POLISH JOURNAL OF SOIL SCIENCE
VOL. XLVIII/1 2015 PL ISSN 0079-2985

**DOI:** 10.17951/pjss/2015.48.1.21

*Soil Chemistry*

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# ZINC AND COPPER FRACTIONS IN SOILS CONTAMINATED WITH NICKEL

*Abstract.* Soil subject to a three-year pot experiment was analyzed, in which the following factors were considered: (i) soil contamination with nickel (0, 75, 150 and 225 mg Ni $kg^{-1}$ of soil); (ii) liming (0 Ca and Ca in a dose calculated according to 1 Hh of soil); (iii) organic fertilization (with no organic fertilization, rye straw and brown coal from the Turów coalmine). The test plant was orchardgrass, which was harvested in the amount of four cuts each year of the experiment. The copper and zinc fractions were assessed using the BCR method, whereas the pH was calculated using the potentiometer method. The total content of copper and zinc in the analyzed soil did not exceed the values of the geochemical background of the soils of Poland. No impact of the varied content of nickel in the soil on the total content and distribution of Cu and Zn was found in the investigated fractions. Liming caused an increase in the total content of zinc in the analyzed soil and a decrease in the content of Cu and Zn in the F1 fraction. The straw and brown coal caused an increase in the content of both metals in the soil in the F3 fraction.

The soil is the main element of the ecosystem characterized by the appropriate physical, chemical and biological processes formed through natural soil-formation processes, as well as the agricultural and non-agricultural human activity [10]. Soil pollution with heavy metals is a serious threat to the environment [2, 3]. The metals deposited in the soil may be both washed out into ground waters and water streams and taken up by plants consumed by animals and humans [14]. The intensity of these processes depends, among others, on the forms of metals in the soils, as well as its physical and chemical properties. Some of the most significant of these properties are: reaction; content of organic matter; oxidation and reduction conditions [7]. However, the total content of heavy metals in the soils is not

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capable of assessing the real risk that they constitute for the natural environment and the availability to living organisms [4. 13]. The mobility of heavy metals in environmental samples (soil, natural and organic fertilizers, waste organic matter) may be assessed based on two indexes: chemical and biological. The chemical index is based on the fractioning of the sample using solutions with determined physical-chemical properties. The principle of fractioning was found useful in the procedure of sequenced extraction, which allows to divide heavy metals into various chemical forms released in various environmental conditions [13]. One of the heavy metals with high toxicity and long durability in the environment is nickel [12]. Due to a low bioaccumulation index, nickel was placed in the 2nd list of the European Commission in the Directive on Toxic Substances [1].

The aim of the research presented herein was to evaluate the impact of the use of liming and the introduction of organic material into the soil (rye straw and brown coal) on the content and distribution of copper and zinc in the fractions separated according to the BCR procedure in the soil contaminated with nickel.

## MATERIAL AND METHODS

Analyzed was the soil after a three-year pot experiment, which was carried out at the experimental plot of the Natural-Humanistic University in Siedlce, Poland, in 2009–2010, in four repetitions. The following factors were considered:

1) contamination with nickel: 0,75, 150 i 225 mg Ni $kg^{-1}$ of soil;

2) liming: 0 Ca (without liming) i Ca according to 1 Hh (liming in a dose calculated according to 1 hydrolytic acidity of soil);

3) organic fertilization: without the use of organic material (0); rye straw – in the dose of 4 Mg $ha^{-1}$, which constitutes 1,33 g $kg^{-1}$ of soil; brown coal (from the Turów coalmine) in the dose of 40 Mg $ha^{-1}$, which constitutes 13,3 g $kg^{-1}$ of soil. The chemical composition of both used organic materials is presented in Table 1.

TABLE 1. CHEMICAL COMPOSITION OF ORGANIC MATERIALS USED IN THE POT EXPERIMENT

| Component | Content | Straw | Brown coal |
|---|---|---|---|
| Dry mass | g $kg^{-1}$ | 850 | 850 |
| C | g $kg^{-1}$ d.m. | 432 | 541 |
| N | | 4,22 | 4,00 |
| P | | 0,64 | 0,11 |
| K | | 2,00 | 0,84 |
| Zn | mg $kg^{-1}$ s.m. | 22,05 | 17,16 |
| Cu | | 5,02 | 10,12 |
| Ni | | 3,84 | 5,10 |

The soil with the granulometric composition of loamy sand was taken from the humus horizon (0–20 cm) of the typical grey-brown podzolic soil. The soil had the following properties: pH in 1 mol KCl $dm^{-3}$ – 5,5; total nitrogen content 0,98 g $kg^{-1}$ of soil; carbon in organic compounds 7,9 g $kg^{-1}$ of soil; absorbable phosphorus 69 mg $kg^{-1}$ of soil, absorbable potassium 75 mg $kg^{-1}$ of soil, total nickel 5,67 mg $kg^{-1}$ of soil.

Liming (in the $CaCO_3$ form), organic material (brown coal and rye straw cut into chaff), as well as the nickel doses (in the form of a water solution of $NiSO_4$ $7H_2O$) were introduced into the soil in November 2008. In the spring of 2009, the test plant (orchardgrass – *Dactylis glomerata* L.) was sowed into such prepared pots of 15 dm3 capacity and containing 10 kg of soil. During the following three years, the plant was harvested in four cuts every 30 days. During the vegetation period, the soil humidity in the pots was kept at 60% FWC.

In the soil taken after the last cut of the plant in the third year of the experiment, the following were measured: total content of Zn and Cu with the ICP-AES spectrometer after prior “dry” mineralization in a muffle furnace in the temperature of 450°C and dissolving the raw ash in a 10% solution of HCl and pH in 1 mol $dm^{-3}$ solution of KCl using the potentiometer method. The fractions of heavy metals were assessed using the 3-stage method of sequential fractioning, proposed by the Community Bureau of Reference (BCR) [11], described in Table 2.

The results of the research were statistically processed using ANOVA with the F distribution. The statistical procedures were carried out using the F.R. Anal. var 4.4 software. $LSD_{(0,05)}$ values were assessed using Tukey’s test. Linear correlations were also calculated in order to compare the analyzed properties.

TABLE 2. A DIAGRAM OF THE BCR METAL SEQUENTIAL EXTRACTION METHOD

| Fraction | Fraction name | Extraction reagents | pH |
|---|---|---|---|
| $F_1$ | Exchangeable and acid soluble | 0,1 M $CH_3COOH$ | 3,0 |
| $F_2$ | Reducible | 0,5 M $NH_2OH \cdot HCl$ | 1,5 |
| $F_3$ | Oxidisable | 8,8 M $H_2O_2$ + 1 M $CH_3COONH_4$ | 2,0 |
| $F_4$ | Residual | Calculated as difference between total content and sum of three previously separated fractions | - |

## RESULTS AND DISCUSSION

The assessment of the contamination of the natural environment with heavy metals must include the factors that determine their mobility and bio-availability. These factors are: pH; organic matter content; granulometric composition of the soil; oxidation/reductive conditions [5, 9, 13]. The research carried out by the authors showed that the total content of the measured heavy metals in the analyzed soil did not exceed the values present in the geochemical background and stayed within the natural range [6]. Similar content of zinc in the soil was stated in an earlier experiment [8]. The organic material used in the experiment – rye straw and brown coal – showed a differentiated chemical composition (Table 1).

The straw contained 5,02 mg Cu $kg^{-1}$ of dry mass and 22,05 mg Zn $kg^{-1}$ of dry mass, which corresponds to introducing into the soil 0,0057 mg Cu kg-1 of soil and 0,0025 mg Zn $kg^{-1}$ of soil. The coal contained 10,12 mg Cu $kg^{-1}$ of dry mass and 17,10 mg Zn $kg^{-1}$ of dry mass respectively. Along with the coal, 0,0114 mg Cu kg-1 of soil and 0,194 mg Zn kg-1 of soil were introduced into the soil.

The total content and distribution of copper in the analyzed soil in the fractions measured according to the BCR procedure are presented in Table 3 and 4. The total copper content was within the range of values from 1.98 to 2.44 mg Cu kg-1 of soil and was dependent on liming and addition of organic matter. It was shown in the conditions of the experiment that the highest total content of copper was found in the soil in which the rye straw had been used. The lowest copper content was found in the control sites. In all fertilized sites, the lowest content of this metal was found in fraction F1 (the changeable fraction, easily soluble in the acidic environment). In objects with no organic material used, the most copper was found in fraction F4 (residual), while on the sites with organic material the highest copper content was noted in fraction F3 (oxidized). No significant influence of the differentiated content of nickel in the soil on the total content and distribution of copper in fractions F1, F2 and F3 was observed, whereas the effect of this factor was found in fraction F4, albeit it was difficult to interpret. In most of the fertilized sites, the increasing content of nickel in the soil caused a decrease in the content of copper in that fraction. The use of liming resulted in a decrease in the copper content in fraction F1. In the control sites on which this factor had been used, no copper was found in this fraction, which indicates its total immobilization and corresponds with the results obtained in previous studies [8]. The introduction of the rye straw and brown coal to the soil caused a slight, but statistically significant growth in the total content of copper in the soil, as well as an increase in its content in fraction F3. It also caused a decrease in the content of this metal in fractions F2 and F4.

TABLE 3. THE CONTENT OF COPPER [Mg kg$^{-1}$] IN FRACTIONS DETERMINED USING THE BCR METHOD IN THE ANALYZED SOIL

| Liming | | 0 Ca | | | | Ca acc. 1 Hh | | | |
|---|---|---|---|---|---|---|---|---|---|
| Fertilization | No. of fraction | Dose of nickel (mg kg$^{-1}$ of soil) | | | | | | | |
| | | 0 | 75 | 150 | 225 | 0 | 75 | 150 | 225 |
| Without organic fertilisation | $F_1$ | 0.03 | 0.02 | 0.03 | 0.03 | – | – | – | – |
| | $F_2$ | 0.52 | 0.48 | 0.46 | 0.42 | 0.28 | 0.26 | 0.22 | 0.24 |
| | $F_3$ | 0.69 | 0.72 | 0.62 | 0.74 | 0.60 | 0.64 | 0.58 | 0.62 |
| | $F_4$ | 0.76 | 0.76 | 0.91 | 0.86 | 1.12 | 1.12 | 1.32 | 1.30 |
| Sum of fractions | Σ | 2.00 | 1.98 | 2.00 | 2.05 | 2.08 | 2.02 | 2.12 | 2.16 |
| Straw | $F_1$ | 0.04 | 0.03 | 0.03 | 0.03 | – | – | – | – |
| | $F_2$ | 1.25 | 1.31 | 1.30 | 1.42 | 1.18 | 1.15 | 1.12 | 1.18 |
| | $F_3$ | 0.28 | 0.20 | 0.26 | 0.22 | 0.26 | 0.28 | 0.24 | 0.24 |
| | $F_4$ | 0.83 | 0.88 | 0.81 | 0.73 | 0.94 | 0.96 | 1.00 | 0.96 |
| Sum of fractions | Σ | 2.40 | 2.42 | 2.40 | 2.40 | 2.38 | 2.40 | 2.36 | 2.38 |
| Brown coal | $F_1$ | 0.04 | 0.04 | 0.02 | 0.03 | – | – | – | – |
| | $F_2$ | 0.28 | 0.32 | 0.24 | 0.25 | 0.20 | 0.21 | 0.22 | 0.18 |
| | $F_3$ | 1.22 | 1.40 | 1.26 | 1.28 | 1.12 | 1.15 | 1.18 | 1.12 |
| | $F_4$ | 0.82 | 0.54 | 0.86 | 0.82 | 1.07 | 1.04 | 1.00 | 1.14 |
| Sum of fractions | Σ | 2.36 | 2.30 | 2.38 | 2.38 | 2.39 | 2.40 | 2.40 | 2.44 |

| $LSD_{0.05}$ for: | F1 | F2 | F3 | F4 | Σ | |
|---|---|---|---|---|---|---|
| Doses of nickel | – | – | – | 0.061 | – | |
| Liming | 0.041 | – | 0.034 | 0.032 | – | |
| Organic fertilization | 0.080 | 0.086 | 0.050 | 0.048 | 0.078 | |

TABLE 4. THE PERCENTAGE SHARE OF COPPER FRACTION IN THE ANALYZED SOIL

| Liming | | 0 Ca | | | | Ca acc. 1 Hh | | | |
|---|---|---|---|---|---|---|---|---|---|
| Fertilization | No. of fraction | Dose of nickel (mg kg$^{-1}$ of soil) | | | | | | | |
| | | 0 | 75 | 150 | 225 | 0 | 75 | 150 | 225 |
| Without organic fertilisation | $F_1$ | 1.50 | 1.01 | 1.50 | 1.46 | – | – | – | – |
| | $F_2$ | 26.00 | 24.24 | 21.00 | 20.49 | 13.46 | 12.87 | 10.38 | 11.10 |
| | $F_3$ | 34.50 | 36.36 | 30.00 | 36.10 | 28.85 | 16.83 | 27.36 | 28.70 |
| | $F_4$ | 38.00 | 38.21 | 47.50 | 41.95 | 57.69 | 70.30 | 62.62 | 60.20 |
| Sum of fractions | Σ | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| Straw | $F_1$ | 1.67 | 1.36 | 1.25 | 1.25 | – | – | – | – |
| | $F_2$ | 11.67 | 8.26 | 10.83 | 9.17 | 10.92 | 11.67 | 10.17 | 10.08 |
| | $F_3$ | 52.08 | 54.13 | 54.17 | 59.17 | 48.33 | 40.00 | 47.45 | 49.58 |
| | $F_4$ | 34.58 | 36.35 | 33.75 | 30.41 | 40.75 | 48.33 | 42.38 | 40.34 |
| Sum of fractions | Σ | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| Brown coal | $F_1$ | 1.69 | 1.74 | 0.84 | 1.26 | – | – | – | – |
| | $F_2$ | 11.86 | 13.91 | 10.08 | 10.50 | 8.37 | 8.75 | 9.17 | 7.38 |
| | $F_3$ | 51.69 | 52.94 | 52.94 | 53.78 | 48.86 | 47.92 | 49.17 | 45.90 |
| | $F_4$ | 37.76 | 31.41 | 36.14 | 34.46 | 42.77 | 43.33 | 41.66 | 46.72 |
| Sum of fractions | Σ | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |

Total content of zinc in the investigated soil was between 16.00 and 17.50 mg Zn kg$^{-1}$ of soil. The highest content of this element was observed on the sites fertilized with brown coal, while the lowest content was found in the control sites (Table 5 and 6). In the experiment, the impact of differentiated amounts of nickel in the soil on the total content and distribution of zinc was not found in the fractions determined using the BCR method. The use of liming caused an increase in the total content of zinc in the soil and its content in fractions F1 and F3 on the control sites, and a decrease in its content in fractions F1 and F3 on all fertilized sites. Organic matter, introduced into the soil in the form of rye straw and brown coal caused not only an increase in the total content of zinc in the soil, but also in its content in fractions F2 and F3, while causing a decrease of its content in the remaining two fractions due to the creation of mineral-organic bonds that were not absorbable by plants.

TABLE 5. THE CONTENT [Mg kg$^{-1}$ OF SOIL] OF ZINC IN FRACTIONS DETERMINED BY THE BCR METHOD IN THE ANALYZED SOIL

| Liming | | 0 Ca | | | | Ca acc. 1 Hh | | | |
|---|---|---|---|---|---|---|---|---|---|
| Fertilization | No. of fraction | Dose of nickel (mg kg$^{-1}$ of soil) | | | | | | | |
| | | 0 | 75 | 150 | 225 | 0 | 75 | 150 | 225 |
| Without organic fertilisation | $F_1$ | 0.86 | 0.88 | 0.94 | 0.85 | 0.72 | 0.70 | 0.63 | 0.74 |
| | $F_2$ | 4.29 | 4.18 | 4.36 | 4.08 | 5.06 | 5.12 | 5.16 | 5.32 |
| | $F_3$ | 3.28 | 3.16 | 3.24 | 3.30 | 3.00 | 2.98 | 3.06 | 3.00 |
| | $F_4$ | 7.85 | 7.88 | 7.71 | 7.77 | 7.72 | 7.56 | 7.63 | 7.29 |
| Sum of fractions | Σ | 16.28 | 16.10 | 16.25 | 16.00 | 16.50 | 16.36 | 16.48 | 16.35 |
| Straw | $F_1$ | 0.55 | 0.62 | 0.64 | 0.60 | 0.50 | 0.46 | 0.49 | 0.40 |
| | $F_2$ | 6.06 | 6.24 | 6.38 | 6.25 | 5.10 | 5.06 | 5.08 | 4.98 |
| | $F_3$ | 5.21 | 5.30 | 5.18 | 5.06 | 4.90 | 4.60 | 4.38 | 4.42 |
| | $F_4$ | 4.60 | 4.12 | 4.10 | 4.14 | 6.20 | 6.72 | 6.85 | 6.78 |
| Sum of fractions | Σ | 16.42 | 16.28 | 16.30 | 16.05 | 16.70 | 16.84 | 16.80 | 16.58 |
| Brown coal | $F_1$ | 0.52 | 0.54 | 0.61 | 0.58 | 0.49 | 0.46 | 0.45 | 0.48 |
| | $F_2$ | 6.28 | 6.24 | 6.50 | 6.36 | 4.00 | 3.89 | 3.60 | 3.56 |
| | $F_3$ | 6.06 | 6.24 | 6.18 | 6.04 | 5.36 | 5.38 | 5.42 | 5.36 |
| | $F_4$ | 4.38 | 3.67 | 3.41 | 3.70 | 7.61 | 7.75 | 8.03 | 8.00 |
| Sum of fractions | Σ | 17.24 | 16.70 | 16.70 | 16.68 | 17.46 | 17.48 | 17.50 | 17.40 |
| $LSD_{0.05}$ for: | | | F1 | F2 | F3 | F4 | Σ | | |
| Doses of nickel | | | n.s | n.s. | n.s. | n.s. | n.s. | | |
| Liming | | | 0.041 | 0.122 | 0.133 | 0.188 | 0.198 | | |
| Organic fertilization | | | 0.060 | 0.181 | 0.241 | 0.279 | 0.238 | | |

Table 7 includes the pH value of the analyzed soil in a 1M solution of KCl, which was in the range between 5.14 and 6.54. No impact of the differentiated amount of nickel in the soil on the pH value was observed. Despite the 3-year period from the use of liming, the positive influence of this procedure on the pH value was significant. The experiment showed also the significant impact of the used organic materials on the pH. Brown coal caused an increase and the rye straw caused a decrease in the pH value.

TABLE 6. THE PERCENTAGE SHARE OF ZINC FRACTION IN THE ANALYZED SOIL

| Liming | | 0 Ca | | | | Ca acc. 1 Hh | | | |
|---|---|---|---|---|---|---|---|---|---|
| Fertilization | No. of fraction | Dose of nickel (mg kg$^{-1}$ of soil) | | | | | | | |
| | | 0 | 75 | 150 | 225 | 0 | 75 | 150 | 225 |
| Without organic fertilisation | $F_1$ | 5.28 | 5.47 | 5.78 | 5.31 | 4.34 | 4.28 | 3.82 | 4.53 |
| | $F_2$ | 26.35 | 25.96 | 26.83 | 25.50 | 30.67 | 31.30 | 31.31 | 32.54 |
| | $F_3$ | 220.15 | 19.63 | 19.94 | 20.63 | 18.18 | 18.22 | 18.57 | 18.35 |
| | $F_4$ | 48.22 | 48.94 | 47.45 | 48.56 | 46.81 | 46.20 | 46.30 | 44.58 |
| Sum of fractions | Σ | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| Straw | $F_1$ | 3.35 | 3.82 | 3.93 | 3.74 | 2.99 | 2.73 | 2.92 | 2.41 |
| | $F_2$ | 36.91 | 38.33 | 39.14 | 38.94 | 30.54 | 30.05 | 30.24 | 30.04 |
| | $F_3$ | 31.73 | 32.56 | 31.78 | 31.53 | 29.34 | 27.32 | 26.07 | 26.66 |
| | $F_4$ | 28.01 | 25.29 | 25.15 | 25.79 | 37.13 | 39.90 | 40.77 | 40.89 |
| Sum of fractions | Σ | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| Brown coal | $F_1$ | 3.02 | 3.23 | 3.65 | 3.48 | 2.81 | 2.63 | 2.60 | 2.76 |
| | $F_2$ | 36.43 | 37.37 | 38.92 | 38.13 | 22.91 | 22.25 | 20.57 | 20.46 |
| | $F_3$ | 35.15 | 37.37 | 37.01 | 36.21 | 30.70 | 30.79 | 30.97 | 30.80 |
| | $F_4$ | 25.40 | 22.03 | 20.42 | 22.18 | 43.58 | 44.33 | 45.86 | 45.98 |
| Sum of fractions | Σ | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |

TABLE 7. pH OF THE SOIL IN 1M KCL

| Liming | 0 Ca | | | | Ca acc. 1 Hh | | | |
|---|---|---|---|---|---|---|---|---|
| Fertilization | Dose of nickel (mg kg$^{-1}$ of soil) | | | | | | | |
| | 0 | 75 | 150 | 225 | 0 | 75 | 150 | 225 |
| Without organic fertilisation | 5.36 | 5.29 | 5.26 | 5.30 | 6.38 | 6.36 | 6.40 | 6.38 |
| Straw | 5.16 | 5.14 | 5.20 | 5.16 | 6.25 | 6.22 | 6.20 | 6.30 |
| Brown coal | 5.76 | 5.72 | 5.70 | 5.68 | 6.46 | 6.50 | 6.54 | 6.52 |
| $LSD_{0.05}$ for: | | | | | | | | |
| Doses of nickel | | | n.s. | | | | | |
| Liming | | | 0.040 | | | | | |
| Organic fertilization | | | 0.062 | | | | | |

It should be noted that the total content of copper and zinc, as well as their content in the fractions derived using the BCR procedure did not depend on the differentiated amount of nickel in the soil. Liming resulted in a decrease in the content of both metals in fraction F1 (changeable), which limited the bio-availability of these elements – a result corresponding with that obtained by Lipinski and Lipinska [9] and earlier research studies [8]. The use of organic materials – rye straw and brown coal – increased the total content of both metals in the soil and increased their content in fraction F3 (reducible).

The correlation analysis revealed important relationships between the pH value of the soil and the content of copper and zinc in the measured fractions (Table 8 and 9). Especially important are the high negative values of the correlation coefficients between the pH and the content of both metals in fractions F1 and F2, as well as the high positive correlations between the pH and the content of copper and zinc in fraction F4 (residual).

TABLE 8. SIMPLE CORRELATION COEFFICIENTS BETWEEN COPPER FRACTIONS AND SELECTED SOIL PROPERTIES

| Parameter | Fraction | | | |
|---|---|---|---|---|
| | $F_1$ | $F_2$ | $F_3$ | $F_4$ |
| Cu total | n.s. | – 0.766** | 0.901** | n.s. |
| pH | – 0.886** | – 0.528** | n.s. | 0.733** |

n.s. – not significant, **$\alpha \leq 0{,}01$, *$\alpha \leq 0{,}05$.

TABLE 9. SIMPLE CORRELATION COEFFICIENTS BETWEEN ZINC FRACTIONS AND SELECTED SOIL PROPERTIES

| Parameter | Fraction | | | |
|---|---|---|---|---|
| | $F_1$ | $F_2$ | $F_3$ | $F_4$ |
| Zn total | -0.713** | n.s. | 0.552** | n.s. |
| pH | -0.523** | – 0.446** | n.s. | 0.511* |

n.s. – not significant, **$\alpha \leq 0{,}01$, *$\alpha \leq 0{,}05$.

## CONCLUSIONS

1. Total content of zinc and copper in the studied soil did not exceed the values typical of the geochemical base of the soils of Poland.

2. No significant impact of the differentiated content of nickel in the soil on the total content of copper and zinc and on their distribution in the fractions separated using the BCR method was found.

3. Liming resulted in an increase in the total content of zinc in the investigated soil, as well as a decrease in the content of copper and zinc in fraction F1.

4. The organic materials used caused an increase in the total content of zinc and copper in the analyzed soil, as well as an increase in their content in fraction F3 (oxidizable).

## REFERENCES

[1] Eisler R.: Handbook of Chemical Risk Assessment: Health Hazards to Humans, Plants, and Animals. Vol. 1. Metals. Levis Publishers, 2000.
[2] Gondek J.: Acta Agrophysica, **8**(4), 825, 2006.
[3] Gorlach E., Gambuś F.: Zesz. Probl. Post. Nauk. Roln., **472**, 275, 2000.
[4] Jamali M. K., Kazi T. G., Afridi H. I., Arain M. B., Jalbani N., Memon A. R.: J. Environ. Sci. Health, **42**, 649, 2007.
[5] Jaske A., Gworek B.: Ochrona Środowiska i Zasobów Naturalnych, **49**, 209, 2011.
[6] Kabata-Pendias A., Pendias H.: Biogeochemia pierwiastków śladowych. Wyd. PWN, Warszawa, 1999.
[7] Kennedy V. H., Sanchez A. L., Oughton D. H., Rowland A. P.: Analyst., **122**, 89, 1997.
[8] Kuziemska B., Kalembasa S.: Proc. ECOpole, **7**(1), 215, DOI: 10.2429/proc.2013.7 (1) 028, 2013.
[9] Lipiński W., Lipińska H.: Zesz. Probl. Post. Nauk. Roln., **479**, 187, 2001.
[10] Odum H. T.: Heavy Metals in the Environment: Using Wetlands for Their Removal. Levis Publishers, 2000.
[11] Rauret G., Lopez-Sanchez J.F., Sahuquillo A., Rugio R., Davidson C., Ure A., Quevauculler Ph.: J. Environ. Monit., **1**, 57, 1999.
[12] Reid K.M., Spencer K. L., Shotbolt L.: J. Soils., Sediments, **11**, 518, DOI: 10.1007/s/11368–011–0340–9. 2011.
[13] Szumska (Wilk) M., Gworek B.: Ochrona Środowiska i Zasobów Naturalnych, **41**, 42, 2009.
[14] Świetlik R., Trojanowska M.: Monitoring Środowiska Przyrodniczego. Kieleckie Towarzystwo Naukowe. Kielce, 9, 29, 2008.

## FRAKCJE CYNKU I MIEDZI W GLEBIE ZANIECZYSZCZONEJ NIKLEM

Analizowano glebę po trzyletnim doświadczeniu wazonowym, w którym uwzględniono następujące czynniki: 1. zanieczyszczenie gleby niklem (0,75, 150 i 225 mg Ni $kg^{-1}$ gleby); 2. wapnowanie (0 Ca i Ca w dawce wyliczonej wg 1 Hh gleby); 3. nawożenie organiczne (bez nawożenia organicznego, słoma żytnia i węgiel brunatny pochodzący z kopalni w Turowie). Rośliną testowa była kupkówka pospolita, której w każdym roku eksperymentu zebrano po cztery pokosy. Frakcje miedzi i cynku oznaczono metodą BCR, a pH metodą potencjometryczną. Ogólna zawartość miedzi i cynku w analizowanej glebie nie przekraczała wartości tła geochemicznego gleb Polski. Nie wykazano wpływu zróżnicowanej ilości niklu w glebie na zawartość ogólną i rozmieszczenie Cu i Zn w wydzielonych frakcjach. Wapnowanie spowodowało zwiększenie ilości ogólnej cynku w analizowanej glebie oraz zmniejszenie udziału Cu i Zn we frakcji $F_1$. Słoma i węgiel brunatny spowodowały zwiększenie w glebie ilości obu metali oraz ich udziału we frakcji $F_3$.