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ORIGINAL PAPER

CONTENT OF ORGANIC CARBON, TOTAL NITROGEN AND AVAILABLE FORMS OF MACRONUTRIENTS IN SOIL CONTAMINATED WITH COBALT*

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ABSTRACT

Cobalt plays a special role in living organisms. However, it becomes harmful to their growth after its concentration exceeds an acceptable level. The aim of this study was to determine the effect of increasing levels of cobalt in soil (0, 20, 40, 80, 160, 320 mg kg⁻¹ d.m. of soil) following the application of neutralising substances on the content of C_{org}, total-N and available forms of P, K and Mg in soil. The neutralising substances applied in the experiment included manure, loam, charcoal, zeolite at 2% of the soil weight, and calcium oxide at a dose corresponding to one unit of HAC. The same levels of materials were also applied to the soil. Spring barley was the main crop, and white mustard was the successive crop. Applying both increasing levels of cobalt and neutralising substances to soil had a significant effect on the content of C_{org}, the macronutrients under study and the C:N ratio in soil. Increasing levels of cobalt in the series with no neutralising substances increased the content of C_{org} and available K, widened the C:N ratio and reduced the content of total-N in soil. Among the neutralising substances under study, charcoal increased the content of C_{org} and widened the C:N ratio the most and, in the case of total-N, the greatest and negative effect was caused by calcium oxide. The addition of manure to soil increased the content of available P, K and Mg the most. Among the other neutralising substances, zeolite had the greatest effect, as it reduced the content of C_{org}, available P, K and Mg and reduced the C:N ratio in soil. A similar effect of charcoal on the content of total-N and P and of calcium oxide on the content of K was observed.

Keywords: cobalt, neutralizing substances, soil, organic carbon, total-N, C:N ratio, available elements.

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INTRODUCTION

Greatest amounts of cobalt are accumulated in igneous and sedimentary rocks, as well as in such minerals as: cobaltite, sphaerocobaltite, linneite and saphlorite (LUO et al. 2010). Weathering causes the release of a cobalt-to-soil solution as a divalent cation, with the highest availability to plants (SWARNALATHA et al. 2013). The content of cobalt in soil is also affected by other factors closely related to human activity. These include: mining metal ores, including those of cobalt, combustion of coal and oil or sludge (HUANG et al. 2013, SINGH, CAMEOTRA 2013, ZUPANČIČ, SKOBE 2014). Cobalt plays a special role in living organisms. However, it becomes harmful to their growth after its concentration exceeds an acceptable level. High concentrations of cobalt in soil have an effect on immobilisation or excessive release of other metals. This can be potentially harmful to plant growth, but also to humans and animals (LANGE et al. 2014). Therefore, it is important to seek for methods to reduce the cobalt content in soil when its concentrations are excessively high. Adding to soil different substances which have a positive effect on sorption capacity, e.g. compost, manure, zeolite, bentonite, loam, and charcoal or calcium oxides, contributes to limiting the uptake of many elements by plants (FENG et al. 2007). Detailed effects of cobalt on soil (with sources, forms, mobility, etc.) and the role of neutralising substances in ameliorating the effect of cobalt pollution on the soil properties were discussed in earlier publications (KOSIOREK, WYSZKOWSKI 2016*a,b*).

The aim of this study was to determine the effect of increasing levels of cobalt in soil following the application of neutralising substances on the content of organic carbon, total nitrogen and available forms of phosphorus, potassium and magnesium in soil (model studies).

MATERIAL AND METHODS

An experiment was conducted in a plant growing room at the University of Warmia and Mazury, Olsztyn, in polyethylene pots with a capacity of 9 kg of soil with the texture composition of loamy sand (sand fraction, 74%; silt fraction, 2%; clay fraction, 24%). The soil had the following properties: pH in 1 M KCl – 5.05; hydrolytic acidity – 28.40 mmol(+) kg⁻¹; total exchangeable bases – 46.50 mmol(+) kg⁻¹; cation exchange capacity – 74.90 mmol(+) kg⁻¹; saturation of the sorptive complex with alkaline cations – 68.08%, content of organic carbon – 12.15 g kg⁻¹, total nitrogen – 0.73 g kg⁻¹, available forms of: phosphorus – 40.99 mg kg⁻¹, potassium – 46.29 mg kg⁻¹ and magnesium – 116.21 mg kg⁻¹, total cobalt – 2.98 mg kg⁻¹ of soil. The soil was contaminated with increasing levels of cobalt (cobalt chloride) at 0, 20, 40, 80, 160 and 320 mg kg⁻¹ d.m. of soil. The neutralising substances applied in the experi-

ment included manure, loam, charcoal, zeolite at 2% of the soil weight, and calcium oxide at a level corresponding to one unit of hydrolytic acidity (HAC). The same levels of nutrients were also applied to the soil (100 mg N; 35 mg P; 100 mg K; 50 mg Mg; 0.33 mg B; 5 mg Mn and 5 mg Mo kg⁻¹ d.m. of soil). Spring barley (*Hordeum vulgare* L.), cultivar Mercada, was the main crop, and white mustard (*Synapis alba* L.), cultivar Bamberka, was the successive crop. Moisture content was maintained at 60% of the capillary water capacity during plant growth. Spring barley was harvested during the ear emergence stage (55 days after sowing) and white mustard was harvested during the flowering stage (37 days after sowing). The experiment was conducted with three replications.

Soil samples were collected after the successive crop was harvested and were then dried and sifted through a 1 mm mesh sieve. The following were determined in the samples: organic carbon – by the Tiurin method, total nitrogen – by the Kjeldahl method, available forms of: phosphorus and potassium – by the Egner-Riehm method, and magnesium (Mg) – by the Schachtschabel method. The properties of soil prior to the experiment were analyzed: pH – by the potentiometric method at 1 mole KCl dm⁻³, hydrolytic acidity (HAC) and the total exchangeable bases (TEB) – by the Kappen method. Cation exchange capacity (CEC) and base saturation (BS) were calculated from the formulas: CEC = TEB + HAC; BS = (TEB : CEC) 100. The results were processed statistically with a two-way analysis of variance (ANOVA) in a Statistica software package. The effect of contamination with cobalt and the impact of the neutralising substances on the soil properties under study were assessed by the principal component analysis (PCA) and with the Pearson's correlation coefficients.

RESULTS AND DISCUSSION

The experiment showed that applying both increasing levels of cobalt and substances which neutralise its harmful effect to soil had a significant effect on the content of organic carbon and the analysed macronutrients in the soil (Tables 1, 2). The content of organic carbon was higher and the content of total nitrogen was lower in the series with no neutralising substances in the soil contaminated with cobalt than in the control, although the changes were not linear and were not larger than about a dozen per cent. The organic carbon-to-total nitrogen ratio was wider in soil contaminated with cobalt. Increasing levels of cobalt increased the content of available potassium and they had a very small but significant effect on the content of available phosphorus and magnesium. The dose of 320 mg Co kg⁻¹ increased the content of available potassium by 119% compared to the control (no Co). The negative effect of cobalt on the uptake of phosphorus, potassium and magnesium from soil was confirmed by FAUCON et al. (2009). Studies by

Table 1

Effect of cobalt contamination and neutralising substances on the content of organic carbon, total nitrogen and C:N ratio in soil (SD for the average from a series)

Level of cobalt (mg kg ⁻¹ d.m. of soil)	Without added substances	Manure	Loam	Charcoal	Zeolite	Calcium oxide	Average
Organic carbon (g kg ⁻¹ d.m.)							
0	11.10	12.30	13.50	15.60	11.70	11.25	12.58
20	10.50	13.65	12.30	15.90	11.10	13.50	12.83
40	12.30	15.15	13.35	15.15	11.70	12.30	13.33
80	11.85	14.70	12.30	13.80	10.80	12.00	12.58
160	12.30	15.00	13.65	13.65	11.25	11.70	12.93
320	11.85	11.85	15.60	13.35	11.55	11.40	12.60
Average	11.65±0.71	13.78±1.42	13.45±1.21	14.58±1.10	11.35±0.36	12.03±0.82	12.80±0.29
<i>r</i>	0.435	-0.343	0.826**	-0.832**	0.059	-0.434	-0.243
LSD	a - 0.68**; b - 0.68**; a · b - 1.67**						
Total nitrogen (g kg ⁻¹ d.m.)							
0	0.82	0.65	0.71	0.65	1.03	0.78	0.77
20	0.71	0.76	0.64	0.58	1.01	0.77	0.75
40	0.71	0.80	0.68	0.63	0.85	0.39	0.68
80	0.68	0.69	0.78	0.62	0.77	0.36	0.65
160	0.80	0.69	0.82	0.64	0.73	0.62	0.72
320	0.72	0.64	0.67	0.63	0.76	0.65	0.68
average	0.74±0.06	0.71±0.06	0.72±0.07	0.63±0.02	0.86±0.13	0.60±0.18	0.71±0.05
<i>r</i>	-0.101	-0.516*	0.088	0.199	-0.713**	-0.017	-0.422
LSD	a - 0.05**; b - 0.05**; a · b - 0.12**						
C:N ratio							
0	13.54	18.92	19.01	24.00	11.36	14.42	16.88
20	14.79	17.96	19.22	27.41	10.99	17.53	17.98
40	17.32	18.94	19.63	24.05	13.76	31.54	20.87
80	17.43	21.30	15.77	22.26	14.03	33.33	20.69
160	15.38	21.74	16.65	21.33	15.41	18.87	18.23
320	16.46	18.52	23.28	21.19	15.20	17.54	18.70
Average	15.82±1.53	19.56±1.56	18.93±2.64	23.37±2.34	13.46±1.88	22.21±8.08	18.89±1.58
<i>r</i>	0.328	0.101	0.511*	-0.716**	0.774**	-0.176	0.039
LSD	a - 1.98**; b - 1.98**; a · b - 4.95**						

LSD for: a – cobalt level, b – kind of neutralising substance, a · b – interaction; significant at ** $P \leq 0.01$ * $P \leq 0.05$; *r* – correlation coefficient.

CAPPUYNS and MALLAERTS (2014) also found positive correlations between the content of cobalt and organic carbon in soil. On the other hand, GAD (2012) found that the content of nitrogen was increased by cobalt.

Table 2

Effect of cobalt contamination and neutralising substances on content of available phosphorus, potassium and magnesium in soil (SD for average from series)

Level of cobalt (mg kg ⁻¹ d.m. of soil)	Without added substances	Manure	Loam	Charcoal	Zeolite	Calcium oxide	Average
Available phosphorus (mg kg ⁻¹ d.m.)							
0	58.44	81.02	59.27	58.94	46.34	62.14	61.03
20	61.14	70.19	60.59	60.65	53.13	61.58	61.21
40	59.70	71.78	59.48	51.28	46.21	65.69	59.02
80	60.77	78.35	58.94	50.06	50.80	60.94	59.98
160	57.83	87.32	61.15	48.83	47.43	57.17	59.96
320	61.56	81.59	74.58	55.05	56.86	59.63	64.88
Average	59.91±1.52	78.38±6.45	62.34±6.06	54.14±4.88	50.13±4.28	61.19±2.83	61.01±2.06
<i>r</i>	0.309	0.524 ⁺	0.908 ^{**}	-0.295	0.652 ^{**}	-0.574 ⁺	0.736 ^{**}
LSD	a - 2.80 ^{**} ; b - 2.80 ^{**} ; a · b - 6.85 ^{**}						
Available potassium (mg kg ⁻¹ d.m.)							
0	43.24	122.96	42.25	53.20	30.49	35.66	54.63
20	46.36	131.59	42.87	64.15	31.34	34.94	58.54
40	53.73	141.94	53.74	69.38	31.64	43.41	65.64
80	84.32	161.98	65.95	93.05	43.47	45.05	82.30
160	89.11	193.46	80.39	109.56	49.10	79.62	100.21
320	94.51	201.75	112.12	121.78	65.56	81.07	112.80
Average	68.55±23.23	158.95±32.76	66.22±26.77	85.19±27.24	41.93±13.86	53.29±21.35	79.02±23.64
<i>r</i>	0.846 ^{**}	0.926 ^{**}	0.992 ^{**}	0.927 ^{**}	0.984 ^{**}	0.910 ^{**}	0.951 ^{**}
LSD	a - 2.70 ^{**} ; b - 2.70 ^{**} ; a · b - 6.24 ^{**}						
Available magnesium (mg kg ⁻¹ d.m.)							
0	124.96	134.48	127.69	128.46	124.34	125.50	127.57
20	126.81	133.07	129.96	126.08	125.12	125.56	127.77
40	126.28	134.81	129.32	126.09	124.11	126.14	127.79
80	124.82	135.80	127.91	126.26	125.73	125.46	127.66
160	125.77	136.78	127.34	127.12	127.30	123.93	128.04
320	130.27	136.70	128.75	127.20	128.00	125.21	129.36
Average	126.49±2.00	135.27±1.43	128.50±1.02	126.87±0.93	125.77±1.58	125.30±0.74	128.03±0.67
<i>r</i>	0.798 ^{**}	0.785 ^{**}	-0.143	0.091	0.922 ^{**}	-0.442	0.948 ^{**}
LSD	a - 1.08 [*] ; b - 1.08 [*] ; a · b - 2.66 ^{**}						

LSD for: a – cobalt level, b – kind of neutralising substance, a · b – interaction; significant at ^{**} $P \leq 0.01$ ^{*} $P \leq 0.05$; *r* – correlation coefficient.

Applying a neutralising substance to soil had a significant effect on the content of the elements under study and the organic carbon-to-total nitrogen ratio in soil (Tables 1, 2). Applying loam, manure and charcoal to soil had a

beneficial effect on the content of organic carbon, increasing its average content by 15%, 18% and 25%, respectively, and widening the C:N ratio considerably, compared to the series with no additives. Calcium oxide also widened the average C:N ratio in soil. Zeolite increased the average content of total nitrogen in soil. Manure had the greatest effect on the content of available forms of the elements under study, significantly increasing the content of phosphorus and potassium while slightly increasing the content of magnesium in soil. The increase was by 31%, 131% and 7%, respectively, compared to the series with no additives. Among the other neutralising substances, zeolite had the greatest and significant effect; it reduced the average content of available forms of phosphorus by 16% and that of potassium by 39%, and it narrowed down the C:N ratio in soil by 15%. A similar effect of charcoal on the content of total nitrogen and available phosphorus and of calcium oxide on the content of potassium was observed. Charcoal reduced the average content of total nitrogen by 15% and available phosphorus by 10%, and calcium oxide decreased the content of available potassium by 22% compared to the series with no additives in the soil.

The study found a significant relationship between the content of some elements and the C:N ratio, acidity and the sorption properties of soil, which was shown by the PCA (Figure 1) and the correlation coefficients (Table 3). The highest positive correlation coefficients were observed between:

- the available phosphorus and potassium and magnesium,
- potassium and magnesium,
- organic carbon and available phosphorus, potassium and magnesium,
- total nitrogen and soil pH.

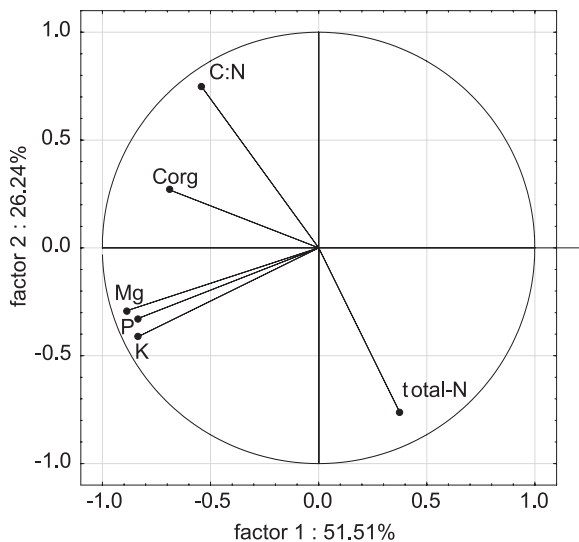


Fig. 1. Content of elements in the soil illustrated with the PCA method.

Vectors represent analysed variables (content of C_{org} , total-N, available P, K, Mg and C:N ratio)

Table 3

Correlation coefficients (*r*) between content of organic-C, total-N, C:N ratio and available forms of P, K and Mg and some properties of soil

Factor	C _{org}	Total-N	C:N ratio	Available		
				P	K	Mg
pH _{KCl}	-0.124	0.339**	0.063	0.166	-0.152	-0.084
HAC	0.056	-0.266*	-0.162	-0.106	0.207	0.121
TEB	-0.158	0.267*	0.158	0.075	-0.285*	-0.223
CEC	-0.192	0.253*	0.148	0.057	-0.302*	-0.253*
BS	-0.097	0.279*	0.136	0.099	-0.248*	-0.155
C _{org}		-0.206	0.534**	0.307**	0.442**	0.367**
Total-N			-0.654**	-0.053	-0.013	-0.205
C:N ratio				0.214	0.137	0.189
P					0.706**	0.779**
K						0.789**

pH_{KCl} – pH in 1M KCl, HAC – hydrolitic acidity, TEB – total exchangeable bases, CEC – cation exchange capacity, BS – base saturation; *n* = 108, significant at ** $P \leq 0.01$ * $P \leq 0.05$; *r* – correlation coefficient;

pH_{KCl}, HAC, TEB, CEC and BS were earlier published (KOSIOREK, WYSZKOWSKI 2016b).

A negative correlation was found to exist between the content of total nitrogen and the C:N ratio (Table 3).

The relationships between the soil properties under study, especially between the content of available phosphorus, potassium and magnesium, were confirmed by a PCA analysis (Figure 1). It must be stressed that the content of available phosphorus, potassium and magnesium, as well as the C:N ratio, were reproduced very well on the vectors, while the content of total nitrogen and organic carbon was not. The principal components represented 77.75%, with the first component responsible for 51.51% and the second one - for 26.24%. A greater effect of manure and zeolite than the other substances on the soil properties under study was confirmed (Figure 2).

According to TARNOCAI et al. (2009), the content of carbon is closely related to the presence of organic matter in soil, which also explains the significant increase in the content of organic carbon in soil following the application of charcoal, manure and loam, as observed in this study. Manure has been found (GLISIC et al. (2009) to increase the content of humus in soil. The C:N ratio plays an important role in the immobilisation of nutrients in soil (WYSZKOWSKI, WYSZKOWSKA 2009, WYSZKOWSKA et al. 2013) and their absorption by plants, as well as the regulation of process of releasing toxic forms of metals into soil (VAN-CAMP et al. 2004). An excessively wide C:N ratio can result in a deficit of nitrogen available to plants because if the content of this element in organic matter is too low, microorganisms will absorb considerable amounts of it from the soil solution. OSTROWSKA et al. (1991) found that

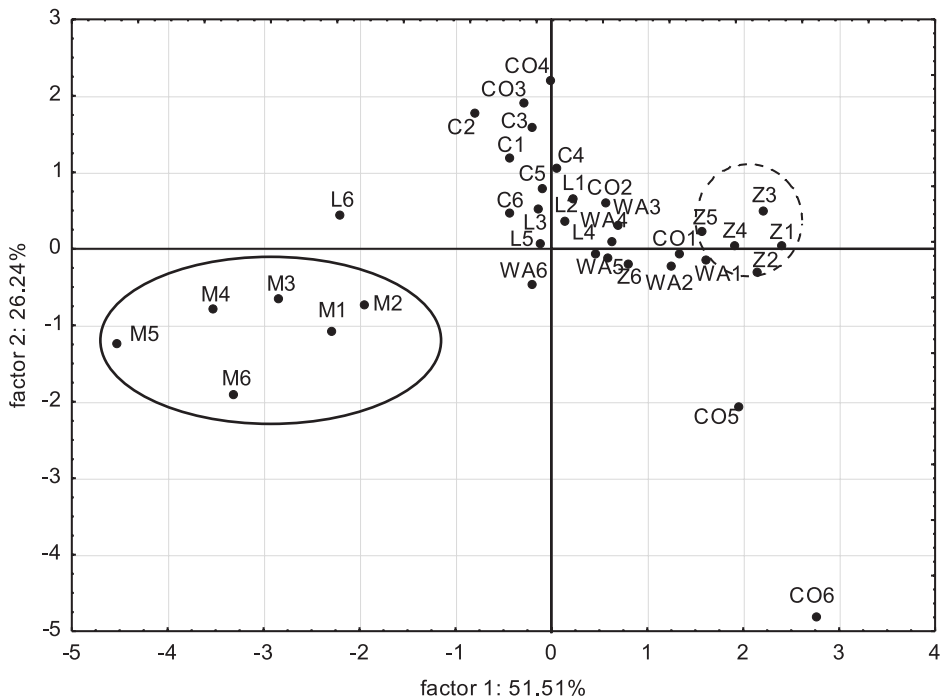


Fig. 2. Effect of neutralising substances on the content of macroelements and C:N ratio in the soil illustrated with the PCA method. Points show soil samples with macroelements and C:N ratio: WA – without added substances, M – manure, L – loam, C – charcoal, Z – zeolite, CO – calcium oxide; 1 – 0, 2 – 20 mg, 3 – 40 mg, 4 – 80 mg, 5 – 160 mg, 6 – 320 mg Co kg⁻¹ d.m. of soil

if the C:N ratio in arable soil is lower than 10, intensive humification and mineralisation of organic matter takes place, whereas if it is higher than 30, the intensity of biological processes decreases significantly, which indicates high accumulation. According to TSAI et al. (2012), the application of manure also significantly increases the content of macronutrients in soil. This was confirmed by SIENKIEWICZ et al. (2009), who observed an increase in available forms of potassium, calcium and magnesium following the application of manure.

An increase in the soil pH following the application of manure (KOSIOREK, WYSZKOWSKI 2016a) raised the content of available macronutrients in soil. AGBENIN (2002) found that fertilisation of soil with manure or nitrogen, phosphorus and potassium reduced the content of cobalt by 0.8 to 1.1 g Co m⁻² of soil. MICÓ et al. (2008) showed that a large content of calcium in soil significantly reduces the uptake of phosphorus by barley. According to DE SCHAMPHELAERE and JANSSEN (2002) as well as HEIJERICK et al. (2002), Ca²⁺ ions in the soil solution compete with Co²⁺ ions for a binding site, which significantly reduces cobalt toxicity to plants. Adding zeolite to soil either increases the availability of potassium to plants (JAYASINGHE et al. 2010) or

does not have any effect on available phosphorus, potassium and magnesium in soil (WYSZKOWSKI, SIVITSKAYA 2012), which is a consequence of special ion-exchange properties of the substance. The large extent of potassium release from a zeolite network to the soil solution was shown by TREACY and HIGGINS (2001), who observed a decrease in the available potassium content in soil with zeolite previously absorbed by plants.

CONCLUSIONS

1. Increasing levels of cobalt in the series with no neutralising substances increased the content of organic carbon and available potassium, widened the C:N ratio and reduced the content of total nitrogen in soil.

2. Among the neutralising substances under study, charcoal increased the content of organic carbon and widened the C:N ratio the most, whereas the strongest and negative effect on total nitrogen was caused by calcium oxide.

3. The addition of manure to soil increased the content of available phosphorus, potassium and magnesium the most.

4. Among the other neutralising substances, zeolite had the greatest effect, as it reduced the content of organic carbon, available phosphorus, potassium and magnesium and reduced the C:N ratio in soil. A similar effect of charcoal on the content of total nitrogen and phosphorus and of calcium oxide on the content of potassium was observed.

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