ECOLOGICAL CHEMISTRY AND ENGINEERING A

Vol. 16, No. 10 2009

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MACROELEMENT CONTENT IN YIELD OF OATS (*Avena sativa* L.) CULTIVATED ON SOILS CONTAMINATED WITH COPPER, ZINC, TIN, COBALT AND MANGANESE

ZAWARTOŚĆ MAKROPIERWIASTKÓW W PLONIE OWSA (*Avena sativa* L.) UPRAWIANEGO NA GLEBACH ZANIECZYSZCZONYCH MIEDZIĄ, CYNKIEM, CYNĄ, KOBALTEM I MANGANEM

Abstract: The aim of study was to compare the effect of contamination of soil with copper, zinc, tin, cobalt and manganese applied in the following doses: 0 (control), 20, 40, 80, 120, 240 and 480 mg $\cdot$ kg^{-1} of soil on macroelement content in the aboveground parts of oats (*Avena sativa* L.). The effect of heavy metals on macroelement content in oats depended both on the element and on its dose. The greatest changes were observed in calcium content. Copper increased the content of magnesium, nitrogen and, more than others, calcium, in the aboveground parts of oats. A similar relationship was observed for phosphorus, potassium and sodium, but only after relatively low doses of copper were applied; the effect of high doses was distinctly negative. Contamination of soil with high doses of zinc increased the content of phosphorus, but not nitrogen, sodium, magnesium, potassium or calcium, in oats. Tin favoured the accumulation of sodium and, when applied in low doses, also phosphorus, nitrogen and calcium, in plants; in addition, it reduced the content of magnesium and potassium in oats. Cobalt had a significantly negative effect on potassium content in the aboveground parts of oats and on the other hand positively affected the content of phosphorus, sodium, magnesium and, especially, calcium. Manganese generally increased the accumulation of the macroelements under study in plants, but its higher doses reduced the content of sodium and, partly, potassium and magnesium. A strong effect of soil contamination with heavy metals on content of some macroelements in oats was connected with toxic impact of copper, cobalt and, in a smaller degree, manganese on the growth and development of plants.

Keywords: contamination, copper, zinc, tin, cobalt, manganese, oats yield, macroelements content

Contamination of the environment with trace elements in Poland is generally observed in small areas, but locally it may cause some problems, eg in plant cultivation

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[1]. Copper, zinc and manganese are elements which, in small amounts, are necessary for the correct function of organisms [2]. Plants may tolerate elevated concentrations of metals in soil, but their high concentrations are harmful, both to plants and to other organisms [3]. Excessively high metal concentrations may cause stress reactions in plants, depending on the species and on many other factors, mainly the soil properties (interactions between trace elements are of considerable importance) [4]. At the same time, contamination of soil with the elements favours contamination of plants and incorporating them in subsequent links of the trophic chain [5], which in consequence results in their excessive content in food of plant (and sometimes of animal) origin [6]. They cause numerous disorders of various elements' (both macro- and microelements) uptake by plants and of plant growth and development.

Therefore, the aim of a study was to compare the effect of contamination of soil with copper, zinc, tin, cobalt and manganese on macroelement content in the aboveground parts of oats (*Avena sativa* L.).

Material and methods

A vegetative pot experiment was performed in 4 replications in the vegetation hall of the University of Warmia and Mazury in Olsztyn on slightly acidic soil with the granulometric composition of loamy sand, in polyethylene pots. The soil had the following characteristics: pH_{KCl} – 6.9; hydrolytic acidity (HA) – 15.38 mmol $(H^+) \cdot kg^{-1}$; exchangeable basic cations (EBC) – 98.50 mmol(+) $\cdot$ kg^{-1}; cation exchange capacity (CEC) – 113.88 mmol(+) $\cdot$ kg^{-1}; base saturation (BS) – 86.50 %; organic C content – 6.35 g $\cdot$ kg^{-1}. The examined factors included heavy metals: copper ($CuCl_2$), zinc ($ZnCl_2$), tin ($SnCl_2 \cdot 2H_2O$), cobalt ($CoCl_2 \cdot 6H_2O$) and manganese ($MnCl_2 \cdot 4H_2O$) applied in the following doses: 0 (control), 20, 40, 80, 120, 240 and 480 mg $\cdot$ kg^{-1} of soil. Macro- and microelements were added to all the objects in the following amounts, in mg $\cdot$ kg^{-1} of soil, converted to a pure component: N – 120 ($CO(NH_2)_2$), P – 42 (K_2HPO_4), K – 120 (K_2HPO_4 + KCl), Mg – 20 ($MgSO_4 \cdot 7H_2O$), Mo – 5 ($Na_2MoO_4 \cdot 2H_2O$) and B – 0.33 (H_3BO_3); the following were added to selected ones: Zn – 5 ($ZnCl_2$), Cu – 5 ($CuSO_4 \cdot 5H_2O$), Mn – 5 ($MnCl_2 \cdot 4H_2O$). The dose of zinc, copper and manganese at 5 mg $\cdot$ kg^{-1} of soil was applied in those variants where soil was not contaminated with increasing doses of the metals. The examined elements, as well as macro- and micro-elements as aqueous solutions were thoroughly mixed with soil (3.2 kg) and placed in the pots. The effect of the metals was tested on oats (*Avena sativa* L.), 'Borowik' c.v. The experiment, at a density of 12 oats plants per pot, was conducted for 65 days, until the ear formation phase in which the plants were harvested and samples were taken for laboratory analyses. During the experiment, the soil humidity was kept at 60 % of the capillary capacity.

Samples of plant material were cut, dried and ground. The nitrogen content was determined by the Kjeldahl method, phosphorus – by the vanadium-molybdenum method, potassium, calcium and sodium – by atomic emission spectrometry (AES) and magnesium – by atomic absorption spectrometry (AAS). Statistical analysis was performed with the Statistica software pack [7].

Results and discussion

Macroelement content in plants was affected by the metal (Tables 1 and 2). The greatest changes were observed with calcium content.

Table 1

The content of nitrogen, phosphorus and potassium in aboveground parts of oats (*Avena sativa* L.) [$g \cdot kg^{-1}$ d.m.]

Dose [$mg \cdot kg^{-1}$ of soil]	Cu	Zn	Sn	Co	Mn
Nitrogen (N)					
0	6.91	7.83	7.83	7.83	7.83
20	8.10	8.79	6.89	5.20	9.70
40	9.71	12.62	7.83	6.61	9.09
80	7.74	6.32	9.88	6.89	9.13
120	8.06	5.63	9.49	10.67	8.32
240	8.62	6.82	8.32	n.a.	8.47
480	8.97	6.28	6.35	n.a.	8.70
Average	8.30	7.76	8.09	7.44	8.75
LSD	a – 1.11*; b – 1.31*; a · b – 2.83**				
Phosphorus (P)					
0	4.61	4.61	4.61	4.61	4.61
20	5.40	5.18	7.03	5.35	6.63
40	5.26	5.81	8.73	5.64	5.91
80	5.06	5.12	6.99	5.21	8.54
120	4.87	5.46	7.23	5.48	8.74
240	3.41	5.75	6.91	n.a.	8.32
480	2.36	6.60	6.71	n.a.	6.52
Average	4.43	5.50	6.89	5.26	7.04
LSD	a – 0.34**; b – 0.40**; a · b – 0.87**				
Potassium (K)					
0	18.09	18.09	18.09	18.09	18.09
20	20.65	21.74	17.29	19.20	18.69
40	18.85	22.45	18.36	19.57	20.32
80	18.31	21.14	18.19	18.76	18.34
120	17.49	19.58	16.80	15.41	18.13
240	16.58	21.00	17.61	n.a.	18.29
480	14.70	20.80	15.85	n.a.	17.41
Average	17.81	20.69	17.45	18.21	18.47
LSD	a – 1.20**; b – 1.41**; a · b – n.s.				

Explanations for Tables 1 and 2: LSD significant for: a – metal, b – metal dose; *$p \le 0.05$; **$p \le 0.01$; n.s. – non-significant; n.a. – not analysed because of an insufficient amount of plant material.

Table 2

The content of sodium, magnesium and calcium in aboveground parts of oats (*Avena sativa* L.) [g · kg^{-1} d.m.]

Dose [mg · kg^{-1} of soil]	Cu	Zn	Sn	Co	Mn
Sodium (Na)					
0	1.31	1.31	1.31	1.31	1.31
20	1.38	1.49	1.95	1.20	2.60
40	1.38	2.20	2.03	1.45	2.70
80	1.59	1.06	2.15	1.68	2.20
120	1.31	1.16	1.85	1.64	1.97
240	1.21	1.40	2.22	n.a.	1.73
480	1.11	0.81	2.50	n.a.	1.16
Average	1.33	1.35	2.00	1.46	1.95
LSD	a – 0.16**; b – 0.18**; a · b – 0.40**				
Calcium (Ca)					
0	2.61	2.61	2.61	2.61	2.61
20	2.93	4.45	4.77	4.40	5.51
40	2.80	8.29	6.33	6.53	6.15
80	3.01	3.50	6.90	7.23	6.08
120	5.16	4.30	5.83	12.33	6.24
240	5.50	5.40	5.14	n.a.	7.34
480	10.10	5.63	4.53	n.a.	7.61
Average	4.59	4.88	5.16	6.62	5.93
LSD	a – 0.47**; b – 0.55**; a · b – 1.20**				
Magnesium (Mg)					
0	2.00	2.00	2.00	2.00	2.00
20	2.05	2.23	1.67	2.22	2.10
40	2.01	2.12	1.96	2.37	2.12
80	2.25	2.00	2.16	2.17	1.85
120	2.08	1.96	1.66	2.93	1.84
240	2.21	1.92	1.75	n.a.	1.75
480	2.39	1.55	1.71	n.a.	2.12
Average	2.14	1.97	1.84	2.34	1.97
LSD	a – 0.13**; b – 0.15**; a · b – 0.32**				

Explanations see Table 1.

Copper caused an increase in magnesium, nitrogen, and – more than others – calcium content in the aboveground parts of oats (Tables 1 and 2). Following the application of the highest dose of copper – 480 mg Cu · kg^{-1} of soil, the observed increase was as follows, as compared with the control object: magnesium 20 %, nitrogen 30 % and calcium 287 %. A similar relationship was shown to exist for phosphorus, potassium and sodium, but only following the application of small doses of copper; the effect of high doses was always negative. The content of the elements in oats in the object with the highest copper contamination was lower than in the control by 49 %, 19 % and 15 %, respectively.

Contamination of soil with high doses of zinc increased the phosphorus content in oats, but not that of nitrogen, sodium, magnesium, potassium or calcium (Tables 1 and 2). Contamination of soil with zinc at 480 mg Zn · kg^{-1} of soil increased the phosphorus content in the aboveground parts of oats by 43 %. Low doses of zinc increased the contents of the other macroelements, whereas high doses decreased the content of nitrogen, sodium, magnesium, potassium and calcium. It should be noted that the potassium and calcium content, even in the object with the highest dose of zinc (480 mg Zn · kg^{-1}), was higher than in the control object.

Tin favoured the accumulation of sodium and small amounts of phosphorus, nitrogen and calcium in plants, but it reduced the content of magnesium and potassium in oats (Tables 1 and 2). It is noteworthy that a linear increase was observed only in the sodium content which was higher by 91 % with 480 mg Sn · kg^{-1} as compared with the control object. The accumulation of phosphorus, nitrogen and calcium in the aboveground parts of oats was maximal with 40, 80 and 80 mg Sn · kg^{-1} of soil, respectively, whereas a higher contamination with tin reduced their content as compared with objects with lower doses of Sn. The highest dose of tin (480 mg Sn · kg^{-1} of soil) produced a relatively small, but significant, decrease in potassium and magnesium content in the aboveground parts of oats. The decrease was 12 % for potassium and 15 % for magnesium content.

Cobalt had a negative effect on potassium content in the aboveground parts of oats and a positive effect on the content of phosphorus, sodium, magnesium and, especially, calcium (Tables 1 and 2). The decrease in potassium content was relatively small, by 15 %, while the phosphorus content increased by 19 %, that of sodium – by 25 %, magnesium – by 47 %, and calcium – by as much as 372 %. The nitrogen content fluctuated. However, it should be added that the changes were related to the doses ranging from 0 to 120 mg Co · kg^{-1} of soil, as higher doses of cobalt were toxic to plants, making it impossible to obtain a sufficient mass of plants for chemical analyses.

Manganese generally increased the accumulation of the examined macroelements in plants, but its higher doses restricted the content of sodium and partly potassium and magnesium (Tables 1 and 2). The highest content of nitrogen in the aboveground parts of oats was determined in the soil contaminated with 20 mg Mn · kg^{-1}, that of potassium, sodium and magnesium – 40 mg Mn · kg^{-1}, phosphorus – 120 mg Mn · kg^{-1}; only the content of calcium increased until the dose of manganese was 480 mg Mn · kg^{-1}. Of all the macroelements, the growth of calcium content was the strongest – nearly three-fold in relation to the object without manganese. The highest manganese dose (480 mg Mn · kg^{-1} of soil) decreased the content of most macroelements in oats, but only in the case of sodium and potassium was it lower than in the control variant.

Contamination of soil with heavy metals has a strong effect on content of some macroelements in oats. This effect correlated with toxic impact on the growth and development of plants, which causes a decrease in their mass, especially in objects with copper, cobalt, in a smaller degree with manganese (Fig. 1). Contamination of soil with zinc and tin resulted in relatively small changes of the aboveground parts mass. The highest dose (480 mg · kg^{-1} of soil) of copper, cobalt and manganese caused 94, 99 and 35 % reduction of the mass of aboveground parts of oats, compared with the variant without heavy metals application.

Other authors [2–4, 8–14] have pointed out that trace elements have a strong and varied effect on the macroelement content in plants, which has been confirmed in the author's own study. In an experiment conducted by Eleiwa [8] copper strongly affected nitrogen

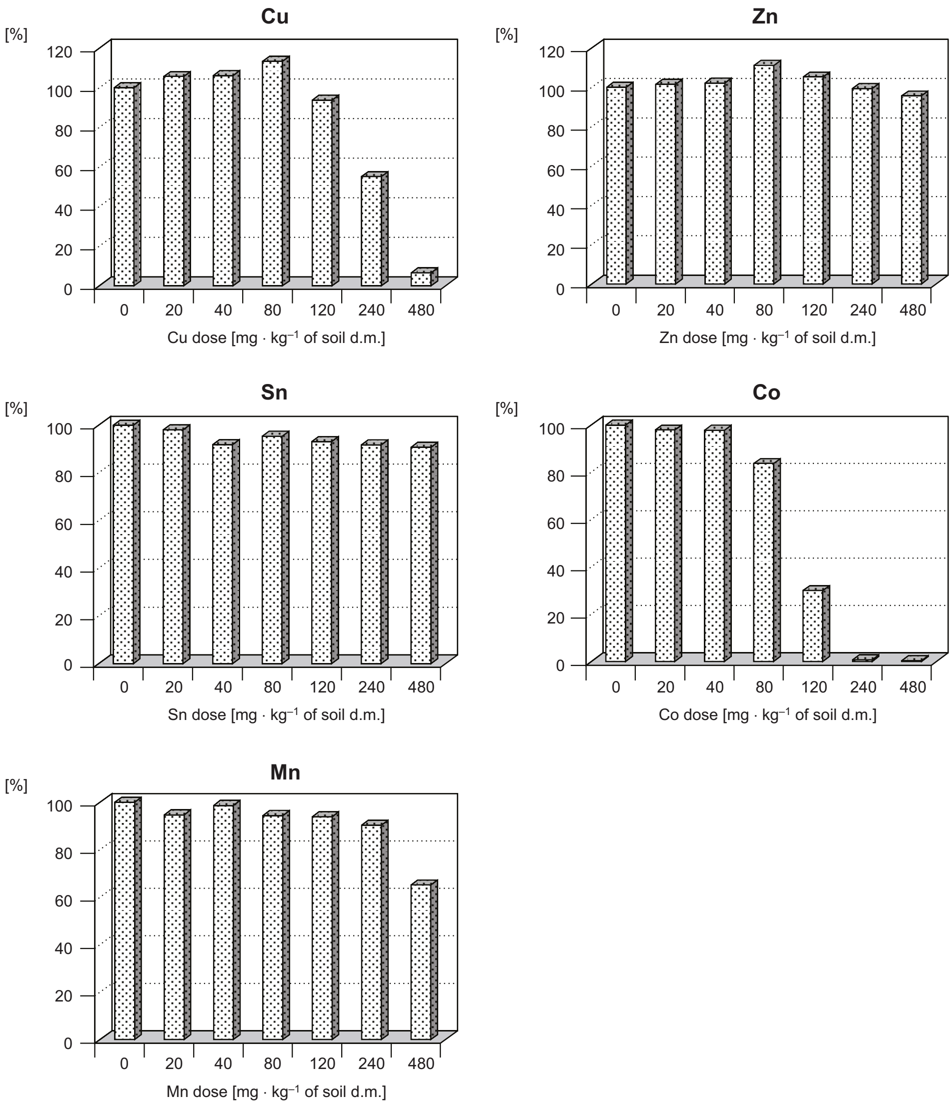

Fig. 1. The variability of aboveground parts mass of oats (*Avena sativa* L.) fresh matter [% of F.M.] depending on soil contamination with Cu, Zn, Sn, Co and Mn; relative number, control = 100 %

assimilation in wheat and lupine. Copper and zinc also reduced nitrogen, sodium, potassium and calcium content in plants and, to a lesser degree, they affected phosphorus and magnesium content. Contamination of soil with copper may result in a nitrogen content increase in spring barley [3].

According to Sienkiewicz-Cholewa and Wrobel [9], copper determines a good supply of nitrogen to plants as it takes part in nitrogen compound transformations. Copper can also have an antagonistic effect on other elements [3]. Zinc is one of the mobile elements in the soil [10]. Zinc can also increase nitrogen content in plants [11], whereas the effect of cobalt on nitrogen content is a result of its participation in nitrogen fixation, where it is a component of a coenzyme, although this only regards the papilionaceous plants [2]. Trace elements, particularly copper and zinc and, to a lesser extent, tin, manganese and cobalt, especially when applied in low and medium doses, favour the accumulation of nitrogen in some plants, eg in spring barley [12]. The findings of experiments conducted by Parker [13] and Kitaeva [14] indicate that growing contamination of soil with zinc may decrease phosphorus content in plants. According to Kozera et al [4], copper may decrease potassium content and increase that of calcium, while zinc favours accumulation of sodium in potato tubers. In the study conducted by Wyszkowski and Wyszkowska [3] and by Wyszkowski et al [12], copper increased the content of calcium, sodium, magnesium and potassium, but not phosphorus, in spring barley. According to Kabata-Pendias and Pendias [2], there is an antagonism between copper and calcium and between zinc and magnesium. The findings of an experiment conducted by Wyszkowski et al [12] indicate that zinc may increase the content of calcium, magnesium, potassium and partly phosphorus and sodium in plants. High doses of zinc decreased phosphorus and sodium content in spring barley, whereas tin increased the accumulation of calcium and decreased magnesium content.

Conclusions

1. The effect of heavy metals on macroelement content in oats depended both on the element and on its dose. The greatest changes were observed in calcium content.
2. Copper increased the content of magnesium, nitrogen and, more than others, calcium, in the aboveground parts of oats. A similar relationship was observed for phosphorus, potassium and sodium, but only after relatively low doses of copper were applied; the effect of high doses was distinctly negative.
3. Contamination of soil with high doses of zinc increased the content of phosphorus, but not nitrogen, sodium, magnesium, potassium or calcium, in oats.
4. Tin favoured the accumulation of sodium and, when applied in low doses, also phosphorus, nitrogen and calcium, in plants; in addition, it reduced the content of magnesium and potassium in oats.
5. Cobalt had a significantly negative effect on potassium content in the aboveground parts of oats and a positive effect on the content of phosphorus, sodium, magnesium and, especially, calcium.

6. Manganese generally increased the accumulation of the macroelements under study in plants, but its higher doses reduced the content of sodium and, partly, potassium and magnesium.

7. A strong effect of soil contamination with heavy metals on content of some macroelements in oats was correlated with toxic impact of copper, cobalt and, in a smaller degree, manganese on the growth and development of plants.

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ZAWARTOŚĆ MAKROPIERWIASTKÓW W PLONIE OWSA (*Avena sativa* L.) UPRAWIANEGO NA GLEBACH ZANIECZYSZCZONYCH MIEDZIĄ, CYNKIEM, CYNĄ, KOBALTEM I MANGANEM

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Abstrakt: Celem przeprowadzonych badań było określenie wpływu zanieczyszczenia gleby miedzią, cynkiem, cyną, kobaltem i manganem w dawkach 0 (kontrola), 20, 40, 80, 120, 240 i 480 mg · kg^{-1} gleby na zawartość makroelementów w częściach nadziemnych owsa (*Avena sativa* L.). Na zawartość makroelementów w roślinach, oprócz poziomu zanieczyszczenia, duży wpływ miał rodzaj metalu. Oddziaływanie metali ciężkich na zawartość makroelementów w owsie było związane z poszczególnymi pierwiastkami i ich dawkami. Największe zmiany zaobserwowano w zawartości wapnia. Miedź wywołała zwiększenie zawartości magnezu, azotu i w największym stopniu wapnia w częściach nadziemnych owsa. Podobną zależność wykazano w przypadku fosforu, potasu i sodu, ale tylko po zastosowaniu niewielkich dawek miedzi, podczas gdy duże dawki działały zdecydowanie ujemnie. Zanieczyszczenie gleby dużymi dawkami cynku spowodowało wzrost zawartości fosforu w owsie, w odróżnieniu od azotu, sodu, magnezu, potasu i wapnia. Cyna sprzyjała nagromadzaniu sodu, a w niewielkich dawkach także fosforu, azotu i wapnia w roślinach, jednocześnie ograniczała zawartość magnezu i potasu w owsie. Kobalt działał wyraźnie ujemnie na zawartość potasu w częściach nadziemnych owsa, a dodatnio na zawartość fosforu, sodu, magnezu i szczególnie wapnia. Mangan na ogół powodował zwiększenie nagromadzania w roślinach badanych makropierwiastków, jednakże większe jego dawki ograniczały zawartość sodu oraz częściowo potasu i magnezu. Silny wpływ zanieczyszczenia gleby metalami ciężkimi na zawartość niektórych makroelementów w owsie był skorelowany z toksycznym oddziaływaniem miedzi, kobaltu i, w mniejszym stopniu, manganu na wzrost i rozwój roślin.

Słowa kluczowe: zanieczyszczenie, miedź, cynk, cyna, kobalt, mangan, plon owsa, zawartość makroelementów