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EVALUATION OF THE IMPACT OF THE COPPERWORK "GLOGOW" ON THE TOTAL CONTENT OF MANGANESE AND ITS MOBILE FORMS IN THE VICINITY OF ARABLE SOILS

OCENA ODDZIAŁYWANIA HUTY MIEDZI „GŁOGÓW" NA ZAWARTOŚĆ CAŁKOWITĄ MANGANU ORAZ JEGO FORM MOBILNYCH W OKOLICZNYCH GLEBACH UPRAWNYCH

Abstract: The occurrence of manganese in soils depends *eg* on its content in the parent rock as well as on the soil-formation process determining its profile distribution. Moreover clay soils are richer in this metal than sandy soils.The properties and transformations of manganese compounds are defined by redox conditions as well as the reaction and the content of organic substance and calcium carbonate.

The aim of the present research was to determine the total contents of manganese and its mobile forms in the profiles of Luvisols in the vicinity of the Copperworks "Glogow".

The research material was made up of the profiles of arable Luvisols located at different distances from the Copperworks "Glogow". There were made four soil test pits located at varied distances from the emitter: P1 – 6.8 km (southwards), P2 – 6.6 km (south-eastwards), P3 – 5.7 km (eastwards) and P4 – 6.5 km (southwards). In the soil samples from each genetic horizon the following soil analyses were made: texture using Cassagrande method with the modification by Pruszynski, pH in H_2O and in the KCl solution (1 mol/dm^3) using potentiometric method, C_{org} using Tiurin method, content of $CaCO_3$ by Scheibler volume method [3]. The total content of manganese was defined with the AAS method following the mineralization in the mixture of HF and $HClO_4$ acids and the content of mobile manganese forms, according to the modified sequence analysis by Miller et al (1986). The soils investigated were classified as the subtype of Haplic Luvisols showing the reaction ranging from slightly acid to alkaline and the content of C_{org} in horizons Ap from 6.7 g · kg^{-1} to 31.2 g · kg^{-1}. The total content of manganese ranged from 102.40 g · kg^{-1} to 332.80 mg · kg^{-1}. The Mn-richest horizons were the humus horizons, while Mn lowest contents were observed in the horizons of the parent rock in all the profiles investigated. In the sequential analysis the most important share (about 41 %) in the total content of manganese was reported for fraction IV (connected with organic matter) and fraction VI – connected with crystalline iron oxides (24 %) and fraction III – with free manganese oxides (15 %). The share of fractions 1, 2 and 5 was below 5 % of the total content of the metal. A considerable content of Mn fractions connected with organic matter and iron and manganese oxides points to its temporary immobilization, which

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is connected with the changes in the redox potential. The total contents do not exceed the geochemical background level, which allows for considering the soils of that region to be unpolluted with manganese.

Keywords: soil, total manganese, mobile forms, sequential analysis

Introduction

Manganese is one of the metals classified as representing the group posing a high potential threat for the environment [1, 2]. It occurs in the soil mostly in a form of free oxides or silicates from which, as a result of the process of weathering, Mn^{2+} ions get released, entering the soil solution. The content of manganese in soil undergoes many fluctuations, and the variation in its content, next to manganese richness of the soils parent rocks, is affected by the physicochemical conditions of the environment. Besides the redox conditions, also the reaction and the content of organic substance and calcium carbonate determine the transformations of manganese compounds in soil. The anthropogenic factors resulting in the increase in the content of heavy metals in the agricultural environment include dust emissions from the copper smelter and refinery of non-ferrous metals, which is especially dangerous in soils due to their adsorption in mineral and organic colloids. In Poland the main copper producer is KGHM POLSKA MIEDZ S.A. It covers the Copperworks "Glogow" I and II as well as the Copperworks "LEGNICA". They are located at a small distance from the areas under the agricultural use, which makes their contamination with the emissions from the Copper Smelter and Refinery more likely.

The aim of the present research was to evaluate the impact of the Copperworks "Glogow" on the total content of manganese and its mobile forms in the arable profiles of Luvisols.

Material and methods

The research of the soil cover involved the area located in the vicinity of the Copperworks "Glogow". There were made four soil test pits located at varied distances from the emitter: P1 – 6.8 km (southwards), P2 – 6.6 km (south-eastwards), P3 – 5.7 km (eastwards) and P4 – 6.5 km (southwards). During the field research, drawing on the morphological features, in selected soil profiles there were separated genetic horizons from which soil was sampled and the following laboratory analyses were made: the grain size composition with the Cassagrande method modified by Proszynski, pH with the potentiometric method in H_2O and in the KCl solution at the concentration of 1 mol · dm^{-3}, C_{org} applying the Tiurin method, the content of $CaCO_3$ with the volumetric method by Scheibler [3]. The total contents of manganese were determined following the soil mineralization in the mixture of HF and $HClO_4$ acids, using Crock and Severson's procedure [4]. The extraction of mobile forms of manganese was made drawing on the modified [5] sequential analysis according to Miller et al [6], which allowed the separation of metal fractions, following: FI – exchangeable and soluble in water fraction, FII – forms soluble in acids, F3 – forms occluded on manganese oxides, FIV – forms associated with organic matter, FV – lead bound to amorphous iron oxides, FVI – forms associated with crystalline iron oxides, FVII – residual forms. There was

also made the analysis of certified material Till-3 and SV-M. The measurements of the contents of total and mobile Mn forms were performed with the *Atomic Absorption Spectrometry* (AAS) applying the PU 9100X spectrometer. The analysis mas made in three repetitions. The statistical evaluation of the results was made with the use of Statistica 10.0 software.

Results and discussion

The arable soil profiles selected for the present research have been classified to represent a good wheat complex. While applying agricultural categories [7], they belong to medium heavy soils (P1 and P2) and heavy soils (P3 and P4). According to the PTG 2008 soil classification, they have been considered to represent Haplic Luvisols produced from silts [8] with the sequences of genetic horizons (Ap, Eet, Bt, C) typical for those soils.

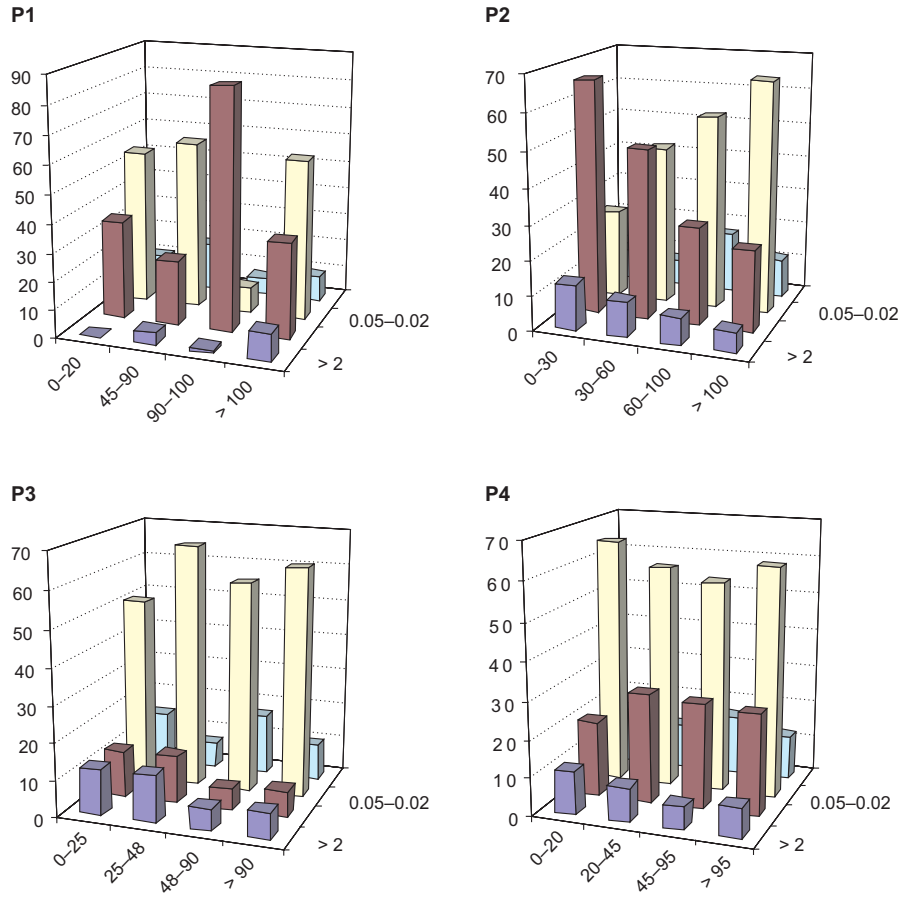

Fig. 1–4. Percentage of fraction with diameter [mm]

The feature characteristic for the grain size composition of the soils investigated was a low content of skeleton fractions (5; 15) %, which facilitates their classification as poor-skeleton formations [7].

In the parent rocks of the soils analysed there occurs the grain size composition of silt loams (Fig. 1–4), and in the enrichment horizons – silt loams. In all the profiles there was found a clear enrichment of illuvial horizons with all the clay fraction in which the sub-fraction of fine clay (∅ 0.0002 mm) prevailed. In the humus and eluvial horizons of the profiles investigated (except for profile P2), the grain size composition corresponds to silt loams (Fig. 1–4). The grain size composition results from the aerometric analysis demonstrated that the dominant grain size composition group in the profiles analysed was silt loam [7]. The content of the clay fraction, next to the content of C_{org} and the reaction, is the factor which has a considerable effect on the availability of heavy metals [9]. The soils showed the content of organic carbon, typical for the soils of that region, which in the humus horizons ranged from 7.0 g · kg^{-1} to 18.1 g · kg^{-1} (Table 1). The organic substance in the soil and that introduced with fertilisers result in limiting the availability of heavy metals and thus their toxicity decreases [10]. The reaction of the soils investigated was neutral and close to alkaline pH_{H_2O} (7.33; 8.55) and pH_{KCl} (5.81; 7.75). The more acid the soil, the more soluble and the more available the manganese compounds. Besides, the higher pH values, the higher concentration of Mn^{2+} ions available to plants. Clearly lower pH values were recorded in the illuvial horizons (Table 1). The alkaline reaction of the soils investigated could have been affected by intensive liming of arable soils around the Copperworks, which was to limit the uptake of heavy metals from the sorption complex of soils and manganese leaching to deeper horizons [9]. What is noteworthy is the presence of calcium carbonate (0.43; 11.6) % in most samples, which, however, does not always determine a high pH value (Table 1). The total contents of manganese in the profiles investigated assumed the values in the range 59.2 mg · kg^{-1} to 332.8 mg · kg^{-1} (Table 2). The occurrence of manganese in soils depends on the anthropogenic factors and on its content in the parent rock as well as on the soil-formation process determining its profile distribution [11, 12]. The manganese content is usually higher in the soils rich in the clay fraction [13]. The soil richness in the fraction of colloidal clay as well as the humus content affect the availability of heavy metals to plants [9]. Manganese deficits can be due to its immobilisation in organic soils and containing carbonates. In all the soils investigated clearly higher total manganese contents were in the humus horizons, while the lowest contents were reported in the horizons of the parent rock (Table 2). The high content of C_{org} was accompanied by the highest total manganese content (profile P1). There was no correlation between the total content of manganese and the content of fraction with ∅ < 0.002 mm, differently to other authors [13]. The pollution of soils with manganese is connected with its form and not with the amount. The knowledge of the total contents of heavy metals in soils does not provide the picture of their real availability to plants and the possibility of entering into the biological circle [15] which however, is possible with the sequential analysis [16]. Application of sequential extraction allows the evaluation of metals behavior in soil environment and the possibility of their migration to biochemical circulation [17]. This may be the result of the increased accumulation of

heavy metals in the agricultural areas located within the range of metalliferous dusts emission [9].

In the sequential analysis applied [5, 6] there were separated seven manganese fractions: FI – exchangeable and soluble in water fraction, FII – forms soluble in acids, F3 – forms occluded on manganese oxides, FIV – forms associated with organic matter, FV – lead bound to amorphous iron oxides, FVI – forms associated with crystalline iron oxides, FVII – residual forms (Table 2).

Table 1

Physico-chemical properties of the soils

Profile Horizon	Depth [cm]	pH		$CaCO_3$ [%]	C_{org} [$g \cdot kg^{-1}$]
		H_2O	KCl		
P1					
Ap	0–20	7.33	6.07	< 1	18.1
Eet	20–45	7.54	5.91	< 1	3.2
Bt	45–90	7.95	5.81	< 1	n.o.
C	90–100	8.16	6.62	< 1	n.o.
C1	> 100	8.14	6.58	< 1	n.o.
P2					
Ap	0–30	7.53	6.89	< 1	7.2
Eet	30–60	8.20	7.50	< 1	3.9
Bt	60–100	7.82	6.46	11.6	n.o.
C	> 100	8.48	7.65	< 1	n.o.
P3					
Ap	0–25	8.19	7.49	1.93	7.0
Eet	25–48	8.55	7.72	< 1	1.2
Bt	48–90	8.13	7.30	6.72	n.o.
C	> 90	8.38	7.75	8.58	n.o.
P4					
Ap	0–20	7.55	7.22	< 1	18.4
Eet	20–45	7.53	7.05	< 1	4.9
Bt	45–95	7.67	6.98	3.46	n.o.
C	> 95	8.01	7.30	5.82	n.o.

The contents of manganese forms soluble in water (fraction I) were below the detection threshold, which could have been due to a high pH of the soils. Growing acidification strengthen the airing of minerals processes and the accumulation of their products in soil profile [18, 19].The exchangeable fraction (F II) accounted for 0.1–4 % of the total Mn content only, and its content in the profiles ranged from 0.8 $mg \cdot kg^{-1}$ to 14.0 $mg \cdot kg^{-1}$.

A low content of the most mobile forms (FI and FII) points to a low bioavailability and toxicity of manganese in the soils. The presence of calcium carbonate is a factor

which limits the availability of manganese and its leaching into deeper soil layers. The fraction occluded (coprecipitated) on Mn oxides (FIII) was most abundant in the humus horizons (Table 2). Similarly, the humus horizons also demonstrated the highest content of fractions VI and VII; the forms connected with crystalline iron oxides and the residual forms. The fraction dominant in the profiles investigated was the one connected with organic substance (FIV) and its contents ranged from 30.0 mg · kg^{-1} to 130.0 mg · kg^{-1}. Manganese connected with organic substance can be temporarily immobilized. In the polluted soils there is observed a considerable share of the fractions connected with organic substance [16]. A considerable content of the least mobile Mn forms (FVI and FVII) points to a clear tendency to Mn occluding with iron oxides of soil minerals [17]. Determining the manganese mobility facilitated the evaluation of its possibility to enter the biogeochemical circle [20].

Table 2

The total content of manganese and metal fractions in soils

Profile Horizon	Total Mn [mg · kg^{-1}]	F I	F II	F III	F IV	F V	F VI	F VII*
		[mg · kg^{-1}]						
P1								
Ap	44.64	b.d.	14.0	26.8	130.0	17.6	100.4	44.0
Eet	31.36	b.d.	4.0	9.2	57.6	18.4	98.0	26.8
Bt	30.16	b.d.	2.4	5.2	30.0	14.0	73.2	27.2
C	27.16	b.d.	1.6	3.6	52.0	9.2	34.0	15.6
C1	27.36	b.d.	1.6	1.6	36.0	0.8	7.2	12.0
P2								
Ap	31.44	b.d.	2.4	26.8	90.0	8.4	60.0	30.0
Eet	23.84	b.d.	2.0	14.4	104.4	10.8	50.0	22.0
Bt	24.48	b.d.	2.4	9.2	34.0	7.6	25.2	24.0
C	21.96	b.d.	0.8	76.6	69.2	2.8	20.0	15.6
P3								
Ap	34.68	b.d.	3.2	60.8	144.0	9.6	45.2	32.0
Eet	17.56	b.d.	0.8	23.2	109.2	8.4	16.8	17.2
Bt	22.44	b.d.	1.6	68.8	74.0	2.0	25.2	27.6
C	17.40	0.24	1.2	76.0	49.2	0.8	16.8	20.4
P4								
Ap	45.36	b.d.	4.4	35.2	84.0	9.2	51.2	24.0
Eet	34.80	b.d.	4.0	26.0	76.0	8.4	46.0	20.0
Bt	32.44	b.d.	2.8	9.6	82.0	16.0	56.8	18.8
C	28.72	b.d.	1.2	6.0	48.0	12.4	42.0	20.8

* FI – exchangeable and soluble in water fraction, FII – forms soluble in acids, F3 – forms occluded on manganese oxides, FIV – forms associated with organic matter, FV – lead bound to amorphous iron oxides, FVI – forms associated with crystalline iron oxides, FVII – residual forms, b.d. – below detection limit.

Conclusions

1. In the soil profiles in the vicinity of the Copperworks "Glogow" the total manganese contents fell within the range of (59.2; 332.8) mg · kg^{-1}. A clear enrichment in that element was found in the humus horizons, however, the contents did not exceed the geochemical background level.

2. In the sequence analysis the most considerable share in the total manganese content was reported for fraction IV (forms associated with organic matter), which accounted for (20; 62) % of the total content, and fraction VI (forms associated with crystalline iron oxides), – for (10; 48) % of the total content.

3. In the soils a low share of the most mobile fractions (FI and FII) can suggest a low manganese mobility and demonstrates its low bioavailability and toxicity.

4. The proximity of Copperworks "Glogow" did not affect on the increase of manganese concentration in nearby arable soils, which does not eliminate the investigated soils from their agricultural use.

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OCENA ODDZIAŁYWANIA HUTY MIEDZI „GŁOGÓW" NA ZAWARTOŚĆ CAIKOWITĄ MANGANU ORAZ JEGO FORM MOBILNYCH W OKOLICZNYCH GLEBACH UPRAWNYCH

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Abstrakt: Występowanie manganu w glebach zależy m.in. od jego zawartości w skale macierzystej, jak również od procesu glebotwórczego decydującego o jego profilowym rozmieszczeniu. Obecne w skale macierzystej metale ciężkie są na ogół mało ruchliwe i uwalniane są dopiero w wyniku procesów wietrzenia. O właściwościach i przeobrażeniach związków manganu decydują poza warunkami redoks, także odczyn oraz zawartość substancji organicznej i węglanu wapnia.

Celem przedstawionych badań było określenie całkowitych zawartości manganu oraz jego form mobilnych w profilach gleb płowych z sąsiedztwa Huty Miedzi Głogów.

Materiał badawczy stanowiły profile uprawnych gleb płowych położonych w różnej odległości od Huty Miedzi „Głogów". Wykonano cztery odkrywki glebowe zlokalizowane w różnej odległości od emitora: P1 – 6,8 km (w kierunku południowym), P2 – 6,6 km (w kierunku południowo-wschodnim), P3 – 5,7 km (w kierunku wschodnim) i P4 – 6,5 km (w kierunku południowym). W wybranych profilach glebowych wyodrębniono poziomy genetyczne, z których pobrano próbki glebowe i wykonano następujące analizy laboratoryjne: uziarnienie metodą Casagrande'a w modyfikacji Prószyńskiego, pH metodą potencjometryczną w H_2O i w roztworze KCl o stężeniu 1 mol · dm^{-3}, C_{org} metodą Tiurina, zawartość $CaCO_3$ metodą objętościową Scheiblera [3].

Całkowitą zawartość manganu oznaczono metodą AAS po mineralizacji w mieszaninie kwasów HF i $HClO_4$, a zawartość form mobilnych manganu, wg zmodyfikowanej analizy sekwencyjnej Millera i in. (1986). Badane gleby zaliczono do podtypu gleb płowych typowych o odczynie w zakresie od lekko kwaśnego do zasadowego i zawartości C_{org} w poziomach Ap w przedziale (6,7; 31,2) g · kg^{-1}. Całkowita zawartość manganu wynosiła (102,40; 332,80) mg · kg^{-1}. Najzasobniejsze w mangan były poziomy próchniczne, natomiast najmniejsze jego zawartości stwierdzono w poziomach skały macierzystej we wszystkich badanych profilach. W analizie sekwencyjnej najbardziej znaczący udział w zawartości całkowitej manganu miała frakcja IV – związana z materią organiczną (około 41 %) oraz VI – związana z krystalicznymi tlenkami żelaza (24 %) i III – związana z wolnymi tlenkami manganu (15 %). Udział frakcji 1, 2 i 5 był poniżej 5 % zawartości całkowitej badanego metalu. Znaczna zawartość frakcji manganu związanych z materią organiczną oraz tlenkami żelaza i manganu wskazuje na jego czasową immobilizację, co związane jest ze zmianami potencjału oksydacyjno-redukcyjnego. Zawartości całkowite nie przekraczają poziomu tła geochemicznego, co pozwala uznać gleby tego regionu za niezanieczyszczone manganem.

Słowa kluczowe: gleba, mangan całkowity, formy mobilne, analiza sekwencyjna