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EFFECT OF BOTTOM DEPOSIT SUPPLEMENT ON TRACE ELEMENT CONTENT IN LIGHT SOIL

WPŁYW DODATKU OSADU DENNEGO NA ZAWARTOŚĆ PIERWIASTKÓW ŚLADOWYCH W GLEBIE LEKKIEJ

Abstract: The research aimed at an assessment of bottom deposit supplement effect on the content and mobility of selected trace elements in light soil. The investigations demonstrated a positive effect of bottom deposit on increasing light soil pH. After a two-year research period the soil pH was 6.24 on the control treatment, 6.49 on the treatment with a 5 % supplement of the deposit and 6.86 on the treatment containing 10 % of the deposit. Bottom deposit supplement to light soil significantly diminished the content of zinc, lead and manganese available forms extracted with 1 mol HCl $\cdot$ dm^{-3} and bioavailable forms of cadmium, manganese and iron extracted with 0.01 mol CaCl$_2$ $\cdot$ dm^{-3}. No apparent influence of the soil pH on diminishing the availability of a majority of analyzed elements was found, which has been confirmed by negative and insignificant values of correlation coefficients between pH value and element content in soil.

Keywords: bottom deposit, trace elements, light soil, 0.01 mol CaCl$_2$ $\cdot$ dm^{-3} extract, 1 mol HCl $\cdot$ dm^{-3} extract

Dredging water reservoirs is a commonly used measure allowing to maintain them in a proper state so that they fulfill their economic and environmental functions [1–3]. In pursuance of the regulation of the Minister of the Natural Environment [4], bottom deposit (the output) is a waste marked with 1705 code, which requires an appropriate management. The research conducted by Wisniowska-Kielian and Niemiec [5] revealed that the extracted deposits, showing a neutral or alkaline reaction and high fraction of silt and clay fractions, may be used for an improvement of physicochemical properties of light and acid soils. On the other hand, Pelczar et al [6] report that despite high content of fertilizer substances, bottom deposits are unsuitable for agricultural application because of heavy metal contamination. These deposits should be used as a material

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for reclamation of mine waste landfills and fly ash disposal sites [6]. At this point it should be mentioned that the form in which trace elements occur in soils (total or soluble) or in bottom deposits are very important from ecological viewpoint because some are toxic (Pb, Cd) and in excess all are harmful for living organisms. Frequently total element contents are considered and used for indications of the degree of soil environment contamination [7]. However, total contents are not the best indicator of element availability and mobility in soil. Therefore an analysis of bioavailable element form concentrations seems justified, since they are a potential source of minerals for plants and may pose a hazard for the soil environment when they are too high. The research aimed at an assessment of the effect of bottom deposit on the content and mobility of selected trace elements in light soil.

Material and methods

A two-year pot experiment (2006–2007) was conducted on light soil with granulo-metric composition of weakly loamy sand (Tables 1, 2). The bottom deposit originated from a small retention reservoir located in Zeslawice village at 8.7 km of the Dlubnia River course (Malopolska province) [8].

Table 1

Characteristics of selected properties of soil and bottom deposit

Component	pH_{KCl}	C org.	N total	P_2O_5	K_2O
		[g · kg^{-1} d.m.]		[mg · kg^{-1} d.m.]	
Soil	6.21	9.37	0.36	78.70	165.96
Bottom sediment	7.35	15.80	1.0	44.61	69.76

Table 2

Contents of heavy metals in soil and bottom deposit

Component	Cr	Zn	Pb	Cu	Cd	Ni	Fe	Mn
	[mg · kg^{-1} d.m.]							
Soil	5.93	62.0	29.75	4.00	0.68	4.15	3010	150
Bottom sediment	15.0	76.31	12.85	12.23	0.35	11.0	7550	140

The material was qualified to ordinary silt deposit group with pH_{KCl} = 7.35. Moreover the deposit revealed low content of bioavailable phosphorus and potassium but high content of magnesium. According to standards concerning the quality of bottom deposits, heavy metal concentrations in the analyzed deposit did not exceed the content permissible for the output [9] or for group B soil and earth [10]. According to the IUNG assessment, comprising a 6-degree soil classification regarding heavy metal concentrations, considering the reaction and granulometric composition, the analyzed deposit, revealed the natural contents (degree 0). On the other hand, according to the

limit heavy metal contents, the soil used for the experiment showed elevated content of Zn and Cd (degree I) [7]. The experimental design comprised 3 treatments in 4 replications: soil without bottom deposit (control) (I), soil with a 5 % supplement of bottom deposit (II) and soil with a 10 % addition of the deposit (III). Equal NPK fertilization was applied on all treatments in doses respectively: 1.8 g N; 1.1 g P; 2.2 g K per pot (8 kg of soil d.m.). Mineral salts as NH_4NO_3; KH_2PO_4 and KCl were applied once before the test plant (maize) sowing. Air-dried bottom deposit was added to the soil in the first year of the investigations.

In the soil samples collected in the second year of the experiment pH was assessed in 1 mol KCl · dm^{-3} by potentiometer and the content of selected trace elements (iron, manganese, zinc, copper, nickel, chromium, lead and cadmium) was determined. Total element content in soil was assessed after hot mineralization in the mixture of HNO_3 and $HClO_4$ acids (2:1). The soluble forms of Zn, Cu, Ni, Pb, Cr, Cd, Fe and Mn were extracted from the soil with 1 mol · dm^{-3} HCl solution (Rinkis method) and with 0.01mol · dm^{-3} $CaCl_2$ solution [11–13]. Extraction of the soluble element forms was conducted at the soil to solution ratio 1:10 and during extraction lasting 1 hour (1 mol HCl · dm^{-3}) and 2 hours (0.01 mol $CaCl_2$ · dm^{-3}). The element concentrations in the solutions were assessed using ICP-AES apparatus (JY 238 ULTRACE, Jobin Yvon). The obtained results were verified statistically using one-way ANOVA at significance level $\alpha = 0.05$, by means of Statistica 8.1 programme.

Results and discussion

In conditions of acid soil reaction solubility of most elements toxic for plants increases, whereas solubility of main nutrients decreases [14, 15]. After a two-year period of investigations the soil pH, depending on the experimental treatment, was 6.42 on the control, 6.49 on the treatment with a 5 % bottom sediment supplement and 6.86 on the treatment with a 10 % sediment addition. Therefore, bottom deposit supplement to the soil caused an increase in light soil pH value by 17 % (5 % deposit supplement) and by 23 % (10 % addition of the sediment) in relation to the control treatment, whereas the increase reached 5 and 10 % in comparison with the initial soil.

The effect of bottom sediment admixture on the content and mobility of the analyzed trace elements was shown in Table 3. Total content of zinc in the soil after the experiment completion was not significantly diversified and fluctuated from 61.54 to 62.34 mg · kg^{-1} d.m. On the other hand, bottom deposit supplement to the soil markedly diversified the content of this metal forms soluble both in 0.01 mol $CaCl_2$ and in 1 mol HCl · dm^{-3} (Table 3). On the treatments with 5 % and 10 % share of the bottom deposit, on average 44 % and 45 % increase in zinc forms soluble in 0.01 mol $CaCl_2$ · dm^{-3} extract was assessed in comparison with the control. On the other hand under the influence of 1 mol HCl · dm^{-3} a decreased availability of this metal was observed by 41 % (at 5 % of the deposit addition) and by 26 % (at 10 % of bottom deposit). The share of soluble zinc forms extracted with 0.01 mol $CaCl_2$ · dm^{-3} was between 23 and 33 % and extracted with 1 mol HCl · dm^{-3} between 44 % and 75 % of this element total content (Fig. 1).

Table 3

Contents of heavy metals in soil after 2nd year of the experiment [mg $\cdot$ kg^{-1} d.m.]

Treatment	Zn	Cu	Ni	Cr	Cd	Pb	Fe	Mn
0.01 mol CaCl$_2$ $\cdot$ dm^{-3}								
Soil without sediment	14.20	1.57	0.40	0.20	0.56	13.78	221.25	64.13
Soil+ 5 % sediment	20.50	1.37	0.24	0.19	0.46	10.38	124.75	40.03
Soil + 10 % sediment	20.53	1.83	0.57	0.22	0.48	10.82	145.50	46.13
LSD$_{0.05}$	1.77	ns*	ns	ns	0.05	1.13	31.13	10.84
1 mol HCl $\cdot$ dm^{-3}								
Soil without sediment	46.50	2.34	0.48	0.65	0.64	21.37	836.19	100.58
Soil + 5 % sediment	27.65	2.35	0.34	0.64	0.49	18.79	784.29	84.49
Soil + 10 % sediment	34.55	2.26	0.59	0.80	0.50	19.76	891.87	98.70
LSD$_{0.05}$	10.14	ns	ns	0.07	ns	1.45	ns	9.89
Total content								
Soil without sediment	61.54	4.48	4.13	5.88	0.76	26.03	3432.2	137.64
Soil+ 5 % sediment	62.34	5.40	4.55	6.81	0.51	22.25	3530.9	137.60
Soil + 10 % sediment	61.91	4.90	4.10	6.58	0.56	22.36	3718.4	141.50
LSD$_{0.05}$	ns	0.67	0.24	ns	0.09	ns	ns	ns

ns – statistically nonsignificant.

Both doses of bottom sediment added to the soil significantly increased the total copper content. On the treatments which received 10 % share of the deposit the increase was 9 % and on the treatments with 5 % deposit share – 21 % in comparison with the soil without the deposit (Table 3). The soil concentrations of soluble copper forms were not markedly diversified depending on the percent share of the bottom deposit in the soil. Copper soluble in 0.01 mol CaCl$_2$ $\cdot$ dm^{-3} constituted between 25 and 37 % of this metal total content. However, in effect of 1 mol HCl $\cdot$ dm^{-3} copper solubility generally diminished in the direction of: control treatment > 10 % deposit supplement > 5 % deposit supplement and constituted from 44 % to 52 % of the total copper content in the researched soil (Fig. 1).

Total content of nickel in soil after the finished experiment was significantly diversified depending on bottom sediment addition to the soil and fluctuated from 4.10 mg to 4.55 mg $\cdot$ kg^{-1} d.m. The highest content of this metal was assessed on the treatment with a 5 % deposit supplement, whereas the lowest on the treatment with its 10 % share. Bottom deposit did not significantly diversify nickel soluble forms content in the soil (Table 3). The share of nickel forms soluble in 0.01 mol CaCl$_2$ $\cdot$ dm^{-3} ranged from 5 to 14 % of its total content. Available forms of nickel determined in 1 mol HCl $\cdot$ dm^{-3} were on a similar level and ranged from 7 to 14 % of this metal total content (Fig. 1).

The investigations did not demonstrate any marked effect of bottom deposit on total content of chromium and its soluble forms determined in 0.01 mol CaCl$_2$ $\cdot$ dm^{-3} extract
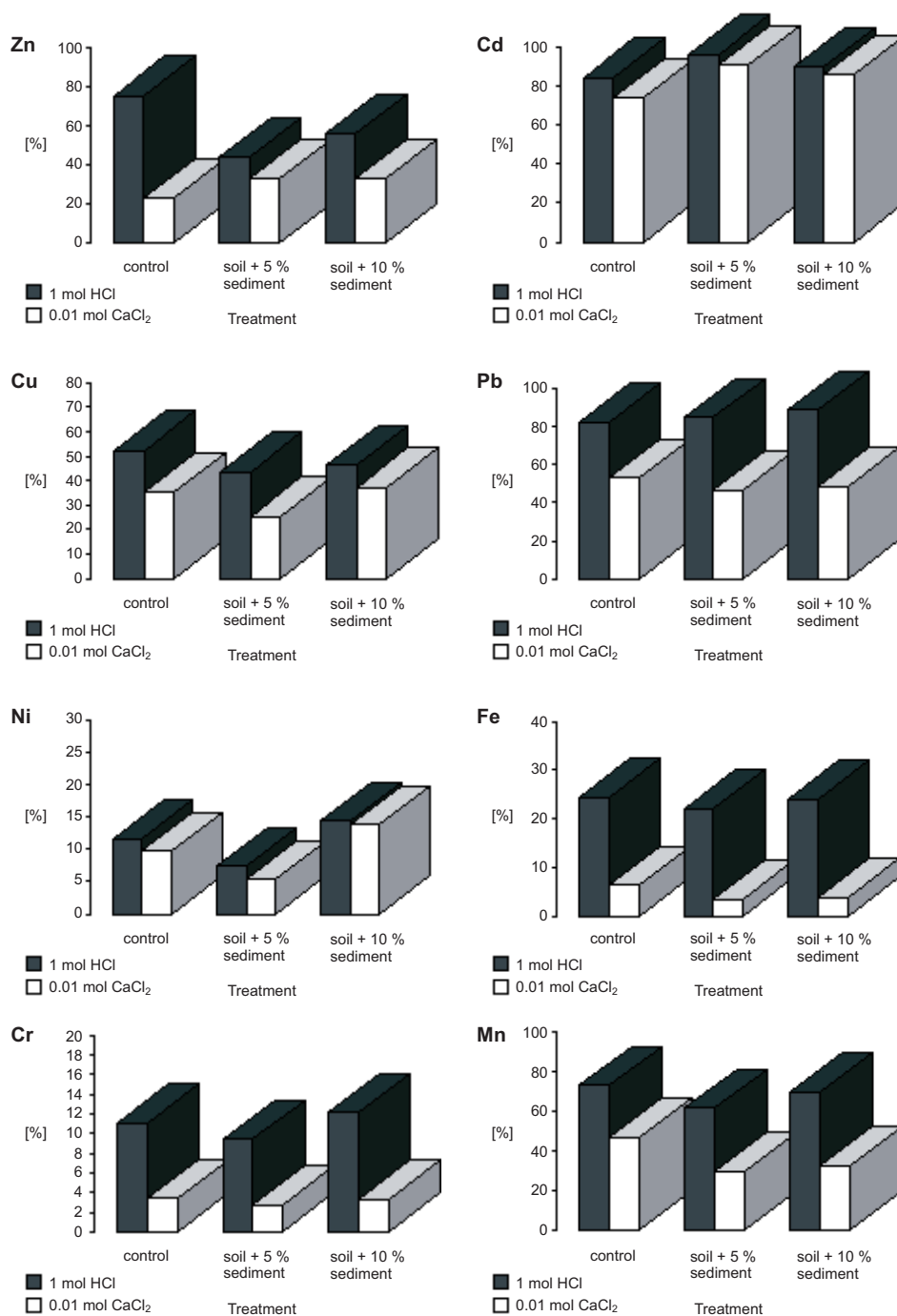
Fig. 1. Percent share of available forms of trace elements in their total contents in soil

(Table 3). The highest value of available chromium forms was found on the treatment with a 10 % addition of bottom sediment, however for extraction with 1 mol HCl $\cdot$ dm^{-3} the dependence was statistically significant. The content of soluble chromium forms in soil constituted from 2.8 to 3.4 % (0.01 mol CaCl$_2$ $\cdot$ dm^{-3}) and from 9 to 12 % (1 mol HCl $\cdot$ dm^{-3}) of this element total content in the researched soil (Fig. 1).

An apparent decline in total cadmium content in relation to the control treatment was demonstrated in the soil with a 5 % share of the deposit, where it diminished by 33 % and in the soil with 10 % deposit supplement showing a 26 % decrease. An admixture of bottom sediment to the soil also affected diminishing the content of this element soluble forms and the dependencies were significant for the extraction with 0.01 mol CaCl$_2$ $\cdot$ dm^{-3} (Table 3). On the treatments with a 5 % deposit admixture a 18 % decrease in cadmium soluble forms in soil was revealed (0.01 mol CaCl$_2$) and a 23 % decline (for 1 mol HCl extraction), whereas on the treatments with a 10 % deposit share, respectively 14 % and 22 % decrease. Generally the soluble cadmium forms content in soil was diminishing in the direction of: control treatment > 10 % deposit supplement > 5 % deposit supplement. Soluble forms of cadmium determined in 0.01 mol CaCl$_2$ $\cdot$ dm^{-3} constituted between 74 and 90 % of this metal total content in soil, whereas determined in 1 mol HCl $\cdot$ dm^{-3} made up between 84 and 96 % (Fig. 1).

When the experiment was completed, total lead content in soil was not significantly diversified in result of bottom sediment admixture and fluctuated from 22.25 to 26.03 mg $\cdot$ kg^{-1} d.m. Application of bottom sediment to the soil significantly diversified the content of this metal soluble forms (Table 3). The treatments with 5 % and 10 % share of bottom deposit revealed a decrease in lead soluble forms content in soil respectively by 25 % and 21 % (0.01 mol CaCl$_2$ $\cdot$ dm^{-3}) and by 12 % and 24 % (1 mol HCl $\cdot$ dm^{-3}) in relation to the treatment without the deposit. Lead forms extracted with 0.01 mol CaCl$_2$ $\cdot$ dm^{-3} constituted between 47 % and 53 %, and those extracted with 1 mol HCl $\cdot$ dm^{-3} from 82 % to 84 % of this metal total concentration (Fig. 1).

Both doses of applied bottom deposit slightly increased total content of iron in soil (Table 3). Also the content of iron soluble forms assessed in 1 mol HCl $\cdot$ dm^{-3} was not dependent significantly on bottom sediment admixture and was diminishing in the direction of: a 10 % deposit addition > control treatment > a 5 % sediment addition. On the other hand, application of bottom deposit to the soil apparently increased the content of this metal bioavailable forms determined in 0.01 mol CaCl$_2$ $\cdot$ dm^{-3} (Table 3). On the treatments with a 5 % supplement of bottom deposit to the soil iron content decreased by 44 % and on treatments with a 10 % admixture by 34 % in comparison with the control. Iron forms soluble in 0.01 mol CaCl$_2$ constituted between 4 % and 6 % of this metal total content in soil, whereas those soluble in 1 mol HCl $\cdot$ dm^{-3} between 22 % and 24 % (Fig. 1).

Total content of manganese in soil after the experiment has been competed fluctuated from 137.64 to 141.50 mg $\cdot$ kg^{-2} d.m. An admixture of bottom deposit to the soil significantly decreased the content of this metal forms soluble both in 0.01 mol CaCl$_2$ and in 1 mol HCl $\cdot$ dm^{-3} in comparison with the control (Table 3).On the treatment where 5 % and 10 % of bottom sediment was applied a decline respectively by 38 and 28 % in solubility of manganese determined in 0.01 mol CaCl$_2$ $\cdot$ dm^{-3} was found. On the

other hand, in effect of 1 mol HCl $\cdot$ dm^{-3} a 15 % decrease in this metal bioavailability was registered (for a 5 % deposit addition) and by 2 % (for a 10 % deposit admixture) in comparison with the control. The share of soluble forms of manganese extracted with 0.01 mol CaCl$_2$ $\cdot$ dm^{-3} was from 29 % to 47 %, whereas the forms extracted with 1 mol HCl $\cdot$ dm^{-3} made up between 61 and 73 % of this element total soil concentrations (Fig. 1).

The process of learning mineral biovailability is important in view of proper plant supply with these components. The issue of trace element bioavailability, which should be addressed is an assessment of their readily soluble forms. It is obvious that element content in plants is the bigger, the more numerous easily available forms of these elements are present in soil [12, 16]. The presented investigations applied a non-specific method using two extraction solutions: 1 mol HCl and CaCl$_2$ $\cdot$ dm^{-3} for the extraction of trace element available forms from the soil mixed with bottom deposit. Application of the test with 1 mol HCl $\cdot$ dm^{-3} is a routine procedure, commonly used by chemical-agricultural stations and by IUNG for the assessment of trace element available forms content in soils [17]. Also the 0.01 mol CaCl$_2$ $\cdot$ dm^{-3} test suggested by Houba et al [13] as a physiological soil solution balanced with the soil solution which may be used for an assessment of nutrient availability to plants [12, 18]. Moreover, according to many authors the 0.01 mol CaCl$_2$ $\cdot$ dm^{-3}, unlike 1 mol $\cdot$ dm^{-3} is counted among solutions with low extraction powers and determining so called bioavailable (active) fraction of trace elements [19,16]. According to expectations in the presented investigations smaller amounts of the analyzed elements were found in the 0.01 mol CaCl$_2$ $\cdot$ dm^{-3}. The content of zinc in this extract was between 26 % and 69 % lower, copper between 19 % and 24 %, nickel from 3 % to 29 %, chromium from 69 % to73 %, cadmium 4–16 %, lead 36–45 %, iron from 74 % to 84 % and manganese from 36 % to 53 % in relation to the studied element content in 1 mol HCl $\cdot$ dm^{-3} extract. Generally, hydrochloric acid leaches metals bound to exchangeable, carbonate, Fe/Mn oxides and organic matter fractions. Moreover, as reported by Dziadek and Waclawek [15], in case of strongly polluted soils, extraction with such strong substance as 1 mol HCl $\cdot$ dm^{-3} does not show the real hazard for plants. It has been commonly accepted that copper, lead, chromium and nickel are the least mobile elements in soil, while zinc and cadmium are counted among the most mobile, whereas manganese and iron place in between them [14]. Mobility of the elements analyzed in the presented investigations looked as follows: Cd > Pb > Mn > Zn > Cu > Fe > Ni = Cr (1 mol HCl $\cdot$ dm^{-3}) and Cd > Pb > Zn > Mn = Cu > Ni > Cr > Fe (0.01 mol CaCl$_2$ $\cdot$ dm^{-3}). It was also demonstrated that bottom deposit supplement to light soil diminished the content of available forms of zinc, cadmium, lead, iron and manganese extracted with 1 mol HCl $\cdot$ dm^{-3} and copper, nickel and chromium (a 5 % admixture of bottom deposit), cadmium, lead, iron and manganese extracted with 0.01 mol CaCl$_2$ $\cdot$ dm^{-3} in relation to these elements content in the soil without the deposit supplement. Numerous investigations have shown that soil reaction, humus content and granulometric composition may affect trace element mobility and therefore their uptake by plants. Increased mobility, particularly of heavy metals in the environment influences their greater accumulation in plants posing a grave hazard for living organisms. According to a prevailing opinion, trace elements may pass into less

soluble forms at higher pH values, which leads to their uptake by plants and diminishes their toxicity for plants [20]. Presented research did not find any significant effect of soil pH on diminishing the availability of most analyzed elements. The fact was confirmed by the negative, but insignificant values of correlation coefficients between pH values and element content in soil (Table 4).

Table 4

Correlation coefficient between pH and contents of the analyzed trace elements in soil

Zn			Cu			Ni			Cr		
I	II	III	I	II	III	I	II	III	I	II	III
–0.13	0.68*	–0.42	0.15	–0.17	0.29	–0.20	0.75*	0.40	0.28	0.20	0.78*
Cd			Pb			Fe			Mn		
I	II	III	I	II	III	I	II	III	I	II	III
–0.41	–0.63*	–0.51	–0.60	–0.66*	–0.26	0.28	–0.54	0.45	–0.06	–0.51	0.04

I – total content, II – 0.01 mol $CaCl_2 \cdot dm^{-3}$, III – 1 mol $HCl \cdot dm^{-3}$, * r significant $p < 0.05$.

In conclusion, applied bottom deposit revealed in its composition a considerable share of silt and clay fractions, alkaline reaction and low total heavy metal content, therefore it may be applied as an admixture to light soils to improve their productivity. The experiment demonstrated that the applied bottom deposit supplement positively affected improvement of the analyzed soil and decreased both total and available content of elements toxic for plants, ie lead and cadmium. Moreover, as reported by Pelczar et al [6] bottom deposits may be used for reclamation of mining wastes. The authors revealed that adding bottom deposit to mining wastes changes their buffer properties, porosity and capability for water retention, increases the contents of organic substance, fertilizer components and causes an increase in enzymatic activity of soil.

Conclusions

1. A positive effect of bottom deposit on the increase in light soil pH value was revealed. After a two-year period of research light soil pH value was 6.24 on the control treatment, 6.49 on the treatment with a 5 % sediment supplement and 6.86 on the treatment with a 10 % deposit admixture.

2. Bottom deposit supplement to the light soil significantly diminished the contents of available forms of zinc, lead and manganese extracted with 1 mol $HCl \cdot dm^{-3}$ and bioavailable forms of cadmium, lead, manganese and iron extracted with 0.01 mol $CaCl_2 \cdot dm^{-3}$.

3. The experiment did not reveal any significant effect of the soil pH on diminished availability of most analyzed elements as it has been confirmed by negative and insignificant values of correlation coefficients between pH and element content in soil.

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WPŁYW DODATKU OSADU DENNEGO NA ZAWARTOŚĆ PIERWIASTKÓW ŚLADOWYCH W GLEBIE LEKKIEJ

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Abstrakt: Celem badań była ocena wpływu dodatku osadu dennego na zawartość i mobilności wybranych pierwiastków śladowych w glebie lekkiej. W badaniach wykazano dodatni wpływ osadu dennego na zwiększenie wartości pH gleby lekkiej. Po 2-letnim okresie badań wartość pH gleby wyniosła: 6,24 w obiekcie kontrolnym, 6,49 w obiekcie z 5 % dodatkiem osadu i 6,86 w obiekcie z 10 % dodatkiem osadu dennego. Dodatek osadu dennego do gleby lekkiej zmniejszył znacznie zawartość form przyswajalnych cynku, ołowiu, i manganu ekstrahowanych 1 mol HCl $\cdot$ dm^{-3} oraz biodostępnych kadmu, ołowiu, manganu i żelaza ekstrahowanych 0,01 mol CaCl$_2$ $\cdot$ dm^{-3}. W badaniach nie stwierdzono istotnego wpływu odczynu gleby na zmniejszenie dostępności większości badanych pierwiastków, potwierdzeniem tego są ujemne i statystycznie nieistotne wartości współczynników korelacji pomiędzy wartością pH a zawartością pierwiastków w glebie.

Słowa kluczowe: osad denny, pierwiastki śladowe, gleba lekka, wyciągi: 0,01 mol CaCl$_2$, 1 mol HCl $\cdot$ dm^{-3}