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THE PINE BARK AND TOPSOIL AS AN INDICATOR OF POLLUTIONS CAUSED BY INDUSTRY AND TRANSPORT

ZASTOSOWANIE KORY SOSNY I WIERZCHNIEJ WARSTWY GLEBY DO OCENY ZANIECZYSZCZEŃ PRZEMYSŁOWYCH I KOMUNIKACYJNYCH

Abstract: Concentrations of Pb, Cd, Ni were determined in topsoil and in samples of necrotic bark of *Pinus sylvestris* L. collected along transects around the Skawina industry center and in parts of Bielansko-Tyniecki Landscape Park in Krakow (southeast Poland). The suitability of bark and topsoil for monitoring of these heavy metals and acidifying gases pollution was investigated. After comparing the concentration of heavy metals and pH value in pine bark with topsoil, it was observed that topsoil is better biomonitor for lead and nickel than bark of *Pinus sylvestris* and that bark appear to be suitable bioindicator of atmospheric deposition only for cadmium and acidifying components.

Keywords: *Pinus sylvestris* L., necrotic bark, heavy metals, topsoil, pine bark reaction, biomonitoring

Introduction

Intensive development of industry (metallurgy, burning of energetic raw materials) and steadily increasing car transport constitute the main source of contamination by heavy metals and acidic compounds (SO_2, SO_3 and NO_x) of soils adjacent to the industrial areas and traffic paved roads.

The consequence of the accumulation of metals and their toxic impact is biological deactivation of the soil subsystem. Additionally, terrestrial ecosystems productivity decreases [1-3]. Heavy metals and acidifying compounds are one of the most durable and toxic contaminates of the soil subsystem.

The anthropogenic processes that cause the emission of acidifying compounds are the cause of the spreading of many metals and the growth of their toxic impact on living organisms [4]. Respectively, the content of heavy metals (especially Pb, Ni or Cd) in soils can be treated as an indicator of the environmental degradation of different branches of the industry and car transport.

Tree bark is an ideal natural absorbent as it is dead tissue that does not grow anymore. The pine bark surface is very porous and the absence of metabolic processes makes it highly unreactive for inorganic and organic substances [5, 6]. The changes in the chemical composition of the surface layers can be documented. Kuik and Wolterbeek [7] and another [8, 9], proposed the use of tree bark samples as biomonitors of heavy metals. Monitoring of the environment with the use of bark not only enables evaluation of present layer of the accumulation of elements and polluting compounds, but also evaluation of the course of the process in the previous years. Adjacent trees are supposed to demonstrate a similar degree of pollution accumulation s and may be used consequently to determine the

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extent of the pollutants. Similarly the results on the bark of model trees analysis taken on surfaces at different distances from source emission can illustrate the problem of the spread of pollutions. Tree bark is a good bioindicator because it remains in place for an extended period of time, it is easily accessible and sampling does not damage the tree [9]. What is more, sampling and analysis of necrotic bark is fast and economical. Kuik and Wolterbeek [7] study demonstrated the potential of bark as a biomonitor on a larger scale.

The aim of the present work was the recognition of contamination by Pb, Cd and Ni and acidifying compounds of the surface soil (topsoil) and tree bark of approximately similar aged trees at localities situated at different distances from industrial and transport emitters.

Materials and methods

Characteristic of area analyzed

The samples were taken in spring 2012 at 5 different distances from the source of emission. The 3 sites (1, 2, 3) examined are situated in Skawina - a city characterized by heavy industrialization (aluminium-works, power plant and others), densely populated and situated approximately 18 km southwest from the center of Krakow and the 2 sites (4, 5) situated in the Bielansko-Tyniecki Landscape Park of Krakow - park encompassed by the Krakow city limits.

Samples collection and analysis

For evaluation of pollutions of air and soil by heavy metals and acidifying compounds necrotic pine bark (*Pinus sylvestris* L.) and topsoil from the pines' surroundings were used as the accumulative cumulative bioindicators. The temperature, soil moisture and pH of topsoil and bark were examined and the content of Pb, Cd and Ni was determined. The topsoil reaction (pH) was examined on place with a pH-meter- WTW pH 330, placed into the soil to a depth of 5 cm. The topsoil samples were taken by forcing a 5 cm diameter steel cylinder to a depth of 5 cm. At each site the 4 soil samples were taken at eastern side (before the trees) and the 40 samples of bark 3 mm thick from the trunk of 4 trees at the high of around 1.5 m from the soil, 5 in the eastern side of each tree and 5 on the western side. The trees analyzed were from 2 to 4 m distance from each other, had similar breast height diameter (35 to 40 cm) and had a similar age (around 30 years).

The samples were dried in a temperature of 65 degrees for 3 hours, then milled to a powder. One gram of powdered bark from each sample was weighed and mixed with 5 cm^3 of distilled water. After 48 hours the pH reaction was measured using a ELMETRON type CPC-401 pH-meter. Chemical analyses of heavy metals in the topsoil and bark were conducted by mapping the content of the general forms of Cd, Pb, Ni, determined by the FAAS method. Dried samples of topsoil and bark (1 g each) were mineralized. For this purpose dried samples of soil and pine bark were mixed with 3 cm^3 of 65% HNO_3, the solution was heated to a temperature of 110ºC and left for 4 hours to cool. The filtered liquid was poured into measuring flasks and filled with distilled water. In the solutions of soil and bark prepared, the content of heavy metals was determined by atomic absorption spectrometer (AAS-Cole-Parmer, BUCK 200A).

Statistical analysis

As variances showed no parametrical distribution (Shapiro-Wilk test, $p > 0.05$), we used non parametric Kruskal-Wallis ANOVA. The correlations between metal concentrations, pH and sites were calculated using the Pearson correlation coefficient and Students` test. Statistical significance was defined at $p < 0.05$. All analyses were performed using STATISTICA 12 computer program.

Results and discussions

The pH value is subjected to the quickest changes when exposed to external factors and, among others, it directly and indirectly influences many mechanisms releasing heavy metals in soils [10]. In normal conditions the pH of *Pinus sylvestris* bark is 3.5 [8], whereas the average pH of pine bark at sites analyzed indicated high acidity and fluctuated from 2.68 to 3.44. The average value of soil pH fluctuated from 4.31 to 6.04 (Table 1).

Table 1

pH value in studies sites

	Cardinal directions	**Site 1**	**Site 2**	**Site 3**	**Site 4**	**Site 5**
Pine bark pH	East	3.14 (2.98-3.24)	2.68 (2.60-2.82)	3.18 (2.63-3.94)	3.29 (3.05-3.46)	3.12 (3-3.23)
	West	3.28 (3.05-3.59)	2.99 (2.61-3.49)	3.44 (2.78-3.78)	3.14 (3.01-3.27)	3.02 (2.88-3.23)
Top soil pH	East	6.04 (5.34-6.79)	4.25 (3.79-5.47)	4.4 (4.01-5.03)	4.61 (4.37-5.05)	4.69 (4.52-5.21)

Site 1 - Skawina 700 m from the aluminium works and about 5 meters north of a heavy used road
Site 2 - Skawina 2400 m from the power plant and aluminium works
Site 3 - Skawina 1200 m from the power plant and 450m from the aluminium works and approximately 200 m from the road
Site 4 - Bielansko-Tyniecki Landscape Park 4 km north east from the power plant and 5 km from the aluminium works
Site 5 - Bielansko-Tyniecki Landscape Park 5 km north east from the power plant and 6km from the aluminium works, and around 200 m west from the ring road

Comparison of the pH reaction indicated considerably higher acidity of pine bark verses topsoil at each sites, and these differences were statistically significant (Table 2).

Table 2

Statistical significance of pH value and of heavy metals concentrations

	pH	**Pb**	**Cd**	**Ni**
Pine bark East-West	0.0040*	0.000013*	0.019198*	0.000001*
Pine bark East - Topsoil	0.000000*	0.000000*	0.000046*	0.000000*
Pine bark West - Topsoil	0.000000*	0.000000*	0.078504	0.000000*

*differences statistically significant at $p < 0.05$

The highest acidity (pH lower than 4.5) was observed in soils at sites 2 and 3. At the same time similar, almost parallel increasing or decreasing tendencies of pH of bark and topsoil were noticed regarding all sites. The pH value of pine bark on the eastern and on the western side did not differ much, however at sites 1, 2, 3 situated at the closest distance and west of industrial emitters, a slightly higher acidity on the eastern side of trunk was observed. The lowest average pH value of bark and of soil was recorded at site 2 (Table 1). It is probably that here polluted air touched with the north-east winds from the north-east part of Krakow, where is located a steelworks and electro-thermal power plant. Site 5 situated furthest away from the industrial emitters, but approximately 200 m from a ring road was characterized by high bark acidity, as well as the highest content of Pb in the topsoil (Fig. 1). This result proves a big impact of transport pollutions flowing with frequently occurred natural wind currents blowing from the ring road.

The low soil pH is negative from the ecological perspective - in acidic soil the mobility of heavy metals (mainly Cd and Ni) increases which facilitates transfer of these metals into the circulation of matter. The results of presented research indicate that the pH value of pine tree bark must be regarded as an indicator for air acidification.

The content of xenobiotic elements

Amongst the metals examined Ni is the only one that is indispensable (for humans 25-35 µg/day) for the proper functioning of the organisms. Its overdose, however, can have very negative consequences. Cd and Pb do not have any positive influences on organisms and constitute some of the most dangerous heavy metals; the accepted dose determined by the WHO is: Pb - 415-550 µg/day, Cd - 57-71 µg/day [11]. The occurrence of heavy metals in soil and plants can be treated as an indicator of the quality of the environment and *Pinus silvestris* is commonly used in fitoindication [12]. Intensity and scope of the contamination of soils and plants by trace elements depend on many factors at local conditions. Additionally, the important source of heavy metals accumulated on the surface of soils and plants is so-called long distance emission related to the spreading of pollutions over large distances.

The climatic conditions (rainfalls, temperature, direction and wind speed) play an important role in dispersion and deposition of air pollutants. For an estimation of the environmental health and threat of heavy metals, an evaluation of their mobility, that is, possibility of their transmission to biogeochemical circulation, is necessary [13]. High mobility of Cd, Ni and the relatively low mobility of Pb in soils is regulated by their pH and modified by the other soil qualities such as content of organic substances, occurrence of other metals and humidity. In oxidative environments with acidic reactions, Cd and Ni are characterized by high mobility, to the lesser extent the mobility of Pb increases as well [14]. Among metals measured in topsoil the concentration of Pb was the highest and its amount was higher than the average natural occurrence in the soils of Poland [15] (Fig. 1).

Lead - a component of commonly used, until recently, leaded petrol is the contamination attributed to transport and to various industrial activities. The other main sources of Pb emission are coal burning and metallurgical industries. It is a metal typical for low emitters and non-organized emissions. Pollutions from this source do not spread over long distances [16]. According to the literature [11] natural concentrations of this metal should not exceed 20 mg/kg for most soils. The Pb content in soils analyzed fluctuated from 29.37 mg/kg at site 4 furthest away from industrial emitters, ring road and busy road to 62.26 mg/kg at site 5 which is remote from industry, but situated close to a ring road (Fig. 1).The highest Pb content was observed in topsoil (site 5) approximately 200 m away from the ring road and in bark (at site 1) adjacent to the busy road (Fig. 1). Soils of habitats analyzed contain slightly higher amount of Pb that the natural average content in soils in Poland. However, only in soil at site 5 the amount of Pb is averagely 2 times higher than in soils of remaining sites and exceeds acceptable content according to the standards of soils and earths qualities [15]. The greatest effect of traffic Pb pollution on the soil subsystem was observed up to a distance of 200 m away from the motorway (Fig. 1), which proves higher influence of busy roads than in the results presented by Ruhling and Tyler (2004) [17]. Their studies of Pb accumulation in many plants growing next to busy roads in Sweden, show the most intensive accumulation of Pb up to 150 m from the road. Observations of Jaworska and Murowana [18] stating the impact of distance up to 300 m from the road on plants are similar to the results of presented research.

The content of Pb spanning from 2 to more than 6 times higher in soil than in bark was detected here, the exception is site 1 (Fig. 1). The highest Pb concentration in pine bark at site 1 can be explained by the proximity to the heavy traffic road. With increasing distance from the emission center (car transport and power plant) the Pb content of bark decreases. The lowest Pb content in bark as well as in topsoil, was observed at site 4 situated furthest away from roads (Fig. 1). Therefore it is probable that the main emitter of Pb on area analyzed is car transport.

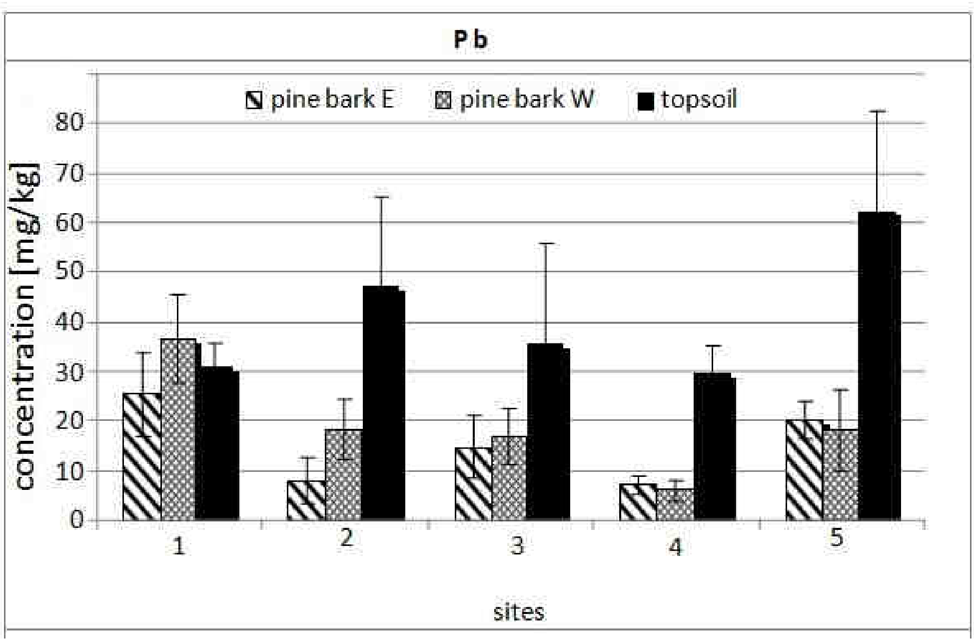

Fig.1. Pb concentrations in studies sites

Cadmium, that is emitted by metal works, is one of the most dangerous heavy metals for the environment [19]. What is more, along roads, the source of contaminations are for example greases used in vehicles, tyre abrasion and other parts of vehicles. Cd is accumulated mainly in surface soil levels and the higher the reactivity (pH) of soil, the more readily it is absorbed by it. Cadmium is more easily activated and mobile in soils of pH 4.5-5.5. With higher pH values Cd is immobilized forming carbonates [20]. In soils examined it occurs in natural amounts or slightly elevated ones and fluctuated from 0.41 to 0.97 mg/kg (Fig. 2). In 6-degree IUNG classification 0.5 mg/kg d.m. is considered as natural amount of Cd in soil. On this basis it was stated that topsoils at sites 1, 4 and 5 exceed this amount (Fig. 2). The highest Cd concentration was detected in soil with the least situated near a ring road. Whereas in tree bark the highest Cd content was detected at site (3) situated nearest to the aluminium works and power plant (Fig. 2), and the highest content of the general forms of this element was noted on the eastern side of tree-trunks. Higher Cd content on the eastern side of tree-trunk (differently than in case of Pb) can prove that the main source of emission of this element is industry. As the research indicate, Cd accumulates best in bark - according to Samecka-Cymerman et al. [21] they state that bark is a better accumulator of Cd compared to *Pinus schreberi*, whereas in soil its content is considerably lower. However in soils at sites situated near roads (1 and 5) the Cd content is similar to the content observed in barks at the same localities (Fig. 2).

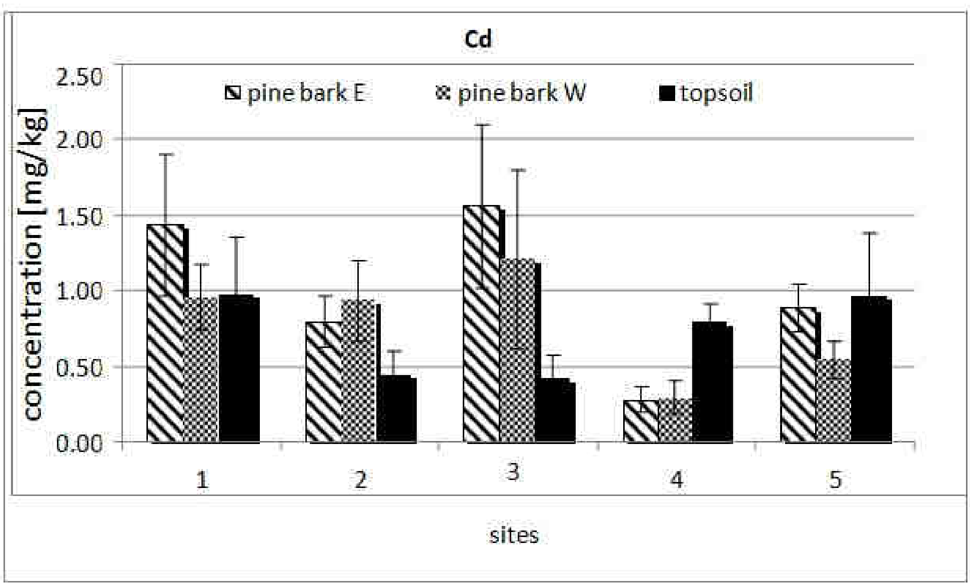

Fig. 2. Cd concentrations in studies sites

In spite of the statement presented in literature that emissions released at the height [16] can be observed in case of Cd and Ni, because they are emitted mainly from tall smokestacks. The results prove that apart from industrial emissions, car transport influences heavily the content of Cd. The results obtained by Marko-Worlowska et al. [22] confirm at the same time, that motorways are the main emitters of Pb and big emitter of Cd, in the immediate vicinity nearest and up to 200 m away from the motorway.

Nickel is emitted mainly by the metallurgical industry and during coal burning and petrol use [23]. In the case of Ni considerably higher amounts were observed in soils at all sites analyzed (from 2.73 to 4.41 mg/kg), whereas in barks the amount was from 0.4 to 1.9 mg/kg (Fig. 3).

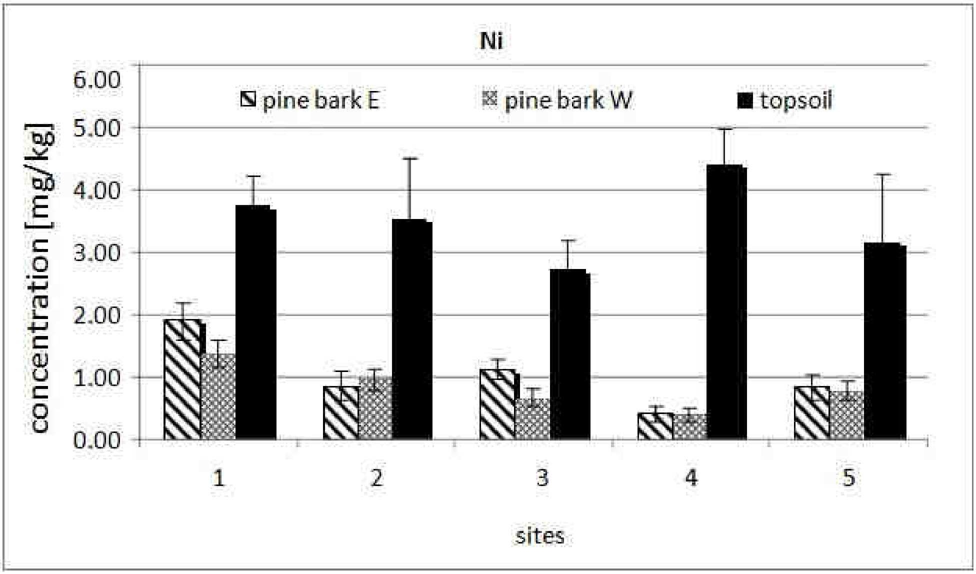

Fig. 3. Ni concentrations in studies sites

Natural concentrations of this metal in soil are 25 mg/kg d.m. [10]. In all soils analyzed its content was much lower. In tree-bark the highest content of Ni (different than in case of Pb, and similar to the case of Cd) was noted on the eastern side of the trees (Fig. 3). It proves the significant influence of industry on Ni emissions.

In most circumstances, a positive correlation is observed between lead and cadmium concentrations in soil and pine bark, which predicts the higher the lead content the higher the cadmium concentration. Concentrations of Cd and Pb in topsoil and in bark were influenced by the distance from industrial emitters and busy roads. Concentration of Ni in topsoil was not influenced by these distances, whereas concentrations of Cd, Pb, Ni in bark were not influenced by concentration of this element in soil (Figs. 1-3).

Conclusions

1. The results obtained confirm the negative impact of aluminium work, power plant and transport on quality and number of environmental pollutants at the sites situated near these industries and road with intensive traffic. Therefore, the constant monitoring of these localities is necessary.

2. Topsoil is better biomonitor for lead and nickel than pine bark.
3. Pine bark appears to be better bioindicator of atmospheric acidifying compounds and cadmium deposition and with comparison with another bioaccumulators can be suitable biomonitor for environmental pollution by heavy metals.

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ZASTOSOWANIE KORY SOSNY I WIERZCHNIEJ WARSTWY GLEBY DO OCENY ZANIECZYSZCZEŃ PRZEMYSŁOWYCH I KOMUNIKACYJNYCH

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Abstrakt: W wierzchniej warstwie gleby oraz w próbkach kory sosny zwyczajnej *Pinus sylvestris* L. zebranych wokół centrum przemysłowego w Skawinie oraz na terenie Bielańsko-Tynieckiego Parku Krajobrazowego w Krakowie, położonego w południowo-wschodniej Polsce, oznaczono stężenia takich metali ciężkich, jak, Pb, Cd, Ni. Celem badań było wykazanie przydatności kory martwicowej i wierzchniej warstwy gleby do monitorowania zanieczyszczenia środowiska tymi metalami ciężkimi i związkami zakwaszającymi. Na podstawie porównania stężenia metali ciężkich w wierzchniej warstwie gleby i korze sosny oraz wartości pH kory sosnowej stwierdzono, że gleba jest lepszym biomonitorem dla ołowiu i niklu, natomiast kora sosny zwyczajnej *Pinus sylvestris* L. wydaje się być odpowiednim bioindykatorem depozycji atmosferycznej tylko dla kadmu i składników zakwaszających.

Słowa kluczowe: *Pinus sylvestris* L., kora martwicowa, metale ciężkie, wierzchnia gleba, odczyn kory sosny, biomonitoring