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INFLUENCE OF THE GŁOGÓW COPPER WORKS ON THE CONTENT OF MOBILE FORMS OF COPPER AND ZINC IN ARABLE SOILS

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Abstract

The aim of this research has been to investigate the influence of the Głogów Copper Works on profile distribution and mobility of copper and zinc in cultivated soils in the vicinity of the plant.

The following were determined in soil samples from 4 cultivated soil profiles classified as Luvisols: soil texture, pH in KCl, pH in H_2O, organic carbon, total Cu and Zn content using the ASA method after mineralization in HF and $HClO_4$ acids and the content of mobile forms of Cu and Zn using the sequential method. In terms of grain size distribution, the profiles were classified as loamy silt. The soil pH was in range of pH_{H_2O} 7.33-8.55 and pH_{KCl} 5.81-7.75. Except for P1 profile, the presence of $CaCO_3$ was observed in all soil profiles. C and Bt horizons were the richest in $CaCO_3$. The content of C-organic in humus horizons was in the range of 7.0-18.1 g kg^{-1}. The total Cu content was in the range of 4.04-57.75 mg kg^{-1}. In Ap horizons, the total Cu content was significantly higher, but in C horizons it was the lowest, which indicates that Ap horizons had been enriched with Cu by human activity. The results of the sequential analysis indicate the dominant share of fraction V, associated with organic matter, in the surface horizons. In the remaining horizons, the Cu fraction associated with iron oxides dominates. The total content of Zn was in the range of 3.34-42.65 mg kg^{-1}. The highest content of this element was observed in Ap horizons, and the lowest occurred in Eet horizons. The speciation analysis showed the highest content of Zn in the form associated with crystalline iron oxides (fraction VI), and the lowest in fractions I and II, i.e. soluble in water and exchangeable forms. Most of the investigated soils (apart from P1 profile) may be classified as unpolluted with Cu and Zn, which shows that the proximity of the Głogów Copper Works does not preclude agricultural use of the analyzed soils (with one exception).

Keywords: soils, copper, zinc.

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WPŁYW HUTY MIEDZI GŁOGÓW NA ZAWARTOŚĆ MOBILNYCH FORM MIEDZI I CYNKU W OKOLICZNYCH GLEBACH UPRAWWNYCH

Abstrakt

Celem badań była ocena wpływu Huty Miedzi Głogów na profilową dystrybucję oraz mobilność miedzi i cynku w okolicznych glebach uprawnych. Materiał badawczy stanowiły profile glebowe położone w odległości 5,7-6,8 km w kierunku południowo-wschodnim od emitora. W próbkach glebowych pochodzących z 4 profili gleb uprawnych sklasyfikowanych jako gleby płowe typowe oznaczono: uziarnienie, pH KCl (1 mol dm^{-3}) i pH w H_2O, C-organiczny oraz całkowitą zawartość Cu i Zn metodą ASA po mineralizacji w kwasach HF i $HClO_4$, a zawartość form mobilnych Cu i Zn metodą analizy sekwencyjnej. Pod względem uziarnienia badane profile zaliczono do pyłów gliniastych. W badanych glebach pH było w zakresie pH_{H_2O} 7,33-8,55 oraz pH_{KCl} 5,81-7,75, przyjmując najniższe wartości w poziomach Bt. Stwierdzono obecność węglanu wapnia, oprcz profilu (P1), którego zawartość wynosiła 0,43%-11,60%. Najzasobniejsze w $CaCO_3$ były poziomy C oraz poziomy Bt. Zawartość C-organicznego w poziomach próchnicznych wynosiła 7,0-18,1 g kg^{-1}, całkowita zawartość Cu 4,04-57,75 mg kg^{-1}. Stwierdzono wyraźnie wyższą całkowitą zawartość Cu w poziomach Ap oraz najniższą w poziomach C, co wskazuje na antropogeniczne wzbogacenie poziomów Ap w Cu. Wyniki analizy sekwencyjnej wskazują na dominujący udział w poziomach powierzchniowych frakcji V, tj. form związanych z materią organiczną, w pozostałych poziomach przeważa frakcja Cu związana z tlenkami żelaza. Całkowita zawartość Zn wynosiła 3,34-42,65 mg kg^{-1}, a najwyższą zawartość tego pierwiastka stwierdzono w poziomach Ap, najniższą w poziomach Eet. Analiza specjacyjna wykazała najwiekszą zawartość Zn w formie związanej z krystalicznymi tlenkami żelaza (frakcja VI), a najniższą we frakcji I i II, tj. w formach wodnorozpuszczalnych i wymiennych. Badane gleby w większości (oprócz profilu P1) można zaklasyfikować do gleb niezanieczyszczonych Cu i Zn, co wskazuje, że bliskość Huty Głogów (oprócz jednego przypadku) nie eliminuje badanych gleb z użytkowania rolniczego.

Słowa kluczowe: gleba, miedź, cynk.

INTRODUCTION

The Głogów II Copper Works in Żukowice near Głogów has operated since 1978. It is a subsidiary plant of the Mining and Copper Industry Polska Miedź S.A. It is located in the Glogau-Baruther Urstromtal (*Pradolina Głogowska*), which is an area of agricultural and industrial use. Most of the area is occupied by cultivated soils. The Głogów Copper Works emits to the atmosphere metalliferous dusts, which permeate soil through the sedimentation process. Most of the dust emitted by non-iron works falls on soil, causing various changes. Heavy metals from dusts emitted by copper works show significantly higher solubility than lithogenic metals. They are mostly in the form of oxides, sulfides, sulfates and carbonates. Post-processing dusts emitted to the atmosphere are carriers of heavy metals, mostly Cu, Pb, Cd, Zn and As (ROSADA 2008). Emitted cement dusts affect the soil environment and the quality of crops grown on such soils.

The aim of this research has been to evaluate the influence of the Głogów Copper Works on the profile distribution and mobility of copper and zinc in arable soils in the vicinity of the plant.

MATERIAL AND METHODS

The research material consisted of 4 cultivated soil profiles, located 3.0--6.8 km away from the copper works. During the field tests, genetic horizons from which soil samples were taken were identified morphologically. The following laboratory analysis were performed on the soil samples: soil texture using Cassagrande method modified by Pruszyński, pH using the potentiometric method in H_2O and in KCl solutions (1mol dm^{-3}), organic C using Tiurin method, and content of $CaCO_3$ using Scheibler volumetric method. The total content of copper and zinc was determined after soil mineralization in a mixture of HF and $HClO_4$ acids (Crock, Severson 1980). The extraction of mobile lead was conducted by the sequential analysis according to Miller et al. (1986) with the modification of Dąbkowska-Naskręt (1998). The results were verified by analysis of certified material Till-3 (1995). Measurements of the content of total and mobile forms of Cu and Zn were performed using the atomic spectrometry method (ASA) in a spectrometer PU 9100X. The analyses were performed in triplicate. Statistical evaluation of the results was accomplished using Statistica 6.0 software.

RESULTS AND DISCUSSIONS

The analyzed cultivated soil profiles were classified as typical Luvisols formed from silt (PTG 1989). In agricultural categories (PTG 2008), they are medium (P1 in Wierzchosławice and P2 in Modła) and heavy soils (P3 in Kurowice and P4 in Nielubia). In the humus and eluvial horizons of the investigated profiles (apart from P2), the texture was similar to clay silt and loamy silt (Table 1), while the illuvial horizons represented clay silt (Table 1). These horizons were characterized by a low content of skeletal fraction (<8%) and sand fraction (23-28%). Three of the four examined profiles were found to contain calcium carbonate (the exception was profile P1). The richest in calcium carbonate were illuvial and bedrock horizons (Table 2), where the content of this compound was in the range of 3.46% to 11.60%. The pH of the soils was in the range of pH_{H_2O} 7.33-8.55 and pH_{KCl} 5.81--7.75, with the lowest values usually detected in the enrichment horizons of the investigated samples (Table 2). The neutral and higher values of pH were not always accompanied by a high content of $CaCO_3$, which indicates

Table 1

Soli texture

Profile	Horizon	Depth (cm)	Percentage of fraction in diameter (mm)					
			2 - 0.1	0.1 - - 0.5	0.05 - - 0.02	0.02 - - 0.002	0.002 - - 0.0002	< 0.0002
P1 Wierzchowice	Ap	0-20	19	16	35	15	5	10
	Eet	20-45	12	13	39	18	6	12
	Bt	45-90	12	15	34	16	6	17
	C	90-100	82	3	5	2	2	6
	C1	>100	22	12	39	14	4	9
P2 Modła	Ap	0-30	59	7	17	6	2	9
	Eet	30-60	37	11	27	12	3	10
	Bt	60-100	18	10	35	16	4	17
	C	>100	11	13	40	20	5	11
P3 Kurowice	Ap	0-25	15	20	33	13	5	14
	Eet	25-48	10	16	45	16	6	7
	Bt	48-90	14	11	35	17	6	17
	C	90-150	14	12	46	14	4	10
P4 Nielubia	Ap	0-20	14	6	46	19	5	10
	Eet	20-45	17	12	35	15	5	16
	Bt1	45-70	17	11	37	19	6	10
	Bt2	70-95	22	7	36	17	5	13
	C	> 95	15	12	40	21	5	7

Table 2

Physicochemical properties of soils

Profile	Horizon	pH		C- org. (g kg^{-1})	$CaCo_3$ (%)
		H_2O	KCl		
P1 Wierzchowice	Ap	7.33	6.07	18.1	<1
	Eet	7.54	5.91	3.2	<1
	Bt	7.95	5.81	-	<1
	C1	8.14	6.58	-	<1
	C	8.16	6.62	-	<1
P2 Modła	Ap	7.53	6.89	7.2	<0.64
	Eet	8.20	7.50	3.9	<1
	Bt	7.82	6.46	-	11.60
	C	8.84	7.65	-	<1
P3 Kurowice	Ap	8.19	7.49	7.0	1.93
	Eet	8.55	7.72	1.2	0.43
	Bt	8.13	7.30	-	6.72
	C	8.38	7.75	-	8.58
P4 Nielubia	Ap	7.55	7.22	13.0	0.93
	Eet	7.53	7.05	9.3	<1
	Bt1	7.67	6.98	-	3.46
	C	8.01	7.30	-	5.82

presence of other forms of metals alkalizing the soil environment in the soil solution and sorption complex, either in the form of salts or hydroxides (KABATA-PENDIAS, PENDIAS 2001). The content of organic carbon in the humus horizons of the analyzed soils was typical of local soils, ranging from 7.0 to 18.1 g kg^1 (STRĄCZYŃSKI, ANDRUSZCZAK 1996, KARCZEWSKA 2002, ROSADA 2008) Table 2.

The total content of Cu varied from 1.98 to 57.75 mg kg^{-1} (Table 3). Significant enrichment with this element was observed in the humus horizons of the soils, which may be the result of high sorption capacity of or-

Table 3

The total content of Cu and metal fractions

Profile Horizon	Cu total (mg kg^{-1})	F I	F II	F III	F IV	F V	F VI	F VII
		(mg kg^{-1})						
P1 Wierzchowice								
Ap	24.91	0.70	0.86	1.59	1.06	7.05	9.19	1.83
Eet	9.40	0.69	0.64	0.28	1.70	2.11	2.33	1.60
Bt	11.66	0.44	0.48	0.21	0.97	1.64	2.27	2.88
C	4.85	0.60	0.71	0.15	1.18	0.86	1.27	1.03
C1	9.08	0.82	0.74	0.16	0.96	1.41	1.79	2.51
P2 Modła								
Ap	6.58	0.43	0.58	0.65	2.70	1.63	2.12	1.33
Eet	6.16	0.41	0.69	0.83	2.54	1.43	1.87	1.40
Bt	9.63	0.37	0.76	0.72	2.43	1.35	2.83	2.17
C	7.08	0.40	0.62	1.10	2.25	1.42	1.75	1.53
P3 Kurowice								
Ap	30.62	0.70	0.71	3.50	2.47	11.19	3.52	2.52
Eet	4.04	0.41	0.43	0.72	0.88	0.70	1.37	1.64
Bt	4.85	0.43	0.43	0.80	1.32	1.21	1.03	1.76
C	1.98	0.30	0.32	0.49	0.68	0.55	0.62	0.83
P4 Nielubia								
Ap	57.75	0.51	0.91	4.45	2.70	25.71	22.11	3.11
Eet	10.40	0.60	0.71	0.56	1.10	3.86	3.72	1.11
Bt	4.98	0.34	0.59	0.21	0.93	1.42	2.08	0.86
C	4.48	0.36	0.62	0.24	1.07	1.55	0.94	1.59

FI – exchangeable and soluble in water forms, FII – forms soluble in acids, FIII – forms occluded on manganese oxides, FIV – forms related to organic matter, FV – forms related to amorphous iron oxides, FVI – forms related to crystal iron oxides, FVII – residual form

ganic substances towards Cu, forming associations of different mobility (MIGASZEWSKI et. al. 2004). It may have also been caused by man-made enrichment due to the proximity of the copper works. The indicators of Cu arrangements were calculated from the ratio of this element in a given horizon to its average content in the bedrock, assuming value >1, which may prove its anthropogenic origin (Table 3). The highest content of Cu in surface horizons was reported by other authors (WEBER 1995, STRĄCZYŃSKI, ANDRUSZCZAK 1996, KARCZEWSKA 2002). This finding indicates the dependence on the distance to the copper works (P4 profile) and the content of organic substances. The factors which influence solubility, migration and availability of Cu are organic substances, clay minerals and pH (DĄBKOWSKA-NASKRĘT et al. 2002). In the analyzed soils, correlation between the total Cu content and pH in 1M KCl was found.

Sequential extraction helps to evaluate behavior of metals in soil environment and their possible migration in the biochemical circulation (GWOREK 1985). The sequential analysis performed in this study extracted 7 fractions of metals (Table 3). The results of copper sequential extraction were varied within and between the profiles (Table 3) and the share of each copper fraction in the total copper content in each genetic horizons of the investigated profiles can be ordered as follow:

Ap- FV> FVI> FIII> FIV> FVII> FII> FI

Eet- FVI> FV> FIV> FVII > FII> FIII> FI

Bt- FVI> FVII> FIV> FV> FII> FIII> FI

C- FVII> FVI> FIV> FV> FII> FIII> FI

Fraction V, composed of forms associated with organic matter, dominates in the humus horizons, and especially in Ap horizon of P4 profile, the closest to the emitter, where it equalled 44.52% of the average total Cu content. However, P2 profile was an exception in that its Ap horizon *did* contain a high amount of fraction V but the dominant form of copper was fraction IV, i.e. forms related to manganese oxides. The lowest content of high mobility fractions (FI and FII) and the highest share of hardly soluble forms (FV and FVI) were observed in the humus horizons of the examined soils, which proves the low mobility of Cu in the surface horizons – a desirable characteristic when soils are used for agricultural purposes. Similar results for soils from the environs of a copper smelter were obtained by ROSADA (2008), who confirms the predominant role of organic matter in association of Cu in surface samples, mostly in soils with silt texture. This author demonstrated a 5-fold higher content of Cu in fraction III (forms related to carbonates) in Ap horizons of soil profiles than in deeper horizons, a finding attributable to routine liming of fields, which was recommended as the simplest method of soil reclamation to be carried out during peak emission of dust from copper works (ROSADA 2008). In the deeper genetic horizons of the investigated soils, the highest content of Cu forms associated to iron oxides was observed. In Eet and Bt horizons, the Cu forms related to

amorphous iron oxides (FV) and crystalline iron oxides (FIV) make 3.97% and 26.38% of the average total Cu content, respectively, and in the parent horizon, where Cu forms related to crystal iron oxides (FVI) were dominant, it equalled 28.53% of the average total Cu content. In the bedrock horizons of the analyzed soils, the average percentage of Cu related to fractions of the highest mobility (FI – 8.30% and FII – 10.16%) is 4-fold higher than in the average total Cu content in the humus horizons (FI – 1.95% and FII – 2.55%), which may indicate copper release from the bedrock to higher horizons, where it is bound by clay minerals (Bt) and organic substance (Ap).

The total Zn content in the investigated soil profiles ranged from 3.34 to 42.65 mg kg^{-1} (Table 4). The highest total Zn content was observed in Ap horizons of P1 and P4 profiles, which may be related to the fact that organic matter forms fairy stable associations with zinc (Kabata-Pendias, Pendias 2001), and in Bt horizons of P2 and P3 profiles, which may be attributed to the well-developed illuvial horizon and progressing illuvial process. Highly significant statistical correlation was found between the total content of Zn and C-org. content in the soils (0.96 p=0.0500). Simultaneously, the eluvial horizons were the poorest in total Zn. The role of pH is very significant for Zn sorption by organic substance, optimal pH is 5.8 (Kabata-Pendias et. al. 1993). Acidification usually favours the weathering of minerals and accumulation of their products in a soil profile (Allen, Fanning 1983, Dudka 1992, Gondek 2010). In the analyzed soil profiles, such a low value of pH was observed only in Bt horizon of P1 profile and it does not confirm the above dependences. The indicator of Zn distribution is >1 for surface profiles P1, P2 and P4, which indicates its anthropogenic accumulation. It was only in P3 profile that this value was <1 (0.76), proving its lithogenic character. In the conducted sequential analysis, the following order of the shares of Zn fractions in relation to the average total Zn content was observed (Table 4):

Ap- FVII> FVI> FIII> FIV> FV> FII> FI

Eet- FVII> FVI> FIII> FV > FIV> FII> FI

Bt- FVII> FVI> FIII> FV> FIV> FII> FI

C- FVII> FV> FIII> FVI> FIV> FII> FI

In all the genetic horizons of the profiles, forms of zinc related to crystalline iron oxides (FVI) and to amorphous iron oxides (FV) were clearly dominant. Such high levels of Zn in the least mobile forms indicate a significant tendency to Zn occlusion by soil mineral oxides (Rosada 2008). Moreover, in soils with low pH, a particularly significant content of mobile and easily absorbed forms of heavy metals was observed on iron oxides (Karczewska 2002). The relatively high pH of the investigated soils (pH_{KCl} 5.81--7.75) led to a very low content of labile Zn fractions (soluble in water and exchangeable) in all the genetic horizons of the soils. The content of Zn in these forms did not exceed 5% of its total content. The fractions related to organic matter (FIV) varied in the range of 0.56-2.26 mg kg^{-1} and the highest values were observed in Ap horizons (except P2 profile). The content of

Table 4

The total content of Zn and metal fractions

Profile Horizon	Zn total (mg kg^{-1})	F I	F II	F III	F IV	F V	F VI	F VII
		(mg kg^{-1})						
P1 Wierzchowice								
Ap	42.65	0.31	1.48	5.86	2.63	2.18	7.02	9.61
Eet	22.60	0.66	0.64	1.11	1.39	1.88	2.68	5.88
Bt	25.49	0.43	0.66	0.73	1.17	1.69	1.93	5.60
C	3.73	0.16	0.32	0.53	0.75	0.83	0.64	1.04
C1	28.26	0.48	0.57	1.32	1.14	1.48	1.00	4.38
P2 Modła								
Ap	15.91	0.67	0.30	2.45	1.05	1.43	2.63	5.32
Eet	13.43	0.69	0.41	1.65	0.96	1.30	2.11	4.44
Bt	22.63	0.62	0.36	2.04	0.84	1.90	1.02	4.68
C	15.18	0.13	0.49	1.52	0.81	2.28	0.73	4.53
P3 Kurowice								
Ap	15.75	0.31	0.33	3.34	2.10	2.04	4.12	6.41
Eet	6.21	0.18	0.39	1.29	0.76	1.24	1.36	3.05
Bt	22.39	0.33	0.46	2.12	1.09	1.47	4.93	6.72
C	20.85	0.11	0.33	1.64	0.68	1.29	1.91	4.75
P4 Nielubia								
Ap	41.71	0.41	0.70	7.69	2.75	2.66	6.63	9.04
Eet	41.56	0.30	0.48	4.45	2.12	2.07	4.63	7.75
Bt	3.34	0.27	0.41	0.72	0.79	0.56	0.68	0.96
C	24.96	0.49	0.41	1.60	1.07	1.46	1.93	4.21

Key: cf. Table 3. p.d - below detection limit

Zn in the organically bound fraction (IV) was significantly lower than the content of Cu related to fraction IV. The results suggest lower affinity of Zn than Cu to soil organic substances (Kabata-Pendias, Pendias 2001). Furthermore, similarly to Cu, the Zn content in fraction II (forms related to carbonates) was three-fold higher in the humus horizons of the soils. This fraction makes 16.67% of the total Zn content, and its share is comparable to the forms related to amorphous iron oxides in these horizons. Similar results on Zn fractions in soils from the surroundings of a copper smelter are given by Rosada (2008) and Karczewska (2002), which indicates the predominance of Zn in most stable fractions, related to crystalline iron oxides.

CONCLUSIONS

1. The total content of Cu in Ap horizons of the analyzed soil profiles in the vicinity of the copper works was significantly higher than its total content in the bedrock horizon, which was confirmed by the values of the profile arrangement of Cu indicator (>1) and indicates the anthropogenic origin of copper in the soil.

2. In the sequential analysis, Cu forms related to organic matter were dominant among all forms of Cu in Ap horizons, which confirms high affinity of this metal to organic matter. In other soil horizons, the forms of Cu associated iron oxides dominate, which – along with the small share of Cu lower mobility fractions, may indicate low mobility of Cu in the investigated soils. This finding is ecologically advantageous.

3. The highest total Zn content in the investigated soils was observed in the humus horizons. However, it was only a little higher than the content of this metal in the bedrock, which indicates small enrichment of the investigated soils with this element due to human activity.

4. The dominant fraction of Zn in the investigated soils contained forms related to crystalline iron oxides, while smaller amounts of hardly soluble and exchangeable forms, which suggests low mobility of Zn in the soils.

5. Statistical analysis of the results showed significant correlation between the total content of zinc and organic carbon in the surface horizons of the soils.

6. Generally, no negative effect was observed of the Głogów Copper Works on the Cu and Zn content in arable soils in the vicinity of the plant. Thus, the analyzed soils can be used as farmland. However, a slightly higher total Cu content in P4 profile, in the closest proximity of the copper smelter, indicates that these soils should be monitored.

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