Phytoextraction with Maize of Soil Contaminated with Copper after Application of Mineral and Organic Amendments

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Abstract: This study aimed to determine the possibility to increase the the effect of different amendments (compost, bentonite and zeolite) on the shoot yield and the concentration of trace elements in shoots of maize (Zea mays L.) on soil contaminated with Cu. The yield of shoots and concentration of the trace elements in shoots of maize depended on Cu dose and amendment incorporation into the sandy soil. Cu-spiked soil caused an increase the yield of shoots (only to 100 mg Cu/kg of soil), in the concentration of Cu, Co, Mn, Ni and Fe in shoots of maize and, to a smaller degree, in the concentration of Zn and bioconcentration factor (BCF) of all elements except copper, compared to the control soil without Cu. Under the influence of 150 and 200 mg Cu per kg of soil, a decrease in yield of shoots of maize was observed. Compost, bentonite and zeolite increased the yield of shoots and reduced the concentration of Cu, Co, Mn, Fe and Zn in shoots of maize. Bentonite had a more positive effect than compost and zeolite on the yield of shoots and the concentration of Co, Mn and Zn in shoots of maize. The effect of these amendments on the Cu and Fe concentration in shoots of maize was reverse. A reverse effect of these amendments (especially bentonite and zeolite) on the Ni concentration in plants was observed. The amendments applied to soil, especially compost, increased the BCF of Ni and, to a small degree, BCF of Cu in shoots of maize, compared to the control series. Compost, zeolite and especially bentonite are very good amendments in the restoration of maize growth in polluted areas.

Keywords: copper contamination; amendments; Zea mays L.; trace elements

1. Introduction

Growing industrialisation and the associated increased demand for energy is closely related to the need for a systematic energy supply to meet the needs of both industry and the population [1]. In the structure of energy generation in most countries worldwide, solid and liquid fuels are dominant, while the percentage of renewable energy sources, although still on an increase, is, however, insufficient [2]. The combustion of fuels, particularly solid fuels, generates pollutants that are emitted into the air and pollute the environment, especially the soil [3,4]. Other important sources of pollution include transport, especially road transport, and other non-specific urban sources [5]. Therefore, there is a serious hazard of their inclusion into the trophic chain whose first link comprises soil and plant microorganisms [1,4,6]. The cultivation of plants on contaminated soils entails an excessive uptake of more mobile trace elements (e.g., Cd, Ni, Cr(VI), Cu and Zn) and other contaminants by plants [3,7]. The trace elements most toxic to the environment include Hg, As, Cd, Pb, Cr, Ni, Cu...
and Zn [8]. The toxicity of trace elements depends on their chemical properties, dose, time and exposure pathways, as well as sensitivity of the biological receptors and other factors characteristic of organisms [9]. However, the environment is most commonly polluted with Cr, Mn, Ni, Cu, Zn, Cd and Pb [10]. The high concentration of some elements in the soil, mainly Mn and Fe, is related to their concentration in the parent rock. Some forms of trace elements, such as Cr (III) and Pb (II), have low mobility [9]. As regards Cu, a particular hazard is posed by Cu and Zn works, in the vicinity of which environmental pollution may exceed, even by many times, the standards permitted for agricultural soils. Moreover, the use of fertilisers, pesticides and sewage sludge in agriculture can be an additional source of trace elements [4,11,12]. The high concentration of Cu and other trace elements in soil is sometimes related to their concentration in the parent rock [5].

The cultivation of plants under such conditions sometimes results in excessive accumulation of Cu and some other trace elements in individual part organs, particularly in the roots [7]. The toxic concentration content of trace elements in plants per kilogram of dry matter (DM) is: copper 20–100 mg/kg; zinc 100–400 mg/kg; nickel 10–100 mg/kg; manganese 400–1000 mg/kg; cobalt 15–50 mg/kg [9]. However, the hazard to living organisms is mainly due to their presence in the usable parts and their translocation to subsequent links of the trophic chain [3,4,11]. The impact of soil Cu contamination on microorganisms, soil mesofauna and soil enzyme activity is generally greater than that on plants [6]. The uptake of elements by plants is determined by several factors, particularly by the soil properties, mainly including the pH value as well as the humus and floatable fraction concentrations [13,14]. However, an essential role is served by the concentration of these elements in the soil and the surrounding air, as a certain quantity of them can be taken up through the stomatal apparatus or be deposited on the plants and, where they have a wax coating, bind to them permanently [1]. Trace elements and other contaminants which are permanently bound to the wax coating, even though they are found on the surface of plants, are difficult to remove and sometimes prevent the use of the usable parts of these plants as originally intended. Where the plant cuticle is missing, the danger of occurrence of excessive trace element concentrations in the usable parts of plants significantly decreases as the elements are taken up by the roots, and there is a physiological barrier on the boundary between the roots and the shoots which limits their translocation to the organs located above the soil surface [1,15]. This is a specific mechanism that protects the photosynthetic apparatus of plants against the harmful effects of excessive quantities of contaminants originating from the soil [16].

Certain metals, e.g., Cu, Zn, Ni, Cr, Mn, Fe or Co, in small quantities are essential for the proper growth and development of plants and other living organisms [1,4,9]. They increase the resistance to stress and contribute to the growth of plants, biosynthesis and the proper functioning of various biomolecules, e.g., chlorophyll, carbohydrates, nucleic acids and secondary metabolites [17]. Plants growing in contaminated areas are usually characterised by an excessive concentration of Cu and other trace elements [14]. These modify plant metabolism by affecting physiological and biochemical processes. Consequently, their growth is limited, chloroses emerge, the biomass production decreases and, in extreme cases, even plant die-back occurs [1]. Where excessive Cu concentration emerges in plants, it becomes necessary to limit its uptake, preferably through the application of in-situ methods. Remediation of soil contaminated with copper with in-situ and ex-situ techniques is important to restore contaminated soil for safe agricultural production [18]. Immobilization and phytoremediation are considered to be an effective method of rehabilitating soils contaminated with Cu and other heavy metals [19]. This can be achieved by means of phytoremediation and the application of various amendments into the soil, which, through their effect on soil properties, will limit the uptake of Cu and other trace elements by plants [20,21]. The most common phytoremediation methods include phytoextraction and phytostabilisation. Phytoextraction involves the removal of Cu and other metals from the soil using plant cultivation in the harvestable part of the plant. However, given their toxicity, it yields good results where soil contamination is not very high [22]. Excessive Cu and other heavy metal concentration in soils can be reduced by phytoextraction using hyperaccumulators [23]. Phytostabilisation is the process of immobilization of the Cu and other metals
in the soil–root system [22]. Hyperaccumulators can be plants with a high capacity to accumulate trace elements, cultivated especially for this purpose, and the accumulators of these elements can also be typical cultivated plants, particularly those characterised by high biomass, e.g., maize—Zea mays L. [24]. The amendments’ application to soil is used to increase the effect of phytoextraction and phytostabilisation on contaminated soils. The amendments reduce the mobility and uptake of Cu and other trace elements by plants [25]. The level of contaminated soil, the bioavailability of metal contaminants, as well as the accumulation of metals by plant biomass have an important role in the phytoremediation effectiveness [26,27]. Clays, carbonates, phosphates and iron oxides were used to stabilize Cu. They caused the precipitation of non-digestible ones for plants of Cu carbonates and oxyhydroxides or the formation of cation–anionic complexes on the surface of Fe and Al oxyhydroxides [28]. The effect of organic and mineral amendments is different. Organic substances have a positive effect on the sorption properties of soil and immobilize copper and other trace elements. Mineral amendments, such as bentonite and zeolite, change the pH of soil and immobilize trace elements more strongly than organic amendments. Studies by Usman et al. [29] and Abuzaid et al. [30] show that the application of mineral amendments, e.g., bentonite, and humic substances are effective in reducing the labile fraction of copper in soil. The advantages of phytoremediation undoubtedly include low labour input and low costs, as compared to ex-situ methods [22].

Our hypothesis was that amendments can modulate the toxic effects of Cu contamination in maize. Maize was used for phytoextraction of soil contaminated with Cu. This study aimed at determining the possibility to increase the effect of different amendments (compost, bentonite and zeolite) on the shoot yield and of the concentration of trace elements in shoots of maize (Zea mays L.) on the soil contaminated with Cu.

2. Materials and Methods

2.1. Experimental Design

A pot vegetation experiment was carried out on acidic sandy soil. The agricultural typical soil (9 kg) from a 0–25-cm deep layer was added to each pot (height—25 cm, diameter at the top—24 cm and diameter at the bottom—19 cm). The effect of increasing soil Cu contamination in quantities of 0, 50, 100, 150 and 200 mg Cu/kg was tested on maize (Zea mays L.) of the San variety. The study was carried out in four soil treatments: without amendments (control series) and with the application of compost (3%), bentonite (2%) and zeolite (2% in relation to the soil weight). Copper was introduced into the soil in the form of CuCl$_2$ 10 days before sowing. Copper doses were based on the standards for soils from the Regulation of Polish Minister of the Environment of 1 September 2016 on the procedures for the assessment of land surface contamination. The soil properties and the chemical composition of compost, bentonite and zeolite (clinoptilolite) are presented in Tables 1 and 2 and are provided, also, in a previously published study by Wyszkowski [31]. The compost was rich in iron, bentonite in iron and manganese and zeolite in iron and nickel. In addition, fertilizer components were applied to each pot in the following quantities: 100 mg N (NH$_4$NO$_3$); 35 mg P (KH$_2$PO$_4$); 100 mg K (KH$_2$PO$_4$ + KCl); 50 mg Mg (MgSO$_4$ · 7H$_2$O); 5 mg Mn (MnCl$_2$ · 4H$_2$O); 5 mg Mo ((NH$_4$)$_6$Mo$_7$O$_{24}$ · 4H$_2$O); 0.33 mg B (H$_3$BO$_3$) per kg of soil. The soil (9 kg) was thoroughly mixed with copper chloride, compost, bentonite, zeolite and fertilizer components and then transferred to polyethylene pots. Maize grains were sown into each pot. The aize was cultivated with a density of 8 plants per pot. The experiment was performed in three replications. During the study, the moisture concentration was maintained at a level of 60% of water holding capacity. After 82 days since the start of the experiment, plant material samples for laboratory analyses were collected at the time of maize harvest in the end of tassel emergence (BBCH 59).
### Table 1. Properties of the soil.

| Parameter                        | Soil          |
|----------------------------------|---------------|
| Granulometric composition        |               |
| Sand > 0.05 mm (%)               | 86            |
| Silt 0.002–0.05 mm (%)           | 12            |
| Clay < 0.002 mm (%)              | 2             |
| pH value in 1 M KCl/dm³          | 5.53          |
| Hydrolytic acidity—HAC (mM (+)/kg DM) | 27.5        |
| Total exchangeable bases—TEB (mM (+)/kg DM) | 151.1     |
| Cation exchange capacity—CEC (mM (+)/kg DM) | 178.6   |
| Base saturation—BS (%)           | 84.6          |
| Total organic carbon—TOC (g/kg DM) | 9.86        |
| Total nitrogen (g/kg DM)         | 0.71          |
| Available phosphorus (mg P/kg DM) | 86.48       |
| Available potassium (mg K/kg DM) | 108.46        |
| Available magnesium (mg Mg/kg DM) | 85.32       |
| Copper (mg Cu/kg DM)             | 4.24          |
| Zinc (mg Zn/kg DM)               | 15.70         |
| Nickel (mg Ni/kg DM)             | 5.84          |
| Manganese (mg Mn/kg DM)          | 212.3         |
| Iron (mg Fe/kg DM)               | 6954.2        |
| Cobalt (mg Co/kg DM)             | 7.81          |

DM—dry matter.

### Table 2. Properties of amendments.

| Parameter                        | Compost | Bentonite | Zeolite |
|----------------------------------|---------|-----------|---------|
| Total organic carbon—TOC (g/kg DM) | 204.2   | -         | -       |
| Total nitrogen (g/kg DM)         | 11.97   | -         | -       |
| Phosphorus (g P/kg DM)           | 2.39    | 0.52      | 0.12    |
| Potassium (g K/kg DM)            | 1.41    | 2.36      | 23.13   |
| Magnesium (mg Mg/kg DM)          | 1.52    | 5.04      | 0.37    |
| Copper (mg Cu/kg DM)             | 0.81    | 21.3      | 12.38   |
| Zinc (mg Zn/kg DM)               | 4.29    | 11.8      | 14.68   |
| Nickel (mg Ni/kg DM)             | 0.51    | 2.32      | 409     |
| Manganese (mg Mn/kg DM)          | 5.32    | 145       | 2.04    |
| Iron (mg Fe/kg DM)               | 208     | 4260      | 4920    |
| Cobalt (mg Co/kg DM)             | 0.51    | 1.43      | 0.31    |

DM—dry matter.

#### 2.2. Methods of Laboratory and Statistical Analyses

The plant material samples were minced, dried and ground. The prepared plant material was wet-digested in concentrated nitric acid (HNO₃ of analytical grade) with a density of 1.40 g/cm³ in HP 500 Teflon vessels in a MARS 5 microwave reaction system (CEM Corporation, Matthews, NC, USA), in line with the US-EPA30551A method [32]. Following the digestion, the Cu, Zn, Ni, Mn, Fe and Co concentrations were determined by the flame atomic absorption spectroscopy (FAAS) method in an air-acetylene flame, using standard solutions of the Fluka company (Zn 18827, Ni 42242, Mn 63534, Fe 16596 and Co 119785.0100) as well as the Certified Analytical Reference Material NCS ZC 73030 (Chinese National Analysis Centre for Iron and Steel, Beijing, China). The methods for analyzing the soil before the establishment of the experiment and the chemical composition of compost, bentonite and zeolite were developed in a study by Wyszkowski [31]. Moreover, the bioconcentration factors (BCFs) were calculated for individual trace elements according to the following formula: 

\[
\text{BCF} = \frac{C_{\text{plant part}}}{C_{\text{soil}}}
\]

where C is the concentration of a particular element, expressed in mg/kg [33]. Statistical analysis of the study results (two-factor variance analysis ANOVA, the observed variability percentage
using the $\eta^2$ coefficient by the ANOVA analysis, principal component analysis (PCA) and correlation coefficients) was carried out using Statistica 13 software (StatSoft, Inc., Tulsa, Oklahoma, USA) [34]. The two-way ANOVA evaluates both the impact of each independent variable (Cu contamination, amendments application kind) and the interaction between them. Observed variability percentage is a classic measure of the variability of the effect of each examined factor. Principal component analysis (PCA) is very useful technique for analysis of research results because it increases interpretability and minimizes information loss [34].

3. Results

3.1. Yield and Trace Elements in Maize (Zea Mays L.)

Cu contamination and application of compost, bentonite and zeolite into the soil had a significant effect on the yield of shoots and the trace element concentration in the shoots of maize (Tables 3 and 4).

In the series without amendments, the soil Cu contamination increased the yield of shoots (only to the concentration of 100 mg Cu/kg of soil) and the concentrations of most tested trace elements in shoots of maize (Tables 3 and 4). Application of 100 mg Cu/kg of soil increased the yield of shoots by 11%. Under the influence of 200 mg Cu per kg soil, a 48% decrease in yield of shoots ($r = -0.659$) and a 27-fold increase in the Cu concentration in shoots of maize ($r = 0.959$) was demonstrated. Moreover, an increase was noted in the concentration of Co by 75% ($r = 0.731$), of Mn by 49% ($r = 0.778$) and of Fe by 30% ($r = 0.937$) in the shoots of maize as compared to the control pot (without Cu). An increase was also noted in the Zn and Ni concentrations in the shoots of maize by 12% ($r = 0.798$) and 158% ($r = 0.483$), respectively, but only in the pots with 100 mg Cu/kg of soil. The amendments applied to the soil had a significant effect on the yield of shoots and the trace element concentration in maize (Tables 3 and 4). Increased content of some trace elements in compost, bentonite and zeolite did not have a negative effect on their content in maize because trace elements were permanently associated with the amendments (especially with bentonite and zeolite) and the vegetation period was short. Their effect was mostly positive. They increased the yield of shoots and decreased the Cu, Co, Mn, Fe and Zn concentrations in the shoots of maize as compared to the control series (without amendments). It should be stressed, however, that bentonite had a more powerful remedial effect than compost and zeolite on the yield of shoots and the Co, Mn, Fe and Zn concentrations in the shoots of this plant. Bentonite increased the yield of shoots by 26% and decreased the average Co, Mn and Zn concentrations by 84%, 51% and 14%, respectively. Moreover, compost and zeolite had a stronger limiting effect on the Cu and Fe concentrations in maize than bentonite. The effect of the tested amendments (especially bentonite and zeolite) on the Ni concentration of the shoots of plants was the opposite.

Based on the calculation of the variability percentage using the $\eta^2$ coefficient of the ANOVA method, the trace element concentration of the maize (Zea mays L.) shoots was determined to the greatest extent by the application of amendments, particularly for yield of dry weight (DW) shoots and concentrations of Mn, Ni and Co in shoots of maize, in which it accounted for the proportions of 54.4%, 69.6%, 84.9% and 87.9% of this variable’s percentage, respectively (Figure 1). Rather high values were demonstrated for Fe and Zn: 38.0% and 41.0%, respectively. The percentage of Cu contamination was relatively low and ranged from a few to several percent, with the highest value of 18.2% obtained for Mn. The exceptions were concentrations of Cu and Zn and yield of DW shoots of maize at 89.0%, 31.3% and 31.2%, respectively.
Table 3. Effect of copper contamination and amendments on yield of shoots and concentration of copper (Cu), zinc (Zn) and nickel (Ni) on shoots of maize (*Zea mays* L.).

| Copper Dose in mg/kg of Soil | Without Amendments | Compost | Bentonite | Zeolite | Average |
|-----------------------------|-------------------|---------|-----------|---------|---------|
|                             | Yield of shoots, in g DM/pot |         |           |         |         |
| 0  | 80.87 ± 1.54 | 77.15 ± 1.62 | 85.60 ± 1.76 | 70.19 ± 1.46 | 78.45 |
| 50 | 88.53 ± 1.77 | 78.18 ± 1.56 | 106.96 ± 2.16 | 102.75 ± 1.99 | 94.11 |
| 100 | 89.97 ± 1.77 | 100.32 ± 2.01 | 97.46 ± 2.01 | 95.12 ± 1.90 | 95.72 |
| 150 | 83.39 ± 1.53 | 78.74 ± 1.77 | 96.59 ± 1.95 | 91.98 ± 1.79 | 87.68 |
| 200 | 42.17 ± 0.99 | 77.54 ± 1.58 | 97.80 ± 1.86 | 88.11 ± 1.02 | 83.97 |
| Average | 76.99 | 82.39 | 96.88 | 79.63 | 83.97 |
| r | -0.659 * | 0.021 | 0.292 | -0.453 | -0.428 |
| LSD for: | Cu dose—0.92 ** | amendments application—1.02 ** | interaction—2.05 ** |

| Copper (Cu), in mg/kg DM |         |           |         |         |         |
|--------------------------|---------|-----------|---------|---------|---------|
| 0  | 1.01 ± 0.02 | 1.78 ± 0.04 | 2.14 ± 0.04 | 1.38 ± 0.03 | 1.58 |
| 50 | 4.51 ± 0.09 | 2.76 ± 0.06 | 3.92 ± 0.08 | 3.59 ± 0.07 | 3.70 |
| 100 | 8.57 ± 0.17 | 7.40 ± 0.15 | 7.95 ± 0.16 | 7.00 ± 0.14 | 7.73 |
| 150 | 14.15 ± 0.28 | 10.40 ± 0.21 | 10.43 ± 0.21 | 11.10 ± 0.22 | 11.52 |
| 200 | 26.88 ± 0.54 | 17.07 ± 0.34 | 19.33 ± 0.39 | 14.75 ± 0.30 | 19.51 |
| Average | 11.02 | 7.88 | 8.75 | 7.56 | 8.81 |
| r | 0.959 ** | 0.972 ** | 0.957 ** | 0.995 ** | 0.973 ** |
| LSD for: | Cu dose—0.57 ** | amendments application—0.63 ** | interaction—0.27 ** |

| Zinc (Zn), in mg/kg DM |         |           |         |         |         |
|------------------------|---------|-----------|---------|---------|---------|
| 0  | 25.54 ± 0.51 | 21.99 ± 0.38 | 24.82 ± 0.48 | 22.59 ± 0.34 | 23.74 |
| 50 | 25.31 ± 0.48 | 23.75 ± 0.48 | 20.76 ± 0.40 | 24.34 ± 0.47 | 23.54 |
| 100 | 28.53 ± 0.57 | 25.54 ± 0.56 | 22.81 ± 0.49 | 24.57 ± 0.55 | 25.36 |
| 150 | 28.43 ± 0.49 | 26.18 ± 0.55 | 21.69 ± 0.36 | 25.51 ± 0.49 | 25.45 |
| 200 | 28.03 ± 0.56 | 24.49 ± 0.49 | 26.58 ± 0.53 | 25.64 ± 0.38 | 26.19 |
| Average | 27.17 | 24.39 | 23.33 | 24.53 | 24.86 |
| r | 0.798 ** | 0.718 ** | 0.298 | 0.939 ** | 0.930 ** |
| LSD for: | Cu dose—n.s., amendments application—2.45 *, interaction—n.s. |

| Nickel (Ni), in mg/kg DM |         |           |         |         |         |
|-------------------------|---------|-----------|---------|---------|---------|
| 0  | 0.66 ± 0.01 | 3.80 ± 0.08 | 5.20 ± 0.06 | 5.50 ± 0.07 | 3.79 |
| 50 | 0.21 ± 0.00 | 4.40 ± 0.09 | 7.15 ± 0.12 | 6.40 ± 0.09 | 4.54 |
| 100 | 1.70 ± 0.03 | 5.20 ± 0.05 | 6.65 ± 0.01 | 7.45 ± 0.11 | 5.25 |
| 150 | 1.45 ± 0.02 | 6.30 ± 0.11 | 6.15 ± 0.09 | 7.40 ± 0.05 | 5.33 |
| 200 | 0.95 ± 0.02 | 6.40 ± 0.08 | 7.35 ± 0.13 | 7.55 ± 0.12 | 5.56 |
| Average | 0.99 | 5.22 | 6.50 | 6.86 | 4.89 |
| r | 0.483 | 0.980 ** | 0.605 * | 0.905 ** | 0.944 ** |
| LSD for: | Cu dose—0.84 ** | amendments application—0.75 ** | interaction—n.s. |

Values are average ± standard deviation; LSD—least squares deviation; significant for: ** *p ≤ 0.01, * p ≤ 0.05; n.s.—non-significant; r—correlation coefficient.
Table 4. Effect of copper contamination and amendments on concentration of manganese (Mn), iron (Fe) and cobalt (Co) on shoots of maize (*Zea mays* L.).

| Copper Dose in mg/kg of Soil | Without Amendments | Compost | Bentonite | Zeolite | Average |
|-----------------------------|-------------------|---------|-----------|---------|---------|
|                             | Mn, in mg/kg DM   |         |           |         |         |
| 0                           | 237.2 ± 4.2       | 236.2 ± 4.7 | 144.2 ± 2.2 | 168.2 ± 1.8 | 196.5   |
| 50                          | 339.9 ± 5.4       | 269.5 ± 5.2 | 152.3 ± 2.8 | 203.3 ± 2.6 | 241.3   |
| 100                         | 347.3 ± 3.5       | 294.0 ± 5.9 | 170.2 ± 3.4 | 261.8 ± 5.2 | 268.3   |
| 150                         | 350.9 ± 7.0       | 278.8 ± 4.4 | 179.5 ± 3.6 | 252.9 ± 4.5 | 265.5   |
| 200                         | 354.6 ± 6.1       | 277.5 ± 5.1 | 160.5 ± 0.7 | 339.3 ± 6.4 | 283.0   |
| Average                     | 326.0             | 271.2   | 161.3     | 245.1   | 250.9   |
|                             | r                 | 0.778 ** | 0.677 ** | 0.675 ** | 0.815 ** | 0.920 **|
| LSD for:                    | Cu dose—12.1 **   | amendments application—10.9 ** | interaction—24.3 ** |
| Iron (Fe), in mg/kg DM      |                   |         |           |         |         |
| 0                           | 71.20 ± 0.71      | 86.40 ± 1.32 | 65.50 ± 1.31 | 83.40 ± 1.29 | 76.63   |
| 50                          | 74.75 ± 1.50      | 60.10 ± 1.20 | 66.00 ± 1.35 | 69.00 ± 1.00 | 67.46   |
| 100                         | 88.80 ± 1.61      | 63.50 ± 1.27 | 63.40 ± 1.22 | 49.85 ± 1.09 | 66.39   |
| 150                         | 90.80 ± 1.33      | 63.00 ± 1.11 | 65.00 ± 1.30 | 59.10 ± 1.25 | 69.48   |
| 200                         | 92.30 ± 1.73      | 46.90±0.85 | 70.20 ± 1.38 | 63.65 ± 1.27 | 68.26   |
| Average                     | 83.57             | 63.98   | 66.02     | 65.00   | 69.64   |
|                             | r                 | 0.937 ** | −0.845 ** | 0.525 * | 0.981 ** | −0.573 * |
| LSD for:                    | Cu dose—5.54 **   | amendments application—4.95 ** | interaction—11.08 ** |
| Cobalt (Co), in mg/kg DM    |                   |         |           |         |         |
| 0                           | 0.253 ± 0.004     | 0.414 ± 0.004 | 0.109 ± 0.002 | 0.033 ± 0.001 | 0.202   |
| 50                          | 0.438 ± 0.007     | 0.370 ± 0.007 | 0.074 ± 0.001 | 0.063 ± 0.001 | 0.236   |
| 100                         | 0.426 ± 0.009     | 0.302 ± 0.005 | 0.053 ± 0.004 | 0.056 ± 0.001 | 0.209   |
| 150                         | 0.441 ± 0.008     | 0.267 ± 0.002 | 0.045 ± 0.000 | 0.115 ± 0.002 | 0.217   |
| 200                         | 0.442 ± 0.009     | 0.297 ± 0.005 | 0.044 ± 0.001 | 0.119 ± 0.002 | 0.226   |
| Average                     | 0.400             | 0.330   | 0.065     | 0.077   | 0.218   |
|                             | r                 | 0.731 ** | −0.885 ** | −0.918 ** | 0.893 ** | 0.322   |
| LSD for:                    | Cu dose—0.033 *   | amendments application—0.030 ** | interaction—0.068 ** |

Values are average ± standard deviation; LSD—least squares deviation; significant for: ** p ≤ 0.01, * p ≤ 0.05; n.s.—non-significant; r—correlation coefficient.

The performed PCA analysis (Figures 2 and 3) and the calculated correlation coefficients (Table 5) confirm significant relationships between the individual trace element concentrations in the shoots of maize and in the soil and certain other properties of the soil. The PCA analysis in the form of vector variables presents the accumulated effects of soil Cu contamination (for all series with mitigating amendments—compost, bentonite and zeolite) on the yield of shoots and the selected trace element concentrations in the shoots of maize (Figure 2). The total correlation of the data set in the first group of elements (yield of shoots, Co, Mn, Zn and Fe) was at a level of 51.85%, and in the second group (Ni), at a level of 20.35%. The Zn and shoot DW yield vectors were by far the shortest, which indicates its lesser importance, as compared to other elements, in the proportion of variability. The location of vectors indicates rather strong positive correlations between Co and Fe and Mn and between Zn and Mn and less strong correlations between Cu and Mn and Zn. Moreover, strong negative correlations between shoot DW yield and Cu and Mn concentration and between Ni and the other elements (except Cu), particularly Co and Fe, were demonstrated in the shoots of maize. The calculated correlation coefficients (Table 5) also indicate highly negative correlations between shoot DW yield and hydrolytic acidity and negative correlations with the base saturation and Cu concentration of soil. Strong positive correlations were also noted between the Ni concentrations of the plants and soil, as opposed to Co.
Analogous relationships were demonstrated between shoot DW yield and base saturation and Mn and Fe concentration in soil, between the Fe and Co concentrations of shoots of maize and Mn in the soil and between the Mn, Fe and Co concentrations in the shoots of maize and the hydrolytic acidity. Strong negative relationships were observed between the Ni concentration of plants and Mn in the soil and between the Mn, Fe and Co concentrations in the shoots of maize (Figure 3).

Figure 1. Per cent contribution of variable factors according to the concentration of trace elements in shoots of maize (Zea mays L.): CuC—Cu contamination; AA—amendments application; CuC · AA—interaction between Cu contamination and amendments application.

Figure 2. Yield of dry weight (DW) shoots and concentration of trace elements in shoots of maize (Zea mays L.) illustrated with the principal component analysis (PCA) method. Results of PCA performed with yield of DW shoots and concentration of Cu, Zn, Ni, Mn, Fe and Co in shoots of maize.
and rather high for Mn and Zn (1.563 and 2.188, respectively). For Fe, Co and Cu were low (on average, 0.012, 0.086 and 0.168, respectively), medium for Ni (0.640) particularly, for Ni, while reducing the BCF values for the other elements. However, the BCF values for Zn, Mn and Fe and concentration of trace elements in shoots of maize (WA—without amendments; C—compost; B—betonite; Z—zeolite; 1—0 mg; 2—50 mg; 3—100 mg; 4—150 mg; 5—200 mg Cu/kg of soil.

In the series without amendments, soil Cu contamination increased the bioconcentration factors of all elements. All of the amendments, particularly compost, increased the Ni and, to a small degree, the BCF value of Cu in shoots of maize, as applied to the soil modified the BCF value of all elements. The increase was the lowest for Zn and Fe and the highest for Co. Reverse relationships were noted for Co. Bentonite increased the bioconcentration factor for Zn, and, to an increase in the Zn, Mn and Fe BCF values, with the changes being relatively minor.

The increase was the lowest for Zn and Fe and the highest for Co. All of the amendments, particularly, for Ni, while reducing the BCF values for the other elements. However, the BCF values for Zn, Mn and Fe and concentration of trace elements in shoots of maize (WA—without amendments; C—compost; B—betonite; Z—zeolite; 1—0 mg; 2—50 mg; 3—100 mg; 4—150 mg; 5—200 mg Cu/kg of soil.

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The exception was Cu. The BCF value of Cu decreased with the increasing soil contamination.

### Table 5. Correlation coefficients (r) between yield of DW shoots, concentration of trace elements in shoots of maize (Zea mays L.) and concentration of trace elements and some other properties of soil.

| Factor          | Shoot DW yield | Maize            | Concentration of Trace Elements in Maize |
|-----------------|----------------|-----------------|------------------------------------------|
|                 | Cu             | Zn              | Ni                                       | Mn  | Fe  | Co  |
| Shoot DW yield  | −0.423 **      | −0.214          | 0.353 *                                  | 0.020| 0.402 *| 0.086| 0.163 |
| Cu              | −0.214         | 0.353 *         | −0.348 *                                 | 0.484 *| 0.342| 0.321 |
| Zn              | 0.237          | 0.020           | −0.348 *                                 | −0.528 *| −0.631 | −0.755 |
| Ni              | −0.495 **      | 0.402 *         | 0.484 **                                 | −0.528 **| 0.274| 0.750 |
| Mn              | −0.275         | 0.086           | 0.342 *                                  | −0.631 **| 0.274| 0.462 |
| Co              | −0.318 *       | 0.163           | 0.321 *                                  | −0.755 **| 0.750 | 0.462 |

| Factor          | pH<sub>KCl</sub> | HAC              | TEB         | CEC         | BS          | Cu         | Zn         | Ni         | Mn         | Fe         | Co         |
|-----------------|------------------|-----------------|-------------|-------------|-------------|------------|------------|------------|------------|------------|------------|
| Shoot DW yield  | 0.362 *          | −0.366 *        | 0.074       | −0.076      | 0.015       | −0.262     | −0.163     |
| Cu              | −0.343 *         | 0.190           | −0.186      | 0.183       | −0.194      | −0.134     | −0.225     |
| Zn              | 0.483 **         | −0.480 **       | −0.372 *    | 0.370 *     | −0.568 **   | −0.476 **  | −0.545 **  |
| Ni              | −0.361 *         | 0.958 **        | 0.486 **    | −0.028      | 0.454 **    | 0.161      | 0.212      |
| Mn              | 0.182            | −0.105          | 0.012       | −0.222      | 0.267       | 0.076      | 0.299      |
| Fe              | −0.109           | 0.112           | −0.017      | 0.460 **    | −0.182      | −0.231     | −0.584 **  |
| Co              | 0.422 **         | −0.317 *        | 0.116       | −0.604 **   | 0.026       | 0.452 **   | 0.500 **   |
| pH<sub>KCl</sub>| 0.510 **         | −0.335 *        | −0.192      | −0.351 *    | −0.334 *    | 0.234      | 0.237      |

**p<sub>KCl</sub>**—pH in 1 mol/dm<sup>3</sup> KCl; HAC—hydrolytic acidity; TEB—total exchangeable bases; CEC—cation exchange capacity; BS—base saturation. Significant at **p ≤ 0.01, *p ≤ 0.05; r—correlation coefficient.
3.2. Bioconcentration Factors

In the series without amendments, soil Cu contamination increased the bioconcentration factors (BCF) for all tested trace elements in shoots of maize as compared to the uncontaminated soil (Figure 4). The exception was Cu. The BCF value of Cu decreased with the increasing soil contamination.

**Figure 4.** Bioconcentration factor (BCF) of copper (Cu), zinc (Zn), nickel (Ni), manganese (Mn), iron (Fe) and cobalt (Co) in shoots of maize (*Zea mays* L.). LSD significant for: ** $p \leq 0.01$, * $p \leq 0.05$; n.s.—non-significant.
The increase was the lowest for Zn and Fe and the highest for Co. All of the amendments applied to the soil modified the BCF value of all elements. All of the amendments, particularly compost, increased the Ni and, to a small degree, the BCF value of Cu in shoots of maize, as compared to the control series (without amendments). Compost contributed to a decrease and zeolite to an increase in the Zn, Mn and Fe BCF values, with the changes being relatively minor. Reverse relationships were noted for Co. Bentonite increased the bioconcentration factor for Zn and, particularly, for Ni, while reducing the BCF values for the other elements. However, the BCF values for Fe, Co and Cu were low (on average, 0.012, 0.086 and 0.168, respectively), medium for Ni (0.640) and rather high for Mn and Zn (1.563 and 2.188, respectively).

4. Discussion

4.1. The Effect of Copper Soil Contamination on Plants Used or Phytoremediation

According to Murakami and Ae [23], maize (Zea mays L.) has a high potential for copper phytoextraction. However, maize is more sensitive to soil Cu contamination than, for example, energy plants [22]. Its use can yield good results for minor or medium soil contamination with Cu, but it depends on providing the plants with sufficient water.

The phytotoxicity of Cu is determined by the soil properties, including the presence of other elements which may have an antagonistic or synergistic effect. In an experiment by Wyszkowski [31], soil Cu contamination resulted in a very high increase in the Cu concentration and a relatively low increase for Cd in acidic sandy soil and a decrease in Ni, Pb, Zn, Mn, Fe and Co concentrations of the soil. The reduction in the content of trace elements in the soil was related to their lower uptake by plants in the more polluted soil. The highest doses of copper limited the plant biomass and the uptake of trace elements from the soil. Copper toxicity to plants, including maize, is determined by the labile copper and free Cu$^{2+}$ ion concentrations in the soil [15]. A study by Tiecher et al. [35] indicated that in soils contaminated with Cu and Zn, an increase in Zn amount had no effect on Cu toxicity to maize. However, increasing soil contamination with this element has an adverse effect on maize growth and development as well as chlorophyll concentration. It should be stressed, however, that Cu, Zn and Ni concentrations were the highest in the roots, lower in the stem and the leaves and the lowest in maize cobs [22,26]. The increasing soil Cu contamination can limit the root uptake of other elements. In Tao et al. [36], with an increase in the soil contamination with Cu, the Mn and Fe concentrations decreased down to deficiency level in three plant species, namely Brassica juncea, Brassica rapa and Brassica napus. Consequently, chlorosis of the shoots of the plants was noted. Here, an increase in the soil Cu contamination contributed to a decrease in plant biomass and an increase in the concentrations of most trace elements in maize, including Mn and Fe.

Considerable differences are observed in individual metalloid phytoextraction by the same plant species. According to Tao et al. [36], Brassica spp. remove Zn from the soil more quickly and more effectively than they remove Cu. However, if both elements are present in them at the same time in large quantities, their removal by plants is less effective than for contamination with one of the elements (Cu or Zn).

Bioconcentration factors (BCF) for trace elements in maize (e.g., Cu, Zn, Cr, Pb or Cd) are correlated with soil contamination and their concentrations in plants [37]. According to Aladesanmi et al. [7], bioconcentration factors for Zn and Cu and certain other trace elements (e.g., Cd) in maize are high due to their easy accumulation in plants. According to Wang et al. [37], bioconcentration factors for trace elements in maize cobs were ranked in the following order: Pb < Cr < Zn < As < Cu < Cd < Hg. They amounted to 0.054, 6.65 · 10$^{-4}$, 7.94 · 10$^{-4}$, 0.0044, 0.028, 0.13 and 0.19, respectively.

4.2. The Effect of Amendments on Plants Cultivated on Soil Contaminated with Copper

The solubility of trace elements can be regulated by controlling soil properties, such as the pH, organic matter concentration and the mineral composition [38]. The effectiveness of phytoremediation
can, therefore, be enhanced by applying various amendments into soil. A particular role is served by amendments containing large quantities of organic matter which, while enriching the soil, have a positive effect on the development of soil microorganisms that mostly have a limiting effect on the availability of trace elements to plants [13].

According to Oorts [39], copper is found in soil mainly as Cu$^{2+}$ and tends to bind with organic matter. Most soil-soluble Cu (even as much as over 90%) is found in complexes with dissolved organic matter. Copper toxicity in soils with a good sorption complex and with a neutral reaction is significantly lower than in acidic soils of poor quality or in strongly alkaline soils. The application of an organic substance into the soil (especially to acidic sandy soil) has a positive effect on several other soil properties [40], especially on the available macronutrient form concentration [41], which is not neutral for the uptake of trace elements by plants. In a study by Wyszkowski [31], compost reduced Cu, Cd, Cr, Ni and Co concentrations and, to a lesser extent, Pb and Mn concentrations in acidic sandy soil. In an experiment by Urunmatsoma et al. [13], an organic substance applied into sandy clay loam soil bound Cu, Cr and other heavy metals. They were found in the soil in both organic and residual forms and were taken up by plants in reduced quantities, which had a positive effect on maize growth and development. A positive effect of compost, expressed by an increase in the yield of shoots and in root length, a decrease in metal uptake by plants and an increase in the pH value and nutrients in soil contaminated with Cu, was also observed by Farrell et al. [21]. According to Janoš et al. [42], most Zn in soil (over 60%) is rather strongly bound in the residual fraction and is characterised by low mobility. With an increase in the clayey part concentrations of the soil, the binding of trace elements in the sorption complex increases their mobility, among others, and their uptake by plants decreases [14]. Positive changes in soil properties can prove to be insufficient to neutralise the phytotoxicity of Cu, especially in soils severely contaminated with this heavy metal for a long time (over 3000 mg Cu/kg of soil), which, despite the application of humus, can prevent maize germination and development [15].

According to Zołnowski et al. [43] and Lam et al. [44], the application of an organic substance into soil reduces the bioconcentration factors for trace elements in plants, including in maize. In a study by Sigua et al. [45], manure had a similar effect on the bioconcentration factor values for Zn and Cd in the shoots and roots of maize. This was confirmed in the author’s own study, in which compost reduced the concentrations of most trace elements in maize; the exception was Ni.

Changes in pH value following the application of calcium and other de-acidifying agents, or even an organic substance, have a very positive effect on the trace element concentration of maize [36]. An increase in soil pH to a value close to neutral has an immobilising effect on trace elements in soil [14]. However, in an acidic environment, high variability is observed in the mobility of individual trace elements. Certain metals, e.g., Ni, Zn or Cd, are characterised by very high mobility, while others, e.g., Cu and Pb, by low mobility in the soil, which is directly reflected in their concentration in plants [13]. The solubility of Cu, Zn and other trace elements increases with a decrease in the soil pH value, e.g., for Zn and Cu, while a decrease in the soil pH to 6.2 and 5.5, respectively, increases their mobility, bioavailability and toxicity [38]. According to Tao et al. [36], during the maize growing period, there is an increase in the pH and organic carbon concentration and the microbial count in the maize rhizosphere, which affects the mobility of Cu and other trace elements and their concentration in plants. However, due to the relatively minor effect of soil pH on Cu, this effect appears to be greater on other trace elements.

A study by Ling et al. [20] indicates that bentonite can be a very good sorbent of heavy metals. They concluded that bentonite was most effective in immobilising copper (Cu$^{2+}$) in soils contaminated for a long time. Its application into the soil was effective within a broad pH range of 2.5–7.0. Bentonite also contributes to overall improvement in soil quality. In the neutralisation of heavy metals, natural zeolites characterised by a high capacity for ion exchange can be used. One of them, clinoptilolite, which was used in the author’s own study, exhibits a high selectivity towards certain ions of trace elements, e.g., Cu$^{2+}$ and Zn$^{2+}$ [8]. In a study by Wyszkowski [31], the application of bentonite and zeolite decreased the Cu, Zn, Cr and Cd concentrations and, partially, the Pb and Mn concentrations in acidic
sandy soil. Zeolite had an analogous effect on Fe, as did bentonite on Zn accumulation in acidic sandy soil. The effect of zeolite was greater than that of bentonite. Janoš et al. [42] concluded that application of zeolite reduced the mobility of Cu and, to a lesser degree, of Zn in the soil. In an experiment by Wyszkowski and Sivitskaya [46], bentonite decreased Cu and Fe concentrations, but bentonite and zeolite had no positive effect on the Cr and Mn concentrations of soil (loamy sand). According to ˙Zołnowski et al. [43], the application of mineral additives (zeolite) into loamy sand soil contributed to a reduction in the bioconcentration factor for maize in the soil. Here, bentonite and zeolite contributed to a decrease in the concentration of all trace elements (except Ni) in maize.

In summary, it can be concluded that composts [21,47,48], similarly to zeolite [31,48] and bentonite [20,49] are very suitable to assist in the restoration of plant growth in polluted areas. The beneficial effect of organic matter (compost) on the plant and soil properties was completely different from the mineral amendments (bentonite and zeolite) [31,41].

5. Conclusions

The yield of shoots and the trace element concentration in the shoots of maize was influenced by soil Cu contamination and amendment incorporation into the soil. In the unamended series, Cu-spiked soil increased the yield of shoots (only up to the concentration of 100 mg Cu/kg of soil) and the Cu, Co, Mn, Ni and Fe concentrations in the shoots of maize and, to a lesser extent, contributed to the accumulation of Zn, as compared to the control pot (without Cu). Under the influence of 150 and 200 mg Cu per kg soil, a decrease in yield of shoots of maize was observed. It also increased the bioconcentration factors (BCF) for all tested trace elements in maize shoots, particularly Co. The exception was Cu. The bioconcentration factors of Cu decreased with increasing soil contamination.

All amendments had a significant effect on the yield of shoots and the trace element concentration in shoots of maize. Compost, bentonite and zeolite increased the yield of shoots and decreased the Cu, Co, Mn and Zn concentrations in the shoots of maize. Bentonite had a more positive effect than compost and zeolite on the yield of shoots and the concentration of Co, Mn and Zn in shoots of maize. As for Cu and Fe, opposite relationships were noted. All amendments, especially bentonite and zeolite, increased the Ni concentration in the shoots of maize. The amendments applied into the soil, particularly compost, increased the Ni and, to a small degree, Cu BCF in the shoots of maize, as compared to the control series (without amendments). The BCFs for other trace elements in shoots of maize were determined by the type of substance applied to the soil. Compost, zeolite and especially bentonite are very good amendments in the restoration of maize growth in polluted areas.

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