Electronic Journal of Polish Agricultural Universities is the very first Polish scientific journal published exclusively on the Internet, founded on January 1, 1998 by the following agricultural universities and higher schools of agriculture: University of Technology and Agriculture of Bydgoszcz, Agricultural University of Cracow, Agricultural University of Lublin, Agricultural University of Poznan, Higher School of Agriculture and Teacher Training Siedlce, Agricultural University of Szczecin, and Agricultural University of Wroclaw.

ELECTRONIC JOURNAL OF POLISH AGRICULTURAL UNIVERSITIES

2006
Volume 9
Issue 2
Topic
ENVIRONMENTAL DEVELOPMENT

WYSZKOWSKI M. , WYSZKOWSKA J. , WŁODKOWSKA L. 2006. CORRELATIONS BETWEEN MACROELEMENTS CONTENT OF SPRING BARLEY AND THE ENZYMATIC ACTIVITY OF SOIL CONTAMINATed WITH COPPER, ZINC, TIN AND BARIUM **Electronic Journal of Polish Agricultural Universities**, Environmental Development, Volume 9, Issue 2.
Available Online http://www.ejpau.media.pl/volume9/issue2/art-02.html

CORRELATIONS BETWEEN MACROELEMENTS CONTENT OF SPRING BARLEY AND THE ENZYMATIC ACTIVITY OF SOIL CONTAMINATED WITH COPPER, ZINC, TIN AND BARIUM

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ABSTRACT

This experiment aimed at determining the effect of copper, zinc, tin and barium administered to soil at doses of 4, 40, 400 mg/kg on the contents of macroelements in spring barley and their correlations with the enzymatic activity of soil. The elements applied were found to be the most favourable for nitrogen accumulation in spring barely, however, the most beneficial effect was usually observed at their lowest (4 mg/kg) and medium doses (40 mg/kg). The highest increase in nitrogen content was evoked by zinc and copper. An increased zinc content of soil was accompanied by a rise in the contents of calcium, magnesium, potassium and partly phosphorus and sodium in plants. High doses of zinc resulted in decreased levels of phosphorus and sodium in spring barley. Copper contributed to an increase in the contents of calcium, sodium, magnesium and potassium, and a decrease in the phosphorus content of spring barley. Soil contamination with tin and barium was found to affect to the greatest extent the contents of calcium, magnesium and phosphorus, however, in the case of magnesium its effect was definitely negative, whereas in the case of calcium it was positive. The correlations between the activity of urease in the soil and nitrogen content of plant were usually negative, and between the activity of alkaline phosphatase and the phosphorus content of spring barley was usually positive.

Key words: copper, zinc, tin, barium contamination, spring barley, content of macroelements, enzymatic activity.

INTRODUCTION

The contamination of the environment has significant implications for reduced usability and application of field crops for consumption purposes. The most dangerous and prevailing contaminants include heavy metals [3, 10]. Their high concentrations in the soil exerts negative effects on the growth and development of plants, evoking disturbances in the absorption, transport and assimilation of individual elements and contributing to changes reflected in reduced yields and fluctuating contents of some micro- and macroelements [7, 15, 17, 21, 22, 24]. Zinc and copper belong to the group of elements whose minimal doses are indispensable for the proper functioning of organisms, and excessive amounts exert detrimental effects [8, 9, 10]. Plants usually demonstrate a high tolerance towards increased contents of metals, however, excessive concentrations of metals in the soil are harmful to plants due to the ease of their accumulation, which is likely to result in diminished volume and deteriorated quality of yields [4, 22, 24]. Increased levels of xenobiotics in soil have also been reported to affect the growth of microorganisms and the enzymatic activity of soil [23, 25, 26].

The aim of this research was to determine the impact of soil contamination with copper, zinc, tin and barium, administered to soil at different doses, on the contents of macroelements in spring barley and their correlations with the enzymatic activity of soil.

MATERIALS AND METHODS

Investigations were carried out based on a pot experiment established in a greenhouse of the University of Warmia and Mazury in Olsztyn, on soil with the granulometric composition of light loamy sand characterised by the following properties: pH_{KCl} – 6.0, hydrolytic acidity (Hh) – 11.0 mmol H^+/kg, $C_{org.}$ – 7.1 g/kg, sum of exchangeable bases (S) – 94.5 mmol/kg, total exchangeable capacity of a sorption complex (T) – 105.5 mmol/kg, and base saturation of soil (V) – 89.6%. All analyses were carried out in 4 repetitions. All objects were administered with the following macro- and microelements (converted into a crude component): N – 120 mg/kg [$CO(NH_2)_2$], P – 42 mg/kg [K_2HPO_4], K – 120 mg/kg [K_2HPO_4+KCl], Mg – 20 mg/kg [$MgSO_4 \cdot 7H_2O$], Mn – 5 mg/kg [$MnCl_2 \cdot 4H_2O$], Mo – 5 mg/kg [$Na_2MoO_4 \cdot 2H_2O$], and B – 0.33 mg/kg [H_3BO_3]. Soil prepared in this way was contaminated with copper, zinc, tin and barium at the following doses: 4, 40 and 400 mg/kg of soil. The elements were applied in the form of water solutions of their easily-soluble salts: copper – $CuCl_2$, zinc – $ZnCl_2$, tin – $SnCl_2 \cdot 2H_2O$, and barium – $BaCl_2 \cdot 2H_2O$. Micro- and macroelements were mixed with 3.2 kg of soil which was then transferred into pots. The experiment was carried out for 56 days. Over the experimental period, the moisture content of soil was kept at the level of 60% of capillary water capacity. Analyses were carried out on spring barley cv. Start (12 plants in each pot).

During the harvest, samples of plant material were collected, comminuted, dried and ground. The contents of macroelements in plants were analysed with the following analytical methods: nitrogen – with Kiejdahl's method; phosphorus – with the vanadium-molybdenum method; potassium, calcium and sodium – with the emission atomic spectrometry (EAS); and magnesium – with the atomic absorption spectrometry (AAS). The soil was determined for the activities of: urease (Ure) – according to Alef and Nannipieri [1] as well as acid phosphatase (Pac) and alkaline phosphatase (Pal) – according to Alef et al. [2]. Results of these assays were used to determine the correlations between the contents of nitrogen and phosphorus in plants and the enzymatic activity of the soil. The results were elaborated statistically with Statistica 6 software [20] using the ANOVA analysis of variance.

RESULTS AND DISCUSSION

Soil contamination with the elements applied in the study (Cu, Zn, Sn, Ba) was reflected in the correlations between the contents of selected macroelements in the aerial parts of spring barley (tab. 1-2).

The contamination of soil with these elements contributed to a considerable increase in the nitrogen content of the aerial parts of spring barley, however, the increase appeared to be the highest (2.6-fold) upon contamination with zinc, at all applied doses (tab. 1). The other elements were also observed to increase the content of nitrogen, however, only when applied at doses of 4 mg (barium) or 40 mg/kg (zinc and copper). For those objects, the increase accounted for 78, 68 and 117%, respectively, compared to the control variant (without the addition of metals). A subsequent increase in the contents of barium, tin and copper in the soil produced a decrease in nitrogen content of plants. The increased nitrogen content in variants with copper and zinc was reflected in its average concentrations in those series which were substantially higher than in the objects with tin and barium. The effect of trace elements on nitrogen concentration in plants has been confirmed by the findings of other authors [14, 22]. Zinc has been found to affect nitrogen metabolism [14], thus increasing the yield, which was also demonstrated by Domska et al. [5] and Krauze [12] who investigated its effect on the yield and grain quality of winter wheat, and by Domska et al. [6] in their research into the changes in nitrogen content of amaranth seeds as affected by zinc.

According to Sanders and Adams [18], a high concentration of zinc in soil enhances both nitrogen absorption by plants and saccharide synthesis in the plants. Soil contamination with copper has been reported to be likely to increase nitrogen content of winter wheat [5] and spring barley [22, 24].

Table 1. The content of nitrogen, phosphorus and potassium in above-ground parts of spring barley, in g per kg of D.M.

Dose in mg · kg^{-1} of soil	Cu	Zn	Sn	Ba
Nitrogen (N)				
0	9.43	9.43	9.43	9.43
4	15.16	16.25	15.86	16.83
40	20.51	16.25	15.88	15.08
400	19.85	24.62	13.53	13.07
Average	16.24	16.64	13.68	13.60
LSD	a – 0.52**; b – 0.52**; a · b – 1.03**			
Phosphorus (P)				
0	2.79	2.79	2.79	2.79
4	3.26	4.95	3.15	2.74
40	2.72	3.97	2.74	3.82
400	2.29	2.96	2.97	3.14
Average	2.77	3.67	2.91	3.12
LSD	a – 0.29**; b – 0.29**; a · b – 0.58**			
Potassium (K)				
0	21.41	21.41	21.41	21.41
4	21.98	22.17	20.02	20.92
40	21.92	24.06	21.35	20.97
400	24.00	26.38	21.99	21.52
Average	22.33	23.51	21.19	21.21
LSD	a – 0.44**; b – 0.44**; a · b – 0.88**			

LSD significant for: a – kind of metal, b – metal dose, c – interaction; * p=0.05; **p=0.01

Table 2. The content of sodium, magnesium and calcium in above-ground parts of spring barley, in g per kg of D.M.

Dose in mg · kg^{-1} of soil	Cu	Zn	Sn	Ba
Sodium (Na)				
0	0.37	0.37	0.37	0.37
4	0.37	0.38	0.37	0.37
40	0.44	0.42	0.37	0.38
400	0.54	0.36	0.37	0.37
Average	0.43	0.38	0.37	0.37
LSD	a – 0.03**; b – 0.03**; a · b – 0.06**			
Magnesium (Mg)				
0	2.11	2.11	2.11	2.11
4	1.97	2.06	2.02	1.90
40	2.13	2.30	1.96	1.81
400	2.59	2.95	1.71	1.70
Average	2.20	2.36	1.95	1.88
LSD	a – 0.09**; b – 0.09**; a · b – 0.18**			
Calcium (Ca)				
0	3.71	3.71	3.71	3.71
4	3.47	3.83	3.82	3.73
40	4.66	5.10	4.32	4.06
400	6.99	8.83	4.86	4.31
Average	4.71	5.37	4.18	3.95
LSD	a – 0.05**; b – 0.05**; a · b – 0.10**			

Explanations under table 1

Correlations of phosphorus content (tab.1) depending on soil contamination with copper, zinc, tin and barium were slightly different. The application of the lowest dose of metals (4 mg/kg of soil) produced an increase in the concentration of phosphorus, ranging from 13% in the case of tin to 77% in the case of zinc. In contrast, the content of this element was observed to decrease upon higher doses of Cu, Zn and Sn (40 and 400 mg/kg). This was especially apparent at soil contamination with 400 mg Cu/kg where the phosphorus content of spring barley was lower by as much as 18%, compared to the control variant. The only exception was barium which was observed to increase the concentration of phosphorus in spring barley when applied at doses up to 40 mg/kg of soil. The average content of phosphorus in the aerial parts of barley was substantially higher in objects with zinc. The results obtained were consistent with reference data [9, 11, 13, 16, 22, 24]. Interactions between zinc and phosphorus have been explored by Parker [16] and Kitaeva [11] who demonstrated that contamination with zinc, hence its increased concentration in the soil, causes the phosphorus content of a plant to decline. According to Spiak [19], zinc may partly reduce phosphorus transport from roots of a plant to its aerial parts. Opposite tendencies were, however, reported in the research of Wyszkowski and Wyszkowska [24]. Increasing doses of copper were found to enhance the accumulation of that element in plant tissues [9, 13] and exert an antagonistic effect on other elements by displacing them, which has been confirmed in the investigations of Kuduk [13] and Wyszkowski and Wyszkowska [22] into the effect of copper on spring barley. Another experiment of Wyszkowski and Wyszkowska [24] demonstrated that soil contamination with copper had no significant effect on phosphorus content of oat.

Soil contamination with copper and zinc was observed to contribute to an increase in the contents of potassium (by 12 and 23%, respectively) and magnesium (by 23 and 40%, respectively) in spring barley (tab.1-2). As a result of soil contamination with zinc and copper, the content of sodium was also observed to increase in the aerial parts of spring barley, nevertheless, zinc displayed this positive effect only when applied at a dose of 40 mg/kg of soil. On the contrary, tin and barium exerted no significant effects on the contents of potassium and sodium. Their increased concentrations in the soil were accompanied by a 19% decrease in magnesium content of spring barley, compared to the control variant (not contaminated with Sn nor Ba).

More significant and explicit changes were caused by the microelements examined in respect to the content of calcium (tab. 2). Each of the microelements was observed to evoke an increase in the Ca content of spring barley. When applied at a dose of 400 mg/kg, zinc and copper caused a 138 and 88% increase, whereas tin and barium had as low as a 31 and 16% increase, respectively, in calcium content of the aerial parts of barley. The beneficial effect of copper on the concentrations of potassium, sodium, calcium and magnesium in spring barley has also been pointed out in the results of the previous experiments by Wyszkowski and Wyszkowska [22]. The concentrations of potassium, magnesium and calcium have also been reported to increase in oat cultivated on soil contaminated with zinc [24].

The effect of the elements examined on the contents of macroelements in spring barely has been observed to change depending on the type of soil and the level of its contamination from a “stimulatory effect”*, through “no effect”**, to a “negative effect”***. The strength of this activity can be expressed by the following orders:

- the content of nitrogen: $Zn^{*} > Cu^{*} > Sn^{*} = Ba^{*}$,
- the content of phosphorus: $Zn^{*} > Ba^{*} > Sn^{*} > Cu^{***}$,
- the content of potassium: $Zn^{*} > Cu^{*} > Sn^{**} = Ba^{**}$,
- the content of sodium: $Cu^{*} > Zn^{*} > Sn^{**} = Ba^{**}$,
- the content of magnesium: $Zn^{*} > Cu^{*} > Sn^{***} > Ba^{***}$,
- the content of calcium: $Zn^{*} > Cu^{*} > Sn^{*} > Ba^{*}$.

Apart from affecting the contents of macroelements, the application of the microelements analysed was also observed to produce significant changes in the biological properties of soil expressed by the activities of urease, as well as acid and alkaline phosphatase. The activities of these soil enzymes were significantly higher in pots with high doses of copper, zinc, tin and barium. The analyses carried out within the experiment measured the correlation between the activity of urease and nitrogen content as well as between activities of acid and alkaline phosphatase in the soil and phosphorus content of spring barley (fig. 1-3). The content of macroelements in spring barley was determined by the enzymatic activity of the soil. The activity of urease was positively correlated with the content of nitrogen in plants only in objects contaminated with barium, compared to the variants with copper, zinc and tin where the correlations appeared to be negative. The phosphorus content of spring barley was found to correlate positively with the activity of acid phosphatase in the soil contaminated with copper and zinc, and with that of alkaline phosphatase – in the variants with copper, zinc and barium. In the case of tin (acid phosphatase) and barium (acid and alkaline phosphatase), the correlations appeared to be negative. The results of analyses carried out in this study confirm the outcomes of our previous experiments which demonstrated the correlations between the enzymatic activity of soil and nitrogen and phosphorus contents of spring barley, however, the tendencies of these correlations were determined by the presence of various contaminants in the soil [23, 25, 26].

Fig.1. Relationships between the urease activity in soil contaminated with Cu, Zn, Sn or Ba and nitrogen content in above-ground parts of spring barley

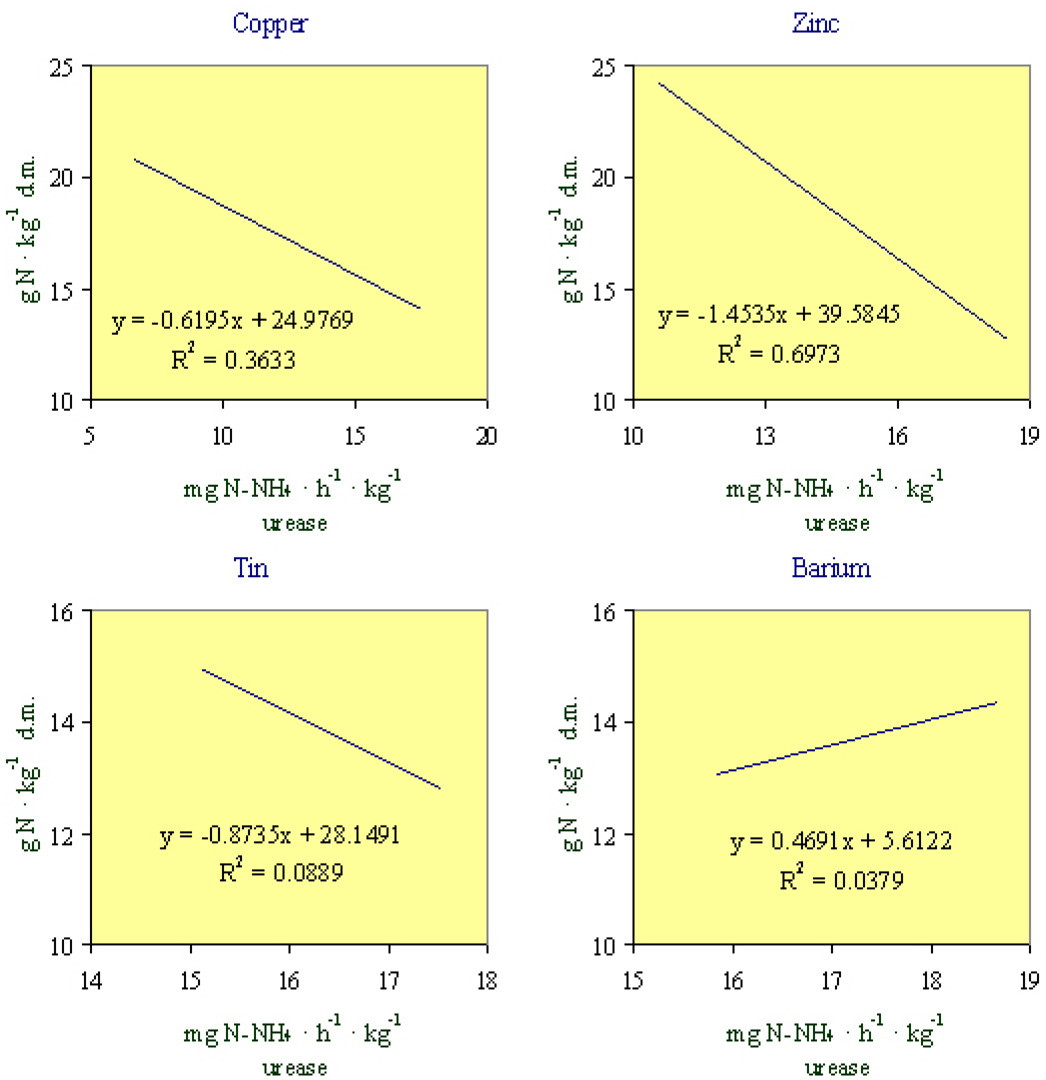


Fig.2. Relationships between the acid phosphatase activity in soil contaminated with Cu, Zn, Sn or Ba and phosphorus content in above-ground parts of spring barley

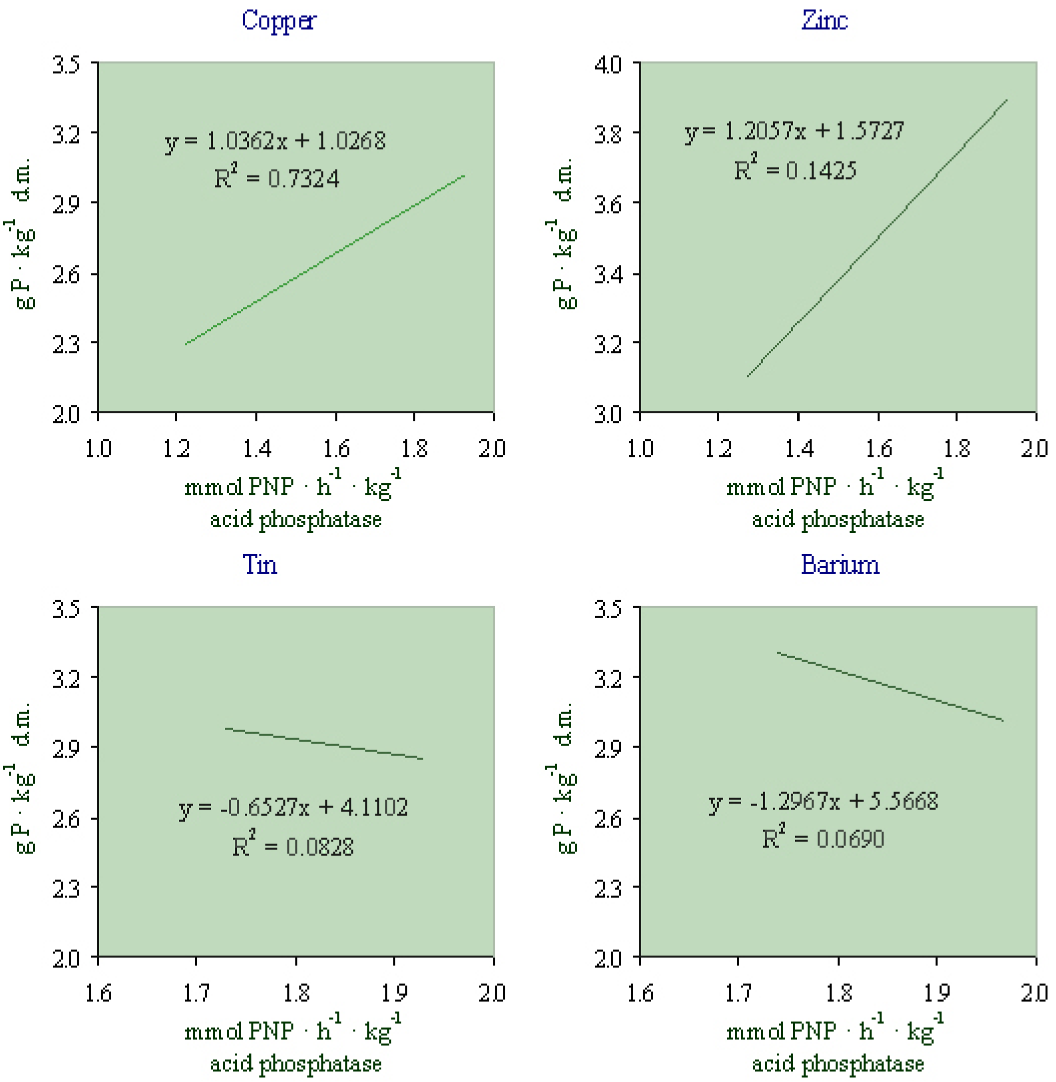
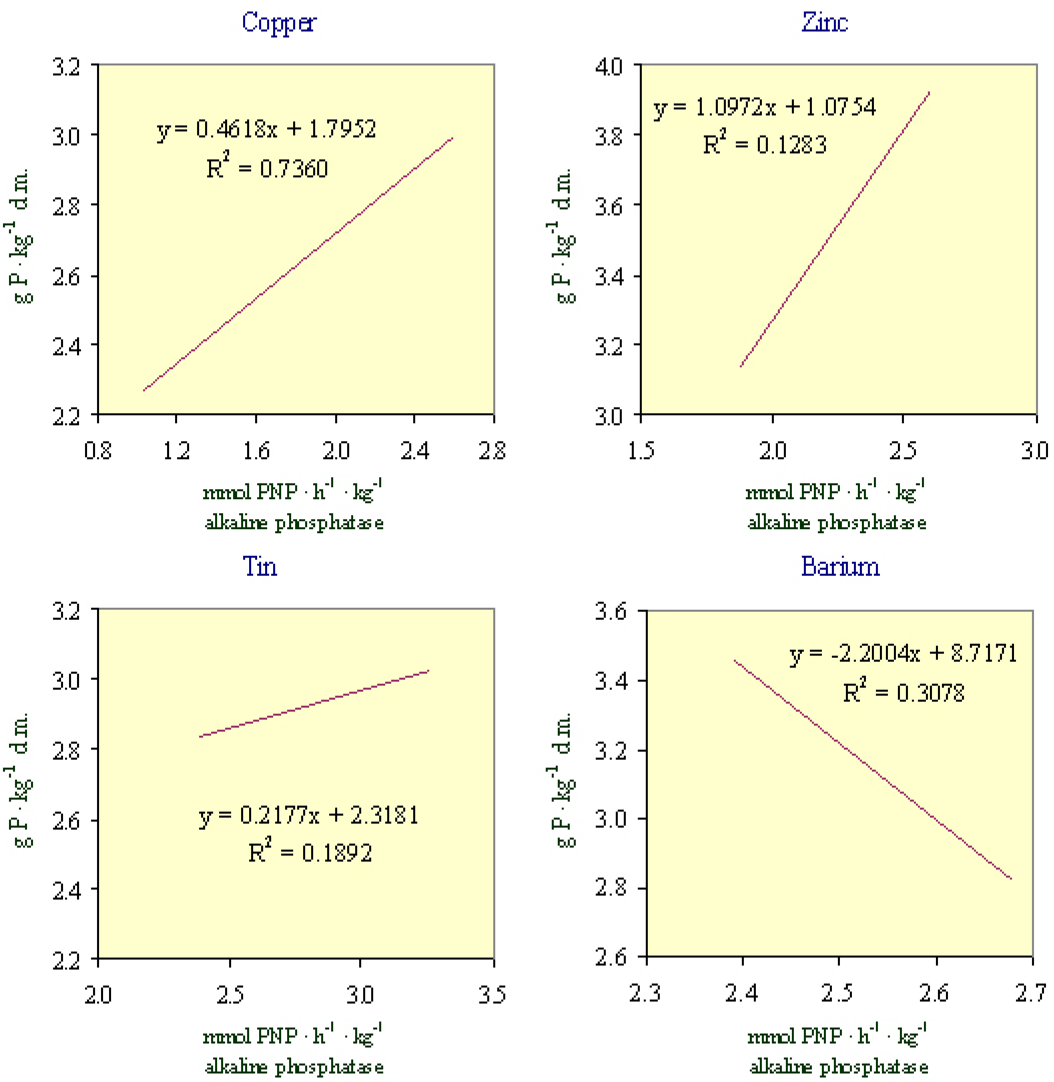


Fig.3. Relationships between the alkaline phosphatase activity in soil contaminated with Cu, Zn, Sn or Ba and phosphorus content in above-ground parts of spring barley



CONCLUSIONS

1. The microelements applied in the study were found to exert the most beneficial effect on nitrogen accumulation in spring barely, however, their positive activity was usually observed at their lowest (4 mg/kg) and medium doses (40 mg/kg). The highest increase in nitrogen content was caused by zinc and copper.
2. Higher doses of zinc in the soil were accompanied by increasing concentrations of calcium, magnesium, potassium and partly phosphorus and sodium in plants. The high doses of zinc affected a decrease in phosphorus and sodium contents of spring barley.
3. Copper was observed to contribute to increased contents of calcium, sodium, magnesium and potassium, compared to phosphorus, in spring barley.
4. Soil contamination with tin and barium exerted the strongest impact on the contents of calcium, magnesium and phosphorus, however, in the case of magnesium the effect was definitely negative, whereas in the case of calcium it was positive.
5. The correlations between the activity of urease in the soil and nitrogen content of plants were usually negative, whereas those between the activity of alkaline phosphatase and phosphorus content of spring barley were usually positive.

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