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SOME REGULARITIES IN ACCUMULATION AND MIGRATION OF HEAVY METALS (Cd, Cu, Pb AND Zn) IN THE SOILS ADJACENT TO STREETS OF LUBLIN

NIEKTÓRE PRAWIDŁOWOŚCI W AKUMULACJI I MIGRACJI METALI CIĘŻKICH (Cd, Cu, Pb I Zn) W GLEBACH SĄSIADUJĄCYCH Z ULICAMI LUBLINA

Abstract: This study attempted to determine the contamination with heavy metals (Cu, Cd, Pb and Zn) of the soils neighbouring on selected streets in Lublin and the effect of the trolley bus line (with uninsulated copper wires). The comparative study was made possible by opening or extensive repair of major traffic routes in Lublin, which was taken into account in selecting the study sites. The total content of copper at the sites ranged from 9.6 to 208.6 mg/kg, lead – from 11.3 to 167 mg/kg, cadmium – from 0.02 to 4.9 mg/kg, and zinc – from 22.9 to 300.6 mg/kg. The portion of bioavailable species in the general pool of heavy metals ranged from 6.7 to 35.3 % for copper, from 7.4 to 36.2 % for lead, from 3.3 to 90.1 % for cadmium, and from 1.7 to 10.7 % for zinc. Soil at the sites situated near the routes with new trolley buses lines contained less common species of the metal as compared with the traffic routes used for several decades. The total content of Cu, Cd, Pb and Zn did not exceed the limit concentrations of heavy metals in class C soils, as laid down in the Regulation of Minister of Environment on the soils and earth quality standards (J. of Laws 02.165.1359 of 04.10.2002).

Keywords: heavy metals, urban soils, traffic pollution

Road transport is a source of considerable contamination with heavy metals of soils adjacent to traffic routes. They come from emission of gas from combustion engines, brake discs, additions of heavy metals to oils, etc. It is particularly important in cities which variable and congested traffic, with a high level of dust in the air and with disturbed air flows. Major pollutants associated with traffic include lead – a component of leaded petrol which was in common use until not long ago. Traffic pollution is more dangerous than that produced by industry because it spreads in relatively high concentrations at low altitudes, in the immediate vicinity of breathing people, animals and plants [1, 2]. Although public transport, including trolley buses, is an environ-

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mentally-friendly alternative to common use of cars in cities, it is one of the factors which contribute to increased concentration of traffic pollution.

The content of heavy metals (especially lead, copper, zinc and cadmium) in soils may be regarded as an indicator of environmental nuisance of roads [3–5]. Moreover, there is a dense network of trolley bus lines with uninsulated copper wires. In recent years it has been expanded and now covers new residential quarters of the town. Trolley buses do not require special railways because they move among other vehicles; however, the surface layer of electric wires gets rubbed out. Additionally, there is pollution originating from tyre wear and from brake discs.

The aim of the study was to evaluate contamination with Cu, Cd, Pb and Zn of selected traffic routes in Lublin and the effect of trolley bus lines on the content of common and bioavailable species of selected heavy metals in soils in the immediate vicinity of the most busy street of Lublin. The opportunity of conducting the study was provided by opening new trolley bus lines in Lublin, which was taken into account when the study sites were selected. This also made it possible to conduct a comparative study of the soils adjacent to streets where trolley bus lines have existed for several decades with new trolley bus lines and selected traffic routes with no trolley bus lines.

Materials and methods

Eighteen sites were selected for the study, with different characteristics in accordance with the adopted study objectives. Two representative surface soil samples were taken at each site (20–30 cm and 2 m away from the street edge).

The following were determined: pH in 1M KCl – potentiometrically, *total organic carbon* – by the Turin's method, *total exchangeable alkaline cations* as the sum of Ca, Mg, K and Na, extracted from soil with 1 M ammonium acetate and determined by AAS, *hydrolytic acidity* (Hh) by the Kapen's method. Bioavailable forms of Pb, Cu, Cd and Zn were extracted by Lindsey's and Norvell's method; samples were mineralised with *aqua regia* in order to determine total heavy metals; determination was performed by AAS [6, 7].

Results and discussion

Chemical analysis of the soils (Table 1) revealed neutral to alkaline reaction with little variability, ranging from 6.74 to 7.38. Hydrolytic acidity was low and ranged from 0.45 cmol(+)/kg to 1.13 cmol(+)/kg. The soils also had good buffering properties. *Sorptive capacity* (T) varies greatly and ranges from 12.33 to 102.57 cmol(+)/kg. The sorptive complex is almost fully saturated with alkaline cations with calcium cations dominating (Table 1). Such characteristics of total alkaline cations with distinct portion of sodium beside calcium is *a proof of the effect of chemical snow melting agents*.

Surface layers of soil under examination showed varied content of organic carbon (from 8.7 to 45.8 g/kg).

Total copper content in the analysed soils ranged from 9.6 to 208.6 mg/kg, that of lead – from 11.3 to 167 mg/kg, that of cadmium – from 0.02 to 4.9 mg/kg, and that of zinc – from 22.9 to 300.6 mg/kg (Fig. 1). The share of bioavailable species in the total pool of heavy metals ranged from 6.7 to 35.3 % for copper, from 7.4 to 36.2 % for lead, from 3.3 to 90.1 % for cadmium, and from 1.7 to 10.7 % for zinc. Mean total contents of heavy metals (Cu, Cd, Pb, Zn) decreased in the following order Zn > Cu > Pb > Cd, whereas the order was different for mean contents of bioavailable species (Cu > Pb > Zn > Cd).

Table 1

Selected characteristics of analysed soils

Statistical data	pH 1 M KCl	C_{org} [%]	Hh [$cmol^+ \cdot kg^{-1}$]	S [$cmol^+ \cdot kg^{-1}$]	T [$cmol^+ \cdot kg^{-1}$]
min.	6.74	0.52	0.45	11.88	12.33
mean value	7.0	2.54	0.81	31.04	31.85
max	7.38	4.58	1.5	101.97	102.57

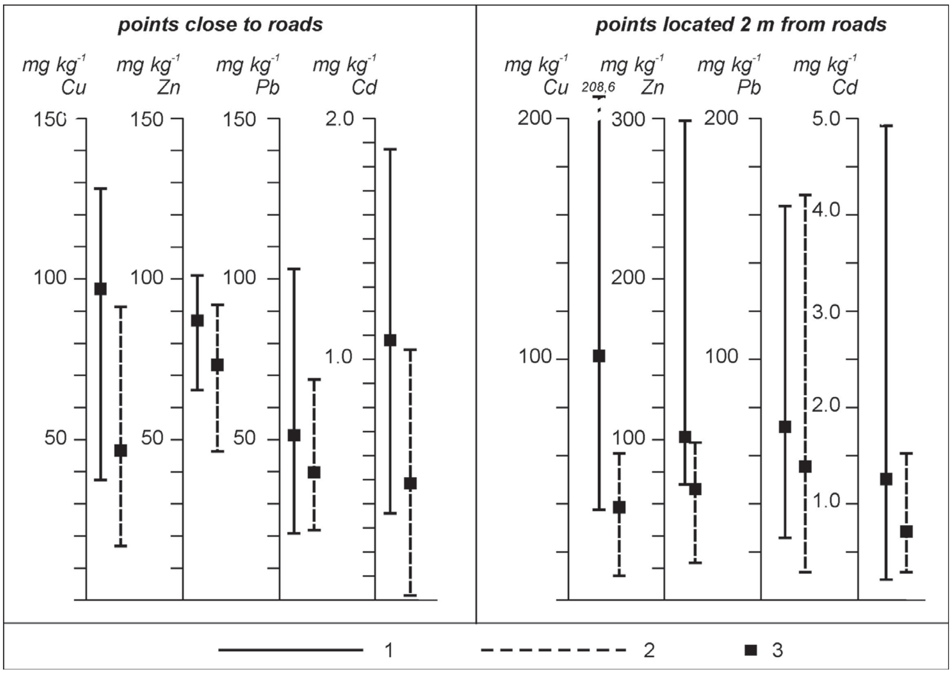

Fig. 1. Total content of selected heavy metals in soils analyzed: 1 – range of concentrations for points with old traction, 2 – range of concentrations for points with new traction, 3 – mean values

Relatively low variability of concentration of *bioavailable species* of the metals at sites situated close to the road edge and 2 m away from it shows that the effect of distance from the source of emission is imperceptible. It is quite *different with common species* of heavy metals, which are distinctly variable. Similarly, as most authors point out, the heavy metal content decreases with increase of the distance from a traffic route [8–10].

The level of contamination of the soils with Cu, Cd, Pb and Zn was assessed based on the limit values, laid down in the Regulation of Minister of Environment on the standards of soil quality and standards of earth quality (J. of Laws 02.165.1359 of 04.10.2002). No limit values for Cu, Pb, Cd or Zn were found to be exceeded in group C soils, which include industrial soils, surface mining land and soils close to traffic routes. The soils under examination contained the metals at amounts which are referred to as acceptable for the soils group. At one site (point 18), a slightly elevated content of copper and lead was recorded.

The experiment results indicate the effect of trolley bus traffic on the total content of copper in the soils neighbouring on the electric line. The soils situated close to the new trolley bus lines contained lower total amounts of the metal. Similar tendencies could be observed by analysing distribution of concentrations of bioavailable species. Soils taken from the study sites situated close to the streets with the newly built trolley bus lines usually contained lower amounts of copper as compared with the sites near the streets where trolley bus lines have existed for several decades.

Moreover, the variable position of the study points show that the effect of traffic on the content of heavy metals in soils near traffic routes is significant [5, 10, 11]. Larger accumulation of the heavy metals under study is usually found in surface samples from the vicinity of routes which have been in use for several decades as compared with the streets which were have been opened or thoroughly repaired within the past several years or months. The average content of common species of heavy metals in the newly opened or thoroughly repaired streets of Lublin were equal to: Cu 35.56 mg/kg, Cd 0.6 mg/kg, Pb 33.55 mg/kg, and Zn 66.98 mg/kg whereas the concentrations in the vicinity of old traffic routes were equal to: Cu 97.29 mg/kg, Cd 1.11 mg/kg, Pb 65.87 mg/kg, and Zn 95.14 mg/kg. Similar regularities were recorded for the species available to plants, which in the soils situated near newly opened or thoroughly repaired roads of Lublin were equal to: Cu 8.6 mg/kg, Cd 0.2 mg/kg, Pb 8.59 mg/kg, and Zn 4.61 mg/kg, whereas near the old traffic routes, the concentrations were equal to Cu 15.71 mg/kg, Cd 0.23 mg/kg, Pb 15.17 mg/kg, and Zn 5.06 mg/kg (Fig. 2).

The statistical analysis of the concentration of heavy metals *vs* variability of organic carbon in the soil under examination reveals statistically significant, strongest correlation with total and bioavailable Cu, somewhat weaker for Pb and Zn, no statistically significant correlation of organic carbon with the content of common species of cadmium and poor correlation in a bioavailable form. Although heavy metals form complexes with humus, which is a way of binding them, the complexes are not particularly stable or dominating.

The statistical analysis did not reveal any significant correlations between total content and the content of bioavailable species of cadmium and zinc and the sorptive capacity of the soils under examination (Table 2). Slightly greater effect on both species were exerted by sorptive capacity T in the case of lead, where primarily bioavailable species showed medium strength correlation. It is difficult to say which component of the sorptive complex has the greatest effect on the content, distribution and mobility of the heavy metals under examination [12].

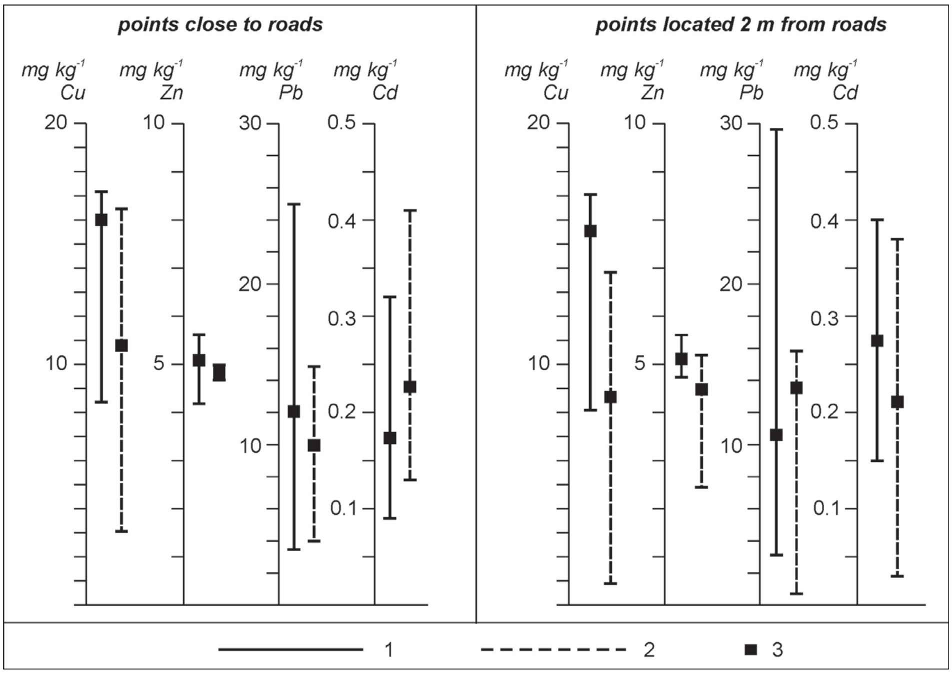

Fig. 2. Content of available form of selected heavy metals in soils analyzed: 1 – range of concentrations for points with old traction, 2 – range of concentrations for points with new traction, 3 – mean values

An analysis of heavy metals concentration in their common and bioavailable species in soils in the immediate vicinity of streets in Lublin *vs* variability of granulometric composition of the soils shows the absence of statistically significant correlations or the presence of only weak ones. Only copper as both species showed medium strength correlation for each of the isolated fractions. Many authors have indicated strong relationships between profile distribution of heavy metals with the smallest fractions; however, no such relationships were shown to exist in the soils in the vicinity of streets in Lublin [13, 14].

Heavy metals undergo various processes in the soil, including accumulation and migration. Metal accumulation depends on various factors, which have been widely discussed in the literature, with the content and nature of organic substances or the content of small grain fractions or the type of land use being dominant [2, 11–13]. The profile distribution of heavy metals in soils in the immediate vicinity of streets depends mainly on the origin of the surface layers which were brought to a site, and on the distance from sources of contamination with heavy metals, *ie* a street. These regularities are valid for young soils which were formed anew as a result of repairs and reconstructions and such soils which have been present close to traffic routes for decades. Current quality of the soils in Lublin, which is expressed as the content of heavy metals (Cd, Cu, Pb, Zn), is affected by origin of the soil layers which have been brought to the site, but also by various anthropogenic factors, the traffic factor being the main one.

Table 2

Chosen correlations between soil parameters (significant at $p < 0.05$)

	pH KCl	pH H_2O	C_{org}	H	Na	K	Mg	Ca	S	T	V	Cu t	Cu dtpa	Zn t	Zn dtpa	Pb t	Pb dtpa	Cd t	Cd dtpa
pH KCl																			
pH H_2O	0.68																		
C_{org}	–0.42																		
H	–0.66	–0.59	0.46																
Na																			
K	–0.51	–0.42	0.42																
Mg																			
Ca			0.46				0.88												
S			0.45				0.89	0.99											
T			0.46				0.89	0.98											
V		0.44		–0.47			0.44	0.65	0.64	0.63									
Cu t			0.5		0.41														
Cu dtpa			0.53		0.41							0.74							
Zn t			0.37									0.7							
Zn dtpa	–0.49		0.4									0.43	0.54						
Pb t			0.43					0.43	0.42	0.42	0.37	0.43	0.38	0.4					
Pb dtpa			0.45					0.49	0.47	0,47	0.44		0.37			0.85			
Cd t																			
Cd dtpa	–0.53		0.35	0.6				0.47	0.47	0.48									

Explanations: H, Na, K, Mg, Ca – exchangeable cations, S – sum of base cations, T – sorptive capacity, V – base saturation, X t – total form of an element, X dtpa – bioavailable form of an element.

Conclusions

1. Total concentration of Cu, Cd, Pb and Zn did not exceed the limit values of concentrations of copper, cadmium, lead or zinc for class C soils, which include industrial areas, surface mining land and traffic areas, laid down in the Regulation of Minister of Environment on the standards of soil quality and standards of earth quality (J. of Laws 02.165.1359 of 04.10.2002), however, the exceeded concentrations of Cu, Pb and Zn of the so called geochemical background show that the area under study is under strong influence of anthropopressure.

2. The proportion of bioavailable species in the total heavy metal pool was varied, which makes it difficult to establish which of the metals under study was the most mobile.

3. The content of common species of heavy metals decreases as the distance from the street edge increases, whereas no significant tendency of this kind was recorded for concentrations of bioavailable species of Cu, Cd, Pb and Zn.

4. Despite being regarded as practically unburdensome to the environment, trolley bus traffic affects the content of common and bioavailable species of copper in the soils adjacent to the electric line. Lower total content of the metal was found at the study sites situated on the routes with new trolley bus lines as compared with the traffic routes which have been in use for decades.

5. Current quality of the soils under study, containing heavy metals (Cd, Cu, Pb, Zn), is affected by the origin of surface layers of soils, which have been brought to the site, but also by a complex of various anthropogenic factors, with the traffic factor dominating.

References

[1] Klimowicz Z, Melke J. Rocz Glebozn. 2000;51(3/4):37-46.
[2] Maciejewska A, Skłodowski P. Zesz Probl Post Nauk Rol. 1995;418(1):271-280.
[3] Niesiobędzka K, Krajewska E. Ochr Środow i Zasob Natural. 2007;31:278-283.
[4] Hanna K, Lassabatere L, Bechet B. J Hazard Mater. 2009;161:1499-1505. 10.1016/j.jhazmat. 2008.04.124
[5] Kalembasa D, Pakuła K, Becher M. J Elementol. 2005;10(2):315-324.
[6] ISO 11466: International Standart, Soil quality-extraction of trace elements soluble in aqua regia. First edition, Geneve: 1995.
[7] Lindsay WL, Norvell WA. Soil Sci Soc Amer J. 1978;42:421-435.
[8] Kabata-Pendias A, Pendias H. Biogeochemia pierwiastków śladowych. Warszawa: PWN; 1999.
[9] Olajire AA, Ayodele ET. Environ Int. 1997;23(1):91-101.
[10] Czarnowska K, Bednarz I. Rocz Glebozn. 2000;51(3/4):29-36.
[11] Ma L.Q, Tan F, Harris WG. J Environ Qual. 1997;26:769-775
[12] Sipos P, Nemeth T, Kovacs Kis V, Mohai I. Chemosphere. 2008;73:461-469. 10.1016/j.chemosphere. 2008.06.046,
[13] Uziak S, Brogowski Z, Komornicki T. Acta Agrophys. 2005;124:1-157.
[14] Basta NT, Ryan JA, Chaney RL. Environ Qual J. 2005;34:49-63.

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Abstrakt: W pracy została podjęta próba oceny stopnia zanieczyszczenia metalami ciężkimi Cu, Cd, Pb i Zn gleb sąsiadujących z wybranymi ciągami komunikacyjnymi Lublina, oraz wpływu trakcji trolejbusowej (zbudowanej z nieizolowanych drutów miedzianych). Zaplanowane badania porównawcze umożliwił fakt otwarcia, bądź gruntownego remontu ważniejszych arterii komunikacyjnych w Lublinie, co zostało uwzględnione przy wyborze punktów badawczych. Zawartość ogólna miedzi w analizowanych glebach wahała się od 9,6 do 208,6 mg/kg, ołowiu od 11,3 do 167, mg/kg, kadmu od 0,02 do 4,9 mg/kg, a cynku od 22,9 do 300,6 mg/kg. Udział form dostępnych dla roślin w puli ogólnej metali ciężkich stanowił dla miedzi od 6,7 do 35,3%, dla ołowiu od 7,4 do 36,2%, kadmu od 3,3 do 90,1%, a dla cynku 1,7 do 10,7%. Stanowiska zlokalizowane przy trasach z nowymi liniami trolejbusowymi charakteryzowały się mniejszą zawartością ogólną tego pierwiastka, w porównaniu do szlaków komunikacyjnych charakteryzujących się kilkudziesięcioletnim użytkowaniem. Całkowite stężenia Cu, Cd, Pb i Zn nie przekroczyły zawartości granicznych metali ciężkich dla gruntów zaliczanych do grupy C, zamieszczone w Rozporządzeniu Ministra Środowiska w sprawie standardów jakości gleby oraz standardów jakości ziemi (Dz. U. 02.165.1359 z dn. 04.10.2002 r.).

Słowa kluczowe: metale ciężkie, gleby miejskie, zanieczyszczenia komunikacyjne