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CONTENT OF HEAVY METALS IN SOIL AND IN PINE BARK IN SKALKI TWARDOWSKIEGO LANDSCAPE PARK IN KRAKOW

ZAWARTOŚĆ METALI CIĘŻKICH W GLEBIE I KORZE SOSNY W PARKU KRAJOBRAZOWYM SKAŁKI TWARDOWSKIEGO W KRAKOWIE

Abstract: Among the components of natural environment, the soil is the main center of accumulation of many chemical substances, among others pollutions such as heavy metals. In order to evaluate pollution of the environment the soil samples were taken with the use Morris square frame 25 cm by 25 cm in around 40-year old pine grove as well as in the meadow situated nearby, in Skalki Twardowskiego Landscape Park, that is a part of Bielansko Tyniecki Landscape Park. In the grove, necrotic bark of the common pine (*Pinus sylvestris* L.) was taken as well. The environmental condition was analyzed owing to the detection of reaction of the soil, its humidity, content of heavy metals, pH and content of the metals in the pine bark obtained near the area where the soil samples were taken. It was detected that the soils of the researched areas had slightly alkaline reaction, whereas humidity was slightly higher in the meadow. What is more, the analysis of the results concerning the pine barks from the grove indicates considerable acidity (pH 3.33–3.97). The concentration of the metals such as Pb, Zn and Cd was higher in the soil of pine grove, while Cu slightly higher in the meadow. In meadow and grove soil content of the Cd was almost two times above the norm, whereas content of the other metals complied with norms. The content of Cu in bark pine was similar to content of Cu in soil, while content of Pb, Cd and Zn in bark was lower than it was in the soil.

Keywords: heavy metals, necrotic bark of pine, pH soil, pH bark pine

The ever-increasing soil pollution resulting from environmental emission of various pollutants produces substantial adverse changes in the soil that manifest, among others, as its acidification or alkalisation, saltiness, ionic equilibrium disturbance and an increase in its heavy metals content. Among components of natural environment, the

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soil is the principal centre of accumulation of chemical substances, including pollutants. Like in the case of acidification processes, the degree of heavy metal soil pollution depends on its resistance resulting from its sorption capacity. Due to the sorption complex and intense exchange of matter and energy with other environmental components, the soil is able to retain chemical substances migrating through water and the air [1]. In this way, in the process of pollutant circulation, the soil plays the role of a protective filter against compounds that enter waters and, at the same time, becomes increasingly polluted. Soil also belongs among the components of the natural environment more sensitive to the effects of pollution, including pH changes caused by human activity. For this reason, many habitat experts define it as a "mirror" of the environment [2].

Physicochemical properties of the soil affect the plant uptake of various elements and their incorporation into food chain. A pH value greater than 6.5 definitely decreases the amount of soluble forms of metals in the soil and limits their uptake and accumulation by plants [3]. Acidity is one of the key factors determining the course of many soil processes, affecting the functioning and efficiency of entire geoecosystems. Basically, it affects the living conditions of soil organisms, the availability of macro- and micronutrients necessary for plant growth, and the processes of nitrification and the presence of toxic heavy metals, especially aluminium.

In an acidic environment, plants may take up large amounts of these elements (particularly cadmium, zinc, nickel) even from not very polluted soils [4, 5]. Trace elements systematically brought into the soil accumulate in its top layer, because they are bonded by the soil sorption complex and only very slowly move into the depths of the soil profile.

Because of its sensitivity and constant presence in the test site, exposed to the impact of the changing environment, tree bark is a good bioindicator [6]. The bark of deciduous trees is inherently less acidic than the bark of coniferous trees [7]. Clear changes occur in its physical and chemical properties due to air pollution [8]. The method based on the use of aqueous extracts of the tree bark is simple, cheap and appropriate in the assessment of air pollution. It has been used by many researchers [7, 9]. Using it may determine the pH, which decreases under the influence of sulphur dioxide and nitrogen oxides in the air, as well as the electrolytic conductivity, the concentration of sulphates in the bark extract, and the absorption capacity of certain chemical elements. The pH also depends on the species, age and the health of the trees, and on the soil they grow on, the storage tests, techniques, harvest time and the degree of porosity of the cortex [9–11]. Last time the bark is also used to asses the poluttion of organic and inorganic compounds, such as polycyclic aromatic hydrocarbons (PAHs), organochlorine compounds, ammonium nitrate [12].

An exceptionally sensitive biomarker of environmental pollution is the outer bark of common pine (*Pinus sylvestris* L.) – the most widespread tree species in Poland, from which it is easy to collect its outer layer [10]. To evaluate the pollution level are applied, among others, such physicochemical properties of the bark as the pH of water extracts and the capability to absorb some chemical elements.

The aim of the studies was to determine the acidification degree and Pb, Cd, Cu and Zn accumulation in the soil and the outer bark of the pine on sites located in a protected area in the Park Skalki Twardowskiego belonging to the Bielansko-Tyniecki Landscape Park in Krakow.

Material and methods

In order to evaluate pollution of the environment the soil samples were taken with the use of Morris square frame 25 cm by 25 cm in around 40-year old pine grove as well as in the meadow situated nearby, in Skalki Twardowskiego Landscape Park in Krakow. The frame was thrust into the soil on the depth of 10 cm. In each particular site a series consisted of 16 tests on the surface of 1 m^2. Series of samples was taken on the selected sites during autumn 2008. In the grove, necrotic bark of the common pine (*Pinus sylvestris* L.) was taken as well. The environmental condition was analyzed owing to the detection of reaction of the soil, its humidity, content of heavy metals, pH and content of the metals in the pine bark obtained near the area where the soil samples were taken.

In a pine grove, from which soil was sampled, outer bark samples were taken from four *ca* forty year old trees, having similar size of 40 to 50 cm breast height diameter, *ca* 2 to 4 m away from each other. The bark, four samples from each tree, was taken from the trunk at the height of 1.5 m above the ground. The determination of the bark toxicity level was carried out by evaluating its pH value and, next, lead, cadmium, copper and zinc contents were determined.

In order to determine the pH value, the bark samples were dried at 65 ^oC for 3 hours, and next they were ground in mortar and pulverised using impact mill. From each sample, 2 g each of bark powder was weighed and 8 cm^3 distilled water added. After 48 hours, pH was measured using a WTW 330 pH-meter.

Chemical analyses of heavy metals were performed by determining the contents of general forms of lead, cadmium, copper and zinc using the AAS method. Dried samples of bark and soil (2.5 g) were subjected to mineralisation process. For this purpose dry water was poured over 3 cm^3 of 65 % HNO_3 and heated for about 4 hours. The filtered liquid was poured into measure flasks and filled with distilled water to volume of 25 cm^3. In solutions of the soil prepared in that manner the content of heavy metals on the spectrometer of atomic absorption was determined (Cole-Parmer, BUCK 200A).

Results and discussion

The soil from the studied sites in the Landscape Park Skalki Twardowskiego showed slightly alkaline pH, from 7.36 to 7.78 (Table 1). The moisture content of the soil from the meadow was 28.6 % and was by several per cent higher than in the soil from the grove (Table 1).

Table 1

Soil moisture and pH in the soil and in the pine bark

Selected parameters	Soil in the grove	Soil in the meadow	The pine bark
Dampness of soil [%]	20.95 (20.2–21.7)	28.55 (25.2–31.9)	—
pH value	7.65 (7.56–7.74)	7.57 (7.36–7.78)	3.71 (3.31–3.97)

However, the results concerning the bark from *ca* 40-year old pine trees from the grove point to its significant acidity. The pH of the analysed pine bark from the studied grove ranged from pH 3.33 to pH 3.97, despite the fact that the soil from this site was slightly alkaline, which resulted from its location on calcareous ground (Table 1). Similar pH values of the pine bark obtained in their study Samecka-Cymerman et al [7] and Harju et al [8].

Average concentrations of heavy metals studied in a pine grove soil were as follows: Pb 59 mg $\cdot$ kg^{-1} d.m., Zn 72 mg, Cu 11 mg and Cd 2 mg $\cdot$ kg^{-1} d.m. However, in the meadow soil demonstrated more than 51 mg of Pb, 65 mg Zn, 13 mg Cu and Cd about 2 mg $\cdot$ kg^{-1} d.m. The concentration of metals such as Pb, Zn and Cd was higher in the pine grove soil, whereas Cu slightly higher in the meadow in the landscape park (Fig. 1). The critical concentrations of the metals in the soils containing the anthropogenic contaminations, according to Kabata-Pendias et al are: 70 mg Pb, 150 mg Zn and 1 mg Cd/kg [13, 14]. The obtained results concerning cadmium are characterised by exceeding the levels indicated by Kabata-Pendias [13]. In the grove soil and in the meadow, the limit value was exceeded more than twice, and in the meadow, almost twice (Table 2).

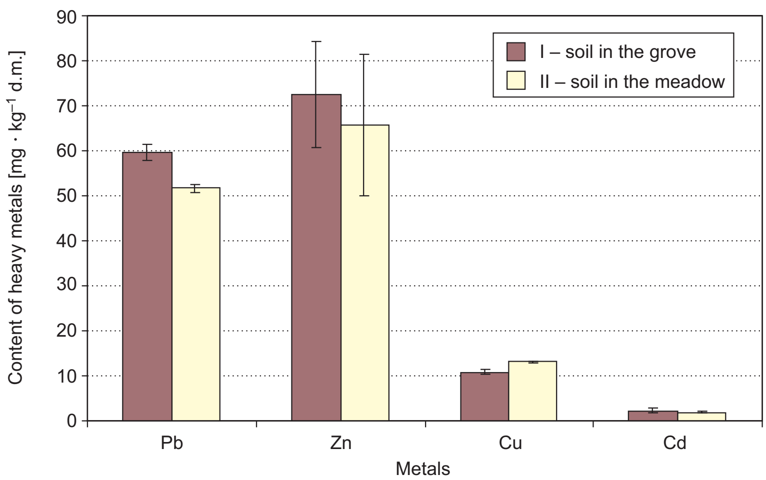

Fig. 1. Content of heavy metals in soil

Table 2

Content of Pb, Zn, Cu, Cd in soil and in pine bark [mg · kg^{-1}]

Heavy metals	Soil in the grove	Soil in the meadow	The pine bark	The critical concentrations	
				Kabata-Pendias*	Minister of Environment Regulation**
Pb	59.63 (58.29–60.96)	51.70 (51.08–52.33)	41.86 (24.16–59.55)	70	100
Zn	72.47 (64.07–80.87)	65.72 (54.54–76.91)	32.37 (30.75–33.99)	150	300
Cu	10.85 (10.43–11.26)	13.05 (12.91–13.2)	10.23 (5.07–15.39)	—	150
Cd	2.32 (2.03–2.6)	1.90 (1.82–1.98)	1.56 (1.49–1.62)	1	4

* The critical concentrations according to Kabata-Pendias [13]; ** limit values for the heavy metal content set out in the Minister of Environment Regulation on the soil quality and farmland quality standards (Polish Journal of Laws DzU 2002, No. 165, item 1359 of 4 October 2002 [15].

However, concentrations of heavy metals found do not exceed the limits stipulated in the Minister of Environment Regulation on the soil quality and farmland quality standards (Polish Journal of Laws DzU 2002 No. 165, item 1359 of 4 October 2002) (Table 2).

No cases of exceeding the limit values for metals were found for Group B soils (a group covering the land rated as farmland excluding the land under ponds and the land under ditches, the woodland and tree- and bush-covered land, wasteland, as well as built-up and urban areas, excluding industrial areas, mine lands and transport areas) [15].

In the soil environment, heavy metals demonstrate diverse mobility. Lead is strongly bonded by organic matter of soil top layer and only slightly migrates into the depth of the profile, copper is a little more mobile, and zinc relatively easily moves into the depths of the soil. The total metal content of forest litter is determined, beside the deposition rate, also by the humification conditions of the vegetable material and the balance of metal accumulation and leaching processes. Heavy metal toxicity depends on the roles they play in the metabolic processes of the organisms and their susceptibility to bioaccumulation. Metal toxicity is not only the result of its content in the environment, but primarily its biochemical role in metabolic processes and mechanisms of absorption, accumulation and excretion by living organisms. The capability of heavy metals to penetrate to higher plants depends on the soil properties and the conditions prevailing in the environment, as well as the physical and chemical form in which the element occurs.

The lead and zinc contents in the pine bark were significantly lower than in the soil, in which the studied trees grow. Zinc is an essential element in the process of regulating the metabolism of living organisms. In comparison with other trace elements, zinc is much less toxic to animals and humans. Zinc is a common element in the tissues of plants and animals. Just as in plants, in animals zinc interacts with a variety of physiological processes and with various elements, primarily cadmium and copper.

Soils are the place where most of the lead of anthropogenic origin, such as from vehicle exhausts, waste incineration, lead smelting, and use of paint, accumulates. This element is strongly bound in soils and accumulates in the humus layer. Although it is barely mobile, in acidic and sandy conditions can easily be absorbed by plants, which poses an immediate threat to living organisms participating in the food chain. In the soils studied, lead concentration was 51.7–59.6 ppm d.m. and in the pine bark 41.8 ppm. In the studies, the Pb content did not exceed the limit value [13, 15].

In the pine bark, 10.23 mg/kg copper was found and this value was comparable with that analysed in the grove soil (Table 2, Fig. 2).

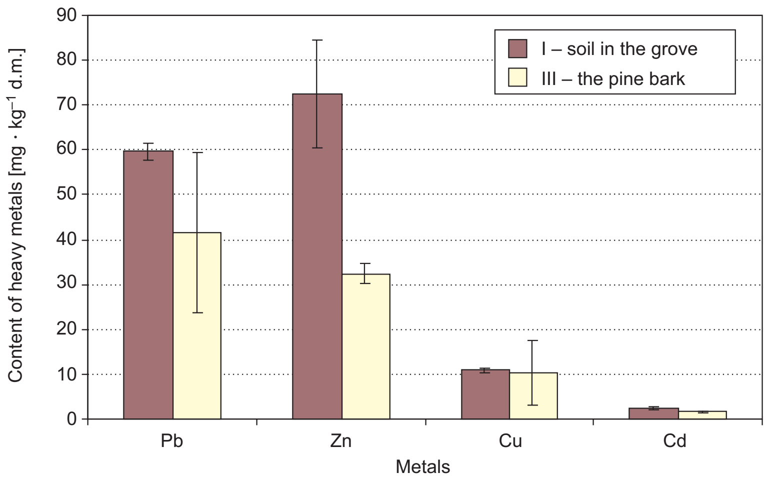

Fig. 2. Content of heavy metals in soil and in pine bark

Copper is a metal present in the soil in the form of very mobile bonding. Its content is closely related to the particle size composition and the pH of the soil; lowering the pH will increase the occurrence of copper. The natural copper content in soils not contaminated ranges from 10 mg/kg for light soils to 25 mg/kg for heavy soils [13]. The copper content in the analyzed soils does not exceed the acceptable limit given by the Regulation of the Minister of the Environment on soil and land quality standards [15].

The lowest cadmium content was found in the pine bark. It was *ca* 1.56 mg per kg, but according to Kabata-Pendias, it was also a value slightly in excess of the limit [13]. Cadmium content in the pine bark from the grove was slightly lower than in the grove soil and meadow in the Landscape Park Skalki Twardowskiego (Table 2, Fig. 1, 2).

Cadmium is relatively easily and intensively taken up by plants, in general proportionally to its concentration in the environment [14] Cadmium introduced into the soil is readily soluble in an acidic medium, and its mobility increases in light soils. It then becomes readily taken up by plants and incorporated into the food chain. It is considered dangerous to humans and animals as it is easily absorbed and long remains in the body. Plants accumulate cadmium in the roots, and its toxic effects may interfere with the processes of photosynthesis.

The cadmium concentration in the bark of necrotic pine correlated with its concentration in the soil. Slosarz [16] obtained a higher Cd content in the bark of pine trees in the Niepolomicka primeval forest (2 ppm) than in the soil (0.88 ppm d.m.) in which the trees grew [16].

Slosarz's results of the research carried out in the Niepolomicka primeval forest in fresh mixed forest indicate that the soil accumulated larger quantities of copper, zinc and lead, while the bark accumulated larger amounts of cadmium [16].

The results indicate that both the pine bark and the soil contaminants are good indicators of acidifying compounds and investigated metals. Confirm the results of Marko-Worlowska and Slosarz [16, 17].

Conclusions

1. The results indicate that the concentrations of heavy metals do not exceed the standards set out in the Regulation of the Minister of the Environment on soil quality standards and earth quality standards for group B – a group covering the land rated as farmland excluding the land under ponds and the land under ditches, the woodland and tree- and bush-covered land, wasteland, as well as built-up and urban areas, excluding industrial areas, mine lands and transport areas (Polish Journal of Laws DzU 2002, No. 165, item 1359 of 4 October 2002).

2. The results of the analysis of the tree bark collected from model trees with surfaces at varying distances from the source of emissions may be used to illustrate the dispersion range of the pollution.

3. The pH of pine bark indicated its much higher acidity than that of the soil in which these pine trees grew.

4. The soil had higher accumulation of lead, cadmium and zinc occurs in the soil than in the pine outer bark.

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ZAWARTOŚĆ METALI CIĘŻKICH W GLEBIE I KORZE SOSNY W PARKU KRAJOBRAZOWYM SKAŁKI TWARDOWSKIEGO W KRAKOWIE

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Abstrakt: Spośród komponentów środowiska przyrodniczego gleba jest głównym ośrodkiem akumulacji wielu substancji chemicznych, w tym również zanieczyszczeń, takich jak metale ciężkie. Dla oceny zanieczyszczenia środowiska pobierano próbki glebowe przy użyciu ramy Morrisa o wymiarach 25 × 25 cm w ok. 40-letnim zagajniku sosnowym oraz na pobliskiej łące w Parku Skałki Twardowskiego w Krakowie należącym do Bielańsko-Tynieckiego Parku Krajobrazowego. W zagajniku pobierano również korę martwicową sosny zwyczajnej (*Pinus sylvestris* L.). Badano stan środowiska, określając odczyn gleby, jej wilgotność, zawartość metali ciężkich oraz pH i zawartość metali w korze sosny pozyskanej w pobliżu miejsca pobierania gleby. Stwierdzono, iż gleby badanych stanowisk wykazywały odczyn słabo zasadowy, zaś wilgotność była nieznacznie większa na łące. Natomiast wyniki dotyczące kory sosen z zagajnika wskazują na jej znaczne zakwaszenie (pH 3.33–3.97). Koncentracja metali, takich jak Pb, Zn i Cd była wyższa w glebie zagajnika sosnowego, natomiast Cu nieznacznie wyższa na łące. W glebie łąki, jak i w glebie zagajnika ilość kadmu przekraczała prawie dwukrotnie normę, a pozostałych metali mieściła się w normie. Zawartość miedzi w korze sosny była porównywalna do zawartości w glebie, podczas gdy ilość Pb, Cd i Zn w korze była mniejsza niż w glebie.

Słowa kluczowe: metale ciężkie, kora sosny, pH gleby, pH kory sosny