Necrotic bark of common pine (Pinus sylvestris L.) as a bioindicator of environmental quality

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Abstract The aim of this study was to determine the pH and the concentration of lead, cadmium, nickel, copper and zinc in aqueous extracts of necrotic bark Pinus sylvestris L. and in adjacent soil, located in two types of forest habitat in different parts in the Niepolomice Forest in southern Poland. The Niepolomice Forest is located about 35 km east of an urban-industrial agglomeration Kraków. Despite the lack of significant differences in pine bark reaction studied, there was a clear difference in contamination of both bark and soil with heavy metals. There was a correlation between the distribution of pollutants in the forest, and the direction of the prevailing winds. More heavy metals were accumulated in the pine bark and soil from the west than the east. The high content of lead, zinc, cadmium and copper in the soils most likely results from the inflow of gas and dust pollutants from the urban-industrial agglomeration of Kraków.

Keyword Heavy metals · Necrotic pine bark · pH reaction · Niepolomice Forest

Introduction

Biosphere pollution imposes a need to search for bioindicators enabling evaluation of the quality of environment and identification of trends in its changes. Using biological materials in the determination of environmental pollution as indicators is a cheap and reliable method (Faggi et al. 2011). Various types of plant, lichens, mosses, bark and leaves of higher plants have been used to detect the deposition, accumulation and distribution of metal pollution (Grodzińska 1982; Sawidis et al. 2011; Serbula et al. 2013). Tree bark is a sensitive indicator of environmental pollution, particularly of acidifying compounds and heavy metals (Al-Asheh and Duvnjak 1997). These contaminants affect the physicochemical properties of bark (Świeboda and Kalemba 1979; Santamaría and Martín 1997). The pH depends on the species, age and health of the trees and on the soil they grow on (Medwecka-Kornaś et al. 1989; Szczepanowicz and Gawroński 2000). Among the studied barks of pine tree are Turkish red pine Pinus brutia Ten. (Baslar et al. 2009), Italian stone pine Pinus pinea L. (Oliva and Mingorance 2006), Austrian pine Pinus nigra Arnold. (Coskun 2006), Masson pine Pinus massoniana Lamb. (Kuang et al. 2007) and Scots pine (Pinus sylvestris L.) (Świeboda and Kalemba 1979; Huhn et al. 1995; Lippo et al. 1995; Poikolainen 1997; Schulz et al. 1999; Pöykiö et al. 2005; Saarela et al. 2005; Samecka-Cymerman et al. 2006). In Poland, atmospheric pollution may be well detected with the bark of common pine (P. sylvestris L.), being a sensitive and common (over 70 % of all Polish trees) bioindicator, located at fixed sites, constantly influenced by the surrounding environment and easily sampled and analysed (Grodzińska 1978, 1982; Marko-Worłowska et al. 2011; Chrzan and Marko-Worłowska 2012). Examination of water extracts from tree bark provides data on its pH reaction (lowered by SO₂ and NOₓ in the air), electrolytic conductivity, ability to absorb chosen chemical elements and concentration of sulphates in extract (Schulz et al. 1999).

Soil also belongs among the components of the natural environment more sensitive to the effects of pollution, including pH changes caused by human activity (Kowalkowski 2002; Hernandez et al. 2003). Acidity is one of the key factors determining the course of many soil processes, affecting the functioning and efficiency of entire geosystems. 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 (Gambuś and Gorlach 2001; Gruc-Królikowska and Wacławek 2006).

The study aimed to determine the pH reaction and concentration of lead, cadmium, nickel, copper and zinc in water extracts from necrotic bark of P. sylvestris L. and in soil surrounding the analysed trees, situated in two forest habitat types of the western and southern part of the Niepolomice Forest located in southern Poland, as well as to evaluate the environmental pollution in this area on the basis of abovementioned parameters.

Materials and methods

The study area covered the Niepolomice Forest, located ca. 35 km from Kraków and since many years considered as its “green lungs”. The area extends at ca. 10,758 ha, includes ca. 80 % of forest surface in the Niepolomice Forest District and includes several parts, presently separated, however once integrated.

Species composition in stands of the Niepolomice Forest is dominated by pine, attaining a frequency of 62 %. Bark was sampled from even-aged specimens of common pine growing in two sectors of the Niepolomice Forest, namely the fresh mixed broadleaved forest (in the western part of the southern complex of the Niepolomice Forest, in the Sitowiec Forestry), and the moist mixed broadleaved forest (in the ecotone zone of the southern part of the Niepołomice Forest, in the Baczków Forest District, near a highway, built at that time) (Fig. 1). The areas were covered by soils of similar type, namely brown acidic soils and podzols. All the samples were collected in the autumn in October.

Both sectors included trees of similar size (diameter at breast height of ca. 40–45 cm) and age (ca. 45 years) and spaced at ca. 3–5 m from each other. For each tree, three samples of necrotic bark were collected, using a sharp knife, from all four sides of the trunk (southern, northern, western and eastern), at ca. 1.5 m from the ground. Surfaces covered with lichens or resin was avoided. Sampling was performed after a no-rainfall period, as recommended by other authors using the “bark test” (Medwecka-Kornaś et al. 1989). Additionally, topsoil samples, each of ca. 10 dag, were collected with a soil samples from the surrounding of examined trees, from the depth of ca. 5 cm. In total, 96 samples of pine necrotic bark (P. sylvestris L.) and 24 soil samples were taken.

The obtained bark was dried in open air at ca. 25 °C, for ca. 30 days, and ground to powder in an electric grinder. Samples were prepared by mixing ca. 1 g of the powdered bark with 8 ml of distilled water, at room temperature, and after 24 h were subjected to pH measurements using a WTW 330 pH meter. Similarly, all soil samples were dried and used to prepare solutions, including 10 g of soil and 25 ml of distilled water, in which pH was measured after 24 h from pouring water on to the soil. The next step of analytical studies involved preparation of soil and bark for mineralization. From each sample, 0.5 g of bark or ca. 1 g of soil was weighted out into a vial, afterwards filled with 4 ml of 65 % nitric acid. After mineralization (2–3 h at 110 °C) solutions were poured to volumetric flasks and filled with distilled water to 10 ml. Content of heavy metals (lead, cadmium, copper and zinc) in the mineralized soil and bark samples was determined in the AAS atomic absorption spectrophotometer (Cole-Parmer, BUCK 200A).
All the analyses were performed using STATISTICA 10 computer program. Results were subjected to analysis of variance with repeated measurements and Tukey’s test. Relationships between the pH reaction in bark and soil and metal content in bark and soil were assessed with the Pearson linear correlation coefficient. The p value assumed as statistically significant was $p<0.05$ and statistically highly significant was $p<0.01$.

**Results and discussion**

The pH of pine bark *P. sylvestris* L. indicated its much higher acidity than that of the soil in which these pine trees grew. The pH of the analysed pine bark ranged from pH 2.92 to pH 3.25 (Table 1). Similar acidity of pine bark (2.97–3.16) showed Bąbelewska (2013) in forest reserves, “Zielona Góra” and “Sokole Góry” near Częstochowa in Poland. Santamaria and Martin (1997) also recorded similar bark acidity for *P. sylvestris* L (3.17) in Navarra, Spain. A little lower pH values of the pine bark obtained in a study in the Niepołomice Forest by Grodzińska (1978, 1982). The Niepołomice Forest, located just a few kilometers from the large agglomeration of Krakow and a steel mill, reported acidification of pine bark in the range 2.2–3.0 (Grodzińska 1982). Grodzińska (1978) reported similar values of pH reactions in pine barks of Kraków and polluted areas of southern Sweden.

The low pH of pine bark was also reported in Ojcowski National Park (2.6–3.5) (Medwecka-Kornaś et al. 1989), the most polluted national park in Poland.

Lowering the pH of pine bark below 3.0 is dangerous and can result in changes in the health of the forest ecosystem. pH of common pine bark lower than 3.0 may increase the accessibility of heavy metals to plant tissues and therefore threaten the healthiness of forest ecosystems (Bąbelewska 2013).

Differences between the pH reaction of bark collected from various sides of the examined pine trunks appeared to be highly significant ($F=31.49; p<0.0001$), with the highest values recorded for the western and eastern side (mean pH 3.1). These two groups did not differ statistically from each other ($p=0.9027$), however showed significantly higher values than bark pH at the northern side (mean 2.92). The lowest bark pH was determined for the southern side (mean 2.76), statistically different from pH at W ($p=0.0002$), E ($p=0.0003$) and N ($p=0.003$).

Soil pH was generally higher, with values ranging between 3.9 and 6.35 and attaining a mean of ca. 4.5 (Table 1). The investigated forest habitat types showed only small differences in soil and bark pH, being slightly higher in the fresh than in the moist forest (Fig. 2). However, no statistically significant relationship was established between bark and soil pH at any of examined sides ($p=0.5174; p=0.7253$).

Concentration of metals in bark varied at particular sides of collection and was also different from soil. At the western side, necrotic bark of the examined trees displayed the highest heavy metal concentrations, with Pb accumulated at greatest values (42.35 mg kg$^{-1}$ d.m.), followed by Zn (40.85 mg kg$^{-1}$ d.m.), Cu (25.63 mg kg$^{-1}$ d.m.) and Cd (2.08 mg kg$^{-1}$ d.m.). Such high metal accumulation in the west-side bark may result from the direction of air movement in the Niepołomice Forest, dominated by western winds, carrying dust from the industrial agglomeration of Kraków. In contrast, the lowest metal content was generally recorded for bark from the southern side of trees (Zn—12.92 mg kg$^{-1}$ d.m., Pb—9.63 mg kg$^{-1}$ d.m., Cu—4.74 mg kg$^{-1}$ d.m.).

In areas less intensively affected by anthropogenic activity, accumulation of Zn is lower than in industrial areas and roadsides (Baslar et al. 2009).

The minimum mean zinc value was determined as 8.4 mg kg$^{-1}$ d.m. in control areas, and the maximum mean value was determined as 14.1 mg kg$^{-1}$ d.m. in industrial areas and roadsides in Western Anatolian part of Turkey (Baslar et al. 2009). Higher concentrations of Zn (up to 189 mg kg$^{-1}$ d.m.) showed by Schulz et al. (1999) in Rösa, a polluted area in Germany.

Cadmium concentration in bark was the lowest at the northern side (0.62 mg kg$^{-1}$ d.m.), while at the southern side,

| Parameters | X  | SD | Min | Q25 | Me  | Q75 | Max |
|------------|----|----|-----|-----|-----|-----|-----|
| pH bark W  | 3.10 | 0.05 | 3.02 | 3.06 | 3.08 | 3.12 | 3.21 |
| pH bark E  | 3.13 | 0.08 | 2.99 | 3.06 | 3.12 | 3.19 | 3.25 |
| pH bark N  | 2.92 | 0.17 | 2.66 | 2.83 | 2.87 | 3.05 | 3.25 |
| pH bark S  | 2.76 | 0.09 | 2.63 | 2.70 | 2.74 | 2.79 | 2.97 |
| pH soil W  | 4.66 | 0.68 | 4.11 | 4.20 | 4.38 | 4.98 | 6.35 |
| pH soil S  | 4.14 | 0.17 | 3.89 | 4.01 | 4.10 | 4.27 | 4.45 |

$X$ mean, $SD$ standard deviation, $Min$ minimum, $Q25$ lower quartile, $Me$ median, $Q75$ upper quartile, $Max$ maximum, $W$ West, $E$ East, $N$ North, $S$ South

**Fig. 2** Comparison of the soil pH and pine bark in the studied types of forest habitat MMBF—moist mixed broadleaved forest, MFBF fresh mixed broadleaved forest
it showed a significant ($p=0.0403$) and negative ($r=−0.9456$) correlation with Cd concentration in soil (Fig. 3). Schulz et al. (1999) showed in their work significantly lower mean of the metal—three times lower in Jostedalsbreen National Park in Norway, Syktyvkar in Russia and Neuglobsow in Germany, twice lower in Rösa, a polluted area in Germany, and only 1.5 times lower (0.4 mg kg$^{-1}$ d.m.) in Białowieża, Poland.

Amounts of Zn, Cu and Pb attained much higher values in soil than in bark (Figs. 3 and 4).

Compared to bark, mean Zn content in soil was over six times greater in the southern part of the forest and three times greater (119.33 mg kg$^{-1}$ dry weight) in the western part (Fig. 3). However, correlations between soil and bark for Zn concentration were not statistically significant ($p>0.05$). A significant positive correlation was observed for Cu content in soil at the western side and in bark at the eastern side ($p=0.0422$, $r=0.9404$).

Soils, specifically their humic horizon, are the main site of accumulation and strong fixation of anthropogenically derived lead. Soil Pb contamination is rather the result of many years of deposition enriched in transboundary leaded gasoline particles than of a local or regional industrial sources (Hernandez et al. 2003). The element, though of low mobility, in acidic and sandy grounds may become easily accessible to plants and consequently can be incorporated into food chains and impose a direct threat to organisms (Kabata-Pendias and Pendias 1999). In Poland, lead concentration in soil attains a mean value of 18 mg kg$^{-1}$ and is most frequently recorded at amounts not exceeding 100 mg kg$^{-1}$. Soil of the examined fresh mixed broadleaved forest included 52 mg kg$^{-1}$ Pb (Table 2). However, Pb from airborne particles represents the present-day atmospheric conditions, whereas the soil surface reflects several years of atmospheric deposition.

This value was significantly and positively correlated with Pb content in bark ($p=0.0449$, $r=0.9404$). However, no correlation between concentration in soil and bark was established for other metals ($p>0.05$).

The obtained results indicate increased content of copper, zinc, lead and cadmium in the investigated soils of the Niepolomice Forest. Much lower concentration of Pb (average 12.45 mg kg$^{-1}$ d.m.), Cu (10.44 mg kg$^{-1}$ d.m.) and Zn (39.5 mg kg$^{-1}$ d.m.) were showed in a natural reserve in Dinghushan in China (Kuang et al. 2007). The obtained results are in consent with studies by Hernandez et al. (2003), who concluded that high metal content in soils may be recorded both close to pollution sources and at greater distances, what results from the geographic location of sites and spreading of pollutants by winds, in the direction of their movement.

Enrichment of forest topsoil with heavy metals is likely to evidence their anthropogenic origin. Such a quality of soil environment results possibly from the inflow of gas and dust pollutants carried by western winds, mainly from the urban-industrial agglomeration of Kraków. Consequently, soils of the western part of the Niepolomice Forest accumulated more zinc and copper, while soils of the southern part of the forest, adjacent to a highway, accumulated more cadmium and lead (Fig. 4).

Research of other authors (Härtel and Grill 1972; Poikolainen 1997; Harju et al. 2002; Kuang et al. 2007; Kakulu 2003; Sawidis et al. 2011; Guéguen et al. 2012) has confirmed that industrial activity tends to increase the concentration of metallic contaminants of barks. According to Huhn

![Fig. 3 Content of heavy metal in pine bark milligram per kilogram d.m. W West, E East, N North, S South](image3)

![Fig. 4 Content of heavy metal in topsoil milligram per kilogram d.m. W West, S South](image4)

**Table 2** The average of heavy metal concentrations (mg kg$^{-1}$ d.m.) in soil and pine bark in Niepolomice Forest

| Metal | MMBF soil | MFBF soil | MMBF bark | MFBF bark |
|-------|-----------|-----------|-----------|-----------|
| Zn    | 89.44 (20.81) | 119.33 (87.98) | 14.33 (3.13) | 37.23 (6.54) |
| Cu    | 15.86 (1.55)  | 26.00 (16.9)  | 5.46 (1.31)  | 19.39 (8.19)  |
| Cd    | 0.93 (0.16)   | 0.88 (0.69)   | 0.76 (0.24)   | 2.06 (0.42)   |
| Pb    | 76.11 (25.35) | 51.76 (22.28) | 12.48 (4.08) | 29.93 (14.98) |

Numbers in the bracket are the standard deviations of the concentrations (SD)
et al. (1995) and Schulz et al. (1999), heavy metal concentrations of the barks were generally found to correlate very well with the heavy metals deposition.

The results of researches from Niepolomice indicate that concentrations of analysed heavy metals do not exceed boundary values defined in the Regulation of the Minister of Environment on soil quality standards and earth quality standards for group B soils, including the forest, tree-covered and shrub-covered soils, wastelands and built-up and urbanized areas, however excluding industrial areas, mining grounds and transport areas (Regulation 2002). Similar results were reported by other authors (Ciesiła et al. 1994; Skwaryło-Bednarz 2006).

Conclusions

Tree bark is a sensitive indicator of environmental pollution, particularly of heavy metals. The presented results confirm the usefulness of water extracts from bark of common pine (P. sylvestris L.) in research on the spatial variation and distribution of pollution in forests. Bark of trees examined in the western part of the Niepolomice Forest showed higher concentrations of Pb, Cd, Zn and Cu than in the southern part, most likely due to accumulation of pollutants inflowing from the urban-industrial agglomeration of Kraków with the dominant western winds.

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