Macroelement content in plants after amendment application to cobalt-contaminated soil

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Abstract

Aim The study was undertaken to determine the effect of amendments used in remediation of cobalt-contaminated soil on the macroelement content of all organs of spring barley (the main crop) and white mustard (the after-crop).

Methods In the experiment, six blocks were selected: without amendments; with manure (bovine, granulated); clay; charcoal; zeolite; and with calcium oxide (50%). In each of the blocks, increasing doses of cobalt were applied: 0, 20, 40, 80, 160, and 320 mg kg⁻¹ of soil.

Results Cobalt-contaminated soil and amendments application had a significant effect on macroelement content of all organs of both plants.

Conclusions In blocks without amendments, 80 mg Co kg⁻¹ contributed the most increase in nitrogen, sodium, and calcium contents of both organs of spring barley. Cobalt-contaminated soil increased content of all macroelements in white mustard organs. Application of amendments to soil had strong impact on phosphorus, sodium, and calcium contents of organs of both plant species, compared to the control block (without amendments). Among the amendments, manure had the greatest effect on the content of macroelements in plants. Manure increased phosphorus, potassium, and sodium contents of all organs of both plants. The optimal content of macroelements is extremely important for the growth and development of plants, especially on soils contaminated with trace elements, including cobalt.

Keywords Cobalt · Amendments · Spring barley · White mustard · Macroelements

1 Introduction

The dry matter of plants contains both essential and unnecessary minerals as well as minerals with yet-unknown modes of operation (Stanisławska-Głubiak and Korzeniowska 2007). In terms of chemical properties, plant species, biochemical functions, and the volume of demand, minerals are usually divided into two or more categories (Loomis and Shull 1937). The essential minerals are referred to as macroelements (which are found in large quantities in plant tissues) and include nitrogen, phosphorus, potassium, magnesium, calcium, and sulphur. On the other hand, a significant role in the composition of plants,

the structure and activation of a variety of enzymes (copper, iron, molybdenum, manganese, zinc, and nickel), osmoregulation, metabolic regulation (chlorine, copper, manganese, iron, zinc), electron carriers, and increasing the resistance to both biotic and abiotic stress, is played by microelements (Sharma 2006). Ensuring the proper microelement content of a plant allows the effective use of essential macroelements during a biomass increase to be made (Stanisławska-Głubiak and Korzeniowska 2007; Brodowska and Kaczor 2009). A variety of factors have a strong effect on microelement uptake by plants in quantities necessary to ensure their proper growth and development. Most often, they include a number of soil properties, moisture content, atmospheric conditions, and their quantity in the soil (Ronan 2007; Gąsiorowska et al. 2011).

One of the microelements which may be found in certain soils in elevated quantities that poses a potential hazard to the development of plants is cobalt (Chatterjee and Chatterjee 2000). In addition to its naturally high content, which may be found in soils, the great accumulation thereof is most

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influenced by activities involving mining, processing, and the use of this metal in a variety of technological solutions (ATSDR 2004). The vast majority of cobalt is obtained as a by-product in the mining of copper and nickel (van den Brink et al. 2020). Therefore, places such as areas adjacent to roads or industrial and power distribution plants are most exposed to contamination with cobalt (ATSDR 2004). With great cobalt accumulation in the soil, the pH value can decrease, which results in more intense uptake by plants (Gál et al. 2008; Kosiorek and Wyszowski 2016). It also has an adverse effect on the microbiological and biochemical activity of soils (Zaborowska et al. 2016). The occurrence in a plant of excessive quantities of microelements, which include cobalt as well, may have an effect on the occurrence of interactions between the other accumulated elements (Ronan 2007). The toxicity of cobalt to plants is related to inhibition of photosynthesis and iron deficiency as well as oxidative stress (Morrissey et al. 2009). There are plants which exhibit no toxic symptoms when significant quantities of accumulated cobalt are present, for example *Alyssum murale* or *Bulbostylis pseudoperennis* (Collins and Kinsela 2011; Saad et al. 2012), but cereals, for example, belong to the group of plants sensitive to contamination with this element (Kabata-Pendias and Pendias 2001). Cobalt accumulation and cobalt tolerance mechanisms are still poorly understood (Lange et al. 2017). One of the ways to reduce the content of this metal in the soil and to restore balance in the environment through, *inter alia*, increasing the availability of other elements with great potential significance, is phytoremediation treatments (Pszczółkowski et al. 2012). These treatments often involve the use of energy plants which are not used to produce food (Grzesik and Romanowska-Duda 2009) but also, *inter alia*, various varieties of mustard which belong to the group of plants known as hyperaccumulators (Baker et al. 1994). Phytoremediation is increasingly used to remove trace elements from contaminated soils (Awa and Hadibarata 2020; Saleh et al. 2019). A significant role is also attributed to operations associated with the use of a variety of soil-applied amendments improving the physico-chemical properties of soils, which consequently have an effect on increases in metals availability for plants (Kwiatkowska and Maciejewska 2008).

Therefore, studies were conducted to determine the impact of amendments used in the remediation of cobalt-contaminated soil on the macroelement content of all organs of spring barley and white mustard.

2 Materials and methods

2.1 Methodological approach

The vegetation pot experiment was established in vegetation hall belonging to University of Warmia and Mazury (Poland).

The research was carried out in polyethylene pots (9 kg of soil) in Olsztyn (north-eastern Poland). The soil used in experiment was characterised by granulometric composition of loamy sand. Detailed soil and amendments characteristics were included in the previously published paper (Kosiorek and Wyszowski 2020). In the experiment, six blocks were selected: without amendments; with manure (bovine, granulated); with clay; with charcoal; with zeolite (clinoptilolite); and with calcium oxide (50%). Most of amendments (manure, clay, charcoal, zeolite) were applied at 2% of the amount of soil. The exception was calcium oxide, which was added to the soil in an amount equivalent to 1 hydrolytic acidity (1.30 g CaO kg⁻¹). In each blocks with above-mentioned amendments, increasing doses of cobalt (CoCl₂) were applied: 0, 20, 40, 80, 160, and 320 mg kg⁻¹ of soil. Moreover, the following were also introduced to each pot in one dose: 100 mg of nitrogen, 35 mg of phosphorus, 100 mg of potassium, 50 mg of magnesium, 0.33 mg of boron, 5 mg of manganese, and 5 mg of molybdenum per kg of soil. Nitrogen was used as (NH₄NO₃), phosphorus as KH₂PO₄, potassium as KH₂PO₄+KCl, magnesium as MgSO₄·7H₂O, boron as H₃BO₃, manganese as MnCl₂·4H₂O, and molybdenum as (NH₄)₆Mo₇O₂₄·4H₂O. The above-mentioned soil amendments, cobalt, and elements were applied while setting up the experiment (in three replications). The amendments were selected based on their positive effect on physico-chemical properties of soil, while the selection of cobalt doses was based on the cobalt acceptable levels in soil (Regulation 2016). Cobalt doses are multiples of the acceptable cobalt level (20 mg kg⁻¹) in agricultural soils in Poland. The spring barley (*Hordeum vulgare* L.) and white mustard (*Sinapis alba* L.) were test plants. The spring barley (main crop) var. Mercada was sowing in density of 15 plants per pot. The spring barley was harvested in the heading stage, after 52 days from sowing. Next, the white mustard var. Bamberka (after-crop) was sowing to the same soil in density of 9 plants per pot. After 36 days, in the flowering stage, all organs of white mustard were harvested. The selection of spring barley for the study was based on its high percentage in the cereal cropping pattern in Poland; on the other hand, white mustard was selected due to the recommendations for sowing this plant as an aftercrop (following cereal cultivation) and its hyperaccumulatory properties towards metals found in the soil. The content of cobalt in plants was previously published in paper Kosiorek and Wyszowski (2020).

2.2 Methods of laboratory and statistical analyses

The harvested shoots and roots of both test plants were dried at 60°C and then ground in an electric grinder. The plant material was subjected to a “wet” mineralisation procedure in concentrated (95%) H₂SO₄. The following contents were then determined: total nitrogen—by Kjeldahl method (Bremner 1965),

phosphorus—by colorimetric method (Ostrowska et al. 1991), other macroelements (K, Ca, Mg, Na)—by AAS (atomic absorption spectroscopy) method (Ostrowska et al. 1991). The Statistica 13 package (Dell Inc. 2016) with ANOVA variance analysis, correlation coefficients (r), and the PCA analysis were used for the statistical analysis of research results.

3 Results

The cobalt introduced to the soil and all amendments in form of manure, clay, charcoal, zeolite, and calcium oxide had an effect on macroelement contents of all organs of test plants.

3.1 Nitrogen

In the objects without amendments, the 3rd cobalt dose (80 mg Co kg⁻¹ of soil) had maximum effect on an increase in nitrogen content of spring barley shoots (17%, $r=0.93$) and roots (28%, $r=0.86$) and in white mustard shoots (53%, $r=0.92$); in turn, 1st cobalt dose (20 mg Co kg⁻¹ of soil) had the uttermost impact on its accumulation in white mustard roots (50%, $r=0.45$) (Table 1). The introduction of all amendments to soil had little effect on nitrogen content of spring barley shoots. Clay had the strongest impact on an increase in the content of nitrogen in roots of this plant (9%), compared to the control block (no amendments). The applied amendments had no significant impact on nitrogen content of white mustard, while charcoal contributed to the greatest reduction, both in shoots (11%) and in roots (23%). Zeolite and calcium oxide also reduced the nitrogen content of white mustard.

3.2 Phosphorus

In the blocks without amendments, contamination of the soil with 3rd cobalt dose (80 mg Co kg⁻¹) contributed to maximum reduction in phosphorus content (22%, $r=-0.94$) in spring barley shoots, and an increase in this macroelement content in roots of this plant (13%, $r=0.98$) and in white mustard shoots (34%, $r=0.94$) (Table 2). After the application of 2nd cobalt dose (40 mg Co kg⁻¹ of soil), a 9% ($r=0.55$) increase in phosphorus content of white mustard roots was noted. The highest increase in the phosphorus content of spring barley shoots was demonstrated after the introduction of zeolite to soil (46%), and in roots—after introduction of manure (56%), compared to the control block (without amendments). Manure also had an effect on an increase in its content in after-crop shoots (12%) and roots (25%). In other blocks, a decrease in phosphorus content of after-crop was observed, especially in objects with CaO. In calcium oxide blocks, a decrease in its content of white mustard shoots (16%) and roots (15%) was noted. Charcoal exhibited a similar action in shoots and clay in roots of white mustard.

3.3 Potassium

In the control blocks, the application of 80 mg Co kg⁻¹ of soil increased potassium content of shoots of spring barley (7%, $r=0.96$) and white mustard (17%, $r=0.93$); in turn, introduction of 40 mg Co kg⁻¹ of soil decreased phosphorus content of spring barley roots (8%, $r=-0.76$), and its increased in white mustard roots (28%, $r=0.95$) (Table 3). In the objects with charcoal, a slight potassium increase was noted in main crop shoots and a greater increase was noted in this plant roots (11%) and in after-crop shoots (6%), compared to the control block (no amendments). Addition of manure to soil had the greatest effect on an increase in potassium content of white mustard roots (10%). Among applied amendments, only zeolite had a strongest decreasing effect on content of this macroelement, both in shoots (7%) and roots (7%) of spring barley and in shoots (8%) and roots (20%) of white mustard.

3.4 Sodium

In the objects without amendments, a 3rd cobalt dose (80 mg Co kg⁻¹ of soil) had the greatest effect on the increase in sodium content of spring barley shoots (28%, $r=1.00$) and roots (35%, $r=0.98$), while a 2nd cobalt dose (40 mg Co kg⁻¹) reduced by half also contributed to the increase in this macroelement content in white mustard shoots (20%, $r=0.73$) and roots (16%, $r=0.94$) (Table 4). The soil application of zeolite resulted in an increase in sodium content of spring barley shoots (on average, by 107%) and roots (by 66%) and its content of white mustard shoots (by 71%) and roots (by 45%), compared to the control block (without amendments). Charcoal exerted an opposite effect in the objects with this addition and the sodium content of white mustard shoots decreased by 11% and in its roots by 13%. Reverse relationships were observed in blocks with manure in all parts of plants and in objects with charcoal and calcium oxide in shoots of spring barley.

3.5 Calcium

In the blocks without amendments, a 3rd cobalt dose (80 mg Co kg⁻¹ of soil) had a significant effect on an increase in calcium content of main crop shoots (26%, $r=0.67$) and roots (133%, $r=0.96$) as well as its content in after-crop shoots (49%, $r=0.99$) (Table 5). When the soil was contaminated with a 2nd cobalt dose (40 mg Co kg⁻¹ of soil), a highly significant increase (112%, $r=0.94$) in calcium content in white mustard roots was noted. The introduction of calcium oxide to soil resulted in an increase in content of calcium in tested plant parts. In spring barley shoots, it was 46%, in its roots 59%, and in white mustard roots of 37%, compared to the control block (no amendments). It was low in

Table 1 Nitrogen content in plants

Cobalt dose (mg kg ⁻¹ of soil)	Kind of amendment						
	Without amendments	Manure	Clay	Charcoal	Zeolite	Calcium oxide	Average
Spring barley—shoots							
0	27.41	27.83	26.39	27.83	28.95	25.73	27.35
20	27.76	28.12	26.16	28.49	28.25	28.07	27.81
40	28.00	27.98	28.82	28.40	28.58	28.74	28.42
80	32.01	29.12	30.15	30.40	29.77	28.46	29.98
160	n.a.	29.79	37.94	35.18	33.62	29.14	33.13
320	n.a.	35.96	n.a.	n.a.	n.a.	34.56	35.26
Average	28.79	29.80	29.89	30.06	29.83	29.11	30.33
<i>r</i>	0.93	0.97	0.98	0.98	0.94	0.94	0.97
LSD _(0.01)	Cobalt dose—0.90, kind of amendment—0.90, interaction—2.20						
Spring barley—roots							
0	20.67	23.57	23.21	21.86	22.68	21.84	22.30
20	20.60	19.92	23.63	22.72	19.11	20.37	21.06
40	20.37	19.50	22.70	20.53	23.98	21.19	21.38
80	26.53	22.45	26.83	23.73	23.26	21.81	24.10
160	n.a.	23.94	n.a.	n.a.	n.a.	24.94	24.44
320	n.a.	26.95	n.a.	n.a.	n.a.	n.a.	26.95
Average	22.04	22.72	24.09	22.21	22.26	22.03	23.37
<i>r</i>	0.86	0.80	0.81	0.47	0.39	0.87	0.93
LSD _(0.01)	Cobalt dose—0.45, kind of amendment—0.45, interaction—1.10						
White mustard—shoots							
0	32.80	37.92	33.64	33.32	37.99	35.32	35.16
20	33.95	38.80	39.10	30.08	33.34	35.88	35.19
40	47.02	41.79	44.84	34.37	37.70	36.63	40.39
80	50.28	44.70	47.97	47.39	40.44	38.03	44.80
160	n.a.	51.96	n.a.	n.a.	n.a.	46.17	49.06
320	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Average	41.01	43.03	41.38	36.29	37.37	38.40	40.92
<i>r</i>	0.92	1.00	0.95	0.88	0.59	0.97	0.96
LSD _(0.01)	Cobalt dose—1.72, kind of amendment—1.72, interaction—4.22						
White mustard—roots							
0	14.02	16.61	12.69	12.85	14.63	13.77	14.09
20	21.02	15.16	14.14	12.95	13.74	12.39	14.90
40	17.20	18.25	18.22	14.37	15.47	14.93	16.41
80	n.a.	18.81	n.a.	n.a.	n.a.	14.82	16.82
160	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
320	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Average	17.41	17.21	15.02	13.39	14.61	13.98	15.55
<i>r</i>	0.45	0.76	0.96	0.90	0.48	0.61	0.93
LSD _(0.01)	Cobalt dose—0.46, kind of amendment—0.46, interaction—1.12						

r, correlation coefficient; *n.a.*, not analysed

shoots of white mustard. Clay, manure, and charcoal had a positive effect on calcium content of spring barley roots. Zeolite had a positive effect on its content in white mustard roots. After the application of manure, calcium

content of spring barley shoots decreased by 48%, while in white mustard shoots by 17%. Charcoal, zeolite, and manure contributed to decrease in the calcium content in white mustard shoots.

Table 2 Phosphorus content in plants

Cobalt dose (mg kg ⁻¹ of soil)	Kind of amendment						
	Without amendments	Manure	Clay	Charcoal	Zeolite	Calcium oxide	Average
Spring barley—shoots							
0	1.25	1.53	1.19	1.38	1.69	1.42	1.41
20	1.11	1.62	1.17	1.53	1.81	1.52	1.46
40	1.14	1.90	1.01	1.16	1.67	1.41	1.38
80	0.97	1.58	1.30	1.28	1.56	1.59	1.38
160	n.a.	1.46	1.37	1.37	1.41	1.16	1.35
320	n.a.	1.41	n.a.	n.a.	n.a.	1.28	1.35
Average	1.12	1.58	1.21	1.35	1.63	1.40	1.39
<i>r</i>	−0.94	−0.59	0.70	−0.13	−0.92	−0.59	−0.74
LSD _(0.01)	Cobalt dose—0.08, kind of amendment—0.08, interaction—0.19						
Spring barley—roots							
0	1.10	1.21	1.53	1.24	1.20	1.20	1.25
20	1.12	1.82	1.57	1.19	1.07	1.20	1.33
40	1.19	1.88	1.71	1.10	1.37	1.14	1.40
80	1.24	2.00	1.39	1.18	1.44	1.30	1.43
160	n.a.	1.93	n.a.	n.a.	n.a.	1.28	1.60
320	n.a.	2.00	n.a.	n.a.	n.a.	n.a.	2.00
Average	1.16	1.81	1.55	1.18	1.27	1.22	1.50
<i>r</i>	0.98	0.55	-0.45	-0.41	0.79	0.68	1.00
LSD _(0.01)	Cobalt dose—0.04, kind of amendment—0.04, interaction—0.09						
White mustard—shoots							
0	1.55	1.79	1.49	1.60	1.69	1.55	1.61
20	1.82	1.88	1.73	1.29	1.70	1.55	1.66
40	1.78	1.92	1.73	1.59	1.83	1.47	1.72
80	2.07	1.87	2.01	1.84	1.94	1.45	1.86
160	n.a.	2.63	n.a.	n.a.	n.a.	1.58	2.11
320	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Average	1.81	2.02	1.74	1.58	1.79	1.52	1.79
<i>r</i>	0.94	0.91	0.97	0.67	0.97	0.24	1.00
LSD _(0.01)	Cobalt dose—0.08, kind of amendment—0.08, interaction—0.19						
White mustard—roots							
0	1.03	1.19	0.83	1.03	1.13	0.96	1.03
20	0.96	1.17	0.94	1.08	1.02	0.93	1.02
40	1.12	1.46	1.06	1.13	1.26	0.77	1.13
80	n.a.	1.36	n.a.	n.a.	n.a.	0.88	1.12
160	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
320	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Average	1.04	1.30	0.95	1.08	1.14	0.88	1.08
<i>r</i>	0.55	0.66	1.00	1.00	0.55	−0.49	0.77
LSD _(0.01)	Cobalt dose—0.09, kind of amendment—0.09, interaction—0.22						

r, correlation coefficient; *n.a.*, not analysed

3.6 Magnesium

In the objects without amendments, a 3rd cobalt dose (80 mg Co kg⁻¹ of soil) had no significant effect on

magnesium content of main crop both organs and on its content of after-crop shoots (Table 6). Only after application of 2nd cobalt dose (40 mg Co kg⁻¹ of soil) the magnesium content of white mustard roots significantly increased

Table 3 Potassium content in plants

Cobalt dose (mg kg ⁻¹ of soil)	Kind of amendment						
	Without amendments	Manure	Clay	Charcoal	Zeolite	Calcium oxide	Average
Spring barley—shoots							
0	16.81	16.92	15.52	17.30	16.53	16.75	16.64
20	17.25	16.99	16.45	18.03	15.54	17.42	16.95
40	17.21	16.87	17.21	17.88	15.90	17.82	17.15
80	17.98	17.15	17.16	18.31	16.36	17.04	17.33
160	n.a.	17.18	17.56	18.97	16.22	17.90	17.57
320	n.a.	19.08	n.a.	n.a.	n.a.	18.03	18.56
Average	17.31	17.37	16.78	18.10	16.11	17.50	17.36
<i>r</i>	0.96	0.93	0.81	0.95	0.18	0.68	0.99
LSD _(0.01)	Cobalt dose—0.31, kind of amendment—0.31, interaction—0.77						
Spring barley—roots							
0	15.09	13.61	14.98	16.22	14.26	15.61	14.96
20	14.86	15.18	15.48	16.33	13.50	15.39	15.12
40	13.56	15.42	14.47	15.71	13.60	15.56	14.72
80	13.90	15.06	14.32	15.27	12.12	14.62	14.22
160	n.a.	14.96	n.a.	n.a.	n.a.	13.96	14.46
320	n.a.	16.00	n.a.	n.a.	n.a.	n.a.	16.00
Average	14.35	15.04	14.81	15.88	13.37	15.03	14.91
<i>r</i>	−0.76	0.66	−0.74	−0.93	−0.96	−0.96	0.57
LSD _(0.01)	Cobalt dose—0.16, kind of amendment—0.16, interaction—0.39						
White mustard—shoots							
0	17.34	18.17	17.85	18.29	18.03	19.32	18.17
20	18.36	19.56	18.50	19.15	16.44	19.82	18.64
40	19.90	20.42	18.79	20.39	16.84	18.96	19.21
80	20.29	20.43	20.00	22.41	18.17	18.96	20.04
160	n.a.	19.64	n.a.	n.a.	n.a.	21.86	20.75
320	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Average	18.97	19.64	18.78	20.06	17.37	19.79	19.36
<i>r</i>	0.93	0.39	0.99	1.00	0.28	0.76	0.97
LSD _(0.01)	Cobalt dose—0.01, kind of amendment—0.01, interaction—0.03						
White mustard—roots							
0	14.13	17.17	14.31	15.19	13.33	15.21	14.89
20	15.02	16.34	14.79	15.96	11.06	15.62	14.80
40	18.05	17.61	16.71	16.08	13.50	16.05	16.34
80	n.a.	17.90	n.a.	n.a.	n.a.	15.47	16.68
160	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
320	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Average	15.74	17.26	15.27	15.74	12.63	15.59	15.68
<i>r</i>	0.95	0.68	0.95	0.92	0.06	0.26	0.90
LSD _(0.01)	Cobalt dose—0.16, kind of amendment—0.16, interaction—0.38						

r, correlation coefficient; *n.a.*, not analysed

(by 17%, $r=0.92$). Soil amendments did not affect the content of this macroelement in spring barley both organs or white mustard shoots. Among all amendments only the

effect of manure was positive, as it lead to a 9% increase in magnesium content in after-crop roots, compared to the control block (without amendments).

Table 4 Sodium content in plants

Cobalt dose (mg kg ⁻¹ of soil)	Kind of amendment						
	Without amendments	Manure	Clay	Charcoal	Zeolite	Calcium oxide	Average
Spring barley—shoots							
0	0.65	1.46	0.65	0.81	1.58	0.77	0.98
20	0.69	1.53	0.67	0.82	1.57	0.79	1.01
40	0.74	1.50	0.84	0.92	1.78	0.73	1.09
80	0.83	1.63	0.88	1.01	1.83	0.80	1.16
160	n.a.	1.66	0.80	1.67	0.79	0.86	1.15
320	n.a.	0.64	n.a.	n.a.	n.a.	0.81	0.73
Average	0.73	1.40	0.77	1.04	1.51	0.79	1.02
<i>r</i>	1.00	−0.78	0.57	0.96	−0.73	0.59	−0.61
LSD _(0,01)	Cobalt dose—0.05, kind of amendment—0.05, interaction—0.13						
Spring barley—roots							
0	0.83	0.88	0.99	0.88	1.48	0.97	1.00
20	0.86	1.42	1.02	0.90	1.40	0.93	1.09
40	0.92	1.46	1.05	0.91	1.54	0.95	1.14
80	1.12	1.50	1.14	1.00	1.73	0.98	1.24
160	n.a.	1.57	n.a.	n.a.	n.a.	1.19	1.38
320	n.a.	1.82	n.a.	n.a.	n.a.	n.a.	1.82
Average	0.93	1.44	1.05	0.92	1.54	1.00	1.28
<i>r</i>	0.98	0.79	0.99	0.96	0.89	0.91	1.00
LSD _(0,01)	Cobalt dose—0.02, kind of amendment—0.02, interaction—0.05						
White mustard—shoots							
0	1.29	1.95	1.31	1.06	2.38	1.19	1.53
20	1.33	2.04	1.37	1.22	2.28	1.29	1.59
40	1.55	2.10	1.53	1.21	2.53	1.27	1.70
80	1.48	2.22	1.68	1.55	2.47	1.36	1.79
160	n.a.	2.43	n.a.	n.a.	n.a.	1.51	1.97
320	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Average	1.41	2.15	1.47	1.26	2.41	1.32	1.72
<i>r</i>	0.73	1.00	0.98	0.96	0.56	0.98	0.99
LSD _(0,01)	Cobalt dose—0.04, kind of amendment—0.04, interaction—0.10						
White mustard—roots							
0	1.27	1.83	1.26	1.11	1.95	1.18	1.43
20	1.30	1.82	1.41	1.18	1.90	1.22	1.47
40	1.47	1.81	1.48	1.21	2.04	1.29	1.55
80	n.a.	1.79	n.a.	n.a.	n.a.	1.33	1.56
160	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
320	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Average	1.35	1.81	1.38	1.17	1.96	1.25	1.50
<i>r</i>	0.94	−1.00	0.98	0.97	0.65	0.97	0.91
LSD _(0,01)	Cobalt dose—0.02, kind of amendment—0.02, interaction—0.04						

r, correlation coefficient; *n.a.*, not analysed

3.7 PCA analysis and correlation coefficients

The conducted PCA analysis (Figs. 1, 2, 3, 4, 5, 6, 7, and 8) and calculated correlation coefficients (Table 7) confirmed the

significant relations between contents of particular macroelements in organs of both plant species.

Figure 1 shows the contents of macroelements in spring barley shoots under the influence of cobalt and the selected

Table 5 Calcium content in plants

Cobalt dose (mg kg ⁻¹ of soil)	Kind of amendment						
	Without amendments	Manure	Clay	Charcoal	Zeolite	Calcium oxide	Average
Spring barley—shoots							
0	0.47	0.14	0.32	0.28	0.32	0.41	0.32
20	0.36	0.18	0.41	0.35	0.32	0.43	0.34
40	0.42	0.16	0.44	0.38	0.40	0.63	0.40
80	0.59	0.24	0.53	0.55	0.37	0.57	0.47
160	n.a.	0.32	0.81	0.82	0.79	0.82	0.71
320	n.a.	0.38	n.a.	n.a.	n.a.	1.18	0.78
Average	0.46	0.24	0.50	0.47	0.44	0.67	0.51
<i>r</i>	0.67	0.95	0.99	1.00	0.93	0.98	0.95
LSD _(0.01)	Cobalt dose—0.04, kind of amendment—0.04, interaction—0.10						
Spring barley—roots							
0	0.15	0.44	0.22	0.23	0.19	0.26	0.25
20	0.15	0.23	0.20	0.23	0.20	0.28	0.22
40	0.21	0.16	0.25	0.24	0.23	0.29	0.23
80	0.35	0.22	0.34	0.39	0.26	0.32	0.31
160	n.a.	0.24	n.a.	n.a.	n.a.	0.57	0.40
320	n.a.	0.28	n.a.	n.a.	n.a.	n.a.	0.28
Average	0.22	0.26	0.25	0.27	0.22	0.35	0.28
<i>r</i>	0.96	−0.10	0.93	0.92	1.00	0.95	0.43
LSD _(0.01)	Cobalt dose—0.00, kind of amendment—0.00, interaction—0.01						
White mustard—shoots							
0	1.01	0.84	1.03	0.96	1.07	1.12	1.00
20	1.14	0.91	1.18	1.07	1.03	1.17	1.08
40	1.32	1.00	1.31	1.14	1.16	1.21	1.19
80	1.50	1.08	1.43	1.33	1.30	1.33	1.33
160	n.a.	1.30	n.a.	n.a.	n.a.	1.52	1.41
320	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Average	1.24	1.03	1.24	1.13	1.14	1.27	1.21
<i>r</i>	0.99	0.99	0.97	1.00	0.93	1.00	0.95
LSD _(0.01)	Cobalt dose—0.04, kind of amendment—0.04, interaction—0.09						
White mustard—roots							
0	0.17	0.19	0.19	0.24	0.27	0.24	0.22
20	0.20	0.21	0.26	0.24	0.21	0.24	0.23
40	0.36	0.24	0.29	0.19	0.33	0.43	0.31
80	n.a.	0.29	n.a.	n.a.	n.a.	0.41	0.35
160	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
320	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Average	0.24	0.23	0.25	0.23	0.27	0.33	0.28
<i>r</i>	0.94	1.00	0.96	−0.85	0.50	0.80	0.96
LSD _(0.01)	Cobalt dose—0.02, kind of amendment—0.02, interaction—0.06						

r, correlation coefficient; *n.a.*, not analysed

amendments, using PCA analysis. The contents of calcium, potassium, magnesium, and nitrogen accounted for 51.02% of total correlation of data set, and the contents of sodium and phosphorus accounted for 26.60%. The potassium vector

was shortest of the remaining macroelement vectors, which indicates the smallest effect was in share of variability. In first group of macroelements, the occurrence of a strong positive correlation was noted between nitrogen and magnesium, while

Table 6 Magnesium content in plants

Cobalt dose (mg kg ⁻¹ of soil)	Kind of amendment						
	Without amendments	Manure	Clay	Charcoal	Zeolite	Calcium oxide	Average
Spring barley—shoots							
0	3.13	3.10	3.11	3.10	3.13	3.11	3.11
20	3.13	3.11	3.13	3.14	3.14	3.12	3.13
40	3.15	3.11	3.15	3.13	3.14	3.15	3.14
80	3.17	3.17	3.15	3.16	3.14	3.14	3.16
160	n.a.	3.20	3.22	3.24	3.23	3.17	3.21
320	n.a.	3.24	n.a.	n.a.	n.a.	3.23	3.23
Average	3.14	3.15	3.15	3.15	3.16	3.15	3.16
<i>r</i>	0.97	0.94	0.98	0.98	0.94	0.96	0.96
LSD _(0.01)	Cobalt dose—0.01, kind of amendment—0.01, interaction—0.04						
Spring barley—roots							
0	2.97	3.08	2.97	2.97	2.88	2.91	2.96
20	3.00	3.06	2.89	2.92	2.87	2.91	2.94
40	3.02	3.02	3.00	2.93	2.90	2.94	2.97
80	3.13	3.02	3.10	3.10	3.02	2.99	3.06
160	n.a.	3.08	n.a.	n.a.	n.a.	3.19	3.13
320	n.a.	3.13	n.a.	n.a.	n.a.	n.a.	3.13
Average	3.03	3.06	2.99	2.98	2.92	2.99	3.03
<i>r</i>	0.97	0.71	0.82	0.77	0.93	0.97	0.86
LSD _(0.01)	Cobalt dose—0.01, kind of amendment—0.01, interaction—0.02						
White mustard—shoots							
0	3.28	3.28	3.14	3.21	3.23	3.20	3.22
20	3.32	3.32	3.18	3.24	3.23	3.24	3.25
40	3.34	3.31	3.19	3.25	3.26	3.26	3.27
80	3.38	3.33	3.26	3.31	3.29	3.28	3.31
160	n.a.	3.37	n.a.	n.a.	n.a.	3.32	3.34
320	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Average	3.33	3.32	3.19	3.25	3.25	3.26	3.28
<i>r</i>	0.99	0.96	0.98	0.99	0.98	0.95	0.98
LSD _(0.01)	Cobalt dose—0.02, kind of amendment—0.02, interaction—0.04						
White mustard—roots							
0	2.45	2.78	2.44	2.60	2.81	2.53	2.60
20	2.51	2.75	2.70	2.64	2.56	2.41	2.59
40	2.87	2.86	2.81	2.49	2.76	2.79	2.76
80	n.a.	3.00	n.a.	n.a.	n.a.	2.76	2.88
160	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
320	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Average	2.61	2.85	2.65	2.57	2.71	2.62	2.71
<i>r</i>	0.92	0.95	0.97	−0.73	−0.20	0.72	0.95
LSD _(0.01)	Cobalt dose—0.08, kind of amendment—0.08, interaction—0.19						

r, correlation coefficient; *n.a.*, not analysed

in second group of macroelements, there was a strong positive correlation between sodium and phosphorus. A weaker positive correlation was also noted between calcium and potassium. Figure 2 indicates that zeolite and manure had greatest

effect (and charcoal and calcium oxide had smallest effect) on contents of analysed macroelements in spring barley shoots.

The contents of the macroelements concerned in spring barley roots, being under influence of both test factors used

Table 7 Correlation coefficients (r) between macroelement content in plants

	P	K	Na	Ca	Mg
Spring barley—shoots					
N	−0.083	0.536**	−0.010	0.636**	0.894**
P		−0.325	0.651**	−0.374**	−0.163
K			−0.246	0.388*	0.509**
Na				−0.330	−0.013
Ca					0.699**
Spring barley—roots					
N	0.238	−0.135	0.271	0.532**	0.569**
P		0.150	0.650**	−0.165	0.341
K			−0.302	−0.237	−0.167
Na				−0.096	0.197
Ca					0.632**
White mustard—shoots					
N	0.734**	0.596**	0.328	0.679**	0.616**
P		0.180	0.611**	0.257	0.618**
K			−0.207	0.497**	0.461**
Na				−0.089	0.335
Ca					0.339
White mustard—roots					
N	0.452**	0.465**	0.345	0.127	0.527**
P		0.363	0.650**	−0.186	0.544**
K			−0.126	0.227	0.501**
Na				0.030	0.589**
Ca					0.574**

Significant for ** $P \leq 0.01$, * $P \leq 0.05$ **Fig. 1** Macroelement content in spring barley shoots calculated with PCA method. Vectors represent variable (N, P, K, Na, Ca, Mg) as PCA results

in experiment, are presented in Fig. 3. The first group of microelements, including nitrogen, magnesium, and potassium, accounted for 40.09% of total correlation of data set, while the second group (phosphorus, sodium, and calcium) accounted for 27.33%. Similarly to shoots of spring barley, the potassium vector was shortest, which indicates its slight effect in the share of variability. A strong positive correlation was noted between nitrogen and magnesium, and between sodium and phosphorus. A strong negative correlation was observed between calcium and potassium. Of the applied soil amendments, manure had maximum effect, and calcium oxide had smallest effect, on the contents of selected macroelements in spring barley roots (Fig. 4).

The PCA analysis presented in Fig. 5 illustrates the effects of cobalt and soil amendments on the macroelement content of white mustard shoots. The total correlation of data set for first group of macroelements (nitrogen, magnesium, and phosphorus) amounted to 52.36%, while for second group (sodium, potassium, and calcium) it amounted to 26.00%. Due to the shortest lengths of magnesium and calcium vectors as compared with other vectors, their effect in share of variability was small. Both in the first and in the second group of macroelements, the occurrence of a strong positive correlation was noted between macroelements—a weaker correlation between nitrogen and magnesium, and a strong correlation between potassium and calcium. No negative correlations between analysed macroelements were found. Manure definitely had maximum impact on the contents of macroelements in the white mustard shoots (Fig. 6).

The effects of cobalt and soil amendments on the contents of macroelements in white mustard roots are shown in Fig. 7. For nitrogen, magnesium, potassium, and phosphorus, the total correlation of data set was 47.45%, while for calcium and sodium, it was 23.39%. Potassium and nitrogen were characterised by shortest lengths of vectors, which explains their slight effects in share of variability. A strong positive correlation was found between phosphorus and sodium and a weaker correlation was found between magnesium and nitrogen. Similarly to white mustard shoots, no negative correlations were noted. Figure 8 indicates that calcium oxide, manure, and charcoal had a greatest effect on macroelement contents of white mustard roots than remaining amendments.

4 Discussion

4.1 Effect of cobalt contamination on macroelement content in plants

Cobalt belongs to the group of microelements whose content in relation to the dry matter of plants ranges from 0.5 to 10 mg kg^{−1} (Lohry 2007). At low contents, cobalt stimulates physiological processes, while at high contents it can result in the

Fig. 2 Effect of amendments and cobalt dose on macroelement content in spring barley shoots calculated with PCA method. Points show element content in plant shoots (WA—without amendments, M—manure, L—clay, C—charcoal, Z—zeolite, CO—calcium oxide, 1—0 mg, 2—20 mg, 3—40 mg, 4—80 mg, 5—160 mg, 6—320 mg Co kg⁻¹ of soil)

emergence of toxic symptoms, consequently leading to reduced yielding of plants (Ali et al. 2010). The effect of high doses of cobalt on the reduction in yielding of plants was also confirmed in the author's own study. Since for objects with doses of 160 and 320 mg Co kg⁻¹ of soil (spring barley all organs and white mustard shoots) and with doses of 80, 160, and 320 mg Co kg⁻¹ of soil (white mustard roots) the gain of plants was slight, it was not possible to perform an analysis of the contents of the macroelements concerned in these objects. Macroelements (phosphorus, nitrogen, potassium, calcium, magnesium, and sulphur) play a very important role in the first

stages of plant vegetation. Macronutrients determine the rapid growth, formation of seeds and fruits, and the correct chemical composition of plants. The correct proportions and the correct macronutrient content of plants are desirable. An imbalance in the level of macronutrient concentrations can affect plant growth, delay fruit ripening, and production of nutrient-poor plants (Al-Obaidi 2020). Kosiorek and Wyszowski (2016) found that the introduction of increasing doses of cobalt to soil contributed to a decrease in the pH value. With the decrease in pH value of the soil, the availability of cobalt increases considerably, which promotes its increased accumulation in plant tissues (Gál et al. 2008). Cobalt contamination of soil increases its content in plant organs, especially in roots (Boros-Lajszner et al. 2020). At high cobalt contents, disturbances to the uptake of other elements occur in a plant, among other symptoms (Chatterjee and Chatterjee 2000; International Plant Nutrition Institute 2015). The above relationship is also confirmed by own study, in particular in the objects with 2nd and 3rd doses (40 and 80 mg Co kg⁻¹), which had maximum impact on an increase in contents of analysed macroelements in both test plants (except phosphorus, whose accumulation decreased in spring barley shoots and in white mustard roots).

As reported by Kabata-Pendias and Pendias (2001), cobalt is necessary in structure of porphyrins, which are responsible for formation of coenzyme cobalamin which is involved in binding N₂. Studies by International Plant Nutrition Institute (2015) reveal that fertilising soil with cobalt has a positive effect on the increase of nitrogen, phosphorus, and potassium contents in peanuts. An increase in calcium and magnesium contents and a decrease in sodium content in the stems and roots of tomato (varieties Moneymaker and Edcaw) after the application of 15 mg of cobalt per kg of soil were

Fig. 3 Macroelement content in spring barley roots calculated with PCA method. Vectors represent variable (N, P, K, Na, Ca, Mg) as PCA results

Fig. 4 Effect of amendments and cobalt dose on macroelement content in spring barley roots calculated with PCA method. Points show element content in plant roots (WA—without amendments, M—manure, L—clay, C—charcoal, Z—zeolite, CO—calcium oxide, 1—0 mg, 2—20 mg, 3—40 mg, 4—80 mg, 5—160 mg, 6—320 mg Co kg⁻¹ of soil)

demonstrated by Gad (2005). Increasing doses of cobalt increased the content of majority macroelements (phosphorus, sodium, magnesium, and calcium) and decreased content of potassium in oats (Wyszkowski et al. 2009). In other research, cobalt soil contamination increased the content of nitrogen, phosphorus, calcium, and sodium in oat organs—grain, straw, and roots (Kosiorek and Wyszkowski 2019). The same relations between cobalt contamination and macroelement contents (except potassium) in plants, especially white mustard, were observed in the present study. According to Chatterjee

and Chatterjee (2000), a 0.5-mM concentration of cobalt sulphate applied to seedlings of cauliflower *Brassica oleracea* L., variety Maghi, after 86 days of growth has an effect on the decrease in phosphorus accumulation from roots to the stem, and then to the leaves, which amounts to, respectively, 0.62 ± 0.05 , 0.29 ± 0.02 , and $0.30 \pm 0.02\%$.

4.2 Effect of remediation with amendments on macroelement content in plants

The negative effect of cobalt and other trace elements on plants can be limited by the application of various amendments, such as organic substance (Liu et al. 2018), liming (Doskočil and Pekař 2012), and other sorbents (Kosiorek and Wyszkowski 2019, 2020). It is especially important to restore the balance in soils, including the correct air-water relations, the number of microorganisms, and soil enzymatic activity. They determine the uptake of nutrients and the correct content and proportions of the elements in plants (Boros-Lajszner et al. 2020). This has a major impact on the growth and development of plants.

According to Chaudhari et al. (2017), manure is characterised by long-term properties of metal adsorption and has a positive effect on increase of soil quality in terms of biology and on an increase in the content of primary elements in the soil. Palm et al. (2001) concluded that after the introduction of organic fertilisers to the soil, the availability of primary macroelements which have an effect on the growth and development of plants, *inter alia* nitrogen, phosphorus, and potassium, considerably increases. Compost can lead to an increase in nitrogen content of spring rape and oats (Wyszkowski and Ziółkowska 2009), potassium and calcium

Fig. 5 Macroelement content in white mustard shoots calculated with PCA method. Vectors represent variable (N, P, K, Na, Ca, Mg) as PCA results

Fig. 6 Effect of amendments and cobalt dose on macroelement content in white mustard shoots calculated with PCA method. Points show element content in plant shoots (WA—without amendments, M—manure, L—clay, C—charcoal, Z—zeolite, CO—calcium oxide, 1—0 mg, 2—20 mg, 3—40 mg, 4—80 mg, 5—160 mg, 6—320 mg Co kg⁻¹ of soil)

contents of maize shoots (Sivitskaya and Wyszowski 2013), and the magnesium content of various plant species (Ciećko et al. 2004, 2005). Compost also resulted in a decrease in phosphorus content of maize shoots (Sivitskaya and Wyszowski 2013) and in potassium content of various plants (Ciećko et al. 2004, 2005). The manure increased the content of nitrogen, phosphorus, potassium, and sodium in all organs of oats—grain, straw, and roots (Kosiorek and Wyszowski 2019). The above relationships are also confirmed by own study, as in the objects with the addition of manure, an increase in phosphorus content was noted in white mustard and

spring barley shoots, and an increase in potassium and magnesium contents in white mustard roots. Mucheru-Muna et al. (2014) found a strong effect of organic fertilisation combined with mineral fertilisation on an increase in contents of the element forms available to plants in the soil.

Kosiorek and Wyszowski (2016) indicated that application of manure, particularly calcium oxide to soil results in an increase in soil pH value of, respectively, 6 and approx. 7.5. According to McCauley et al. (2017), maintaining soil pH

Fig. 7 Macroelement content in white mustard roots calculated with PCA method. Vectors represent variable (N, P, K, Na, Ca, Mg) as PCA results

Fig. 8 Effect of amendments and cobalt dose on macroelement content in white mustard roots calculated with PCA method. Points show element content in plant roots (WA—without amendments, M—manure, L—clay, C—charcoal, Z—zeolite, CO—calcium oxide, 1—0 mg, 2—20 mg, 3—40 mg, 4—80 mg, 5—160 mg, 6—320 mg Co kg⁻¹ of soil)

value at a level from 5.5 to 7.5 increased content of available phosphorus in soil, while from 6.5 to 8 has a positive effect on calcium content. Therefore, it can be assumed that in own study in objects with these amendments, the contents of both macroelements in main and after-crop were the highest. This relationship was confirmed for phosphorus in blocks with manure in white mustard and spring barley roots and for calcium in blocks with calcium oxide in both test plants. In objects with calcium oxide, a much higher soil pH value was maintained than for manure, which promoted an increase in phosphorus content of soil according to the assumptions of McCauley et al. (2017); however, in this study, an opposite effect was obtained, as the phosphorus content of white mustard decreased. Kaniuczak et al. (2004a, b) demonstrated that liming of soils promotes a decrease in cobalt content of the spring barley grains and of potato tubers and green matter of fodder sunflower. Calcium oxide decreased the content of most macronutrients in oat grain, straw, and roots (Kosiorek and Wyszowski 2019). Therefore, it can be concluded that manure and calcium oxide applied in this experiment are amendments which not only have a positive effect on properties of soil and an increase in selected macroelement content in test plants, but, most importantly, can lead to reduction toxic cobalt content in plants.

According to Adeyemi and Idowu (2017), the charcoal application to soil considerably increases organic carbon content of soil, which translates into an improvement in soil fertility. Kolb et al. (2008) found that presence of carbon amendments in four moderate soils, namely Mollisol, Alfisol, Entisol, and Spodosol, significantly increases both bacterial and microbial activity in soil and availability of elements. A positive effect of charcoal on increase in availability of selected macroelements was also noted in own study, as in objects with addition of charcoal, there was a significant increase in nitrogen content of spring barley shoots, and in the potassium content of spring barley all organs and white mustard shoots. The effect of charcoal and zeolite on the macroelement content in oat organs was less equivocal (Kosiorek and Wyszowski 2019).

As reported by Mumpton (1999) and Kithome et al. (1999), zeolites are amendments that exhibit potent properties of both precipitation and water accumulation and the ability to exchange cations with no significant changes appearing in their structure. In turn, the application of zeolites in agriculture has a major influence on the increase in phosphorus and potassium contents in a soil poor in elements (Dwairi 1998). Zeolite can increase the nitrogen content of spring rape and oats (Wyszowski and Ziolkowska 2009), phosphorus, magnesium, and calcium contents of various plant species (Sivitskaya and Wyszowski 2013; Wyszowski and Modrzewska 2015), as well as potassium content, and a decrease in phosphorus content of maize shoots (Sivitskaya and Wyszowski 2013). In own study, zeolite only increased

phosphorus content of the main crop shoots and sodium content of both plants, while for potassium, it exhibited an opposite effect. The negative effect of zeolite on potassium content in plants was observed in Manolov et al. (2005) experiment.

In the research by Kosiorek and Wyszowski (2020), spring barley and white mustard were plants suitable for phytoremediation, especially phytostabilisation, as they retained cobalt well in the roots.

5 Conclusions

Cobalt-contaminated soil and amendments application to soil significantly differentiated macroelement content of all organs of test plants. In objects without amendments, a 3rd cobalt dose (80 mg Co kg⁻¹ of soil) contributed the most to an increase in nitrogen, sodium, and calcium contents of both organs of spring barley, and an increase in the potassium content of its shoots. Phosphorus content increased in roots and decreased in shoots of this plant. Cobalt application to soil resulted in a decrease in potassium content of spring barley roots. Under influence of cobalt, the contents of all macroelements in white mustard organs increased. Application of amendments to soil had the strong impact on differentiation of phosphorus, sodium, and calcium contents of all organs of both plant species, compared to the control block (without amendments). Among the amendments, the clearest and most potent impact had manure, which increased the phosphorus, potassium, and sodium contents of all organs of both plants. It should also be stressed that zeolite addition to soil caused a large increase in sodium content, and calcium oxide application increased calcium content of both plants. The effects of clay and charcoal on the macroelement contents of plants were less clear.

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