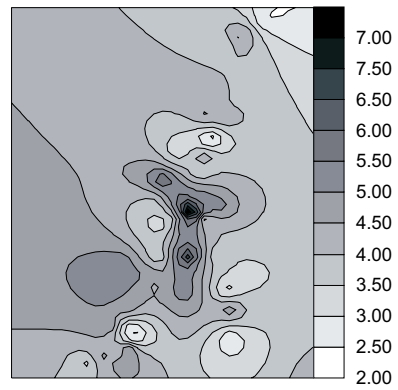


Fig. 3. Distribution of Cu concentrations in beech leaves from BdnP [$\mu\text{g/g}$]

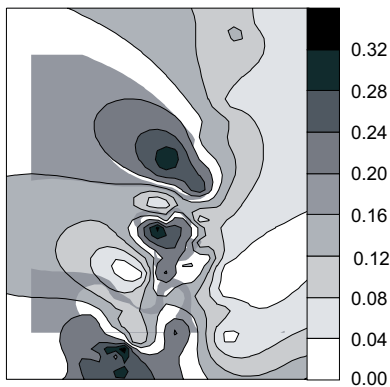


Fig. 4. Distribution of Cd concentrations in beech leaves from BdnP [$\mu\text{g/g}$]

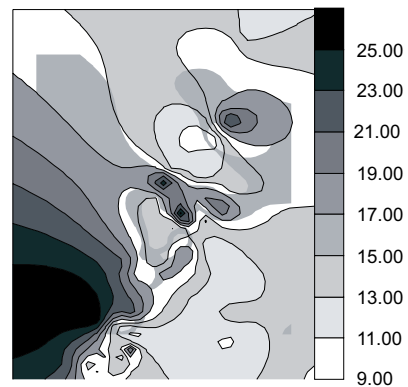


Fig. 5. Distribution of Zn concentrations in beech leaves from BdnP [$\mu\text{g/g}$]

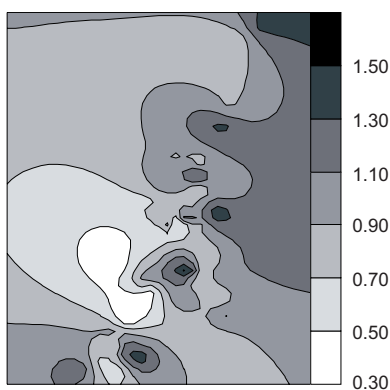


Fig. 6. Distribution of Cd concentrations in soil from BdnP [$\mu\text{g/g}$]

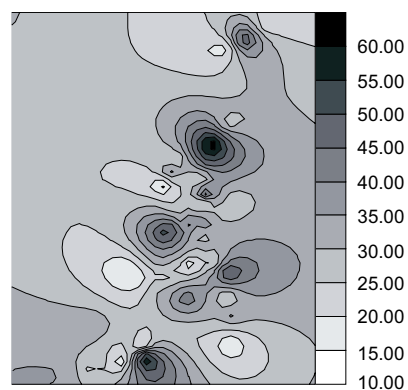


Fig. 7. Distribution of Pb concentrations in soil from BdnP [$\mu\text{g/g}$]

Results and discussion

The content of heavy metals in the leaves of European beech (*Fagus sylvatica* L.) and in the top layer of soil was presented by means of isolines at the Figs. 2–7. The lowest values of concentration were marked with the bright color and the highest with the dark one.

The average zinc concentration in the soils from different countries is within the limits of 30–120 $\mu\text{g/g}$. The average zinc content for the non-polluted soils in Poland is 40 $\mu\text{g/g}$ [8]. The permitted content of zinc in the soils of protected areas amounts to 100 mg/kg.

In the investigated soil material the content of zinc was within the range of 7.54–26.7 $\mu\text{g/g}$. The average concentration of zinc in the Bieszczady National Park was 13.7 $\mu\text{g/g}$ [9].

In the top layer of soil in the Roztocze National Park Rycman noted 3.10–6.85 $\mu\text{g Zn/g}$ [10]. Kuc found the content of zinc in the Tatra National Park within the range 15.90–150.47 $\mu\text{g/g}$. In the Slotwina reserve in the Podkarpace Region the average content of zinc was 3 $\mu\text{g/g}$. Ciepal and Lipka [11] found 350 $\mu\text{g Zn/g}$ in the surface layer of soil in the Gora Chelm Reserve and in the Smolen Reserve 200 $\mu\text{g Zn/g}$. Lukasik [5] in the upper level of soil in the Parkowe Reserve found that an average concentration of zinc equals 85 $\mu\text{g/g}$. On Babia Gora the content of zinc was from 105.0 to 215 $\mu\text{g/g}$ and on Mt Pilsko 185.0–325.0 $\mu\text{g/g}$ [12].

The obtained results concerning zinc contents in the soil of the Bieszczady National Park are within the average content of zinc for the non-polluted areas and the permitted zinc content was not exceeded.

In case of plants, zinc is necessary for proper growth. To cover physiological requirements of plants, its concentration in the leaves at the level of 15–30 $\mu\text{g/g d.m.}$ is sufficient and in the aboveground parts of a plant, which are not affected by pollution, it should be around 10–70 $\mu\text{g/g}$ [8].

Zinc concentrations in the examined leaves are within the range of 8.51–32.1 $\mu\text{g/g}$ [9].

In the area of the Babia Gora National Park Sawicka-Kapusta noted content level of zinc 15–30 $\mu\text{g/g}$ [13]. Ciepal observed the content of zinc in the reserve of the Beskid Slaski within the range of 95.5–170.4 [1], and Lukasik determined the zinc concentrations in the area of Wyzyna Slasko-Krakowska at 33–99 $\mu\text{g/g}$ [5].

The content of zinc in European beech (*Fagus sylvatica* L.) leaves from the Bieszczady National Park area does not exceed the norms and even shows zinc deficiency.

The average content of cadmium in the soils of Poland amounts to 0.2 $\mu\text{g/g}$ [8].

In the top layer of soil in the Bieszczady National Park the content of cadmium varied from 0.13–1.75 $\mu\text{g/g}$ and slightly exceeded permitted concentration of this element in the soil in the protected areas.

The results of the soil analysis carried out in this research concerning the concentration of cadmium are comparable with the results obtained by Rycman in the Roztocze National Park (0.9 $\mu\text{g/g}$) [10] and Kuc in the Tatra National Park (1.12–2.83 $\mu\text{g/g}$) [14].

Kimsa and others [15] determined in the surface layer of soil in the the Swietokrzyski National Park a cadmium concentration amounting to 2.7–3.4 $\mu\text{g/g}$. Ciepal and others [16] noted 2.0 $\mu\text{g/g}$ of Cd in the top layer of soil in the Bukowica Reserve, whereas in the Lipowiec Reserve it was 4.0 $\mu\text{g/g}$ of Cd. Ciepal and Lipka [11] present the cadmium content in the top layers of soil in the Smolen Reserve at the level of 17.0 $\mu\text{g/g}$ and for Gora Chelm 16 $\mu\text{g/g}$. Lukasik [5] noticed the concentration of Cd in the soil of the Parkowe Reserve at the level of 1.5 $\mu\text{g/g}$.

In the case of plants, cadmium is considered highly toxic. Sawicka-Kapusta [13] presents a range of cadmium occurrences in plants from not contaminated areas: 0.12–0.5 $\mu\text{g/g}$ d.m., whereas Kabata-Pendias and Pendias [8] state that in such areas content of cadmium does not exceed 1 $\mu\text{g/g}$ d.m. Content of cadmium at the level of 5–10 $\mu\text{g/g}$ d.m. for susceptible plants and 10–30 $\mu\text{g/g}$ d.m. for resistant plants is considered phytotoxic [17].

The average content of cadmium for the investigated area was 0.2 $\mu\text{g/g}$ d.m. [9].

Szarek and others [18] discovered the average amount of cadmium 2.6 $\mu\text{g/g}$ d.m in plants of ground cover in the beech forest in the area of the Ojcow National Park. Ciepal and Rycman in an analogous material from the Roztocze National Park noted that the content of cadmium was within the range from 0.6 to 1.05 $\mu\text{g/g}$ d.m. [19]. The obtained results indicate that content of cadmium in European beech (*Fagus sylvatica* L.) leaves does not exceed the level characteristic for plants from non-polluted areas.

Copper belongs to the biogenic group of elements used by plants in many metabolic traces [8]. In the upper layer of Polish soils copper total is within the range 1–60 $\mu\text{g/g}$ and usually it amounts to 10–30 $\mu\text{g/g}$ [20].

Content of Cu in investigated soil was 1.99–11.43 $\mu\text{g/g}$.

The average, physiological content of copper in the leaves of different species is at the level of 5–30 $\mu\text{g/g}$ d.m.

The concentrations of copper in the analysed samples are within the normal ranges from 1.97–8.9 $\mu\text{g/g}$ [9].

Witkowski determined in the Bieszczady National Park the average content of copper at the level 3–4 $\mu\text{g/g}$ [6]. In another protected area of Poland Rycman described the range of copper occurrences in plants from the Roztocze National Park at 7.25–11.62 $\mu\text{g/g}$ [10]. In the examined plant material, concentrations of copper do not exceed the permitted values and in some part of the Bieszczady National Park present even a deficiency of copper in the assimilation apparatus of European beech (*Fagus sylvatica* L.).

Similarly to the case cadmium, lead is also considered a very toxic element. Kabata-Pendias and Pendias [8] describe an average content of lead for soils of Poland not exceeding 20 $\mu\text{g/g}$. Permitted concentration of Pb in soils for the protected area on the basis of law regulations regarding protection of nature amounts to 50 $\mu\text{g/g}$.

Kimsa and others [14] determined in the surface layer of soil in the Swietokrzyski National Park lead concentration amounting to 18.0–19.0 $\mu\text{g/g}$. Ciepal informs that this value for the protected areas in Silesia and Malopolska is 60–350 $\mu\text{g/g}$ [1].

The obtained results concerning the lead contents in the upper layers of soil in the Bieszczady National Park are between 11.8–66.7 $\mu\text{g/g}$, which indicates that the permitted content of lead for the protected areas was exceeded.

The regular content of lead in plants varies from 5 to 14 $\mu\text{g/g}$ d.m., and the amount of 30 μg Pb/g d.m. is considered toxic [8].

The concentration of lead in the analyzed material falls between 0.01–0.9 $\mu\text{g/g}$ [9].

Witkowski in the Bieszczady National Park found content of lead amounting to 6–7 $\mu\text{g/g}$ [6]. Rycman for the Roztocze National Park noted it as ranging from 0.25 to 1.25 μg Pb/g [10].

The results concerning lead content in European beech (*Fagus sylvatica* L.) leaves from the Bieszczady National Park indicate an insignificant threat of this metal.

Conclusion

The results obtained in the research show that there is no excessive heavy metals load in the Bieszczady National Park. The values of the investigated heavy metals concentration are different depending on the region of the Park. However, their concentrations in the upper layer of soil and in the leaves of European beech (*Fagus sylvatica* L.) in most cases were lower than the average values noted in the sources and the values permitted for the protected areas. Only lead displays excessive concentration in the soil, which indicates that the soil is polluted with this metal.

On the basis of this research investigating the content of heavy metals in the soil and in the leaves it can be stated that the Bieszczady National Park is a good control stand for such studies.

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BIOMONITORING METALI CIĘŻKICH W BIESZCZADZKIM PARKU NARODOWYM PRZY UŻYCIU GLEBY I LIŚCI *Fagus sylvatica* L.

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Abstrakt: Przeprowadzono badania dotyczące zawartości metali ciężkich (Zn, Cd, Cu i Pb) w liściach *Fagus sylvatica* L. i w wierzchniej (0–10 cm) warstwie gleby na terenie Bieszczadzkiego Parku Narodowego.

Próbki gleby oraz materiał roślinny został zebrany w sezonie wegetacyjnym 2007 z 63 wyznaczonych wcześniej stanowisk. Zawartości Zn, Cd i Cu w liściach i glebie nie przekraczały dopuszczalnych norm dla terenów niezanieczyszczonych. Najniższe i średnie (4,4 µg/g s.m.) stężenie miedzi w liściach *Fagus sylvatica* L. jest zdecydowanie niższe niż stężenie określane jako „normalne”, co świadczy o niedoborze tego pierwiastka. Stwierdzono przekroczenie (śr. 31 µg/g s.m.) dopuszczalnego poziomu Pb dla terenów chronionych analizowanych próbkach gleby.

Słowa kluczowe: metale ciężkie, *Fagus sylvatica* L., Bieszczadzki Park Narodowy