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The bioaccumulation of heavy metals in *Brassica napus* L. in the area around Turów Power Station, Poland

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Abstract. *Brassica napus* L. is a known bioaccumulator of copper, zinc, cadmium, lead, chromium, nickel and arsenic from soils. The metal ions are accumulated in the roots, stems, leaves and seeds of the oilseed rape. The samples of soils and plants were collected in the area around the Turów power station (Bogatynia city, Lower Silesia). The soil samples were collected from the surface layer of 0-25 cm. Roots, stems and pods of the oilseed rape were used in the study. The environmental samples were digested in HNO_3, 60%, using the Microwave Digestion System. Metal concentrations have been dermined through the FAAS method. Three heavy metals - zinc, copper and lead – have been analyzed. The content of zinc was higher than the content of copper in all samples (plants and soils). In the roots of the oilseed rape higher concentration of metals compared to other parts of the plant was observed. In the soil samples, there was no correlation between the concentration of pollution and the distance from the power plant. Permissible concentrations of heavy metals relative to the standard according to the Polish Ministry of Environment Regulation from September 1st, 2016, have not been exceeded. The permissible pollution indexes (Wn) in soils were exceeded compared to the geochemical background in uncontaminated soils of Poland. The bioaccumulation coefficients of heavy metals indicate lower metal concentrations in plants than in soils

1 Introduction

The main factor for the contamination of soil with metals is the industrial activity. In Poland, soils contaminated with heavy metals are usually observed in heavily industrialized areas. The processes of mining, also the extraction of metal ores, as well transporting, remaking and finally utilizing the products, are the leading sources of anthropogenic contamination of soils. Large amounts of pollutants are brought into the soil and the land from the metallurgical waste on landfills, and also as a result of gas and dust emissions created during the processing of fossil fuels in power and heating plants. Heavy metals can also get into the soil from the exhaust of road and railway transport vessels [1–3].

Heavy metals are are the persistent contamination and are accumulated in biotic elements of the ecosystem. Traditional methods of soil remediation are based on the immobilization of metals or, optionally, immobilization and removal from the environment

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(*in situ* and *ex situ* methods). The phytoremediation process can be used in industrial areas and along the roads, utilizing plants to purify the soil-water environment [4-6]. Plants have a natural ability to dispose, collect or remove contaminants from the soil. In phytoremediation specific species of plants are used, which can have lesser ability to acquire the pollutant, but their rate of growth is very high. These include e.g. the oilseed rape (*Brassica napus* L.), mustard greens (*Brassica juncea* L.), maize (*Zea mays* L.). The oilseed rape (*Brassica napus* L.) is known to accumulate copper, zinc, cadmium, lead, chromium, nickel and arsenic from the soil. Metals accumulate in the roots, stem, leaves and seeds [7].

2 Materials and methods

Samples of soil and oilseed rape were collected in June 2016 from the farmlands along road no. 352 in Lower Silesia (district of Zgorzelec, municipality of Bogatynia), in the immediate neighborhood of the Turów power station. In each location three soil samples were collected from ca. 4 m^2 soil surface. Soils from a given location were sieved and averaged after drying, giving one laboratory sample. The soil samples have been collected from the surface layer of the soil profile (up to 25 cm of depth).

Fig. 1 Locations of sampling.

Samples with location no. 2 were collected the nearest to the Turów power station. The remaining sampling places were at a greater distance from the source of the pollution emissions (Fig. 1, Table 1).

Table 1. The origin of environmental samples.

No.	Location
1	Laboratory of the Sewage Research and Sludge Processing Station.
2	Turów Power Station
3	Działoszyn
4	Działoszyn – Bratków Road
5	Bratków
6	Lutkogniewice
7	Krzewina

Analogically, three plants were collected at the same soil surface. Roots, stems and pods of the oilseed rape after separation were dryed and homogenized, giving an averaged laboratory samples. Soil samples of approx. 0.2 g of dry matter and plant samples of approx. 0.15 g of dry matter (the same amount of root, stem and pods) were digested in 8 cm^3 of HNO_3, 60%. Microwave mineralization process was conducted in a closed system in a condition of linear temperature rise (up to about 220 °C) and microwave radiation (power 500 W). The measurments of the concentration of metals were conducted through the FAAS method, with the use of the iCE 3500 Thermo Solaar. The spectroscopy analysis of three heavy metals (zinc, copper and lead) was carried out. The measurements in solutions were made in six replicates (six readings on the apparatus) and then arithmetic mean were calculated.

The accumulation index (Wn) of metal in soil was calculated as the ratio of the average content of chemical element in the contaminated soil versus to the geochemical background. The bioaccumulation coefficient (WB) of metal in a plant (separately for roots, stems or pods the oilseed rape) was calculated as the ratio of the average content of chemical element in a part of a plant to the metal concentration in the soil.

Chemical analyses have been carried out in the certified Laboratory of Toxycology and Environmental Research in the Faculty of Environmental Engineering at the Wroclaw University of Science and Technology.

3 Results

3.1 The content of zinc, copper and lead in soils

The highest content of copper and zinc was identified in soil samples collected from the location closest to the source of emissions, the Turów power station (Fig. 2).

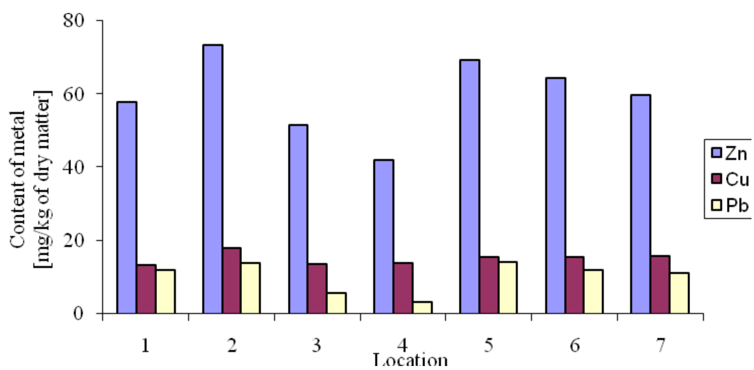

Fig. 2. The content of zinc, copper and lead in soils.

The content of zinc in soil sample no. 2 was 73.3 mg/kg of dry matter. This value is higher than the average zinc content in the Lower Silesia soils (59.8 mg/kg of dry matter [8]). In the area of Bogatynia, from where the samples were collected, the average content of zinc is even higher, 207.7 mg/kg of dry matter. The values of zinc content in soils are in the limit of the average value occurring in the region. The content of copper in soil sample no. 2 was 17.98 mg/kg of dry matter (in the Lower Silesia soils it is 21.5 mg Zn/kg of dry matter and in the area of Bogatynia it is in the range of 7.3 - 19.2 mg Zn/kg of dry matter) [8]. High concentrations of zinc and copper in the soil were also observed in samples no. 5, 6 and 7, collected a few kilometers away from the source of pollution emissions. The

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highest concentration of lead in sample no. 5 is 14.10 mg/kg of dry matter. Comparable concentrations of Pb were observed in soil samples, in descending order, no. 2, 1 and 6.

Copper is present in soil samples within the range of 13.37 to 17.98 mg/kg of dry matter. In sample no. 1 the lowest copper content in soil was observed. The concentration of zinc is within the range of 42.11 to 73.34 mg/kg of dry matter and the lowest content of Zn is in sample no. 4. Concentrations of zinc and copper exceeded the geochemical background level in surface soils for the whole Poland (background values: Cu – 6.5 mg/kg, Zn – 33 mg/kg, Pb – 18 mg/kg [9]). The concentration of lead in all measurement points was below the geochemical background and ranges from 3.35 to 14.10 mg Pb/kg of dry matter. Its content is the lowest in location no. 4.

The concentration of metals in soils is lower than the limit values according to the standard (the Polish Ministry of Environment Regulation from September 1st, 2016, regarding the manner of conducting the assessment of the contamination of ground [10]) and indicates lack of soil contamination of the investigated area

3.2 The pollution indexes of soils for zinc, copper and lead

Pollution indexes (Wn) were calculated for soil samples, informing about the enrichment of the soil with heavy metals. The Wn factor is expressed as the ratio of the metal in soil to the geochemical background in Poland [9]. The highest, above 2-fold, was the enrichment of all soil samples with copper (fig. 3), in relation to the average value of the geochemical background in Poland (Cu of 6.5 mg/kg [9]). The pollution indexes ranged from 2.1 to 2.8 in the case of copper. The maximum value Wn of 2.8 for copper occured in location no. 2.

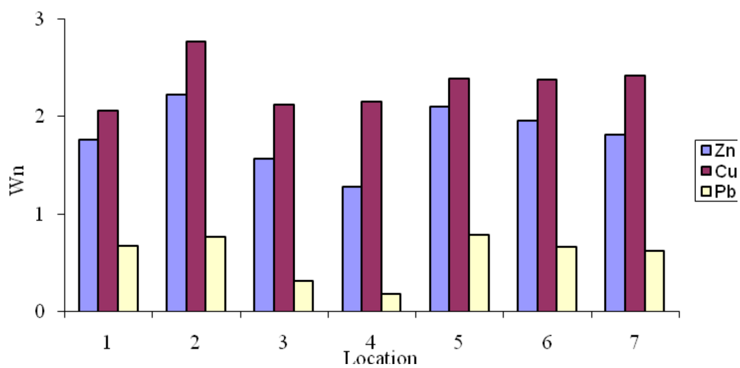

Fig. 3. Wn indexes for heavy metals.

The Wn values for zinc were in the range of 1.3 – 2.2. The maximum accumulation of zinc occured in sample no. 2 (Wn of 2.2). The lowest Wn value of 1.3 was recorded in location no. 4. The concentrations of zinc in soils, as in the case of copper, in all measurement samples were higher than the geochemical background in Poland (Zn of 33 mg/kg [9]).

The Wn values obtained for lead (0.20-0.80) indicated a small accumulation of metal in the soil samples. The pollution indexes do not show the excess of lead relative to the geochemical background (Pb of 18 mg/kg [9]). The highest enrichment of soils with this element were found in samples no. 2 and 5 (Wn 0.80). The minimum value was observed in soil no. 4 (Wn 0.19).

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3.3 The content of zinc and copper in the oilseed rape (*Brassica napus* L.)

In the roots, stems and pods of the oilseed rape (*Brassica napus* L.) the content of zinc, copper and lead was assayed through the FAAS method. The concentrations of lead in the biomass were below the quantification limit for the flame technique of the atomic absorption spectroscopy.

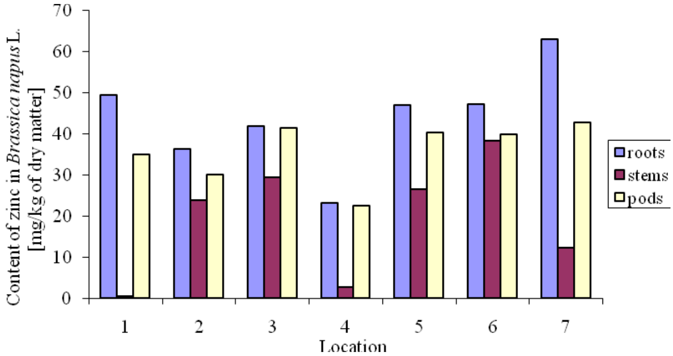

Fig. 4. The content of zinc in *Brassica napus* L.

The highest concentrations of zinc were observed in the roots of the oilseed rape (Fig. 4). The content of Zn ranged from 23.2 to 63.0 mg/kg of dry matter. Decreasing amount of metal was observed sequentially in samples no. 7, 1, 6, 5, 3, 2 and 4. The content of zinc in the pods of the oilseed rape were in the range of 22.5 to 42.8 mg/kg of dry matter.

The stems of the oilseed rape in samples no. 2 and 4 had the content of zinc below 3 mg/kg of dry matter. In other samples content of 12.0 to 38.4 mg Zn/kg of dry matter was observed. Maximum concentration of zinc in the stem was identified in sample no. 6. Comparison of the results with the allowable concentration of Zn in the forage plants from the grassland (50–100 mg Zn/kg of dry matter [11]) showed no exceedance of the 100 mg/kg of dry matter value in the oilseed rape. In sample no. 7 the highest value of 63.0 mg Zn/kg of dry matter was recorded.

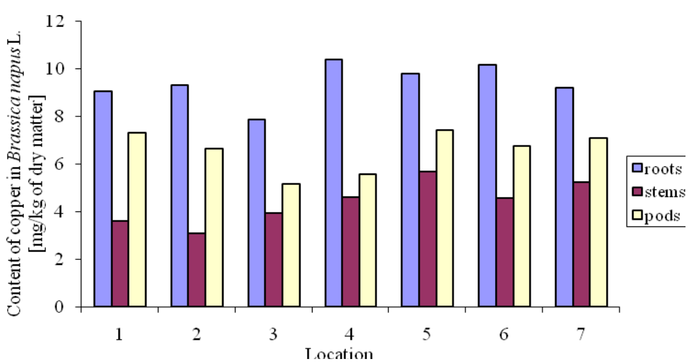

Fig. 5. The content of copper in *Brassica napus* L.

The concentrations of copper in the oilseed rape (*Brassica napus* L.) were significantly lower than those of zinc. Similarly to zinc, the highest concentration of copper was observed in the roots of the oilseed rape from 7.8 to 10.4 mg/kg of dry matter (Fig. 5). Accumulation of copper in the pods was in the range of 5.2 - 7.4 mg/kg of dry matter. The lowest concentration of copper, ranging from 3.1 to 5.7 mg/kg of dry matter, was observed in the stems. Essentially, the copper content in the plants did not exceed the permissible concentration for forage plants (10 mg Cu/kg of dry matter [11]). The exceptions are samples from locations no. 4 and 6, because the values in roots of the oilseed rape were slightly exceeding the limit value for Cu (ca. 0.5 mg/kg of dry matter).

3.4 The bioaccumulation coefficients of zinc and copper in *Brassica napus* L.

In order to check the possibility of accumulation of heavy metals by the oilseed rape (*Brassica napus* L.) the bioaccumulation coefficient, expressed as content of metal in the plant organs to the content of metal in the soil, was calculated. The highest bioaccumulation of zinc in the oilseed rape occurred in the roots, with smaller bioaccumulation observed in pods and stems (Fig. 6).

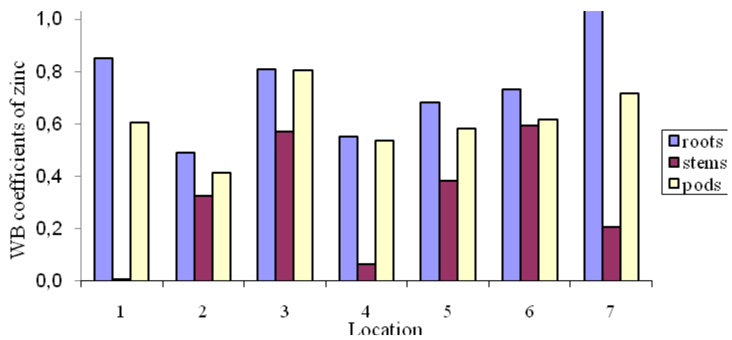

Fig. 6. WB coefficients for zinc.

The WB coefficients for zinc in the roots of the oilseed rape ranged from 0.50 to 1.05, in the pods from 0.41 to 0.80 and in the stems up to 0.60. In sample no. 7 the highest value of the bioaccumulation coefficient of 1.05 for zinc was recorded in the roots. High value of the WB for zinc was also identified in samples of the roots in locations no. 1 and 3: 0.83 and 0.81, respectively. Average values of the bioaccumulation coefficient for zinc indicate smaller bioaccumulation in the tissues of the oilseed rape relative to the concentration of metal in the soil.

Copper is the element bioaccumulated by the oilseed rape to a lesser extent than zinc (Fig.7). The values of the bioaccumulation coefficients in roots are in the range of 0.52 to 0.74, in the pods 0.37–0.55 and in stems of 0,17–0,37. The majority of copper accumulated in roots of the oilseed rape was observed in a sample from location no. 4. The WB coefficient values of bioaccumulation for copper, similarly to those for zinc, indicated lower concentrations of metal in the oilseed rape than the concentration of copper in the soil. Due to the excess of copper and zinc in soil samples relative to the geochemical background in Poland, the oilseed rape can be used for the phytoremediation process of soils enriched with these metals.

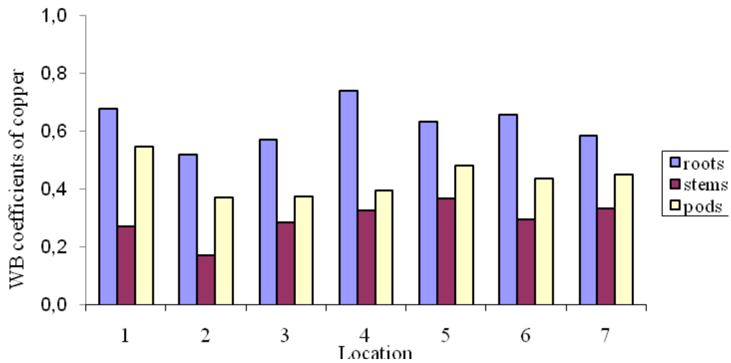

Fig. 7. WB coefficients for copper.

Phytoremediation of soils contaminated with heavy metals conducted under greenhouse conditions and field conditions in the region of Apulia (Italy) confirms the ability of metal bioaccumulation in shoots and roots of the oilseed rape in the following order of Cr > Zn > Cu > Pb. Additionally, the presence of compost and strains of *Bacillus licheniformis* stimulates the removal of metals from the soil and accumulation in the tissues of the oilseed rape. A higher contents of Cr, Pb, Zn, Cd, Ni, and Cu were found in roots than in stems [12]. In biomass of *Brassica napus* L. from agricultural fields irrigated with sewage was accumulated about twice more of Zn and Cu in compared with control [13].

In process of phytoremediation, an important are not only the number of heavy metals and their contents in soil but also interaction between trace elements. Increase of Pb, Cd, Zn contents in the soil cause an increased concentration of these metals in the roots, stems and seeds of *Brassica napus* L. Lead is accumulated mostly in roots, while zinc is present in aerial parts of the oilseed rape. Lead and zinc together in the soil affect the increasing of lead concentration in stems and much lower content of lead in the roots of the oilseed rape, compared with the process conducted in the soil contaminated only through one heavy metal [14]. The oilseed rape shows moderate tolerance to heavy metals and can be used in land remediation moderately polluted with heavy metals [15-16].

In presented studies confirmed the ability to bioaccumulation of heavy metals in *Brassica napus* L. collected from moderately polluted soils around of the Turów power station. The oilseed rape collected from fields can be used as feed. Because contents of zinc and copper in biomass do not exceed of the limit values: 100 mg Zn/kg and 30 mg Cu/kg [11].

4 Conclusion

1. The content of metals in soil samples does not exceed permissible concentrations set by the Polish Ministry of Environment Regulation from September 1st, 2016 (the soil depth of 0 to 0.25 m).
2. In all soil samples enrichment with copper and zinc (average of 2-fold, with respect to the geochemical background in Poland) was observed.
3. Comparison of the content of copper and zinc in soils with average concentrations of these metals in the soils of Lower Silesia (21.5 mg Cu/kg, 59.8 mg Zn/kg) proved that the results are within the average values for the region. In four samples (location no. 2, 5, 6, 7) the content of metals exceeded 1.5-times the average content of metals for the province of Lower Silesia.
4. The pollution indexes (Wn) for copper in soil are higher than for zinc and lead.

5. Sample no. 2 collected from a location nearest to the Turów power station has the highest Wn values for copper (2.8) and zinc (2.2).
6. There has been little excess of copper content in the roots of the oilseed rape (sample no. 4:10.36 mg Cu/kg of dry matter, sample no. 6: 10.14 mg Cu/kg of dry matter) compared with the permissible concentration of these metals for the forage plants from grassland (10 mg Cu/kg of dry matter). There were no exceedances of zinc content in *Brassica napus* L.
7. The values of the bioaccumulation coefficient (WB) for zinc in the oilseed rape are higher than for copper and are as follows: roots - 0.74 (Zn) and 0.63 (Cu), pods – 0.61 (Zn) and 0.44 (Cu), stems - 0.31 (Zn) and 0.29 (Cu). The most substantial accumulation of metals in *Brassica napus* L. was observed in the roots, slighter in the pods and then in the stems.
8. The remediation process of moderately polluted soil with heavy metals around the Turów power station can be carried out with the oilseed rape using.
9. The oilseed rape harvest from the studied areas around the Turów power station can be used as feed.

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