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CONTENT AND FRACTIONAL COMPOSITION OF NICKEL IN ARABLE SOILS DEPENDING ON PHYSICOCHEMICAL PROPERTIES

ZAWARTOŚĆ I SKŁAD FRAKCYJNY NIKLU W GLEBACH UPRAWNYCH ZALEŻNIE OD ICH WŁAŚCIWOŚCI FIZYKOCHEMICZNYCH

Abstract: The aim of this study was estimation of pseudo-total nickel content and its fractional composition in arable soils depending on their physicochemical properties.The research material consisted of samples taken from arable soil in 81 points of Podlasie Province. The content of pseudo-total nickel in soils and its fractional composition was determined with BCR method. The correlations between pseudo-total content of nickel, as well as its individual fractions and physicochemical properties of soils were evaluated.

It was found, that pseudo-total content of nickel was typical for uncontaminated soils and ranged from 2.0 to 14.4 mg · kg^{-1}. The share of acid soluble and exchangeable fraction was above 20 %, as compared to pseudo-total content. Reducible fraction comprised 20–40 %. The most of nickel was bound to organic matter. The factors which influenced fractional composition of nickel were determined. For the light soils it was content of soil fraction < 0.02 mm, granulometric composition and pH, while for medium-heavy soils, organic carbon and magnesium content, granulometric composition and content of soil fraction < 0.02 mm. The factors related to the changes of Ni content in light soils in fraction II and IV and for medium-heavy soils in fraction I, were not determined.

Keywords: nickel, soil, BCR method, metal fraction

Introduction

The natural content of elements, including trace elements, in arable soils is dependent on lithogenesis and pedogenesis [1]. The other sources of trace elements, such as mineral and organic fertilization, plant pesticides, irrigation, as well as wet and dry precipitation, are related to anthropogenic activity [2, 3]. It is well known, that they

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occur in soil in different forms, which are more or less mobile, that means bioavailable. Trace elements of anthropogenic origin are, in general, more mobile, than these of natural origin [4]. Mobility of metals is influenced mainly by physicochemical properties of soil, pH, content of organic matter, granulometric composition and management practices [5].

There are many methods for estimation of metal forms and their changes in soil, sequential extraction for example [6, 7]. There are a lot of schemes of this method [8]. For unification purposes the BCR method [9, 10] with its modifications [11] is increasingly used.

Nickel is essential for proper plant growth and development (it forms the active metallocenter of the enzyme urease) [12]. Excessive Ni amounts inhibit a large number of plant enzymes, cause disturbance of cation-anion and water balance in plant as well as inhibit development of lateral roots. Its total content in non-contaminated soils is up to 35 $mgNi \cdot kg^{-1}$ (in sandy soils about 15 $mgNi \cdot kg^{-1}$ and in heavy textured soils about 30 $mgNi \cdot kg^{-1}$) [13]. The total content of nickel is not adequate to estimate its behavior in soils. It's necessary to identify quantitative changes of its chemical forms.

The aim of this study was estimation of pseudo-total nickel content and its fractional composition in arable soils using BCR method, depending on their physicochemical properties.

Materials and methods

The research material consisted of samples taken from arable soil in 81 points of Podlasie Province. One point was selected in the majority of its districts. Each point was located on mineral soil used as arable land, without external source of contamination, like roads or industrial plants. The samples were collected from arable layer (0–30 cm) after plant harvest. Maize was cultivated in 14 points, cereals in 53 points, rape in 2 points, buckwheat in 2 points and the rest was taken from under grass on field cultivation. Basic physicochemical properties of soil samples there were determined: granulometric composition by Cassagrande's method with Proszynski's modification, organic carbon content by Tiurin's and pH in 1 $mol \cdot dm^{-3}$ KCl solution by potentiometric method. Available phosphorus and potassium by Egner-Riehm method, as well as magnesium by Schachtschabel method in soils were also determined. Based on the content of soil fraction < 0.02 mm, soils were divided into two groups: very light and light and medium-heavy soils. Heavy soil was not taken into account, because this type does not occur in Podlasie Province. The pseudo-total nickel content was determined, after previous digestion in *aqua regia*, by means of FAAS technique using Varian AA-100 apparatus.

Modified BCR method with usage of ultrasonic probe Sonics VCX 130 was used to evaluate fractional composition of Ni in soil samples. Extraction included four stages (fractions):

1. Acid soluble and exchangeable fraction (fraction I) – 1 g of soil in 100 cm^3 centrifuge tube with 40 cm^3 of 0.11 $mol \cdot dm^{-3}$ acetic acid was sonicated for 7 minutes (power – 20 W) at temperature 22 ± 5 ^oC. Then, the mixture was centrifuged for 20

minutes at 3000 g. Extract was separated for analysis. Residue with 20 cm^3 of deionized water was sonicated for 5 minutes (power – 20 W) and centrifuged for 20 minutues at 3000 g. Water was discarded.

2. Reducible fraction, bound to Fe/Mn oxides (fraction II) – to the residue from the first step was added 40 cm^3 of 0.5 mol · dm^{-3} hydroxylamine hydrochloride fresh solution, pH = 1.5, and sonicated for 7 minutes (power – 20 W) at temperature 22 ± 5 °C. Then, the mixture was centrifuged for 20 minutes at 3000 g. Extract was separated for analysis. The residue was rinsed with deionized water, like in the first step.

3. Oxidizable fraction, bound to organic matter (fraction III) – to the residue from the second step was added 20 cm^3 of 30 % hydrogen peroxide and sonicated for 2 minutes (power – 20 W) at temperature 22 ± 5 °C. Then, the volume of H_2O_2 was reduced to approx. 1 cm^3 using water bath. To the moist residue was added 50 cm^3 of 1 mol · dm^{-3} ammonium acetate and sonicated for 6 minutes (power – 20 W) at temperature 22 ± 5 °C. Then, the mixture was centrifuged for 20 minutes at 3000 g. Extract was separated for analysis. The residue was rinsed with deionized water, like in the previous steps.

4. Residual fraction (fraction IV) – the residue from the third step was extracted using concentrated HNO_3 with addition of 30 % H_2O_2. Extract was separated for analysis.

The content of studied element in fractions was determined by means of GFAAS technique using Varian AA-100 apparatus. The share of individual fractions in pseudo-total content of nickel was calculated.

Pearson correlation coefficients between all sets of data were calculated. It was assumed that they are significant above 0.65 or below –0.65. Since the correlation coefficients were non-siginificant, canonical factor analysis was made. Based on this analysis, for both groups of soil, factors which influenced fractional composition of nickel were determined.

Results and discussion

The content of soil fraction < 0.02 mm in very light and light soils ranged from 4 to 19 % (12 % on average) and in medium-heavy soils from 21 to 28 % (22 % on average) (Table 1).

The pH of the first group of studied soils was very differentiated and varied from 4.0 to 7.6. Among 35 soil samples, twelve were very acidic (pH < 4.5), eight were acidic (pH = 4.6–5.5), nine was slightly acidic (pH = 5.6–6.5) and the rest soils were neutral (pH = 6.6–7.2). The most of medium-heavy soils was characterized by higher pH values: only three samples came from very acidic soils, eleven samples were acidic and the rest were light acidic and neutral. Investigated soils were typical for Podlasie Province, that is light and acidic.

The content of organic carbon in both groups of soil was differentiated. In very light and light soils ranged from 8 to 37 g · kg^{-1} (18 g · kg^{-1} on average), and in medium-heavy soils from 7 to 42 g · kg^{-1} (24 g · kg^{-1} on average). The most of soils contained average amounts of phosphorus and magnesium, as well as low amount of potassium.

Table 1

Physicochemical properties of soils

Studied soils		Share of soil fraction < 0.02 mm [%]	pH	C_{org} [g · kg^{-1}]	P_2O_5	K_2O	Mg	Pseudo-total content of Ni
					[mg · kg^{-1}]			
Very light and light soils n = 35	range	4–19	4.0–7.6	8–37	43–440	25–290	7–150	2.0–9.1
	$\bar{x}$	12	5.3	18	155	107	47	5.5
	median	13	5.2	15	121	9.5	38	5.25
Medium-heavy soils n = 46	range	21–28	4.1–7.8	7–42	22–420	32–484	17–226	2.6–14.4
	$\bar{x}$	22	6.1	24	137	132	97	7.8
	median	22	6.1	21	115	106	93	7.5

The pseudo-total content of nickel in very light and light soils ranged from 2.0 to 9.1 mg · kg^{-1} and in medium-heavy soils from 2.6 to 14.4 mg · kg^{-1}. It means that studied soils contained natural amount of nickel, which is mainly influenced by parent rock.

Many authors report high differentiation of pseudo-total content of nickel in soils. According to Terelak et al [14] the content of nickel in soil ranged from 0.10 to 173 mg · kg^{-1}, in contrast, Gworek and Misiak [13] report that content ranged from 0.2 to 35.0 mgNi · kg^{-1}. The higher amounts of nickel can be found in soils derived from igneous and sedimentary rocks and the lower ones in soils derived from loams and sandy deposits [15]. The total content of metals indicates only degree of possible threat of soil, but not the binding forms of each element. That's why the sequential analysis is made, which shows the type of chemical binding forms of an element and potential threats related to its high bioavailability.

The percentage of nickel in fraction I of very light and light soils (Fig. 1) was increasing simultaneously with pH value and ranged from 17 to 25 %, as compared to

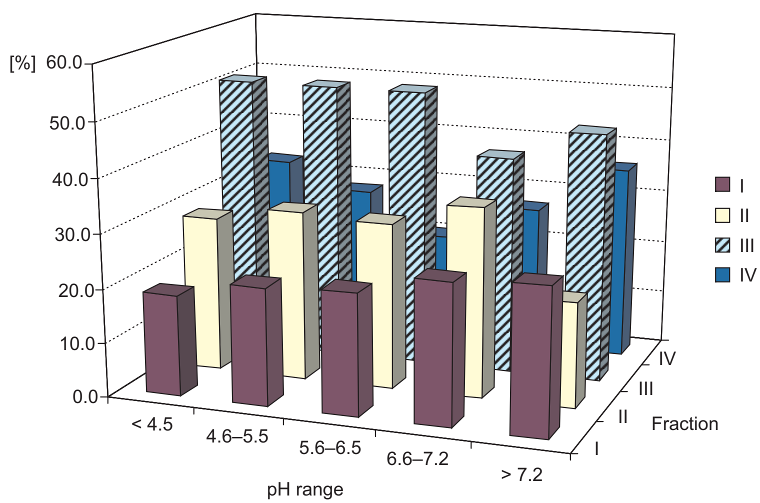

Fig. 1. Percentage of nickel fractions in pseudo-total its content in light and very light soils, depending on pH

pseudo-total content. Sloot et al [16] stated that the increase of nickel content in soil solution of soils with high pH values might be connected with the rise of solubility of organic matter. Due to this process the nickel can be released, what causes its content increase in soluble and exchangeable fraction in soils with neutral and alkaline reaction. In medium-heavy soils opposite trend was observed (Fig. 2).

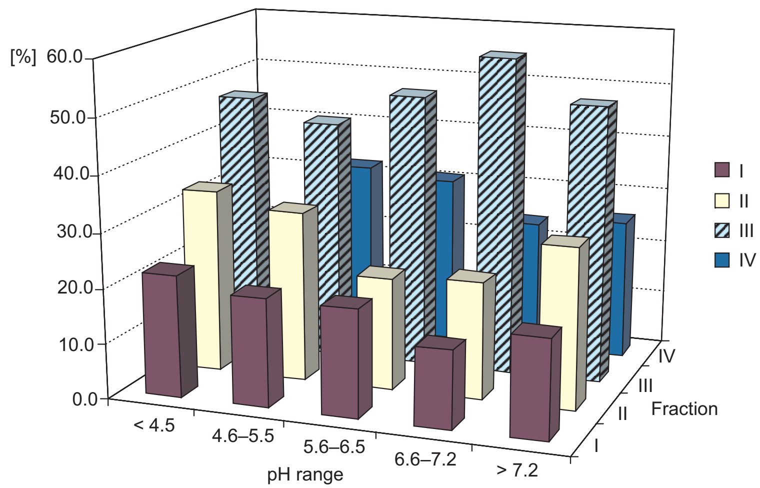

Fig. 2. Percentage of nickel fractions in pseudo-total its content in medium soils, depending on pH

In the most of light soils with very acidic, acidic and slightly acidic reaction the percentage of nickel bound to Fe/Mn oxides and hydroxides was increasing with pH value and decreased in soils with pH > 7.2.

In medium-heavy soils with pH ≤ 7.2 the percentage of Ni in fraction II was decreasing with increase of pH value. In soils with pH > 7.2 the rise of percentage of Ni in fraction I and II was noted. Rooney et al [17] are reporting that sorption of nickel by Fe/Mn hydroxides is increasing simultaneously with decrease of soil acidity, what is proved by obtained results.

The organic matter applied to soil in large amounts causes the decrease of content of available for plants forms of metals, such as nickel [18]. The organic fertilizers are applied to soil in Podlasie Province even each year, due to the well developed cattle farming. It may contribute to decrease of mobility of trace elements, mainly in medium-heavy soils, what can be seen in the results of our studies.

The most of nickel was bound to organic matter (Figs. 1 and 2). The percentage of nickel in fraction III was influenced in small degree by soil reaction. It was similar in very light and light soils with very acidic, acidic and light acidic reaction. Among soils from this group with higher pH values the decrease of share of Ni about 10 % in discussed fraction was noted. The opposite trend was observed in medium-heavy soils (Fig. 2). The share of nickel in residual fraction of both groups of soils was mainly lower than 30 % of pseudo-total content.

Investigating distribution of nickel in individual fractions in dependence on content of organic carbon in soil, can be stated, that more of nickel in exchangeable fraction was in light soils (Fig. 3).

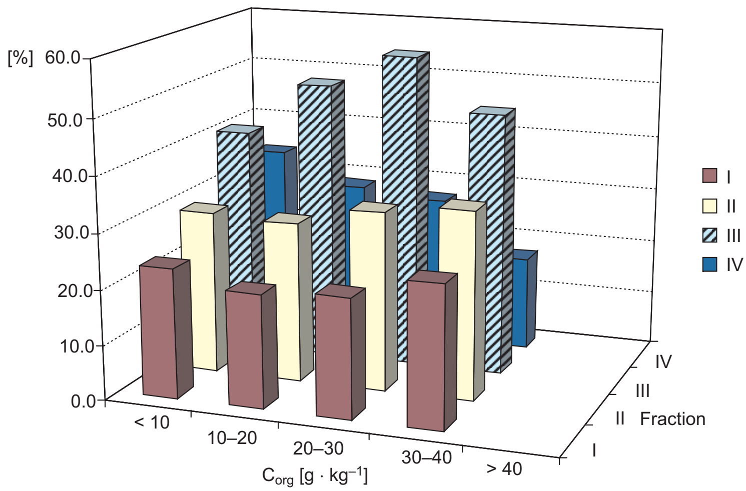

Fig. 3. Percentage of nickel fractions in pseudo-total its content in light and very light soils, depending on organic carbon content

The percentage of nickel in this case was about 20 % and was similar in all the investigated soils. In medium-heavy soils it was lower than 20 % (Fig. 4) and differentiated by content of organic carbon.

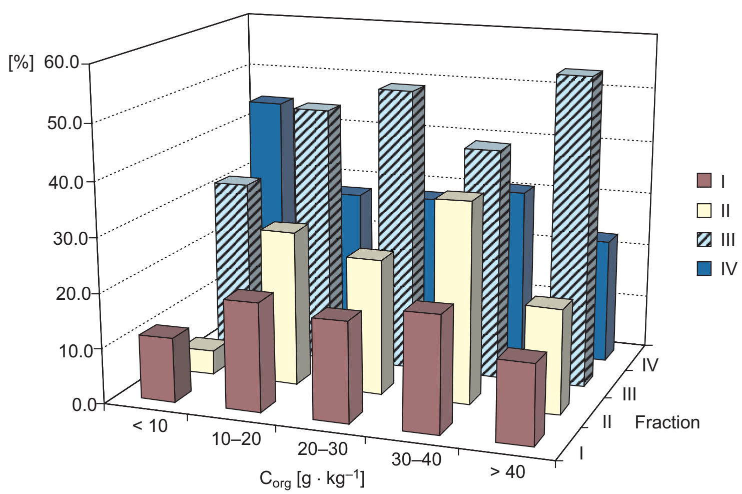

Fig. 4. Percentage of nickel fractions in pseudo-total its content in medium-heavy soils, depending on organic carbon content

The share of Ni in fraction II in very light and light soils was about 30 %, increasing with rise of organic carbon content. In medium-heavy soils such tendency was not observed and percentage of nickel in this fraction was lower. The most of nickel was in fraction III, bound to organic matter. The percentage in this case was increasing at the same time as the content of organic carbon in both groups of soil was rising and reached the most 50 %. The percentage of nickel in residual fraction, in both groups of soil, was the highest in soils which contained below 10 $gC_{org} \cdot kg^{-1}$ of soil and was decreasing simultaneously with increase of carbon content.

Many authors [17, 19, 20] emphasis, that availability and mobility of nickel in soil is dependent on lot of factors, including content of organic matter and iron compounds, as well as reaction. Canonical factor analysis, for both groups of soil, explains the above mentioned statement (Tables 2 and 3). In very light and light soils determined two factors which influenced the percentage of nickel in fraction I and III.

Table 2

Factor analysis of nickel fraction contents in light and very light soils

Factor	Content of Ni			
	Fraction I	Fraction II	Fraction III	Fraction IV
pH	0.02	–0.11	**–0.69**	0.10
C_{org}	0.45	–0.32	–0.01	0.40
P_2O_5	–0.10	–0.09	–0.46	0.47
K_2O	–0.13	–0.03	–0.09	–0.09
Mg	0.21	0.47	–0.28	0.32
Content of soil fraction < 0.02 mm	0.88	0.06	–0.57	–0.12
Granulometric composition	**–0.82**	–0.01	–0.51	–0.53

Table 3

Factor analysis of nickel fraction contents in medium-heavy soils

Factor	Content of Ni			
	Fraction I	Fraction II	Fraction III	Fraction IV
pH	–0.51	–0.25	0.08	0.53
C_{org}	–0.53	**–0.72**	–0.21	0.24
P_2O_5	0.12	0.17	0.52	0.04
K_2O	–0.02	0.00	0.02	0.12
Mg	–0.24	–0.16	–0.10	**0.80**
Content of soil fraction < 0.02 mm	–0.62	–0.25	**–0.91**	0.45
Granulometric composition	0.56	0.08	**–0.91**	0.58

The factors which explain the content of nickel in fraction I consisted of content of soil fraction < 0.02 mm and granulometric composition. The factor which affected the

Ni content in fraction III was pH of soil. The factors conditioning the changes of Ni content in fraction II and IV were not determined.

In studied medium-heavy soils were determined three factors which influenced the percentage of nickel in fraction II, III and IV. The content of organic carbon was the factor conditioning the changes of percentage of Ni in fraction II. The factors which explain the content of nickel in fraction III consisted of the content of soil fraction < 0.02 mm and granulometric composition. The factor which affects the Ni content in fraction IV was the content of magnesium. The factors which influenced the changes of nickel content in fraction I were not determined.

Conclusions

1. The studied soils were characterized by natural content of pseudo-total nickel.
2. The percentage of nickel in studied soils was the highest in fraction bound to organic matter and similar in other fractions.
3. The percentage of nickel in fraction I, in very light and light soils, was affected by content of soil fraction < 0.02 mm and granulometric composition, while in fraction III by pH. The percentage of nickel in fractions II, III and IV in medium-heavy soils was determined by organic carbon, granulometric composition and content of soil fraction < 0.02 mm, as well as magnesium content.

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ZAWARTOŚĆ I SKŁAD FRAKCYJNY NIKLU W GLEBACH UPRAWNYCH ZALEŻNIE OD ICH WŁAŚCIWOŚCI FIZYKOCHEMICZNYCH

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Abstrakt: Celem niniejszej pracy było określenie całkowitej zawartości niklu i jego frakcji w glebach uprawnych Podlasia oraz określenie zależności między zawartością niklu i jego frakcji a własnościami fizykochemicznymi gleb. Materiał badawczy stanowiły próbki pobrane z gleb uprawnych w 81 punktach województwa podlaskiego. Oznaczono zbliżoną do ogólnej zawartość niklu i jego frakcji metodą BCR. Obliczono zależności korelacyjne między zawartością ogólną niklu i jego poszczególnych frakcji, a właściwościami fizykochemicznymi gleb.

Stwierdzono, że zawartość niklu ogółem była typowa dla gleb uprawnych niezanieczyszczonych i wahała się w szerokich granicach od 2,0 do 14,4 mg $\cdot$ kg^{-1}. Udział frakcji wymiennej w ogólnej zawartości niklu w badanych glebach wynosił ponad 20 %. Frakcja redukowalna stanowiła 20–40 % zawartości ogólnej. Najwięcej niklu było związane z substancją organiczną. Wyodrębniono czynniki wpływające na udział niklu w poszczególnych frakcjach. Dla gleb lekkich był to skład granulometryczny, zawartość frakcji spławialnej i pH, a w przypadku gleb średnich zawartość węgla organicznego, skład granulometryczny, zawartość frakcji spławialnej i zawartość magnezu. Nie wyznaczono czynników warunkujących zawartość niklu w II i IV frakcji gleb lekkich, a w przypadku gleb średnich zawartość tego metalu we frakcji I.

Słowa kluczowe: nikiel, gleba, metoda BCR, frakcje metali