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FRACTIONATION OF SELECTED HEAVY METALS IN AGRICULTURAL SOILS

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Abstract: The content of trace elements in soils varies widely and their mobility and availability depends not only on the total content but also on the form of in which these elements occur. The aim of this study was to determine the total content of nickel, lead, zinc and copper in soils used for agriculture, and assess the mobility and phytoavailability of these metals against a background of physical and chemical properties of these soils. In samples taken from three soil profiles (*Phaeozem* and 2 *Fluvisols*) the contents of Ni, Pb, Zn and Cu were determined using atomic absorption spectroscopy in the solutions obtained according to the protocol of modified BCR sequential extraction procedure supplemented with *aqua regia* digestion. The total content of the analyzed metals in most cases corresponded to the natural values, often not exceeding the geochemical background level. It was only in the one profile of the *Fluvisols* (*Endogleyic Fluvisol*) that a higher concentration of zinc and lead was noticed (especially in the surface horizon), slightly exceeding the legal limit. Among the studied metals the lowest phytoavailability was characterized by copper (exchangeable forms on average 4.73% of the total), and the highest by zinc (11.49%). Nickel was the most permanently bound with soil solid phase, and its content in the residual fraction reached 84.46% of the total. Approximately a half of the total lead content was determined as a fraction bound with iron and manganese oxides, while in the case of this metal a significant role in binding of this metal was playing organic matter (fraction bound with organic matter and sulphides - an average of 27.5%). Significant role in the binding of all investigated metals was credited to iron and manganese compounds.

Keywords: nickel, lead, zinc, copper, BCR, sequential extraction procedure, agricultural soils

Introduction

Soil is the first link in the food chain determines the chemical composition of plants, and finally the health of humans and animals. Determining the parameters of elements such as bioavailability, toxicity or mobility certainly cannot be done on the basis of their total content. Knowledge of the interactions between trace elements (their forms) and soil components is essential to assess their behaviour in the environment. There are many analytical procedures consisting of single or sequential extraction for determination of metals in soil. The most comprehensive information about the metal forms in soils and sediments provided by sequential analysis, yet because of the diversity of methods and the

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modifications introduced by the researchers, their results are difficult to compare [1-5]. One of the most popular methods of sequential analysis to determine trace elements in sediments and soils studies is a three-step extraction developed by the *European Community Bureau of Reference - BCR* in order to standardize the methodology in this field throughout the European Union.

The aim of this study was to determine the total content of nickel, lead, zinc and copper in soils used for agriculture, and to assess the mobility and bioavailability of these metals in comparison with the physicochemical properties of these soils, as a way to understand chemical behaviour and fate of analysed metals in the environment.

Material and methods

The object of the study were soils from the area of Swiecka Plateau and Fordonska Valley. These are adjacent regions located in the north of Bydgoszcz city (Poland). The research in this study included three soil profiles: *Endogleyic Phaeozem* (profile no. 1), *Endogleyic Fluvisol* (profile no. 2), and *Haplic Fluvisol* (profile no. 3) [6]. In the samples the following were determined: texture, pH, carbonate content, organic carbon content, the free and amorphous iron oxides content, and cation exchange capacity using methods commonly applied in soil science. The contents of Pb, Ni, Zn and Cu were determined by atomic absorption spectrometry in a air-acetylene flame in solutions received in accordance with the three-step sequential extraction procedure followed the modified BCR protocol [3] supplemented with *aqua regia* digestion [7] (Table 1).

Table 1

Modified BCR three-step sequential extraction scheme with an aqua regia digestion

| Extraction step* | Reagents | Operational definition | Nominal target phase |
|------------------|--|------------------------|--|
| 1 | 0.11 M CH ₃ COOH | Acid-extractable | Soil solution, carbonates, exchangeable metals |
| 2 | 0.5 M NH ₂ OH·HCl | Reducible | Iron/manganese oxyhydroxides |
| 3 | 8.8 M H ₂ O ₂ & 1 M CH ₃ COONH ₄ (pH 2) | Oxidizable | Organic matter and sulphides |
| 4 | Aqua regia | Residual | Remaining, non-silicate bound metals |

* - Steps 1-3 modified BCR protocol, 4 step aqua regia digestion

Results and discussion

The studied profiles represent the two types of soils of different texture, which is mainly the effect of lithogenesis. *Endogleyic Phaeozem* (profile no. 1), was formed of the glacial material (glacial till), which was characterized by a content of clay ranged from 19 to 23%. Only surface horizon, has shown lower content of fractions less than 0.002 mm at 8% level. Different texture of the analysed *Fluvisols* (profile no. 2, 3) was the result of different sedimentation conditions under which they were formed. *Endogleyic Fluvisols* (profile no. 2) was characterized by a relatively constant texture throughout the soil profile. Separated horizons were classified as silty clay, silty clay loam and silt loam [8]. The content of fractions below 0.002 mm ranged from 20 to 42% and decreased with depth (Table 2). *Haplic Fluvisol* (profile no. 3) was characterized by a varied texture across the profile. Horizons were classified as loamy sand, sandy loam, loam, and sand. Lithogenic discontinuity of presented

Fluvisols, confirmed in previous studies [9], is the result of the specificity of the alluvial process, characterized by the variability of conditions in which it occurs [10].

The content of organic carbon in surface horizons ranged up to $18.75 \text{ g} \cdot \text{kg}^{-1}$ (*Phaeozem*), and 23.45 and $18.00 \text{ g} \cdot \text{kg}^{-1}$ (*Fluvisols*), reaching the lowest values in the horizons of parent material (0.10 , 11.65 and $7.30 \text{ g} \cdot \text{kg}^{-1}$ respectively). Both found the content and profile distribution of organic matter was a typological feature of the analysed soils. The research of many authors [11-15] shows that similar organic carbon content was found in various soil types of many regions in Poland. The high content of C_{org} in the alluvial soils (in all layers of the profile) are characteristic of most soils of this type occurring in European river valleys [10, 16, 17].

Table 2

Physico-chemical properties of the analysed soils

| Profile no. | Horizon | Depth | <0.002 mm | C _{org} | pH | | CEC | CaCO ₃ | Fe _d | Fe _o |
|---------------------|---------|--------|-----------|-------------------------|------------------|------|-------------------------------|-------------------|-------------------------|-----------------|
| | | [cm] | [%] | [g · kg ⁻¹] | H ₂ O | KCl | [mmol(+) · kg ⁻¹] | [%] | [g · kg ⁻¹] | |
| Endogleyic Phaeozem | | | | | | | | | | |
| 1 | Ap | 0-35 | 8 | 18.75 | 6.22 | 5.78 | 138.33 | < 1 | 1.83 | 0.67 |
| | AC | 35-48 | 23 | 4.85 | 6.97 | 5.79 | 150.93 | < 1 | 2.32 | 0.26 |
| | Cg1 | 48-95 | 22 | 1.95 | 7.50 | 6.38 | 132.12 | < 1 | 10.54 | 0.52 |
| | Cg2 | 95-140 | 20 | 0.10 | 7.55 | 6.47 | 107.00 | < 1 | 5.29 | 0.40 |
| | Cgk3 | <140 | 19 | 0.33 | 7.85 | 7.31 | 106.83 | 5.00 | 5.28 | 0.55 |
| Endogleyic Fluvisol | | | | | | | | | | |
| 2 | Ap | 0-20 | 42 | 23.45 | 7.48 | 7.08 | 317.22 | 7.16 | 18.90 | 8.05 |
| | AC | 20-45 | 29 | 20.35 | 7.56 | 7.02 | 252.10 | 5.01 | 15.09 | 6.36 |
| | Cg1 | 45-70 | 26 | 14.05 | 7.68 | 7.09 | 236.70 | 4.28 | 13.48 | 5.86 |
| | Cg2 | 70-100 | 21 | 11.65 | 7.81 | 7.21 | 198.59 | 4.29 | 10.63 | 4.72 |
| | Cg3 | <100 | 20 | 11.65 | 7.80 | 7.21 | 196.94 | 3.49 | 10.13 | 3.42 |
| Haplic Fluvisol | | | | | | | | | | |
| 3 | Ap | 0-15 | 7 | 18.00 | 7.04 | 6.70 | 93.34 | < 1 | 3.70 | 1.97 |
| | C1 | 15-55 | 10 | 8.65 | 7.44 | 7.20 | 98.63 | < 1 | 4.42 | 2.46 |
| | C2 | 55-73 | 15 | 6.85 | 7.57 | 7.16 | 153.07 | 1.84 | 6.96 | 3.78 |
| | C3 | 73-90 | 13 | 9.85 | 7.65 | 7.27 | 139.69 | 2.03 | 6.07 | 3.43 |
| | C4 | <90 | 2 | 7.30 | 7.82 | 7.42 | 19.63 | < 1 | 0.93 | 0.43 |

C_{org} - organic carbon, CEC - cation exchange capacity, Fe_d - free iron oxides, Fe_o - amorphous iron oxides

The active acidity ranged from 6.22 to 7.85 pH and exchangeable acidity from 5.78 to 7.42 pH (Table 2). These values within the investigated profiles were mainly dependent on the content of calcium carbonate. Soils with relatively low differentiation of reaction at all profile horizons were *Fluvisols* (profiles no. 2 and 3). Calcium carbonate content in excess of 1% was found only in parts of the studied soil profiles, only in the *Endogleyic Fluvisol* (profile no. 2) the presence of CaCO_3 was found in all profile horizons (3.49-7.16%). At the same time it was the only profile in which the content of this component decreased with the depth.

The cation exchange capacity of soils (CEC) ranged from 19.63 to $317.22 \text{ mmol}(+) \cdot \text{kg}^{-1}$ (Table 2). Soil with extremely high cation exchangeable capacity was *Endogleyic Fluvisol* (profile no. 2). In the surface horizon of this soil CEC was $317.22 \text{ mmol}(+) \cdot \text{kg}^{-1}$ and decreased with the depth to $196.94 \text{ mmol}(+) \cdot \text{kg}^{-1}$.

The free iron oxides content ranged from 0.93 to $18.90 \text{ g} \cdot \text{kg}^{-1}$ and was mainly depended on the content of clay. Fe_d as compounds with a diameter much smaller than $2 \mu\text{m}$ (usually not exceeded 500 nm in diameter) are part of the colloidal clay fraction of soils [18, 19].

Amorphous iron oxides took values from 0.26 to 8.05 g · kg⁻¹ and did not show a high variety in profile.

The total nickel content in the studied soils ranged from 2.776 to 39.118 mg · kg⁻¹. Its content in the *Endogleyic Phaeozem* and in the *Haplic Fluvisol* (profiles no. 1 and 3) was characteristic of uncontaminated soils of Europe [14, 20] and close to the geochemical background values [21]. Much higher values were found in *Endogleyic Fluvisol* (profile no. 2 - 39.118 mg · kg⁻¹ at the surface horizon). The total Ni concentration was highly correlated with the content of free and amorphous iron oxides and clay fraction ($r = 0.91$, $r = 0.85$, $r = 0.87$ respectively, $p < 0.05$). Among the studied metals nickel was strongest bound with the soil solid phase, the residual forms (F4) were from 48.83 to 84.84% of the total (Table 3). A very important role in the binding of this element was played by iron and manganese compounds (F2 on average 20.18%), which was confirmed by very high positive correlation coefficients between these forms and content of free and amorphous iron oxides ($r = 0.87$, $r = 0.93$ respectively, $p < 0.05$). The exchangeable forms (F1) and the associated with organic matter (F3) were mostly a few percent of the nickel total content (Table 3).

Table 3

The total content of nickel and its fractions in analysed soils

| Profile no. | Horizon | Depth | F1* | F2 | F3 | F4 | Tot. | F1 | F2 | F3 | F4 |
|---------------------|---------|--------|--------------------------|--------|--------|--------|--------|-------|-------|-------|-------|
| | | [cm] | [mg · kg ⁻¹] | | | | | [%] | | | |
| Endogleyic Phaeozem | | | | | | | | | | | |
| 1 | Ap | 0-35 | 0.739 | 0.948 | 0.469 | 4.176 | 6.332 | 11.67 | 14.97 | 7.41 | 65.95 |
| | AC | 35-48 | 0.201 | 0.551 | 1.584 | 12.693 | 15.029 | 1.34 | 3.67 | 10.54 | 84.46 |
| | Cg1 | 48-95 | 0.391 | 1.223 | 0.777 | 12.988 | 15.379 | 2.54 | 7.95 | 5.05 | 84.45 |
| | Cg2 | 95-140 | 0.664 | 2.154 | 0.895 | 10.982 | 14.695 | 4.52 | 14.66 | 6.09 | 74.73 |
| | Cgk3 | <140 | 0.585 | 1.552 | 0.458 | 10.951 | 13.546 | 4.32 | 11.46 | 3.38 | 80.84 |
| Endogleyic Fluvisol | | | | | | | | | | | |
| 2 | Ap | 0-20 | 2.489 | 15.119 | 2.408 | 19.102 | 39.118 | 6.36 | 38.65 | 6.16 | 48.83 |
| | AC | 20-45 | 1.523 | 5.836 | 1.109 | 14.143 | 22.611 | 6.74 | 25.81 | 4.90 | 62.55 |
| | Cg1 | 45-70 | 1.212 | 9.658 | 1.036 | 19.291 | 31.197 | 3.88 | 30.96 | 3.32 | 61.84 |
| | Cg2 | 70-100 | 1.443 | 8.437 | 1.467 | 18.339 | 29.686 | 4.86 | 28.42 | 4.94 | 61.78 |
| | Cg3 | <100 | 1.192 | 6.357 | 1.012 | 15.934 | 24.495 | 4.87 | 25.95 | 4.13 | 65.05 |
| Haplic Fluvisol | | | | | | | | | | | |
| 3 | Ap | 0-15 | 1.320 | 2.156 | b.d.l. | 5.776 | 9.252 | 14.27 | 23.30 | - | 62.43 |
| | C1 | 15-55 | 1.394 | 2.785 | b.d.l. | 8.232 | 12.411 | 11.23 | 22.44 | - | 66.33 |
| | C2 | 55-73 | 0.788 | 4.196 | b.d.l. | 11.708 | 16.692 | 4.72 | 25.14 | - | 70.14 |
| | C3 | 73-90 | 0.662 | 4.422 | b.d.l. | 10.006 | 15.090 | 4.39 | 29.30 | - | 66.31 |
| | C4 | <90 | 0.651 | b.d.l. | b.d.l. | 2.125 | 2.776 | 23.45 | - | - | 76.55 |

* - F1 - acid-extractable, F2 - reducible, F3 - oxidizable, F4 - residual, Tot - sum total of fractions, b.d.l. - below the detection limit.

The total content of lead ranged from 11.611 to 105.297 mg · kg⁻¹. These values are characteristic of uncontaminated soils with the exception of sample from the surface horizon of the *Endogleyic Fluvisol* (profile no. 2), in which the Pb content slightly exceeded the permissible standards [22]. At the same sample excess of the total content of zinc was also noticed. The main role in the binding of lead in the studied soils was played by iron and manganese compounds (F2 on average 51.31%) and organic matter (F3 on average 27.50%). It was reflected by the relationship between the total lead content and organic carbon content ($r = 0.62$, $p < 0.05$). The amount of lead bound by organic matter is often correlated with the

soil pH [23], which was statistically confirmed also in the analysed soils (pH KCl $r = 0.54$, $p < 0.05$). A small part of the metal was permanently bound with the soil solid phase (F4 on average 15.73%), and even less was potentially available to plants (F1 on average 5.46%). A similar condition was found in the soils of Slovakia and the UK [24, 25], a slight variation in the dominant role of iron oxides alternating with organic compounds in binding this metal was mainly associated with the typological diversity of the soils.

Table 4

The total content of lead and its fractions in analysed soils

| Profile no. | Horizon | Depth | F1 | F2 | F3 | F4 | Tot. | F1 | F2 | F3 | F4 |
|---------------------|---------|--------|--------------------------|--------|-------|-------|---------|-------|-------|-------|-------|
| | | [cm] | [mg · kg ⁻¹] | | | | | [%] | | | |
| Endogleyic Phaeozem | | | | | | | | | | | |
| 1 | Ap | 0-35 | 0.859 | 5.507 | 6.352 | 1.751 | 14.469 | 5.94 | 38.06 | 43.90 | 12.10 |
| | AC | 35-48 | 0.201 | 4.318 | 6.984 | 2.737 | 14.240 | 1.41 | 30.32 | 49.04 | 19.22 |
| | Cg1 | 48-95 | 0.848 | 3.609 | 5.592 | 1.562 | 11.611 | 7.30 | 31.08 | 48.16 | 13.45 |
| | Cg2 | 95-140 | 1.584 | 4.681 | 5.053 | 1.406 | 12.724 | 12.45 | 36.79 | 39.71 | 11.05 |
| | Cgk3 | <140 | 1.125 | 3.917 | 5.265 | 2.401 | 12.708 | 8.85 | 30.82 | 41.43 | 18.89 |
| Endogleyic Fluvisol | | | | | | | | | | | |
| 2 | Ap | 0-20 | 0.565 | 88.878 | 7.175 | 8.679 | 105.297 | 0.54 | 84.41 | 6.81 | 8.24 |
| | AC | 20-45 | 1.131 | 16.157 | 4.521 | 4.269 | 26.078 | 4.34 | 61.96 | 17.34 | 16.37 |
| | Cg1 | 45-70 | 1.111 | 32.747 | 5.024 | 4.348 | 43.230 | 2.57 | 75.75 | 11.62 | 10.06 |
| | Cg2 | 70-100 | 0.674 | 32.431 | 4.499 | 5.283 | 42.887 | 1.57 | 75.62 | 10.49 | 12.32 |
| | Cg3 | <100 | 0.331 | 24.514 | 4.648 | 4.346 | 33.839 | 0.98 | 72.44 | 13.74 | 12.84 |
| Haplic Fluvisol | | | | | | | | | | | |
| 3 | Ap | 0-15 | 1.673 | 12.808 | 4.634 | 3.014 | 22.129 | 7.56 | 57.88 | 20.94 | 13.62 |
| | C1 | 15-55 | 0.909 | 19.737 | 5.331 | 3.813 | 29.790 | 3.05 | 66.25 | 17.90 | 12.80 |
| | C2 | 55-73 | 1.403 | 12.017 | 6.163 | 3.496 | 23.079 | 6.08 | 52.07 | 26.70 | 15.15 |
| | C3 | 73-90 | 1.179 | 8.709 | 4.716 | 4.505 | 19.109 | 6.17 | 45.58 | 24.68 | 23.58 |
| | C4 | <90 | 1.905 | 1.541 | 5.847 | 5.301 | 14.594 | 13.05 | 10.56 | 40.06 | 36.32 |

* - F1 - acid-extractable, F2 - reducible, F3 - oxidizable, F4 - residual, Tot - sum total of fractions.

The total zinc content in the analysed soils ranged from 7.877 to 386.925 mg · kg⁻¹ (Table 5). The increase in Zn content with depth was found in the *Endogleyic Phaeozem* (profile no. 1), and in the investigated *Fluvisols* the content decreased with depth. Almost half of the total metal content was determined as the residual (F4 on average 47.16%), and a third was associated with Fe and Mn compounds (F2). The relatively low amount of zinc was associated with organic matter (average 7.87%), and its mobile form was on the level of 11.49% (average) of the total content of this metal. Comparison of the phytoavailable forms with threshold content (0.8 mg kg⁻¹), below which there is deficit in zinc for plants, indicates that the analysed soils are reach in this element, and the deficit should not occur in practice [26]. Whereas high availability and mobility of zinc in *Endogleyic Fluvisol* (profile no. 2) may be a risk of biotoxicity or migration of this metal to the deeper soil horizons. In organo-mineral soils, with acid reaction, zinc occurs in exchangeable and mobile forms sometimes exceeding 60% of total [25]. The results published by other authors suggest that a similar share of the soil components in the binding of this metal were found in soils with similar physicochemical properties [4, 27].

The concentration of copper took much lower values in comparison with zinc content and ranged from 6.238 to 52.614 mg · kg⁻¹ (Table 6). Distribution of this element was similar to the distribution of zinc, but showed relatively lower variation in total content in

each soil profiles. Also percentage content of the determined forms of this metal was similar, according to the following sequence: F4 > F2 > F3 > F1. In comparison with the results of other researchers [28, 29] draws attention to a small role of organic matter in binding copper in the studied soils. In organo-mineral soils the amount of copper associated with organic matter exceeds even 80% of the total, while easily soluble, exchangeable and reducible forms are on the level of few percent [25]. Relatively high concentration of reducible Cu forms (F2 on average 38.54%) may be the result of increased extraction in the second step of the modified procedure in comparison with the original BCR protocol [30]. Schramel et al [31] found that the original BCR procedure overestimates the amount of Cu present in the residual phase and underestimates the amount of Cu associated with the oxidizable fraction. In investigated soils the share of acid-extractable Cu forms (F1 on average 4.73%) was the lowest among analysed metals, which confirms that copper is one of the least mobile trace elements in soils, mainly because of its great ability to chemical interaction with mineral and organic components of soil [32, 33]. This situation (except *Endogleyic Fluvisol*) can lead to copper deficiency for plants, which concerns up to 36% of soils in Poland [34].

Table 5

The total content of zinc and its fractions in analysed soils

| Profile no. | Horizon | Depth | F1 | F2 | F3 | F4 | Tot. | F1 | F2 | F3 | F4 |
|---------------------|---------|--------|--------------------------|---------|--------|---------|---------|-------|-------|-------|-------|
| | | [cm] | [mg · kg ⁻¹] | | | | | [%] | | | |
| Endogleyic Phaeozem | | | | | | | | | | | |
| 1 | Ap | 0-35 | 2.866 | 6.643 | 1.921 | 14.917 | 26.347 | 10.88 | 25.21 | 7.29 | 56.62 |
| | AC | 35-48 | 0.788 | 5.274 | 2.308 | 26.842 | 35.212 | 2.24 | 14.98 | 6.55 | 76.23 |
| | Cg1 | 48-95 | 1.650 | 7.264 | 2.035 | 24.429 | 35.378 | 4.66 | 20.53 | 5.75 | 69.05 |
| | Cg2 | 95-140 | 0.347 | 12.132 | 1.711 | 26.877 | 41.067 | 0.84 | 29.54 | 4.17 | 65.45 |
| | Cgk3 | <140 | 0.405 | 11.763 | 1.607 | 27.575 | 41.35 | 0.98 | 28.45 | 3.89 | 66.69 |
| Endogleyic Fluvisol | | | | | | | | | | | |
| 2 | Ap | 0-20 | 84.095 | 95.083 | 52.856 | 154.891 | 386.925 | 21.73 | 24.57 | 13.66 | 40.03 |
| | AC | 20-45 | 8.881 | 42.301 | 10.505 | 44.199 | 105.886 | 8.39 | 39.95 | 9.92 | 41.74 |
| | Cg1 | 45-70 | 22.366 | 112.561 | 18.882 | 69.271 | 223.080 | 10.03 | 50.46 | 8.46 | 31.05 |
| | Cg2 | 70-100 | 24.334 | 96.362 | 18.674 | 61.469 | 200.839 | 12.12 | 47.98 | 9.30 | 30.61 |
| | Cg3 | <100 | 13.989 | 58.047 | 11.148 | 44.864 | 128.048 | 10.92 | 45.33 | 8.71 | 35.04 |
| Haplic Fluvisol | | | | | | | | | | | |
| 3 | Ap | 0-15 | 29.152 | 39.033 | 6.488 | 31.348 | 106.021 | 27.50 | 36.82 | 6.12 | 29.57 |
| | C1 | 15-55 | 9.318 | 23.265 | 4.329 | 24.419 | 61.331 | 15.19 | 37.93 | 7.06 | 39.82 |
| | C2 | 55-73 | 5.473 | 26.246 | 5.117 | 30.903 | 67.739 | 8.08 | 38.75 | 7.55 | 45.62 |
| | C3 | 73-90 | 3.537 | 14.982 | 3.768 | 24.653 | 46.940 | 7.54 | 31.92 | 8.03 | 52.52 |
| | C4 | <90 | 2.460 | 2.349 | 0.917 | 2.151 | 7.877 | 31.23 | 29.82 | 11.64 | 27.31 |

* - F1 - acid-extractable, F2 - reducible, F3 - oxidizable, F4 - residual, Tot - sum total of fractions.

In the analysed soils, with the exception of the case of Pb oxidizable forms described above, there was no statistical correlation between the pH and any determined form of metals. This may result from low diversity of neutral and close to neutral reaction of studied samples, what for example in comparison with the case of acid reaction soils effects usually higher mobility of metals [25].

Total content of all investigated metals was highly correlated with clay fraction (below 2 µm), Fe oxides and, despite the relatively low concentration, with the organic carbon (with exception of Ni). This is of course the consequence of chemical reactivity of these soil

constituents and moreover in the case of clay and Fe oxyhydroxides the result of similar particle size (what complicating assessment). It is also important to observe the comparison of results determined according to the modified and the original BCR protocol in particular for Cu and Pb [30]. Moreover, in the case of Ni the BCR extraction gives lots of problems in evaluation of results [23]. Finally, differences in the obtained results may also arise from differences in sample preparation like drying, homogenization or sample weight [35].

Table 6

The total content of copper and its fractions in analysed soils

| Profile no. | Horizon | Depth | F1 | F2 | F3 | F4 | Tot. | F1 | F2 | F3 | F4 |
|---------------------|---------|--------|--------------------------|--------|-------|--------|--------|-------|-------|-------|-------|
| | | [cm] | [mg · kg ⁻¹] | | | | | | [%] | | |
| Endogleyic Phaeozem | | | | | | | | | | | |
| 1 | Ap | 0-35 | 0.121 | 1.593 | 0.361 | 4.163 | 6.238 | 1.94 | 25.54 | 5.79 | 66.74 |
| | AC | 35-48 | 0.481 | 2.323 | 0.274 | 3.341 | 6.419 | 7.49 | 36.19 | 4.27 | 52.05 |
| | Cg1 | 48-95 | 0.161 | 2.564 | 0.426 | 6.786 | 9.937 | 1.62 | 25.80 | 4.29 | 68.29 |
| | Cg2 | 95-140 | 0.196 | 3.185 | 0.421 | 5.849 | 9.651 | 2.03 | 33.00 | 4.36 | 60.61 |
| | Cgk3 | <140 | 0.031 | 4.129 | 0.441 | 5.621 | 10.222 | 0.30 | 40.39 | 4.31 | 54.99 |
| Endogleyic Fluvisol | | | | | | | | | | | |
| 2 | Ap | 0-20 | 1.149 | 27.268 | 5.491 | 18.706 | 52.614 | 2.18 | 51.83 | 10.44 | 35.55 |
| | AC | 20-45 | 1.022 | 9.205 | 1.592 | 8.136 | 19.955 | 5.12 | 46.13 | 7.98 | 40.77 |
| | Cg1 | 45-70 | 1.010 | 12.661 | 1.804 | 13.687 | 29.162 | 3.46 | 43.42 | 6.19 | 46.93 |
| | Cg2 | 70-100 | 0.734 | 13.306 | 1.926 | 13.901 | 29.867 | 2.46 | 44.55 | 6.45 | 46.54 |
| | Cg3 | <100 | 1.129 | 11.422 | 1.465 | 9.014 | 23.030 | 4.90 | 49.60 | 6.36 | 39.14 |
| Haplic Fluvisol | | | | | | | | | | | |
| 3 | Ap | 0-15 | 0.625 | 4.742 | 1.419 | 6.441 | 13.227 | 4.73 | 35.85 | 10.73 | 48.70 |
| | C1 | 15-55 | 1.015 | 5.426 | 1.007 | 6.359 | 13.807 | 7.35 | 39.30 | 7.29 | 46.06 |
| | C2 | 55-73 | 0.889 | 7.091 | 1.942 | 8.011 | 17.933 | 4.96 | 39.54 | 10.83 | 44.67 |
| | C3 | 73-90 | 0.941 | 6.143 | 1.407 | 7.337 | 15.828 | 5.95 | 38.81 | 8.89 | 46.35 |
| | C4 | <90 | 1.515 | 2.606 | 1.251 | 3.871 | 9.243 | 16.39 | 28.19 | 13.53 | 41.88 |

* - F1 - acid-extractable, F2 - reducible, F3 - oxidizable, F4 - residual, Tot - sum total of fractions.

Conclusions

1. The total content of studied metals in most profiles correspond to the natural values, often not exceeding the geochemical background level. Only in the surface horizon of the *Endogleyic Fluvisol* high content of zinc and lead slightly exceeded the legal limit.
2. Nickel was strongest bound by soil solid phase (up to 84.46% in the residual fraction), while the important role in its binding played Fe and Mn compounds.
3. Approximately half of the total lead content was associated with iron and manganese oxides, and about one-third with the organic matter.
4. Zinc and copper occurred mostly in the residual forms (ca 50%), and the rest was associated mainly with iron and manganese oxides.
5. The studied metals generally characterized by low mobility and phytoavailability, which especially in the case of copper can lead to its deficiency for plants.

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FRAKCYONOWANIE WYBRANYCH METALI CIĘŻKICH W GLEBACH UPRAWNYCH

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Abstrakt: Zawartość pierwiastków śladowych w glebach waha się w szerokich granicach, a ich mobilność i dostępność uzależniona jest nie tylko od całkowitej zawartości, lecz również od formy, w jakiej występują. Celem niniejszej pracy było poznanie zawartości całkowitej niklu, ołowiu, cynku i miedzi w glebach użytkowanych rolniczo oraz ocena mobilności i fitodostępności tych metali na tle właściwości fizykochemicznych tych gleb. W próbkach pobranych z 3 profili glebowych (czarna ziemia i 2 profile mad rzecznych) oznaczono zawartość Ni, Pb, Zn i Cu metodą atomowej spektroskopii absorpcyjnej w roztworach otrzymanych zgodnie z protokołem zmodyfikowanej procedury ekstrakcji sekwencyjnej BCR uzupełnionej roztwarzaniem w *aqua regia*. Zawartość całkowita badanych metali odpowiadała w większości przypadków wartościom naturalnym, często nie przekraczając poziomu tła geochemicznego. Tylko w przypadku jednej z badanych mad stwierdzono podwyższoną zawartość cynku i ołowiu, szczególnie w poziomie powierzchniowym, przekraczającą nieznacznie dopuszczalne normy. Najniższą fitodostępnością spośród badanych metali charakteryzowała się miedź (formy wymienne średnio na poziomie 4,73% zawartości całkowitej), a najwyższą cynk (11,49%). Najtrwalej z fazą stałą gleby związany był nikiel, którego zawartość we frakcji rezydualnej sięgała 84,46% zawartości całkowitej. Średnio połowa zawartości całkowitej ołowiu oznaczona została jako frakcja związana z tlenkami żelaza i manganu, jednocześnie w przypadku tego metalu znaczącą rolę w jego wiązaniu odgrywała materia organiczna (frakcja związana z materią organiczną i związkami siarki - średnio 27,5%). Wyraźnie znaczącą rolę w wiązaniu wszystkich badanych metali odgrywały związki żelaza i manganu.

Słowa kluczowe: nikiel, ołów, cynk, miedź, BCR, analiza sekwencyjna, gleby uprawne