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The Effect of Zeolites on Copper Uptake by Plants Growing in Contaminated Soils

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Abstract. Three-year pot experiments were carried out in a greenhouse with the aim of reducing the copper content in the 2nd link of the soil–plant–animal (man) trophic chain. For this purpose, synthetic zeolites of the 3A, 4A, 5A and 13X type were introduced into copper contaminated soils at levels of 1, 2 and 3% by weight in relation to the soil mass. Mono- and dicotyledonous plants were cultivated in mixtures of soils with the zeolites. The copper content in lettuce grown in the contaminated soil decreased in the presence of zeolites by 29–77%, in grass by 41–78%, in oats by 45–64% and in beets by 21–41%, as compared to the control.

Key words. Contaminated soils, copper, zeolites, plants.

1. Introduction

Copper belongs to the group of elements which are of greatest potential threat to the environment. The toxicity of copper to living organisms is caused by its biochemical and biological properties and, among other things, its susceptibility to bioaccumulation in the parenchymatic organs of mammals (liver, kidneys, heart) [1]. It is an element which is widely used in various branches of industry (e.g. rubber, dye-works, electronics, etc.) as well as in the production of pesticides and fertilizers. As a result of such wide applications copper passes into ecosystems and into the soil–plant–animal (man) trophic chain [2–5]. Despite the biological barriers that protect living organisms against an excessive accumulation of heavy metals, their accumulation in the last link of the trophic chain is taking place.

The aim of the present investigations was to limit the passage of copper from the first to the second link of the trophic chain, i.e. from soil to plant, by applying synthetic aluminosilicate zeolites of types 3A, 4A, 5A and 13X. Synthetic zeolites were used because natural zeolites are not available in Poland and they are not so uniform as the synthetic types. Mono- and dicotyledonous plants were used as indices of the effect of zeolite introduction into copper contaminated soil.

2. Material and Methods

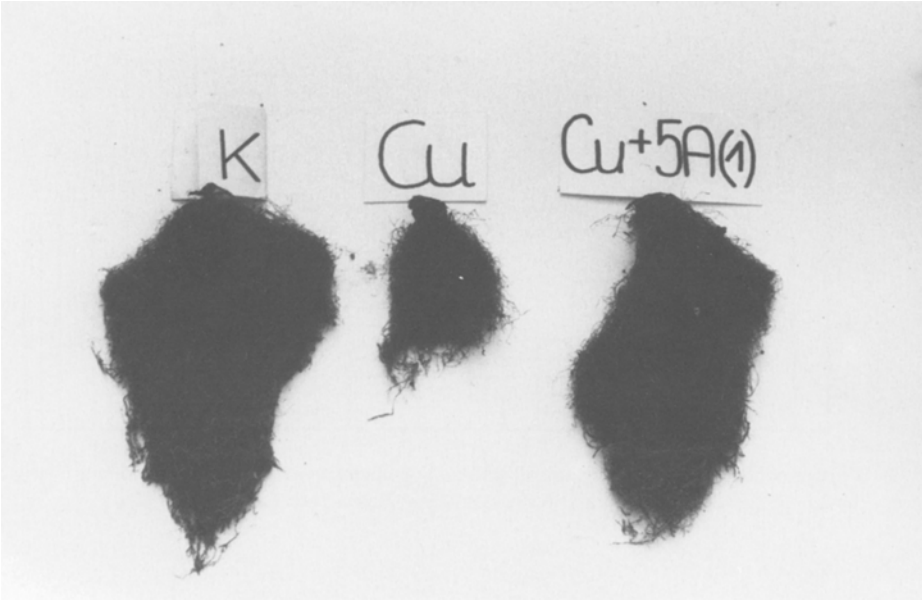
The experiments were carried out in pots having a soil capacity of 4 kg in a greenhouse for 3 years. Soil (silty sandy loam) for the experiments was taken from an accumulation horizon with the following properties: pH (1M KCl) 6.2, organic carbon content 1.21% and copper content 4.2 mg Cu/kg of soil dry matter (dm). Before the start of the experiment the soil was artificially contaminated with doses of 150 and 75 mg Cu/kg soil dry matter applied by means of an aqueous solution of $Cu(NO_3)_2 \cdot 3H_2O$. The basic macroelemental fertilization amounted to 0.20 g N/kg of soil d.m., as well as 0.28 g P, 0.30 g K, 0.06 g Mg in the form of NH_4NO_3, KH_2PO_4 and $Mg(NO_3)_2$. Synthetic zeolites 3A, 4A, 5A and 13X (granule diameter 4–5 mm: Polish Chemical Company) were then introduced into the soil in doses of 1 or 3% by weight in relation to the soil bulk. A mixture of 4A and 13X type zeolites was also applied at 1% by weight because it was felt that a mixture would probably increase their activity [6, 7]. The control was soil artificially contaminated with copper and fertilized with macroelements without the addition of zeolites. The test plants included 2-week-old seedlings of lettuce, cv 'Volburg's Wonder (Cud Wolburgu)' and oats, cv 'Dragon' sown directly into pots, perennial ryegras (*Lolium perenne*) and beet cv 'Red Ball (Czerwona Kula)'. Lettuce was fertilized in the 3rd week of growth and oats in the tillering phase with nitrogen via an aqueous solution of NH_4NO_3. Lettuce was cultivated two additional times in the same pots. Lettuce was cut after reaching the consumption stage, i.e. after 6 weeks of growth. Oats were cut after reaching full maturity. The growth of beets took place from May to October. Grass was cut three times in the growing season at different time intervals. Plants were watered during growth with redistilled water up to 60% of the maximum field capacity. Plant material was washed in redistilled water (except for straw, chaff and oat grain), dried at a temperature of 60°C, and calcined in a muffle furnace at 480°C. The ash was dissolved in HCl and the copper content determined directly from the solution by the AAS technique. Statistical calculations were performed by the method of two-way analysis of variance using the Tukey test.

3. Results and Discussion

All the test plants cultivated in the soil contaminated with 150 and 75 mg Cu/kg of soil dry matter were chlorotic, as were the plants cultivated in the presence of zeolites. Copper is capable of exerting a distinctly inhibiting effect upon root system development (see Photograph).

The results on the copper content in the particular organs of plants are presented in graphical form by arithmetic means for 3 years ($n = 12$), as the variability coefficients varied within the limits of 3.4–6.2%.

The cultivation of plants in soil with contamination doses of 150 and 70 mg Cu/kg of soil dry matter shows that copper is taken up by plants in relation to its concentration in soil (Figures 1, 3, 5–7). The copper concentration in the plant can greatly exceed its actual requirement for this element [2]. The copper accumulation was the highest in the roots of the plants analyzed (except for beetroots) and amounted in the control to: 38.2 mg in beetroots, 365.0 mg in grass roots, 41.4–412.0 mg in lettuce roots and 105.3–559.0 mg Cu in oat roots (Fig. 1–7). The copper accumulation in roots is connected with the effect of biological barriers limiting its transport to the above-ground parts. Copper, in this process, is strongly bound to proteins and is deposited in intracellular spaces or in cells [6, 8]. The lowest copper concentrations were found in the oat grain, the average values being 7.6 and 9.5 mg/kg of soil dry matter. It is widely accepted that generative parts of plants accumulate much less heavy metals in comparison to their vegetative parts. In the remaining vegetative parts of the test plants the copper content varied,



Photograph. Lettuce roots cultivated in a soil contaminated with a 75 mg kg^{-1} dose of Cu. *Legend*: (a) = uncontaminated soil; (b) = contaminated by copper; (c) = contaminated by copper with the addition of 1% weight 5A zeolite.

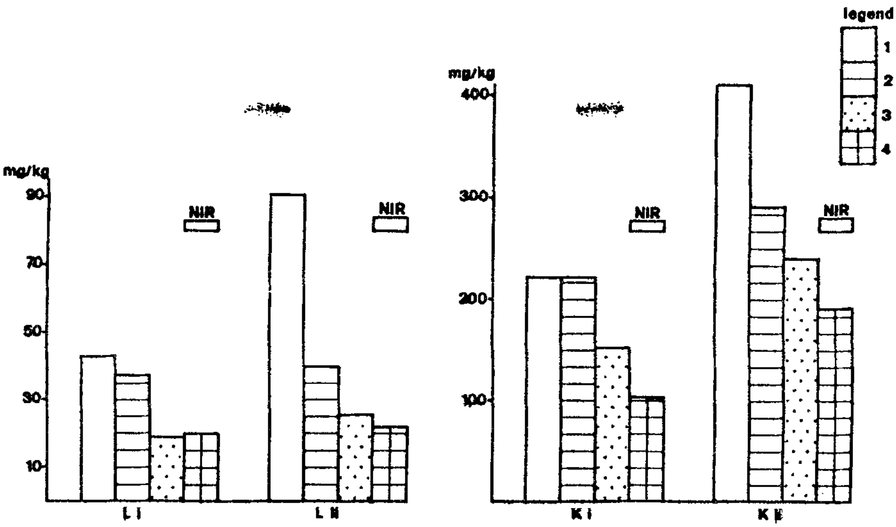


Fig. 1. Copper content in lettuce grown in soil artificially contaminated with a dose of 150 mg Cu/kg of soil dry matter. $L_{I\text{-}II}$ = Leaves of second successive harvest lettuce; $K_{I\text{-}II}$ = Lettuce roots. *Legend*: **1** – variant without addition of zeolites (control); **2** – variant with addition of 3% weight of 4A-type zeolite; **3** – variant with addition of 3% weight of 13X-type zeolite; **4** – variant with addition of 1% weight of 4A- and 13X-type zeolites. NIR – LSD – least significant differences (0.05).

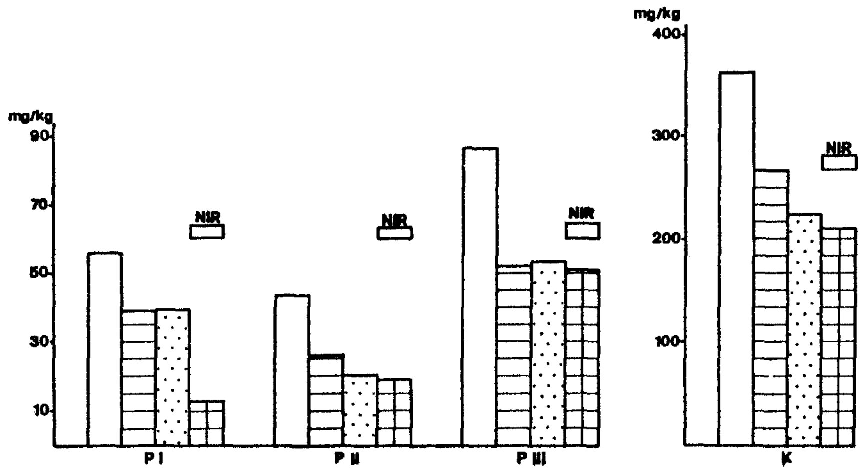


Fig. 2. Copper content in grass grown in soil artificially contaminated with a dose of 150 mg Cu/kg of soil dry matter. $P_{I\text{-}III}$ = cuts of the grass; K = grass roots. *Legend*: see Fig. 1.

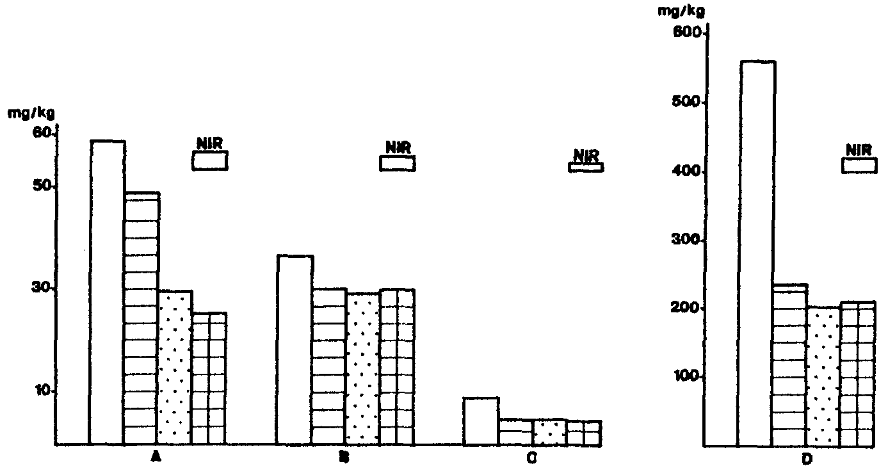


Fig. 3. Copper content in oats grown in soil artificially contaminated with a dose of 150 mg Cu/kg of soil dry matter. B = straw, C = grain, D = roots. *Legend*: see Fig. 1.

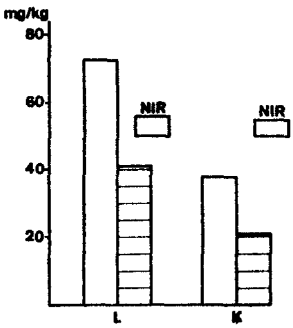


Fig. 4. Copper content in beets grown in soil artificially contaminated with a dose of 150 mg Cu/kg of soil dry matter. L = leaves, K = roots. *Legend*: see Fig. 1.

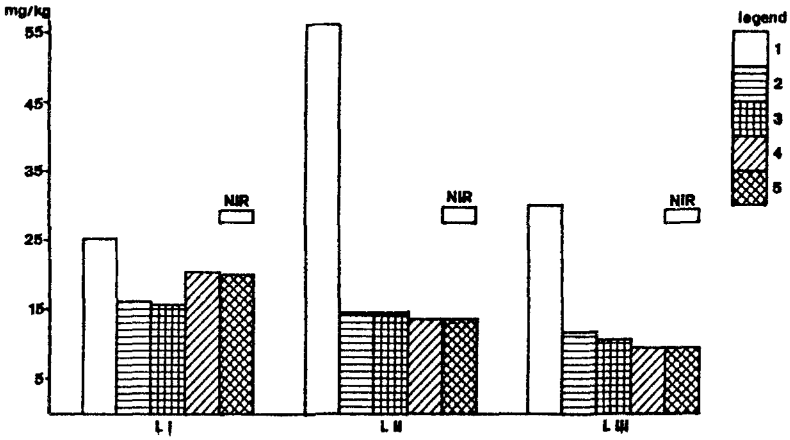


Fig. 5. Copper content in leaves of lettuce grown in soil artificially contaminated with a dose of 75 mg Cu/kg of soil dry matter. II + III = leaves of second successive harvest of lettuce. *Legend*: **1** – variant without addition of zeolites (control); **2** – variant with addition of 1 weight % of 3A-type zeolite; **3** – variant with addition of 3 weight % of 3A-type zeolite; **4** – variant with addition of 1 weight % of 5A-type zeolite; **5** – variant with addition of 3 weight % of 5A-type zeolite.

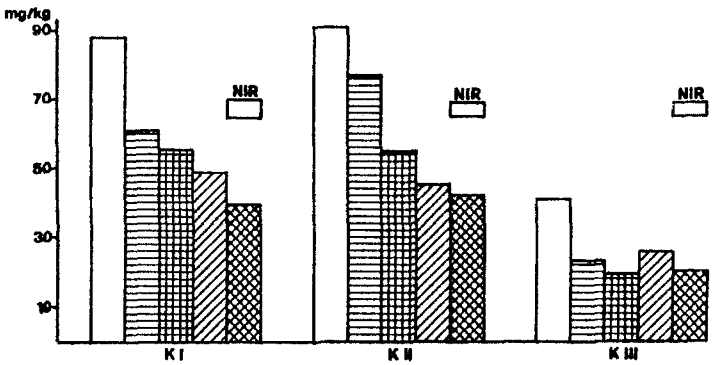


Fig. 6. Copper content in roots of lettuce grown in soil artificially contaminated with a dose of 75 mg Cu/kg of soil dry matter. K_{I-III} = roots of second successive harvest of lettuce. *Legend*: see Fig. 5.

irrespective of the dose of simulated contamination, within the range 25.4–90.6 mg/kg of soil dry matter.

The introduction of synthetic zeolites into contaminated soils resulted in a significant lowering of the copper content in the analyzed parts of the cultivated plants (Figures 1–7). One exception is the grain of oats cultivated in soil contaminated with a dose of 75 mg Cu/kg of soil dry matter (Figure 7). The amount of copper in lettuce leaves cultivated in the contaminated soil was reduced, irrespective of the type and dose of the zeolites, by 29–77% as compared to the control (Figures 1, 5), and in lettuce roots by 52–62% (Figures 1, 6).

The amount of copper in three subsequent cuts of grasses decreased, irrespective of the type and dose of the zeolite, by 41–78% and in grass roots by 42% as compared to the control (Figure 2). The copper content in the individual parts of oats confirms the significant reduction of the element in the plants (Figures 3, 7).

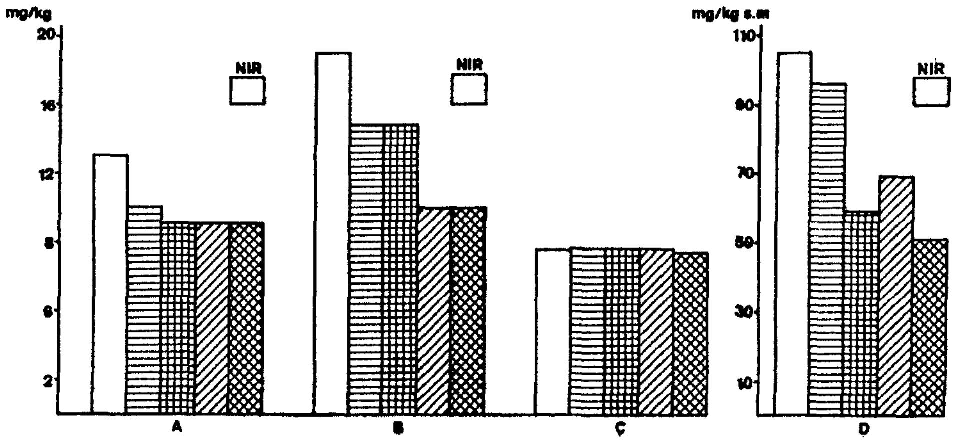


Fig. 7. Copper content in oats grown in soil artificially contaminated with a dose of 75 mg Cu/kg of soil dry matter. A = chaff, B = straw, C = grain, D = roots. *Legend*: see Fig. 5.

The greatest reduction of copper was found in oat roots (64%), in chaff (49%) in straw (47%) and in grain (45%). Beets cultivated in soil with zeolites contaminated with copper also showed a 21% lower content of copper in roots and 41% lower in leaves as compared to the control.

On the basis of the copper content in plants, as well as an index of immobilization of this element in soil by synthetic zeolites, it can be stated that the 13X type zeolite showed greater selectivity in relation to Cu^{2+} ions and its effect was more rapid than that of the remaining zeolite types. This can be seen by the Cu content in lettuce leaves after 6 weeks of growth. This selectivity is most probably connected with the diameter of the microchannels inside the crystals of these minerals and with the hydration state of the Cu^{2+} ions which most often occur in soils in a hydrated form [1]. The diameter of channels inside the 13X synthetic zeolite is 7.4 Å, that of 3A = 3.8 Å, 4A = 4.2 Å, and 5A = 5.9 Å [9]. Moreover, the zeolite with the greatest diameter (13X) absorbs more quickly than the one with the smallest diameter (4A) with the same doses of Cu application to the soil, due to the exchangeable sorption of hydrated Cu^{2+} cation, and the potassium–sodium type (3A) and the calcium–sodium type (5A). This is connected with the desorption energy, which is higher for Na^{+} than for K^{+} and Ca^{2+}. Along with the increase in incubation time of zeolites in soil, the maximum copper reduction in the leaves of lettuce and its subsequent plantings was shifted in favor of the calcium–sodium zeolite (Figure 5). This is most probably due to the tendency for substituting Ca^{2+} ions with Cu^{2+} ions in siliceous minerals.

The sorption capacity of both natural and synthetic zeolites is higher than the sorption potential of soil humus. Moreover, heavy metals can be occluded in channels of intercrystalline minerals [6, 7].

The pot experiments have demonstrated that the application of a dose of 3% (by weight) zeolite in relation to the soil mass as compared to the dose of 1% is not feasible from the economic viewpoint.

The investigation of results concerning the addition of natural zeolites into soils and the binding of heavy metals by natural and synthetic zeolites as presented by other authors (in model, pot (greenhouse), and field experiments) confirms the possibility of reducing toxic levels of these elements in the trophic chain [1–7, 10–16].

The added zeolites can subsequently be excavated from the soil at any time, along with the absorbed heavy metals. This results in a permanent removal of an excess of carcinogenic and teratogenic elements from the soil. The method of mechanical application of appropriate zeolites over wider areas has been reported [16]. Moreover, there exists the possibility of repeated regeneration of the removed zeolites and their reapplication for the same purpose.

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