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ZINC, COPPER AND CHROMIUM CONTENT IN SOILS AND NEEDLES OF THE SCOTS PINE (*Pinus silvestris* L.) FROM THE KRAKOW AGGLOMERATION TERRAIN

ZAWARTOŚĆ CYNKU, MIEDZI I CHROMU W GLEBACH ORAZ SZPILKACH SOSNY ZWYCZAJNEJ (*Pinus silvestris* L.) Z TERENU AGLOMERACJI KRAKOWSKIEJ

Abstract: The aim of the study was to determine soils pollution by heavy metals (Zn, Cu and Cr) and their content in pine needles taken from terrain of Krakow Agglomeration.

It was found large changeability of individual trace metals content in analyzed plants and soils material. The metals content in soils amounted to: 12.64–631.9 mg Zn, 1.24–35.06 mg Cu and 2.39–158.9 mg Cr $\cdot$ kg^{-1} dm. The average content of zinc, copper and chromium in soil samples from the city of Krakow terrain was visibly higher than in the analogous material taken from neighboring localities. Variation coefficients of individual trace elements content were: 102.8 % for Cr, 72 % for Zn and 54.2 % for Cu. The highest amounts of analyzed heavy metals was found in soils from places of Krakow Agglomeration located in zones of large intensity of road traffics and in Old Town where the influence of anthropopressure lasts the longest. High their contents were observed also in soil samples taken from the periphery of Krakow and in localities with dense one-family buildings situated along the main traffic routes. The relatively low content of these metals in soils were observed in multifamily dwelling housing estates and in smaller villages from the periphery of the Agglomeration. On average, the most pollution of studied soils with Cu and Zn was found in the eastern part of the Agglomeration, while the lowest in western one. The highest average Cr content was observed in the soil samples taken from northern part of the Krakow Agglomeration while the lowest in southern part. Contents of zinc and copper in soil were significant positively correlated with organic matter content in soil.

The average contents of analyzed trace metals in pine needles taken from the city of Krakow terrain and from neighboring localities were differed slightly. The average content of these metals in pine needles from the Agglomeration terrain amounted to: 55.45 mg Zn, 4.76 mg Cu and 2.54 mg Cr $\cdot$ kg^{-1} d.m. Individual metals content in plant was differentiated in diverse extent. The largest variation was found in case of Cr (V = 40 %), lower for Zn (V = 30.8 %), and the lowest in case of Cu (26.4 %). The highest average analyzed heavy metals content was found in needles of pine grown in southern part of the Krakow Agglomeration. The smallest Cu and Cr contents were observed in needles taken from the trees grown in northern part of the city and neighboring localities, while the smallest Zn content was noted in samples from the northern part of the Krakow Agglomeration. Obtained results did not prove a substantial correlation between heavy metals content

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in soil and in pine needles, what points at origin of Zn, Cu and Cr from deposition from the atmosphere. The bioaccumulation coefficients of analyzed elements had higher values in case of samples taken from countryside than those taken from city Krakow terrain.

Keywords: heavy metals, soils, pine needles, bioaccumulation

The Krakow Agglomeration constitutes an area of 4069 km^2 composed of 51 communes of the Malopolska province, inhabited by ca 1.45 mln people. Currently, atmospheric air pollution poses one of the main hazards for human beings and the natural environment. Dust and gaseous pollutant emission from industries, classifies this region among the worst in Poland, despite continuous efforts at reducing of pollution. On the other hand, emission originating from the city of Krakow area places the city among the ones most seriously threatened with dust emission. Atmospheric air quality in the Malopolska province is additionally worsened by winds blowing from the west and south-west, which cause pollutants translocation from the Silesia province, which dominates in the pollutant emission in the whole country [1]. Air pollutants including trace metals penetrate to the soil with wet and dry deposition but are also dispersed depending on the direction as well as speed of wind and the temperature [1, 2]. Trace elements which in excessive amounts find their way to the environment pose a serious hazard to plants, animals and man. Therefore, constant monitoring of their contents in individual components of the environment is necessary. Anthropopressure causes major disturbances in element cycle in the nature, leading to pollution of individual components of the environment with them. High contents of heavy metals in soil usually lead to their high concentrations in plants [3], whereas their presence in soil and plants is an indicator of the natural environment quality [4]. Trace elements systematically supplied to the soil accumulate in the topsoil because they are bound by the soil sorption complex and very slowly penetrate into the soil profile [5]. However, plant pollution is usually permanent, what means that elements and chemical compounds accumulated in tissues may remain in them during the whole growth period [4]. Phytoindication is a method based on the use of plants for an assessment of the environment quality and the changes occurring in it. One of the plant species, which is a particularly useful phytoindicator of soil and air pollution, is Scots pine (*Pinus silvestris* L.) [4]. Chemical composition of its needles reflects tree abundance in nutrients but also shows the degree of the environmental pollution. Monitoring conducted using technical methods registers the level and distribution of environmental pollution. Phytoindication supplements the data with the information describing response of living organisms to the level of harmful substances in the environment [6].

The investigations aimed at determining the contents of zinc, copper and chromium in the soil and needles of Scots pine (*Pinus silvestris* L.) collected from the area of the Krakow Agglomeration as a basis for an assessment of anthropopressure level.

Material and methods

Material for the analyses constituted soil samples and pine needles collected from the area of Krakow Agglomeration (Fig. 1).

Fig. 1. Localisation of sampling points

A total 50 samples both of soil and pine needles, including 29 from the Krakow city terrain and 21 from the neighbouring localities within 30 km from the city, were collected in November 2008. The samples were dried at room temperature, whereas the pine needles in a dryer with forced air flow at the temperature of 65 ^{o}C. Total contents of heavy metals in the soil samples were assessed after dry mineralization of organic matter and hot dissolving in a mixture of HNO_3 and $HClO_4$ acids (3:2), whereas in the plant material after mineralization in a mixture of HNO_3 and H_2SO_4 [7]. Metal concentrations in the obtained solutions were determined using ICP-AES method in JY 238 Ultrace apparatus.

Results and discussion

Zinc is an element commonly occurred in the environment. It reveals considerable mobility in the soil from which it is intensively absorbed by plants, what causes that it easily enters both animal and human food chains. In the proper amounts this metal is crucial for proper development of living organisms, whereas in excess it becomes toxic for them. Pollution of the natural environment with zinc is mainly caused by dust pollutant emission from zinc works, coal and waste burning. Zinc also finds its way to soils with phosphorous fertilizers and plant protection preparations [2]. The greatest amount of zinc (631.88 mg $\cdot$ kg^{-1} d.m.) was found in the soil material from Piastowska Street in Krakow and the smallest one (12.64 mg $\cdot$ kg^{-1}) in the samples from Kryspinow (Table 1). The soil samples collected from the most urbanized parts of Krakow (Medweckiego, Stanislawa ze Skalbmierza and Swoszowicka Streets) and from the localities surrounding the city (Wielka Wies, Proszowice, Zabierzow) revealed the largest quantities of this element. The smallest amounts of Zn were noted in the soils of city residential areas (Czarnogorska and Okolna Streets, Oswiecenia estate) and in small villages near Krakow (Raczna, Morawica, Igolomia). Considering the limit contents of heavy metals in the topsoil elaborated by ISSPC [18], 16 % of soil samples revealed the natural Zn content (0^o of pollution), 40 % of soils had elevated Zn content (I^o of pollution), 34 % showed weak (II^o) and 8 % medium pollution (III^o), whereas 2 % of samples revealed strong pollution by this metal (IV^o). Mean content of zinc in the analyzed soil material from the Krakow Agglomeration indicated a weak pollution (II^o) with this element. However, it should be pointed out that average Zn content in the soil samples from the city of Krakow area was much higher than its medium content in the soils collected from the neighbouring localities. Pine needles collected in Krzeszowice town contained the highest Zn amounts – 108.19 mg · kg^{-1} d.m., while the smallest ones were found in the needles of pine growing at Palacha Street in Krakow – 32.1 mg · kg^{-1} dm (Table 1). Zinc content in plants is considered natural within the range from 20 to 100 mg · kg^{-1} d.m. [2]. Following this criterion zinc content in all samples of pine needles may be considered natural.

Copper is a natural trace element of the Earth crust [2]. As a microelement, it is crucial for proper functioning of plants, animals and man. Either a deficiency or excess of copper leads to disturbances of living organism activities and therefore the balance in the environment [9]. In strongly industrialized areas the heaviest contamination of the environment with copper is caused by local mines and metal works processing this metal. Copper concentrations increases in the dust emitted to the atmosphere in city Agglomerations due to intensified road traffic and electric transport [2]. Analogously as in case of zinc, the highest amounts of copper (38 mg · kg^{-1} d.m.) were found in the soil material collected in Piastowska Street in Krakow and the smallest ones (1.24 mg · kg^{-1} d.m.) in the soil from Kryspinow (Table 1).

Table 1

Zn, Cu and Cr contents of soil samples and pine needles
and organic matter contents at top soil layer

Sampling points	Pine needles			Soil samples			Organic matter [%]
	Zn	Cu	Cr	Zn	Cu	Cr	
	[mg · kg^{-1} d.m.]						
ul. Pradnicka	44.44	3.68	1.59	176.25	13.00	13.38	2.16
ul. Gornickiego	45.56	2.87	0.82	123.25	12.88	24.06	2.92
ul. S. ze Skalbmierza	50.50	7.94	2.83	402.50	24.25	158.88	4.29
ul. Lepkowskiego	38.00	3.29	2.56	177.50	12.18	39.88	2.47
ul. Powstancow	55.13	5.71	2.10	123.94	14.94	25.63	2.79
os. Oswiecenia	35.44	4.36	2.89	68.13	9.15	13.53	1.97
ul. Makuszynskiego	42.38	5.11	2.19	118.94	11.80	24.38	2.79
ul. Medweckiego	47.09	4.73	2.40	465.63	29.25	30.44	3.77
al. Pokoju	38.06	6.24	2.63	196.88	24.13	33.00	3.33
ul. Cystersow	57.69	5.93	2.97	237.63	25.94	36.94	5.89
ul. Swoszowicka	61.91	5.54	6.35	330.00	9.38	8.05	2.34
ul. Krzywda	67.95	5.18	2.84	133.75	25.13	19.00	4.18

Table 1 contd.

Sampling points	Pine needles			Soil samples			Organic matter [%]
	Zn	Cu	Cr	Zn	Cu	Cr	
	[mg · kg^{-1} d.m.]						
ul. Jerzmanowskiego	33.98	3.90	1.83	211.88	20.31	11.44	3.33
ul. Okolna	36.41	4.22	2.58	44.31	12.23	8.03	1.57
ul. Czarnogorska	58.69	5.26	1.79	43.25	7.05	6.56	1.54
ul. Szwedzka	52.73	6.09	3.66	185.00	23.38	13.05	3.67
ul Wl. Tetmajera	47.51	6.26	1.77	244.38	18.94	20.31	1.92
ul. Jeleniowa	60.15	3.99	3.43	222.50	13.05	22.94	5.65
al. Kasztanowa	35.40	4.25	1.71	148.13	13.69	16.81	3.42
ul. P. Listopadowego	58.65	3.29	2.71	133.13	35.06	15.56	2.57
ul. Juliusza Lea	47.14	4.72	1.81	141.88	28.81	11.93	6.46
ul. Lindego	46.81	5.01	3.98	157.50	24.13	11.66	5.13
ul. Na Blonie	54.25	5.39	4.65	93.31	7.21	10.16	4.55
ul. Majora Lupaszki	48.00	3.83	1.80	186.88	16.88	16.69	3.99
ul. Palacha	32.10	4.08	1.26	130.63	16.69	10.96	2.92
ul. Piastowska	40.50	4.30	2.13	631.88	38.00	12.13	4.58
ul. Nad Sudolem	46.06	5.09	3.47	147.50	10.79	10.37	2.39
ul. Pachonskiego	68.19	3.26	1.17	95.25	10.25	22.31	2.90
ul. Pasteura	51.13	4.09	1.48	80.00	8.50	9.58	2.15
Zielonki	95.56	4.63	2.34	97.81	9.59	12.53	5.25
Maslomiąca	71.94	4.62	3.19	77.63	5.69	22.44	3.04
Iwanowice	63.56	3.99	2.16	105.69	12.22	18.19	2.72
Slomniki	36.75	2.34	2.14	101.75	13.31	26.69	3.86
Kocmyrzow	50.38	4.41	2.01	175.63	15.69	26.38	8.28
Koniusza	61.88	5.42	2.19	209.38	11.04	29.38	3.52
Proszowice	63.31	4.73	3.42	253.00	28.94	31.88	2.97
Karwin	37.00	4.68	3.60	77.13	12.71	13.69	4.05
Igolomia	29.56	2.56	3.57	59.44	11.89	15.25	2.14
Niepolomice	59.88	4.90	1.98	203.75	17.00	31.81	4.21
Wieliczka	95.56	6.05	2.96	147.50	19.50	20.31	7.50
Mogilany	69.50	4.96	1.61	72.63	10.62	18.44	4.56
Skawina	76.06	9.63	3.46	162.50	31.25	14.38	2.57
Raczna	60.38	5.17	3.37	25.13	3.39	4.16	1.26
Kryspinow	64.56	5.72	3.86	12.64	1.24	2.39	0.56
Liszki	57.94	3.41	2.72	70.50	9.44	16.56	1.75
Morawica	47.69	4.18	1.58	34.88	5.18	16.75	1.49
Zabierzow	73.38	5.67	3.03	233.75	14.81	11.36	4.10
Krzeszowice	108.19	4.99	1.28	51.69	5.20	8.25	1.33
Skala	87.50	4.03	1.75	155.63	6.44	26.44	2.22
Wielka Wies	60.19	4.44	1.30	350.63	23.00	33.44	3.47
Average	**55.45**	**4.76**	**2.54**	**162.61**	**15.70**	**21.17**	**3.37**
CV [%]	**30.80**	**26.50**	**40.00**	**72.00**	**54.20**	**102.80**	**46.90**

Relatively large quantities of copper were registered in the soils from the city area (Powstania Listopadowego, Medweckiego and Lea Streets) but also in town around Krakow (Skawina and Proszowice). The localities mentioned above are characterized by compact settlement pattern and busy traffic routes running in their vicinity. Copper content in the analyzed soils of Krakow Agglomeration pointed to only slightly elevated content of this element (I^o of pollution) on a six degree scale proposed by ISSPC [8], of which 72 % of soils revealed natural content (0^o) and 28 % had elevated Cu concentrations (I^o). Average copper content in the Agglomeration soils was 15.7 mg $\cdot$ kg^{-1} d.m. (Table 1) and was approximate (the same level of pollution) to average Cu contents registered in the research conducted by Gambus [10] on the soils of the former Krakowskie province. Copper content in aboveground parts of the plant is quite diversified and depends on many factors (species, kind of soil, antagonism with other elements), therefore it is difficult to determine the limit numbers for its natural content in tissues and toxicity threshold. As reported by Kabata-Pendias and Pendias [2], an average Cu content in aerial part o the plants fluctuates from 5 to 20 mg $\cdot$ kg^{-1} d.m. Mean copper content in pine needles growing in the Krakow Agglomeration area was 4.76 mg $\cdot$ kg^{-1} d.m. The greatest amounts were found in pine needles growing in places with highly intensive traffic, close to busy traffic routes (Skawina and Tetmajera Street in Krakow, Pokoju Avenue in Krakow), while the smallest were noted in small villages outside the city boundaries (Slomniki, Igolomia).

Chromium is a natural component of the Earth's crust. This element is present in various quantities and its natural content in soil fluctuates from trace amounts to over 0.1 %. Its role in plant growth and development has not been fully identified. However, chromium is indispensable for life to animals and humans but excessive its concentrations are harmful to all living organisms. Despite many anthropogenic sources of chromium pollution, there is no risk of global contamination of the natural environment with this metal. However, this element may be introduced into the environment components locally, which may cause its excessive entering the biogeochemical cycle [2, 9]. Similarly as for Zn and Cu the smallest quantities of Cr were found in the soil samples collected in Kryspinow (2.39 mg $\cdot$ kg^{-1} d.m.), whereas about 70 times bigger were assessed in Stanislawa ze Skalbmierza Street in Krakow (158.88 mg $\cdot$ kg^{-1} d.m.) (Table 1). Considerable amounts of this element were also found in soil samples collected in Lepkowskiego and Cystersow Streets, in Pokoju Avenue and in Medweckiego Street in Krakow, but also in Wielka Wies, Proszowice and Niepolomice localities. It was also found that 84 % of the collected samples revealed natural content of chromium (0^o of pollution), 14 % had increased content of this metal (I^o) and 2 % revealed medium pollution with this metal (III^o). Mean chromium content noted in the Agglomeration soils was 21.17 mg $\cdot$ kg^{-1} d.m., which according to the West European criteria classifies these soils to clean ones [9]. The least of chromium (0.82 mg $\cdot$ kg^{-1} d.m.) was assessed in needle samples of pine growing in Gornickiego Street in Krakow whereas the greatest amounts were found in Swoszowicka Street (6.35 mg $\cdot$ kg^{-1} d.m.) (Table 1). Average content of chromium in pine needles growing in the Krakow Agglomeration area, ie 2.54 mg $\cdot$ kg^{-1} d.m. is higher than average content of this element in plants for consumption (0.02–1 mg $\cdot$ kg^{-1} d.m.) stated by Kabata-Pendias and Pendias [2].

The contents of the analyzed heavy metals (Zn, Cu and Cr) in the soil material collected from the area of the Krakow Agglomeration were diversified to various degrees. The highest variability was assessed for Cr (coefficient of variation, CV = = 102.8 %), slightly smaller for Zn (CV = 71.2 %) and the lowest for Cu (54.2 %). Similar diversification of the studied trace element values may be observed in soils of other agglomerations in Poland [11]. Also in the collected pine needles chromium content revealed the greatest variability (V = 40 %), then zinc (V = 30.8 %), while the lowest value of variability coefficient was registered for copper (V = 26.4 %). The reason for such considerable variability of the analyzed elements content might be the locally uneven distribution of soil and atmospheric air pollution with heavy metals. Heavier pollution with zinc, copper and chromium is usually observed along traffic routes and within a radius of several hundred meters from factories. The changeability is also caused by climatic factors such as wind or temperature [1].

According to the literature of the subject, there are numerous factors affecting phytoavailability and trace metal contents in the arable layer. The most frequently mentioned soil physicochemical properties which influence the metal availability include: type and granulometric composition of soil, organic matter content, sorption capacities as well as pH and oxidation-reduction potential [12]. According to Siuta [9] there is a positive correlation between organic matter content in soil and the amount of trace elements retained in its top layer. Obtained results confirmed the thesis, as evidenced by the values of correlation coefficients between organic matter content and the quantity of heavy metals determined in soil. The contents of Zn and Cu were positively correlated with organic matter content in soils. The correlation coefficients were respectively $r_{0.05} = 0.32$ and $r_{0.01} = 0.42$. Similar dependence was not found for Cr in the studied soils of Krakow Agglomeration. No significant correlation was found either between heavy metal content in the soil and needles of pines growing in the individual places. It points out on origin of Zn, Cu and Cr from the atmospheric deposition. According to Siuta [9], there are numerous factors conditioning heavy metal absorption by plants. Gorlach [13] also states that various species and even varieties of plants growing under the same conditions may reveal different ability of heavy metal uptake from soil. Other authors state, that the soil content of heavy metal forms available to plants is also affected by the course of climatic conditions, which to a considerable degree modify the soil properties and therefore influence the level of these elements content in plants [14]. Moreover, Siuta [9] emphasizes that in practice heavy metal concentrations are assessed only in the topsoil. For this reason, most frequently no dependence is assessed between the elements content in soil and their concentrations in plants, especially perennials.

Intensity and scale of soil and plant pollution with trace elements depends on many local factors, however a serious source of heavy metals deposited on the soil and plant surface is so called far emission connected with pollutants dispersion and translocation for long distances [15]. Climatic conditions (precipitation, temperature, wind direction and strength) also play an important role in pollutant dispersion. Analysis of soil samples pollution revealed the highest medium pollution with Zn and Cu in the eastern part of Krakow Agglomeration, whereas Cr contamination was the highest in the northern part. Average lowest contents of all analyzed elements were registered in the southern part of the Krakow city and in the eastern part of the neighboring localities. It may be due to the fact that winds from the west and south west prevail in the area of Krakow and its neighborhood, which causes a dispersion of pollutants from the west and south towards the east and north. On the other hand, the highest average speeds are noted for the winds from the west [1]. Analysis of the chemical composition of pine needs showed the highest mean contents of all studied elements in the material collected in the southern part of Krakow Agglomeration. Pine needles taken in the eastern part of the Agglomeration contained the lowest quantities of zinc, whereas the least amounts of copper and chromium were determined in pine needles growing in the northern part of this region.

Bioaccumulation coefficient (BC) expresses the ratio of element concentration in plant to its content in soil. Analysis of the obtained BC values for Zn, Cu and Cr demonstrated that under conditions of soil pollution with heavy metals needles more easily cumulate Zn and Cu, than Cr. Zinc is an element very easily absorbed by plants from the soil, therefore Zn bioaccumulation coefficient assumed the highest values among the studied elements both in the city of Krakow and in the other research points situated in the neighboring areas. It is caused by a relatively considerable mobility of this element in the soil, including its exchangeable forms and compounds with organic matter. It has been confirmed by the highest mean value of bioaccumulation coefficient for zinc 0.71 in comparison with BC 0.5 for Cu and 0.21 for Cr. On the other hand the lowest BC value noted for chromium is caused by a poor translocation of this element from soil to plant tissues [9]. On average, bioaccumulation coefficient for Zn, Cu and Cr assumed higher values for rural areas as compared with the city (Fig. 2).

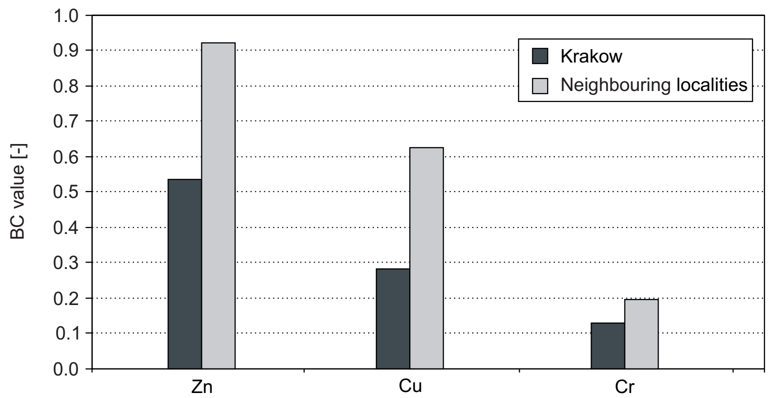

Fig. 2. Average values of bioaccumulation coefficient of metals in pine needles

Conclusions

1. The Zn, Cu and Cr content in soils and pine needles taken from Krakow Agglomeration showed large changeability. Significantly higher amounts of individual elements were observed in places of large intensity of road traffics and in Old Town, as well as in the larger localities nearby Krakow.

2. The average Zn, Cu and Cr content in soil samples taken from Krakow was visibly higher than in the material taken from neighboring localities.

3. The average contents of Zn, Cu and Cr in pine needles taken from Krakow terrain and from neighboring localities were differed slightly and pointed at their natural content.

4. The highest average contents of analyzed metals were found in needles of pine grown in southern part of Krakow Agglomeration.

5. On average, the biggest pollution of soils with Cu and Zn was found in the eastern part of the Agglomeration, while Cr in northern one.

6. Contents of Zn and Cu in soil were significant positively correlated with organic matter content in soil.

7. The bioaccumulation coefficients had higher values in case of samples taken from neighboring localities than those taken from city Krakow terrain.

8. Obtained results did not prove a substantial correlation between heavy metals content in soil and in pine needles, what may point at absorption of metals deposed from the atmosphere.

9. Needles of the Scot pine are good indicator of environment pollution level.

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ZAWARTOŚĆ CYNKU, MIEDZI I CHROMU W GLEBACH ORAZ SZPILKACH SOSNY ZWYCZAJNEJ (*Pinus silvestris* L.) Z TERENU AGLOMERACJI KRAKOWSKIEJ

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Abstrakt: Celem pracy było określenie zanieczyszczenia gleb metalami ciężkimi (Zn, Cu i Cr) oraz ich zawartości w szpilkach sosen z terenu aglomeracji krakowskiej.

Stwierdzono duże zróżnicowanie zawartości poszczególnych metali śladowych w analizowanym materiale glebowym i roślinnym. Gleby zawierały: 12,64–631,88 mg Zn, 1,24–38 mg Cu oraz 2,39–158,9 mg Cr · kg^{-1} s.m. Średnie zawartości cynku, miedzi i chromu w próbkach glebowych z terenu miasta Krakowa były wyższe niż w analogicznym materiale pobranym z okolicznych miejscowości. Współczynniki zmienności zawartości poszczególnych metali przyjmowały wartości: 102,8 % dla Cr, 72 % dla Zn i 54,2 % dla Cu. Najwięcej metali zawierały gleby pobrane z punktów aglomeracji krakowskiej, zlokalizowanych w rejonach o dużym natężeniu ruchu drogowego oraz na terenie Starego Miasta, które najdłużej podlegają antropopresji. Duże ich zawartości zanotowano także w próbkach gleb pobranych na obrzeżach Krakowa oraz w miejscowościach o zwartej zabudowie domów jednorodzinnych, usytuowanych przy głównych szlakach komunikacyjnych. Stosunkowo mało tych metali zawierały gleby z osiedli o zabudowie wielorodzinnej oraz z mniejszych wsi położonych na obrzeżach aglomeracji. Średnio największe zanieczyszczenie badanych gleb Zn i Cu stwierdzono we wschodniej części aglomeracji, a najmniejsze w części zachodniej. Największą średnią zawartością Cr odznaczały się gleby z północnej, a najmniejszą z południowej części aglomeracji krakowskiej. Zawartość cynku i miedzi w glebie były istotnie dodatnio skorelowane z zawartością materii organicznej.

Średnie zawartości badanych metali śladowych w szpilkach sosen pobranych z terenu miasta Krakowa oraz z pobliskich miejscowości różniły się nieznacznie. Przeciętna zawartość tych metali w igliwiu sosen rosnących na terenie aglomeracji wyniosła: 55,45 mg Zn, 4,76 mg Cu i 2,54 mg Cr · kg^{-1} s.m. Zawartości poszczególnych metali ciężkich były zróżnicowane w niejednakowym stopniu. Największą zmienność stwierdzono w przypadku Cr (V = 40 %), następnie Zn (V = 30,8 %), a najmniejszą w przypadku Cu (26,4 %). Średnio najwięcej wszystkich analizowanych metali stwierdzono w szpilkach sosen rosnących w południowej części aglomeracji krakowskiej. Najmniej Cu i Cr zawierały igły pobrane z drzew z północnej części miasta oraz z graniczących z nią miejscowości, natomiast najmniejszą zawartość Zn zanotowano w próbkach pobranych w północnej części aglomeracji. Nie wykazano statystycznie istotnej korelacji między zawartością badanych metali w glebie i igliwiu sosny, co wskazuje na ich pobieranie z depozycji z atmosfery. Współczynniki bioakumulacji badanych metali przyjmowały znacznie większe wartości w przypadku próbek pobranych na terenach wiejskich w porównaniu z pobranymi na terenie miasta Krakowa.

Słowa kluczowe: metale ciężkie, gleby, szpilki sosny, bioakumulacja