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Author: Marta Kandziora, Ryszard Ciepał, Aleksandra Nadgórska-Socha

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Marta KANDZIORA¹, Ryszard CIEPAŁ¹ and Aleksandra NADGÓRSKA-SOCHA¹

HEAVY METALS AND SULPHUR ACCUMULATION IN THE *Picea abies* L. Karst. NEEDLES AND SOIL OF THE FOREST PROMOTIONAL COMPLEX "LASY BESKIDU SLASKIEGO"

AKUMULACJA METALI CIĘŻKICH I SIARKI W SZPILKACH *Picea abies* L. Karst I GLEBIE NA TERENIE LEŚNEGO KOMPLEKSU PROMOCYJNEGO "LASY BESKIDU ŚLĄSKIEGO"

Abstract: The investigation of zinc, cadmium, lead, copper and sulphur contents was carried out in the soil and in the needles of *Picea abies* L. Karst. in the Forest Promotional Complex "Lasy Beskidu Slaskiego". Samples of soil (from the level 0–10 cm) and annual, biennial and triennial needles of spruce were collected in autumn 2005 and 2006 from top parts of mountains: Rownica, Barania Gora and Czantoria. The highest heavy metals concentration were determined in triennial needles of *Picea abies* collected from Czantoria and Barania Gora. The lowest content of sulphur and investigated metals was found in soil samples and heavy metals in plant material from the Równica. Cadmium content (1.2 μ g/g) was higher than normal level (0.2–0.8 μ g/g) only triennial needles collected from Czantoria. The lead concentration (118–165 μ g/g) in the soil of all investigated areas was exceed, lead level considered as allowable. Relatively low microelement concentrations in the soil and the needles of *Picea abies* L. Karst. indicated poor plant nutrition.

Keywords: heavy metals, sulphur, Picea abies L. Karst., Beskid Slaski

Introduction

Spruce (*Picea abies* L. Karst.) is one of the most endangered species of trees in Europe, with the highest percentage of damaged trees (30 %). There is a close relation between the amount of trees damaged and the level of pollution in a given area. The chemical composition of the assimilation apparatus of spruce does not only indicate the contents of nutrients but also shows the degree of the environmental pollution [1].

¹ Departament of Ecology, Silesian University, ul. Bankowa 9, **40-007** Katowice, Poland, email: marta.kandziora@yahoo.pl

Thus, the most endangered spruce are those from Poland, the Czech Republic and Germany, which is a result of high deposition of pollution in those countries [2].

Strong anthropopressure is characteristic of Forest Promotional Complex "Lasy Beskidu Slaskiego". It results from the vicinity of large industrial areas of the Upper Silesia, Ostrava and Karvina District in the Czech Republic [2], as well as from the pollution emitted by transport and agriculture. On the basis of the analysis of assimilation apparatus, spruce trees from Beskid Slaski have been categorized into the 1st and 2nd classes of damage [2]. It is assumed that the high level of pollution until mid-90s had a huge impact on the condition and vitality of the trees. The first symptoms of the spruce forests dying out were observed in the 50s in Beskid Mały, in the 70s the problem was discovered in Beskid Slaski, and later also in Beskid Zywiecki [4]. In 2006 the amount of dead wood and coarse woody debris was estimated at 118,000 m³ in the forests of Beskid Śląski, which was ten times more than in the previous years. In addition, every year the number of sanitary cuts increases which is caused by the unfavourable weather conditions and the increasing threat of the insect pests [5].

Dying out of the spruce forests cannot of course be attributed just to one disadvantageous factor. The bad condition of the stands results from a variety of causes, accumulated over a period of time, which overlap and strengthen the final effect – dying out of a forest. Among diverse factors which have a negative influence on the stand, the industrial pollution, mostly heavy metals and sulphur, is the most significant factor in this process.

The research aimed at estimating heavy metals (Cd, Pb, Zn and Cu) as well as sulfur accumulation in the upper levels of the forest soil and in the accumulation apparatus of spruce in the stands of Forest Promotiona Complex "Lasy Beskidu Slaskiego" in relation to dying of the spruce forest.

Material and methods

The investigation was carried out in the soil and needles of *Picea abies* L. Karst. in the Forest Promotional Complex "Lasy Beskidu Slaskiego". Samples of soil (from the level 0–10 cm) and annual, biennial and triennial needles of *Picea abies* were collected in autumn 2005 and 2006 from top parts of mountains: Rownica, Barania Gora and Czantoria). In order to determine the heavy metal concentration, spruce needles were divided into three groups (one-, two- and three-year-old), dried at 105 °C to a constant weight, ground to a powder, then mineralized and dissolved in 10 % HNO₃. After filtration Cd, Pb, Zn and Cu content were determined using flame Atomic Absorption Spectrometry (AAS) [6]. Soil was air dried and extracted with 10 % HNO₃ and measurements were made using the conventional Atomic Absorption Spectrometry (AAS) [6]. The sulphur (total sulphur) content in plants and soil was determined with colorimetric method [6, 7]. The quality of analytical procedures was controlled by using the reference material (Certified Reference Material CTA–OTL–1 Oriental Tabacco Leavs). The data were processed using software Statistica.

Results and discussion

Results are shown in Table 1, 2.

Table 1

Content of cadmium, lead, zinc, cooper [$\mu g/g$] and sulphur [%] in the needles *Picea abies* L. Karst. Values with the same letter are statistically the same for p<0.05

| Location | Sample | Cd | Pb | Zn | Cu | S |
|--------------|-------------------|-----------------|--------|------------------|----------------|-----------------|
| | | [µg/g] | [µg/g] | [µg/g] | [µg/g] | [%] |
| Barania Gora | annual needles | 0.27b | 0.53a | 25.2a | 1.75a | 0.052a |
| | biennial needles | 0.325a | 0.38a | 25.0 4 5a | 1.685a | 0.0 4 5a |
| | triennial needles | 0.35 4 a | 1.2a | 2 4 .115a | 1.29a | 0.026a |
| Czantoria | annual needles | 0.755a | 0.535a | 22. 4 15a | 1.285a | 0.087b |
| | biennial needles | 0. 4 9b | 1.155a | 25. 4 6b | 2.298a | 0.0 4 3a |
| | triennial needles | 1.175b | 1.625b | 5 4 .225b | 4 .237a | 0.065b |
| Rownica | annual needles | 0.5 4 a | 0.32a | 15.67b | 1.32a | 0.063a |
| | biennial needles | 0. 4 3c | 1.01a | 11.23a | 1.1 4 b | 0.0 4 2a |
| | triennial needles | 0.76c | 0.37c | 9. 4 35c | 1.7b | 0.060b |

Table 2

Content of cadmium, lead, zinc, cooper and sulphur $[\mu g/g]$ and in the upper layer of the soil Values with the same letter are statistically the same for p < 0.05

| Location | Cd [µg/g] | Рb [µg/g] | Zn [µg/g] | Си [µg/g] | S [μg/g] |
|--------------|----------------|--------------|----------------|---------------|-----------------|
| Barania Gora | 1.62a | 165.6a | 37. 4 a | 9. 4 a | 1 4 7.3a |
| Czantoria | 1.2 4 b | 155.6b | 26.9b | 6.9b | 100.1b |
| Rownica | 0.96c | 118.6b | 11.5c | 6.6b | 81.0b |

The concentration of cadmium, which is considered highly toxic, fluctuates in the examined material from 0.27 μ g/g dry mass in the needles of one-year-old spruce from Barania Gora to 1.175 μ g/g in the needles of three-year-old from Czantoria. Cadmium concentration in the soil remains within the normal range, from 0.96 μ g/g on Rownica to 1.62 μ g/g on Barania Gora. In the plant material from Czantoria and in the soil from Barania Gora the content of cadmium was exceeded, 0.2–0.8 μ g/g Cd in plants and to 1 μ g/g Cd in the soil [8].

Lead is also considered a very toxic element and its content in the plants shows the influence of anthropogenic factors. The concentration of lead in the analyzed material falls between $0.32 \ \mu g/g$ in one-year-old needles from Rownica and $1.625 \ \mu g/g$ in three-year-old needles from Czantoria, and in the soil between 118.6 $\ \mu g/g$ on Rownica to 165.6 $\ \mu g/g$ on Barania Gora. Hence, it can be concluded that in all investigated areas, the normal range of lead (100 $\ \mu g/g$ Pb) [8] has been exceeded.

Zinc is an element which is indispensable to a proper functioning of living organisms. Its content may fluctuate in a wide range from 10 to 100 μ g/g [8]. The concentration of

zinc in the examined samples of plant material was in the range from 9.435 μ g/g (in the three-year-old spruce needles from Rownica) to 54.225 μ g/g (in the three-year-old spruce needles from Czantoria) and in the soil from 11.5 μ g/g on Rownica to 37.4 μ g/g on Barania Gora, which does not exceed the norms and even shows zinc deficiency.

The concentrations of copper in the analysed samples are within the normal ranges from 1.14 μ g/g in the two-year-old spruce needles from Czantoria and do not exceed the norms (2–20 μ g/g Cu) [8]. Similarly, the content of copper in the soil from 6.6 μ g/g on Rownica to 9.4 μ g/g on Barania Gora are within the normal range of concentration (1–140 μ g/g Cu) [8].

Sulphur, similarly to zinc and copper, is absolutely crucial for the development of living forms. Its higher concentration in the plants is often a result of air pollution caused by sulphur dioxide. The content of sulphur fluctuated between 0.026 % in the threeyear-old needles form Barania Gora to 0.087 % in one-year-olds from Czantoria. Sulphur content in the soil falls between 81.0 % (Rownica) and 147.3 % (Barania Gora).

The research showed, that heavy metals concentration in spruce needles and soil was similar to those of Zwolinski study (Cd 0.09–0.46 µg/g, Pb 1.9–2.5Xµg/g, Zn 11.0-28.2 µg/g, Cu 2.0-2.8 µg/g, S 0.096-0.12 % in spruce needles and Zn 20-56 µg/g, Cu 7-13Xµg/g, Cd 0,6-1 µg/g in soil) [3]. Only lead concentrations (118.6–165.6Xµg/g) in soil were considerably higher than Zwolinski results. This study differed from data for 'Male Pieniny [1], only concentration of zinc (12.5-43.5 µg/g) was similar but concentrations of cadmium $(0.01-0.1 \,\mu g/g)$ and sulphur (mean 0.023 %) were lower and the content of lead $(1.0-2.0 \text{ }\mu\text{g/g})$ was higher than in this study. Similar situation was reported in the research conducted in Podhale Region. The concentrations of zinc (31.8-34.4 µg/g) and lead (1.6-1.7 µg/g) were lower and the content of cadmium (0.24–0.34 µg/g) was higher [1, 9]. The content of sulphur in Forest Promotional Complex "Lasy Beskidu Slaskiego" was lower than previously reported by Barszcz and Malek (annual needles 0.103-0.138 %, biennial needles 0.094-0.121 %) [10]. The concentrations of zinc in annual, biennial and triennial needles were similar to German research results (annual – 30.7 µg/g, biennial 27.6 µg/g, triennial 24.8 µg/g) [11]. The contents of cadmium and lead were higher than in Norway (0.011–0.173 μ g/g Cd, 0.03-0.89 µg/g Pb), but lower than in Slovakia (1.19 µg/g Cd, 1.73 µg/g Pb) [11, 12].

The spruce forests in Beskid Slaski do not show an excessive accumulation of heavy metals in the needles. The content of metals both in the soil and in the needles is within the normal range. Only lead displays excessive concentration in the soil, which indicates that the soil is polluted with this metal. It is also noticeable that those forests are deficient in the basic nutrients, which has been noticed also in his studies by Zwolin-ski [2].

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AKUMULACJA METALI CIĘŻKICH I SIARKI W SZPIŁKACH Picea abies L. Karst. I GLEBIE NA TERENIE LEŚNEGO KOMPLEKSU PROMOCYJNEGO "LASY BESKIDU ŚLĄSKIEGO"

Katedra Ekologii, Uniwersytet Śląski

Abstrakt: Prowadzono badania dotyczące zawartości metali ciężkich (Zn, Pb, Cu, Cd) w glebie i szpiłkach *Picea abies* L. Karst. na terenie Leśnego Kompleksu Promocyjnego "Lasy Beskidu Śląskiego". Próbki gleby (z górnego poziomu) oraz szpiłki jedno-, dwu- i trzyletnie świerka pobierano ze szczytowych partii gór: Równicy, Baraniej Góry i Czantorii jesienią 2005 i 2006 r. Stwierdzono najwyższe stężenia metali cięż-kich w igłach trzyletnich zbieranych na Baraniej Górze i Czantorii. Najniższe koncentracje badanych metali i siarki zanotowano w próbkach gleby oraz w materiale roślinnym z Równicy. Zawartość Cd (1.2 μ g/g) w trzyletnich igłach świerka pobieranych na Czantorii była wyższa od określanych jako stężenie normalne (0.2–0.8 μ g/g). Stwierdzono przekroczenie dopuszczalnego poziomu dla Pb w glebie wszystkich badanych powierzchni (118–165 μ g/g). Stosunkowo niskie stężenia mikroelementów zarówno w glebie, jak i igłach świerka wskazywać mogą na zły stan odżywienia roślin.

Słowa kluczowe: metale ciężkie, siarka, świerk pospolity Picea abies L. Karst., Beskid Śląski