Polish J. of Environ. Stud. Vol. 18, No. 4 (2009), 645-650

Original Research

The Influence of Mineral Fertilization on Heavy Metal Fraction Contents in Soil. Part II: Copper and Nickel

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Received: 23 April 2008
Accepted: 3 March 2009

Abstract

The aim of our study was to estimate the influence of mineral fertilization on the contents of various copper and nickel forms in soil. It was based upon a field experiment made up of ten plots. In average soil samples taken in 2002-04, the pseudo-total copper and nickel content was determined. Chemical forms of these metals, by modified BCR method, were also determined.

The nickel content in particular fractions can be arranged quantitatively (average values) in order as follows: F2 (21%) > F3 (18%) > F1 (8%), in the case of copper: F2 (37%)>F3 (14%)>F1 (11%). The accumulation of nickel in the soil during the experiment was not observed. Whereas slight copper accumulation in some plots (with Polifoska 6, Polimag 305, calcium sulfate tetraurea and phosphogypsum) was noted. During the experiment the most mobile nickel and copper forms (soluble + exchangeable fraction) increased.

Keywords: copper fractions, nickel fractions, soil, mineral fertilization, BCR method

Introduction

Heavy metal contamination of arable land is mainly related to atmospheric deposition of industrial dust [1] as well as the application of biosolids and mineral fertilizers (especially containing phosphorus) [2-4]. Fertilization can lead to heavy metal accumulation and fractional composition changes in the soil. The influence of fertilization with mixed fertilizers on fractional composition of heavy metals in the soil, including copper and nickel, is examined to a small degree.

Copper is essential for proper plant growth and development. It participates in many physiological processes (e.g. photosynthetic electron transport, mitochondrial respiration, oxidative stress responses and cell wall metabolism) [5]. Excessive Cu amounts inhibit plant growth and impair important cellular processes (e.g. photosynthetic electron transport). Deficiency also negatively influences a plant's metabolism, affecting mostly young leaves and reproductive organs [6].

Nickel is essential only for some plant species. It forms the active metallocenter of the enzyme urease (EC 3.5.1.5.) in plants [7]. It's toxic at high concentrations [8]. Nickel inhibits a large number of plant enzymes, such as those of nitrogen metabolism [9] and sulphate assimilation [10].

The plant uptake of both elements is usually directly proportional to concentration in the soil. It was found, that copper from anthropogenic sources is more available, as compared to Cu from natural sources.

The aim of our study was to evaluate changes (after application of mineral fertilizers) in copper and nickel content in soil fractions during the three years of the experiment.

Table 1. Chemical composition of mineral fertilizers used in experiment.

Fertilizer	N	P	K	Mg	Zn	Cu	Pb	Ni	Cd
	$g \cdot kg^{-1}$				$mg \cdot kg^{-1}$				
Urea	460	-	-	-	-	-	-	-	-
Agrecol	-	96	266	-	-	-	-	-	-
Polifoska 6	60	87	250	-	31.2	1.7	1.19	38.0	3.12
Polifoska 8	80	105	200	-	159.3	3.9	2.45	35.1	16.17
Polifoska B	80	48	200	-	87.2	2.8	2.11	33.0	11.40
Polimag 305	50	70	200	48	28.5	2.8	1.50	97.0	1.61
Polimag 405	50	44	166	36	36.4	1.3	1.59	295.1	1.22
Calcium sulfate tetraurea	280	2	-	-	3.3	1.9	3.81	1.5	2.19
Granulate	61	21	108	6	560.0	217.0	89.97	26.0	1.13
Chloride potassium salt	-	-	498	-	436.0	9.3	1.17	0.4	0.01
Phosphogypsum	-	6	-	-	9.2	5.5	11.03	4.3	6.10
Salmag	-	275	-	24	153.4	2.5	0.07	0.6	0.09
Triple superphosphate	-	201	-	-	16.1	21.6	0.04	6.5	4.82

Experimental Procedures

The description of the experiment is presented in the first part of our paper [11] . Pseudo-total content of copper and nickel was determined in mean samples (after previous digestion in 30% H_2O_2 with 1:1 HCl addition). Modified BCR method [12] was used to describe fractional composition of the studied metals in each sample.

Extraction included three stages: 1 g of the soil was weighed and placed in a centrifuging tube, then subjected to sequential extraction according to the scheme:

F1 – soluble + exchangeable fraction using 0.11 mol · dm^{-3} CH_3COOH in a ratio of 1:40 (m/V),

F2 – metals bonded to iron and manganese oxides using 0.5 mol · dm^{-3} $NH_2OH \cdot HCl$ in a ratio of 1:40 (m/V),

F3 – metals bonded to organic matter applying 8.8 mol · dm^{-3} H_2O_2 in a ratio of 1:10 (m/V),

and then (after evaporation) using 1 mol·dm^{-3} CH_3COONH_4 in a ratio of 1:50 (m/V), pH 2.

The mixture was centrifuged after every stage and extracts were stored until analysis at 4ºC. All determinations were made by means of GFAAS technique using a Varian AA100 apparatus. Certified Reference Material (CRM023-050, Sandy Loam) from the Resource Technology Corporation was used for the validation of pseudo-total metal content.

The urea, Polifoska 6, Polifoska 8, Polifoska B, Polimag 305, Polimag 405, chloride potassium salt, triple superphosphate and phosphogypsum came from the ZCh “Police” S.A. chemical plant. The granulate was produced by the Instytut Chemicznej Przeróbki Węgla (Institute for Chemical Processing of Coal) in Zabrze. It consisted of about 70% sewage sludge and about 30% potassium nitrate (KNO_3). The calcium sulphate tetraurea was produced by Instytut Nawozów Sztucznych (Fertilizers Research Institute) in Puławy. It was prepared by grinding a stoichiometric mixture of urea and calcium sulfate.

The Salmag came from Zakłady Azotowe Kędzierzyn S.A. (Nitrogen Works Kędzierzyn) and Agrecol from AGRECOL Sp. z o.o. in Wieruszów.

Copper and nickel contents in fractions were statistically processed applying three-factor variance analysis and differences were evaluated by Tukey’s test. Sorption capacity was evaluated by means of Kappen’s method, pH in 1 mol · dm^{-3} KCl – potentiometrically and organic carbon content – using a ThermoEuroglas TOC 1200 apparatus.

Table 1 lists the contents of general nutrients and some heavy metals in mineral fertilizers applied.

Results and Discussion

In all objects, pseudo-total copper and nickel content (Table 2) was within the range for agricultural soils [13].

The accumulation of nickel in soil during the experiment was not observed. Similar results were obtained by Bartl et al. [14] in their six-year experiment. Authors didn’t observe nickel accumulation in the soil fertilized with mineral fertilizers.

In the case of copper, slight accumulation was noted in some objects, as compared to the control. Such accumulation was caused by neighbouring car exchange rather than applied fertilizers. This pertains to objects fertilized with Polifoska 6, Polimag 305, calcium sulfate tetraurea and phosphogypsum.

Table 2. Pseudo-total Cu and Ni content (mg·kg^{-1} DM), pH (in 1 mol·dm^{-3} KCl), organic matter content (%) and CEC (mmol(+)·kg^{-1}) in soil.

object	pseudo-total Cu			pseudo-total Ni			pH			organic matter			CEC		
	2002	2003	2004	2002	2003	2004	2002	2003	2004	2002	2003	2004	2002	2003	2004
1	9.9	12.7	11.2	13.0	9.2	10.2	7.49	7.44	7.47	2.48	2.51	2.53	46.6	45.8	46.8
2	10.6	13.1	11.9	17.1	11.6	10.8	7.48	7.42	7.43	2.96	2.94	3.11	48.8	47.6	49.1
3	9.6	12.9	12.0	17.8	10.9	10.5	7.48	7.43	7.47	3.06	2.85	3.32	46.8	46.5	46.3
4	10.3	9.3	10.9	16.3	9.9	11.0	7.49	7.44	7.44	3.04	2.94	3.13	46.1	47.6	46.5
5	9.6	10.0	9.1	15.8	10.6	10.3	7.53	7.39	7.45	3.10	2.98	3.24	48.8	47.7	49.0
6	9.6	11.8	11.8	14.8	9.1	9.3	7.49	7.47	7.42	2.92	2.67	2.93	47.9	47.5	47.9
7	10.2	11.0	9.1	19.2	11.1	12.4	7.60	7.46	7.44	3.02	2.93	3.16	48.4	47.1	47.9
8	10.4	11.6	13.9	14.4	11.8	11.4	7.49	7.46	7.37	2.39	2.70	2.58	48.7	48.2	48.9
9	12.0	10.0	12.2	18.5	11.0	12.6	7.48	7.38	7.47	2.19	2.25	2.37	48.9	49.8	49.8
10	10.0	12.2	14.0	17.0	9.2	13.5	7.52	7.34	7.37	2.05	2.01	2.16	48.7	46.9	48.8

As compared to years 2002 and 2004, elevated copper content in some objects in 2003 occurred probably due to the intensified car exchange activity or errors associated with the analytical phase.

The highest nickel level was observed in 2002. In 2003 content decrease occurred, due to the metal shifting from residual fraction into the mobile fractions, especially to the first fraction (exchangeable). Soil microbiological activity was the cause of such redistribution. Because of that, part of the metal was leached deep into the soil profile. The large nickel content increase in object with phosphogypsum, in 2004 as compared to 2003, occurred due to errors in the analytical phase.

pH values, organic matter content and sorption capacity in soil samples during the experiment are described in part I of the paper [11].

Copper

The content of mobile copper forms was significantly differentiated by applied fertilization (Table 3). The highest amount was found in objects with Polifoska B (23.7%), and the lowest amount in control object (19%). Copper mobility decrease was noted in all objects. Only in four objects (with Polifoska 6, Polimag 305, calcium sulfate tetraurea and phosphogypsum) was decrease greater than in the control object.

The significant differences of copper content in soil samples in the particular years were stated. The decrease of the mobile pool of this metal was observed during the experiment. The highest copper content was in the year 2002 (27.2% on an average). The least amount of copper (16.6 %) was observed after the third year. It was significantly less compared to the first year of the experiment. Jakubus et al. [15] investigating the long-term influence of mineral fertilization on the trace metal fractions in the soil, has stated increased easily soluble copper fraction percentages in the total content. Results obtained by Gondek [16] in the three-year experiment were different. He studied the content of soluble copper forms, extracted with hydrochloric acid (conc. 1 mol · dm^{-3}), in soil fertilized with mineral fertilizers. After three years the mobile copper pool was on the similar level as in the first year of the experiment.

The copper content in fractions, during the experiment, was significantly differentiated. Fraction F2 contained the least amount of Copper (10.6%).The highest copper amount (37.4% on an average) was in fraction F2 (Fe/Mn oxides). This is the result of low solubility of copper oxides and hydroxides as well as relatively high solubility of copper carbonates. The Cu^{2+} ion is the most strongly adsorbed of all the divalent transition and heavy metals on Fe/Al oxides and oxyhydroxides [17]. Even stronger Cu^{2+} is specifically adsorbed on Mn oxides [18].

Agbenin et al. [19] obtained similar results studying dynamics of copper fractions and its solubility in savanna soil fertilized for 50 years with mineral fertilizers. Copper bounded with amorphous Fe/Mn oxides, Mn oxides and crystalline Fe oxides in the top layer of soil (0-20cm) constituted 40.4% of total content. The least copper amount was noted in a water-soluble fraction, only 1.2%.

Laboratory studies on the influence of mineral fertilization (N, P, K) on fractional copper content in red soil were carried out by Tu et al. [20]. Application of urea (200 mg N kg^{-1}) significantly decreased the soluble plus exchangeable fraction, but increased the specifically adsorbed and/or Fe/Mn oxides bound. Supply of 80 mg P kg^{-1} caused a decrease in the soluble plus exchangeable fraction, and a rise in the specifically adsorbed fraction of Cu. The addition of 100 mg K kg^{-1} led to an increase in the soluble plus exchangeable fraction, while a decrease in the specifically adsorbed and/or Fe/Mn oxides bound fraction. Applying chemical fertilizers had no significant influence on the other copper fractions. Authors suggest that in soil contaminated with heavy metals, applying fertilizers does not only provide plants with nutrients, but may also act to change the speciations and thus bioavailability of heavy metals.

Table 3. Copper fractions (% of pseudo-total Cu) in studied soil.

object	2002			2003			2004			$\bar{x}$ B·C			$\bar{x}$ C
	F1	F2	F3	F1	F2	F3	F1	F2	F3	F1	F2	F3	
1	5.3	38.5	34.8	9.2	33.1	2.4	11.6	34.5	1.8	8.7	35.4	13.0	19.0
2	5.3	37.4	34.0	12.4	34.3	2.9	13.6	32.7	2.7	10.4	34.8	13.2	19.5
3	6.2	42.7	36.6	9.7	34.6	2.1	13.5	30.1	3.0	9.8	35.8	13.9	19.8
4	4.8	36.4	35.3	14.7	49.2	3.3	15.4	34.3	2.3	11.6	40.0	13.6	21.7
5	4.7	44.0	39.2	13.4	45.5	2.9	17.7	40.8	5.0	11.9	43.4	15.7	23.7
6	6.5	41.7	38.3	12.8	37.6	2.0	13.7	31.6	3.1	11.0	37.0	14.5	20.8
7	5.3	40.0	37.4	12.5	41.1	2.3	17.5	42.0	2.2	11.8	41.0	14.0	22.3
8	5.5	41.1	36.4	13.4	37.5	2.4	11.7	24.5	1.4	10.2	34.4	13.4	19.3
9	5.5	35.1	32.6	13.8	44.7	4.7	13.6	32.5	3.0	11.0	37.4	13.4	20.6
10	5.5	41.4	38.8	11.8	37.1	3.4	12.5	26.5	1.9	9.9	35.0	14.7	19.9
$\bar{x}$ A·B	5.5	39.8	36.3	12.4	39.5	2.8	14.1	33.0	2.6				
	$\bar{x}$ A1 27.2			$\bar{x}$ A2 18.2			$\bar{x}$ A3 16.6						
	$\bar{x}$ B1 10.6			$\bar{x}$ B2 37.4			$\bar{x}$ B3 13.9						

1-control; 2-urea (65 kg·ha^{-1})+64 kg·ha^{-1} P_2O_5 (Agrecol)+94 kg·ha^{-1} K_2O (Agrecol); 3-polifoska 6 (500 kg·ha^{-1}); 4-polifoska 8 (375 kg·ha^{-1}) 5-polifoska B (375 kg·ha^{-1}); 6-polimag 305 (600 kg·ha^{-1}); 7-polimag 405 (600 kg·ha^{-1}); 8-calcium sulfate tetraurea (112 kg·ha^{-1}) +64 kg·ha^{-1} P_2O_5 (Agrecol)+ 94 kg·ha^{-1} K_2O (Agrecol); 9-granulate (430 kg·ha^{-1})+84 kg·ha^{-1} K_2O (potassium salt); 10-phosphogypsum (3,500kg·ha^{-1})+ 30 kg·ha^{-1} N (salmag) + 96 kg·ha^{-1} K_2O (potassium salt) + 40 kg·ha^{-1} P_2O_5 (triple superphosphate).

LSD – α = 0.05 α*=0.01

A – years	1.44	A·B	3.35
B – fractions	1.44	A·C	7.08
C – fertilization	3.61	B·C	not significant

Table 4. Nickel fractions (% of pseudo-total Ni) in studied soil.

object	2002			2003			2004			$\bar{x}$ B·C			$\bar{x}$ C
	F1	F2	F3	F1	F2	F3	F1	F2	F3	F1	F2	F3	
1	6.6	13.2	24.4	12.1	25.0	22.0	7.4	28.2	15.3	8.7	22.1	20.6	17.1
2	5.2	10.8	19.9	11.0	24.8	18.2	7.2	27.9	14.2	7.8	21.2	17.4	15.5
3	4.1	11.1	18.2	13.1	24.9	20.0	6.2	31.1	12.0	7.8	22.4	16.7	15.6
4	4.2	9.2	19.3	17.2	25.8	22.0	5.1	28.2	10.2	8.8	21.1	17.2	15.7
5	5.5	11.3	21.1	15.9	27.4	20.4	7.0	34.3	11.2	9.5	24.3	17.6	17.1
6	5.6	9.1	21.3	13.7	24.9	26.0	7.4	35.4	16.8	8.9	23.1	21.4	17.8
7	3.4	8.4	16.5	10.7	22.2	20.2	6.1	24.3	11.7	6.7	18.3	16.1	13.7
8	5.1	10.9	21.5	11.5	18.4	20.8	6.3	28.4	8.9	7.6	19.2	17.1	14.6
9	4.5	6.7	16.6	12.3	22.5	21.8	5.9	24.2	9.3	7.6	17.8	15.9	13.8
10	4.7	9.2	18.7	11.9	24.8	22.9	6.0	24.0	8.9	7.5	19.3	16.8	14.6
$\bar{x}$ A·B	4.9	10.0	19.8	12.9	24.1	21.4	6.5	28.6	11.9				
	$\bar{x}$ A1 11.5			$\bar{x}$ A2 19.5			$\bar{x}$ A3 15.6						
	$\bar{x}$ B1 8.1			$\bar{x}$ B2 20.9			$\bar{x}$ B3 17.7						

1-control; 2-urea (65 kg·ha^{-1})+64 kg·ha^{-1} P_2O_5 (Agrecol)+94 kg·ha^{-1} K_2O (Agrecol); 3-polifoska 6 (500 kg·ha^{-1}); 4-polifoska 8 (375 kg·ha^{-1}) 5-polifoska B (375 kg·ha^{-1}); 6-polimag 305 (600 kg·ha^{-1}); 7-polimag 405 (600 kg·ha^{-1}); 8-calcium sulfate tetraurea (112 kg·ha^{-1}) +64 kg·ha^{-1} P_2O_5 (Agrecol)+ 94 kg·ha^{-1} K_2O (Agrecol); 9-granulate (430 kg·ha^{-1})+84 kg·ha^{-1} K_2O (potassium salt); 10-phosphogypsum (3,500kg·ha^{-1})+ 30 kg·ha^{-1} N (salmag) + 96 kg·ha^{-1} K_2O (potassium salt) + 40 kg·ha^{-1} P_2O_5 (triple superphosphate).

LSD – α = 0.05 α*=0.01

A – years	1.06	A·B	2.48
B – fractions	1.06	A·C	5.25*
C – fertilization	2.67	B·C	not significant

Redistribution of the studied metal from the fraction bound with organic matter (F3) directly into exchangeable fraction (F1) was observed after the second year. This is confirmed by similar average copper levels in fraction F2 during the whole experiment. It was caused by soil microbiological activity. This thesis is confirmed by investigations by Inaba and Takenaka [21], who studied the influence of forest soil microbiological activity on the copper fractional composition changes. During their experiment, which lasted three months, authors stated part of the copper shifting from residual fraction into carbonate fraction. According to the authors, soil microorganism activity was the cause of releasing part of the metal from residual fraction.

The copper content in fraction F1 (most mobile) increased during the experiment. This means that applied fertilization positively influenced the increase of bioavailability of this element.

Clear decrease of the copper mobile pool amount in 2003 and 2004 (mean values) during our investigations can be connected with redistribution part of the copper from fraction F3 into F1. As a result, some of the metal was leached and part of it was uptaken by plants.

Nickel

The content of mobile nickel forms was also significantly differentiated by applied fertilization. Fertilization with Polimag 305 and Polimag 405 influenced the most nickel mobility increase during the experiment. It can be connected with the high nickel content in above-mentioned fertilizers, as compared to other fertilizers used in the experiment.

The average nickel content in particular years, like in the case of copper, was significantly differentiated. After the first two years of experiment the metal content increased and after the third year decreased, but to a higher level than in 2002. Zhao et al. [22] obtained different results in a six-year experiment on Andisoil. According to the authors, the influence of mineral fertilization on the nickel fractional composition in the soil was not significant.

Most of the nickel during the experiment, 20.9% on average, was noted in fractions bound with Fe/Mn oxides. The least amount of Ni (8.1%) was accumulated in fraction F1. The content in particular fractions was significantly differentiated. The average nickel content in fraction F2 increased during the experiment, as a result of shifting some of the metal from fraction F3 into F1.

This fact confirms the thesis that nickel affinity to manganese and iron oxides is lower than in the case of copper [14]. Copper content in fraction F2 remained all the time almost at the same level. This means that this fraction already after the first year of experiment accumulated the maximum metal amount.

The influence of mineral fertilization on the fractional composition of heavy metals in contaminated soil (from the galvanizing plant area) in the laboratory study, was investigated by Liu et al. [23]. After four months of soil fertilization with urea, authors stated the highest nickel level (30.0% of total content), similar to our experiment, in the fraction bounded with Fe/Mn oxides. Fertilization with phosphorus (as KH_2PO_4) and potassium (as KCl) caused nickel content to decrease in discussed fraction.

In 2002 nickel had the largest summary content in the control object (44.2%). It's rather the result of a low total nickel content in this object, than influence of fertilization on the mobile metal pool amount in other objects. A similar situation occurred in 2004, in an object with Polimag 305.

The nickel content in fraction F1, similarly to copper, increased during the experiment in all objects. This of course means an increase of bioavailability of this element.

In the year 2003, as compared to the first year of our experiment, a significant nickel mobility increase occurred. This is the result of total metal content decrease, as stated before. Decrease of mobile metal pool amount in the year 2004 occurred due to plant uptake, leaching and organic matter decomposition (nickel has shifted to fractions F2 and F1).

Conclusions

1. The accumulation of nickel in the soil was not observed, while slight copper accumulation in some objects (with Polifoska 6, Polimag 305, calcium sulfate tetraurea and phosphogypsum) was noted.
2. Mineral fertilization significantly influenced the content of nickel and copper mobile forms in the soil.
3. The nickel content (mean values) in particular fractions can be arranged quantitatively in a sequence: F2 (21%) > F3 (18%) > F1 (8%), in the case of copper: F2 (37%) >F3 (14%) > F1 (11%).
4. The amount of most mobile nickel and copper forms (soluble + exchangeable fraction) increased during the experiment.

Acknowledgements

Our investigations were subsidized with statutory project No. S/JJŚ/24/08.

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