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# IMPACT OF BOTTOM SEDIMENTS ON ASSIMILABILITY OF COPPER AND ZINC IN LIGHT SOIL

## WPŁYW OSADÓW DENNYCH NA PRZYSWAJALNOŚĆ MIEDZI I CYNKU W GLEBIE LEKKIEJ

**Abstract:** The aim of the research was to evaluate an effect of bottom sediment addition on the content of soluble forms of copper and zinc in light soil as well as to evaluate the bioaccumulation of these elements by energetic plants, *ie Miscanthus giganteus* and *Sida hermaphrodita*. In order to reach the research goal, a field experiment was set up in autumn 2010 in Lipie near Rzeszow using the method of random blocks. The experimental design included 3 doses of the bottom sediment added to soil and a control treatment without sediment supplement. Doses of the bottom sediment were calculated based on soil hydrolytic acidity and the content of calcium carbonate in the sediment. The bottom sediment used in the experiment was taken from the Rzeszow Reservoir and was characterized by alkaline reaction and silt texture. Moreover, it showed an 8-times greater content of soluble forms of copper and zinc in comparison to the experimental soil. The soil of experimental field had granulometric composition of weakly clayey sand with very acid reaction ($pH_{KCl} = 4.53$), as well as low content of soluble and bioavailable forms of copper and zinc. *Miscanthus giganteus* and *Sida hermaphrodita* were chosen for test plants. In autumn 2011 and 2012, soil samples were collected from the experimental plots. In those samples, the contents of copper and zinc soluble forms extracted with 1 mol $HCl \cdot dm^{-3}$ were determined according to Rinkis method. The content of copper and zinc in soil samples and the above-ground parts of plant was determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES). On the basis of the obtained results, the bioaccumulation factor [BF] of both metals in the above-ground plant biomass was calculated. The obtained results were elaborated statistically using a one-way analysis of variance and Tukey's test at a significance level of $\alpha = 0.01$.

The addition of the bottom sediments to the light soil caused a change its reaction in all the experimental treatments in relation to the control treatment. The applied doses of bottom sediments did not cause exceeding the permissible concentrations of copper and zinc in the examined soil. The content of available for plants soluble forms of copper and zinc in light soil under *Miscanthus giganteus* and *Sida hermaphrodita* cultivation increased as consequence of rising bottom sediment doses introduced to the substratum. The addition of the bottom sediments to the soil resulted in a decrease of values of the bioaccumulation factor of copper and zinc in selected energetic plants.

**Keywords:** bottom sediments, copper, zinc, soluble forms, bioaccumulation factor

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## Introduction

Sediments that are deposited at the bottom of water bodies as a result of sedimentation have a very varied chemical composition. Apart from nutrients, they also contain toxic substances that get into waters with surface flow, with industrial and municipal sewage or with inflow waters. Bottom sediments are important in the functioning of water ecosystems and constitute an integral part of the water environment [1, 2]. Bottom sediment management or disposal after their extraction from the bottom of rivers, dam reservoirs, ponds, channels or ports is currently an important ecological problem [3–5]. Agricultural use of chemically and biologically uncontaminated bottom sediments may be the most rational way of using them, as reported by many authors [3, 6–9]. It is commonly known that mineral-organic materials might be used to enrich marginal soils with assimilable minerals [7]. One of the materials might be bottom sediments, especially the ones with neutral or basic reaction and with a large amount of silt and clay fractions [9].

With relation to the above, the aim of the research was to evaluate an effect of the bottom sediment addition on the amount of soluble forms of copper and zinc in light soil, as well as on bioaccumulation of copper and zinc in energetic plant biomass.

## Material and methods

The research on the effect of bottom sediment addition to light soil was conducted in the years 2011–2012 in field experiment conditions. In order to reach the research goal, a field experiment was set up in autumn 2010 in Lipie near Rzeszow using the method of random blocks. Two energetic plants, *ie Miscanthus giganteus* and *Sida hermaphrodita,* were chosen as test plants. The field experiment comprised 32 plots, with an area of 10 $m^2$ each. In spring 2011, *Miscanthus giganteus* seedlings were planted on 16 of them, and *Sida hermaphrodita* seedling were planted on the remaining 16 plots. Doses of the bottom sediment introduced to soil were calculated based on the content of calcium carbonate in the sediment and on soil hydrolytic acidity (Hh), *ie* doses of CaO were calculated according to a half, one and two hydrolytic acidity values.

The experimental design comprised 4 treatments (each in 4 replications) which differed in the dose of the introduced bottom sediments: I – control, II – soil + 5.625 $Mg \cdot ha^{-1}$ of sediment DM, III – soil + 11.25 $Mg \cdot ha^{-1}$ of sediment DM, IV – soil + 22.5 $Mg \cdot ha^{-1}$ d.m. of sediment. Additionally, treatments in which *Miscanthus giganteus* or *Sida hermaphrodita* were the test plants were marked with M and S symbols, respectively.

The bottom sediment used in the experiment came from the Rzeszow Reservoir and was characterized by alkaline reaction ($pH_{KCl}$ = 7.89) as well as sandy silt granulometric composition. The contents of copper and zinc in the bottom sediment did not exceed the permissible values for output according to the Regulation of the Minister of Environment of 16 April 2002 on the types and concentrations of substances that cause the output is contaminated [10] and according to the Regulation of the Minister of Environment of 9 September 2002 on soil quality standards and earth quality standards [11]. The experimental soil had granulometric composition of weakly clayey sand and very acid reaction ($pH_{KCl}$ = 4.53). The contents of available copper and zinc forms in soil and sediment are presented in Table 1.

Table 1

Content of assimilable forms of copper and zinc as well as pH value of soil and of bottom sediments used in the experiment

| Specification | Cu | Zn | $pH_{KCl}$ |
|---|---|---|---|
| | soluble in 1 mol HCl · $dm^{-3}$ [mg · $kg^{-1}$] | | |
| Light soil | < 4 | 14.1 | 4.53 |
| Bottom sediment | 27.1 | 105.7 | 7.89 |

In autumn 2011 and 2012, soil samples weighing approximately 0.5 kg were collected from the experimental plots. In those samples, $pH_{KCl}$ was measured potentiometrically, and the contents of copper and zinc soluble forms extracted with 1 mol HCl · $dm^{-3}$ were determined according to Rinkis method by means of atomic absorption spectrometry (AAS).

After vegetation, in November 2011 and 2012, the above-ground biomass obtained in the experiment was gathered and homogenized using a mechanical cutter. Samples of plant material were collected from such prepared cumulative samples (from individual plots). The biomass collected in this way was subjected to dry mineralization at a temperature of 450 $^{o}$C, and the obtained ash was dissolved in 20 % nitric acid. The content of copper and zinc in the above-ground parts of both test plants was determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES). On the basis of the obtained results, the bioaccumulation factor (BF) was calculated for the above-ground parts as a ratio of the content of copper and zinc in plant to their content in soil. The obtained results were elaborated statistically, taking into consideration a one-way analysis of variance and Tukey's test at a significance level of $\alpha = 0.01$.

## Results

Total amount of the both studied elements introduced to the soil was calculated basing on the total content of copper and zinc in the bottom sediment (Table 2). The results of $pH_{KCl}$ measured in the soil samples after harvest of *Miscanthus giganteus* and *Sida hermaphrodita* taken from individual treatments are presented in Table 2.

Table 2

Total content of copper and zinc introduced into the soil with bottom sediment and $pH_{KCl}$ of soil

| Treatments* | Cu | Zn | $pH_{KCl}$ | |
|---|---|---|---|---|
| | [kg · $ha^{-1}$ d.m.] | | *Miscanthus giganteus* | *Sida hermaphrodita* |
| I | — | — | 4.53 | 4.53 |
| II | 1.90 | 7.42 | 5.50 | 5.15 |
| III | 3.81 | 14.86 | 6.00 | 5.79 |
| IV | 7.62 | 29.72 | 6.43 | 6.57 |

* For explanations see methods.

When analyzing the soil reaction in individual treatments, it was found that addition of the bottom sediment to light soil changed the soil reaction, depending on applied dose. In the treatment where half a dose, *ie* according to 0.5 Hh, was used, soil pH was 5.50 in the case of *Miscanthus giganteus* cultivation, and pH = 5.15 when *Sida hermaphrodita* was cultivated. Addition of a full sediment dose, *ie* according to 1 Hh, improved the soil reaction (to pH = 6.0) in the treatment where *Miscanthus giganteus* constituted vegetation cover for soil, and to pH = 5.79 in the treatment with *Sida hermaphrodita*. A double sediment dose, *ie* according to 2 Hh, changed the reaction of light soil to pH = 6.43 (*Miscanthus giganteus*) and pH = 6.57 (*Sida hermaphrodita*) (Table 2).

Copper content was within a narrow range, from 2.47 to 4.81 mg · kg$^{-1}$ of soil d.m. in the 1st year of the experiment, and from 1.64 to 3.47 mg · kg$^{-1}$ of soil d.m. in the 2nd year of the experiment in the case of *Miscanthus giganteus* cultivation, and from 2.59 to 4.92 mg · kg$^{-1}$ of soil d.m. and from 1.78 to 3.22 mg · kg$^{-1}$ of soil d.m. in the 1st and 2nd year of the experiment, respectively, when *Sida hermaphrodita* was cultivated (Table 3).

Table 3

Content of soluble forms of copper and zinc in light soil

| Treatments* | Years of research | | | |
|---|---|---|---|---|
| | 2011 | 2012 | 2011 | 2012 |
| | Cu | | Zn | |
| | [mg · kg$^{-1}$ d.m.] | | | |
| M I | 2.47$^{a}$ | 1.64$^{a}$ | 9.66$^{a}$ | 9.36$^{a}$ |
| M II | 2.78$^{a}$ | 1.92$^{a}$ | 9.81$^{a}$ | 9.92$^{a}$ |
| M III | 4.12$^{a}$ | 2.73$^{a}$ | 10.82$^{a}$ | 11.66$^{a}$ |
| M IV | 4.81$^{a}$ | 3.47$^{a}$ | 11.14$^{a}$ | 12.74$^{a}$ |
| S I | 2.59$^{a}$ | 1.78$^{a}$ | 10.07$^{a}$ | 9.75$^{a}$ |
| S II | 3.05$^{a}$ | 2.01$^{a}$ | 10.51$^{ab}$ | 10.37$^{a}$ |
| S III | 3.43$^{a}$ | 2.38$^{ab}$ | 10.80$^{ab}$ | 11.32$^{a}$ |
| S IV | 4.92$^{b}$ | 3.22$^{b}$ | 13.98$^{b}$ | 12.60$^{a}$ |

* For explanations see methods.

In the treatment where *Miscanthus giganteus* constituted the vegetation cover, the content of soluble forms of copper increased proportionally to the increase of the bottom sediment dose in the first and second year of the experiment. Those differences were not statistically significant. The highest content of the copper soluble forms, amounting to 4.92 mg · kg$^{-1}$ of soil d.m., was found in the soil on which *Sida hermaphrodita* was cultivated in the treatment where the sediment dose according to 2 Hh was applied. The smallest copper content, amounting to 1.78 mg · kg$^{-1}$ of soil d.m., was stated in control without addition of bottom sediment (Table 3). It was established that the differences in copper content in the biomass of *Sida hermaphrodita* were statistically significant. The contents of the soluble form of copper in the second year of the experiment decreased on average by 32 % in treatments where *Miscanthus giganteus* was cultivated, and by 33 % in treatments where *Sida hermaphrodita* was cultivated (Table 3).

Zinc content in soil in the case of *Miscanthus giganteus* cultivation was increasing along with the increase in the bottom sediment amount added to soil, and it was, respectively: from 9.66 mg · kg$^{-1}$ of soil d.m. in control treatment to 11.14 mg · kg$^{-1}$ of soil d.m. in the treatment with double sediment dose in the 1st year, and from 9.36 mg · kg$^{-1}$ of soil d.m. to 12.74 mg · kg$^{-1}$ of soil d.m. in the 2nd year (Table 3). Zinc content in the soil in the second year of the experiment in the control treatment diminished by 3 %, whereas in treatments with addition of the sediment that content increased on average by 7 %. Those differences were not statistically significant. In the treatment where *Sida hermaphrodita* constituted the soil cover, a statistically significant diversification in soluble form of zinc contents was found and they amounted from 10.07 mg · kg$^{-1}$ of soil d.m. in the control treatment to 13.98 mg · kg$^{-1}$ of soil d.m. in the treatment with a double dose of the bottom sediment after the 1st year of plant vegetation, and from 9.75 mg · kg$^{-1}$ of soil d.m. in the control treatment to 12.60 mg · kg$^{-1}$ of soil d.m. in the treatment with the biggest dose of the sediment after the 2nd year of plant vegetation (Table 3). The soil abundance in zinc increased in the second year of the experiment only in the treatment with single dose of the bottom sediment, and in other treatments it decreased on average by 5 %, and the differences were not statistically significant (Table 3).

When analyzing the copper content in the biomass of *Miscanthus giganteus*, a small diversification in concentrations of this element can be found, ranging from 1.79 mg · kg$^{-1}$ of d.m. in the control treatment to 2.10 mg · kg$^{-1}$ of d.m. in the treatment with a double dose of the sediment. Similar contents were found in the biomass of *Sida hermaphrodita*, ranging from 1.80 mg · kg$^{-1}$ of d.m. in the control treatment to 2.49 mg · kg$^{-1}$ of d.m. in the treatment with a double dose of the sediment (Table 4).

Table 4

Content of copper and zinc in plant biomass

| Treatments* | Years of research | | | |
|---|---|---|---|---|
| | 2011 | 2012 | 2011 | 2012 |
| | Cu | | Zn | |
| | [mg · kg$^{-1}$ d.m.] | | | |
| M I | 1.79$^{a}$ | 1.88$^{a}$ | 31.67$^{b}$ | 44.22$^{a}$ |
| M II | 1.82$^{a}$ | 1.95$^{a}$ | 27.72$^{ab}$ | 37.17$^{a}$ |
| M III | 1.85$^{a}$ | 2.11$^{a}$ | 27.63$^{ab}$ | 35.06$^{a}$ |
| M IV | 1.99$^{a}$ | 2.10$^{a}$ | 26.45$^{a}$ | 35.70$^{a}$ |
| S I | 1.80$^{a}$ | 2.28$^{a}$ | 15.87$^{b}$ | 39.07$^{a}$ |
| S II | 2.06$^{a}$ | 2.32$^{a}$ | 11.56$^{a}$ | 29.53$^{a}$ |
| S III | 1.89$^{a}$ | 2.33$^{a}$ | 10.19$^{a}$ | 28.85$^{a}$ |
| S IV | 1.98$^{a}$ | 2.49$^{a}$ | 10.27$^{a}$ | 27.51$^{a}$ |

* For explanations see methods.

Results of analyses confirm the effect of bottom sediment addition on the copper content in the biomass of energetic plants increasing its level, although these differences are not statistically significant. Moreover, an increase in the copper content was found in the second year of the experiment in the biomass of *Miscanthus giganteus* on average by 7 %, and in the biomass of *Sida hermaphrodita* – on average by 18 % (Table 4). Zinc content in the biomass of *Miscanthus giganteus* in the 1st year of the experiment was between 26.45 mg · kg$^{-1}$ of d.m. in the treatment with a double dose of the sediment and 31.67 mg · kg$^{-1}$ of d.m. in the control treatment, and in the 2nd year of the experiment this content was between 35.06 mg · kg$^{-1}$ of d.m. in the treatment with single dose of the sediment and 44.22 mg · kg$^{-1}$ of d.m. in the control treatment (Table 4). The zinc content in the biomass of *Sida hermaphrodita* after the 1st year of vegetation was between 10.19 and 15.87 mg · kg$^{-1}$ of d.m., and between 27.51 mg · kg$^{-1}$ and 39.07 mg · kg$^{-1}$ of d.m. after the 2nd year of vegetation (Table 4). Differences in zinc content in the biomass of *Miscanthus giganteus* and *Sida hermaphrodita* were statistically significant only in the 1st year of the experiment. It needs to be stated that the addition of half a dose of the bottom sediment to the soil caused a decrease in zinc content in the biomass of *Miscanthus giganteus*, on average by 17 %, and in the biomass of *Sida hermaphrodita* – by 34 % (Table 4). The simple and double doses of the bottom sediment addition to the soil on average influenced to a lesser degree the zinc content, lowering its concentration in the biomass of the test plants (Table 4).

Bioaccumulation factor of copper in biomass of *Miscanthus giganteus* ranged from 0.41 to 1.14, and in biomass of *Sida hermaphrodita* fluctuated from 0.40 to 1.28 (Table 5). Bioaccumulation factors for copper were decreasing along with an increase of the bottom sediment addition to the soil in both years of the experiment, as well as in the case of both cultivated test plants.

Table 5

Values of bioaccumulation factor of copper and zinc in plant biomass

| Treatments* | Years of research | | | |
|---|---|---|---|---|
| | 2011 | 2012 | 2011 | 2012 |
| | Bioaccumulation factor [BF] | | | |
| | Cu | | Zn | |
| M I | 0.72 | 1.14 | 3.28 | 4.72 |
| M II | 0.65 | 1.01 | 2.82 | 3.75 |
| M III | 0.45 | 0.77 | 2.55 | 3.01 |
| M IV | 0.41 | 0.60 | 2.37 | 2.80 |
| S I | 0.69 | 1.28 | 1.57 | 4.01 |
| S II | 0.67 | 1.15 | 1.10 | 2.85 |
| S III | 0.55 | 0.98 | 0.94 | 2.55 |
| S IV | 0.40 | 0.77 | 0.73 | 2.18 |

* For explanations see methods.

The computed values of the bioaccumulation factor of zinc in biomass of *Miscanthus giganteus* varied from 2.37 to 4.72, and in biomass of *Sida hermaphrodita* ranged from 0.73 to 4.01 (Table 5). Similarly as in the case of copper, the bioaccumulation factor of zinc was decreasing along with the increase of the bottom sediment addition to the soil, regardless of the year of experiment or tested plant.

## Discussion

The bottom sediment used in the field experiment had alkaline reaction, and after adding and mixing with the very acid soil used in the experiment it significantly improved soil pH and increased productivity of soil. The change in soil reaction in individual experimental treatments depended on the applied sediment dose and on calcium carbonate that was introduced along with the sediment.

According to the previously mentioned regulations, the contents of copper and zinc in the studied experimental treatments did not exceed their permissible contents for output [10], as well as for group B soil quality and ground quality [11]. With relation to the above, it is rational to utilize bottom sediment for agricultural purposes. Despite the introduction of 7.62 kg $\cdot$ ha$^{-1}$ of copper and 29.72 kg $\cdot$ ha$^{-1}$ of zinc (Table 2) to the soil along with the sediment, the content of assimilable forms of both these elements did not increase significantly, which can be attributed to the change in soil reaction. It is commonly known that soil reaction has high effect on metal mobility, and increase in pH value causes a decrease of solubility of copper and zinc in soil [12–15].

A small increase in the content of assimilable forms of copper and zinc in soil of treatments in which bottom sediment was used is beneficial from agricultural point of view, because it may have stimulating effect on the increase in biomass yield from cultivated energetic plants.

The value of the bioaccumulation factor (BF) determines plant sensitivity to elements and also reflects the plant capacity to uptake the element from soil, and it informs about the transfer of this metal from the soil solution to the above-ground parts of a plant and roots [16–18]. This factor is the ratio of the content of an element in a plant to its content in soil. The calculated values of bioaccumulation factors for copper and zinc showed a medium degree of accumulation (BF; 0.1–1), as well as intensive accumulation (BF; 1–10). In comparison to control treatments, the increase of the bottom sediment addition to light soil influenced the decrease in accumulation of copper and zinc in the energetic plants used in the experiment (Table 5).

In all variants that were used, the addition of the bottom sediment influenced the decrease in the bioaccumulation factor for copper and zinc in the biomass of energetic plants (Table 5). When describing the bioaccumulation factor for Cu and Zn, Kabata-Pendias and Pendias [19] stated that despite the higher copper and zinc content in a soil solution, these elements are intensively uptaken by plants. The obtained results point out to a different degree of uptake of the studied elements by the test plants, *ie Miscanthus giganteus* and *Sida hermaphrodita*. It is undoubtedly connected with the physiology of these plants and their different soil requirements.

## Conclusions

1. The bottom sediment addition to the soil caused a change in light soil reaction of all experimental treatments in relation to the control treatment.

2. The content of soluble forms of copper and zinc in light soil in the case of *Miscanthus giganteus* and *Sida hermaphrodita* cultivation increased along with an increase of the bottom sediment dose.

3. The applied doses of the bottom sediment did not exceed the permissible concentrations of copper and zinc in the studied soil.

4. The bottom sediment addition to the soil caused the decrease in the value of bioaccumulation factor of copper and zinc in selected energetic plants.

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# WPŁYW OSADÓW DENNYCH NA PRZYSWAJALNOŚĆ MIEDZI I CYNKU W GLEBIE LEKKIEJ

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**Abstrakt:** Celem badań była ocena wpływu dodatku osadu dennego na zawartość rozpuszczalnych form miedzi i cynku w glebie lekkiej oraz ocena bioakumulacji tych pierwiastków przez rośliny energetyczne, tj. *Miscanthus giganteus* i *Sida hermaphrodita*. Dla realizacji tego celu badań założono doświadczenie polowe jesienią 2010 r., w miejscowości Lipie koło Rzeszowa, metodą losowanych bloków. Schemat doświadczenia obejmował 3 dawki osadu dennego stosowanego do gleby oraz obiekt kontrolny bez dodatku osadu. Dawki osadu obliczono na podstawie wartości kwasowości hydrolitycznej gleby oraz zawartości węglanu wapnia w osadzie. Wykorzystany w doświadczeniu osad denny pobrany ze Zbiornika Rzeszowskiego miał odczyn alkaliczny oraz skład granulometryczny pyłu. Ponadto wykazywał 8-krotnie większą zawartość rozpuszczalnych form miedzi i cynku, w porównaniu z glebą użytą w doświadczeniu. Doświadczenie założono na glebie o składzie granulometrycznym piasku słabo gliniastego, o odczynie bardzo kwaśnym ($pH_{KCl}$ = 4,53) oraz niskiej zawartości przyswajalnych form miedzi i cynku. Jako rośliny testowe wybrano miskant olbrzymi i ślazowiec pensylwański. Z poletek doświadczalnych jesienią 2011 i 2012 r. pobrano próbki glebowe, w których oznaczono zawartość rozpuszczalnych form miedzi i cynku ekstrahowanych 1 mol $HCl \cdot dm^{-3}$ według metody Rinkisa. Zawartość miedzi i cynku w glebie oraz częściach nadziemnych roślin oznaczono metodą atomowej spektometrii emisyjnej opartej na palniku indukcyjnie wzbudzonej plazmy (ISP-AES). Na podstawie uzyskanych wyników obliczono współczynniki bioakumulacji [WB] w nadziemnej biomasie roślin. Uzyskane wyniki opracowano statystycznie stosując jednoczynnikową analizę wariancji i test Tukeya przy poziomie istotności $\alpha = 0,01$.

Dodatek osadu dennego do gleby lekkiej spowodował zmianę odczynu gleby we wszystkich obiektach doświadczalnych w stosunku do obiektu kontrolnego. Analiza wykazała zwiększenie zawartości dostępnych dla roślin rozpuszczalnych form miedzi i cynku w glebie pod uprawą obydwu roślin testowych na skutek wprowadzenia do niej wzrastających dawek osadu dennego. Zastosowane dawki osadu dennego nie spowodowały przekroczenia dopuszczalnych zawartości miedzi i cynku w badanej glebie. Dodatek osadu dennego do gleby skutkował zmniejszeniem wartości współczynnika bioakumulacji miedzi i cynku w wybranych roślinach energetycznych.

**Słowa kluczowe:** osady denne, miedź, cynk, formy rozpuszczalne, współczynnik bioakumulacji