ESTIMATION OF OAK STAND POLLUTION WITH HEAVY METALS ON THE KROTOSZYN PLATEAU

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ABSTRACT

The content of heavy metals – Zn, Cd, Pb and Cu – in oak wood of *Quercus robur* L. and in the soil was investigated. The studies were carried out in five areas: on the Krotoszyn Plateau, in two areas of the Copper Basin, in the area of Zawiercie and in the control area in Kórnik. The results showed an elevated content of copper in the wood of oaks from the Krotoszyn Plateau as compared with oaks from the other investigated areas. The copper content in the examined oaks was 0.6 µg/g in Kórnik, 1.1 µg/g in Zawiercie, 3.9-15.8 µg/g in the Copper Basin, whereas in the oaks of the Krotoszyn Plateau it amounted to 7.0-26.5 µg/g. It was also noticed that there is a correlation between the copper content in the wood and sanitary condition of the trees. The content of other toxic metals in the oak stands of the Krotoszyn Plateau was on the level of non-polluted areas ranging between 0.08-0.21 µg/g for Cd, 0.12-0.45 µg/g for Pb and 9.1-14.7 µg/g for Zn.

KEY WORDS: *Quercus robur*, Krotoszyn Plateau, copper, zinc, cadmium, lead

INTRODUCTION

A complex of oak stands on the Krotoszyn Plateau (the area under the District Forest Administration in Krotoszyn, Piaski, Jarocin and Taczanów, in West-Central part of Poland), is one of the most valuable forest objects in Europe. In addition to their natural beauty and value, these forests are of great economical importance, regularly providing national economy with high-quality wood assortments (Filipiak and Zaradny 1991). Unfortunately, these stands have been declining for a dozen or so years. Therefore, the oak stands of the Krotoszyn Plateau are now an object of intense studies and observations aimed at finding the cause or causes of oak diseases and decline (Siwecki 1987). According to the above authors, oak decline might be affected by different abiotic (mainly drought in 1982-1983) and biotic factors (feeding of the pea-green oak roller moth *Tortrix viridiana* causing defoliation and development of fungi from the genus *Ophiostoma* (*Ceratocystis*); the problem, however, has not been clearly explained. The influence of environment contamination, mostly by industrial pollutants, has not been sufficiently investigated, either.

The aim of the present paper was to determine the degree of pollution with heavy metals – Zn, Pb, Cd and Cu of the oak stands on the Krotoszyn Plateau. Therefore the contents of Zn, Cd, Pb and Cu in the wood of oaks and in the soil were analysed. The Krotoszyn Plateau is located in the wind zone from the Copper Smelter in Głogów. This creates the possibility for pollution of the forest area with heavy metals. The studies covered the oak stands on five investigated areas established by the Polish Academy of Sciences – Institute of Dendrology in Kórnik. On account of the small number of

reference monographs concerning heavy metal content in the wood of oaks (Greszta 1982, Queirolo and Valenta 1987, Queirolo et al. 1990) and only a few papers dealing mostly with Pb (Ault et al. 1970, Szopa et al. 1973, Herrmann et al. 1978, Kardell and Larsson 1978) the studies also included stands located in the copper region (near the Głogów Smelter), in Zawiercie (near a Steel Mill) and in Kórnik (Experimental Forest Zwierzyniec – completely free of heavy metal contamination).

MATERIALS AND METHODS

The characteristics of the oak stands under study are presented in Table 1. All the stands contained the same oak species – *Quercus robur* L.

Wood samples were taken from several oak trees on each investigated forest area with a Pressler's bore at a height of 1.30 m above the ground. They were dried up (105 °C, 24 h), and then disintegrated. Wood mineralization and determination of Zn, Cd, Pb and Cu contents were done as described by Opydo and Zembruski (1993) (by differential pulse anodic stripping voltammetry using a hanging mercury drop electrode). Soil samples were taken at three depths: 0-20 cm, 20-40 cm and 40-60 cm. Metals were extracted from the soil samples by a mixture of hydrochloric and nitric acids in the ratio 3:1 (Wolf et al. 1984). The extract was evaporated adding 30% hydrogen peroxide at the end of evaporation to mineralize organic compounds contained in the sample. The obtained deposit was dissolved in several drops of concentrated hydrochloric acid, and iron (III) was reduced using 0.1 M ascorbic acid. The contents of Cd, Pb, Cu and Zn were determined as in the wood.

TABLE 1. The state of oak stands under study

Location of stand	Research area	Age of trees	Sanitary condition of trees
Krotoszyn Plateau	Jasne Pole 1	136	numerous mortality
	Jasne Pole 2	106	healthy stand
	Jasne Pole 3	104	intense dieback
	Potarzyca	106	diseased stand
	Jarocin breeding nursery	about 100	healthy stand
Copper Basin	Biechów – 2 km from Głogów Smelter	about 80	diseased and healthy trees
	Bogomice – 3 km from Głogów Smelter	about 80	diseased and healthy trees
Zawiercie	3 km from Zawiercie Steel Mill	about 130	healthy trees
Kórnik	Experimental Forest Zwierzyniec	about 100	healthy trees

RESULTS AND DISCUSSION

Results of the soil analysis are summarized in Table 2. They show that in all the cases the metal content was significantly higher in the surface layer (0-20 cm) than in the two other layers at the depth of 20-40 cm and 40-60 cm. This indicates that penetration of these metals into the soil was slow and not large.

The concentration of Zn in the surface soil layer from the Krotoszyn Plateau is comparable with that from Kórnik, but is definitely lower than that from the copper region and Zawiercie. Nevertheless, in all the cases the concentration of this metal is very low. Literature reports on this subject (Kabata-Pendias and Pendias 1979) give 5-220 µg/g concentrations of Zn in bleached soils, 17-127 µg/g in loess and slimy soils and

TABLE 2. Concentration of copper, zinc, lead and cadmium (µg/g) in soil samples near the investigated trees. Confidence intervals of means, at 95% confidence level of Cu, Zn and Pb were determined for the surface layer

Sampling location	Soil layer	Copper	Zinc	Lead	Cadmium
Jasne Pole 1	0-20 cm	14.6±3.0	8.5±1.0	18.6±1.5	0.06
	20-40 cm	8.0	6.3	7.2	0.05
	40-60 cm	4.8	4.3	9.3	0.04
Jasne Pole 2	0-20 cm	9.1±2.5	8.5±1.2	13.8±2.0	0.05
	20-40 cm	4.4	5.8	7.7	0.03
	40-60 cm	3.8	5.9	7.2	0.03
Jasne Pole 3	0-20 cm	12.7±1.6	14.4±3.6	19.4±5.0	0.11
	20-40 cm	6.2	9.3	9.2	0.07
	40-60 cm	6.0	7.7	6.6	0.05
Potarzyca	0-20 cm	12.1±1.5	11.2±2.0	18.3±1.8	0.09
	20-40 cm	7.4	7.7	8.2	0.05
	40-60 cm	5.2	7.1	6.5	0.05
Jarocin	0-20 cm	8.2±1.5	8.8±1.2	13.3±1.5	0.06
	20-40 cm	4.0	6.5	6.3	0.03
	40-60 cm	2.0	6.4	3.1	0.03
Biechów	0-20 cm	86.8±22	45.2±7.0	81.5±19	0.34
	20-40 cm	9.6	26.6	11.4	0.08
	40-60 cm	7.1	18.9	5.6	0.04
Bogomice	0-20 cm	22.3±7.6	16.1±3.0	79.5±20	0.25
	20-40 cm	8.9	7.3	14.1	0.03
	40-60 cm	9.5	6.5	2.1	0.03
Zawiercie	0-20 cm	5.7±1.0	90.5±8.0	120.1±22	0.25
	20-40 cm	4.1	24.9	10.6	0.06
	40-60 cm	3.2	15.0	5.4	0.05
Kórnik	0-20 cm	6.5±2.0	8.7±1.2	12.7±1.2	0.06
	20-40 cm	3.5	6.2	7.2	0.03
	40-60 cm	2.4	6.9	2.2	0.03

TABLE 3. Concentration of Zn, Cd, Pb and Cu ($\mu\text{g/g}$) in the wood of oaks

Location of stand	Research area	Zinc	Cadmium	Lead	Copper
Krotoszyn Plateau	Jasne Pole 1	13.3 $\pm$ 2.0	0.12 $\pm$ 0.02	0.45 $\pm$ 0.05	26.5 $\pm$ 2.5
	Jasne Pole 2	14.8 $\pm$ 1.5	0.09 $\pm$ 0.02	0.21 $\pm$ 0.05	7.5 $\pm$ 2.0
	Jasne Pole 3	9.0 $\pm$ 2.2	0.12 $\pm$ 0.02	0.22 $\pm$ 0.04	11.5 $\pm$ 2.0
	Potarzyca	9.2 $\pm$ 2.0	0.08 $\pm$ 0.02	0.12 $\pm$ 0.05	25.3 $\pm$ 2.8
	Jarocin breeding nursery	14.2 $\pm$ 1.6	0.21 $\pm$ 0.03	0.25 $\pm$ 0.08	7.0 $\pm$ 1.2
Copper Basin	Biechów healthy trees	10.3 $\pm$ 2.1	0.14 $\pm$ 0.02	0.52 $\pm$ 0.08	4.0 $\pm$ 1.2
	Biechów diseased trees	11.3 $\pm$ 2.1	0.12 $\pm$ 0.02	0.57 $\pm$ 0.12	14.8 $\pm$ 2.7
	Bogomice healthy trees	10.9 $\pm$ 1.7	0.14 $\pm$ 0.02	0.82 $\pm$ 0.14	3.9 $\pm$ 1.0
	Bogomice diseased trees	12.8 $\pm$ 2.3	0.15 $\pm$ 0.03	0.99 $\pm$ 0.06	15.8 $\pm$ 2.5
Zawiercie	near a Steel Mill	25.1 $\pm$ 2.3	0.12 $\pm$ 0.02	0.38 $\pm$ 0.08	1.1 $\pm$ 0.1
Kórnik	Experimental Forest Zwierzyniec	7.5 $\pm$ 1.1	0.20 $\pm$ 0.02	0.45 $\pm$ 0.05	0.6 $\pm$ 0.1

$\pm$ confidence intervals of means at a 95% confidence level

13-362 $\mu\text{g/g}$ in loamy soils. Other reports mention 53-222 $\mu\text{g/g}$ (Andruszczak et al. 1986) and 20-108 $\mu\text{g/g}$ Zn (Kabata-Pendias et al. 1981) determined in the soils from the copper basin.

In the case of lead, its concentration in the surface layer is also significantly lower in the soil from the Krotoszyn Plateau and from Kórnik than in the remaining soils. The literature (Kabata-Pendias and Pendias 1979) reports on 14-32 $\mu\text{g/g}$ Pb concentrations in non-polluted soils. In the soils of the copper basin the concentrations of Pb amounted to 95-645 $\mu\text{g/g}$ (Andruszczak et al. 1986) and to 325 $\mu\text{g/g}$ (Kabata-Pendias et al. 1981). These data indicate that the area of the Krotoszyn Plateau is not polluted with lead.

The natural Cd content in soils is within 0.0X-X $\mu\text{g/g}$ (Kabata-Pendias and Pendias 1979). Therefore, its 0.06-0.11 $\mu\text{g/g}$ concentrations found in the soil from the Krotoszyn Plateau (at the depth of 0-20 cm) permit to qualify the studied soil as free of cadmium contamination (cadmium-blank).

According to literature (Kabata-Pendias and Pendias 1979), copper content ranged between 1-26 $\mu\text{g/g}$ in bleached soils, 8-54 $\mu\text{g/g}$ in slimy and loess soils and 17-36 $\mu\text{g/g}$ in loamy soils. There are also reports on Cu concentrations amounting to 830 $\mu\text{g/g}$ (Kabata-Pendias et al. 1981) and 71-1244 $\mu\text{g/g}$ (Andruszczak et al. 1986) in the surface layers of the copper basin. The Cu content in the soil from the Krotoszyn Plateau, ranging between 8.2-14.6 $\mu\text{g/g}$, is relatively small as against these data. This, however, is an increased concentration of Cu in comparison with the reference area in Kórnik (6.5 $\mu\text{g/g}$) and with the soil from Zawiercie (5.7 $\mu\text{g/g}$).

The contents of Zn, Pb, Cd and Cu in the studied oak stands are given in Table 3. These results are based on measurements repeated 8 times and performed in a complete measuring cycle.

The content of Zn in the wood of oaks in the Krotoszyn Plateau ranging between 9.1-14.7 $\mu\text{g/g}$ is a little higher than that in the oak wood from Kórnik (7.5 $\mu\text{g/g}$) and is comparable with the Zn content in the stands of the copper basin (10.8-12.9 $\mu\text{g/g}$). Similar concentrations of Zn (17-18 $\mu\text{g/g}$) were determined in oak wood of seedlings grown in the control, non-polluted areas (Greszta 1982). It may, therefore, be assumed that the concentration of Zn found in the studied oak stands on the Krotoszyn Plateau is at natural level of that metal.

Similar results concerning Cd content do not show a large differentiation. Cd concentrations range between 0.08-0.21 $\mu\text{g/g}$, which may be recognized as normal level of Cd content in the wood of oaks. The literature also reports (Queirolo et al. 1990) on 0.03-0.13 $\mu\text{g/g}$ Cd in the oak wood growing in a non-polluted area and on 0.10-0.14 $\mu\text{g/g}$ concentrations of this metal in the wood of oaks growing in an area polluted with heavy metals.

The content of Pb in the oak stands of the Krotoszyn Plateau is between 0.12-0.45 $\mu\text{g/g}$. Similar concentrations of this metal were found in oak wood from Kórnik (0.45 $\mu\text{g/g}$) and Zawiercie (0.38 $\mu\text{g/g}$). These concentrations are lower than those found in oak wood from the copper basin, where they attained values ranging between 0.82-0.99 $\mu\text{g/g}$ (in Bogomice). Queirolo et al. (1990) report 0.04-0.14 $\mu\text{g/g}$ Pb in oak wood from clean areas and about 0.65 $\mu\text{g/g}$ Pb in the oaks from polluted areas. It may, therefore, be estimated that the oak stands of the Krotoszyn Plateau are rather not contaminated by lead.

Significantly more differential are the results obtained for copper. A considerably elevated copper content can be found in the oak stands located on the Krotoszyn Plateau as compared with copper concentrations in the oaks from other stands. The concentration of Cu is 0.6 $\mu\text{g/g}$ in Kórnik, 1.1 $\mu\text{g/g}$ in Zawiercie, 3.9-15.8 $\mu\text{g/g}$ in the copper basin and 7.0-26.5 $\mu\text{g/g}$ in the area of the Krotoszyn Plateau. The literature reports Cu concentrations in oak wood ranging between 0.8-1.8 $\mu\text{g/g}$ (Queirolo et al. 1990). Other reports inform on 5-8 $\mu\text{g/g}$ Cu found in the wood of oak seedlings from the control areas and on 17 $\mu\text{g/g}$ Cu detected in the xylem of seedlings grown in the soils containing 3850 $\mu\text{g/g}$ Cu (Greszta 1982). It should also be remembered that xylem is that part of the tree which cumulates heavy metals to the lowest degree. Thus, for example, in the paper of Greszta cited above, the seedlings containing 17 $\mu\text{g/g}$ Cu in the xylem simultaneously contained 870 $\mu\text{g/g}$ Cu in the roots, 119 $\mu\text{g/g}$ Cu in the bark and phloem as well as 30 $\mu\text{g/g}$ Cu in the leaves. In comparison to the above data the content of Cu found in the oak stands of the Krotoszyn Plateau seems to be fairly high.

A comparison of Table 3 with Table 1 leads to another striking conclusion. A higher content of copper can be found in the oak stands characterized by a worse health condition.

This regularity exists in the oak stands of both the Krotoszyn Plateau and the copper basin. Thus, the largest concentration of Cu was found in the oak stands located on the research areas Jasne Pole 1 and 3 and Potarzyca. There the condition of trees is very bad (Siwecki 1987). Oak dieback and decline are characteristic of these areas. Many symptoms of oak disease can be also encountered there.

Similar conclusions may be drawn after the analysis of results concerning the copper basin. In both Biechów and Bogomice, the copper content is about 3.5-fold higher in diseased than in healthy trees. A lower copper uptake by oaks in the copper region, as compared with the Krotoszyn Plateau, despite a higher Cu content in the soil, is probably caused by different copper mobility in both the environments. It is known, for instance, that the degree of copper assimilation by plants is influenced by such factors as temperature, soil pH and the contents of Al, Ca, Fe, Zn, P and N in the soil (Kabata-Pendias and Pendias 1979). The reaction of soils from the areas of the Krotoszyn Plateau is very acid (pH or 1 M KCl in some places amounts to 3), and the content of exchangeable aluminium in the research areas Jasne Pole 1 and Potarzyca is within 20-54 mg/100g (Opydo, own data).

On the basis of the obtained results it is difficult to state that copper is responsible for the process of oak decline. There is no report in the literature concerning the limits of Cu toxicity to oaks. But, without doubt, the content of copper is higher in diseased than in healthy stands. It, therefore, cannot be excluded that copper may be one of the factors causing weakening of trees, which become more susceptible to the development of pathogenic fungi and to the attacks of harmful insects.

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OCENA STOPNIA ZANIECZYSZCZENIA METALAMI CIĘŻKIMI DRZEWOSTANÓW DĘBOWYCH PŁYTY KROTOSZYŃSKIEJ

STRESZCZENIE

W pracy zbadano zawartość metali ciężkich – Zn, Cd, Pb i Cu – w drewnie dębów *Quercus robur* L. oraz w glebie. Badaniami objęto drzewostany dębowe zlokalizowane na pięciu powierzchniach badawczych Płyty Krotoszyńskiej, w zagłębiu miedziowym, w Zawierciu oraz w terenie kontrolnym w Kórniku. Przeprowadzone badania wykazują podwyższenie zawartości miedzi w drewnie dębów z Płyty Krotoszyńskiej w porównaniu z drzewostanami zlokalizowanymi na innych terenach. Zawartość miedzi w dębach z Kórnika wynosi 0,6 µg/g, z Zawiercia 1,1 µg/g, z zagłębia miedziowego 3,9-15,8 µg/g a z Płyty Krotoszyńskiej 7,0-26,5 µg/g. Zaobserwowano również korelację między zawartością miedzi w drewnie i kondycją drzew. Zawartość pozostałych metali w drzewostanach Płyty Krotoszyńskiej kształtuje się na poziomie charakterystycznym dla terenów nie zanieczyszczonych i wynosi dla Cd 0,08-0,21, dla Pb 0,12-0,45 oraz dla Zn 9,1-14,7 µg/g.

SŁOWA KLUCZOWE: *Quercus robur*, Płyta Krotoszyńska, miedź, cynk, kadm, ołów.

LITERATURE CITED

- ANDRUSZCZAK E., STRĄCZYŃSKI S., CZERNIAWSKA W., RADWAN B., 1986. Zawartość niektórych składników w glebach i roślinach uprawnych znajdujących się pod wpływem emisji hut miedzi. Roczn. Glebozn. 37 (4): 47-66.
- AULT W. U., SENECHAL R. G., ERLEBACH W. E., 1970. Isotopic composition as a natural tracer of lead in the environment. Environ. Sci. Technol. 4: 305-313.
- GRESZTA J., 1982. Correlation between the content of copper, zinc, lead and cadmium in the soil and the content of these metals in the seedlings of selected forest tree species. Frag. Flor. Geobot. 28: 29-52.
- FILIPIAK T., ZARADNY S., 1991. Oak decline in the Krotoszyn Forest District. In: Oak decline in Europe. Siwecki R., Liese W. (eds). Proc. Intern. Symposium, Kórnik, Poland, May 15-18, 1990, PWRiL – Oddz. w Poznaniu, pp. 299-305.
- HERRMANN R., NEULAND H., BUSS G., 1978. Zur Geschichte der Spurenmetallverunreinigung der Luft: Eine Zeitreihenanalyse der Metallgehalte in Baumringen. Staub-Reinhold Luft 38: 366-369.
- KABATA-PENDIAS A., PENDIAS H., 1979. Pierwiastki śladowe w środowisku biologicznym. Wydawn. Geolog., Warszawa.
- KABATA-PENDIAS A., BOLIBRZUCH E., TARŁOWSKI P., 1981. Impact of a copper smelter on agricultural environments. Roczn. Glebozn. 32: 3, 207-214.
- KARDELL L., LARSSON J., 1978. Lead and cadmium in oak tree rings (*Quercus robur* L.). Ambio 7: 117-121.
- OPYDO J. AND ZEMBRZUSKI W., 1993. Determination of Cd, Pb, Cu and Zn in wood by differential pulse anodic stripping voltammetry. Chem. Anal. (Warsaw) 38: 823-827.
- QUEIROLO F., VALENTA P., 1987. Trace determination of Cd, Cu, Pb and Zn in annual growth rings by differential pulse anodic stripping voltammetry. Fresenius Z. Anal. Chem. 328: 93-98.
- QUEIROLO F., VALENTA P., STEGEN S., BRECKLE S. W., 1990. Heavy metal concentrations in oak wood growth rings from the Taunus (Federal Republic of Germany) and the Valdivia (Chile) regions. Trees 4: 81-87.
- SIWECKI R., (ed), 1987. Ocena występowania, metody zapobiegania i zwalczania zjawiska zanieczyszczenia drzewostanów dębowych Płyty Krotoszyńskiej. Ekspertyza zespołowa. Instytut Dendrologii PAN Kórnik.
- SZOPA P. S., MCGUINNESS E. A., PIERCE J. O., 1973. Distribution of lead within the xylem elements of trees exposed to airborne lead compounds. Wood Sci. Technol. 6: 72-77.
- WOLF A., SCHRAMMEL P., LILL G., HOHN H., 1984. Bestimmung von Spurenelementen in Moos- und Bodenproben zur Untersuchung der Eignung als Indikatoren für Umweltbelastungen. Fresenius Z. Anal. Chem. 317: 512-519.