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HEAVY METALS AVAILABILITY IN SOILS EXPOSED TO TRAFFIC POLLUTION

DOSTĘPNOŚĆ METALI CIĘŻKICH Z GLEB NARAŻONYCH NA EMISJE ZANIECZYSZCZEŃ KOMUNIKACYJNYCH

Abstract: Evaluation of a degree of soils pollution with heavy metals is usually conducted basing on total content of elements. This evaluation should be supplemented by analysis of content of heavy metals forms directly available for living organisms as well as forms which can be relatively easily mobilized. The aim of the research was to determine the content of selected fractions of copper, zinc and chromium in soils located near road No. 957 in the Zawoja passage. The research material consisted of soil samples taken from 13 points (in each point in the distance of 5 and 200 meters from the road edge). The soil samples underwent sequential chemical extraction using Zeien and Brümmer's method. Extracted were 3 fractions of heavy metals: easily soluble forms, exchangeable forms and bonds with manganese oxides.

In general, mean contents of the examined fractions of heavy metals were higher in case of the soils located in the distance of 5 m from the road edge than in the soils located in the distance of 200 m from the road. Copper occurred in soils generally as bound with manganese oxides, whereas zinc and chromium – as exchangeable forms.

Keywords: soil, traffic pollution, copper, zinc, chromium, sequential extraction

Evaluation of a degree of soils pollution with heavy metals is usually conducted basing on content of total forms of elements [1]. This evaluation should be supplemented by analysis of content of heavy metals forms directly available for living organisms as well as forms which can be transformed into available forms within short period of time. Soil is the first link of a "soil – plant – animal – human" food chain [2]. The higher the content of available heavy metals forms in soil, the higher the risk of accumulating these elements in plants, and eventually in following chain links. Human activity may lead to an increase in the content of available metals forms in soil directly

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through introducing metals to soil or indirectly as a result of influencing soil properties (reaction, sorption capacity) regulating elements availability.

The research aimed at determining the influence of traffic pollution on the content of the 3 fractions of heavy metals in soils. The content of easily soluble, exchangeable and bound with manganese oxides forms of copper, zinc and chromium in the soils located near road No. 957 in the Zawoja passage was analyzed.

Material and methods

The research material consisted of soil samples collected in 2008 from 13 points located along regional road No. 957 in Zawoja (the Malopolska province). The samples were collected from both sides of the 18.5 km long section of the road (the distance between the sampling points reached from 0.3 to 5.2 km). Road No. 957 is the only communication route to Zawoja, Skawica and the Babia Gora National Park (Babiogórski Park Narodowy). Within 24 hrs approximately 4827 road vehicles pass that road, including 367 heavy goods vehicles, 77 buses, about 20 motorcycles and 10 agricultural tractors [3]. In each point the material was collected from grass covered places (where tree vegetation did not occur) distant 5 and 200 m from the road edge. Soil samples were collected from the layer of 0–10 cm depth. The data concerning properties of the analyzed soils are shown in the paper by Filipek-Mazur and Tabak [4].

Analyses on air-dried material sifted through a sieve with 1 mm mesh were conducted. The content of the selected heavy metals fractions was assessed according to the method of sequential chemical extraction given by Zeien and Brümmer [5]. Extracted were 3 fractions of heavy metals:

– easily soluble metals forms (F_I),
– exchangeable metals forms (F_I),
– bonds of metals with manganese oxides (F_{III}).

The extraction conditions are shown in Table 1.

Table 1

Conditions of heavy metals extraction

Fraction	Extraction agent, time of extraction
F_I*	1 mol · dm^{-3} NH_4NO_3, 24 hrs
F_{II}	1 mol · dm^{-3} CH_3COONH_4, 24 hrs
F_{III}	1 mol · dm^{-3} $NH_2OH \cdot HCl$ + 1 mol · dm^{-3} CH_3COONH_4, 30 mins

* F_I – easily soluble metals forms; F_{II} – exchangeable metals forms; F_{III} – metals bound with manganese oxides.

A content approximate to the total content of heavy metals was assessed in separate aliquots of soils. For this purpose the samples were incinerated (8 hrs, 450 ^oC), evaporated with a mixture of nitric(V) and chloric(VII) acids, then the remainder was

dissolved in hydrochloric acid [6]. The assessment of the heavy metals content was made using ICP-AES method on JY 238 Ultrace apparatus.

Results and discussion

As a rule, higher mean contents of the examined heavy metals fractions were noted in case of the soils located in the distance of 5 m from the road edge than in the soils located in the distance of 200 m from the road (Table 2).

Gondek et al [7] generally stated higher contents of heavy metals (extracted with 1 mol · dm^{-3} HCl) in soils distant 50 m from road than in soils located in a distance of 100 m. However, the authors did not state dependence between the distance of the soils from the road and the content of metals fraction extracted with 1 mol · dm^{-3} NH_4NO_3 [7]. Bieniek and Lachacz [8] obtained similar results to Gondek et al [7] in regard to mobile heavy metals forms (extracted using 1 mol · dm^{-3} HCl). The highest contents of mobile metals forms in surface horizons were marked in soils located closest to the road [8]. Moreover, these soils revealed an elevated content of some metals. A higher share of mobile heavy metals forms in the soils with an increased content of elements than in the soils with a natural content suggests their anthropogenic origin in the soils with the increased content [8]. Elements derived from natural sources (parent rock) would occur as silicate forms [8]. The soils analyzed in the Authors' own studies were generally characterized by a natural or elevated content of heavy metals (two samples weakly polluted with zinc were noted) [1, 4]. An elevated content and weak pollution were noted in the soils located in the distance of 5 m and 200 m from the road edge [1, 4].

The highest copper content was noted in the third fraction (bonds with manganese oxides), whereas zinc and chromium occurred mainly as an exchangeable form (Table 2). For the soils distant 5 m from the road edge the share of the sum of the three copper fractions in its total content ranged from 7.47 % to 32.84 % while for the soils in the distance of 200 m this share ranged from 5.10 % to 22.46 %. In the case of zinc the share amounted respectively from 0.23 % to 12.04 % (for the 5 m distance) and from 0.26 % to 11.94 % (for the 200 m distance). The chromium fractions constituted from 0.33 % to 4.50 % of the total element content in the soils located in the distance of 5 m from the road edge and from traces to 3.16 % in the soils located in the distance of 200 m.

According to other authors' researches, analyzed elements are present in soils mainly as hardly soluble or insoluble forms, which limits possibility of these elements uptake by plants. Copper occurs mainly as bonds with organic matter and as bonds with amorphous and crystalline iron oxides, a relatively high content of copper is also registered in residual fraction (in minerals) [9–11]. Zinc occurs as bonds with amorphous and crystalline iron oxides, in residual fraction and as bonds with organic matter [11–13]. Kalembasa et al [10] registered a high content of an exchangeable fraction of zinc. Chromium occurs as bonds with amorphous and crystalline iron oxides as well as in a residual fraction [10, 11, 14].

Table 2

Content of copper, zinc and chromium in soils [mg · kg^{-1} d.m.]

Distance from the road	Parameter	Approximate to total content of heavy metals			Content of heavy metals fractions								
					Cu			Zn			Cr		
		Cu	Zn	Cr	F_I*	F_{II}	F_{III}	F_I	F_{II}	F_{III}	F_I	F_{II}	F_{III}
5 m (n = 13)	arithmetic mean	14.61	109.81	31.98	0.29	0.59	1.09	0.55	3.27	2.31	0.16	0.33	0.10
	minimum	8.66	77.40	17.65	trace	trace	0.32	trace	trace	trace	trace	trace	trace
	maximum	31.63	166.65	39.69	1.35	2.44	2.14	4.01	10.48	7.76	0.50	0.82	0.49
	standard deviation	6.11	24.36	5.61	0.38	0.60	0.58	1.05	2.77	2.62	0.19	0.23	0.15
200 m (n = 13)	arithmetic mean	14.38	115.00	31.64	0.16	0.47	1.44	1.98	2.85	1.93	0.11	0.28	0.10
	minimum	8.71	80.15	26.54	trace	trace	0.30	trace	trace	trace	trace	trace	trace
	maximum	22.88	157.53	38.44	1.02	1.20	3.32	10.58	6.54	4.56	0.34	0.67	0.43
	standard deviation	3.71	22.20	3.85	0.29	0.43	0.97	2.86	2.05	1.68	0.11	0.25	0.15

* See Table 1.

Conclusions

1. In general, in the soils located in the distance of 5 m from the road edge higher mean contents of the examined fractions of heavy metals were noted than in the soils distant 200 m from the road. Only the contents of easily soluble zinc forms and bonds of copper with manganese oxides were higher in the distance of 200 m.

2. The highest copper content was noted in the fraction of bonds with manganese oxides, whereas zinc and chromium occurred mainly as exchangeable forms.

3. The content of zinc in soil samples showed that content to be elevated (1st and 2nd level of pollution).

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Abstrakt: Ocena stopnia zanieczyszczenia gleb metalami ciężkimi przeprowadzana jest zazwyczaj na podstawie całkowitej zawartości pierwiastków. Uzupełnieniem tej oceny powinna być analiza zawartości bezpośrednio dostępnych dla organizmów żywych form metali ciężkich oraz form, które stosunkowo łatwo mogą ulec uruchomieniu. Celem niniejszych badań było określenie zawartości wybranych frakcji miedzi, cynku i chromu w glebach położonych w pobliżu drogi nr 957 na odcinku Zawoi. Materiał badawczy stanowiły próbki gleb pobrane z 13 punktów (w każdym punkcie z miejsc oddalonych o 5 i 200 m od brzegu jezdni). Próbki gleb poddano sekwencyjnej ekstrakcji chemicznej według metody Zeiena i Brümmera. Wyekstrahowano 3 frakcje metali ciężkich: formy łatwo rozpuszczalne, formy wymienne oraz połączenia z tlenkami manganu.

Z reguły większe średnie zawartości badanych frakcji metali ciężkich stwierdzono w odniesieniu do gleb położonych w odległości 5 m od brzegu jezdni niż gleb w odległości 200 m od jezdni. Miedź występowała głównie w formie połączeń z tlenkami manganu, natomiast cynk i chrom – jako formy wymienne.

Słowa kluczowe: gleba, zanieczyszczenia komunikacyjne, miedź, cynk, chrom, ekstrakcja sekwencyjna