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Soil Chemistry

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## CONTENT OF CHOSEN HEAVY METALS IN GARDEN AND ARABLE SOILS

*Abstract.* The studies were conducted to determine the impact of the anthropogenic factors in the form of horticultural cultivation and urban environment on soils of allotment and household gardens and the role of humus substance in binding heavy metals and the distribution of elements in a soil profile. The research covered the area of south-eastern Poland, where 3 cities were selected for sandy soils and 3 for silty soils. The high enrichment factor of humus horizons for Cd, Cr and Ni was observed in sandy soils but it was lower in the silty soils. Significant negative correlation coefficients between fractional composition of humus and content of Cd, Cr and Ni were only observed in sandy soils. There were no significant relations in terms of the content of mercury.

The problem of heavy metals inter alia in garden soils was widely discussed in the literature. However, most of the research was focused on humus horizons, which is motivated by the location of gardens in the urban areas and their exposure to accumulation of substance precisely in surface horizons [1–4, 6–9, 11, 14–16, 18–20, 22–26]. However, few authors have paid attention to the combination of properties characteristic of the garden soil which was created in the specific conditions, with accumulation of heavy metals. In addition, it is important to reference the concentration of elements from humus horizons to soil parent material, which proves the anthropogenic origin of the analyzed metals [21].

The aim of this research was to determine the influence of organic matter formed by intensive horticultural cultivation on the content of mercury in humus horizons and cadmium, chromium and nickel in garden soil profiles with regard to arable soils.

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## MATERIALS AND METHODS

Soils from the area of south-eastern Poland were chosen for the research, they represented sandy soils (from the cities of: Biała Podlaska, Lubartów, Tarnobrzeg) and silty soils (Lublin, Przemyśl, Zamość). The samples were taken from household and allotment gardens located in urban areas and compared with arable soils in their neighborhood. The content of mercury was determined in humus horizons with the MA-2 analyzer by Nippon. Total content of cadmium, chromium and nickel was determined in above mentioned soil profiles after mineralization of soil samples in a solution of concentrated acids (nitric and perchloric 1:1) – by means of the ICP-AES method using the Leeman PS 950 analyzer. Granulometric composition of soil samples with the Bouyoucos Cassagrande areometric method modified by Prószyński, the pH in H<sub>2</sub>0 and in 1 mol KCl·dm<sup>-3</sup> suspension, potential acidity by means of the Kappen method, content of basic exchangeable cations using the Pallman method in 1mol CH<sub>2</sub>COONH<sub>4</sub> dm<sup>-3</sup> solution of pH 7, content of organic carbon with the Tiurin method modified by Simakow and fractional composition of humus compounds by the Kononowa-Bielczikowa method were also determined.

Obtained results were statistically analyzed with Statistica 10.0. Correlation coefficients were calculated between the total content of heavy metals in humus horizons and fractional composition of humus.

#### **RESULTS AND DISCUSSION**

The analyzed soils from gardens in Tarnobrzeg and a household garden from Biała Podlaska were classified as gley. In allotment gardens in Biała Podlaska and Lubartów the soils were classified as podzolic and in a household garden in Lubartów – brown podzolic. However, arable soils were defined as podzolic (Biała Podlaska) and brown podzolic (Lubartów i Tarnobrzeg). Horticultural grounds were characterized with slightly diverse soil texture – there were loamy sands on sands in the gardens of Biała Podlaska, in Lubartów household garden – loamy sands to sands, in an allotment garden – loamy sands and in a household garden in Tarnobrzeg – loamy sands and sandy loam, in an allotment garden – loamy sand on sandy loam. Arable soils in all localities showed granulometric composition of sands.

In the case of silty soils, all were classified as gray brown podzolic soils according to the WRB classification – *Luvisols*. The studied profiles of soils in Przemyśl and Zamość and from an allotment garden and arable soil in Lublin were characterized by texture of silt loam. Only the household garden in Lublin showed granulometric composition of loamy sand. The other basic physic-ochemical properties were presented and described in previous publications of the author [12, 13].

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	T and mee		Horizon thickness	Cd	Cr	Ni	Hg
Ully area	Land use	1011001100	(cm)		mg·kg <sup>-1</sup>		μg·kg <sup>-1</sup>
		Ap	0-20	0.42	7.84	8.35	6.86
		Α	20–36	0.49	8.33	9.02	
	Household garden	A/C	36-65	0.33	5.77	6.69	
		CG	65–111	0.12	9.18	6.95	
		G	>111	0.23	5.89	5.49	
		Ap	0-20	0.22	15.20	13.88	1.99
Dick Dodlock		Α	20–32	0.19	14.85	7.83	
Diata rouiaska	Allotment garden	Ees	32–69	0.14	13.95	7.20	
		Bfe	69–91	0.14	7.63	5.37	
		CG	>91	0.15	7.88	7.42	
		Ap	0-27	0.24	1.95	1.32	83.43
	1: v	Ees	27-47	0.16	6.56	1.50	
	ATADIC SOII	Bhfe	47–82	0.16	3.42	2.81	
		С	>82	0.12	7.74	2.88	
		Ap	0-20	0.29	10.38	3.99	17.94
	سامسم الماميسامين	Υ	20–35	0.25	12.40	6.00	
	nousenoia garaen	Bv	35-65	0.17	12.50	4.26	
		С	>65	0.13	7.94	3.62	
		Ap	0-20	0.25	8.13	4.85	32.94
Thoutó		Υ	20–35	0.17	4.85	4.26	
LUDALIUW	Allotment garden	Bhfe	35-50	0.13	3.59	4.35	
		G	50-67	0.21	4.67	4.73	
		С	29<	0.08	1.64	3.07	
		Ap	0-20	0.22	7.85	4.47	110.11
	Arable soil	Bv	20–50	0.21	10.35	5.19	
		С	>50	0.13	17.35	6.20	

#### CONTENT OF HEAVY METALS IN GARDEN AND ARABLE SOILS

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49.96					117.27						18.28				
16.78	16.40	16.63	18.68	17.83	9.33	9.48	9.78	8.75	18.33	18.80	7.00	5.73	6.01	3.22	4.50
21.23	23.70	23.58	23.52	18.48	19.20	11.72	16.85	11.19	18.23	18.92	7.46	5.47	3.26	1.69	3.25
0.59	0.52	0.45	0.36	0.38	0.37	0.25	0.16	0.08	0.23	0.40	0.16	0.13	0.08	0.10	0.21
0-20	20–40	40-65	65–90	>100	0-20	0-20 20-40 40-60 60-80 80-100 >100						20–32	32-55	55-130	>130
Ap	Α	Α	AG	U	Ap	A A A A G G G C C						Α	Bv	Bv/C	С
		Household garden									Arable soil				
							Tomotomo	Ialilouizeg							

TABLE 1. CONTINUATION

	I and use	Soil horizon	Horizon thickness	Cd	Cr	Ni	Hg
דמוות ה			(cm)		mg kg <sup>-1</sup>		μg kg <sup>-1</sup>
		Ap	0–27	0.28	9.11	4.08	111.55
Поче	المسطمة المطم	A/Eet	27–60	0.16	11.45	4.33	
SUUT	enoia garaen	Bt	60–85	0.16	11.45	4.42	
		С	>85	0.24	11.55	5.74	
		Ap	0–25	0.22	22.45	13.18	102.07
011 V	and and and and	Eet	25-45	0.21	17.73	12.13	
AIIC	oument garden	Bt	45-55	0.18	16.92	11.73	
		С	>55	0.19	19.70	13.08	
		Ap	0–25	0.26	37.40	17.13	63.59
		Eet	25-50	0.18	30.30	15.63	
4		Bt1	50-60	0.29	28.70	20.58	
AIS		Bt2	60–80	0.29	35.10	21.41	
		Bt/C	80-100	0.29	30.28	19.08	
		С	100-120	0.26	22.22	14.58	
		Ap	0–20	0.46	23.60	22.08	80.33
		Α	20–41	0.40	24.55	17.88	
П	and and an	Eet	41–67	0.44	36.35	21.18	
	usciiulu galucii	Bt1	67–130	0.45	38.65	26.31	
		Bt2	130–150	0.41	26.60	24.30	
		С	>150	0.43	28.72	25.13	
		Ap	0–20	0.37	31.42	22.53	10.88
		Α	20–33	0.40	31.12	21.13	
11	atmost condor	Eet	33–59	0.30	29.23	17.18	
ΠN		Bt1	59-95	0.36	29.58	17.63	
		Bt2	95–128	0.35	27.78	19.38	
		С	>128	0.45	31.42	24.55	
		db	0–25	0.50	28.40	25.93	96.14
<		Bt1	25-40	0.54	30.75	24.18	
R		Bt2	40–88	0.49	27.95	25.96	
		С	>88	0.50	31.45	26.46	

TABLE 2. CADMIUM, CHROMIUM, NICKEL AND MERCURY IN SILTY SOILS

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90.28				98.63			45.94			
10.73	11.73	12.43	17.13	21.83	20.78	28.03	19.58	19.48	24.63	15.83
21.32	41.80	22.57	29.60	33.25	32.27	39.15	36.47	28.03	26.23	19.90
0.51	0.47	0.24	0.23	0.36	0.28	0.22	0.37	0.29	0.30	0.30
0–24	24-60	60 - 104	>104	0-27	27-82	>82	0-23	23–39	39–101	>101
Ap	Eet	Bt	CG	Ap	Bt	С	Ap	Eet	Bt	С
			<u> </u>		Allotment garden					
					Lamosc					

TABLE 2. CONTINUATION

The total content of cadmium in sandy soils ranged from 0.08 to 0.59 mg×kg<sup>-1</sup> and was determined as natural (Table 1) [5, 10, 17]. Concentration of this element in humus horizons was determined in all profiles regardless to the way the land was cultivated, except for the allotment garden and the arable field in Tarnobrzeg, which was confirmed by the enrichment factor (Table 1, Table 3). The above mentioned coefficient was characterized by higher values (2.17 and 3,23 respectively) in the household and allotment gardens in Lubartów. This could be explained by the location of these objects in the city centre and close to an expressway, respectively (Table 3). The total content of cadmium in silty soils regardless of the usage was characterized by higher values than the sandy soils and ranged between  $0.16-0.54 \text{ mg} \times \text{kg}^{-1}$  (Table 2). There was no greater diversity of the analyzed element in the profiles with the exception of Zamość, where the concentration of cadmium occurred in humus horizons located near a communication route with high traffic, which is confirmed by the high enrichment factor (Table 1, Table 3). Similar relation was determined by many authors in their studies. The authors point to the proximity of a road as a factor influencing the accumulation of cadmium [3, 4, 16, 22, 25]. The content of the analyzed element in literature is defined as diverse in the area of Poland, mostly natural [2, 8, 11, 15, 24] and only in some locations it slightly exceeds the limits [1, 3, 4, 6, 9, 18, 19, 20, 22, 23, 25, 26]. Furthermore, in garden soils of Hungary, the enrichment factor has shown a slight accumulation of the analyzed metal, which indicates precisely the impact of traffic [21]. Similarly, in variously cultivated soils in Ireland, high content of cadmium was found. However, the way the land was used did not influence the accumulation of this element [14].

		Enrichment factor*								
Metal	Land use		Ι			II				
		а	b	с	d	e	f			
	Household garden	1.85	2.17	1.55	1.20	1.09	2.24			
Cd	Allotment garden	1.48	3.23	0.93	1.14	0.82	1.63			
	Arable soil	1.93	1.67	0.75	1.09	1.02	1.23			
	Household garden	1.33	1.31	1.15	0.79	0.82	0.79			
Cr	Allotment garden	1.93	4.96	1.01	1.14	1.00	1.14			
	Arable soil	0.25	0.45	2.30	1.18	0.90	1.18			
	Household garden	1.52	1.10	0.94	0.71	0.88	0.63			
Ni	Allotment garden	1.87	1.58	0.50	1.01	0.92	0.78			
	Arable soil	0.46	0.72	1.56	0.97	0.98	1 24			

TABLE 3. ENRICHMENT FACTOR Cd, Cr, Ni OF SANDY AND SILTY SOILS

I – sandy soils, II – silty soils; a – Biała Podlaska, b – Lubartów, c – Tarnobrzeg, d – Lublin, e – Przemyśl, f – Zamość;

\* Enrichment factor – calculated as concentration of metal in the parent material to surface horizon.

In sandy soils, the total content of chromium fluctuated widely from 1,64 to 23,58 mg×kg<sup>-1</sup> (Table 1). The enrichment factor for this element has pointed to its anthropogenic origin in humus horizons mainly in the allotment gardens in Biała Podlaska and Lubartów and in the arable field in Tarnobrzeg (Table 3). In the case of chromium, there was no tendency to its accumulation in humus horizons in silty soils and the total content of the analyzed element was very diversified in the profiles and ranged from 9,11 to 41,80 mg×kg<sup>-1</sup> (Table 2, Table 3). The total content of chromium was determined as natural, not exceeding the limit values [5], which was similar to the reports in numerous papers on garden soils in the area of Poland [4, 8, 15, 18, 19, 22]. Slight exceeding of permissible concentrations was found in the research of Szerszeń et al. [20], Bielicka et al. [1] and Szolnoki et al. [21] from the area of Hungary. Those author reported that the type of garden had no impact on the concentration of the element. However, according to McGrath [14], the type of land use and especially the localization of the garden influence the accumulation of chromium.

The total content of nickel in sandy soils ranged from 1.32 to 18.80 mg $\times$ kg<sup>-1</sup> (Table 1). The enrichment factor for the analyzed profiles indicated the accumulation of the element in humus horizons in the household and allotment garden in Biała Podlaska, the allotment garden in Lubartów and the arable soil in Tarnobrzeg. However, it did not reach high values (Table 3). Similarly to chromium, the total content of nickel in silty soils has not indicated contamination and concentration in humus horizons and fluctuated in the range of 4,08–28,03 mg×kg<sup>-1</sup> (Table 2, Table 3). In both analyzed soils, the content of nickel was determined as natural [5] and did not exceed the limits for agricultural soils [10, 17]. On the basis of the studies of numerous authors, the total content of nickel in garden soils is defined as a natural [1, 4, 8, 11, 18, 19, 23] and only few pointed to a slight exceeding of its limits [20, 24]. Furthermore, Szolnoki et al. [21] indicated the geochemical origin of the analyzed element on the basis of the obtained enrichment factor in garden soils of Hungary which excluded the impact of different way of cultivating the garden. On the other hand, McGrath [14] observed a higher amount of nickel in the arable soils than in garden soils in urban areas in Ireland.

The analyzed sandy soils were characterized by a natural content of mercury, which ranged between  $1.99-117.27 \text{ mg} \times \text{kg}^{-1}$  (Table 1). However, in silty soils it was slightly higher and ranged from  $10.88-111.55 \text{ mg} \times \text{kg}^{-1}$  (Table 2). According to Kabata-Pendias and Pendias [10], the content of mercury in Polish mineral soils with different granulometric composition amounts to  $0,02-1,5 \text{ mg} \times \text{kg}^{-1}$ . Also the amount of mercury did not exceed the permissible limits, which for Poland amounts to  $0.5 \text{ mg} \times \text{kg}^{-1}$ [5]. Similar results were obtained by Bielicka et al. [1] in garden areas in Gdańsk. In contrast to the results obtained, Gąsiorek at al. [7] found slightly higher values in garden soils from Cracow, which could be attributed to greater pressure of the urban environment. McGrath [14], in

his research comparing different types of soil cultivation in Ireland, indicated a much greater content of the researched element in garden soils in urban localities in comparison to neighboring areas, which does not confirm the results.

# TABLE 4. CORRELATION COEFFICIENTS BETWEEN ALL CONTENT OF Cd, Cr, Ni, Hg AND FRACTIONAL COMPOSITION OF HUMUS SANDY AND SILTY SOILS IN HUMUS HORIZONS REGARDLESS SOIL MANAGEMENT

		Ι		II				
Specification	Cd	Cr	Ni	Hg	Cd	Cr	Ni	Hg
C extracted with a mixture	-0.702*	-	-	-	-	-		-
C extracted 0.1 mol NaOH dm <sup>-3</sup>	-0.809	-0.763	-0.773	-	-	-		-
C extracted 0.05 mol $H_2SO_4$ dm <sup>-3</sup>	-	-	-	-	-	-		-
Humines	0.733	-	-	-	-	-		-
HA extracted with mixture	-	-	-	-	-	-		-
FA extracted with mixture	-0.745	-	-	-	-	-		-
HA extracted 0.1 mol NaOH dm <sup>-3</sup>	-0.747	-0.807	-0.778	-	-	-		-
FA extracted 0.1 mol NaOH dm <sup>-3</sup>	-0.808	-0.714	-0.742	-	-	-		-
C <sub>HA</sub> bound to Ca	-	0.701	0.724	-	-	-		-

Explanations: I - sandy soils, II - silty soils; \* p<0.05

The correlation analysis has indicated significant relations which were mostly negative between the fractional composition of humus compounds and the total content of cadmium, chromium and nickel in sandy soils. However, no significant relations were found in silty soils (Table 4). The positive correlation was only observed between the humin content and cadmium, as well as carbon of humic acids associated with Ca and the total content of chromium and nickel (Table 4). Rogóż [18], analyzing the garden soil with different granulometric composition, found a lack of correlation between the content of organic carbon and the total content of nickel and cadmium, but in the case of chromium there were statistically significant coefficients. Likewise, Dabkowska-Naskret and Kobierski [4] found that the total content of chromium correlated with the content of organic carbon, but also with the the content of cadmium. Similar dependency was obtained in the garden soils from Warsaw [3] and from the convent gardens in Cracow [6]. There were no significant correlations between the content of mercury and fractional composition of humus compounds in both types of soil (Table 4). In their studies, Zhang et al. [27] demonstrated that there was no relation between the content of mercury and the amount of organic carbon.

#### CONCLUSIONS

1. The researched soils were characterized by a natural content of the analyzed elements: mercury, cadmium, chromium and nickel.

2. High values of the enrichment factor for the analyzed metals pointed to their anthropogenic origin. However, they were not dependent on the way the land was cultivated.

3. The obtained correlation coefficients have shown mostly negative relationships between the humus fractional composition and the total content of Cd, Cr and Ni in sandy soils only. There were no significant correlations in terms of the total content of mercury in the analyzed soils.

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# ZAWARTOŚĆ WYBRANYCH METALI CIĘŻKICH W POZIOMACH PRÓCHNICZNYCH ORAZ PROFILACH GLEB OGRODOWYCH I UPRAWNYCH

Badania zostały przeprowadzone w celu określenia wpływu czynnika antropogenicznego w postaci uprawy ogrodniczej oraz środowiska miejskiego na gleby ogrodów działkowych i przydomowych oraz roli związków próchnicznych w wiązaniu metali ciężkich a także rozkładzie pierwiastków w profilu glebowym. Badaniami objęto teren południowo-wschodniej Polski, gdzie wytypowano po 3 miasta dla gleb powstałych z piasków oraz pyłów. Wysokie wskaźniki wzbogacenia poziomów próchnicznych dla Cd, Cr i Ni wystąpiły w glebach piaszczystych a w wytworzonych z pyłu były niższe. Istotne ujemne wskaźniki korelacji pomiędzy składem frakcyjnym próchnicy a zawartością Cd, Cr i Ni wystąpiły jedynie w glebach wytworzonych z piasku. Nie stwierdzono podobnych zależności dla zawartości rtęci.