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TRACE ELEMENT CONTENT IN CEREAL WEEDS AGAINST THE BACKGROUND OF THEIR SOIL CONTENTS PART 3. CADMIUM AND NICKIEL CONTENTS IN SOIL AND WEEDS

ZAWARTOŚĆ PIERWIASTKÓW ŚLADOWYCH W CHWASTACH ROŚLIN ZBOŻOWYCH NA TLE ICH ZAWARTOŚCI W GLEBIE CZ. 3. ZAWARTOŚĆ KADMU ORAZ NIKLU W GLEBIE I CHWASTACH

Abstract: Thirty soil samples were collected from the 0-25 cm layer of arable land in the Brzeźnica commune in the first decade of June 2007. Samples of weeds commonly occurring in cereal crops, *ie* cornflower – *Centaurea cyanus* L., poppy – *Papaver rhoeas* L., corn chamomile – *Anthemis arvensis* and thistle – *Cirsium arvense* (L.) Scop. were collected from the same sites. In both soil and plant material were assessed total contents of cadmium and nickel and their soluble form contents.

Significant differences in cadmium and nickel contents, both approximate to total amount and soluble forms determined in 0.1 mol \cdot dm⁻³ HCl solution were observed in the analyzed soils. The contents of soluble cadmium and nickel forms in soil were to the greatest extent dependent on the soil pH. It was revealed that in slightly acid and neutral soils the amount of extracted cadmium and nickel soluble forms was smaller in relation to the quantity of cadmium extracted from very acid soils with pH_{KCl} < 5.5.

Cadmium and nickel concentrations in the analyzed weeds from cereal crops ranged widely depending on their contents in soil and soil reaction, species and analyzed plant part. Cadmium content was diminishing with increasing pH_{KCl} value over 5.5, whereas the quantity of nickel accumulated in all analyzed weeds, both in their roots and aboveground parts was diminishing irregularly.

Keywords: weeds, soil, cadmium and nickel content, soil pH_{KCl}

The assessment of fodder or nutritive value of plants attaches great importance to their pollution with heavy metals. Weeds collected in cereal crops do not represent any fodder value, but their chemical composition may prove a valuable source of information about the level of the environment pollution with heavy metals. Under conditions of elevated levels of heavy metals in soil, one should seek the methods of

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their management which would allow limit their entering food chain. One of the most dangerous and toxic heavy metals is cadmium.

Heavy metal toxicity for living organisms is apparent when they are accumulated in the environment in excessive quantities [1-3]. Plants containing considerable amounts of heavy metals may constitute a serious source of these elements for humans and animals [1, 4]. Behaviour of heavy metals in soils and their phytoavailability depend on many factors: chemical, physical and biological processes, but also on soil properties [3, 5, 6].

The investigations were conducted to determine the contents of cadmium and nickel in selected weeds originating from cereal crops against these metals contents in soil.

Material and methods

Thirty soil samples were collected from the 0-25 cm layer of arable land in the first decade of June 2007 in order to assess their trace metal contents. The site where the soil samples and 30 samples of weeds most common in cereal crops: poppy – *Papaver rhoeas* L., cornflower – *Centaurea cyanus* L., corn chamomile – *Anthemis arvensis* L. and thistle – *Cirsium arvense* (L.) Scop. were collected was described in the previous part of the article in "Materials and methods" section [7].

Approximate to total contents of trace elements in the analyzed soils were determined following their mineralization at the temperature of 450 °C. Next they were digested in a mixture of perchloric(VII) and nitric(V) acids (2:3, v/v). Mineralized soil material was dissolved in hydrochloric acid (HCl) [8]. The contents of trace elements occurring in soluble compounds (soluble forms) were determined after extraction with 0.1 mol \cdot dm⁻³ HCl solution, and the soil to extraction solution ratio was 1:10.

Collected plant material was washed, divided into the aerial parts and roots, dried, crushed and dry mineralized. The ash was dissolved in nitric(V) acid (1:2). In obtained solutions of the soil and plant samples, cadmium and nickel contents were assessed using ICP-AES method in JY 238 ULTRACE apparatus (Jobin Yvon Emission). Obtained results of these elements contents in soil and analyzed weeds were statistically elaborated.

Results and discussion

Characteristics of collected soil material

Considerable differences of the analyzed soils with reference to their granulometric composition, organic carbon content and pH were observed. The value of soil pH assessed in water suspension ranged from 4.81 to 7.68, whereas in 1 mol KCl \cdot dm⁻³ solution from 3.95 to 6.64. Detailed data on physical and chemical properties of the analyzed soils were given in the previous paper [7]. The analyzed soil samples revealed considerable differences in cadmium and nickel total contents, as well as their soluble forms content.

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Total cadmium content in the studied soils ranged from 0.48 to 3.52 mg \cdot kg⁻¹, at geometric mean 1.12 mg Cd \cdot kg⁻¹, whereas nickel contents ranged from 9.57 to 24.68 mg \cdot kg⁻¹, at geometric mean 12.97 mg Ni \cdot kg⁻¹ (Table 1).

Table 1

	Total c	content	Soluble form content					
Specification	$[{\rm mg}\cdot {\rm kg}^{-1}]$							
	Cd	Cd Ni Cd		Ni				
	pH in 1 mol KCl \cdot dm ⁻³ \leq 5.5							
Arithmetic mean	1.35	14.67	0.79	1.93				
Geometric mean	1.22	14.14	0.78	1.78				
Range	0.68-3.52	10.38-24.68	0.46-0.98	0.71-5.03				
Relative standard deviation [%]	53	30	16	56				
	pH in 1 mol KCl ·	dm^{-3} from 5.5 to 6	.5					
Arithmetic mean	1.16	12.01	0.71	1.64				
Geometric mean	1.05	11.72	0.68	1.44				
Range	0.48-1.45	9.57-10.03	0.38-1.09	0.81-1.43				
Relative standard deviation [%]	50	26	29	57				
pH in 1 mol KCl \cdot dm ⁻³ \ge 6.6								
Arithmetic mean	0.88	11.16	0.67	1.02				
Geometric mean	0.87	11.15	0.66	1.01				
Range	0.81-0.95	10.47-11.86	0.63-0.69	0.91-1.08				
Relative standard deviation [%]	8	6	4	4				

Cadmium and nickel content in soil depending on soil reaction

The content of cadmium and nickel in soluble forms assessed in 0.1 mol \cdot dm⁻³ HCl solution ranged from 0.38 to 1.09 mgCd \cdot kg⁻¹, at geometric mean 0.73 mgCd \cdot kg⁻¹ and from 0.81 to 3.63 mgNi \cdot kg⁻¹, at geometric mean 1.59 mgNi \cdot kg⁻¹ of soil. The amounts of the analyzed elements soluble forms to the greatest extend depended on the soil pH and organic carbon content (Table 2).

The amounts of soluble forms of cadmium and nickel extracted from slightly acid and neutral soils were smaller than the quantities of elements extracted from soil with pH_{KCl} below 5.5 (Table 1). For instance, the amount of nickel extracted with 0.1 mol \cdot dm⁻³ HCl solution from slightly acid and neutral soils was by 19 and 43 % smaller in comparison with the quantity of nickel extracted from soils with pH_{KCl} below 5.5. The share of extracted soluble forms of cadmium and nickel in total content of these elements in soil fluctuated from 16 to 94 % for cadmium and from 7 to 27 % for nickel.

Karczewska [9] and Rogoz [10] demonstrated that a visible increase in metal salts solubility occurs when pH value decreases below 7.2 and therefore metals amount in

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soluble forms available to plants increases. Obtained results revealed that physical and chemical properties of the investigated soils differently affected total contents of cadmium and nickel and their soluble forms, as evidenced by simple correlation coefficients (Table 2).

Table 2

Simple correlation	coefficients (r)) between	cadmium	and nick	el contents	in	soils
	and se	elected soi	1 propertie	s			

Total c	ontents	Soluble forms			
Cd	Ni	Cd	Ni		
-0.351*	-0.413*	-0.375*	-0.344*		
0.272	0.352*	0.599***	0.429*		
Share of fraction with diameter:					
0.038	0.124	0.157	0.232		
0.155	0.359*	0.144	0.337		
	Cd -0.351* 0.272 diameter: 0.038	-0.351* -0.413* 0.272 0.352* diameter: 0.038 0.124	Cd Ni Cd -0.351* -0.413* -0.375* 0.272 0.352* 0.599*** diameter: 0.038 0.124 0.157		

n = number of samples - 30; r significant at: *p = 0.05; **p = 0.01; ***p = 0.001.

On the basis of obtained results the analyzed soils were assessed considering degree of their pollution with cadmium and nickel on the basis of guidelines suggested by Kabata-Pendias et al [11]. Basing on these guidelines 14 samples were classified to soils with natural cadmium contents (0°), 15 samples were classified to soils with elevated content of this element (I°), whereas 1 sample represented a weakly polluted soil (II°). In case of nickel, all analyzed soils were classified to the group with natural content of this element (0°).

Contents of cadmium and nickel in the analyzed weeds

Contents of Cd and Ni in collected cereal weeds depended on: weed species, analyzed plant part and soil properties. Diversified trace element contents in plants depending on abiotic and biotic factors but also on individual variability of plants have been widely documented in the scientific literature [12–14].

Cadmium. Although no physiological role of cadmium has been determined so far, the element is exceptionally easily absorbed by plant, generally proportionately to its concentration in soil. This element contents in plants are greatly diversified, and the amounts most frequently assessed in the aboveground parts range from 0.05 to 0.2 mgCd \cdot kg⁻¹ [3].

Geometric mean content of cadmium in the analyzed roots of weed from cereal crops were arranged according to increasing content: poppy $-0.74 \text{ mgCd} \cdot \text{kg}^{-1}$, thistle $-1.73 \text{ mgCd} \cdot \text{kg}^{-1}$, cornflower $-2.20 \text{ mgCd} \cdot \text{kg}^{-1}$ and chamomile $-3.30 \text{ mgCd} \cdot \text{kg}^{-1}$, whereas in the aerial parts of the weeds geometric mean cadmium content was arranged as follows: poppy $-0.34 \text{ mgCd} \cdot \text{kg}^{-1}$, cornflower $-1.37 \text{ mgCd} \cdot \text{kg}^{-1}$, thistle $-1.94 \text{ mgCd} \cdot \text{kg}^{-1}$ and chamomile $-2.60 \text{ mgCd} \cdot \text{kg}^{-1}$ (Table 3).

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Table 3

	Roots		Aboveground parts	
Mean content	Cd	Ni	Cd	Ni
	Cornflowe	er – Centaurea cyanus	L.; n = 30	
	pH	in 1 mol KCl \cdot dm ⁻³ \leq	5.5	
Arithmetic mean	3.67	4.48	2.06	2.44
Geometric mean	3.29	3.92	1.94	2.17
Range	1.45-7.32	1.11-10.06	0.99–3.58	1.11-6.24
	pH in 1 i	mol KCl \cdot dm ⁻³ from 5	.5 to 6.5	
Arithmetic mean	1.36	2.63	0.95	1.71
Geometric mean	1.18	2.42	0.90	1.41
Range	0.43-1.65	1.37-5.09	0.35-1.28	0.65-3.62
	pH	in 1 mol KCl \cdot dm ⁻³ \geq	6.5	
Arithmetic mean	2.01	3.16	1.15	1.91
Geometric mean	1.84	3.09	1.08	1.83
Range	1.17-3.23	2.29-3.72	0.74-1.73	1.33-2.65
		- Papaver rhoeas L.;		
	pH	in 1 mol KCl \cdot dm ⁻³ \leq	5.5	
Arithmetic mean	1.48	2.47	0.83	1.98
Geometric mean	1.06	2.20	0.46	1.65
Range	0.13-6.45	1.14-5.62	0.11-5.18	0.66-4.61
	pH in 1	mol KCl \cdot dm ⁻³ from 5	.5 to 6.5	
Arithmetic mean	0.47	1.47	0.25	1.29
Geometric mean	0.44	1.30	0.22	1.12
Range	0.24-0.83	0.82-3.80	0.13-0.57	0.85-3.80
	pH	in 1 mol KCl \cdot dm ⁻³ \geq	6.5	
Arithmetic mean	0.54	1.82	0.28	1.52
Geometric mean	0.49	1.70	0.24	1.38
Range	0.33-0.85	1.18-2.81	0.12-0.52	0.91-2.49
	Corn chamor	nile – <i>Anthemis arven</i>	<i>sis</i> L.; n = 30	
	pH	in 1 mol KCl \cdot dm ⁻³ \leq	5.5	
Arithmetic mean	6.21	5.06	4.50	2.78
Geometric mean	4.98	4.31	3.63	2.26
Range	1.82-13.93	1.32–9.28	1.17-10.02	0.73-7.40
	pH in 1	mol KCl \cdot dm ⁻³ from 5	.5 to 6.5	
Arithmetic mean	2.71	2.44	2.24	1.70
Geometric mean	1.99	2.18	1.55	1.46
Range	0.21-7.58	1.11-4.88	0.82-10.12	0.56-3.52

Cadmium and nickel content in cereal weeds depending on soil reaction

Table 3 contd.

Mean content	Roots		Aboveground parts				
Mean content	Cd	Ni Cd		Ni			
	pH in 1 mol KCl \cdot dm ⁻³ \geq 6.5						
Arithmetic mean	1.83	2.24	1.93	1.64			
Geometric mean	1.71	2.05	1.89	1.61			
Range	1.02-2.49	1.11-3.10	1.46–2.37	1.35-2.15			
	Thistle – C	irsium arvense (L.) So	cop. ; n = 30				
	pH	in 1 mol KCl \cdot dm ⁻³ \leq	5.5				
Arithmetic mean	2.79	3.76	4.28	3.77			
Geometric mean	2.47	3.25	3.41	3.02			
Range	1.01-5.42	1.41-8.98	1.05-17.35	1.05-8.69			
	pH in 1	mol KCl \cdot dm ⁻³ from 5	.5 to 6.5				
Arithmetic mean	1.36	2.05	1.09	2.98			
Geometric mean	1.17	1.93	1.01	2.61			
Range	0.64-3.69	1.01-3.62	0.52-1.54	1.33-5.98			
pH in 1 mol KCl \cdot dm ⁻³ \ge 6.5							
Arithmetic mean	0.91	2.07	1.29	1.77			
Geometric mean	0.81	1.79	1.09	1.62			
Range	0.39-1.27	0.79–3.09	0.55-2.29	0.92-2.59			

Nickel. Nickel is an element relatively easily absorbed by plants. If it occurs in soils in its mobile forms, it is taken up proportionately to its content in soil.

Nickel content in the studied weeds was quite diversified depending on the species, analyzed plant part and soil pH. Geometric mean nickel content in the roots of the analyzed cereal weeds can be arranged according to its growing contents: poppy – 1.83 mgNi \cdot kg⁻¹, thistle – 2.51 mgNi \cdot kg⁻¹, corn chamomile – 3.19 mgNi \cdot kg⁻¹ and cornflower – 3.25 mgNi \cdot kg⁻¹, whereas the aboveground parts of these weeds were ordered as follows: poppy – 1.44 mgNi \cdot kg⁻¹, cornflower – 1.78 mgNi \cdot kg⁻¹, corn chamomile – 1.89 mgNi \cdot kg⁻¹ and thistle – 2.57 mgNi \cdot kg⁻¹ (Table 3).

Irrespectively of changes of pH values in the studied soils, higher values of cadmium and nickel were assessed in roots than in the aboveground parts of the analyzed weeds. It evidences poor translocation of these metals from roots to the aboveground parts (Table 3). In their investigations Jurkowska et al [12] revealed considerable interspecies differences in transport of these trace elements from the roots to the aboveground parts in plant species belonging to the same family (legumes).

Cadmium content in roots and aboveground parts of the analyzed weeds of cereal crops was decreasing when the pH_{KCl} value of the analyzed soils was increasing above 5.5. For instance, geometric mean cadmium content in corn chamomile from slightly acid and neutral soils was smaller, respectively by 40 % and 66 % as compared with geometric mean cadmium content in corm chamomile roots from soils with pH_{KCl}

below 5.5 (Table 3). Increase in pH_{KCl} value above 5.5 in the studied soils not unanimously affected nickel contents in the analyzed weeds. Assuming e.g. geometric mean nickel content in the roots and aboveground parts of cornflower grown on soils with $pH_{KCl} \leq 5.5$ as 100, we will see that this element content in the roots of cornflower from slightly acid and neutral soils was smaller by 35 % and 16 % (Table 3).

Statistical analysis of the obtained results revealed that some physicochemical properties of the researched soils not unanimously affected the contents of the analyzed elements in weeds from cereal crops (Table 4). A significantly negative dependence was revealed between the soil pH and cadmium content in cornflower roots, where r = -0.616; p = 0.001 and in the aboveground parts r = -0.672; p = 0.001 (Table 4).

Table 4

Values of simple correlation coefficients (r) between selected soil properties and cadmium and nickel contents in cereal weeds

Properties of soil;	Roots		Aboveground parts			
n = 30	Cd	Ni	Cd	Ni		
Cornflower – <i>Centaurea Cyanus</i> L.; n = 30						
pH _{KCl} value	-0.616***	-0.440*	-0.672***	-0.297		
Total content	0.473**	0.452**	0.389*	0.670***		
Soluble forms	0.253	0.549**	0.342*	0.635**		
Poppy – <i>Papaver rhoeas</i> L.; n = 30						
pH_{KCl} value	-0.473**	-0.327	-0.336*	-0.268		
Total content	—	—	_			
Soluble forms	—	0.343	—	—		
	Corn chamomile – <i>Anthemis arvensis</i> L.; n = 30					
pH_{KCl} value	-0.568**	-0.545**	-0.544**	-0.449**		
Total content	0.594**	0.422*	0.548**	0.591***		
Soluble forms	0.416*	0.447**	0.291	0.518**		
Thistle – <i>Cirsium arvense</i> (L.) Scop.; n = 30						
pH _{KCl} value	-0.636***	-0.541**	-0.458**	-0.314		
Total content	0.054	0.086	0.057	0.182		
Soluble forms	0.370*	0.006	0.207	0.167		

n = number of plant samples; r significant at: *p = 0.05; **p = 0.01; ***p = 0.001.

On the basis of obtained results the contents of cadmium and nickel were assessed in the analyzed plants assuming the guidelines suggested by Kabata-Pendias et al [11] for plants designed for human consumption and animal fodder. Basing on these guidelines exceeded values of critical cadmium content, *ie* 0.5 mgCd \cdot kg⁻¹ were assessed in 70 % of weed samples, whereas no cases of exceeded nickel content were assessed in the studied weeds. High level of cadmium contents in the investigated weeds from cereal crops may suggest that this element contents may have been exceeded also in cereals.

Conclusions

1. Total contents of cadmium and nickel and their soluble forms were diversified in the analyzed soils. With increasing soil pH_{KCl} over 5.5 total contents of these elements and their soluble forms decreased.

2. The contents of cadmium and nickel in the analyzed weeds present in cereal crops ranged widely depending on the species, analyzed plant part, these elements total content in soil and their soluble forms contents, as well as soil reaction.

3. With increasing soil pH_{KCl} over 5.5 the contents of cadmium and nickel decreases in all analyzed weeds, both in their roots and the aboveground parts.

4. The studied plants revealed elevated cadmium contents. In 70 % of weed samples Cd content exceeded permissible value of this element, *ie* over 0.5 mgCd \cdot kg⁻¹ dry mass was assessed.

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ZAWARTOŚĆ PIERWIASTKÓW ŚLADOWYCH W CHWASTACH ROŚLIN ZBOŻOWYCH NA TLE ICH ZAWARTOŚCI W GLEBIE CZ. 3. ZAWARTOŚĆ KADMU ORAZ NIKLU W GLEBIE I CHWASTACH

Katedra Chemii Rolnej i Środowiskowej Uniwersytet Rolniczy im. Hugona Kołłątaja w Krakowie

Abstrakt: W pierwszej dekadzie czerwca 2007 r. na terenie gminy Brzeźnica pobrano 30 próbek glebowych z gruntów ornych z warstwy 0–20 cm. Z tych samych miejsc pobrano próbki chwastów powszechnie występujących w uprawach roślin zbożowych, tj.: chaber bławatek – *Centaurea cyanus* L., mak polny – *Papaver rhoeas* L., rumian polny – *Anthemis arvensis* L. oraz ostrożeń polny – *Cirsium arvense* (L.) Scop. W zebranym materiale glebowym oznaczano całkowite zawartości kadmu i niklu oraz ich zawartości w formach rozpuszczalnych. W materiale roślinnym oznaczano zawartości kadmu i niklu.

Zaobserwowano istotne różnice zbliżonej do całkowitej zawartości kadmu i niklu w badanych glebach, jak również ich w form rozpuszczalnych oznaczonych po ekstrakcji roztworem HCl o stężeniu $0,1 \text{ mol} \cdot \text{dm}^{-3}$.

Zawartość rozpuszczalnych form kadmu i niklu w glebach w największym stopniu zależały od ich odczynu. Wykazano, że w glebach lekko kwaśnych i obojętnych ilość wyekstrahowanych rozpuszczalnych form kadmu i niklu była mniejsza w odniesieniu do ich ilości wyekstrahowanych z gleb bardzo kwaśnych p H_{KCI} < 5,5.

Zawartości kadmu oraz niklu w badanych chwastach rosnących w uprawach roślin zbożowych wahały się w szerokim zakresie w zależności od ich zawartości w glebie i odczynu oraz od gatunku i analizowanej części rośliny. Wraz ze wyrostem wartości pH_{KCI} powyżej 5,5 zmniejsza się zawartość kadmu, natomiast ilość akumulowanego niklu we wszystkich analizowanych chwastach, tak w korzeniach, jak i w częściach nadziemnych, zmniejszała się nieregularnie.

Słowa kluczowe: chwasty, gleba, zawartość kadmu i niklu, pH_{KCl} gleby