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TOTAL CONTENTS AND AVAILABLE FORMS OF NICKEL IN AGRICULTURAL ALLUVIAL SOILS

ZAWARTOŚĆ FORM CAŁKOWITYCH I PRZYSWAJALNYCH NIKLU W ALUWIALNYCH GLEBACH UPRAWNYCH

Abstract: Alluvial soils located in river valleys constitute a diverse cover, which consists of mineral as well as mineral-organic and organic soils, with very different physicochemical properties. The subject of this study was to determine the nickel content in alluvial soils formed from gyttia of the biogenic plain of the Unislawski Basin. Soil samples were collected from seven soil profiles. Selectd physicochemical properties were determined aplying the methods commonly used in soil science laboratories. In the samples analysed the total nickel content was defined after mineralization in a mixture of acids HF + $HClO_4$ and its easily available DTPA-extracted forms. The content of total and mobile forms was reported using the atomic absorption spectrophotometry method using the PU 9100X spectrometer (Philips). The total content of nickel ranged from 0.6 $mg \cdot kg^{-1}$ to 18.04 $mg \cdot kg^{-1}$.The highest content of this element was noted in surface and subsurface horizons and the enrichment horizons of organic matter. In the soil samples the total nickel content was similar to the geochemical background level, while the content of mobile forms of this element was lower than the values considered toxic. In the soils analysed the content of DTPA-extractable forms ranged from 0.14 $mg \cdot kg^{-1}$ to 2.09 $mg \cdot kg^{-1}$.

Keywords: nickel in soil, alluvial soils, total and DTPA-extractable forms

Introduction

A growing interest in microelements resulting from the natural environment pollution calls for the control of the pollution amounts in the air, water and, mostly, in soil, which is obvious since soil is the first link of the food chain, affecting the chemical composition of plant materials determining the human and animal health. Heavy metals are a specific group of pollutions present in soil. This specific nature comes from their character; those are the elements which do not undergo degradation and decomposition, additionally they occur in all the soil types.

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Nickel is a metal which is worth noting in terms of environmental protection. It is not a microelement indispensable for the functioning of living organisms, however, numerous research have shown its presence in the adequate pattern of physiological processes in plants, animals and microorganisms [1–5]. Crops uptake nickel easily, usually proportionally to its concentration in soil, until the level of toxicity is reached. There are, however, differences in the phytoaccumulation and phytotoxicity of nickel depending on its form in soil and on the plant species [6, 7]. The occurrence of that element is connected with the content in the parent rock [8], while the mobility is conditioned by the mineralogical and the granulometric composition of soils [9]. A strong bond with nickel formed by mineral colloids and iron hydroxide limits the mobility of that microelement in the soil environment.

The aim of the present research was to evaluate the total content and the available forms of nickel in alluvial soils formed on gyttias of the biogenic plain of the Unislaw Basin.

Material and methods

The research material involves 7 soil profiles, located in the area of the Unislaw Basin (the Lower Vistula Valley) in the vicinity of Bloto (Fig. 1). The area exposed to the analyses is under agricultural use for the field cultivation of vegetable crops, sugar beet, rape and wheat. The soil material was made up by the carbonate formations, emerged in the stagnant muddy river lakes grown with plants, covered with peat or alluvia, affecting their composition and physicochemical properties.

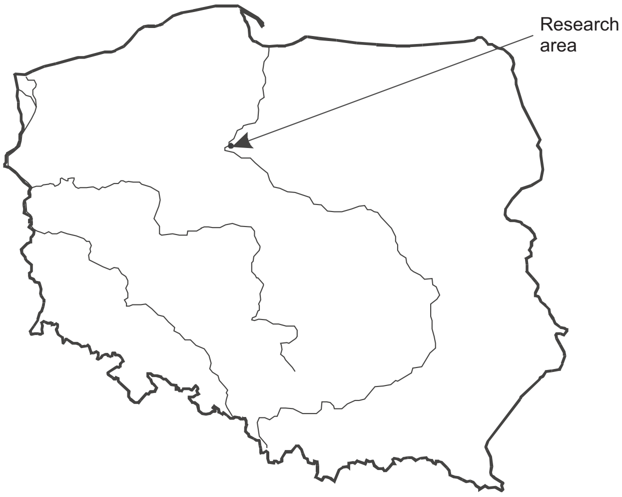

Fig. 1. Research area location

The soils have been classified as Calcari-Mollic Fluvisols, demonstrating high fertility. The soil for laboratory tests was sampled from the morphologically separated layers. The research material was dried and screened through the sieve with the mesh 2 mm in diameter. For the samples prepared in such way, selected physicochemical properties were defined applying the methods commonly used in soil science laboratories. In the samples analysed there was measured the total content of nickel after the mineralization in the mixture of HF + $HClO_4$ acids with the Crock and Severson's method [10] and its easily available forms, extracted with DTPA, according to Lindsay and Norvell [11]. The total contents and mobile forms were determined applying the method of atomic absorption spectroscopy (AAS) with the PU 9100X spectrometer (Philips). To verify the accuracy of the results, the analysis of the certified material SV-M as well as the so-called zero tests were made, which were exposed to the identical analytic procedure as the soil samples. All the assays were made in three repetitions; the paper presents arithmetic means of the results.

Results and discussion

The soils showed a clear variation from most soils in Poland. Next to calcium carbonate, their main component was organic matter. In the earlier reports [12] there was noted the lithologic discontinuity of the soils discussed. The fluctuations in the content of carbonates, organic substance and non-carbonate mineral substance point to the occurrence of many sedimentation cycles in their formation. The characteristic feature of the soil profiles was a high content of carbon carbonate reaching 76.8 %, and organic matter – 355.0 g · kg^{-1} (Table 1). The occurrence of considerable amounts of $CaCO_3$ was observed already in arable and humus horizons (Apca), which, on average, contained 22.0 % of that compound. The analysis of the content of carbonates in respective types of gyttia demonstrated a high variation. Among the gyttias, the lowest amount of carbonates was recorded for claygyttia, while the highest – for lime gyttia. Lime gyttia contained, on average, 63.3 % of $CaCO_3$, at the maximum amounts reaching 76.08 %. Calcium carbonate was also identified in the horizons of low peat, however, those were little amounts, ranging from 4.9 to 6.8 %. Even lower amounts of $CaCO_3$ were noted in the Gleysols in which the content of calcium carbonate did not exceed 4.5 %, at the minimum content of 0.6 %. The analysis of the profile distribution of carbonates showed the occurrence of the highest amounts of that compound in the deepest horizons of the profiles. In the soils investigated the content of organic carbon ranged from 1.4 g · kg^{-1} in the claygyttia horizon to 355.0 g · kg^{-1} in the low peat horizon. The variation in the content of organic carbon was connected with the location of the sampling site in the profile, which is characteristic for multilayer alluvial soils. Definitely highest amounts of C-org. were reported in peat horizons and in the detritus gyttia horizon. Next to the horizons enriched with organic matter, the highest content of organic carbon was noted in the surface horizons. The contents of organic carbon in the profiles analysed decreased with depth. In the soils investigated high amounts of $CaCO_3$ determined the neutral or slightly alkaline reaction of the formations all across the profile. Both the active and exchangeable acidity did not show a considerable variation across the profiles. The active acidity ranged from 7.03 to 7.87 pH units, while exchangeable acidity – from 6.88 to 7.41 (Table 1). All the genetic horizons of the profiles showed a high texture variation, while the grain size composition analysis highlighted the clay nature of the sediments.

Table 1

Selected physicochemical properties of the soils

Profile No.	Horizon	pH		C_{org}	$CaCO_3$	Fraction < 0.002 mm
		H_2O	1 M KCl	$[g \cdot kg^{-1}]$	[%]	
I	Apca	7.67	7.03	55.8	16.2	48.3
	IICgyica	7.76	7.12	77.3	29.8	70.6
	IICgydca	7.51	6.88	195.2	36.7	n.d.
	IICgyca1	7.86	7.24	30.6	59.5	70.7
	IICgyca2	7.86	7.39	9.5	9.8	61.4
II	Apca	7.59	7.13	63.9	21.8	64.0
	Aaca	7.68	7.15	65.9	27.2	60.3
	IICgyica	7.64	7.17	63.9	40.2	81.5
	IICgyca1	7.59	7.2	24.4	68.4	47.6
	IICgyca2	7.63	7.14	59.8	46.0	78.4
	IICgydca	7.64	7.16	112.9	56.5	n.d.
	IICgyca	7.65	7.2	14.7	51.6	35.5
III	Apca	7.84	7.41	60.9	24.4	40.6
	Aaca	7.57	7.27	65.7	25.6	38.5
	Otnica	7.52	7.14	355.0	6.8	n.d.
	Aaca	7.26	6.96	63.1	5.3	11.3
	Gca	7.61	7.09	65.8	2.4	6.7
	IICgyi	7.68	7.14	7.9	8.5	35.0
	IICgyica	7.75	7.30	9.7	39.8	29.8
IV	Apca	7.60	7.30	59.4	26.5	51.0
	Aacag	7.68	7.27	19.7	6.7	18.3
	Gca1	7.87	7.26	4.9	4.5	32.9
	G2	7.79	7.16	5.3	0.6	31.9
	IICgyigg	7.86	7.41	1.4	12.1	42.0
V	Apca	7.60	7.33	80.3	23.6	60.0
	Aacag	7.53	7.26	78.0	24.9	64.5
	IICgyica	7.53	7.21	65.0	39.1	57.2
	IICgyd1	7.30	7.09	342.8	21.0	n.d.
	IICgyd2	7.60	7.12	257.8	22.8	n.d.
	IICgyd3	7.67	7.4	46.5	48.7	n.d.
	IICgyca	7.57	7.48	14.4	76.1	61.9
VI	Apca	7.38	7.20	50.2	15.9	66.5
	Aaca	7.37	7.30	5.1	69.3	29.3
	IICgyicag	7.37	7.3	29.0	35.2	65.1
	IICgyca	7.42	7.25	2.3	70.1	58.1
	IICgyica1	7.44	7.30	4.1	20.5	23.0
	IICgyica2	7.46	7.31	2.8	40.6	19.4
	IICgyica3	7.46	7.35	2.2	37.5	16.2

Table 1 contd.

Profile No.	Horizon	pH		C_{org}	$CaCO_3$	Fraction < 0.002 mm
		H_2O	1 M KCl	[g · kg^{-1}]	[%]	
VII	Apca	7.23	7.20	64.9	25.0	35.6
	IICgyica1	7.27	7.25	58.3	46.8	31.3
	IICgyica2	7.23	7.20	90.6	34.5	21.9
	Otnica1	7.03	6.99	373.4	4.9	n.d.
	Otnica2	7.17	7.10	312.9	6.2	n.d.
	IICgycagg	7.46	7.30	18.0	65.4	12.2

n.d. – not determined.

The total content of nickel ranged from 0.6 mg · kg^{-1} to 18.04 mg · kg^{-1} (Table 2). Its highest contents were noted in humus horizons (Ap and Aa) and in the horizons enriched with organic matter (detritus gyttia, low peat). Kabata-Pendias and Pendias [8] as well as Ruszkowska and Wojcieska-Wyskupajtys [13] confirm a special capacity for nickel bonding by organic substance. The occurrence of nickel in soils determines mostly its content in the parent rocks of soils and their richness with iron and clay minerals [14]. The occurrence of nickel in soils is connected with the alkaline igneous rocks and with sedimentary clay rocks. Nickel most frequently accompanies rock-forming magnesium-iron silicates [15]. Basing on the present research in the arable soils of the Pomorze and Kujawy Region, Piotrowska and Terelak [16] found that the content of nickel ranged from 5.3 mg · kg^{-1} to 7.2 mg · kg^{-1}, and the average content of that element was 6.3 mg · kg^{-1}. As reported in literature [17–19], the content of Ni in the surface horizons of various soils of the region ranged from 1.1 mg · kg^{-1} to 61.8 mg · kg^{-1}. In the Phaeozems of the Kujawy Region the content of total nickel was between 1.4 mg · kg^{-1} and 61.4 mg · kg^{-1}, while in the typologically varied soils of the Inowroclaw Plain the contents were much lower and ranged from 4.5 mg · kg^{-1} to 23.6 mg · kg^{-1}. Similar contents of the element (12.5; 44.2) mg · kg^{-1} were recorded by Kobierski et al [20] in alluvia within the flood banks of the Unislaw Basin as well as by Wojcikowska-Kapusta and Niemczuk [21] in typologically varied arable soils of the Lublin Upland and in the vicinity of Sandomierz (0.5; 46.5) mg · kg^{-1}. In the soils analyzed the total Ni content was similar to the content of the geochemical background [8] and it did not exceed the admissible concentrations for unpolluted soils [22].

Defining the content of phytoavailable forms of Ni in soils is essential due to its availability by the plants determined by the concentration of mobile forms in soil. It is, in general, uptaken proportionally to its concentration in soil [23], and its toxic effect on the plants is visible in disturbed photosynthesis, transpiration and the process of nitrogen binding. In the soils investigated the contents of the forms extracted with DTPA ranged from 0.14 mg · kg^{-1} to 2.86 mg · kg^{-1} (Table 2). The highest contents of the available nickel were noted, similarly as in the case of total forms, in the horizons enriched with organic matter, which can point to a greater Ni concentration in organic matter, which, in turn, coincides with the results reported by Kabata-Pendias and

Table 2

Total Ni contents and its DTPA-extractable forms

Profile No.	Horizon	Total content	Extractable (DTPA)
		[mg · kg^{-1}]	
I	Apca	17.39	1.72
	IICgyica	8.85	1.77
	IICgydca	10.84	2.07
	IICgyca1	5.90	0.58
	IICgyca2	2.66	0.35
II	Apca	12.11	1.31
	Aaca	12.01	1.54
	IICgyica	4.70	0.47
	IICgyca1	3.38	0.76
	IICgyca2	4.73	0.76
	IICgydca	6.09	1.26
	IICgyca	4.39	0.56
III	Apca	12.73	1.43
	Aaca	13.31	1.59
	Otnica	13.91	2.09
	Aaca	6.21	0.67
	Gca	6.09	0.37
	IICgyi	4.98	0.40
	IICgyica	2.29	0.23
IV	Apca	11.86	1.44
	Aacag	5.88	0.74
	Gca1	5.00	0.46
	G2	7.80	0.46
	IICgyigg	1.61	0.40
V	Apca	12.61	1.24
	Aacag	12.96	1.41
	IICgyica	6.80	0.80
	IICgyd1	5.03	1.46
	IICgyd2	9.26	1.96
	IICgyd3	5.03	0.69
	IICgyca	6.34	2.86
VI	Apca	18.04	1.52
	Aaca	3.38	0.46
	IICgyicag	5.70	1.39
	IICgyca	5.30	0.53
	IICgyica1	2.61	0.07
	IICgyica2	2.19	0.28
	IICgyica3	0.66	0.14

Table 2 contd.

Profile No.	Horizon	Total content	Extractable (DTPA)
		[mg · kg^{-1}]	
VII	Apca	10.14	0.56
	IICgyica1	2.89	0.29
	IICgyica2	1.18	0.34
	Otnica1	1.23	0.35
	Otnica2	1.31	0.18
	IICgycagg	10.14	0.56

Pendias [8] showing a high accumulation of nickel in bioliths as well as the occurrence in the soils in the form of bonds with organic matter in a form of mobile chelates. With a low pH, the strength of nickel bond by the organic matter of the soil is low, while in the neutral pH the bond is very strong and it is important in terms of bioavailability [24, 25]. Gebski [26] informs that the mobility of heavy metals increases most probably as a result of the emergence of mobile complexes of heavy metals with organic matter. Such bonds are easily available to plants, which coincides with the reports by Taylor and Olsson [27].

Nickel is considered to be a mobile element. Many authors stress that the availability and the mobility of nickel in soil is affected by very many factors, such as the content of organic matter, the concentration of iron compounds and pH as well as the grain size composition of the soil itself [28–32]. Weng et al [31] claim that the factor determining the mobility of nickel in soil is its reaction, which can be due to the sorption capacity of organic matter of soil towards metals depending strongly on pH [32]. Increased soil acidity enhances the solubility of coordination complexes of nickel in the soil solution and the bioavailability of that element [33]. In the soils of acid reaction its solubility increases considerably, however, its susceptibility to the formation of bonds with organic substance also results in a high mobility of nickel when exposed to neutral or alkaline reaction [8]. Besides, a lower content of organic matter is less important in limiting the bioavailability of nickel, as compared with acid soil [25]. Soil liming is, therefore, a factor limiting the phytoavailability of nickel. In the soil samples investigated there were noted low contents of mobile nickel forms considered to demonstrate non-toxic values, as affected by the neutral or alkaline reaction of the soils (Table 2).

Similarly the soils containing more silt and clay fractions usually show a higher content of that element [34, 35], which is confirmed by the present research in which the statistical analysis identified the correlation between the content of available nickel forms and the content of colloid clay. The highest share of available forms in the total content of the element was noted in most profiles analysed in the horizons of clay and lime gyttia (Fig. 2). Wall [36] reports on a strong dependence between the mechanical composition of soil and the phytoavailability of nickel to plants (buckwheat). The author claims that the lowest concentration of nickel is found in the plants grown in

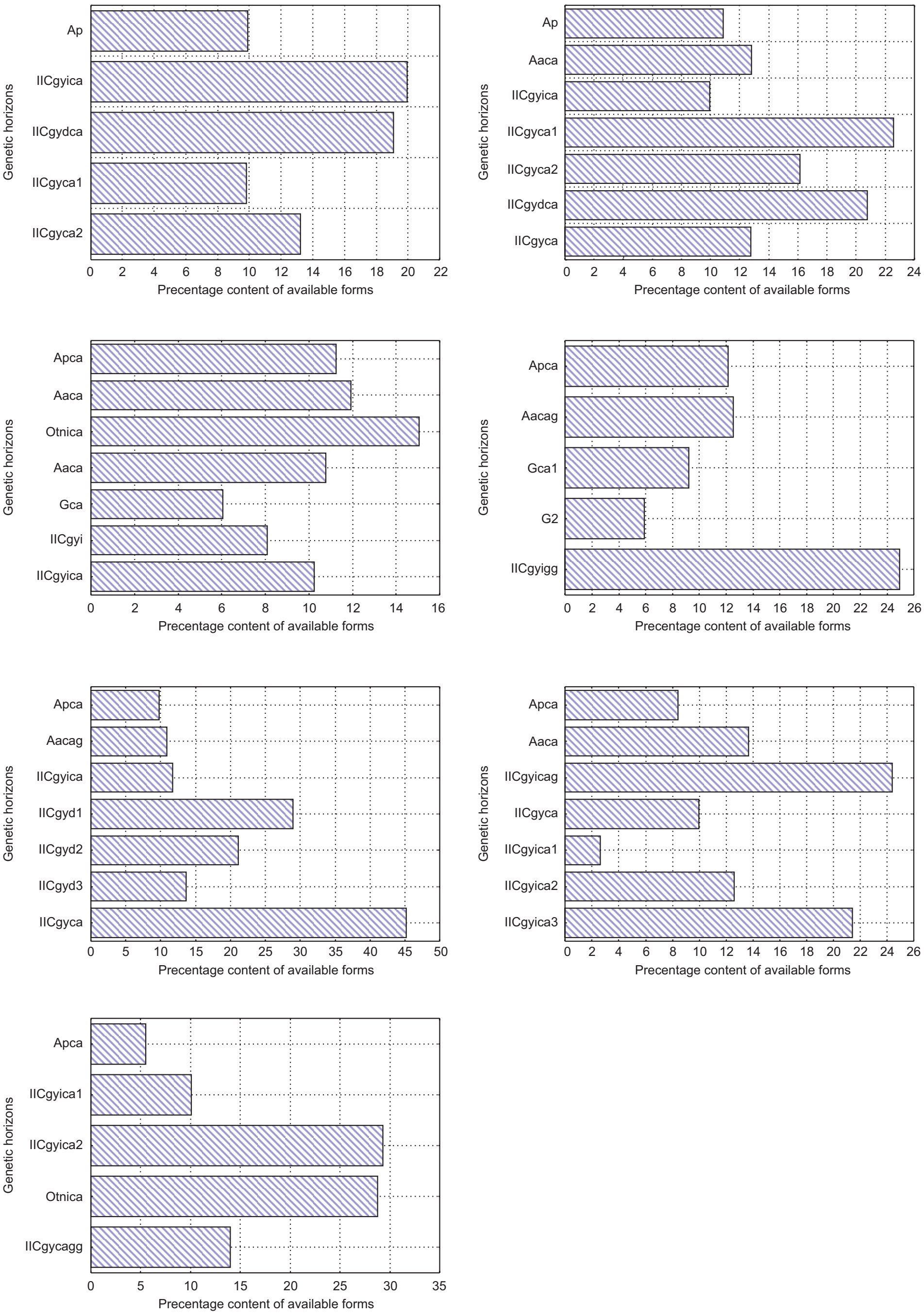

Fig. 2. Percentage content of available nickel forms in the soils

light soils, while the highest – in heavy soils. As reported by Dudek et al [37], in the unpolluted light soils about 65 % of nickel shows a strong bonding with the crystal structure of primary and secondary minerals. Warda [38] draws attention to the fact that an important factor modifying the uptake and the content of nickel by plants is not only the soil type, but mostly the plant species.

Conclusions

1. Drawing on the total content of the element investigated, the soils were considered to be the soils of a natural content of nickel and, as such, they can be allocated to horticultural and agricultural crops.
2. The low concentrations of total Ni suggest that those are natural contents (the geochemical background) and there is no clear effect of the anthropogenic activity on the soils.
3. The contents of the nickel forms extracted with DTPA fell within the range from 0.14 mg $\cdot$ kg^{-1} to 2.86 mg $\cdot$ kg^{-1} and those are the contents below the values considered toxic.

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ZAWARTOŚĆ FORM CAŁKOWITYCH I PRZYSWAJALNYCH NIKLU W ALUWIALNYCH GLEBACH UPRAWNYCH

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Abstrakt: Położone w dolinach rzecznych aluwia stanowią zróżnicowaną pokrywę glebową, na którą składają się zarówno gleby mineralne, mineralno-organiczne, jak i organiczne o bardzo zróżnicowanych właściwościach fizykochemicznych. Przedmiotem badań było określenie zawartości niklu w glebach aluwialnych wytworzonych na gytiach równiny biogennej Basenu Unisławskiego. Próbki glebowe pobrano z 7 profili glebowych, w których oznaczono wybrane właściwości fizykochemiczne metodami powszechnie stosowanymi w laboratoriach gleboznawczych. W analizowanych próbkach dokonano pomiaru całkowitej zawartości niklu po mineralizacji w mieszaninie kwasów HF + $HClO_4$ oraz jego form łatwo przyswajalnych, ekstrahowanych 1 M kwasem dietylenotriaminopentaoctowym (DTPA). Zawartość całkowitą oraz formy mobilne oznaczono przy zastosowaniu metody atomowej spektroskopii absorpcyjnej (AAS) na spektrometrze PU 9100X (Philips). Całkowita zawartość niklu mieściła się w zakresie (0,6; 18,04) $mg \cdot kg^{-1}$. Największe zawartości tego pierwiastka odnotowano w poziomach powierzchniowych i podpowierzchniowych oraz w poziomach wzbogaconych w materię organiczną. W badanych próbkach glebowych stwierdzone całkowite zawartości niklu były zbliżone do zawartości tła geochemicznego. Natomiast zawartości form mobilnych była niższa od wartości uznanych za toksyczne. W badanych glebach zawartości form ekstrahowanych DTPA kształtowały się w zakresie (0,14; 2,09) $mg \cdot kg^{-1}$.

Słowa kluczowe: nikiel w glebie, gleby aluwialne, formy całkowite i ekstrahowane DTPA