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Jacek ANTONKIEWICZ[1]

ASSESSMENT OF CHEMICAL COMPOSITION OF BUSHGRASS (*Calamagrostis epigejos* L.) OCCURRING ON THE LANDFILL SITE OF THE FURNACE WASTE AND CARBIDE RESIDUE LIME

Part 2. CONTENT OF IRON, COBALT MANGANESE, ALUMINIUM AND SILICON

OCENA SKŁADU CHEMICZNEGO TRZCINNIKA PIASKOWEGO (*Calamagrostis epigejos* L.) WYSTĘPUJĄCEGO NA SKŁADOWISKACH ODPADÓW PALENISKOWYCH I WAPNA POKARBIDOWEGO

Cz. 2. ZAWARTOŚĆ ŻELAZA, KOBALTU, MANGANU, GLINU I KRZEMU

Abstract: Furnace ashes and carbide lime deposited on landfills may constitute a valuable raw material, among others for biological reclamation of post-industrial areas. Their environmental management requires the assessment of their suitability not only with respect to concentrations of heavy metals but also other components, including microelements. Ashes originating from hard coal burning are a rich source of microelements, particularly Fe, B, Mn and Co, which is very important for correct growth. However, very high contents of microelements in furnace wastes may influence their excessive uptake by plants, which in consequence lead to their die-back. Although high accumulation of microelements in plants is not always toxic for the plants themselves, it may cause serious pathogenic consequences in people or animals consuming these plants.

The contents of selected elements in bushgrass collected from furnace ash and carbide lime dumps was diversified, ranging from 49.70–1800.0 mg Fe, 0.01–1.17 mg Co, 7.33–146.0 mg Mn, 17.20–120.0 mg Si and 8.68–1500.0 mg Al · kg^{-1} d.m. Higher concentrations of iron, cobalt, manganese and aluminium were registered in plants collected from furnace ash dumps and lower in plants from carbide lime section. Optimal contents of microelements in plants destined for forage are as follows: 40–70 mg Fe, 0.3–1.0 mg Co and 40–60 mg Mn · kg^{-1} d.m. Assessment of the plants according to this criterion revealed over the norm mean content of iron in the samples taken from furnace ashes and carbide lime dump. Optimal content of cobalt was assessed in plants gathered from inactive section of furnace ashes whereas a deficient amount from active section of furnace ashes and carbide lime. Deficient (< 40 mg) manganese contents were found in 13 samples collected from the bowl of furnace ashes and carbide lime landfills. Only in 6 plant samples registered manganese content exceeded its optimal value in fodder. Manganese content in plants gathered from the

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landfill shelves was below the optimal value. Low content of manganese in plants collected from the landfills in comparison with other elements is justified by the fact that in alkaline environment this element passes into compounds unavailable to plants.

Key words: *Calamagrostis epigejos* L. (bushgrass), dumps, incineration ash, lime carbide, Fe, Co, Mn, Al, Si

Considering among others the lack of space for new landfill sites, management of furnace ashes and carbide lime should be a pro-ecological task [1]. Furnace ashes and carbide lime deposited on landfills may be a valuable raw material for among other biological reclamation of post-industrial areas [2–3]. Their environmental applications require an assessment of their usefulness considering not only their heavy metal contents but also with respect to other components including microelements. Ashes originating from hard coal burning provide a rich source of microelements, particularly Fe, B, Mn and Co, which are of key importance for proper plant growth [4–6]. However, very high concentrations of microelements in furnace wastes may also influence their excessive uptake by plants, which in result leads to their dieback [7]. Although high accumulation of microelements in plants is not always toxic for the plants themselves, it may have dangerous pathogenic consequences in people or animals consuming these plants [8].

The investigations aimed at an assessment of Fe, Co, Mn, Al and Si contents in furnace ashes and carbide lime and in bushgrass occurring on these wastes.

Material and methods

The object of investigations was bushgrass (*Calamagrostis epigejos* L.) occurring on furnace waste and carbide lime landfills, the substratum and embankments of these landfills. A detailed description of the above-mentioned landfills was presented in the first part of the paper [9]. The analysis of plant material comprised an assessment of the content of selected elements following their "dry" mineralization. The contents of Fe, Co, Mn, Al and Si in the substratum and bushgrass were assessed using ICP-AES method by sequential spectrometer, JY-238 Ultrace. Statistical computations were made using Statsoft 7.1. programme. Basic statistical parameters: minimum, maximum and medium values as well as variation coefficients were computed. Simple correlation coefficients describing the dependence between the element contents in plants and physical properties (colloidal clay) and chemical properties of the substratum were also calculated.

Results and discussion

A detailed description of physical and chemical properties of furnace ashes and carbide lime was presented in the first part of the paper [9].

The contents of Fe, Co, Mn, Al and Si in wastes. The research revealed that furnace ashes originating from hard coal burning belong to silicate type due to their high concentrations of aluminium, silica and iron [10]. On the other hand, carbide lime is a by-product formed at acetylene production [1].

Total content of selected elements in the samples from the examined landfills ranged quite widely: 1385–38200 mg Fe, 1.00–13.70 mg Co, 28.55–875.0 mg Mn, 264–1285 mg Si and 2545–15950 mg Al · kg^{-1} d.m. (Table 1).

The greatest variability in the content of examined elements was found for iron (V = 87.1 %) and the slightest for aluminium (V = 26.8 %). Experiments have demonstrated that furnace ashes are characterized by a higher content of Fe, Co, Mn, Al and Si in comparison with carbide lime.

In comparison with their total contents, solubility of the tested elements in 1 mol · dm^{-3} HCl solution ranged in limits 0.01–37.38 % Fe, 8.91–36.79 % Co, 13.36–73.53 % Mn and 0.02–42.98 % Al. The greatest solubility in the researched wastes in result of extraction in 1 mol HCl · dm^{-3} was registered for manganese (73 %), then for aluminium (42 %) and the slightest for cobalt and iron (36 %) in relation to total content. For silica greater solubility was registered in 1 mol hydrochloric acid than after a sample digesting in a mixture of nitric(V) and chloric(VII) (3:2) acids.

High contents of microelements in furnace wastes may lead to their excessive uptake by plants [4]. The contents of examined elements in the plants collected from the landfills were diversified and ranged from 49.70 to 1800.0 mg Fe, 0.01–1.17 mg Co, 7.33–146.0 mg Mn, 17.20–120.0 mg Si and 8.68–1500.0 mg Al · kg^{-1} d.m. (Table 1). Among the investigated elements the greatest diversification was registered for aluminium (V = 151.0 %) assessed in bushgrass growing in furnace ashes section and the smallest for iron (V = 28.5 %) in plants occurring in carbide lime section. Similar as in the substratum, higher contents of iron, cobalt and aluminium were assessed in plants collected from furnace ashes dumps, whereas lower from carbide lime section. Manganese contents were on an approximately similar level in the bushgrass gathered from the landfills, whereas greater amounts of silica were registered in bushgrass growing in carbide lime section.

Optimal contents of microelements in plants destined for forage are: 40–70 mg Fe, 0.3–1.0 mg Co and 40–60 mg Mn · kg^{-1} d.m. [11–12]. Assessment of the plants according to this criterion revealed over the norm mean content of iron in the samples taken from furnace ashes and carbide lime dump. Optimal content of cobalt was assessed in plants gathered from inactive section of furnace ashes whereas a deficient amount from active section of furnace ashes and carbide lime. Deficient manganese contents (< 40 mg · kg^{-1}) were found in 13 samples collected from the bowl of furnace ashes and carbide lime landfills. Only in 6 plant samples registered content of manganese exceeded optimal value. Manganese content in plants gathered from the landfill shelves was below the optimal value. Optimal Fe to Mn ratio is 1.5–2.5:1 [12]. Symptoms of manganese toxicity and iron deficiency occur when this value falls below 1, whereas when Fe:Mn ratio is above 2.5 a manganese deficiency and iron excess are noted in plants. The conducted research confirms that mean Fe to Mn ratio in bushgrass occurring on landfill exceeds the optimal value, which demonstrates Fe excess and Mn deficiency.

Table 1

Element contents in plants and substratum of investigated landfills [mg · kg^{-1} d.m.]

Parameter	Plant	Total*	Soluble**	Plant	Total	Soluble	Plant	Total	Soluble
	Fe			Co			Mn		
Quarters incineration ash (N = 30)									
Minimum	49.70	1515.00	193.00	0.01	1.00	0.16	7.33	28.55	8.44
Maximum	1800.00	34900.00	5140.00	1.17	13.70	3.20	129.00	655.00	312.00
Mean	329.99	15754.00	2847.90	0.21	9.44	1.87	32.82	309.97	151.59
V%***	116.16	48.71	39.62	132.11	29.35	31.99	82.09	46.31	48.37
Quarters lime carbide (N = 20)									
Minimum	74.80	1385.00	0.20	0.02	1.00	0.11	8.04	79.00	13.80
Maximum	275.00	38200.00	5210.00	0.22	12.55	2.20	146.00	875.00	339.00
Mean	156.27	10863.50	1740.56	0.09	6.36	1.13	31.26	277.43	121.44
V%	28.54	87.10	108.98	51.61	66.89	75.39	115.10	67.14	78.60

Table 1 contd.

Parameter	Plant	Total	Soluble	Plant	Total	Soluble	Fe:Mn ratio in plants
	Si			Al			
Quarters incineration ash (N = 30)							
Minimum	17.20	394.00	158.00	8.68	2545.00	518.00	1.83
Maximum	73.00	1285.00	9890.00	1500.00	15300.00	5580.00	26.35
Mean	35.81	658.15	5013.23	217.65	11005.83	3518.60	9.65
V%	35.64	28.69	43.46	151.04	26.84	34.34	61.29
Quarters lime carbide (N = 20)							
Minimum	25.40	264.50	203.00	15.20	4845.00	1.04	0.73
Maximum	120.00	735.00	6810.00	309.00	15950.00	4890.00	20.40
Mean	52.31	442.55	3058.55	104.83	10430.50	2115.30	10.09
V%	51.23	34.92	92.82	78.68	39.00	103.20	65.71

* Total content in waste, ** Content of forms soluble in 1 mol HCl $\cdot$ dm^{-3}; *** Variability coefficient.

Correlation coefficients. Occurrence of statistically significant relationships between the contents of Fe, Co, Mn, Si and Al in bushgrass and their amounts in wastes and chemical properties were established by computing simple correlation coefficients at significance level p=0.001 (Table 2 and 3). Fe and Co contents in bushgrass growing on furnace ashes were most strongly affected by the aluminium in plant (Table 2). Total Fe content in the ashes was strongly correlated with total content of manganese and amount its soluble forms. Total Mn content and amount its soluble forms in the ashes were also determined by Co content in this waste. Moreover total content of aluminium and its soluble forms in the ash affected Fe and Co content in this waste. Significant relationships were also found between the contents of Si soluble in 1 mol HCl · dm^{-3} in ash and Fe and Co content. In carbide lime the contents of Co, Mn and Al were strongly correlated with iron content, moreover Mn and Al contents depended on the total content and amount of soluble forms of cobalt in this lime. It was also found that aluminium contents in carbide lime depended on Mn and Si in this waste.

Table 2

Significant (p = 0.001) simple correlation coefficients (r) between element content of plant and wastes

Specification		Plant	Total	Soluble	Plant	Total	Soluble	Soluble	Soluble	Total
		Fe			Co			Mn	Si	Al
Quarters incineration ash (N = 30)										
Soluble**	Fe		0.71						0.68	0.74
Plant	Co	0.95								
Total*			0.64	0.73					0.71	0.75
Soluble						0.70			0.83	
Total	Mn		0.93	0.85		0.71		0.77		
Soluble			0.65	0.91		0.66				0.82
Plant	Al	0.98			0.97					
Soluble				0.69		0.79	0.86		0.93	0.66
Quarters lime carbide (N = 20)										
Soluble	Fe		0.78						0.92	
Total	Co		0.85	0.90					0.95	
Soluble				0.93		0.96			0.97	
Total	Mn		0.87							
Soluble			0.85	0.89		0.89	0.83		0.87	
Total	Al		0.77	0.89		0.97	0.97	0.84	0.96	
Soluble				0.96		0.94	0.98	0.86	0.99	0.95

* Total content in waste; ** Content of forms soluble in 1 mol HCl · dm^{-3}.

Table 3 presents correlation relationships between Fe, Co, Mn, Si and Al contents in bushgrass and wastes with physical and chemical properties of the waste.

Table 3

Significant ($p = 0.001$) simple correlation coefficients (r) between element content of plant and soil and some of its properties

Specification	Plant	Soluble**	Plant	Total*	Soluble	Plant	Soluble	Plant	Soluble	Plant	Total	Soluble
	Fe		Co			Mn		Si		Al		
Quarters incineration ash (N = 30)												
pH_{KCl}						0.64					–0.61	
available K	0.73		0.77							0.78		
Quarters lime carbide (N = 20)												
Clay coloid								0.85		0.78		
pH_{KCl}				–0.82	–0.85				–0.87		–0.87	–0.84
pH_{H_2O}				–0.81	–0.83				–0.86		–0.85	–0.82
Available P				0.81	0.83				0.86		0.81	0.82
Available Mg		0.77		0.86	0.83		0.81		0.91		0.86	0.85

* Total content in waste; ** Content of forms soluble in 1 mol HCl · dm^{-3}.

Fe, Co and Al contents in bushgrass occurring in furnace ashes sections were most depended on the contents of bioavailable potassium, whereas Mn content in plants was most affected by ashes pH_{KCl}. On the other hand, Si and Al content in bushgrass growing in carbide lime section was determined by the presence of colloidal clay. The reaction of furnace ashes was negatively correlated with total content of aluminium in this waste. On the other hand, the reaction of carbide lime and the content of bioavailable phosphorus and magnesium to the highest degree affected the total content of Co and Al and their soluble forms in this waste. It was also found that the content of Si soluble in 1 mol $HCl \cdot dm^{-3}$ was negatively correlated with the pH but positively with bioavailable phosphorus and magnesium contents in carbide lime. The content of bioavailable Mg in carbide lime most affected Fe and Mn solubility in 1 mol $HCl \cdot dm^{-3}$.

Previous investigations have shown that the element contents in plants and wastes may be determined by various physicochemical properties of wastes.

Discussion

Higher contents of Fe, Co, Mn, Al and Si in furnace ashes in comparison with carbide lime demonstrates that furnace ashes constitute a richer source of nutrients for plants. Total microelement content in incineration ashes is comparable with the contents in the ashes was found by Beresniewicz and Nowosielski [4]. Total content of cadmium and cobalt in the analyzed wastes does not basically differ from these elements contents in arable soils [13–14]. On the other hand, it was noted that in the investigated wastes iron and aluminium contents were much higher than in arable soil [15]. From among the analyzed elements manganese revealed the highest and cobalt the slightest solubility. Low solubility of cobalt in arable soils in relation to the total contents was also noted by Straczyk and Drobnica [14].

Furnace ashes constitute a rich source of elements, particularly such as: Fe, B or Si, which may be of crucial importance for plant fertilization [5]. High concentrations of microelements in furnace wastes may influence their excessive uptake by plants [4]. Small content of manganese in plants gathered from the landfills, as compared to the other elements, is justified by the fact that in alkaline environment this element passes into compounds unavailable to plants [16]. Small contents of manganese in plants growing on furnace ash and carbide lime landfills were caused by alkaline reaction of the substratum and presence of a great amount of lime. Research conducted by Maciak et al [17] corroborate the Authors' own investigations showing that in alkaline environment aluminium is intensely cumulated in plants, which on the other hand makes difficult the uptake of other elements, including phosphorus.

Microelement contents in the investigated plants were diversified. According to limit numbers suggested by Falkowski et al [12] and Gorlach [11], a high over-the-limit content of iron was registered, optimal content of cobalt but deficient content of manganese. The Author's own investigations revealed that cobalt contents in bushgrass collected from ash and carbide lime sections were much lower in comparison with plants gathered from incineration ash heap investigated by Andruszczak et al [16]. The research conducted by Macuda et al [18] revealed much bigger contents of cobalt in consumption plants cultivated in the vicinity of petroleum industrial wastes than in plants occurring on the analyzed landfills. On the other hands, investigations conducted by Curylo [19] showed that cobalt content in red fescue and meadow sward was comparable with its amount in plants growing on landfills. Iron content in the Author's own research was considerably bigger than in plants studied by Andruszczak et al [16]. Also Gora [20] found bigger contents of iron and aluminium in plants cultivated in furnace ashes.

Conclusions

1. Furnace ashes contain more Fe, Co, Mn, Si and Al than carbide lime.
2. Bushgrass occurring on furnace ashes revealed higher contents of Fe, Co and Al, whereas Si content was smaller in comparison with carbide lime.
3. Above the norm content of Fe was registered in bushgrass occurring on ashes, close to optimal in the plants from carbide lime section and close to optimal in the plants originating from carbide lime section. Mean content of Mn in plants growing on ashes and carbide lime was below the optimal values. Co content in bushgrass occurring on ashes was on the optimal level, whereas on carbide lime it was deficient.
4. Due to high content of microelements (Fe, Co and Mn) in the incineration ashes and carbide lime they are suggested for use for reclamation measures on post-industrial areas.
5. In case the wastes are not used for reclamation measures, the landfills where the analyzed wastes are deposited should be protected against dusting and migration of elements. Prior to biological turfing of the landfills, a deficient chemistry of ashes and carbide lime should be improved, among other through supplying the nutrients which these wastes lack.

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OCENA SKŁADU CHEMICZNEGO TRZCINNIKA PIASKOWEGO (*Calamagrostis epigejos* L.) WYSTĘPUJĄCEGO NA SKŁADOWISKACH ODPADÓW PALENISKOWYCH I WAPNA POKARBIDOWEGO

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Abstrakt: Zdeponowane na składowiskach popioły paleniskowe i wapno pokarbidowe mogą stanowić cenny surowiec m.in. w biologicznej rekultywacji terenów poprzemysłowych. Ich wykorzystanie w środowisku wymaga oceny przydatności pod względem zawartości nie tylko metali ciężkich, ale także innych składników, w tym mikroelementów. Popioły pochodzące ze spalania węgla kamiennego stanowią bogate źródło mikroelementów, zwłaszcza Fe, B, Mn i Co, mających bardzo duże znaczenie w prawidłowym wzroście. Jednakże bardzo duże zawartości mikroelementów w odpadach paleniskowych mogą powodować nadmierne ich pobieranie przez rośliny, co w konsekwencji prowadzi do ich obumierania. Aczkolwiek duże nagromadzenie mikroelementów w roślinach nie zawsze jest toksyczne dla samych roślin, ale może spowodować groźne następstwa chorobowe u ludzi lub zwierząt spożywających te rośliny.

Zawartość wybranych pierwiastków w trzcinniku piaskowym zebranym ze składowisk odpadów paleniskowych i wapna pokarbidowego była zróżnicowana i wahała się w zakresie: 49,70–1800,0 mg Fe; 0,01–1,17 mg Co; 7,33–146,0 mg Mn; 17,20–120,0 mg Si oraz 8,68–1500,0 mg Al $\cdot$ kg^{-1} s.m. Większe zawartości żelaza, kobaltu, manganu i glinu stwierdzono w roślinności zebranej ze składowisk popiołów paleniskowych, a mniejsze z kwatery wapna pokarbidowego. Optymalna zawartość mikroelementów w roślinach przeznaczonych na paszę wynosi: 40–70 mg Fe; 0,3–1,0 mg Co i 40–60 mg Mn $\cdot$ kg^{-1} s.m. Wyceniając rośliny według tego kryterium, stwierdzono ponadnormatywną zawartość żelaza w próbkach zebranych ze składowiska popiołów paleniskowych nieczynnej kwatery. Natomiast zawartość żelaza w roślinności zebranej ze składowiska wapna pokarbidowego mieściła się w granicach wartości optymalnej. Optymalną zawartość kobaltu stwierdzono w roślinności zebranej z nieczynnej kwatery popiołów paleniskowych, a niedoborową z kwatery czynnej popiołów paleniskowych oraz wapna pokarbidowego. W badaniach własnych stwierdzono niedoborową zawartość manganu (< 40 mg $\cdot$ kg^{-1}) w 13 próbkach pobranych z czaszy składowisk popiołów paleniskowych i wapna pokarbidowego. Tylko w 6 próbkach roślin zawartość manganu przekraczała wartość optymalną. Zawartość manganu w roślinności zebranej z półek składowisk mieściła się poniżej wartości optymalnej. Małą zawartość manganu w roślinności pobranej ze składowisk, w porównaniu z innymi mikroelementami, można uzasadnić tym, że w środowisku alkalicznym pierwiastek ten tworzy połączenia, z których jest trudno dostępny dla roślin.

Słowa kluczowe: trzcinnik piaskowy (*Calamagrostis epigejos* L.), składowiska, popioły paleniskowe, wapno pokarbidowe, Fe, Co, Mn, Al, Si

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Agnieszka BARAN[1]

EFFECT OF ORGANIC WASTES ON ZINC AND LEAD ACCUMULATION IN OAT BIOMASS

WPŁYW ODPADÓW ORGANICZNYCH NA AKUMULACJĘ CYNKU I OŁOWIU W BIOMASIE OWSA

Abstract: The studies on the effect of organic wastes on zinc and lead content in oat were conducted in 2006 as a pot experiment. Mineral salts, farmyard manure, compost, municipal and industrial sludge at two fertilization levels were used in the experiment.

The highest zinc content in plants and its uptake by oat was found in the treatments fertilized with industrial sewage sludge, whereas Pb contents were the biggest in the compost and municipal sewage sludge treatments. The analysis of bioaccumulation coefficient value shows that the aboveground oat biomass accumulated bigger quantities of Zn than Pb, whereas the roots to a greater extent limited lead translocation in the plant. No exceeded lead contents according to plant assessment in view of their fodder usability were detected in oat. The plants revealed over the norm zinc content.

Keywords: farmyard manure, compost, municipal and industrial sewage sludge, zinc, lead, oat

Current reduction of animal organic wastes production makes necessary using other organic wastes (composts or sewage sludges) as unconventional fertilizers for soil and crop treatment [1]. According to Siuta [2] and Mazur [1] it is both environmentally and economically justified. These materials, while increasing soil abundance in humus, macro- and microelements, also improve the soil biological activity and reveal multidirectional effect on the soil and plant [1, 3]. However, usefulness of some wastes (sewage sludge) in agriculture may be limited because of too high contents of heavy metals or other harmful substances [4, 5]. Considering the sanitary aspect, sewage sludges may be decontaminated by means of their mixing with calcium oxide or composting with plant materials. Composting allows for considerable decreasing of heavy metal contents in the sludge in comparison with their initial values [6]. While assessing organic waste usefulness for fertilization one should also consider the response of fertilized crops, heavy metal accumulation in their biomass and their destination [7].

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The investigations aimed at an assessment of the consequent effect of various organic wastes on the content and uptake of zinc and lead by oat.

Material and methods

The studies on the effect of organic wastes on zinc and lead content in oat were conducted as pot experiment in 2006. The paper presents the results obtained for oat cultivated in the third year of the experiment conducted on the soil with granulometric structure of weakly loamy sand, $pH_{KCl} = 4.66$ and organic matter content $19.3\ g \cdot kg^{-1}$. Moreover, the soil revealed a low content of bioavailable phosphorus and potassium, elevated zinc content and natural content of lead [8]. The experimental design comprised 11 treatments differing with the dose and kind of the supplied fertilizers. The sources of nutrients for oat were mineral salts (NH_4NO_3, KH_2PO_4, KCl), farmyard manure, municipal and industrial sewage sludge. Chemical composition of the organic materials was given in Table 1. Two fertilization levels were taken into consideration: the first level: 0.30 g N, 0.11 g P and $0.26\ g\ K \cdot pot^{-1}$ (5 kg of soil) and the second level – double amounts of NPK. The materials and organic wastes were applied in the first year of the experiment under maize and their doses were established on the basis of nitrogen fertilization [9]. Compost of plant wastes was manufactured by Ekokonsorcjum Efekt Ltd. Enterprise in Krakow. Sludges from municipal and industrial sewage originated from "Empos" municipal-industrial sewage treatment plant in Oswiecim. No exceeded permissible norms of heavy metal contents were assessed in the organic wastes, therefore they met the requirements for fertilizers used in agriculture (Table 1) [10].

Table 1

Chemical composition of organic materials

Chemical composition		Farmyard manure	Compost	Municipal sludge	Industrial sludge
Dry mas	[%]	14.56	54.72	18.81	21.84
Organic mater	$[g \cdot kg^{-1}$ d.m.]	855.3	437.3	640.4	482.8
Zinc	$[mg \cdot kg^{-1}$ d.m.]	115.0	228.4	741.6	722.0
Lead		2.37	16.15	38.76	46.25

Zinc and lead contents in the plant material (the shoots and roots) were assessed following the dry mineralization and the ash dissolving in HNO_3 (1:3). Total zinc and lead contents in the soil were determined after hot mineralization in HNO_3 and $HClO_4$ (3:2) mixture. Concentrations of the analyzed elements were assessed in the obtained solutions using inductively coupled plasma emission atomic spectrophotometry (ICP-EAS). Zinc and lead uptake was computed and their bioaccumulation and translocation coefficients in the test plant. The results were elaborated statistically using one-way ANOVA and Tukey test at significance level $\alpha = 0.05$ by means of Statistica 7.0 programme.

Results

Zinc and lead content in plant was diversified depending on the plant part and experimental treatment (Table 2).

Table 2

The content of zinc and lead in oats [mg · kg^{-1}d.m.]

Treatments		Shoots		Roots	
		Zinc	Lead	Zinc	Lead
Without fertilization		103.65	1.07^{bcd}**	197.70^{ab}	4.75^{a}
NPK	1*	124.17	0.64^{ab}	199.70^{ab}	6.61^{ab}
	2	130.45	0.77^{abc}	200.12^{ab}	5.58^{ab}
Farmyard manure	1	117.12	0.82^{abc}	206.32^{ab}	8.10^{ab}
	2	148.27	1.19^{cde}	239.80^{bc}	9.19^{ab}
Compost	1	107.95	1.21^{cde}	170.53^{a}	9.97^{ab}
	2	120.62	1.46^{de}	205.17^{ab}	8.33^{ab}
Municipal sludge	1	138.93	1.56^{f}	253.38^{ab}	10.36^{b}
	2	139.29	0.56^{a}	295.87^{bc}	8.73^{ab}
Industrial sludge	1	137.89	0.50^{a}	335.28^{c}	9.34^{ab}
	2	151.80	0.79^{abc}	412.32^{d}	8.34^{ab}
$LSD_{0.05}$		n.s.***	0.25	34.15	2.98

Explanation for Tables 2–4: * dose; ** homogeneous groups according to the Tukey test; $\alpha = 0.05$; *** n.s. – not significant.

Zinc concentrations in oat in comparison with lead were relatively high, which resulted from introducing considerable amounts of the metal with the organic wastes (Table 1) but also with highly active uptake of his element by the plants. The roots contained between twice and thrice greater quantities of zinc than the aboveground parts depending on the experimental treatment. The organic materials caused an increase in zinc content in the aboveground plant biomass in relation to the control plants, but the differences were statistically insignificant. A notable effect of the dose and kind of organic material on zinc content in the test plant roots was registered (Table 2). The largest zinc content both in oat shoots and roots was registered on the treatment where a double dose of industrial sludge was applied. On this treatment oat contained almost 46 % greater quantities of zinc (aboveground parts) and 108 % (roots) in comparison with the control. The smallest amounts of this metal were assessed in the aerial parts and roots obtained from the object fertilized with a single dose of compost. It may be explained by dissolving of zinc, because plants fertilized with compost produced the largest root biomass [11]. Application of the second fertilization level caused an increase in zinc content in plant. On the other hand, depending on the kind of organic material, zinc content in oat may be ordered in the following descending sequence: industrial sewage sludge > municipal sewage sludge farmyard manure > NPK > compost.

The discussed experiment demonstrated a significant effect of NPK and organic materials on Pb contents in oat (Table 2). Similarly as in case of zinc, oat roots accumulated between 4 and 19 times greater quantities of this metal than the shoots. The obtained results confirm the thesis that Pb becomes accumulated in relatively big quantities on the root surface, which is a mechanism limiting this metal uptake from the soil [12, 13]. Additionally all organic materials and NPK caused an average 78 % increase in Pb content in oat roots in comparison with the control plants. Significantly the greatest lead concentrations were registered in the aboveground biomass and in roots of oat on the treatment receiving a single dose of municipal sewage sludge. In comparison with the unfertilized plants on this treatment, oat contained by over once (aboveground parts) and twice (roots) bigger amounts of lead. On organic treatments the smallest lead content in the oat aboveground biomass was detected after the application of a single dose of industrial sewage sludge and a double dose of municipal sewage sludge, whereas in roots on the treatments receiving a single farmyard manure dose. Sewage sludges led to a decrease in Pb level in the aboveground biomass by 43 % in relation to the control plants. Lead contents in oat may be ordered as follows: compost > municipal sewage sludge ≈ farmyard manure > NPK > industrial sewage sludge (shoots) and municipal sewage sludge > compost > industrial sewage sludge ? farmyard manure > NPK.

Table 3

Uptake of heavy metals by oats [mg · pot^{-1}]

Treatments		Shoots		Roots	
		Zinc	Lead	Zinc	Lead
Without fertilization		0.78^{a**}	0.008^{a}	0.23^{a}	0.006^{a}
NPK	1*	1.87^{ab}	0.010^{ab}	0.35^{abc}	0.012^{ab}
	2	2.04^{abc}	0.010^{ab}	0.26^{ab}	0.008^{ab}
Farmyard manure	1	2.52^{bcd}	0.018^{bcd}	0.39^{abcd}	0.015^{ab}
	2	3.67^{cd}	0.029^{ef}	0.52^{abcd}	0.020^{ab}
Compost	1	2.25^{abc}	0.025^{de}	0.49^{abcd}	0.020^{ab}
	2	2.46^{bcd}	0.031^{ef}	0.40^{abcd}	0.024^{b}
Municipal sludge	1	2.99^{bcd}	0.014^{abc}	0.61^{bcd}	0.019^{ab}
	2	3.55^{bcd}	0.033^{e}	0.63^{cd}	0.025^{b}
Industrial sludge	1	2.99^{bcd}	0.011^{ab}	0.73^{de}	0.020^{ab}
	2	3.97^{d}	0.021^{cd}	1.02^{f}	0.021^{ab}
$LSD_{0.05}$		0.095	0.005	0.20	0.01

The quantity of heavy metals absorbed with the plant biomass is a resultant of the values of obtained yields and their contents of these metals [14]. The absorbed quantities are also influenced by the soil properties, the element form (ion or complex), species features and the plant organ [15]. Considering the share of individual oat parts in total zinc uptake it was found that the aboveground oat biomass took up the biggest quantities of this metal (Table 3).

The aerial biomass accumulated between 77 % and 88 % of the total absorbed amount of Zn, whereas the roots between 11 % and 23 % of this metal. For lead it was found that both oat aboveground parts and roots absorbed comparable amounts of this metal (Table 3). Depending on the experimental treatment, between 35 % and 59 % of Pb was taken up with the aerial biomass, whereas between 41 % and 65 % with roots. On the other hand, the analysis of heavy metal uptake depending on the dose and kind of organic material revealed significant increase in zinc and lead uptake by oat on fertilized treatments in comparison with unfertilized plants. The greatest aggregate heavy metal uptake by oat shoots and roots was determined on the treatments with residual effect of industrial sewage sludge (zinc) and municipal sewage sludge (lead) applied in a double dose. The lowest zinc uptake among the treatments with a consequent effect of fertilizers and organic materials was registered on the treatment with compost, whereas lead uptake on the treatment with industrial sewage sludge. Depending on the experimental treatment an aggregate zinc uptake by oat may be placed in the following descending order: industrial sewage sludge > municipal sewage sludge > farmyard manure > compost > NPK and for lead: compost ? municipal sewage sludge > farmyard manure ≈ industrial sewage sludge > NPK.

Bioaccumulation and translocation coefficients were used for the assessment of the degree and direction of heavy metal movement in plants. The value of bioaccumulation coefficient reflects plant ability to absorb the components from soil. This parameter is a ratio of metal contents in the aerial plant parts to its soil contents [16, 17].

Computed bioaccumulation coefficient values for zinc ranged from 1.61 to 2.38 and for lead from 0.02 to 0.06 (Table 4). These values indicate that oat aboveground biomass more easily accumulated zinc than lead. Additionally they evidence a considerable Zn mobility in comparison with Pb and its relatively easy uptake by plants [15].

Table 4

Bioaccumulation and translocation coefficient of Zn and Pb in oats

Treatments		Bioaccumulation coefficient		Translocation coefficient	
		Zinc	Lead	Zinc	Lead
Without fertilization		1.56	0.04	0.53	0.23
NPK	1*	1.85	0.02	0.62	0.10
	2	2.38	0.03	0.99	0.14
Farmyard manure	1	1.80	0.03	0.57	0.10
	2	2.27	0.05	0.62	0.13
Compost	1	1.61	0.04	0.54	0.12
	2	1.88	0.06	0.71	0.17
Municipal sludge	1	2.19	0.02	0.50	0.06
	2	2.05	0.06	0.47	0.15
Industrial sludge	1	2.01	0.02	0.41	0.05
	2	2.13	0.03	0.37	0.10

Intensive degree of accumulation was registered for zinc (BC; 1–10), whereas weak for lead (BC; 0.01–0.1). The highest values of zinc bioaccumulation coefficient were estimated for the plants fertilized with a double NPK dose, the lowest for the control plats, therefore all applied fertilizer components caused an increase in Zn mobility on average by 32 % in relation to the unfertilized treatment (Table 4). Increasing Zn mobility in oats on fertilized treatments may be ascribed to the fact that the applied fertilizers and organic wastes acidified the soil environment and therefore increased Zn availability to plants. For lead the highest value of bioaccumulation coefficient was determined for the treatments with the consequent effect of a double compost and municipal sewage sludge dose (Table 4). On the other hand, application of a single dose of farmyard manure, compost, municipal sewage sludge, both NPK doses and industrial sewage sludge resulted in a decrease in this coefficient value on average by 36 % in the test plant in comparison with the control plants. In the investigations conducted by Jablonska and Ceglarek et al [18] the plants (cabbage, beetroots and lettuce) fertilized organically also revealed lower value of lead accumulation coefficient than the plants from the unfertilized treatment.

Metal mobility in oat was determined using translocation coefficient. This parameter was computed as a ratio of metal contents in oat aerial parts to its content in the roots [19]. The values of translocation coefficients fell within the range of 0.37–0.99 for Zn and 0.01–0.17 for Pb (Table 4). The analysis of translocation coefficient values shows that oat roots absorbed greater amounts of lead than zinc. Values of translocation coefficient indicate a decrease in Zn mobility from the roots to the aboveground parts on the treatments fertilized with municipal and industrial sewage sludge. All applied fertilizer materials reduced lead mobility from the roots to the aerial parts of plant and the value of translocation coefficient for lead was on average by 50 % lower on the fertilized treatments than on the control. The lowest values of lead translocation coefficient were registered on the treatments with the residual effect of a single sewage sludge dose.

Discussion

Utilization of organic waste materials for crop fertilization may positively affect their chemical composition but also cause an excessive accumulation of heavy metals in plants. Zinc and lead absorbed in excessive quantities may cause the stress conditions for plants and reveal high toxicity. It has been commonly known that individual heavy metals accumulate in various degrees in different plant parts. In the opinion of Gebski et al [20] zinc may accumulate simultaneously in the roots and shoots, whereas lead cumulates mainly in roots. The results confirming this dependency were obtained also in the presented experiments while analyzing bioaccumulation and translocation coefficients. In the discussed experiment the consequent effect of industrial sewage sludge led to a relatively big zinc content and uptake with the yield of the test plant, whereas for lead the similar effect was noted for compost and municipal sewage sludge fertilization. Similar dependencies were determined for ryegrass in the second year of the presented research [21]. The assessment of heavy metal content in oat was based on potential utilization of the produced biomass for fodder, using their limit content: < 100 mg Zn and < 10 mg Pb $\cdot$ kg^{-1} d.m. [22, 23]. Assessing the obtained aboveground oat biomass according to this criterion it was found that it meets the requirements considering lead content. In case of zinc, the plants from all treatments revealed over the norm its content (Table 2).

As stated by Jakubus [24] and Krzywy et al [25] environmental utilization of organic wastes is an efficient method of their disposal and the concept of their management in agriculture has the best perspective of development. It is particularly important in case of sewage sludges because a growing number of sewage treatment plants face the problem of the management of considerable waste amounts, whereas storage of these materials requires considerable space [5]. Moreover, agricultural management of organic materials is of extreme environmental-ecological importance allowing for reducing the use of mineral fertilizers, which ecological effects are less favourable than organic fertilizer effects [26].

Conclusions

1. The highest content and uptake of zinc by oat were stated on treatments with industrial sewage sludge, whereas lead uptake was the highest on the compost and municipal sewage sludge treatments.
2. Tested organic wastes cause an increase in zinc bioacummulation coefficient value. For lead the decrease in this parameter value in oat was the result of application of a majority of organic wastes.
3. All applied organic materials limited lead transport from plant roots to the shoots and for zinc such effect was registered for the application of industrial and municipal sewage sludge.
4. No exceeded admissible values of lead content, used for plant assessment in view of their usability for fodder, were registered in oat. The plants revealed over the norm zinc contents.

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WPŁYW ODPADÓW ORGANICZNYCH NA AKUMULACJĘ CYNKU I OŁOWIU W BIOMASIE OWSA

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Abstrakt: Badania nad wpływem odpadów organicznych na zawartości cynku i ołowiu w owsie przeprowadzono w 2006 r. w doświadczeniu wazonowym. W doświadczeniu użyto sole mineralne, obornik, kompost oraz osady ściekowe komunalny i przemysłowy, które zastosowano w dwóch poziomach nawożenia.

Największa zawartości cynku w roślinach i jego pobranie przez owies została stwierdzone w obiektach nawożonych przemysłowym osadem ściekowym, podczas gdy zawartości Pb były największe w roślinach z obiektów z dodatkiem kompostu i komunalnego osadu ściekowego. Analiza wartości współczynników bioakumulacji i translokacji wykazała, że nadziemna biomasa owsa gromadziła większe ilości Zn niż Pb, podczas gdy korzenie w większym zakresie ograniczały przemieszczanie się ołowiu w roślinie.

Nie stwierdzono przekroczenia zawartości ołowiu w roślinach owsa ocenianej według kryteriów użyteczności paszowej, natomiast rośliny zawierały ponadnormatywne ilości cynku.

Słowa kluczowe: obornik, kompost, komunalny i przemysłowy osad ściekowy, cynk, ołów, owies

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Grażyna ŻUKOWSKA and Iwona MAKUCH

LEAD, NICKEL AND CHROMIUM CONTENT IN GRASS ON LAND RECLAIMED BY SEWAGE SLUDGE AND MINERAL WOOL GRODAN APPLICATION

ZAWARTOŚĆ OŁOWIU, NIKLU I CHROMU W TRAWIE UPRAWIANEJ NA GRUNCIE REKULTYWOWANYM PRZY WYKORZYSTANIU OSADU ŚCIEKOWEGO I WEŁNY MINERALNEJ GRODAN

Abstract: The objective of the present research was to analyze the impact of sewage sludge and post-use mineral wool applied to reclaim the devastated heavily acidified land, on heavy metal content in land reclamation grass seed mixture. The work presents the research findings from the three-year study period. There was analyzed grass obtained from the 1st cut as well as soil samples from 0–20 cm depth.

The experiment was set up on the post-sulfur mining land in Jeziorko. The 5 are-plots underwent the deacidification treatment with post-flotation lime followed by the employment of differentiated mineral wool doses (200, 400 and 800 $m^3 \cdot ha^{-1}$) along with a sewage sludge-amended dose. Ground in all the reclamation variants was characterized by a low content of lead, chromium and nickel.

A grass mixture from all the planting dates showed a natural level of the aforementioned trace elements. A grass Cr and Ni content was shown to be unaffected by sewage sludge and post-use mineral wool use for reclamation purposes. Mineral wool supplement implicated a proportional increase of a grass lead content.

Keywords: reclamation, lead, nickel, chromium, grass, ground, sewage sludge, mineral wool

Problems associated with the agricultural use of sewage sludge include primarily its bacterial and parasitic contamination with a concurrent wide range of toxic metals, in that heavy ones [1]. Sewage sludge application for non-industrial purposes, ground and land parameters as well as natural utilization of the sludge is governed by the stringent acts and regulations [2].

Mineral wool Grodan is produced from naturally occurring inorganic mineral material – magma rock. Rock wool is most widely used as a valuable growing substrate in the production of glasshouse crops but re-use of mineral wool slabs has remained

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a challenge [3]. That led to investigations on its application for devastated soil reclamation [4, 5].

Vegetation produced on sewage sludge-amended soil, especially for feedstuffs, should be examined for heavy metal contents. A few of them, like Cu and Zn (Ni and Cr to less extent) are recognized as essential micronutrients to maintain the life processes in plants/animals including human and animal health, whereas Pb and Cd affect plants most adversely.

The objective of the present study was to analyze the impact of sewage sludge and post-use mineral wool employed for reclamation of land devastated by heavy acidification, on heavy metal (Pb, Cd) content in a land reclamation grass seed mix.

Material and methods

The reclamation research was carried out on the post sulfur mining land in Jeziorko in 2004. The plots of 5-are area underwent the technical reclamation, i.e. deacidification process by post-flotation lime (100 $\mathrm{Mg \cdot ha^{-1}}$) followed by the application of varied rock wool doses (200, 400, 800 $\mathrm{m^3 \cdot ha^{-1}}$) along with a sewage sludge-amended dose (100 $\mathrm{Mg \cdot ha^{-1}}$ d.m.). In spring prior to seed sowing, sewage sludge and mineral wool were applied integrated with ground (coarse sand) by means of a disk harrow and soil miller. The scheme of pre-sowing fertilizer dressing included P (single superphosphate), K (potassium sulfate) and 1/2 N (ammonium nitrate), while post-sowing 1/2 N after the 1st cut harvest.

The characteristics of materials used for reclamation process was presented in the paper by Baran et al [4]. Post-use mineral wool Grodan contained 35.5 $\mathrm{mg\ Pb \cdot kg^{-1}}$, 18.5 $\mathrm{mg\ Cr \cdot kg^{-1}}$ and 9.3 $\mathrm{mg\ Ni \cdot kg^{-1}}$, while sewage sludge supplied by the treatment plant in Stalowa Wola comprised 29.2 $\mathrm{mg\ Pb \cdot kg^{-1}}$, 26.7 $\mathrm{mg\ Cr \cdot kg^{-1}}$ and 55.1 $\mathrm{mg\ Ni \cdot kg^{-1}}$.

The schema of experiment is presented in Table 1. The plots were sown with a reclamation grass seed mix (Baran et al [5]).

Table 1

The schema of experiment

Reclamation variants
Post flotation lime + NPK 80; 40; 60 (control)
Post flotation lime + sewage sludge (control)
Post flotation lime + sewage sludge + wool 200 $\mathrm{m^3 \cdot ha^{-1}}$
Post flotation lime + sewage sludge + wool 400 $\mathrm{m^3 \cdot ha^{-1}}$
Post flotation lime + sewage sludge + wool 800 $\mathrm{m^3 \cdot ha^{-1}}$
Post flotation lime + wool 200 $\mathrm{m^3 \cdot ha^{-1}}$
Post flotation lime + wool 400 $\mathrm{m^3 \cdot ha^{-1}}$
Post flotation lime + wool 800 $\mathrm{m^3 \cdot ha^{-1}}$
Post flotation lime + wool 200 $\mathrm{m^3 \cdot ha^{-1}}$ + NPK (80; 40; 60)
Post flotation lime + wool 400 $\mathrm{m^3 \cdot ha^{-1}}$ + NPK (80; 40; 60)
Post flotation lime + wool 800 $\mathrm{m^3 \cdot ha^{-1}}$ + NPK (80; 40; 60)

For the laboratory examinations, ground samples were collected from the topsoil (0–20 cm) after the soil was prepared for grass seed mix sowing and then, at late vegetation season (October) for three following years. The ground samples were collected in 3 replications (from random squares of 1 m^2 area). In the successive research periods, three cuts of grass were harvested (late spring, summer, autumn). The present study analyzes the results of the first cuts of grass. Having dried the grass, it was mineralized in concentrated acid mixture – HNO_3 and $HClO_4$ for the determination of Pb, Cr and Ni in the extract [6]. The ground samples taken were subjected to mineralization procedure in a mixture of concentrated acids HNO_3 and $HClO_4$ followed by determination of total contents of Pb, Cr and Ni in the ground and plants. The samples were measured using the ICP-AES inductively coupled plasma atomic emission spectrometer, Leeman Labs, model PS 950.

For the analyzed elements, there was calculated a bioaccumulation index (from the ratio between Pb, Cr and Ni content in plant biomass and their soil contents).

Results

Sewage sludge and mineral wool have changed a lead content in the reclaimed ground only to a small extent as compared with control I and II (Table 2). Pb content in 0–10 cm layer of the initial ground averaged 8.4 mg · kg^{-1}. Mean content of the element in ground, subject to an object, was found within 8.1–16.2 mg · kg^{-1} range. In all the fertilizer variants, a lead content increased with the rock wool dose elevation. The ground treated with differentiated doses of mineral wool and NPK showed the highest average lead content. The exception was made by the reclamation variants of lime + wool + NPK, where the ground displayed a higher lead content at the application of wool dose 200 $m^3 \cdot ha^{-1}$ as compared with a 400 $m^3 \cdot ha^{-1}$ dose. The observed differences were most likely to arise from ununiformity of the substrate structure.

Table 2

Content of lead in ground and mix of the grass from experiment
(average values from 3 years of the researches)

Reclamation variants	Ground	Mix of the grass	Bioaccumulation coefficient
	[mg · kg^{-1} d.m.]		
Control: post flotation lime + NPK	8.1	0.90	0.11
Control: post flotation lime + sewage sludge	8.5	0.93	0.11
Post flotation lime + sewage sludge + wool 200 $m^3 \cdot ha^{-1}$	9.0	0.49	0.05
Post flotation lime + sewage sludge + wool 400 $m^3 \cdot ha^{-1}$	10.7	0.40	0.04
Post flotation lime + sewage sludge + wool 800 $m^3 \cdot ha^{-1}$	12.9	1.18	0.09
Post flotation lime + wool 200 $m^3 \cdot ha^{-1}$	9.8	1.53	0.16
Post flotation lime + wool 400 $m^3 \cdot ha^{-1}$	9.7	1.51	0.15
Post flotation lime + wool 800 $m^3 \cdot ha^{-1}$	16.2	1.32	0.08
Post flotation lime + wool 200 $m^3 \cdot ha^{-1}$ + NPK (80; 40; 60)	13.5	0.51	0.04
Post flotation lime + wool 400 $m^3 \cdot ha^{-1}$ + NPK (80; 40; 60)	13.0	1.26	0.10
Post flotation lime + wool 800 $m^3 \cdot ha^{-1}$ + NPK (80; 40; 60)	15.1	1.01	0.07

A chromium content in 0–10 cm layer of the initial ground reached 13.6 mg · kg^{-1} .

Table 3

Content of chromium in ground and mix of the grass from experiment
(average values from 3 years of the researches)

Reclamation variants	Ground	Mix of the grass	Bioaccumulation coefficient
	[mg · kg^{-1} d.m.]		
Control: post flotation lime + NPK	12.7	1.8	0.14
Control: post flotation lime + sewage sludge	11.8	2.2	0.19
Post flotation lime + sewage sludge + wool 200 m^3 · ha^{-1}	14.3	2.3	0.16
Post flotation lime + sewage sludge + wool 400 m^3 · ha^{-1}	18.5	2.2	0.12
Post flotation lime + sewage sludge + wool 800 m^3 · ha^{-1}	24.5	2.1	0.08
Post flotation lime + wool 200 m^3 · ha^{-1}	18.1	2.1	0.12
Post flotation lime + wool 400 m^3 · ha^{-1}	21.8	2.1	0.10
Post flotation lime + wool 800 m^3 · ha^{-1}	30.5	1.9	0.06
Post flotation lime + wool 200 m^3 · ha^{-1} + NPK (80; 40; 60)	22.1	1.8	0.08
Post flotation lime + wool 400 m^3 · ha^{-1} + NPK (80; 40; 60)	24.6	2.0	0.08
Post flotation lime + wool 800 m^3 · ha^{-1} + NPK (80; 40; 60)	36.4	2.0	0.05

A mean Cr level determined from three-year study period of each reclamation variants was in the range between 11.8–36.4 mg · kg^{-1}. A chromium content in all the reclamation variants was shown to rise with increasing mineral wool doses, while in the ground a combination of lime + wool 800 m^3 · ha^{-1}+ NPK, a Cr content showed an over three-fold increase as against control I and II.

Prior to experiment, the initial ground was characterized by a low Ni level – 4.55 mg · kg^{-1}. Its mean content determined in the experimental plot ground ranged within 6.7–14.8 mg · kg^{-1}.

Considering all the fertilizer variants, the highest Ni amount was detected in the ground with the highest mineral wool dose. Alike, the ground under lime + wool + NPK combination was reported to have a higher Ni level compared with control and other fertilizer variants.

A mean lead content in a grass mixture from the plot was found between 0.40 and 1.53 mg · kg^{-1} d.m. (Table 2). The lowest Pb content was established in grass on the plots with sewage sludge and varied mineral wool dressing. In this fertilizer variant, Pb content grew with a rising wool dose. The highest lead content was recorded in grass obtained from the mineral wool-amended plots.

A chromium level in a grass mixture from the plots under study appeared to be slightly differentiated. Waste applied for the reclamation of devastated ground did not affect a Cr content in the grass analyzed (Table 3). A Cr level in the grass mix ranged between 1.8 and 2.3 mg · kg^{-1} d.m., similar values were found in plants from the experimental plots.

Table 4

Content of nickel in ground and mix of the grass from experiment
(average values from 3 years of the researches)

Reclamation variants	Ground	Mi of the grass	Bioaccumulation coefficient
	[mg · kg^{-1} d.m.]		
Control: post flotation lime + NPK	6.7	3.3	0.49
Control: post flotation lime + sewage sludge	7.3	3.1	0.42
Post flotation lime + sewage sludge + wool 200 m^3 · ha^{-1}	7.3	2.7	0.37
Post flotation lime + sewage sludge + wool 400 m^3 · ha^{-1}	9.5	2.8	0.29
Post flotation lime + sewage sludge + wool 800 m^3 · ha^{-1}	11.7	3.0	0.26
Post flotation lime + wool 200 m^3 · ha^{-1}	7.3	2.2	0.30
Post flotation lime + wool 400 m^3 · ha^{-1}	8.8	2.0	0.23
Post flotation lime + wool 800 m^3 · ha^{-1}	14.8	2.3	0.15
Post flotation lime + wool 200 m^3 · ha^{-1} + NPK (80; 40; 60)	11.4	2.2	0.19
Post flotation lime + wool 400 m^3 · ha^{-1} + NPK (80; 40; 60)	10.4	2.0	0.19
Post flotation lime + wool 800 m^3 · ha^{-1} + NPK (80; 40; 60)	13.7	2.3	0.17

A mean nickel content in the analyzed grass was in the 2.0–3.3 mg · kg^{-1} d.m. (Table 4). Alike a Cr content, a grass Ni level was not affected by post-use mineral wool Grodan or sewage sludge applied for land reclamation.

A bioaccumulation index calculated for lead in the grass mix under study was very low and ranged between 0.04 and 0.16. The highest values were detected in grass from the plots, which beside the liming were dressed with varied doses of post-use mineral wool (200 and 400 m^3 · ha^{-1}).Wool at the dose of 800 m^3 · ha^{-1} applied in all the reclamation variants has declined this metal bioaccumulation in grass.

A bioaccumulation index for Cr and Ni in the investigated grass mixture was differentiated but generally, low. The highest values were noted in grass from the control plots, while the lowest from those with the highest mineral wool dose.

Discussion

Sewage sludge and post-use mineral wool Grodan used for the reclamation of land devastated by heavy acidification showed a low Pb, Cr and Ni content. Kuziemska and Kalembasa [7] reported similar Ni levels and tenfold higher Pb levels in the sewage sludge collected from the Siedlce and Sokolow Podlaski region.

Alike, the reclaimed ground also contained small amount of the metals studied. Sewage sludge did not affect these element levels. Only slightly elevated contents of Pb, Ni and Cr were detected in the ground reclaimed with the highest doses of post-use mineral wool.

Contents of Pb and Ni determined in the first cut of the reclaimed grass mix reported it as favourable for forage use [8] with the heavy metal contents most frequently recorded in grasses [9, 10]. Similarly, a Cr level was characteristic of the grasses from the Lublin region [11].

The present studies have not revealed any impact of the waste used in reclamation efforts on Cr and Ni accumulation in a grass mixture. However, there was noted a Pb content increase in the grass on the ground reclaimed by varied post-use mineral wool doses. Alike, in the investigations of Kuziemska and Kalembasa [7] sewage sludge applied did not increase Ni content in the tested plants as compared with those cultivated on manure. Czyzyk [12] in his studies found that Pb, Cr and Ni content in grasses from meadows irrigated with various sewages was dependent on a sewage type and amount of metals it contained. Meadow irrigation by sewages from non-industrialized cities did not cause a significant trace element growth in grasses. Grygierzec et al [10] noted that a grass nickel content was subject to a type of fertilizer dressing applied.

A bioaccumulation index for Pb, Cr and Ni has evidenced low and mean metal accumulation rate in grass mix [13]. Post-use mineral wool used for reclamation at 800 $m^3 \cdot ha^{-1}$ doses has reduced bioaccumulation of Pb, Cr and Ni in grass.

Conclusion

1. Ground reclaimed under all the fertilizer combinations showed a low Pb, Cr and Ni content.
2. Sewage sludge used in reclamation activities had no impact on the studies element contents, but their content increased with growing doses of post-use mineral wool doses.
3. Grass mixture from all the cuts was characterized by a natural content of the discussed heavy metals.
4. Sewage sludge and post-use mineral wool applied for reclamation did not affect chromium or nickel content in grass mix; mineral wool supplement increased proportionally lead accumulation in grass.

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ZAWARTOŚĆ OŁOWIU, NIKLU I CHROMU W TRAWIE UPRAWIANEJ NA GRUNCIE REKULTYWOWANYM PRZY WYKORZYSTANIU OSADU ŚCIEKOWEGO I WEŁNY MINERALNEJ GRODAN

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Abstrakt: Celem niniejszych badań była analiza wpływu osadu ściekowego i poużytkowej wełny mineralnej, zastosowanych do rekultywacji zdewastowanego przez silne zakwaszenie gruntu, na zawartość metali ciężkich w rekultywacyjnej mieszance traw. W pracy przedstawiono wyniki z trzech lat badań. Analizowano trawę z pierwszego pokosu, jak również glebę pobraną z głębokości 0–20 cm.

Doświadczenie założono na terenie byłej kopalni siarki w Jeziórku. Na poletkach o powierzchni 5 arów, po wcześniejszym odkwaszeniu wapnem poflotacyjnym, stosowano zróżnicowane dawki wełny mineralnej (200, 400 i 800 $m^3 \cdot ha^{-1}$), na tle melioracyjnej dawki osadu ściekowego.

Rekultywowany grunt we wszystkich kombinacjach nawozowych charakteryzował się małą zawartością ołowiu, chromu i niklu.

W mieszance traw ze wszystkich pokosów stwierdzono naturalną zawartość omawianych metali ciężkich. Zastosowane do rekultywacji osady ściekowe i poużytkowa wełna mineralna nie miały wpływu na zawartość w niej chromu i niklu. Wzrastające dodatki wełny mineralnej zwiększały proporcjonalnie zawartość ołowiu w trawie.

Słowa kluczowe: rekultywacja, ołów, nikiel, chrom, trawa, grunt, osad ściekowy, wełna mineralna

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EFFECT OF LONG-TERM SEWAGE SLUDGE APPLICATION ON SOIL CHEMICAL INDICES

DZIAŁANIE WIELOLETNIEGO NAWOŻENIA OSADEM ŚCIEKOWYM NA CHEMICZNE WSKAŹNIKI GLEBY

Abstract: Field trial was carried out during the consecutive years 2001–2006 on a lessive soil (Albic Luvisols). The objective was to evaluate the influence of sewage sludge applied at different yearly rates, simultaneously with mineral fertilization, on soil properties, mainly organic carbon and total nitrogen content as well as changes in pH and the level of available phosphorus at the humus layer and the subsoil. Investigations were carried out on two three-years rotation: potatoes – spring barley – winter rye. Sewage sludge was applied at the rates (on dry matter basis) 2.0 Mg $\cdot$ ha^{-1} yearly, 4.0 Mg $\cdot$ ha^{-1}, each two years, 8.0 Mg $\cdot$ ha^{-1} each three years. This corresponded to the legally regulated amounts, ie, 10 Mg $\cdot$ ha^{-1} for a five-year period. Moreover sludge was applied at the rates 4 and 8 Mg $\cdot$ ha^{-1} dry matter, yearly. The control treatment consisted of mineral fertilization, only. It was found, that the application of sewage sludge, irrespective of the rate and the frequency did not exert (in most cases) a significant influence on investigated soil indices. This concerned at whole soil pH, organic carbon and total nitrogen content as well as partly the available phosphorus level. In the case of phosphorus, its amounts decreased during the first three years of investigations, whereas in the second cycle of the rotation, P levels raised extremely at the highest sludge rate. Taking into consideration the biogenic effect of phosphorus as in the case of its accumulation in soils under conditions of long-term sludge application, therefore phosphorus balance at the field level may be a targeted task, particularly for soil rich or very rich in phosphorus.

Keywords: sewage sludge, fertilization, soil properties

The rational use of sewage sludge is a concern, which requires to be solved since few years, mainly organizationally and ecologically. According to GUS [1], more than 501 thousands Mg of sewage sludge dry biomass were produced in municipal sewage treatment plants in Poland, of which 64.2 thousands Mg in the Wielkopolska province. Taking into consideration the way sewage sludge is managed, it appears that at the country scale, 40.6 % of the formed sewage biomass was agriculturally used whereas in the Wielkopolska province, 24 %. In this aspect, sewage sludge has to be considered as

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a source of organic matter and nutrient, in one hand [2, 3] and as a carrier of organic and mineral contaminants on the other hand [4–7]. This is why the agricultural and ameliorative application of sewage sludge is legally regulated in Poland, in order to prevent from unfavorable changes in the soil environment. For this reason, except the fertilizer aspect, chemical changes of soil properties are frequently considered, such as soil reaction (pH), organic carbon content and trace elements, but also phosphorus content. This is due to the necessity of considering its role in the ecosystems and the need for a sustainable fertilization as a system under requirements of environmental protection. Therefore phosphorus topic has to be also considered in given cases as an environmental toxicant.

On the basis of these views, long-term investigations over the influence of sewage sludge applied at different rates on changes of pH, phosphorus, potassium and magnesium at the humus layer and subsoil.

Material and methods

Field trial was carried out during the consecutive years 2001–2006 on a lessive soil (Albic Luvisols) at Zlotniki (52°29′N, 16°50′E) an Experimental-Teaching Station of the University of Life Sciences in Poznan. Selected properties in the soil humus layer are reported in Table 1 and experimental design in Table 2.

Table 1

Selected properties in the soil humus layer (average content)

pH_{KCl}	Organic C	Total N	C : N	Diameter of fraction [%]		Available [$mg \cdot kg^{-1}$]		
	[$g \cdot kg^{-1}$]			< 0.02 mm	< 0.002 mm	P	K	Mg
5.60	6.68	0.60	11.1	14.0	3.0	98.4	118.6	60.3

Table 2

Experimental design

No	Treatment	Fertilization	
1	NPK	According to nutrient requirements of plant	
2	Sewage sludge	2 $Mg \cdot ha^{-1}$ d.m. yearly	+ NPK
3		4 $Mg \cdot ha^{-1}$ d.m. each two years	
4		6 $Mg \cdot ha^{-1}$ d.m. each three years	
5		4 $Mg \cdot ha^{-1}$ d.m. yearly	
6		8 $Mg \cdot ha^{-1}$ d.m. yearly	

Mineral fertilization was elaborated according to nutrient requirements of plant grown on two three-years rotation: potatoes – spring barley – winter rye. Fertilizer rates were accordingly 120–22–83, 50–29–100 and 60–35–90 $kg \cdot ha^{-1}$, respectively for N, P, K.

Each plot (42 m^2) was replicated four times. The area where potatoes were harvested was 42 m^2 and for cereals, 24 m^2.

For each experimental year, sewage sludge was collected from the same sewage treatment plant whose purification technology is based on the mechanical-technological-biological system. Selected properties of the sewage sludge are reported in Table 3.

Table 3

Selected properties of the sewage sludge

Parameter	Unit	Content
pH_{KCl}	—	6.52–7.18
Dry matter	[g · kg^{-1}]	198.2 ± 12.76* (168.0–203.6)**
Organic matter	[g · kg^{-1} d.m.]	736.5 ± 51.85 (668.0–797.0)
Organic carbon ($C_{org.}$)		320.4 ± 15.88 (295.1–341.7)
Total nitrogen (N_{tot})		57.33 ± 5.48 (48.72–62.70)
C : N	—	5.69 ± 0.77 (4.74–6.62)
P	[g · kg^{-1} d.m.]	25.82 ± 2.16 (22.83–28.56)
K		7.06 ± 1.72 (3.95–8.28)
Mg		8.44 ± 3.18 (5.67–14.68)
Ca		16.25 ± 5.40 (11.60–24.83)

* Average; ** range.

Soil chemical analyses were performed as follows:

- pH, potentiometrically in 1 M KCl,
- organic carbon, according to the method of Tiurin,
- total nitrogen by the method of Kjeldahl,
- available phosphorus and potassium by the Egner-Riehm method,
- available magnesium according to the method of Schachtschabel, and further determined by flame atomic absorption spectrometry (FAAS).

The dry biomass of sewage sludge was determined by the dry method at the temperature of 105 ^{o}C, and the organic matter by the ashing method at 550 ^{o}C, total nitrogen by the Kjeldahl method. Calcium and potassium were determined by the atomic emission spectroscopy method (AES) and magnesium by the FAAS method, after ashing the samples at 550 ^{o}C, and hot dissolving the ash in a solution of 3 M HCl.

Results and discussion

Sewage sludge may be used for agricultural purposes with respect to their composition [4, 6]. But the condition for such application is regulated by the standards dealing with the hygienic aspect of sewage sludge and heavy metal contents. From the agricultural point of view, sewage sludges was assessed to date mainly with respect to their effect on pH, organic matter content and fertilizer nitrogen value as well as the problem of heavy metals. It appears from data reported in Table 4, that under experimental conditions the application of sewage sludge influenced slightly pH changes, but a decreasing trend was clearly observed at the last year of field trial.

Table 4

Changes of humus layer of soils pH throughout years of experiments

Treatment	Years of trials					
	2001	2002	2003	2004	2005	2006
1	5.60	5.86	5.44	5.42	5.33	4.85
2	5.82	5.87	5.16	5.35	5.44	5.09
3	5.44	5.87	5.25	5.34	5.46	4.97
4	5.60	5.86	5.08	5.35	5.28	4.96
5	5.87	5.88	5.21	5.40	5.28	5.12
6	5.68	5.84	5.47	5.37	5.34	4.93

The reported decrease concerned not only treatments with sewage sludges, but also those with mineral fertilization exclusively. Since sewage sludge contained relatively notable amounts of calcium (on average 16.25 g · kg^{-1} d.m.) (Table 3), it was expected its effect on pH to be more pronounced. This means that the application of sewage sludge did not exert an influence on the decreasing rate of soil pH. Since the experimental design did not involve a treatment with applied sewage sludge exclusively, therefore it was impossible to assess the main source favorising such pH changes. It should not be excluded that the observed pH decrease was induced mainly by the mineral fertilization which activated the mineralization process of the organic matter [8]. Sewage sludge applied at different frequency in officially permissible rates (treatments 2 to 4) has evoked pH changes as reported above. In general, sewage sludge applied to soil does not lead to pH changes [9] even at high rates [10]. In turn, according to Kuziemska and Kalembasa [11], irrespective of its origin and rates, sewage sludge applied to the soil induced pH decrease. This was earlier reported by Baran [12] who observed a systematic decrease of soil pH along with time after sludge application. The occurrence of organic acids could be one the factors controlling the observed reactions [13, 14].

With respect to the content of organic matter, sewage sludge is considered as its source to the soil, however not significant relationship is always observed in terms of an increase in soil organic carbon after the application of sludge. According to Zukowska and Flis-Bujak [15], changes in soil organic carbon content depended on its content and the rate of applied sludge.

However, a systematic decrease of organic carbon content along with progressing time was observed. Moreover it has been shown that the application of sludge decrease the susceptibility of humic compounds to chemical oxidation with a simultaneous increase of non-hydrolizable fraction of humic substances. An increase in the content of organic carbon in the soil with a simultaneous slight decrease of total nitrogen was reported by Kuziemska and Kalembasa [11]. Results reported in Table 5 indicate that the amounts of organic carbon changes varied with years of experimentation but differences between fertilization treatments were not significant in general, except for years 2004 and 2006.

Table 5

Organic carbon, total nitrogen [g · kg^{-1} d.m.] and C : N at the humus layer of soil

Treatment	Organic carbon ($C_{org.}$)			Nitrogen (N)			C : N		
	Crop rotation		Average	Crop rotation		Average	Crop rotation		Average
	2001– –2003	2004– –2006	2001– –2006	2001– –2003	2004– –2006	2001– –2006	2001– –2003	2004– –2006	2001– –2006
1	6.13	5.75	5.94	0.56	0.56	0.56	10.95	10.20	10.50
2	6.18	6.04	6.11	0.60	0.61	0.61	10.30	10.11	10.18
3	6.10	6.12	6.11	0.58	0.60	0.59	10.52	11.21	10.34
4	6.11	5.66	5.89	0.60	0.56	0.58	10.18	9.88	10.09
5	6.22	5.91	6.06	0.57	0.59	0.58	10.91	10.08	10.41
6	6.32	6.59	6.46	0.61	0.66	0.63	10.36	10.00	10.05
$LSD_{0.05}$	n.s.	0.37	0.33	0.02	0.05	0.03	—	—	—

n.s. – not significant.

By analyzing the dynamics of changes, it should be concluded that the highest organic carbon decrease (23.2 %) in 2006 was observed in the treatment with only mineral fertilization, as compared with organic carbon level at the start of the trial. Furthermore, the application of sludge at the highest rate, ie 8.0 Mg · ha^{-1} d.m. has stabilized the level of organic carbon similar to that of the year 2001 (Start of the trial). Also the systematic yearly application of sludge at the rate 2.0 Mg · ha^{-1} has significantly limited losses of organic carbon by 7.0 % as compared with 19.3 % recorded for the year application of 4.0 Mg · ha^{-1}.

To sum up, it should be mentioned, that next to mineral fertilization, sludge application at agriculturally permissible rates, does not guarantee keeping constant the level of organic carbon. This may be attributed to a possible enhanced mineralization of soil carbon under the control of microorganisms assimilating easily soluble low molecular carbon bonds as well as nitrogen from the sludge. The amounts of these bonds of fulvic acid nature is variable and depends of the way of waste waters purification [12], however they are prevailing most frequently. According to Mazur [16], sewage sludges are characterized by a low value of soil humus formation, and this observation is supported by data reported in Table 3 as referred to the total content of organic carbon. The quality of humic compounds is another topic.

Sewage sludge did not significantly influence the content of nitrogen in the soils (Table 5), irrespective of the applied rates, in spite of its high content in the sludges (Table 3). It is wondering about the transformation of this element, whose amounts varied from 97.4 to 125.4 kg · ha^{-1} at the rate 2.0 Mg · ha^{-1} and from 389.6 to 501.6 kg · ha^{-1} at the rate 8.0 Mg · ha^{-1}. It is basically important that no significant differences were observed for plant yields (unpublished data). One of the reason for such effect of the sewage could be attributed to the relatively low availability of nitrogen in the sludge, where it occurs preponderantly in organic bonds, resistant to breakdown.

According to Kutera [17], the recovery of nitrogen at the first year of sludge application is ca 20 % which appears to be high enough as compared with data from authors in the order 2.5 to 5.0 % [18]. Further investigations are needed in order to elucidate the fate of such high amounts of nitrogen in the soil after the application of both mineral fertilizers and sewage sludge in one way and the lack of its accumulation in the soils, on the other hand.

From the ecological point of view phosphorus is becoming more and more important. Its productive effect is without reservations, but restrictions are needed in terms of sludge application under conditions of soils rich in phosphorus. Therefore sludge application for fertilization purposes should be managed not as a supplement of mineral fertilization but instead of the latter one. This is becoming necessary with respect to exhausting the reserves of mineral resources involved in phosphorus production and also with environmental threat created by this element [19].

When considering the permissible rate of sludge in Poland, ie, 10 Mg d.m. $\cdot$ ha^{-1} for the five-year period, therefore from 228.5 to 285.5 kg P $\cdot$ ha^{-1} were introduced into soils with the sludges tested in the current research. Furthermore with the highest rate it has been applied yearly during the experimental period from 182.6 to 228.5 kg P $\cdot$ ha^{-1}. These amounts are high and exceed those commonly applied in Polish agriculture. In spite of this, just at the first year of experimentation no significant differences were obtained for available phosphorus between the treatments (Table 6).

Table 6

Influence of mineral fertilization and sludge application on changes of available phosphorus, potassium and magnesium average content at the humus soil layer [mg $\cdot$ kg^{-1} d.m.]

Treatment	Phosphorus (P)			Potassium (K)			Magnesium (Mg)		
	Crop rotation		Average	Crop rotation		Average	Crop rotation		Average
	2001–2003	2004–2006	2001–2006	2001–2003	2004–2006	2001–2006	2001–2003	2004–2006	2001–2006
1	86.0	104.6	95.3	96.2	124.0	110.1	59.2	68.8	64.0
2	88.6	105.1	96.8	121.2	146.0	133.6	56.6	68.2	64.2
3	91.0	114.8	102.9	104.0	113.9	116.8	58.0	71.5	64.7
4	90.2	104.5	95.3	93.3	107.5	103.1	57.1	64.5	61.0
5	92.1	109.7	100.9	91.3	102.4	107.0	60.2	63.2	61.1
6	105.3	123.6	107.7	112.7	146.5	129.6	60.7	72.8	66.8
$LSD_{0.05}$	n.s.	n.s.	9.47	15.51	17.93	11.09	n.s.	6.31	n.s.

Simultaneously, its amounts decreased for the next consecutive two years, ie, to the end of the first rotation. It should not be excluded that some amounts of phosphorus underwent chemical changes towards strongly stable forms, for instance for calcium which is an intrinsic component of sludges and occurs in high amounts (Table 2). Data reported by other workers [20] show that the solubility of the available fraction of phosphorus decreased when calcium oxide or ash from brown coal were added to sludge. In turn, during the second rotation an increasing trend in the content of available phosphorus was observed on all treatments, but more in those where sludge was applied. At both rotation periods, lowest levels of available phosphorus occurred in the treatments receiving only mineral fertilization, whereas the more phosphorus-fertile treatment reflected the highest sludge rate. The difference between both extreme treatments for the consecutive rotation was ca 48.3 and 35.3 %, respectively. The most important is the fact, that along with the years elapsing after the year-to-year application of sludge, differences between treatments were getting wider and exhibiting significant differences at the level $p < 0.05$. The influence for such phosphorus behaviour in the soil may be attributed to different factors, among others weather conditions as well as plants growth. Data obtained in the current work indicate also, as reported above, that when applying sludge as fertilizer, phosphorus content should be considered. The latter one will be intended to replace totally or partly phosphorus from mineral fertilizers. This results in the necessity of balancing this element, which next to nitrogen, belongs to the group of biogenic elements in the ecosystem.

Sewage sludge contain usually low levels of potassium (Table 3) which are not considered as an important source for plants. Nevertheless, under conditions of systematic application of sewage sludge, some amounts of available K may accumulate at the humic layer as indicated by results reported in Table 6. Throughout the whole period of experimentation, a distinct increase in the pool of available K forms was observed during the second rotation (2004–2006) as compared with the first rotation (2001–2003), but no explicit trends were recorded, when referring to those which took place in the case of phosphorus. Nevertheless, significant differences in potassium content (Table 6) occurred mainly for the year-to-year application of sludge at the rates 2 $Mg \cdot ha^{-1}$ and 8 $Mg \cdot ha^{-1}$ (on dry weight basis), as compared with the control treatment (without sludge). Therefore, based on such differences, it can be pointed out the fertilizer effect of potassium contained in the sludge. The trends were important and affected mean values of potassium content in the soils for the whole period of investigation.

Decidedly, sludge exerted a slight influence on available magnesium content in the humic layer (Table 6). Moreover, it should be stressed on similar and not significant differences in magnesium content on all treatments, but at a different level between the periods of study.

Conclusions

Sewage sludge is a source of organic matter, nitrogen and additional nutrients, phosphorus among others. On this basis, sewage sludge may be a material of fertilizer nature. However, the results of six years of experiments indicated that sewage applied at recommended and beyond rates did not exert a significant role on the accumulation of organic carbon and total nitrogen in the soil. Furthermore it was observed a decrease in soil pH along with years of experimentation, implying a need for periodic soil liming, even under conditions of applying sludge rich in calcium. Taking into consideration the biogenic effect of phosphorus as in the case of its accumulation in soils under constant sludge application, therefore phosphorus balance at the field level may be a targeted task.

The content of available potassium in the humic layer increased along with the period of experimentation. The highest quantitative and significant differences of potassium forms, as compared with other treatments, were observed on treatments receiving year-to-year sewage sludge at rates 2 and 8 Mg · ha^{-1}.

No significant influence of sewage sludge on available magnesium content was proved in spite of an increase of its content in the humic layer.

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DZIAŁANIE WIELOLETNIEGO NAWOŻENIA OSADEM ŚCIEKOWYM NA CHEMICZNE WSKAŹNIKI GLEBY

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Abstrakt: Doświadczenie polowe przeprowadzono w latach 2001–2006 na glebie płowej. Jego celem było określenie wpływu osadu ściekowego stosowanego w zróżnicowanych corocznych dawkach wspólnie z nawożeniem mineralnym na właściwości gleby, w tym gromadzenie węgla organicznego i azotu ogólnego, oraz na zmiany odczynu i zawartości fosforu przyswajalnego w poziomie próchnicznym i podglebiu. Badania prowadzono w dwóch trzyletnich cyklach zmianowania: ziemniaki – jęczmień jary – żyto ozime. Osad stosowano (w przeliczeniu na suchą masę) w dawkach 2 Mg · ha^{-1} corocznie; 4 Mg · ha^{-1} co dwa lata i 8 Mg · ha^{-1} co trzy lata. Odpowiadało to ilościom normowanym prawem, tzn. 10 Mg · ha^{-1} w okresie pięcioletnim. Poza tym stosowano osad w ilości 4 i 8 Mg · ha^{-1} suchej masy corocznie. Obiektem kontrolnym była kombinacja z wyłącznym nawożeniem mineralnym.

Wykazano, że osad ściekowy bez względu na dawkę i częstotliwość stosowania w większości nie miał znaczącego wpływu na badane wskaźniki gleby. Dotyczyło to w całości odczynu, zawartości węgla organicznego i azotu ogólnego oraz częściowo przyswajalnego fosforu.

W pierwszych trzech latach badań stwierdzono spadek zawartości fosforu, a w drugim cyklu zmianowania systematyczny wzrost, największy przy ekstremalnej dawce osadu. Mając na uwadze gromadzenie się przyswajalnego fosforu w warunkach wieloletniego nawożenia osadem, jak i jego biogenne działanie w środowisku należy ilości wprowadzonego składnika do gleby uwzględnić w bilansie nawozowym pola, szczególnie przy wysokiej i bardzo wysokiej zasobności w ten składnik.

Słowa kluczowe: osad ściekowy, nawożenie, właściwości gleby

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EFFECTS OF CHELATING AGENTS ON COPPER, LEAD AND ZINC SOLUBILITY IN POLLUTED SOILS AND TAILINGS PRODUCED BY COPPER INDUSTRY

WPŁYW DODATKU ZWIĄZKÓW KOMPLEKSUJĄCYCH NA ROZPUSZCZALNOŚĆ MIEDZI, OŁOWIU I CYNKU W GLEBACH SKAŻONYCH ORAZ OSADACH POFLOTACYJNYCH GÓRNICTWA MIEDZI

Abstract: The main aim of this paper was to examine the effects of chelating agents on the mobilization of heavy metals from polluted soils and tailings generated by copper ore processing. Ammonium salts (chloride and nitrate(V)), organic acids (citric and tartaric), amino acids (glycine and histidine) and synthetic chelating agents EDTA (*ethylenediaminetetraacetic acid*) and EDDS (*ethylenediaminedisuccinic acid*) were applied to soil suspension at the rate of 5 mmol · kg^{-1} and shaken. Similar tests were performed also with two kinds of sewage sludge, at various stages of biochemical stability. Examined were 8 samples collected from the dumping sites Zelazny Most and Wartowice, as well as 2 samples of polluted soils from the vicinities of copper smelters Legnica and Glogow were tested.

Total concentrations of metals in tailings were: 1300–3800 mg Cu · kg^{-1}, 80–300 mg Pb · kg^{-1} and 23–35 mg Zn · kg^{-1}, whereas the concentrations of those metals in soils were: 1270–1500 mg Cu · kg^{-1}, 304–336 mg Pb · kg^{-1} and 80–89 mg Zn · kg^{-1}. Efficiency of metals extraction from soils and tailings varied between tested soils and tailings material, metals and chemical agents applied. EDTA appeared the most effective in solubilizing Cu, and extracted 7–39 % of total Cu and 2–18 % Pb from various samples. The efficiency of Cu solubilization from soils and tailings by other agents was in the following order: citric acid (for tailings) > glycine > histidine > EDDS > citric acid (for soils) > tartaric acid > ammonium chloride > ammonium nitrate. The order for extraction of two other metals differed from that obtained for Cu. The tests with sewage sludge did not prove essential increase of Cu and Pb solubility, despite considerable amounts of dissolved organic matter present in one sludge. This effect can be explained by the sorption of chelated forms of metals by highly humified organic matter.

Keywords: soil, heavy metals, solubility, chelates, complexing, sewage sludge

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Copper industry produces huge amounts of wastes, in particular those obtained from flotation process, that are dumped in tailings dumping sites. There are seven such objects in Lower Silesia, of which the largest is still operating, whereas other 6 have been closed and partly reclaimed [1]. Reclamation of those objects is difficult, mainly because of unsuitable physical and chemical properties of tailings, such as lack of organic matter, shortage of bioavailable nutrients (N and P) and high concentrations of metals, in particular Cu and Pb [2]. Grain size composition of tailings depends on the properties of gangue rocks accompanying copper ores, and varies strongly: from sand and sandy silt to silty loam and clay. Tailings material contains certain amounts of limestone or dolomite, and therefore indicates alkaline or neutral reaction. For this reason, heavy metals are believed to remain there in insoluble and non-phytoavailable forms, and their presence should not cause the problems with biological reclamation. Application of organic matter will be needed for successful vegetation on tailings, to supply necessary macro- and micronutrients as well as to improve the physical properties of deposited material. Various organic materials are usually considered as a source of organic matter for reclamation of bare soils or landfills; there are numerous reports on the application of peat or lignite, as well as waste materials, such as manure, sewage sludge or composts. It should be pointed out, however, that poorly humified organic material should not be considered for reclamation of soils rich in heavy metals because of a risk of metals mobilization. Metals solubility may dramatically increase in the presence of low molecular weight organic compounds that act as chelating agents, and may transform metals into soluble chelates both in acidic and neutral or alkaline conditions [3–5]. It has been proved that organic acids present in plant root exudates may act as compounds chelating soil aluminum, iron and heavy metals; similar effects may be caused by fulvic acids and low molecular acids or amino acids produced in considerable amounts during the transformation of soil or waste organic matter, eg before sewage sludge or organic wastes become biochemically stabilized or before the compost reaches the stage of full maturity.

In this study, we examined the effect of copper, lead and zinc solubilization from tailings, as well as from soils highly polluted by copper smelting processes, caused by the application of substances that may act as chelating agents, and might be introduced to soil or tailings, by accident or on purpose, during their reclamation. Inorganic compounds containing ammonium ion that may act as Cu-chelating ligands [3, 5], ie, pure organic acids and amino acids, synthetic chelating compounds, as well as two kinds of sewage sludge and sewage sludge extracts were investigated. In the light of the literature, it is not clear whether the application of sewage sludge into soil (or soil parent rock) containing high concentrations of metals will or not lead to increased metal solubility and bioavailability. There are many reports proving, that sewage sludge application poses the risk of increasing metal solubility in soils [6–9]. Accordingly, legal regulations, introduced in Poland and in other countries, have established maximum permissible contents of heavy metals in soils to be amended with sewage sludge. On the other hand, however, the introduction of organic material, such as compost or sewage sludge, causes an increase of the soil sorption capacity, and therefore leads to the immobilization of potentially soluble metals [10–12]. Thus, metals solubility and bioavailability will decrease rather than increase after the application of sewage sludge. Several authors point out, however, that metal sorption by the solid phase and complexation by dissolved organic ligands must be studied simultaneously, because both processes may counteract one another [13, 14]. This statement prompted us to examine changes in the solubility of metals in polluted soils and in tailings after the application of various pure chelating substances, as well as sewage sludge at various stages of biochemical stability.

Material and methods

Investigations dealt with 8 samples of tailings collected from the surface layers (0–20 cm) in two dumping sites: the operating one Zelazny Most and Wartowice, officially called Iwiny III, closed 30 years ago and not reclaimed. Additionally, 2 soil samples were collected from the surface layers (0–20 cm) of soils in the vicinities of copper smelters Legnica (soil L) and Glogow (soil G). Basic physicochemical and chemical properties of tailings and soils were determined according to the common methods used in soil science [15]. Grain size distribution was analysed by areometric-sieve method according to Polish Norm PN-R-4033, and assigned to the textural groups determined by USDA [16]. The properties of tailings collected from those two objects differed strongly, which was mainly caused by different geological conditions of two copper mining centers [1, 3]. The differences within the groups of four samples collected from the same object were small (with standard deviations below 20 %), which confirms their relative homogeneity. Therefore, all results presented in the paper will be given as mean values for four samples. The tailings from Zelazny Most (described further as tailings ZM) were light in texture and had grain size composition of sand. They contained 1–5 % (with the mean value: 3 %) of clay fraction (< 0.002 mm) (Table 1).

Table 1

Basic properties of soils and tailings tested in the study

Soil / tailings material	Texture	Share of particles [mm]		Organic carbon C_{org} $[g \cdot kg^{-1}]$	pH	$CaCO_3$ [%]	CEC $[mmol(+) \cdot kg^{-1}]$	Total contents of metals		
		< 0.02	< 0.002					Cu	Pb	Zn
		[%]						$[mg \cdot kg^{-1}]$		
Soil L	silty loam	41	11	9.1	6.0	0	125	1270	336	80.3
Soil G	sand	18	4	7.5	6.4	0	96.3	1490	304	89.0
Tailings ZM	sand	8	3	6.5	7.5	9.5	n.d.*	1309	301	22.9
Tailings W	silty loam	64	11	11	7.7	56	n.d.	3780	77.8	35.4

* n.d. – not determined.

The texture of tailings Wartowice (tailings W) was much heavier, determined as silty loam, with 11 % of mean clay contribution, and very high amount (64 %) of the sum of fractions < 0.02 mm. Tailings ZM contained lower amounts of total Cu (0.13 %) than the tailings W (0.38 %), but the mean contents of total Pb were higher in the tailings

ZM (301 mg · kg^{-1}) than in tailings W (78 mg · kg^{-1}). Two soil samples tested in this study (soil L and G) also differed in their textures, that were determined as sand and silty loam, respectively. Concentrations of Cu and Pb in both soils were comparable with those in tailings ZM (Table 1).

Easily soluble forms of metals were determined in soil and tailings material in the common extraction tests with 1 mol · dm^{-3} NH_4NO_3 and 0.01 mol · dm^{-3} $CaCl_2$ [2]. The tests of metals extractability with chelating agents were performed as batch extractions (*m/v*: 1/5), in which the chelating agents were applied to soil suspension at the rate 5 mmol · kg^{-1} soil. The following agents were applied: ammonium chloride and ammonium nitrate(V), citric and tartaric acids, amino acids: glycine and histidine and synthetic chelating agents EDTA (*ethylenediaminetetraacetic acid*) and EDDS (*ethylenediaminedisuccinic acid*). Similar tests were performed also with two kinds of sewage sludge applied at the rate 1 g d.m. per 20 g soil d.m. Sewage sludge material was obtained from two municipal wastewater treatment plants, as freshly produced and mechanically dewatered (sludge 1) and stabilized in methane digestion tank (sludge 2). Basic properties of sludge material, as well as dissolved organic matter content (DOM) and metals contents are presented in Table 2.

Table 2

Basic properties of sewage sludge applied

Sewage sludge	OM [g · kg^{-1}]	pH	$CaCO_3$ [%]	CEC [mmol(+) · kg^{-1}]	DOM [g C · kg^{-1} d.m.]	Total contents of metals		
						Cu	Pb	Zn
						[mg · kg^{-1}]		
1	600	6.0	0	680	56	462	144	820
2	550	6.1	0	750	41	365	155	931

In order to estimate the pure effects of metal mobilization, ie, and to avoid subsequent sorption of soluble chelates by solid sludge organic matter, parallel tests were carried out in which sludge water extracts, obtained from the same amounts of sludge, were used. The extracts were prepared by shaking sludge with water (1/10, *d.m./v*), centrifuging and filtering prior to application to soil suspension.

Results and discussion

Easily soluble forms of metals, as determined by common single extraction method by 0.01 mol · dm^{-3} $CaCl_2$, proved that all metals examined are poorly soluble both in tailings and in polluted soils. Copper forms extracted by 0.01 mol · dm^{-3} $CaCl_2$ remained below 0.4 % of their total contents in soils and below 0.2 % in tailings, which corresponded with absolute values of 4.0–5.2 mg · kg^{-1} and 0.6–2.1 mg · kg^{-1}, respectively (Table 3). Similarly low were contributions of soluble Pb, and absolute amounts of soluble Zn, in soils and tailings. Attention should be paid to strikingly high amounts of "easily soluble" Cu, ie, that extracted both from soils and tailings with 1 mol · dm^{-3} NH_4NO_3, which is the standard method in several countries [2].

Particularly high amounts of Cu were extracted from tailings (61–66 % of total Cu), and this fact may be explained by formation of Cu ammine complexes $[Cu(NH_3)_4]^{2+}$ under alkaline conditions [3–5], as well as by the formation of HNO_3 as a product of ammonium nitrate hydrolysis. Similar data have already been reported [2, 5].

Table 3

Extractable metals determined in the common tests of extractability (mean values)

Soil / tailings material	Easily soluble metals in soils and tailings [mg · kg^{-1}], as extracted by					
	1 mol · dm^{-3} NH_4NO_3			0.01 mol · dm^{-3} $CaCl_2$		
	Cu	Pb	Zn	Cu	Pb	Zn
Soil L	149	5.3	22.3	5.2	1.1	8.9
Soil G	96.5	2.3	9.6	4.9	0.95	5.9
Tailings ZM	807	8.2	0.3	2.1	1.7	0.4
Tailings W	2590	4.3	1.8	0.6	0.9	0.2

High mobilization affinity of Cu present in tailings, and to lesser extent in soils, as caused by the solutions containing high concentrations of ammonium cations, was not reflected however when ammonium salts were applied at low ratio of 5 mmol · kg^{-1}. In that case, the amounts of Cu extracted from tailings and soils remained very low, ie, in the ranges 0.9–6.4 mg · kg^{-1} and 1.25–1.4 mg · kg^{-1}, respectively. Ammonium salts (both chloride and nitrate) applied at that ratio, appeared to have the poorest capacity to mobilize Cu, if compared with other compounds tested in the study.

The most efficient chelating agent was EDTA, that applied at the rate of 5 mmol · kg^{-1} was able to solubilize 254–507 and 284–287 mg Cu · kg^{-1} from tailings and soils, respectively (Table 4). Those amounts corresponded to the range: from 7 % (tailings W) up to 39 % (tailings ZM) of total Cu.

Table 4

Amounts of metals extracted from tailings with chelating agents applied
at the ratio of 5 mmol · kg^{-1}

Chelating agent	Tailings Zelazny Most			Tailings Wartowice		
	Cu	Pb	Zn	Cu	Pb	Zn
	[mg · kg^{-1}]					
EDTA	507	49.9	1.0	254	1.4	1.5
EDDS	97	2.5	2.1	85	1.1	0.9
Glycine	284	0.8	0.2	215	0.4	0.7
Histidine	98	1.1	0.8	101	0.8	0.6
Citric acid	431	9.3	2.6	248	0.4	0.6
Tartaric acid	134	4.8	1.6	6.9	0.7	0.2
NH_4NO_3	3.0	1.1	0.3	0.9	0.4	0.6
NH_4Cl	6.4	1.7	0.5	3.9	0.5	0.8

The orders of mobilizing capacities were different for various materials (tailings vs soils) as well as for various metals. Different reactions of chelating agents with various materials may be partly explained by their various pH-related characteristics [4, 5]. Copper was mobilized from tailings by various chelating agents according to the order: EDTA > citric acid > glycine > tartaric acid (*case of tailings ZM*) >> histidine > EDDS > tartaric acid (*case of tailings W*) >> NH_4Cl > NH_4NO_3 (Table 4).

The order of the capacity to moblilize Cu from polluted soils was as follows: EDTA >> EDDS / glycine / histidine >> citric acid / tartaric acid >> NH_4Cl > NH_4NO_3 (Table 5). None of the compounds proved to mobilize Cu from polluted soils with the efficiency comparable to that of EDTA.

Table 5

Amounts of metals extracted from soils with chelating agents applied at the ratio of 5 mmol · kg^{-1}

Chelating agent	Soil L			Soil G		
	Cu	Pb	Zn	Cu	Pb	Zn
	[mg · kg^{-1}]					
EDTA	287	31.8	5.9	284	23.7	7.1
EDDS	46.3	0.8	1.7	51.7	0.6	2.3
Glycine	36.5	3.7	0.6	65.9	3.9	0.8
Histidine	40.1	0.3	0.45	50.0	0.5	0.7
Citric acid	7.5	1.3	0.4	9.2	1.3	1.3
Tartaric acid	9.6	2.6	0.4	13.1	2.9	1.8
NH_4NO_3	1.2	0.2	0.2	0.3	0.35	0.8
NH_4Cl	1.4	0.2	0.25	0.5	0.25	0.6

The amounts of Pb and Zn solubilized from tailings and soils by chelating agents tested in this study were much lower than those of mobilized Cu. Application of EDTA led to the mobilization of considerable Pb amounts from the tailings ZM (49.9 mg · kg^{-1}) and from soils (23.7–31.8 mg · kg^{-1}). Those values corresponded to the range 8–16 % of total Pb. The mobilization of Pb from the tailings W was much less effective (1.4 mg · kg^{-1}, ie 1.8 % of total Pb).

The effects of Pb mobilization by other chelating agents were much poorer than those obtained with EDTA (Tables 4 and 5), and therefore will not be discussed in details. The effects of chelating agents on Zn solubility should also be considered as negligible, and the amounts of Zn released to the solutions were lower than those determined as easily soluble and exchangeable Zn, extracted by 0.01 mol · dm^{-3} $CaCl_2$.

Results obtained in the tests with two kinds of sewage sludge did not confirm the mobilization of metals from the tailings or soils after biosolids application (Table 6).

The amounts of Cu, Pb and Zn released from the solid to liquid phase of soil + sludge or tailings + sludge suspensions remained lower than those determined as easily soluble. These results support the opinions presented by various authors [10–12], who proved that biosolids application significantly reduced metals mobility and, accordingly, will not cause environmental risk of metal mobilization from polluted soils or metals-rich wastes, such as tailings. On the other hand, however, the amounts of all metals released to the liquid phase after application of sewage sludge extracts were much higher than those observed when untreated sludge were applied in the tests (Table 6).

Table 6

Amounts of metals extracted from soils [mg · kg^{-1}] with sewage sludge and sewage sludge extracts

Metal:	Cu	Pb	Zn	Cu	Pb	Zn
Application of:	Sewage sludge 1			Sewage sludge 2		
Soil L	0.4	0.45	3.2	3.5	0.2	3.7
Soil G	1.2	0.35	5.8	2.9	0.25	4.9
Tailings ZM	0.35	1.05	0.6	1.2	1.1	0.8
Tailings W	0.45	< 0.1	< 0.1	0.2	< 0.1	0.4
Application of:	Extract from sewage sludge 1			Extract from sewage sludge 2		
Soil L	4.9	1.2	4.0	5.5	1.4	4.5
Soil G	9.0	1.5	8.5	10.5	1.3	6.7
Tailings ZM	4.5	1.6	1.3	6.1	1.45	1.35
Tailings W	9.5	< 0.1	0.3	12.2	< 0.1	0.45

This observation stays in accordance with the hypothesis that easily soluble organic substances (DOM) present in various amounts in sewage sludge, do react with heavy metals, particularly with Cu and Pb, and form soluble complexes, like chelates, that potentially may be mobilized to soil solution. At the same time however, those potentially soluble complexes, are effectively adsorbed and immobilized by well-humified organic matter present in sewage sludge or in soil with high sorption capacity.

Therefore, application of sludge or sewage sludge or other organic waste rich in soluble fractions, to calcium carbonate rich soil or limed soil, at pH > 6.8 should be carried out carefully, because in such conditions, the formation of soluble DOM-metal complexes will be possible, which may lead to leaching of metals, especially Cu, from surface soils or reclaimed waste material such as tailings. Consequently, also the phytoavailability of Cu may vitally increase. Possible impacts of the latter effect should be tested in further experiments.

Conclusions

Heavy metals present in tailings, as well as metals present in soils polluted by the processes of copper smelting, may be released from the solid phase into soil solution by various chelating agents. The efficiency of metal solubilization will not be easy to predict, as it strongly depends on the kind of chelating agent, soil or waste properties as well as on the kind of metal. Of three metals examined, the highest affinity to be solubilized by chelating agents has undoubtedly Cu, and the most effective chelator was

EDTA. Several organic compounds, naturally occurring in the environment, such as organic acids or amino acids may also act as considerably effective metal-solubilizing agents. Therefore, special attention is needed when polluted soils or wastes would be treated with biosolids, that may contain soluble organic compounds. Environmental risk caused by metal solubilization when sewage sludge is applied, will be reduced by possible sorption of chelated metals by solid organic matter, and therefore sludge application acts as a factor immobilizing metals rather than mobilizing one. The results of this study may be helpful for planning treatments of chelate-induced soil decontamination or application of organic material in the processes of soil remediation and waste landfills revegetation.

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WPŁYW DODATKU ZWIĄZKÓW KOMPLEKSUJĄCYCH NA ROZPUSZCZALNOŚĆ MIEDZI, OŁOWIU I CYNKU W GLEBACH SKAŻONYCH ORAZ OSADACH POFLOTACYJNYCH GÓRNICTWA MIEDZI

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Abstrakt: Celem pracy było badanie wpływu substancji kompleksujących na rozpuszczalność metali z zanieczyszczonych gleb i osadów poflotacyjnych górnictwa miedzi. Do testów ekstrakcji przeprowadzonych metodą wytrząsania w zawiesinie, zastosowano sole amonowe (chlorek i azotan (V)), kwasy organiczne (winowy i cytrynowy), aminokwasy (glicynę i histydynę) oraz syntetyczne substancje chelatujące EDTA (*kwas wersenowy*, tj. *kwas etylenodiaminotetraoctowy*) i EDDS (*kwas etylenodiaminodibursztynowy*), w dawce 5 mmol $\cdot$ kg^{-1}. Wykonano także podobne testy z dwoma rodzajami komunalnych osadów ściekowych o różnym stopniu stabilizacji biochemicznej. W doświadczeniach badano osiem próbek osadów poflotacyjnych ze składowisk Żelazny Most oraz Wartowice oraz 2 próbki gleb zanieczyszczonych z sąsiedztwa hut miedzi w Legnicy i Głogowie. Całkowite zawartości badanych pierwiastków w osadach wynosiły: Cu: 1300–3800 mg · kg^{-1}, Pb: 80–300 mg · kg^{-1} oraz Zn: 23–35 mg · kg^{-1}. Zawartości tych pierwiastków w glebach wynosiły: Cu: 1270–1500 mg · kg^{-1}, Pb: 304–336 mg · kg^{-1} oraz Zn: 80–89 mg · kg^{-1}. Skuteczność ekstrakcji metali z osadów i gleb była zróżnicowana. Najsilniej rozpuszczająco na Cu działał EDTA, który ekstrahował 7–39 % całkowitej zawartości Cu oraz 2–18 % Pb. Skuteczność rozpuszczania Cu z gleb i osadów pozostałymi odczynnikami układała się w szereg: kwas cytrynowy (dla osadów) > glicyna > histydyna > EDDS > kwas cytrynowy (dla gleb) > kwas winowy > chlorek amonowy > azotan amonowy. Dla pozostałych dwóch metali szereg ten nie był identyczny. Mimo znacznej zawartości łatwo rozpuszczalnej substancji organicznej w nieustabilizowanych osadach ściekowych, w testach z osadami ściekowymi nie stwierdzono znaczącego wzrostu rozpuszczalności Cu i Pb. Praktyczne znaczenie rozpuszczania metali wskutek chelatowania może być ograniczone ze względu na silne sorbowanie połączeń metali przez shumifikowaną substancję organiczną.

Słowa kluczowe: gleba, metale ciężkie, rozpuszczalność, chelaty, kompleksowanie, osady ściekowe

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AEROBIC PROCESS FOR *IN SITU* BIOREMEDIATION OF PETROLEUM-DERIVED CONTAMINATION OF SOIL: A FIELD STUDY BASED ON LABORATORY MICROCOSM TESTS

TLENOWA BIOREMEDIACJA METODĄ *IN SITU* ROPOPOCHODNYCH SKAŻEŃ GRUNTU: PROCES W WARUNKACH POLOWYCH NA PODSTAWIE OPRACOWAŃ LABORATORYJNYCH TESTÓW UKŁADÓW MODELOWYCH

Abstract: The on-site ground-water recultivation project was established in April 2007 and lasted till August ’07. The work was carried out in the area of a fuel station of the chemical industry-production plant, after dismantling and scrapping of three corroded and leaking oil-storage tanks, each of 50 m^3 capacity. Geochemical analyses revealed that the area of approximately 150 m^2 was affected by a significant pollution of ground with migrating oily products whose concentration exceeded permissible standard levels. The average content of high-boiling ($T_b > 105$ ^oC) organic compounds was 3 655 $mg \cdot kg^{-1}$ and the hydrocarbon contamination reached the level of 5.5 m of underground water. Possible pollutant migration with the aqueous phase caused high risk of affecting the nearby river that served as a drinking-water resource.

The aim of the study was to optimize the *in situ* cleanup biotechnology to enable pollution biodegradation within one season of 2007. The treatment was based on biological activities of soil-derived microorganisms. The occurrence of soil autochthonous bacteria was established as $0.8 \cdot 10^6$ cells $\cdot$ g^{-1}.

Tests carried out in microcosm models revealed that contaminant bioremediation was effective only in the presence of oxygen that proved to be a limiting factor for indigenous bacteria proliferation. Then, the additional soil inoculation with specialized, biochemically active microbial consortia enabled to significantly accelerate kinetics of organic compounds removal.

In a field study, an active aeration system was constructed to provide growing microbial biomass with the oxygen. Next, the area became bioaugmented with the active community by applying biomass at initial density of $1.5 \cdot 10^5$ cells per g of soil. The pollution level and cell population dynamics were monitored in soil samples collected at several distinct levels of the first geotechnical layer, ie from 0 to 120 cm. The content of high-boiling organic substances as well as the cell frequency were analyzed with standard procedures.

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The final biodegradation yields of 92.3 %, 68.1 %, 84.3 % and 93.9 % were obtained within 16 weeks for layers 0–30, 30–60, 60–90 and 90–120 cm, respectively. The observed diversity of the resultant effect was due to heterogeneous geochemical structure of the analyzed soil profile. The highest drop in contamination content correlated with a dramatic increase of soil microflora population up to $7.1 \cdot 10^7$ cells $\cdot$ g^{-1}. The method of biological treatment, elaborated and implemented in the study, led to a decrease of pollutant concentration to the limits acceptable for industrial group "C" areas within one bioremediation season.

Keywords: *in situ* bioremediation, petroleum-derived contaminants, biorecultivation of soil, bioaugmentation, autochthonous microorganisms, microbial consortia

The environmental release of petroleum-derived products bears high ecological risk since most of these substances are known to be hazardous agents [1], toxic to a variety of organisms and detrimental to human health. Oily wastes negatively affect physical, chemical and biological characteristics of soil: they lead to dramatic changes in quantity and chemical content of organic substances as well as they disturb the ratio of carbon to nitrogen and phosphorus. Furthermore, these pollutants hamper free gas exchange between soil and the atmosphere, lower soil permeability and water capacity, alter the acidity, ion exchange, and colloidal parameters. As a result, the natural soil live forms become inhibited or extinct. For the above reasons there is a strong need for reclamation of the ground-water environment and full restoration of its original conditions [2–4].

Processes of natural attenuation of hazardous organic waste contamination may be very slow and in some most severe cases can last up to hundreds of years. This process involves both, physicochemical spontaneous breakdown reactions, and bioremediation based on enzymatic action of indigenous microorganisms [5].

So far, a number of technologies have been elaborated and implemented on the industrial scale to substantially improve the rate of pollution removal, with the aim at shortening recultivation period to the order of months. Some of the approaches require the contaminated ground to be removed from its original site (the *ex situ*/off site treatment), whereas the others can be applied directly at areas of pollution release (the *in situ*/on site treatment). Among the most popular physical and chemical processing-based methods are: thermal desorption, air sparging, soil vapor extraction, dual-phase extraction, soil washing, and UV oxidation. On the other hand, several combined technologies employ biological activities of metabolically potent organisms. These are: landfarming, bioventing, biopile formation, bioslurry/bioreactor systems, biosparging, and *in-situ* groundwater bioremediation. The detailed information on the usage conditions and environmental applicability of these techniques can be found in the Guide Manual of the U.S. Environmental Protection Agency [6].

In recent years, there has been a growing interest in employing biological methods, especially bioremediation, which have proved to be efficient and economically favorable. There are numerous strains isolated from contaminated sites that had evolved unique capabilities of biodegrading a variety of recalcitrant xenobiotics [7–10]. Biological breakdown of organics is complex and requires multistage enzymatic action involving either aerobic or anaerobic metabolism [9]. Under aerobic conditions, the oxygen serves as the final electron acceptor and a maximum energetic yield is achieved, which enables biodegradation process to be relatively the most efficient and the shortest [11].

Increasing usage of bioremediation techniques for treatment of environmental pollution results from the following advantageous characteristics, that is:

a) the direct contaminant (xenobiotic) degradation often serves microorganisms as an energy-yielding process and leads to H_2O and CO_2 generation as the final metabolism products,

b) there is no need for contaminant transfer between different media which is typical of several alternative, physical-chemical approaches,

c) relatively low biorecultivation costs.

In addition, when the *in situ* biotechnologies are used, no effect of deterioration and landscape devastation is observed.

Apart from biostimulation of soil autochthonous microflora to accelerate proliferation and metabolism of the contaminant xenobiotics, it is often recommended to bioaugment the cleanup process by introducing additional cultures of specially-selected and adapted, active microorganisms [3, 4, 6, 9]. Such an approach becomes crucial for the cases of sites polluted with toxic waste where no indigenous bacteria can be found or they occur at densities too low to trigger efficient biodegradation.

The aim of this work was to optimize the *in situ* bioremediation of soil polluted with petroleum chemicals based on the results of laboratory microcosm tests. The project was carried out under fully aerobic conditions and was bioaugmented with specialized bacterial suspensions, pre-grown in the presence of hydrocarbon xenobiotics.

Materials and methods

Description of the contaminated site

The ground-recultivation project launched early 2007 was a part of a large-scale modernization plan of a fuel station located in the area of a chemical-industry production plant. According to the Polish regulations [12], the ground-water environment of this site was qualified to the group “C” areas, described as industrial regions, for which the permissible pollution limits are given by the relevant state Methodological Directive [13]. The elevated contamination with petroleum-derived hydrocarbons (the average concentration of high-boiling, $T_b > 105\ ^{o}C$, organic compounds was 3 655 $mg \cdot kg^{-1}$) was reported to affect approximately a 150 m^2 area adjacent to two leaking, corroded, 50 m^3 oil-storage tanks. The tanks were then dismantled and scrapped. Based on hydrogeological and geochemical analyses, significant ground pollution with migrating oily products was established to reach the underground water table at 5.5 m depth. The ground structure was described as very heterogeneous, consisting of Quaternary combined with Tertiary formations containing sand, silt, and a large portion of gravel together with the presence of gluey inclusions. Such morphology facilitated further migration of organic fraction with groundwater. Thus, a high risk was posed to the nearby river as the pollution might reach a drinking water resource.

Approximately 4 weeks before the first inoculation with bacterial consortium (see below), a system of active soil aeration was constructed to stimulate oxidation reactions within soil microflora. It consisted of a network of pipes of 3 cm diameter, connected to an air compressor and penetrating the ground to be reclaimed.

Bacterial consortium used for bioaugmentation

Bioremediation was bioaugmented using the aerobic bacterial biocenosis developed in Biochemistry Department of University of Agriculture in Krakow. All the constituent microorganisms were environmental, autochthonous strains, selected and isolated over years from sites heavily polluted with organic compounds. After integration period, the strains were cultured altogether and were constantly subjected to the selective and adaptational pressure by incubating with sublethal concentrations of organic xenobiotics. The resultant microbial community was highly biodiverse and consisted of a number of bacterial species belonging to various genera. It was then applied as a soil *inoculum* at initial cell density of approx. 10^9 CFU $\cdot$ cm^{-3} (CFU – *colony forming units*). The details of the construction and growing conditions of the consortium are given elsewhere [14].

Laboratory test of soil bioremediation

In a laboratory pot test three identical microcosm systems were constructed, each containing 2 kg of averaged soil collected at the polluted site. One of the containers – the control – was hermetically sealed so that no exogenous oxygen could penetrate into the soil. This sample was not inoculated with any bacterial suspensions, and thus the observed microorganism occurrence was due to indigenous bacteria only. The other two soil samples were supplemented with the mineral salts mix containing (final contents per kg of soil): 23 mmol $(NH_4)_2SO_4$, 1 mmol $MgSO_4 \cdot 7H_2O$, 7 mmol KH_2PO_4, and 1 mmol $CaCl_2 \cdot 5H_2O$. These systems remained unsealed and were systematically, thoroughly mechanically mixed to allow free oxygen penetration. Soil in the third container was additionally inoculated with 10 cm^3 of the pre-grown microbial consortium suspension at the cell density of $0.9 \cdot 10^9$ CFU $\cdot$ cm^{-3}. In all the model systems the soil moisture was kept at approximately 50 % of the maximum sorption capacity. Bioremediation test was conducted for 16 weeks in a dark place at room temperature.

Sample collection in a field study

In a field project, bioremediation process was monitored in the first geotechnical layer whose thickness was estimated as 120 cm. For sample collection, a special tubular soil auger of 5 cm diameter was used. The samples were collected at four independent sites and the material obtained from the respective layers 0–30 cm, 30–60 cm, 60–90 cm, and 90–120 cm was averaged and subjected to further analyses.

Extraction of organic material from soil and analyses of contamination levels

The organic content of soil samples was extracted using petroleum ether. The samples were ground up and averaged mechanically and divided into 10 g specimens. Each one was then acidified with 1 cm^3 18 % HCl, treated with 12.5 g of anhydrous magnesium sulfate, mixed thoroughly and placed in an extraction thimble made of a Whatman filter paper. Extractions, carried out in duplicates, were conducted for approximately 6 h (40–60 runs) with 200 cm^3 of ether in a 65 cm^3 Soxhlet apparatus. After evaporating the excess solvent at 85 ^oC, the flasks containing extracted material were dried at 105 ^oC for 1.5 h, then cooled in a vacuum desiccator and weighed. Soil dry weight was established with a standard method and finally, the total content of high-boiling organic substances was expressed as a % of soil d.w.

Determination of microbial population in soil

Soil bacterial cell population was determined in aqueous microorganism suspensions obtained by suspending 4 g soil samples in 40 cm^3 of distilled, sterile water, and then by vigorously mixing for 2 h at room temperature in 300 cm^3 flasks on rotary shakers (300 rpm). Microbial cell density in the resultant water phase was determined with a Koch plating method by spreading defined volumes of appropriate culture decimal dilutions onto agar-solidified optimal media (2.5 % enriched agar, BTL, Poland), incubating 3 days at 37 ^oC and then by counting CFU. Before making any dilutions, in order to obtain homogeneous cell suspensions, 1 cm^3 of the original bacterial sample was placed in an Eppendorf tube and sonicated under mild conditions for 10 min with a laboratory ultrasound washer (UN-2 Unitra/Unima, Poland).

Petroleum ether, fractions boiling at 40–60 ^oC, was from POCh, Poland. All other chemicals were of analytical grade. Whenever required, fully sterile conditions were applied.

Results and discussion

A laboratory-scale bioremediation experiment (Fig. 1) was carried out in a set of comparative soil microcosm systems to evaluate the importance of oxygen penetration and to verify the process-stimulating role of bioaugmentation with bacterial cultures. Based on the obtained results it can be clearly seen that the lack of any gas exchange totally inhibited bioremediation (a sealed container, Fig. 1A, squares) by hampering proliferation and metabolic activity of bacteria. In Fig. 1B (squares) a gradual decline in autochthonous cell population is shown. This result also reveals that anaerobic processes were not triggered, which suggests that the indigenous soil microflora consisted of aerobic microorganisms, only. On the contrary, free atmospheric oxygen penetration enabled efficient biodegradation of hydrocarbon contaminants. This was observed in both cases studied, that is in bioremediation test guided exclusively by autochthons (Fig. 1, circles) as well as after bioaugmentation with a pre-grown

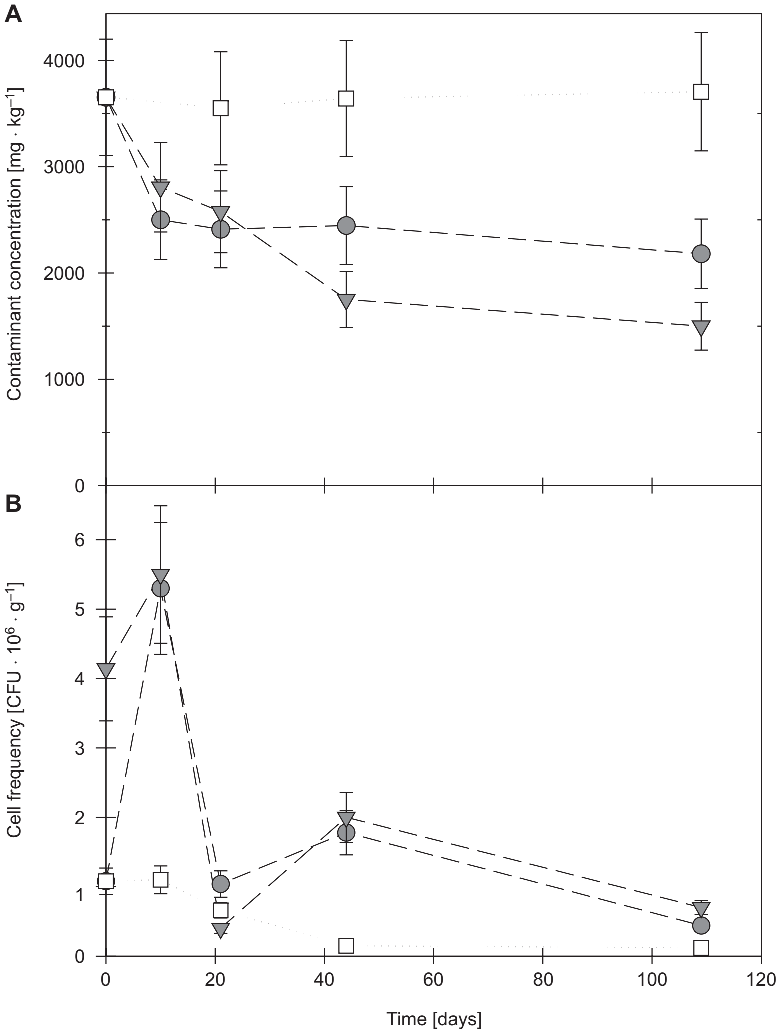

Fig. 1. A microcosm study of organic contaminant bioremediation in soil; squares – a control experiment, lack of oxygen penetration; circles – free gas exchange between air and soil; triangles – soil inoculated with a microbial community to augment xenobiotic biodegradation, free gas exchange between air and soil; (A) kinetics of soil contamination removal; (B) cell population dynamics in the tested soil samples

specialized community (Fig. 1, triangles). Moreover, in the latter case the contaminant removal rate was significantly higher (biodegradation yield of about 59 % as compared with 40 % for the case of uninoculated soil). Such a result proves that bioaugmentation took the advantage of the concerted action of both, indigenous and exogenously-added bacteria. In accordance with the observed biodegradation kinetics, Fig. 1B reveals significant growth of cell population in aerated samples relative to control. This increase of the cell density was especially visible within the first stage of bioremediation (up to 2 weeks) in which the process was launched. During this phase the most accessible fraction of organic carbon was seemingly metabolized, which enabled microbial proliferation.

Based on the laboratory test, a field bioremediation project was established in April 2007. Preliminary monitoring of the site showed that the soil contained autochthonous bacteria at the density of $0.8 \cdot 10^6$ cells · g^{-1}. This original cell population is represented as white bars at time zero in the right-hand panel of Fig. 2. After 4 weeks of active soil venting, cell frequencies in all the tested layers increased by more than one order of

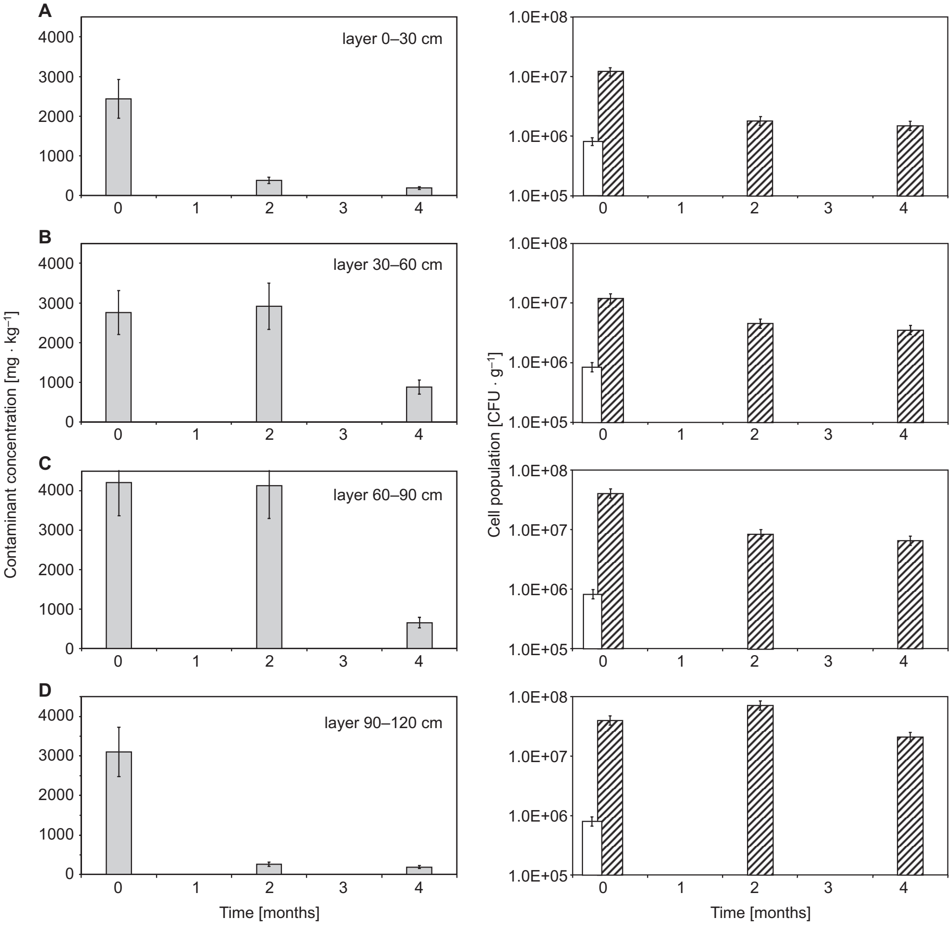

Fig. 2. An *in situ* field project monitoring of soil bioremediation in the area polluted with oil-derived substances; sections (A), (B), (C) and (D) represent the results obtained for different levels of the first geotechnical layer: 0–30 cm, 30–60 cm, 60–90 cm, and 90–120 cm, respectively; the left-hand panel presents biodegradation kinetics, whereas the right-hand one – cell population dynamics during treatment; white bars represent averaged frequency of indigenous bacteria identified in the untreated soil; grey bars at time 0 show autochthonous cell population after 4-week extensive venting of the polluted site, directly before the inoculation with bacterial consortia

magnitude (Fig. 2, the respective grey bars at time zero). This, again, proved the necessity of providing bacteria with the oxygen as a limiting factor for proliferation.

Next, the polluted area became bioaugmented with the active bacterial cultures pre-grown under controlled selective conditions to the logarithmic phase (cell density of $1.2 \cdot 10^9$ CFU $\cdot$ cm^{-3}). The aqueous microbial suspension of 20 dm^3 volume was inoculated twice by introducing directly to the soil; first, at the beginning of the process, and second, in August'07. The latter action was done at the end stage of bioremediation project, and provided the reclamation site with fresh strains to enable more efficient metabolism of the remaining, less-accessible carbon fraction.

Bioremediation project monitoring results are presented for each examined soil layer in Fig. 2A–D. The left-hand panel of Fig. 2 shows the content of high-boiling organic pollutants during the course of the study, whereas the right-hand one represents the cell population dynamics. Upon inoculation no significant increase of the total cell population was observed, which can be explained by substantial dilution of the microbial suspension used for bioaugmenting. However, judging by the degradation results, the microbial process was triggered and its kinetics were satisfactory. During the course of the cleanup project, a slight tendency to decline the cell population was observed, which correlated with the decay of the pollutants that served as carbon sources required for cell growth and energy supply.

It should be noted that for individual layers different contamination removal kinetics and different final bioremediation yields were obtained. In two cases, ie for the layers 30–60 cm and 60–90 cm, bioremediation was not launched within the first 3 months (Fig. 2B and C). We suggest that the above observations were caused mainly by a highly heterogeneous geochemical structure of the reclaimed ground, which led to variable substrate accessibilities and moisture levels in particular soil regions. The latter fact might, in turn, effect in different oxygen solubility and thus could influence the level of oxidation reactions.

The final results of the field bioremediation study are summarized in Table 1.

Table 1

Summary of bioremediation results obtained in the *in situ* field study

Depth of a ground layer [cm]	Concentration of high-boiling organic contaminants		Biodegradation yield [%]
	at the start of the process	at the end of the process (4 months)	
	[mg · kg^{-1} d.m.]		
0–30	2436 ± 487	188 ± 38	92.3
30–60	2762 ± 552	882 ± 176	68.1
60–90	4205 ± 841	660 ± 132	84.3
90–120	3102 ± 620	190 ± 38	93.9

The resultant average biodegradation yield, as achieved within 4 months, was 85 %. For all the soil layers monitored, the resultant organic contaminant concentrations were acceptable in terms of the limits defined as permissible ones for industrial areas of type "C" [12].

Conclusions

1. Laboratory microcosm tests revealed that the process of oil-derived contamination removal from polluted soil was oxygen-limited. Bioaugmentation of the indigenous soil microflora with specialized bacterial consortia stimulated aerobic degradation kinetics significantly.

2. The four-month *in situ* biorecultivation project of the ground-water environment polluted with oily xenobiotics was satisfactory in terms of fulfilling permissible levels defined for type "C" industrial areas. The applied biotechnology which proved effective involved active venting, to stimulate bacterial proliferation and metabolism together with inoculation with pre-grown microbial communities, to enhance pollutant biodegradation potential.

Acknowledgements

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TLENOWA BIOREMEDIACJA METODĄ *IN SITU* ROPOPOCHODNYCH SKAŻEŃ GRUNTU: PROCES W WARUNKACH POLOWYCH NA PODSTAWIE OPRACOWAŃ LABORATORYJNYCH TESTÓW UKŁADÓW MODELOWYCH

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Abstrakt: Prace rekultywacyjne środowiska gruntowo-wodnego prowadzono w okresie kwiecień – sierpień 2007 r. na terenie przebudowywanej stacji paliw w obrębie kompleksu zakładów produkcyjnych przemysłu chemicznego. Po usunięciu starych, skorodowanych i przeciekających zbiorników paliwa o poj. 50 m^3 każdy dokonano geochemicznego rozpoznania stanu środowiska i wykazano znaczące skażenie gruntu migrującymi substancjami ropopochodnymi. Ponadnormatywne poziomy zanieczyszczeń węglowodorowych stwierdzono na obszarze ok. 150 m^2, sięgające w głąb gruntu aż do poziomu lustra wody podziemnej na głębokości ok. 5,5 m. Średnia zawartość wysokowrzących związków organicznych ($T_{wrz.} > 105$ °C) wynosiła 3 655 $mg \cdot kg^{-1}$. Dodatkowo, powstało zagrożenie dalszej migracji skażeń wraz z wodą gruntową do pobliskiej rzeki stanowiącej ujęcie wody pitnej.

Celem pracy była optymalizacja proponowanej biotechnologii oczyszczania ziemi *in situ*, wykorzystującej aktywność biologiczną drobnoustrojów glebowych tak, aby umożliwić biodegradację skażeń w ciągu jednego sezonu. W ziemi stwierdzono występowanie autochtonicznej mikroflory glebowej o liczebności $0{,}8 \cdot 10^6$ komórek $\cdot\ g^{-1}$ gruntu. Testy prowadzone w układach modelowych (ang. *microcosms*) wykazały, że procesy bioremediacji zanieczyszczeń przebiegały wyłącznie w obecności tlenu, umożliwiającego proliferację bakterii autochtonicznych (40 % spadek poziomu skażeń w ciągu 16 tygodni). Dodatkowe zaszczepienie gruntu specjalistycznym konsorcjum aktywnych biochemicznie drobnoustrojów (biopreparatem) pozwoliło przyśpieszyć kinetykę rozkładu skażeń organicznych (wzrost wydajności do 59 %).

W pracach polowych skonstruowano system aktywnego napowietrzania zapewniający dostępność tlenu dla rozwijających się autochtonów, po czym grunt suplementowano aktywnymi drobnoustrojami w ilości ok. $1{,}5 \cdot 10^5$ komórek $\cdot\ g^{-1}$. W próbkach ziemi, pochodzących z poszczególnych poziomów pierwszej warstwy geotechnicznej do głębokości 120 cm prowadzono monitoring poziomu skażeń oraz dynamiki rozwoju populacji drobnoustrojów. Oznaczanie zawartości substancji ropopochodnych prowadzono według standardowej procedury oznaczania wysokowrzących substancji organicznych w glebie. Liczebność mikroorganizmów glebowych określano standardową, płytkową metodą Kocha.

Dla warstw 0–30 cm, 30–60 cm, 60–90 cm oraz 90–120 cm uzyskano końcową efektywność biodegradacji wynoszącą, w ciągu 16 tygodni, odpowiednio: 92,3 %, 68,1 %, 84,3 % oraz 93,9 %. Zróżnicowanie końcowego wyniku wiązało się z heterogeniczną strukturą geochemiczną analizowanego profilu glebowego. Najsilniejszy obserwowany spadek zanieczyszczeń korelował z gwałtownym rozwojem mikroflory glebowej (do $7{,}1 \cdot 10^7$ komórek $\cdot\ g^{-1}$). Opracowana i zastosowana metoda biorekultywacji pozwoliła obniżyć koncentrację skażeń w sezonie 2007 do poziomu akceptowalnego dla obszarów przemysłowych grupy C.

Słowa kluczowe: bioremediacja *in situ*, zanieczyszczenia ropopochodne, biorekultywacja ziemi, bioaugmentacja, drobnoustroje autochtoniczne, biopreparaty

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IMPACT OF LAND USE METHODS ON THE WATER QUALITY OF SMALL PONDS

WPŁYW SPOSOBU UŻYTKOWANIA TERENU NA JAKOŚĆ WÓD OCZEK WODNYCH

Abstract: The objective of this paper was the impact assessment of land use methods on the surface water quality. The small ponds selected for research are located in agricultural, rural, and forested areas. The studies were conducted in the period of two hydrological years eg 2006 and 2007 in order to determine: nitrates(V), nitrates(III), ammonia, phosphates, sulphates, chlorides, calcium, magnesium, dissolved oxygen, reaction and electric conductivity.

Analysis of the collected data allows to affirm that land use methods of the neighbouring area of the reservoir have a direct impact on the water quality of the small ponds. Rural settlements have the most negative influence on the deterioration of the water quality followed by typical agricultural use. Based on the direct quality evaluations of water samples, it has been found that only water of the small pond localised in forested areas can be qualified as belonging to the 1st class of the very good quality water.

Keywords: land use, small ponds, water quality

The stagnant waters, including small ponds, are an important element of the rural areas. They are the integral part of a rural landscape as well as the water reservoir which influence on the waters relations of adjacent terrains. The small pond that is the small reservoir, which area does not exceed 1 ha, it contributes also to increasing species diversity within agrocenosis [1]. Despite so many important functions which small ponds fulfill in the environment, they are subjected to the impact of many negative factors [2, 3]. The main threat for small water reservoirs is their susceptibility to degradation, which can, cause in the extreme case, their disappearance [4, 5]. Rising living standards as well as increasing urbanisation have become the reasons for significant, not always favourable, impact of humans on the natural environment, in this on water resources quality. For this reason protecting water resource quality from pollution is one of the main problems of contemporary civilisation [6, 7].

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The objective of this paper is to compare the water quality of small ponds located in the terrains where the land is used in various ways.

Material and methods

In the work a collation has been made of the impact of land use methods on the water quality of small ponds. For this purpose three small ponds were selected which were located in the agriculturally used land, rural settlements and forested areas, and from which water samples were subjected to physical-chemical analyses which determined 11 quality indicators.

The investigated research sites are located in the Malopolska province, in the district of Bochnia (Bochnia and Nowy Wisnicz communes) and in the district of Brzesko (Brzesko commune) situated within two meso-regions, eg the Bochenski and Wisnicki Foothills [8]. Analysing assigned area around the small pond which was located in agriculturally used area, it has been found that 94 % of the area consist of farm land with a quite large share of meadows and pastures (17 %) and orchards (17 %). With the small pond, located in a settlement-agricultural area, from the south and western side directly border on: internal road and settlements and compacted residential built-up. Examining the whole area adjoined to this small pond, it was found that 86 % of the area makes up agricultural land of what on meadows and pasture falls 16 % and on orchard 15 %. The terrain adjoining the small pond located in a woody area, in 60 % is utilized as forest; meanwhile 36 % of the area is used as farmland, with sufficiently large share of meadows and pastures (20 %) as well as orchards (5 %).

The field studies were conducted from November 2005 to October 2007. Reaction (pH), electric conductivity and dissolved oxygen were determined by equipment from the Elmetron Company. Nitrates(V), nitrates(III), ammonia, phosphates, chlorides were determined by the flow method of colorimetric analysis, and sulphates were determined by a gravimetric analysis (precipitation). Calcium and magnesium were analysed by an atomic absorption spectrophotometer of Unicam Solar M 6 [9].

Based on results obtained by the direct method, the quality of the water was assessed and classified according to regulations established by the Minister of Environment [10].

Results and discussion

The results obtained which concerned the values of selected quality indicators of small ponds located in widely utilised land showed a large difference (Table 1).

The mean values from the investigated period were in the range: for nitrates(V) – 0.77–1.26 mg $\cdot$ dm^{-3}, nitrates(III) – 0.02–0.05 mg $\cdot$ dm^{-3}, ammonium from 0.02 to 1.25 mg $\cdot$ dm^{-3}, phosphates – 0.06–0.86 mg $\cdot$ dm^{-3}, sulphates – 38.25–68.57 mg $\cdot$ dm^{-3}, chlorides – 8.80–52.58 mg $\cdot$ dm^{-3}, calcium – 38.41–176.7 mg $\cdot$ dm^{-3}, magnesium – 11.56–19.18 mg $\cdot$ dm^{-3}, dissolved oxygen – 6.59–9.46 mg O_2 $\cdot$ dm^{-3}, electric conductivity – from 354.54 to 722.21 μS $\cdot$ cm^{-1} and reaction – pH 7.60–7.76. The concentrations of nitrates(V), nitrates(III), ammonium and phosphates were characterised by the highest variability. The smallest coefficient of variability was recorded in the case of reaction, electric conductivity and dissolved oxygen content.

Table 1

The values of selected quality indicators of water in the small ponds located in the various land areas

The quality indicator	Unit	Site	Minimum	Maximum	Mean	Standard deviation	Variability coefficient [%]
NO_3^-	$[\mathrm{mg \cdot dm^{-3}}]$	1	0.035	3.934	0.77	1.13	147
		2	0.095	5.674	1.26	1.50	119
		3	0.063	4.632	1.14	1.46	128
NO_2^-		1	0.003	0.144	0.02	0.03	150
		2	0.007	0.266	0.05	0.07	140
		3	0.003	0.055	0.02	0.01	50
NH_4^+		1	0.006	0.149	0.02	0.04	200
		2	0.203	4.580	1.83	1.25	68
		3	0.007	0.186	0.06	0.04	66
PO_4^{3-}		1	0.018	0.598	0.12	0.13	108
		2	0.037	2.047	0.82	0.66	80
		3	0.006	0.266	0.06	0.08	133
SO_4^{2-}		1	47.38	101.74	68.57	13.23	19
		2	28.00	116.39	50.87	22.94	45
		3	14.23	64.90	38.25	13.88	36
Cl^-		1	36.51	82.00	52.58	12.92	24
		2	24.94	60.00	40.01	7.45	19
		3	4.76	22.46	8.80	3.41	38
Ca^{2+}		1	48.0	150.2	92.57	29.32	32
		2	38.6	176.7	96.63	44.09	46
		3	18.1	78.4	38.41	12.78	33
Mg^{2+}		1	4.8	22.5	13.08	3.65	28
		2	10.8	39.1	19.18	8.13	42
		3	3.6	17.3	11.56	2.70	23
Dissolved oxygen		1	6.45	9.46	8.03	0.78	9
		2	5.21	8.60	6.59	0.83	13
		3	6.14	9.28	7.84	0.74	9
Conductivity	$[\mathrm{\mu S \cdot cm^{-1}}]$	1	443	715	576	114	19
		2	455	873	722	108	15
		3	118	716	354	105	29
Reaction	pH	1	6.87	8.46	7.76	0.37	5
		2	6.74	8.43	7.60	0.42	5
		3	6.95	8.28	7.75	0.35	4

Explanations for Tables 1 and 2: 1 – small pond located in typical agricultural area, 2 – small pond located in agricultural and rural settlement area, 3 – small pond located in forested land.

The small ponds located within agricultural and forest area, are characterized by low eutrophication. During the studies, it has not been found long-lasting water blooms, caused by blue-green algae, as well as a decrease of diversity, abundance of macrophytes and invertebrate fauna. In the small pond located in rural settlement area, numerous water blooms were found, what makes up the base, according to the criteria contained in regulation established by the Minister of Environment [10] to classify its water to high eutrophication degree.

In the work the direct quality assessment of single water samples collected in the period of 24 dates (Table 2) were conducted. Based on this one can conclude that only water in the small ponds located in forested terrain in 5 dates fulfils the criteria of the 1st class of very good quality water. It was shown that the most polluted water was in the small ponds situated in the agricultural-rural settlement areas, which most frequently were classified in the 5th class of bad quality water.

Table 2

Water sample dimensions from the small ponds in particular quality classes, established by a direct method

Site	The number of the sampling collection dates	Water quality classes									
		I		II		III		IV		V	
		n_1	[%]	n_2	[%]	n_3	[%]	n_4	[%]	n_5	[%]
1	24	0	0	12	50	12	50	0	0	0	0
2	24	0	0	2	8.3	4	16.7	7	29.2	11	45
3	24	5	20.8	19	79.2	0	0	0	0	0	0

The greatest impact on lowering water quality of the small pond situated in the area with advantage of farm land had calcium (Fig. 1), which content often fulfilled the criteria of 3rd class of satisfactory quality water. Electric conductivity and contents of phosphates, nitrates(III) and dissolved oxygen decided about classifying water of small

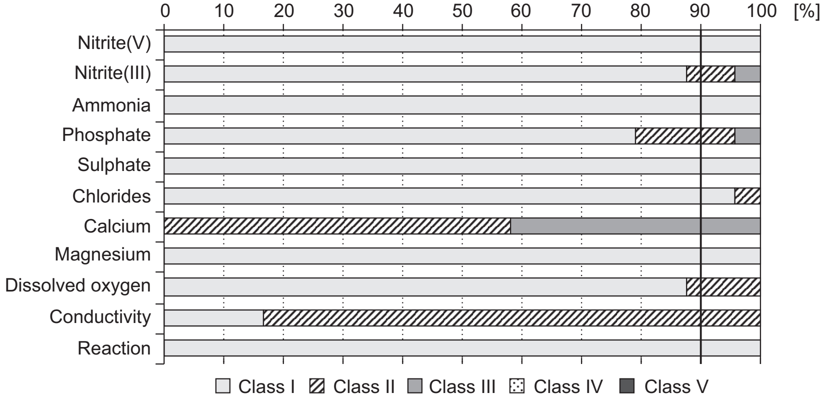

Fig. 1. Distribution frequency [%] of selected quality indicators of water in a small pond located in a typical agricultural land

pond in a typical agricultural terrain to the 2nd class of good quality water. The remaining analysed indicators (concentration of NO_3^-, NH_4^+, SO_4^{2-}, Cl^- and Mg^{2+} as well as pH) placed the water of the small ponds often in the 1st class of very good quality water.

The water quality of the small pond located in rural settlements – agricultural land (Fig. 2) was lowered in the highest degree by excessive concentrations of phosphate (to the 5th class of bad quality water), ammonium (to the 4th class of unsatisfactory quality water) as well as calcium and to low dissolved oxygen concentration (to the 3rd class of satisfactory quality water. Nitrates(III) and magnesium concentrations lowered the water quality to the 2nd class of good quality water. It was established that concentrations of nitrates(V), sulphates and chlorides as well as values of electric conductivity and pH allow for ranking the water of this small pond to the 1st class of very good quality water.

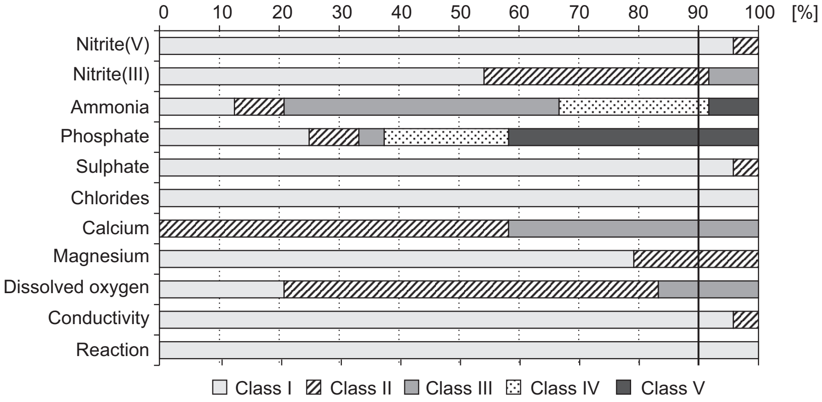

Fig. 2. Distribution frequency [%] of selected quality indicators of water in a small pond located in a rural settlement and agricultural land

Majority of analysed indicators for the water quality of the small pond located in forest area allow, classifying them to the 1st class of very good quality water (Fig. 3). Only calcium qualified often its water to the 2nd class of good quality water. It was found that incidental concentrations of phosphates and dissolved oxygen qualified the water of the small pond also to the 2nd class of good quality water. The remaining analysed quality indicators (NO_3^-, NO_2^-, NH_4^+, SO_4^{2-}, Cl^-, Mg^+, electric conductivity and pH) classified the water of small ponds in forest area to the 1st class of very good quality water.

During the study period, the water quality analysis of stagnant water in variously used land based on a direct method (for frequency 90 %) showed that only nitrates(V), sulphates and chlorides contents as well as pH qualified the water of 3 research sites to the 1st class of very good quality water (Fig. 1).

The tendency for a larger decrease in the water quality of small ponds located in rural settlements and in a typical agricultural area than in the case of woody areas confirmed the results of research conducted by Skwierawski and Szyperek [11]. Based on own

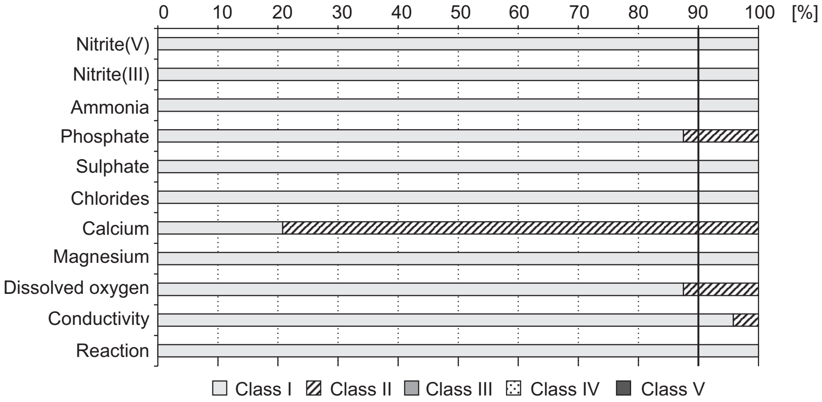

Fig. 3. Distribution frequency [%] of selected quality indicators of water in a small pond located in forest land

studies Koc et al [12] justified it by the impact of agricultural land use, the vicinity of farms, and the lack of sewage systems in compacted built-up areas or scattered housing in which the often encountered practice is the delivery of domestic sewage directly into the small ponds. An unfavourable impact is also caused by leaky sewage tanks, collecting tanks for liquid manure that are not tight enough, and pits.

Conclusion

1. On the basis of a direct quality assessment of single water samples it was found that only water in the forest areas can qualify to the 1st class of very good quality water. The most polluted was water from rural settlements and agricultural areas, which qualified most frequently to the 5th class of bad quality water.

2. The quality analysis by a direct method proved that the indicators which lowered the water quality the most were biogenic compounds and calcium, and the least were sulphates, chlorides and reaction.

3. It has been shown that in the case of small ponds situated in rural settlements and agricultural areas, the water quality was lowered most by excessive phosphate contents (to the 5th class of bad quality water) and ammonia (to the 4th class of unsatisfactory quality water). In small pond located in a typical agricultural area, its quality was decreased only by calcium (to the 3rd class of satisfactory quality water).

4. Water of small ponds in forest areas was characterised by decidedly the better quality. The water quality of this water pond was decided chiefly by calcium, phosphates, and dissolved oxygen, which caused the lowering the water quality to maximum the 2nd class of good quality water.

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WPŁYW SPOSOBU UŻYTKOWANIA TERENU NA JAKOŚĆ WÓD OCZEK WODNYCH

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Abstrakt: Celem badań była ocena wpływu użytkowania terenu na jakość wód powierzchniowych. Wybrane do badań oczka wodne są zlokalizowane na terenie typowo rolniczym, osadniczo-rolniczym i leśnym. Pobrana woda została poddana analizie fizykochemicznej pod względem stężeń: azotanów(V), azotanów(III), amoniaku, fosforanów, siarczanów, chlorków, wapnia, magnezu, tlenu rozpuszczalnego oraz wartości odczynu i przewodności elektrycznej właściwej. Badania wykonano w ciągu dwóch lat hydrologicznych 2006 i 2007.

Uzyskane wyniki badań pozwoliły na stwierdzenie, że na jakość wód oczek wodnych bezpośredni wpływ wywiera sposób użytkowania terenu sąsiadującego ze zbiornikiem wodnym. Największy wpływ na pogorszenie jakości wód mają tereny osadniczo-rolnicze, drugie miejsce zajmują tereny typowo rolnicze. Na podstawie bezpośredniej oceny jakości próbek wody stwierdzono, że tylko wody oczka zlokalizowanego na terenie leśnym mogą być zakwalifikowane do pierwszej klasy wód o bardzo dobrej jakości.

Słowa kluczowe: użytkowanie terenu, oczka wodne, jakość wód

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INFLUENCE OF LIMING AND ORGANIC FERTILIZATION ON YIELD AND CONTENT OF SELECTED HEAVY METALS IN THE BIOMASS OF ORCHARD GRASS

WPŁYW WAPNOWANIA I NAWOŻENIA ORGANICZNEGO NA PLON ORAZ ZAWARTOŚĆ WYBRANYCH METALI W KUPKÓWCE POSPOLITEJ

Abstract: In pot experiment the influence of liming and differentiated organic fertilization on the yield of biomass of orchard grass as well as on the amount of Cu, Zn, Cd and Pb harvested with the biomass were investigated. In the scheme of experiment the following objects were investigated: 1) without liming, 2) with liming in which $CaCO_3$ was applied in the dose equal to 1 unit of hydrolitic acidity. Waste activated sludge, broiler litter and brown coal were used as organic fertilizers and applied in the dose 2 g C $\cdot$ kg^{-1} of soil. In the vegetation period 4 cuts of tested plants were harvested. The biomass of tested plant was air dried and ashed by dry combustion in the furnace at 450 ^{o}C. The ash was dissolved in 10 % HCl and in the obtained solution the contents of lead and manganese were determined by ICP-AES method. The highest yield of biomass (sum of 4 cuts) and the amount of determined heavy metals were harvested from the objects fertilized with waste activated sludge and the lowest ones when brown coal was applied.

Keywords: liming, organic fertilization, orchard grass, heavy metals

Not only macronutrients, organic compounds, but also trace elements contents recognition is important at evaluating the quality of plant-origin products. Excessive content of trace elements in plants is a potential threat for health and life of humans and animals [1–3]. Lower rates of natural and organic fertilizers applied recently forces to search for other sources organic matter and nutrients for plants, but some of them may cause the increase of heavy metals content in soils and plants [4, 5]. Therefore, applying sewage sludge and other waste substances for fertilization purposes requires continuous control for toxic components [6]. The problem is regulated by corresponded legal acts [7–9].

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The present study was aimed at evaluating the influence of liming and varied organic fertilization on yields and contents of selected heavy metals at orchard grass.

Material and methods

The pot experiment in completely randomized pattern was conducted in greenhouse of University of Podlasie, Siedlce in 2004. It included two factors: I – liming, and II – varied organic fertilization. The soil for experiment was collected from plough 0–20 cm layer of Podzol of strong loamy sand granulometric composition characterizing by the following properties: organic carbon 7.9 g · kg^{-1}, total nitrogen 0.98 g · kg^{-1}, available phosphorus 69 mg · kg^{-1}, available potassium 75 mg · kg^{-1}, while pH in 1 mol · dm^{-3} KCl was 5.6. Metals contents amounted to: 23.0 mg Zn, 3.13 mg Cu, 6.60 mg Pb and 0.5 mg Cd · kg^{-1} soil.

The soil material of 10 kg amount was put into the pots of 15 dm^3 capacity. The moisture content was maintained at the level of 60 % of field water capacity during the vegetation period. Objects with liming (in a form of $CaCO_3$ at the rate calculated according to 1 Hh of soil material) or without liming were included within the experiment scheme. Following fertilization using organic material was applied: sewage sludge from purification plant in Siedlce, broiler chickens droppings and brown coal from Brown Coal Mine in Turow (Table 1).

Table 1

Chemical composition of organic materials used in pot experiment

Component	Organic materials		
	Sludge from Siedlce	Broilers droppings	Brown coal
	[g · kg^{-1} d.m.]		
C	371	399.1	541
N	60.5	16.8	4.0
P	31.17	23.6	0.11
K	4.28	20.0	0.84
Ca	39.6	39.2	5.18
Mg	8.42	6.96	2.33
	[mg · kg^{-1} d.m.]		
Zn	1276.8	295.6	17.16
Cd	1.99	15.2	0.07
Pb	50.5	5.00	3.71
Cu	137.7	54.1	10.12
Dry matter [g · kg^{-1}]	180	400	850

All wastes were applied at the introductory dose of 2 g C · kg^{-1} of soil material (about 7 Mg · ha^{-1}). The orchard grass was the test plant. Four cuts of tested grass were harvested during its vegetation period. For four years and for every orchard grass contents of Zn, Cu, Pb and Cu in each cut of test plant were determined by means of ICP-AES technique after dry digestion in muffle furnace at 450 °C and subsequent ash grinding and dissolution in 10 % HCl [10]. Achieved results were statistically processes by means of variance analysis according to F-Fisher-Snedecor's test applying F.R. Anal var. 4.1 software (acc. to Franciszek Rudnicki), while $LSD_{0.05}$ values were calculated on a base of Tukey test.

Results and discussion

Liming and organic fertilization significantly differentiated the yields of orchard grass dry matter (Table 2), which may be attributed to the chemical composition of applied waste materials (Table 1).

Table 2

The yield [g · pot^{-1}] of orchard grass

Number of cut / Organic fertilization	Liming										Mean
	No liming					Liming acc. to 1 Hh					
	I	II	III	IV	Sum	I	II	III	IV	Sum	
Without organic fertilization	3.6	2.1	4.4	0.9	11.0	7.4	1.8	4.4	0.9	14.5	3.2
Waste activated sludge from Siedlce	18.4	7.9	9.1	1.8	37.2	21.6	8.2	9.3	1.8	40.9	9.8
Poultry litter	14.8	4.6	5.9	1.4	26.7	14.8	7.3	8.3	1.4	31.8	7.3
Brown coal	2.5	1.7	4.3	1.1	9.6	6.6	3.1	5.1	0.5	15.3	3.1
Mean	9.8	4.1	5.9	1.3	21.1	12.6	5.1	6.8	1.1	25.6	5.9

$LSD_{0.05}$:	1st cut	2nd cut	3rd cut	4th cut	Sum
for liming	2.578	0.882	0.969	n.s.	3.227
for organic fertilization	4.920	1.683	1.850	0.544	6.159
for interaction of liming × organic fertilization	n.s.	n.s.	n.s.	n.s.	n.s.
for interaction of organic fertilization × liming	n.s.	n.s.	n.s.	n.s.	n.s.

Explanation for Tables 2, 4, 5 and 6: n.s. – non significant.

Sewage sludge from purification plant in Siedlce was the most abundant in macro- and microelements, which was consistent with earlier studies [11]. Brown coal from Brown Coal Mine in Turow appeared to be the least abundant in macro- and microelements (except from organic carbon), which was confirmed by other authors studies [12].

For the 1st cut, applied liming significantly elevated the dry matter yield of orchard grass in all fertilization objects, except from those where poultry droppings were used. In the case of the 2nd and 3rd cuts, the adverse dependence was observed: liming caused considerable increase of the plant yields only on objects where droppings were applied.

Significantly the highest dry matter yields of all cuts of orchard grass were achieved from objects with sewage sludge from purification plant in Siedlce, while the lowest – where no organic fertilization or brown coal was applied (Table 2). Total yield of orchard grass was significantly differentiated by studied factors. Liming made significant increase of the total yield. Considerably the highest yield of tested plant was found on objects where sludge fertilization was used, whereas the lowest – in objects with brown coal.

Copper amounts in orchard grass yield (Table 3) were significantly differentiated by both studied factors as well as interaction between them, which was confirmed by results of other authors [13].

Table 3

The amount of Cu [mg · pot^{-1}] taken up by the biomass of orchard grass

Number of cut / Organic fertilization	Liming										Mean
	No liming					Liming acc. to 1 Hh					
	I	II	III	IV	Sum	I	II	III	IV	Sum	
Without organic fertilization	0.03	0.02	0.01	0.01	0.07	0.04	0.02	0.003	0.01	0.07	0.02
Waste activated sludge from Siedlce	0.18	0.06	0.02	0.01	0.27	0.32	0.08	0.02	0.01	0.430	0.09
Poultry litter	0.13	0.01	0.02	0.02	0.18	0.14	0.04	0.02	0.003	0.20	0.05
Brown coal	0.02	0.01	0.01	0.01	0.04	0.03	0.003	0.003	0.001	0.04	0.01
Mean	0.08	0.03	0.02	0.01	0.14	0.13	0.04	0.01	0.006	0.189	0.04

$LSD_{0.05}$:	1st cut	2nd cut	3rd cut	4th cut
for liming	0.030	0.008	0.002	0.004
for organic fertilization	0.057	0.014	0.003	0.007
for interaction of liming × organic fertilization	0.080	0.020	0.004	0.010
for interaction of organic fertilization × liming	0.059	0.015	0.003	0.007

Liming considerably increased the copper content in the 1st cut yield from objects fertilized with sewage sludge from Siedlce. Significantly the highest concentration of the element was recorded in yield of plants grown on sludge from Siedlce, while the lowest on objects with brown coal from Turow. Liming significantly elevated the content of copper in the 2nd cut yield on objects with sewage sludge (as similar as in the first cut) as well as it caused the decrease of the element content at plants harvested from objects with brown coal applied. Liming significantly decreased the copper amounts in the 3rd cut yield of grass cultivated on objects where brown coal was used as well as on those with no organic fertilization was applied. For the 4th cut, discussed factor caused significant decrease of the yield of analyzed microelement harvested along with the plants grown on brown coal objects (as for the 2nd and 3rd cuts) as well as those where poultry droppings were used. In the case of all combined cuts, the highest copper amounts were recorded in plants grown on sewage sludge from purification plant in Siedlce, whereas the lowest on objects where brown coal was applied, which can be explained by chemical composition of organic materials and the amount of copper introduced along with them into the soil (0.742 mg Cu · kg^{-1} of soil with the sludge from Siedlce, while only 0.037 mg Cu · kg^{-1} of soil with brown coal).

Zinc amounts harvested in the orchard grass yields were presented in Table 4. It was significantly differentiated only by organic fertilization. No influence of liming can be elucidated with the short period after calcium fertilizers application. For all cuts, the highest zinc contents were recorded in plants grown on objects with sewage sludge and poultry droppings, while the lowest on objects with brown coal. As similar as for copper, the fact can be accounted for the amounts of the element introduced into the soil along with these materials: 6.22 mg Zn · kg^{-1} of soil with sewage sludge, 1.48 mg Zn · kg^{-1} of soil with poultry droppings, and only 0.063 mg Zn · kg^{-1} of soil with brown coal.

Table 4

The amount of Zn [mg · pot^{-1}] taken up by the biomass of orchard grass

Number of cut / Organic fertilization	Liming										Mean
	No liming					Liming acc. to 1 Hh					
	I	II	III	IV	Sum	I	II	III	IV	Sum	
Without organic fertilization	0.20	0.11	0.17	0.05	0.53	0.28	0.07	0.13	0.05	0.53	0.013
Waste activated sludge from Siedlce	0.98	0.40	0.32	0.08	1.78	1.11	0.48	0.36	0.09	2.04	0.48
Poultry litter	0.71	0.19	0.21	0.07	1.18	0.64	0.30	0.21	0.05	1.20	0.30
Brown coal	0.13	0.09	0.12	0.06	0.40	0.17	0.09	0.11	0.03	0.40	0.10
Mean	0.51	0.20	0.20	0.006	0.97	0.54	0.24	0.20	0.06	1.40	0.25

LSD$_{0.05}$:	1st cut	2nd cut	3rd cut	4th cut
for liming	n.s.	n.s.	n.s.	n.s.
for organic fertilization	0.235	0.084	0.050	0.028
for interaction of liming × organic fertilization	n.s.	n.s.	n.s.	n.s.
for interaction of organic fertilization × liming	n.s.	n.s.	n.s.	n.s.

The amounts of cadmium harvested with orchard grass yields were significantly differentiated by both studied factors (Table 5) as well as additionally interactions between them in the 2nd and 4th cuts.

Liming elevated the cadmium amounts harvested with the 1st cut yield of plants growing on objects where droppings were used, and in 2nd cut of plants cultivated on objects with droppings plus brown coal and sludge from purification plant in Siedlce. Liming significantly decreased the amount of the element in the 3rd cut of plants grown in objects where no organic fertilization was applied and where brown coal was used; it also caused considerable increase of cadmium content at plants fertilized with sewage sludge and poultry droppings. Liming caused significant decrease of cadmium harvested in the 4th cut along with plants grown on objects with sludge from Siedlce, droppings, and brown coal from Turow. For the 1st, 2nd and 4th cuts, the highest amounts of the metal was found at plants grown on objects with sludge from Siedlce, while for the 3rd cut, with poultry droppings, despite of the fact that its largest quantities were introduced along with the material, amounting 0.076 mg Cd · kg^{-1} of soil.

Tabela 5

The amount of Cd [mg · pot^{-1}] taken up by the biomass of orchard grass

Number of cut	Liming										Mean
	No liming					Liming acc. to 1 Hh					
Organic fertilization	I	II	III	IV	Sum	I	II	III	IV	Sum	
Without organic fertilization	0.003	0.001	0.007	0.002	0.018	0.006	0.001	0.005	0.002	0.014	0.004
Waste activated sludge from Siedlce	0.013	0.006	0.007	0.012	0.038	0.015	0.010	0.012	0.003	0.040	0.010
Poultry litter	0.007	0.003	0.009	0.007	0.026	0.012	0.014	0.013	0.005	0.044	0.004
Brown coal	0.001	0.001	0.006	0.003	0.011	0.004	0.006	0.011	0.001	0.022	0.006
Mean	0.006	0.003	0.007	0.006	0.022	0.009	0.008	0.010	0.003	0.030	0.026

$LSD_{0.05}$:	1st cut	2nd cut	3rd cut	4th cut
for liming	0.003	0.001	0.002	0.001
for organic fertilization	0.006	0.002	0.004	0.002
for interaction of liming × organic fertilization	n.s.	0.003	n.s.	0.003
for interaction of organic fertilization × liming	n.s.	0.002	n.s.	0.002

Significantly lowest amounts of the element was harvested in the 1st and 4th cuts with yield of plants cultivated on objects where brown coal was applied; it contained minimum amounts of cadmium – 0.003 mg Cd · kg^{-1} of soil. The lowest quantities of cadmium were found in the 2nd and 3rd cuts of plants from objects where no organic fertilization was used.

Lead amounts harvested along with orchard grass yields (Table 6) in the 1st cut was differentiated both by liming and organic fertilization.

Table 6

The amount of Pb [mg · pot^{-1}] taken up by the biomass of orchard grass

Number of cut	Liming										Mean
	No liming					Liming acc. to 1 Hh					
Organic fertilization	I	II	III	IV	Sum	I	II	III	IV	Sum	
Without organic fertilization	0.02	0.04	0.15	0.03	0.24	0.07	0.01	0.09	0.03	0.20	0.06
Waste activated sludge from Siedlce	0.16	0.06	0.29	0.05	0.56	0.18	0.09	0.27	0.05	0.59	0.14
Poultry litter	0.05	0.02	0.18	0.04	0.29	0.12	0.22	0.23	0.03	0.60	0.11
Brown coal	0.002	0.01	0.13	0.02	0.18	0.04	0.01	0.08	0.01	0.14	0.04
Mean	0.06	0.03	0.19	0.04	0.32	0.10	0.08	0.17	0.03	0.38	0.09

$LSD_{0.05}$:	1st cut	2nd cut	3rd cut	4th cut
for liming	0.021	0.018	n.s.	n.s.
for organic fertilization	0.041	0.035	0.040	0.015
for interaction of liming × organic fertilization	n.s.	0.050	0.057	n.s.
for interaction of organic fertilization × liming	n.s.	0.037	0.042	n.s.

Liming caused considerable increase of the lead yield harvested with plants grown on objects with poultry droppings as well as those with no organic fertilization. Amount of lead in 2nd cut yield was considerably differentiated by both experimental factor as well as their interaction. Liming significantly decreased the amount of lead from objects without organic fertilization and it caused considerable increase of studied element on objects with poultry droppings and sewage sludge application. For the 3rd cut, the lead amounts were significantly affected by applied organic nutrition as well as interactions between studied factors, while in the case of 4th cut, only by applied organic fertilization.

The largest lead amounts were found in the 1st, 3rd, and 4th cuts of plants from objects where sewage sludge from Siedlce was applied, which can be attributed with its largest amounts of the metal introduced into the soil along with that material (0.272 mg Pb · kg^{-1} of soil). The lowest levels of lead were harvested with plant yields from objects fertilized with brown coal, which can be explained with its lowest quantities introduced to the soil along with that organic material (only 0.014 mg Pb · kg^{-1} of soil) as well as its alkalizing properties.

It can be supposed that applied liming and organic nutrition significantly differentiated the orchard grass yields as well as copper, zinc, cadmium, and lead amounts harvested along with its yield.

The highest total grass yield was harvested from objects fertilized with sewage sludge, while significantly the lowest from objects with brown coal. The largest amounts of studied metals were found at plants grown on sewage sludge from purification plant in Siedlce, which can be attributed with the fact that the highest levels of copper, zinc, and lead were introduced into the soil along with that material, which was consistent with research of other authors [14]. The lowest quantities of discussed metals were harvested with yields of plants cultivated on objects fertilized with brown coal, along which their minimum amounts were introduced into the soil, and which has the sorption properties in relation to cations – according to numerous studies [10, 15].

The highest average copper and zinc amounts were harvested along with plants of the 1st cut, while lead and cadmium of the 3rd cut, which was consistent with earlier results [17], and which can be explained with the highest yields of both cuts (Table 2).

Conclusions

1. Liming not univocally differentiated the orchard grass yields and harvested amounts of copper, zinc, cadmium and lead.
2. Considerably the highest total yield of the test plant was harvested from objects fertilized with sewage sludge from purification plant in Siedlce, while the lowest from those with brown coal.
3. Significantly the highest amounts of studied metals were harvested with yield of plants grown on objects with sewage sludge, whereas the lowest with brown coal.

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WPŁYW WAPNOWANIA I NAWOŻENIA ORGANICZNEGO NA PLON ORAZ ZAWARTOŚĆ WYBRANYCH METALI W KUPKÓWCE POSPOLITEJ

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Abstrakt: W doświadczeniu wazonowym badano wpływ wapnowania i zróżnicowanego nawożenia organicznego na plon kupkówki pospolitej oraz zebrane z tym plonem ilości Cu, Zn, Cd i Pb. W badaniach uwzględniono obiekty bez stosowania wapnowania i ze stosowaniem $CaCO_3$ w dawce równoważnej 1 Hh gleby. W doświadczeniu zastosowano również nawożenie organiczne (osad ściekowy, kurzeniec od brojlerów, węgiel brunatny) w dawce wprowadzającej do gleby 2 g C $\cdot$ kg^{-1}. W sezonie wegetacyjnym zebrano cztery pokosy uprawianej rośliny, w której po wysuszeniu i zmieleniu oznaczono zawartość omawianych pierwiastków metodą ICP-AES po wcześniejszej mineralizacji "na sucho" w piecu muflowym.

Największy plon sumaryczny oraz najwięcej omawianych metali zebrano z obiektów nawożonych osadem ściekowym, a najmniej z obiektów, w których stosowano węgiel brunatny.

Słowa kluczowe: wapnowanie, nawożenie organiczne, kupkówka pospolita, metale ciężkie

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APPLICATION OF THE COMPUTER IMAGE ANALYSES IN THE *Lymnaea stagnalis* L. ACUTE TOXICITY TEST

ZASTOSOWANIE KOMPUTEROWEJ ANALIZY OBRAZU W TEŚCIE TOKSYCZNOŚCI OSTREJ *Lymnaea stagnalis* L.

Abstract: The studies over acute toxicity tests using embryological and juvenile criteria in *Lymnaea stagnalis* L. showed their efficiency in the bioindication of water pollution. These biotests allowed the studies on acute toxicity effects in a wide range of water pollutants. Additionally, one may assess the tendency to causing teratogenic effects by different chemical substances. These tests make a significant supplementation of the applied so far biological methods of the water quality assessment, eg the acute toxicity test on *Daphnia magna* Strauss. The application of methods of the computer image analysis additionally allowed the automatization of this biotest. The computer analysis provided the assessment of the kinetics of the *Lymnaea stagnalis* embryos (up to the late gastrula stage) in the control and polluted environment. The subject of detection was the movement of embryos during their development.

Keywords: Acute toxicity biotest, embryotest *Lymnaea stagnalis,* computer image analysis

"The Framework Water Directive" [1] puts the framework for common actions in water policy of the EU. Following to the recommendations of this legal act, the scope of environmental monitoring was extended by the methods of biomonitoring.

So far biomonitoring have been treated as supplementary monitoring – fulfilling rather a scientific than formal aspect. The studies on new methods of acute or chronic toxicity biotests mainly referred to clinical toxicology. The scientific advance in ecotoxicology and environmental biotechnology proved the need for carrying out biomonitoring to assess the impact of different pollutants on water ecosystems [2]. The assessment of the quality of the aquatic environment cannot be made without using the methods of environmental monitoring. Nowadays, there is a possibility of buying

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toxkits of the acute toxicity for many bioindicators. However, the applied toxkits are still expensive and do not make perfect tools.

The methods of acute toxicity biotests make a very important element of environmental monitoring. Various authors tried to assess acute toxicity applying various methods of bioindication [3–6]. Many commercial versions of biotests were made to allow quick and easy toxicity assessment of the samples of water, wastewater and chemical substances [3, 4].

Traditional methods applied in the toxicity assessment require the researcher's observation, thus there is a risk of getting wrong conclusions. Most of these methods require that scientists and technicians carry out systematic observations and make their assessment visually. Visual observation is a qualitative assessment, and consequently loaded with an error resulting from a subjective assessment by the researcher. It is desirable to invent such methods, which allow quick and precise quantitative and qualitative assessment. Great prospects are brought by the application of methods based on the computer image analysis [7, 8]. The attempts to automatize biotests with the application of the image analysis have already been made. Lewicki [9, 11] created a computer method for the chronic toxicity for *Hydra vulgaris* Pallas and *Lemna minor* L., based on the analysis of morphological changes caused by a toxin. Mazur et al [11] created the method of computer image analysis, allowing the measurement of quickly changing parameters for the biotest on *Daphnia magna* Strauss. This method allows the assessment of kinetic changes (symptoms of the toxicant's effect at given concentration) in the function of time [11].

The process of assessment can be automatized by precise determination of established parameters. The applications of such methods are known in medicine (computer tomography, magnetic resonance, analyses of microscope images etc.). Due to such applications the diagnoses could be made quicker and the chances to correctly detect the pathogenic factor were growing.

Unfortunately, the application of image analysis methods in the aspect of bioindication studies has still been poorly developed. Therefore it is necessary to carry out interdisciplinary research to develop new methods of toxicity biotests, as well as automatization for wider and more efficient application in the assessment of:

– water quality,

– toxicity of chemical substances,

– the quality of treatment in different wastewater treatment stations,

– the impact of investments on aquatic environment (refers to the release of pollutants to surface waters) etc.,

– other chemical and physical factors influencing proper functioning of aquatic ecosystems and their components.

The correct analysis is a "data mine", where one can draw conclusions on many symptoms of the toxicant influence on the organism. It is also possible to obtain in a proper time the information on the course of a toxic process and the answer of the indicator.

The following can be done:

– defining new toxic effects, previously, difficult to observe or record,

– shortening the time of assessment from 24 h, 48 h or even 72 h to the time ranging between several minutes and 4 h,

– better and more comprehensive understanding of the mechanism of a toxic effect and the kind of organism's response,

– defining the character of the stress caused by a chemical substance in the stress theory aspect,

– objective assessment of the "aggressiveness" and toxic character of the analysed compound,

– making a numeric model describing the character of the effect of toxin in a defined concentration on the tested populations,

– studying of other than toxic effects eg: phototaxis, chemotaxis, or the influence of temperature change on the mobility of bioindicators and this way – the definition of the value of the "background" of the biotest.

The introducing by Dobrowolski [12] embryological criteria for the assessment of biological effects of environmental pollution provided scientific premises for more efficient protection of biodiversity and the sustainable use of biological resources. Mazur [13] made a new acute toxicity biotest with the use of the embryos of the great pond snail *Lymnaea stagnalis* L. This species makes a common element of fresh water ecosystems, thus such studies could be useful for the water quality assessment from ecotoxicological point of view. The image analysis increases the objectivity of the assessment in early development, caused already by low concentrations of xenobiotics and even slight changes of pH and temperature.

The authors did detail research on the application of the computer image analysis methods in the newly made by Mazur [13] acute toxicity embryotest on *Lymnaea stagnalis*. It was shown that the assessment of the impact of different water pollutants on embryonic and juvenile stages of *Lymnaea stagnalis* significantly increases the sensitivity on this biotest on acute toxicity. The on-line application of image analysis during the test on embryos, allowed the automatization of this method. The viability of embryos was assessed and kinetic parameters (angular and linear translocation) were analysed. The lack of movement meant death and it was a symptom of the effect of toxicant. Thus this computer method makes another tool allowing precise quantitative and qualitative assessment of the mortality of embryos in the acute toxicity test.

Materials

Stage 1. Traditional biotest

The value of acute toxicity of potassium chloride was assessed in the relation to the embryos of *Lymnaea stagnalis* L. over 24 h. The range of safe concentrations and the LC50 coefficient were determined. The cocoons selected for the test contained the pond snail embryos in best condition, without pathologic or teratogenic changes.

Parameters of the biotest:

– the ratio of geometric progress of solutions: q = 1.25 (determined in *screen* tests),

- the number of repetitions: 5,
- water temperature in the samples: 21.5 °C,
- duration of the test: 72 h.

Results of the first stage of the experiment

Table 1

The mortality of embryos [%] for different potassium chloride concentrations after 72 h

KCl concentration [mg · dm^{-3}]	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
3500.00	100.00	100.00	100.00	100.00	100.00
2800.00	77.78	70.75	75.27	67.52	76.92
2240.00	33.85	43.53	40.48	38.82	45.33
1792.00	20.48	17.14	21.74	23.66	18.49
1433.60	3.17	4.76	5.41	6.78	4.26
1146.88	0.00	0.00	0.00	0.00	0.00
917.50	1.72	0.00	0.00	0.00	1.37
Control	0.00	0.00	0.00	0.00	1.77

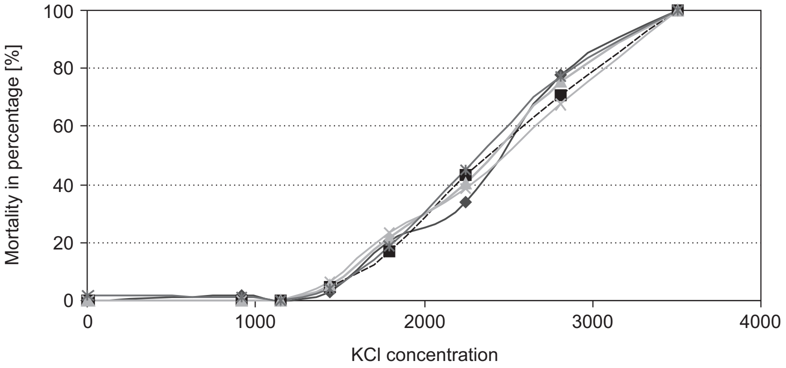


Fig. 1. The graph of cumulated values of the mortality of *Lymnaea stagnalis* embryos [%] for respective KCl concentrations [mg · dm^{-3}] in 72 h

Table 2

The assessment of the degree of toxicity of the studies substances for *Lymnaea stagnalis*

Substance	LC50 value (*Lymnaea stagnalis*)	Toxicity according to:		
		Dockal and Solda	European Union	US EPA
KCl	2346.6 [mg · dm^{-3}]	Slightly toxic	—	Slightly toxic

Stage 2. Application of computer image analysis in the detection of the movement of surviving embryos

This procedure included the studies in the control system and after the application of two concentrations of KCl toxicant ie 1.79 g · dm^{-3} and 1.15 g · dm^{-3}:

– the cocoons with *Lymnaea stagnalis* embryos of the gastrula stage were selected,

– the cocoons were exposed to the toxicant for 72 hours and then time-lapse images were taken (1 image every 1.5″ – for 30 minutes),

– the images were taken with Nikon camera connected with the stereoscope microscope Hund Wetzlar (S/Ns214551),

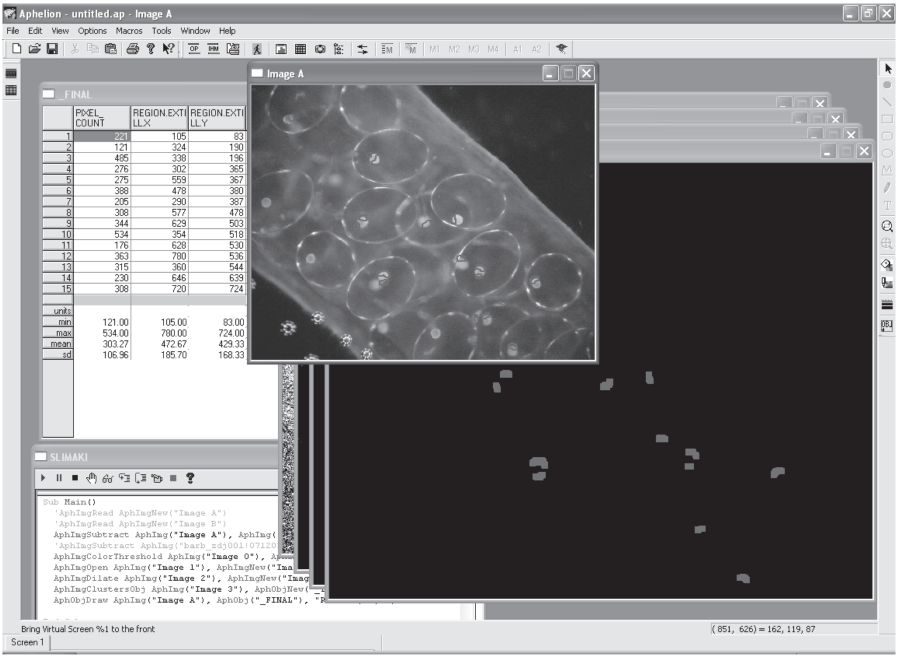
– the magnification of 1 × 200 was applied for detail observation,

– the Aphelion 3.2 environment was used with the authors-made macro, where the movements of embryos were analysed,

– the lack of movement means the death of embryos.

Results of the second stage of the experiment

The produced tool correctly followed the movement of the objects – embryos on the stage of gastrula. In the control group the viability of embryos was shown. In the case of tests groups gradual immobilization was observed, showing the influence of the toxicant.



	PIXEL_ COUNT	REGION.EXTI LL.X	REGION.EXTI LL.Y
1	221	105	83
2	121	324	190
3	485	338	196
4	276	302	365
5	275	559	367
6	388	478	380
7	205	290	387
8	308	577	478
9	344	629	503
10	534	354	518
11	176	628	530
12	363	780	536
13	315	360	544
14	230	646	639
15	308	720	724
units			
min	121.00	105.00	83.00
max	534.00	780.00	724.00
mean	303.27	472.67	429.33
sd	106.96	185.70	168.33

```
Sub Main()
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   'AphImgRead AphImgNew("Image B")
   AphImgSubtract AphImg("Image A"), AphImg(
   'AphImgSubtract AphImg("barb_zdj001!07120
   AphImgColorThreshold AphImg("Image 0"), Ap
   AphImgOpen AphImg("Image 1"), AphImgNew("Ima
   AphImgDilate AphImg("Image 2"), AphImgNew("Imag
   AphImgClustersObj AphImg("Image 3"), AphObjNew(
   AphObjDraw AphImg("Image A"), AphObj("_FINAL"), "
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Bring Virtual Screen %1 to the front

(851, 626) = 162, 119, 87

Fig. 2. The detection of the movements of embryos in the test cocoon (Aphelion environment – image analysis)

Table 3

Detection of the movement of embryos in the tested cocoons (Aphelion environment – image analysis) compared with the number of all the embryos; moving embryos are those that survived

KCl concentration [$g \cdot dm^{-3}$]	Moving embryos (alive) computer detection of movement		Not moving embryos (dead)		Total
	Number	[%]	Number	[%]	100 %
1.79	15	71	6	29	21
1.15	26	100	0	0	26
Control	23	100	0	0	23

Discussion

In the first stage of the experiment the biotest was carried out with a traditional method. The results of the test indicate that potassium chloride was not toxic referring to studied organisms. The range of safe concentrations of this substance for the developing embryos is 0–1.15 $g \cdot dm^{-3}$ of KCl.

The LC50 value within 72 h needs concentration 2.35 $g \cdot dm^{-3}$ KCl and classifies this substance as slightly toxic. Concentrations LC 100 % reach 3.5 $g \cdot dm^{-3}$ KCl and above. The toxicity test carried out with a classical method is based on the observation of embryos and counting the immobilized individuals, compared with all the individuals.

In the second stage of the experiment the methods of computer image analysis were applied for the automatization of the assessment of the survival of individuals exposed on the applied toxicant.

In the case of the control sample and in the sample exposed to KCl concentration 1.15 $g \cdot dm^{-3}$ the tool correctly detected organisms that were alive. In the concentration of 1.79 $g \cdot dm^{-3}$ KCl the computer recognized 15 individuals 71 % of all the exposed embryos moving within the framework of the images. Sample mortality and at the same time concentration, assessed with a standard method and with computer image analysis provides similar results.

The created tool allows the automatization of the embryotest. It properly recognizes objects and allows to define the values of translocations.

Additional information that can be obtained through the image analysis:

– measuring the area of the studied objects can be helpful in measuring the dynamics of the development of embryos in the control and polluted environment; it is possible to detect the impact of the toxicant, manifesting by the disturbances of development such as delays in the speed of the growth of embryos, compared with the control object,

– additionally, due to the analysis of the histogram of the distribution of the surface area for individual embryos in test groups the effect of asynchronization, which is characteristic for the development in polluted environment.

The computer image analysis, also in this case, eliminates the errors resulting from the researcher's subjective assessment and allows unambiguous interpretation of the results. It makes a modern tool in the studies of chronic and acute toxicity [10, 11].

Conclusions

The presented paper brings original new tools of the bioindication for quick assessment of the toxicity of chemical water pollutants, with the use of the computer image analysis for the acute toxicity embryotest on *Lymnaea stagnalis*. It is a biotest with the possibility of application in the wide spectrum of the toxicity assessment of different substances.

The arguments for the application of methods of the computer image analysis in the studies of different scientific disciplines, including biology are the following:

– relatively low prices of computer equipment,

– increasing calculation power of computers,

– user-friendly software,

– the possibility of the archivisation of a large amount of data, which can in future be used in other studies,

– often due to the application of computer methods the objectivity and sensitivity of biotests can be increased,

– these are non-invasive methods, applied to living organisms and allowing the continuation of the experiment.

The application of innovative methods of biological monitoring in environmental engineering will allow earlier detection of direct threat to ecosystems, and indirect – for humans.

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ZASTOSOWANIE KOMPUTEROWEJ ANALIZY OBRAZU W TEŚCIE TOKSYCZNOŚCI OSTREJ *Lymnaea stagnalis* L.

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Abstrakt: Badania nad testami toksyczności ostrej wykorzystującymi kryteria embriologiczne i juwenilne na przykładzie *Lymnaea stagnalis* L. wykazały ich skuteczność w bioindykacji zanieczyszczeń wód. Biotesty te umożliwiają badanie toksyczności ostrej zanieczyszczeń wód w szerokim spektrum badanych substancji. Dodatkowo można ocenić tendencję do wywołania efektów teratogennych przez różne substancje chemiczne. Testy te stanowią ważne uzupełnienie dotychczas stosowanych biologicznych metod oceny jakości wód, np. testu toksyczności ostrej na *Daphnia magna* Strauss. Zastosowanie metod komputerowej analizy obrazu pozwoliło dodatkowo na zautomatyzowanie tego biotestu. Analiza komputerowa dotyczyła oceny kinetyki zarodków *Lymnaea stagnalis* (do stadium późnej gastruli) w środowisku kontrolnym i zanieczyszczonym. Detekcji podlegał ruch embrionów w trakcie rozwoju zarodkowego.

Słowa kluczowe: biotesty toksyczności ostrej, embriotest *Lymnaea stagnalis,* komputerowa analiza obrazu

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and Paweł ZADROŻNY[1]

MERCURY CONTENT IN SOILS OF THE OJCOW NATIONAL PARK

ZAWARTOŚĆ RTĘCI W GLEBACH OJCOWSKIEGO PARKU NARODOWEGO

Abstract: The aim of the study was to evaluate the total mercury content in genetic horizons of soils of the Ojcow National Park (ONP). Most part of all 27 examined soils showed low Hg content, which resulted in classifying them as not polluted soils. The highest concentration of Hg was found in organic horizons of lessive soils. Based on statistical analyze it was found that lessive soils were more polluted in humus horizons than rendzinas. Most part of studied soils humus horizons was characterized by a higher Hg content in comparison with geochemical background, what evidence is accumulation index (AI) values more than 1. Mercury content in examined soils was depended on the content of organic carbon, total nitrogen and C:N ratio.

Keywords: mercury, soil, pollution, the Ojcow National Park

Geographical position of the Ojcow National Park (ONP) within the pollutant range of large industrial centres (Upper Silesian Industrial Region, Olkusz, Jaworzno, Trzebinia-Siersza), a considerable number of windless periods and small wind speed favour persistent air pollution in the park flowing from the west and south-west [1].

According to Grodzinska [2], who in the eighties investigated the problem of contamination in national parks in Poland, the Ojcow National Park was counted among the groups of parks strongly polluted with heavy metals. Moreover, Grodzinska demonstrated that contamination of the Ojcow National Park was the highest among the analyzed parks.

Presented research aimed at determining the total content of mercury in soils of the Ojcow National Park and establishing the degree of these soils pollution with the discussed element.

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Material and methods

The soil material for analyses was collected from 27 soil profiles located in the area of the Ojcow National Park (Fig. 1).

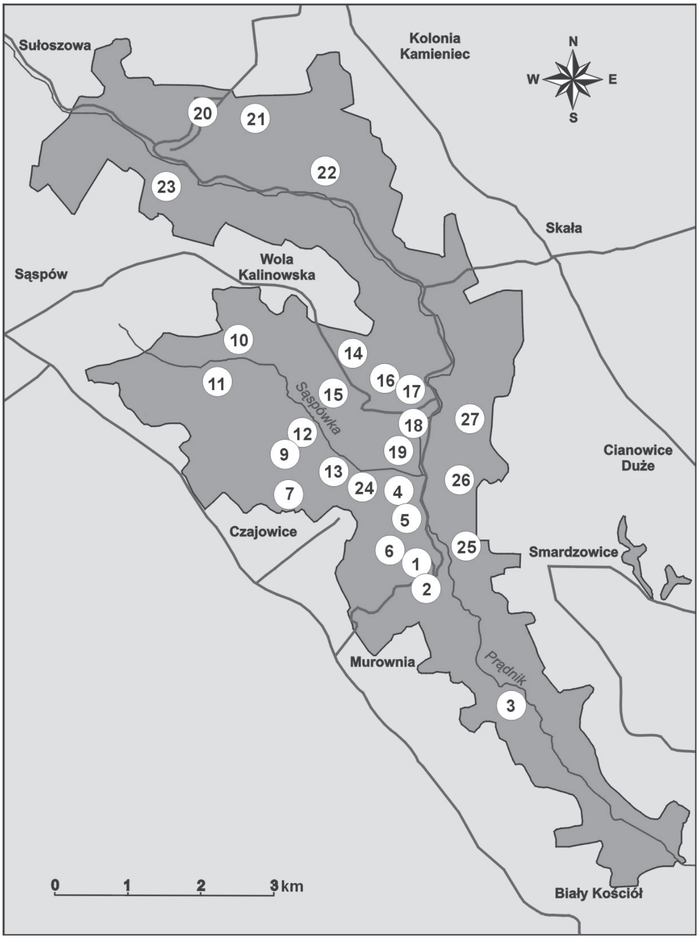

Fig. 1. Location of soil profiles on the Ojcow National Park area

The researched soils represented 5 types [3]:

- rendzinas (16 profiles),
- brown soils (1 profile),
- lessive soils (8 profiles),
- pseudogley soils (1 profile),
- river alluvial soils (1 profile).

Rendzinas were developed from the Jura limestones, brown soils, lessive soils and pseudogley soils formed from loesses deposited on limestones, whereas river alluvial soils from alluvia. The soil profiles were situated in the forest areas and only river alluvial soil (profile 13) was situated on grassland.

Laboratory analyses were conducted on the samples collected from 87 soil genetic horizons. The soil material was dried at room temperature and sifted through a sieve with 1 mm mesh, and subsequently basic physicochemical and chemical properties were determined:

– pH in distilled water using potentiometric method,
– total nitrogen using Kjeldahl method on Kjeltec apparatus (Tecator),
– organic carbon using Tiurin method modified by Oleksynowa,
– granulometric composition using Casagrande method modified by Proszynski,
– total mercury content using atomic absorption spectrometry (AAS) in AMA 254 mercury analyzer (Altech).

The obtained results were subjected to statistical analysis using Statistica 6.1 software; simple correlation coefficients were computed and their significance determined using t-Student test. RIR Tukey test was used to compare mercury contents in rendzinas and lessive soils. Mercury accumulation indices (AI) were also computed as a ratio of the element content in the surface and bottom horizons of the profiles.

Results and discussion

Analyzed rendzinas were characterized by a considerable skeletal content. Granulometric composition of rendzinas was strongly diversified and resulted from the thickness of loess layer lying on carbonate rocks (mixed rendzinas) (Table 1) [4].

Table 1

Chemical and physico-chemical properties of investigated soils

Soil type, profiles number	Horizon	Share of fraction [%] with diameter [mm]				pH (H_2O)	Organic C	Total N
		1–0.1	0.1–0.02	< 0.02	< 0.002		[g · kg^{-1}]	
Rendzinas (16)	O A	— 0–45.5	— 30.5–56	— 19–56	— 3–22	6.0–7.4 5.7–7.8	118.2–326.9 25.4–81.8	1.14–1.63 2.0–7.1
Lessive soils (8)	O A	0.5–24	46–81	29–53	5–15	3.5–5.3 3.2–5.2	204.0–375.0 25.9–82.0	7.0–23.5 2.5–5.6
Brown soils (1)	A	1	56	43	10	4.6	30.1	3.6
Ground gley soils (1)	A	7	55	38	8	3.6	94.6	5.7
River alluvial soils (1)	A	6	62	32	7	6.1	32.3	3.4

A majority of rendzinas revealed granulation of clayey silt, three profiles has clay granulation, one loamy and one sandy granulation. On the other hand, lessive soils were characterized by ordinary silt or clayey silt granulation.

Rendzinas in the surface horizons revealed neutral or alkaline reaction, slightly acid reaction was determined in two profiles and acid reaction in three profiles. Lessive soils were more strongly acidified (strongly acid or acid reaction). Also in surface horizons of brown soil and pseudogley soil strongly acid reaction was determined. On the other hand, river alluvial soil was characterized by a neutral reaction in the surface horizon, whereas in deeper horizons the reaction was alkaline.

A considerable diversification in organic carbon content was found in soils of the Ojcow National Park. The lowest content of organic carbon in organic horizon, amounting 118.2 g · kg^{-1}, was assessed in proper rendzina (profile 7) and the highest, 375.0 g · kg^{-1}, in pseudogley lessive soil (profile 14). On the other hand, in humus horizons organic carbon contents fluctuated from 25.4 g · kg^{-1} in proper rendzina (profile 12) to 94.6 g · kg^{-1} in pseudogley soil (profile 22). Mean carbon contents in organic horizons of lessive soils were higher than in the analogous horizons of rendzinas and reached: 280.4 g · kg^{-1} and 208.5 g · kg^{-1}, respectively. The situation looked similar for humus horizons, where mean content of organic carbon was also higher in lessive soils, i.e. 57.0 g · kg^{-1} and 44.6 g · kg^{-1} for rendzinas.

Nitrogen content in humus horizons remained on a level from 2.0 g · kg^{-1} in proper rendzina (profile 5) to 7.1 g · kg^{-1} in brown rendzina (profile 19). Mean content of total nitrogen in humus horizons of lessive soils was 4.2 g · kg^{-1} and was slightly lower than in rendzinas, ie 4.3 g · kg^{-1}.

Total mercury content in individual genetic horizons of soils in the Ojcow National Park was diversified (Table 2).

Table 2

Mercury content [mg · kg^{-1}] in investigated soils

Profile no., soil subtype	Horizon symbol	Depth [cm]	Hg [mg · kg^{-1}]	Profile no., soil subtype	Horizon symbol	Depth [cm]	Hg [mg · kg^{-1}]
Rendzinas				Lessive soils			
3 brown	A1h	2–4	0.07	1 glossic	Ol	1–2	0.17
	A2h	4–25	0.04		Ah	2–10	0.14
	BbrC1ca	25–58	0.04		AEet	10–35	0.04
	BbrC2ca	58–80	0.05		Eet	35–48	0.02
4 brown	Ah	1–8	0.06		Eet/Btg	48–115	0.02
	BbrCca	8–30	0.05		BtCg	115–150	0.01
5 typical	Ah	2–15	0.08	2 glossic	Ol	2–4	0.19
	ACca	15–25	0.04		Ah	4–12	0.13
	Cca	25–45	0.04		BtCg	80–150	0.02
6 brown	Ah	2–10	0.11	9 typical	Ol	2–6	0.39
7 typical	O1Cca	2–10	0.36		Ah	6–12	0.39
	O2Cca	10–45	0.29		IIBtC	> 75	0.06
8 typical	A1Cca	2–8	0.19	14 pseudogley	Ol	1–4	0.25
	A2Cca	8–35	0.18		Oh	4–7	0.30
10 typical	AhCca	2–15	0.07		AEet	7–13	0.12
11 brown	Ah	1–19	0.14		Eet	13–52	0.04
	AhBbr	19–40	0.12		BtCg	52–125	0.02

Table 2 contd.

Profile no., soil subtype	Horizon symbol	Depth [cm]	Hg [mg · kg^{-1}]	Profile no., soil subtype	Horizon symbol	Depth [cm]	Hg [mg · kg^{-1}]
12 typical	Ah	5–20	0.07	15 pseudo-gley	Ol	1–4	0.31
17 brown	Ol	1–2	0.21		Ah	4–7	0.17
	ACca	2–28	0.16		BtCg	20–100	0.01
	BbrCca	28–40	0.04	16 pseudo-gley	Ol	1–3	0.32
18 inicial	A1Cca	1–6	0.16		Ah	3–9	0.25
	A2Ccaan	6–20	0.13		BtCg	35–100	0.02
19 brown	Ol	1–3	0.16	20 pseudo-gley	A1h	3–6	0.34
	A1Cca	3–20	0.20		IICca	> 59	0.16
	BbrCca	28–48	0.07	26 pseudo-gley	Ol	1–3	0.25
23 brown	Ah	1–16	0.20		Oh	3–6	0.54
	BbrCca	16–38	0.13		AEet	6–35	0.03
24 brown	A1Cca	1–12	0.12		Btg	35–80	0.03
	BbrCca	30–60	0.06		C	80–115	0.02
25 brown	Ah	1–14	0.16		IIC	> 115	0.02
	BbrCca	25–40	0.09	Pseudogley soils			
27 typical	A1Cca	1–10	0.16	21 typical	A1h	2–6	0.23
	A2Cca	10–40	0.13		Gg	12–38	0.03
Brown soils				River alluvial soils			
22 typical	Ah	2–16	0.13	13 typical	Ah	2–10	0.05
	IICca	33–55	0.08		IIG	43–80	0.02

In organic horizons Ol mercury contents ranged between 0.16 and 0.39 mg · kg^{-1} and exceeded natural mean content of this metal in soil, ie 0.1 mg · kg^{-1} [5]. Organic horizons Oh of lessive soils (profiles 14 and 26) revealed high contents of mercury, 0.30 and 0.54 mg · kg^{-1}, respectively. Demers et al [6] point to potential of "internal" mercury binding in O horizons, which escapes in a gaseous form from mineral soil horizons. A lower mercury accumulation was observed in humus horizons in comparison with organic horizons. In their humus horizons rendzinas revealed low contents of the discussed element and 0.20 mg · kg^{-1} was registered only in two profiles (no. 19 and 23). In lessive soils mercury concentration was the highest and reached value 0.39 mg · kg^{-1} (profile 9).

Mean mercury contents computed for humus horizons of rendzinas and lessive soils were 0.13 and 0.24 mg · kg^{-1}, respectively. A statistically significant difference was determined between mercury content in humus horizons of rendzinas and lessive soils at significance level $p = 0.05$ (RIR Tukey test).

In compliance with the Regulation of the Minister of the Environment of 9th September 2002 on soil standards and earth standards, mercury contents in the soils of protected areas cannot exceed 0.5 mg · kg^{-1} [7]. Therefore, the soils of the Ojcow National Park should be considered as unpolluted with the discussed metal. Only in one profile (profile 26) the content of 0.54 mg · kg^{-1} assessed in organic Oh horizon exceeded the admissible value.

Mercury contents determined in soils of the Ojcow National Park were compared with this element contents in black earths from the city area of Krakow and from the southern part of the Nida Basin [8]. Mercury contents in surface horizons of soils from the Nida Basin ranged from 0.078 to 0.390 mg · kg^{-1}, which shows a certain similarity with the park soils, were the values fluctuated from 0.05 to 0.54 mg · kg^{-1}. Mercury content in soils close to the Krakow Gate was slightly higher than in the park and varied within a narrower range (from 0.436 to 0.538 mg · kg^{-1}).

Lower content of mercury was found in surface horizons of forest soils on the Wielun Uppland (from 0.003 to 0.190 mg · kg^{-1}) and on the Tarnobrzeg Plain (from 0.005 to 0.240 mg · kg^{-1}) [9, 10].

Average mercury content in organic horizons of the Babiogorski National Park (BgNP) is 0.32 mg · kg^{-1} and is higher than in soils of the Ojcow National Park (ONP) (0.29 mg · kg^{-1}) [11]. The highest mercury concentrations in the areas of these parks were assessed in the organic horizons: in BgNP it was 0.79 mg · kg^{-1} (the soil covered with spruce trees) and in ONP – 0.54 mg · kg^{-1} (under mixed coniferous forest). In humus horizons, higher mercury contents were found in the soils of ONP than in BgNP and the values were: 0.16 and 0.12 mg · kg^{-1}, respectively.

Profile distribution of Hg contents was different for rendzinas and lessive soil, which is due to different permeability of these soils (Fig. 2).

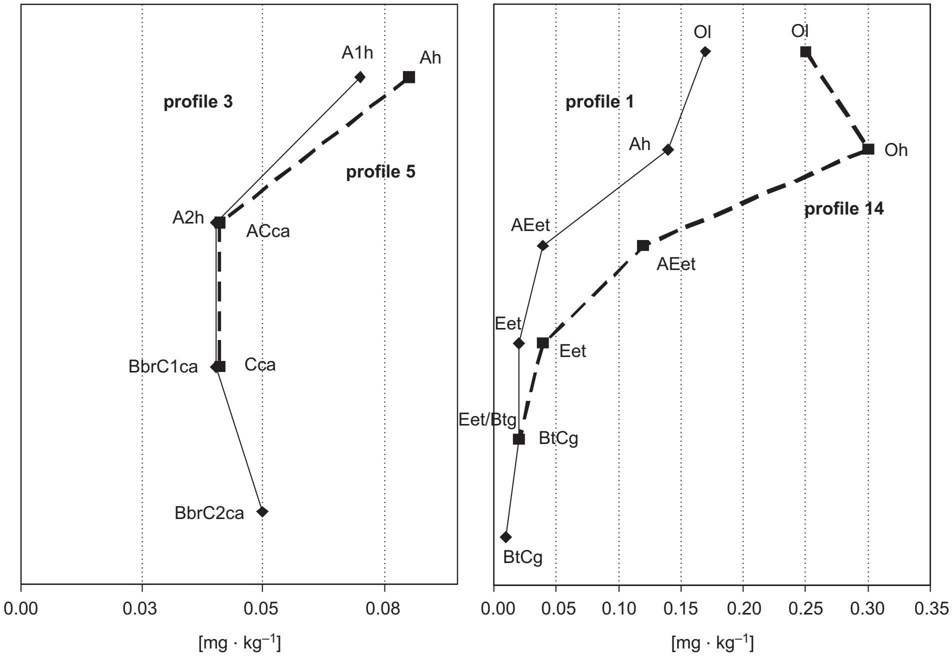

Fig. 2. Mercury profile distribution in chosen rendzinas (profiles 3 and 5) and lessive soils (profiles 1 and 14)

In lessive soils the highest Hg concentrations were found in organic and humus horizons. In deeper, poorly permeable horizons, this element content visibly diminished. In permeable rendzina profiles, mercury content usually varied little in the surface and bottom horizons. Grimaldi et al [12] obtained similar results showing that profile distribution of mercury depends on soil water permeability.

Accumulation indices computed for the analyzed soils of ONP ranged from 1.05 to 16.34 (Fig. 3). Average value of AI determined for lessive soils was 9.32 which is a five-fold higher value in comparison with mean index computed for rendzinas (1.82). Rendzinas are characterized by a high permeability and therefore mercury translocation into deeper horizons is facilitated.

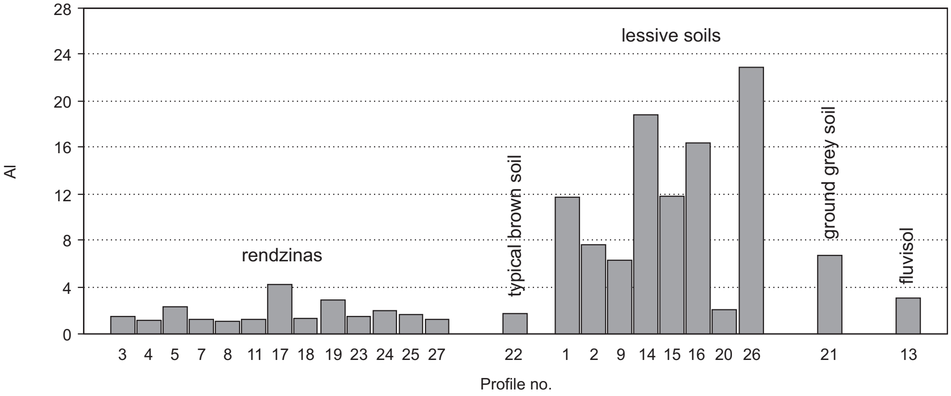

Fig. 3. Accumulation index (AI) calculated for investigated soils

On the basis of computed accumulation indices it may be assumed that the analyzed soil revealed elevated mercury contents as evidenced by AI value higher than assessed in all investigated soil profiles.

Table 3

Linear correlation coefficients between mercury content and some properties of humus horizons of investigated soils

Soil properties	Linear correlation coefficient (r)		
	Rendzinas (16 profiles)	Lessive soils (8 profiles)	Total (27 profiles)
pH (H_2O)	–0.04	0.04	–0.45
Organic C content	0.73***	0.97***	0.87***
Total N content	0.79***	0.96***	0.66***
C:N ratio	–0.27	0.79*	0.60***
Share of fraction < 0.02 mm	0.03	–0.38	–0.22
Share of fraction < 0.002 mm	–0.30	–0.34	–0.33

Significance level: * – $\alpha = 0.05$***; ** – $\alpha = 0.01$; – $\alpha = 0.001$.

Total mercury contents in all analyzed soils were statistically significantly affected by organic carbon and total nitrogen content, as well as C:N ratio, whereas simple correlation coefficients (significant at $p = 0.001$) computed for these relationships were: $r = 0.87$, 0.66 and 0.60, respectively (Table 3). It corroborates previous research results evidencing the strongest Hg binding by soil humus and clayey minerals [13].

In rendzinas the content of discussed element was strictly (significant at $p = 0.001$) dependant on contents of organic carbon ($r = 0.73$) and total nitrogen ($r = 0.79$), similarly as in lessive soils where simple correlation coefficients (significant at $p = 0.001$) were $r = 0.97$ and 0.96, respectively. Moreover in lessive soils statistical analysis revealed weakly significant (at $p = 0.05$) positive correlation with C:N ratio ($r = 0.79$). Strongly significant correlation between C:N ratio and mercury content in the all analyzed soils shows that the lower the degree of organic matter decomposition in humus horizons, the greater mercury accumulation.

Conclusions

1. A majority of the analyzed soils of the Ojcow National Park were characterized by a low content of mercury but the value of accumulation index AI higher than 1 evidence an artificial enrichment of the surface horizons.
2. Mercury content in the analyzed soils was higher in organic horizons than in humus horizons.
3. Accumulation indices revealed higher values for lessive soils than for rendzinas.
4. Mercury content in all investigated soils strictly depended on the contents of organic carbon, total nitrogen and C:N ratio.

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ZAWARTOŚĆ RTĘCI W GLEBACH OJCOWSKIEGO PARKU NARODOWEGO

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Abstrakt: Celem pracy było oznaczenie całkowitej zawartości rtęci w poziomach genetycznych gleb Ojcowskiego Parku Narodowego oraz określenie zależności między wybranymi właściwościami badanych gleb a ilością tego pierwiastka w glebie. Większość badanych gleb charakteryzowała się małą zawartością rtęci. Największą koncentrację tego pierwiastka stwierdzono w poziomie organicznym gleby płowej (0,54 mg $\cdot$ kg^{-1}). Na postawie analizy statystycznej stwierdzono, że gleby płowe w porównaniu z rędzinami charakteryzowały się większą zawartością rtęci w poziomach próchnicznych. W porównaniu z tłem geochemicznym większość badanych gleb wykazywała podwyższoną zawartość rtęci, czego dowodem były wartości współczynnika akumulacji (WA) większe od 1. Zawartość rtęci we wszystkich badanych glebach była uzależniona od zawartości węgla organicznego i azotu ogólnego oraz stosunku C:N.

Słowa kluczowe: rtęć, gleby, zanieczyszczenie, Ojcowski Park Narodowy

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SOIL CONTAMINATION WITH ARSENIC VERSUS THE CONTENT OF ZINC IN PLANTS

ZANIECZYSZCZENIE GLEBY ARSENEM A ZAWARTOŚĆ CYNKU W ROŚLINACH

Abstract: The aim of the study has been to reduce the effect of soil contamination with arsenic (10, 20, 30 and 40 mg As · kg^{-1}) on the content of zinc in plants by the application of several substances (lime, natural zeolite, charcoal, loam, compost and synthetic zeolite in experiments on maize; lime, natural zeolite, charcoal, loam, compost and synthetic zeolite in tests on cocksfoot and yellow lupine; peat, pine bark, dolomite and synthetic zeolite in trials on spring barley and swede). The soil improvers which were added in order to mollify the negative effect of arsenic on plants, in addition to the plant species and organs, were determined as a factor which modified the influence of soil contamination with arsenic on the content of zinc in plants. However, the effect of arsenic in soil on the amounts of zinc in yields of the test crops was ambiguous. Both positive and negative correlations occurred, albeit limited to individual cases, between the increasing quantities of arsenic in soil and the amounts of zinc in the yields of plants. Regarding the trials where no soil improvers had been applied, negative correlation was determined for the aboveground parts and roots of maize, aboveground parts of cocksfoot, roots of yellow lupine as well as grain and straw of barley. Positive correlation was discovered in the case of aboveground parts of Swedish turnip and roots of spring barley. The influence of some of the soil improvers on the content of zinc in the crops was sometimes greater than that of arsenic. Loam, lime, charcoal and compost produced the most evident and typically negative effect on the content of zinc in plant tissues. The influence of the other soil neutralising substances on the content of zinc in plants depended on the plant species or organs.

Keywords: arsenic soil contamination, neutralising substances, crops, zinc content

Depending on the oxidation and reducing conditions prevailing in a given environment, arsenic can be present in four oxidation states: –III, 0, +III and +V. In a strongly reducing environment, elementary (0) and (–III) arsenic can occur. But the two basic forms of this element, that is (+III) and (+V), prevail in nature irrespective of the actual

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hydrogeochemical conditions [1]. Under moderately reducing conditions, arsenic (+III) becomes the dominant form while arsenic (+V) is present as a stable element mainly in strongly oxidizing environments [2]. This means that any transformation from one form of arsenic to the other is a slow process and both forms of this metalloid can be simultaneously present in soil [3]. The presence of arsenic in soil creates the risk of its uptake by plants growing on arsenic polluted soil, which means that the element will enter a food chain. Arsenic (+III) causes metabolic disorders in people and animals. Having chemical affinity for the sulfhydryl group of proteins, arsenic can easily bind with these proteins and inactivate them. This inhibits the activity of many enzymes, especially phosphatase, esterase, lipase and oxidase [4, 5]. The response of a living organism to arsenic is conditioned by the dose of this toxin, type of contact, length of exposure as well as the source and chemical form of arsenic. In the third oxidation state this element is 6-fold more harmful than in the fifth oxidation state; moreover, mineral forms of arsenic can be 100-fold more harmful than organic arsenic [6–8]. In most cases, ingestion of arsenic can lead to death. Even a brief exposure to its influence can cause sudden reactions of the body, including failure of the central nervous system, circulatory collapse, paralysis of the digestive system, with such symptoms as nausea, gastric and intestinal colic and diarrhoea, as well as damage of the kidneys [6]. Arsenic causes numerous disorders of some of macro- and microelements uptake by plants and decrease of plant growth. Arsenic and zinc are elements, which have antagonistic effect on each other [4]. Thus, it is of utmost importance that the risk of excessive uptake of arsenic by crops be eliminated.

Therefore, the aim of the present study has been to compare the effect of contamination of soil with arsenic on zinc content in some of plants and reduce the effect of soil pollution with arsenic on the content of zinc in crops by using various soil improvers.

Material and methods

The tests on soil contamination with arsenic were conducted in a design consisting of five greenhouse pot one-year experiments performed at the University of Warmia and Mazury in Olsztyn, Poland. The plants were grown on three soils, similar in their physicochemical properties, which were taken from the humic layer of proper brown soils characterised by the grain-size distribution typical of light loamy sand. The soils were either acidic or strongly acidic. The effect of soil pollution with arsenic added at 0, 10, 20, 30 and 40 mg As $\cdot$ kg^{-1} of soil was tested on yellow lupine (*Lupinus luteus* L.), Juno cv.; the other test plants, such as maize (*Zea mays* L.), Scandia cv., cocksfoot (*Dactylis glomerata* L.), Nawra cv., Swedish turnip (*Brassica napus* var. *napobrassica*), Sara cv., and spring barley (*Hordeum vulgare* L.), Ortega cv., were grown on soil contaminated with 0, 25, 50, 75 and 100 mg As $\cdot$ kg^{-1} of soil. The following soil improvers were added in the experiments involving maize to reduce the negative influence of arsenic pollution: lime, natural zeolite, charcoal, loam, compost; in the tests on cocksfoot and yellow lupine lime, natural zeolite, charcoal, loam, compost and synthetic zeolite were used, and peat, pine bark, loam, dolomite and synthetic zeolite amended the soil in the trials on spring barley and Swedish turnip. These neutralising agents were introduced to soil at a ratio of 3 % of the soil mass per pot, except lime and dolomite, which were added in the amounts balanced with 1 hydrolytic acidity (Hh). Each pot, in addition to the above, received NPK fertilization, which corresponded to the nutritional demands of the crops. Arsenic was introduced to the soils in the form of sodium arsenate, nitrogen as ammonia, phosphorus as triple superphosphate and potassium as potassium salt. All these components were carefully mixed with the soil, after which the whole mixture was placed in polyethylene pots of the capacity of 9 kg. Finally, the test crops were sown. The soil used for the maize experiments was slightly acidic (pH_{KCl} = 5.91) and moderately rich in available phosphorus, potassium and magnesium. Cocksfoot and yellow lupine were grown on acidic soil (pH_{KCl} = 4.53), moderately rich in available forms of phosphorus, potassium and magnesium. Spring barely and swede were sown to soil of very acidic reaction (pH_{KCl} = 4.16) with moderate amounts of available phosphorus and potassium, but low in available magnesium. The content of arsenic in all the test soils was very low, ranging from 2.21 to 3.58 mg As · kg^{-1} of soil. Also other trace elements occurred in very small contents. The experiments were carried out with the following plant stand per pot: 10 maize plants, 8 cocksfoot and yellow lupine plants, 15 spring barley plants and 3 Swedish turnips. The vegetative pot experiments were performed in 3 replications. The moisture of the soil in the pots was maintained at a level of 60 % field water capacity. The plants were harvested at the technological maturity phase.

Once the plant samples were collected during the harvest, they were fragmented, dried at 60 ^{o}C and ground. The concentration of zinc was determined (in 2 replications) using the atomic spectrophotometric absorption (ASA) method. The results of the determinations underwent statistical elaboration, using a two-factorial analysis of ANOVA variance with the Statistica software package [9]. In addition, relationships between the rate of arsenic and content of zinc in plants were determined using Pearson's simple correlations.

Results and discussion

The effect of growing rates of arsenic in soil on the content of zinc in yields of the test crops was diverse. The content of zinc in the plant material was most often positively correlated with the degree of arsenic contamination of soil. The content of zinc in plant tissues deepened on the plant species, organ and type of a substance used to neutralise arsenic (Tables 1 to 5).

The aboveground parts of maize contained slightly less zinc than its roots (Table 1). The average zinc content in maize aboveground organs and roots was 50.91 and 67.15 mg Zn · kg^{-1} d.m., respectively. The effect on soil pollution with arsenic on the content of zinc in maize was dependent on the plant organ. In the series without any soil improvers, arsenic depressed the maize concentration of zinc by maximum 11 % ($r = -0.871$) in aboveground parts and by 20 % ($r = -0.906$) in roots.

Table 1

Zinc content in aboveground parts and roots of maize (*Zea mays* L.) [mg · kg^{-1} d.m.]

Arsenic dose [mg As · kg^{-1} of soil]	Kind of neutralising substance						Average
	without additions	compost	charcoal	loam	lime	natural zeolite	
Aboveground parts							
0	58.29	48.93	43.97	38.08	53.35	41.59	47.37
25	59.55	44.76	51.01	39.39	54.03	51.37	50.02
50	52.80	44.22	54.90	44.80	57.90	59.70	52.39
75	52.00	44.40	57.40	54.00	59.70	56.20	53.95
100	51.80	44.20	43.70	52.20	65.60	47.40	50.82
Average	54.89	45.30	50.20	45.69	58.12	51.25	50.91
r	–0.871**	–0.761**	0.148	0.935**	0.964**	0.364	0.688*
LSD	a – 3.79**; b – 3.46**; a · b – 8.47**						
Roots							
0	79.20	69.65	67.40	70.25	95.25	87.20	78.16
25	75.30	59.35	62.50	52.95	82.35	88.05	70.08
50	76.90	53.55	44.35	53.75	79.65	90.50	66.45
75	63.65	49.90	40.55	54.75	78.10	77.45	60.73
100	62.97	49.80	40.45	55.75	76.70	76.25	60.32
Average	71.60	56.45	51.05	57.49	82.41	83.89	67.15
r	–0.906**	–0.932**	–0.929**	–0.596	–0.874**	–0.784**	–0.964**
LSD	a – 4.50**; b – 4.11**; a · b – 10.06**						

LSD for: a – kind of additions, b – arsenic contamination; r – simple correlation coefficient; significant level: * p = 0.05, ** p = 0.01; n = 10.

In most of the experimental series, the aboveground parts of maize contained elevated levels of zinc under the effect of arsenic, whereas the roots of maize from all the objects were found to contain less zinc. Nevertheless, the highest arsenic contamination rate also depressed the content of zinc in the aboveground parts of maize. The largest decrease in the zinc content in maize roots, reaching 40 % (r = –0.929) was observed in the objects amended with charcoal. Clearly, the substances added to soil in order to neutralise arsenic affected the content of zinc in both aboveground and underground organs of maize. Regarding the aboveground parts of maize, the highest concentrations of zinc was determined in the objects receiving lime, whereas the lowest ones occurred in the combinations involving compost and loam. In turn, the roots contained the highest amounts of zinc when grown on soil amended with natural zeolite and lime; the lowest levels of zinc in maize roots were found in the case of charcoal amended soil.

The content of zinc in aboveground parts of cocksfoot was slightly lower than in the roots of this plant: 57.54 mg and 66.84 mg Zn · kg^{-1} d.m. (Table 2).

Table 2

Zinc content in aboveground parts and roots of cocksfoot (*Dactylis glomerata* L.) [mg · kg^{-1} d.m.]

Arsenic dose [mg As · kg^{-1} of soil]	Kind of neutralising substance							Average
	without additions	natural zeolite	lime	charcoal	loam	compost	synthetic zeolite	
Aboveground parts								
0	74.80	61.90	54.59	62.36	60.06	61.73	64.52	62.85
25	74.01	50.00	56.25	64.01	60.08	62.05	58.50	60.70
50	57.51	46.23	52.93	67.72	63.71	62.03	56.57	58.10
75	53.00	44.50	46.10	66.80	63.95	72.65	50.60	56.80
100	52.25	36.52	45.19	40.00	52.10	73.18	45.60	49.26
Average	62.31	47.83	51.01	60.18	59.98	66.33	55.16	57.54
r	–0.931**	–0.959**	–0.907**	–0.577	–0.398	0.880**	–0.991**	–0.948**
LSD	a – 3.81**; b – 3.36**; a · b – 8.52**							
Roots								
0	65.02	54.96	59.04	73.12	96.72	56.81	58.40	66.30
25	73.28	70.05	61.80	78.25	86.70	58.49	60.06	69.80
50	70.41	71.25	61.75	78.56	78.00	57.35	66.75	69.15
75	68.25	74.45	60.03	71.50	76.25	54.50	69.70	67.81
100	51.55	74.95	57.05	63.60	53.95	49.25	77.55	61.13
Average	65.70	69.13	59.93	73.01	78.32	55.28	66.49	66.84
r	–0.597	0.857**	–0.456	–0.668*	–0.957**	–0.823**	0.980**	–0.563
LSD	a – 5.53**; b – 4.89**; a · b – 12.38**							

LSD for: a – kind of additions, b – arsenic contamination; r – simple correlation coefficient; significant level: * p = 0.05, ** p = 0.01; n = 10.

Soil contamination with arsenic usually tended to result in depressed zinc concentrations in aboveground parts of the grass and higher levels of this metal in the roots (particularly when the rate of the contaminant was low). The largest decrease in the amount of zinc found in the aboveground parts of cocksfoot (41 %, r = –0.959) was determined in the series with natural zeolite, and in the roots (44 %, r = –0.957) when soil was amended with loam. At the same time, cocksfoot growing on soil treated with natural zeolite accumulated the highest level of zinc in the roots (36 %, r = 0.857). In the series where no soil improvers were applied, the highest arsenic contamination dose caused depressed concentrations of zinc in plants, reaching 30 % (r = –0.931) in aboveground parts and 21 % (r = –0.597) in roots of cocksfoot. The substances used in our experiment to neutralise soil pollution with arsenic produced an evident effect on the concentration of zinc in cocksfoot. Noteworthy is the fact that higher concentrations of zinc were observed in the roots of cocksfoot plants growing on soil amended with loam and charcoal. On the other hand, natural zeolite, lime and synthetic zeolite added to soil caused decrease the zinc in aboveground parts of the grass whereas compost produced an analogous effect in its roots.

The contents of zinc determined in aboveground parts and roots of yellow lupine were approximately identical, reaching on average 71.61 and 76.54 mg Zn $\cdot$ kg^{-1} d.m. (Table 3). Contamination of substrate soil with arsenic caused higher levels of zinc in yellow lupine, with an increase being larger in aboveground parts rather than roots of this crop. When 30 mg As $\cdot$ kg^{-1} of soil was added, the highest increase in zinc content (82 %, r = 0.787) was determined in the objects with compost; regarding the roots of yellow lupine, such an effect occurred in the object neutralised with synthetic zeolite (25 %, r = 0.955), compost (23 %, r = 0.729) and loam (21 %, r = 0.862).

Table 3

Zinc (Zn) content in aboveground parts
and roots of yellow lupine (*Lupinus luteus* L.) [mg $\cdot$ kg^{-1} d.m.]

Arsenic dose [mg As $\cdot$ kg^{-1} of soil]	Kind of neutralising substance							Average
	without additions	charcoal	natural zeolite	synthetic zeolite	loam	compost	lime	
Aboveground parts								
0	61.65	86.59	68.32	71.15	55.55	53.43	54.09	64.40
10	79.50	76.91	65.57	70.42	59.61	79.64	62.00	70.52
20	93.53	74.43	66.23	69.32	68.12	94.22	62.95	75.54
30	103.75	68.11	66.44	67.87	69.12	97.19	62.40	76.41
40	110.14	63.81	58.60	55.00	70.60	88.54	54.53	71.60
Average	89.71	73.97	65.03	66.75	64.60	82.60	59.19	71.70
r	0.983**	–0.983**	–0.786**	–0.824**	0.945**	0.787**	0.045	0.670*
LSD	a – 2.95**; b – 2.49**; a $\cdot$ b – 6.59**							
Roots								
0	83.59	75.48	78.44	70.29	72.91	71.60	67.19	74.21
10	82.91	77.48	78.41	77.72	72.23	69.98	66.67	75.06
20	81.15	77.11	78.95	78.28	76.01	70.15	65.47	75.30
30	76.12	87.45	77.95	87.64	88.37	88.00	65.55	81.58
40	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Average	80.94	79.38	78.44	78.48	77.38	74.93	66.22	76.54
r	–0.924**	0.842**	–0.294	0.955**	0.862**	0.729*	–0.932**	0.850**
LSD	a – 2.44**; b – 2.06**; a $\cdot$ b – 5.46**							

LSD for: a – kind of additions, b – arsenic contamination; r – simple correlation coefficient; significant level: * p = 0.05, ** p = 0.01; n = 10; n.a. – not analysed because of an insufficient amount of plant material.

For comparison, the dose of 40 mg As $\cdot$ kg^{-1} of soil caused the largest increment of zinc in yellow lupine aboveground parts (79 %, r = 0.983) in the series without any neutralising substances, in contrast to the soil amended with charcoal (r = –0.983), natural zeolite (r = –0.786) and synthetic zeolite (r = –0.824). The highest concentration of zinc in both aboveground and underground parts of yellow lupine occurred in the series without soil neutralising agents. The application of any of the neutralising substances caused a large decline in the content of zinc in plants compared to the analogous series without these agents, with the differences being larger in aboveground parts than in roots of yellow lupine. Particularly big changes in zinc contents occurred in aboveground parts of this plant under the effect of lime (on average 34 %), natural and synthetic zeolite and loam (26–28 %) and in the roots – as a result of liming (18 %).

The content of zinc in leaves of swede was on average 88.86 mg, and in the roots of this crop – 26.27 mg Zn · kg^{-1} d.m., which means that three-fold more zinc was present in leaves than in roots (Table 4). Soil contamination with arsenic had some influence on the content of zinc in swede, with the actual effect being correlated with the type of a neutralising agent applied. In some series, arsenic in soil contributed to a higher level of zinc in the plant tissues, but in some other treatments the same pollutant resulted in depressed zinc concentrations in swede. The content of zinc rose rather clearly in the leaves of swede growing on soil without the neutralising agents (r = 0.890) and in the roots of this plant on soil neutralised with synthetic zeolite (r = 0.967).

Table 4

Zinc content in aboveground parts
and roots of swede (*Brassica napus* L. var. *napobrassica* (L.) Rchb.) [mg · kg^{-1} d.m.]

Arsenic dose [mg As · kg^{-1} of soil]	Kind of neutralising substance						Average
	without additions	peat	bark	loam	dolomite	synthetic zeolite	
Aboveground parts							
0	81.45	85.85	111.65	76.85	101.35	98.85	92.67
25	94.95	74.80	97.40	71.90	98.00	111.40	91.41
50	94.20	67.10	90.90	67.20	96.55	122.25	89.70
75	95.90	65.65	87.30	64.40	95.80	112.25	86.88
100	102.55	64.55	88.45	50.35	94.70	101.25	83.64
Average	93.81	71.59	95.14	66.14	97.28	109.20	88.86
r	0.890**	–0.917**	–0.891**	–0.955**	–0.953**	0.095	–0.982**
LSD	a – 6.19; b – 5.65; a · b – 13.84						
Roots							
0	25.75	36.95	31.50	21.53	22.00	21.18	26.49
25	25.50	36.25	23.80	20.75	24.25	23.10	25.61
50	24.90	34.25	21.75	19.30	27.25	31.75	26.53
75	24.45	34.00	21.95	19.10	25.75	33.40	26.44
100	23.50	33.45	20.90	18.60	24.70	36.45	26.27
Average	24.82	34.98	23.98	19.86	24.79	29.18	26.27
r	–0.979**	–0.958**	–0.841**	–0.965**	0.562	0.967**	0.164
LSD	a – 2.22**; b – n.s.; a · b – 4.95*						

LSD for: a – kind of additions, b – arsenic contamination; r – simple correlation coefficient; significant level: * p = 0.05, ** p = 0.01; n.s. – differences non-significant; n = 10.

A reverse relationship, ie depressed levels of zinc under the effect of arsenic in soil, occurred most evidently in the case of leaves in the series treated with peat (r = –0.917) and in roots – in the object neutralised with pine bark (r = –0.841). The substances used to neutralise arsenic pollution of soil differentiated rather extensively the content of zinc in Swedish turnip. The lowest content of zinc in leaves and roots of this crop was found in the series with loam and the highest one – in the series amended with synthetic zeolite (leaves) or peat (roots).

Spring barley grain and straw contained on average 30 % less zinc than its roots (Table 5).

Table 5

Zinc content in grain, straw and roots of spring barley (*Hordeum vulgare* L.) [mg · kg^{-1} d.m.]

Arsenic dose [mg As · kg^{-1} of soil]	Kind of neutralising substance						Average
	without additions	peat	bark	loam	dolomite	synthetic zeolite	
Grain							
0	45.44	47.65	57.86	20.61	25.29	35.17	38.67
25	39.28	31.12	37.31	20.05	25.95	33.29	31.17
50	31.78	29.21	37.32	20.91	28.18	29.17	29.43
75	29.20	28.00	32.12	28.29	29.16	29.38	29.36
100	30.33	28.77	31.28	31.70	30.97	28.93	30.33
Average	35.21	32.95	39.18	24.31	27.91	31.19	31.79
r	–0.918**	–0.779**	–0.853**	0.902**	0.989**	–0.906**	–0.746*
LSD	a – 4.74**; b – 2.32**; a · b – 10.59						
Straw							
0	40.41	43.00	51.89	30.47	28.60	27.92	37.05
25	38.37	38.67	53.25	28.81	29.41	34.40	37.15
50	33.59	36.95	47.13	24.90	30.46	39.24	35.38
75	33.21	36.49	37.42	22.84	34.48	41.68	34.35
100	31.36	29.63	36.24	21.20	44.22	49.48	35.36
Average	35.39	36.95	45.19	25.64	33.43	38.54	35.86
r	–0.963**	–0.947**	–0.935**	–0.989**	0.892**	0.989**	–0.810**
LSD	a – 9.69**; b – n.s.; a · b – n.s.						
Roots							
0	39.88	37.63	47.40	26.65	42.93	44.44	39.82
25	40.20	38.14	53.30	27.08	44.90	55.29	43.15
50	41.26	41.24	88.83	36.30	45.18	55.90	51.45
75	44.03	50.71	96.59	41.23	46.48	56.14	55.86
100	69.63	47.96	94.56	51.78	66.52	62.07	65.42
Average	47.00	43.14	76.14	36.61	49.20	54.77	51.14
r	0.785**	0.890**	0.914**	0.969**	0.790**	0.893**	0.988**
LSD	a – 5.76**; b – 5.25**; a · b – 12.87**						

LSD for: a – kind of additions, b – arsenic contamination; r – simple correlation coefficient; significant level: * p = 0.05, ** p = 0.01; n.s. – differences non-significant.

Arsenic contamination of soil depressed the content of zinc in grain and straw of spring barley in most of the experimental series; in contrast, the concentration of zinc in roots of spring barley increased in most of the treatments. The biggest decrease in the content of zinc in grain occurred in the series with pine bark and peat – on average the level of zinc dropped by 46 % ($r = -0.853$) and 40 % ($r = -0.779$). Regarding the straw, the maximum decline in the zinc content was determined in the series with loam ($r = -0.989$), pine bark ($r = -0.935$) and peat ($r = -0.947$), where it dropped on average by 30–31 %. The increase in zinc concentration in spring barley roots under the effect of 40 mg As $\cdot$ kg^{-1} oscillated from 28 % ($r = 0.890$) in the peat amended objects up to 99 % ($r = 0.914$) in the series with pine bark. Comparison of all the neutralising substances showed that pine bark caused the occurrence of higher levels of zinc in both aboveground and underground parts of spring barley. On the other hand, the lowest content of zinc was determined in the objects neutralised with loam.

Likewise in the present study, Kabata-Pendias and Pendias [4] as well as Paivoke and Simola [10] reported that increasing contamination of soil with arsenic caused increased levels of zinc in plant tissues. However, it should be added that the content of zinc in the analysed plant organs tended to be negatively correlated with the level of soil contamination with arsenic.

The differences in the uptake of zinc by particular species of plants as well as its transfer to plant organs are substantial. According to Lubben [11], carrot, maize and pea seeds are characterised by a low rate of zinc uptake, in contrast to leaves of spinach, roots of radish and other plants, which take up large amounts of zinc. Addition of various substances to soil modifies the content of zinc in plants. Our own results can partly support the results obtained by other authors. Jasic et al [12] showed that the highest levels of zinc occurred in cucumber growing on humus amended soil; the lowest one – when soil received fine-fraction charcoal. Tlustos et al. [13] demonstrated that zinc in spinach declined by 25 % after the soil had been neutralised with straw. Lime contributed to depressed uptake of heavy metals by plants [14], with its effect on zinc possibly larger than on other heavy metals [15]. The actual effect depends also on a plant species. According to Brune [16], levels of zinc in barley grain observed under the effect of soil liming could be depressed by as much as 50 %; Tlustos et al [13] reported than an analogous decrease in spinach could be as high as 75 %. Similar dependences were found by Wallace [17] in the case of maize. Zeolites [18] as well as modified loams [19] seem to be effective too. In a study carried out by Ciecko et al [20], lignite, lime and bentonite in particular were found to have depressed the content of zinc in plants, especially in yellow lupine and radish.

Conclusions

1. The substances added to soil in order to alleviate the negative influence of arsenic pollution as well as the species and organs of plants tested modified the effect of soil contamination with arsenic on the content of zinc in plants.

2. It was not possible to demonstrate an unambiguous effect of soil pollution with arsenic on the content of zinc in yields of the test plants. There were single cases of

either positive or negative correlation between increasing rates of arsenic added to soil and the content of zinc in the analysed organs of plants. As regards the objects not amended with soil improvers, negative correlation between the two factors mentioned above was observed in aboveground parts and roots of maize, aboveground parts of cocksfoot, roots of yellow lupine as well as grain and roots of barley; positive correlation was noticed in aboveground parts of yellow lupine, Swedish turnip and roots of spring barley.

3. The effect of some of the soil additives neutralising the effect of arsenic pollution was even greater than that exerted by arsenic itself. The most unambiguous and typically negative influence on the content of zinc in plants was produced by loam, lime, charcoal and compost. The other soil improvers produced diverse effects on zinc in plants, varying between the plant species or even the plant organs tested.

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ZANIECZYSZCZENIE GLEBY ARSENEM A ZAWARTOŚĆ CYNKU W ROŚLINACH

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Abstrakt: Celem przeprowadzonych badań było zmniejszenie oddziaływania zanieczyszczenia gleby arsenem (10, 20, 30 i 40 mg As · kg^{-1}) na zawartość cynku w roślinach przez stosowanie różnych substancji (wapno, zeolit naturalny, węgiel drzewny, ił, kompost w doświadczeniu z kukurydzą; wapno, zeolit naturalny, węgiel drzewny, ił, kompost i zeolit syntetyczny w badaniach z kupkówką i łubinem żółtym oraz torf, kora sosnowa, ił, dolomit i zeolit syntetyczny w doświadczeniach z jęczmieniem jarym i brukwią pastewną). Substancje zastosowane do złagodzenia wpływu arsenu na rośliny oraz ich gatunek i organ modyfikowały wpływ zanieczyszczenia gleby tym metalem na zawartość cynku w roślinach. Nie wykazano jednoznacznego oddziaływania zanieczyszczenia gleby arsenem na zawartość cynku w plonach badanych roślin. Odnotowano w pojedynczych przypadkach zarówno ujemne, jak i dodatnie korelacje pomiędzy rosnącym zanieczyszczeniem gleby arsenem a zawartością cynku w badanych organach roślin. W obiektach bez dodatków stwierdzono ujemną zależność dla zawartości cynku w częściach nadziemnych i korzeniach kukurydzy, częściach nadziemnych kupkówki, korzeniach łubinu żółtego oraz w ziarnie i słomie jęczmienia, a dodatnią w częściach nadziemnych brukwi pastewnej i korzeniach jęczmienia jarego. Wpływ niektórych dodatków neutralizujących na zawartość cynku był nawet większy niż arsenu. Najbardziej jednoznacznie i na ogół ujemnie na zawartość cynku w roślinach działały ił, wapno, węgiel drzewny i kompost. Wpływ pozostałych dodatków na zawartość cynku był często odmienny u różnych gatunków, a nawet organów testowanych roślin.

Słowa kluczowe: zanieczyszczenie arsenem, substancje neutralizujące, rośliny, zawartość cynku

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EFFECT OF DREDGED BOTTOM SEDIMENT ADDITION TO THE SUBSTRATUM ON THE FODDER VALUE OF PLANT MATERIAL

Part 1. MACROELEMENTS CONTENT

WPŁYW DODATKU BAGROWANEGO OSADU DENNEGO DO PODŁOŻA NA WARTOŚĆ PASZOWĄ MATERIAŁU ROŚLINNEGO

Cz. 1. ZAWARTOŚĆ MAKROELEMENTÓW

Abstract: Pot experiments were conducted in 2004 and 2005 in which light soil, quartz sand and bottom sediment dredged from the Roznow Reservoir were used as a substratum. The experiments aimed at an assessment of the effect of growing bottom sediment share in the substratum on the quality of cultivated crop biomass. The test plants were maize and horse bean, oat and lupine cultivated after each other in 2004 whereas in 2005 the test plant was barley cultivated in the same substrata. The biomass was assessed on the basis of limit values for good quality fodder based on macroelement (P, K, Ca, Mg and Na) contents.

The results show that biomass of most test plants contained too little macroelements considering their use for fodder. Bottom sediment added to the slightly acid soil only slight changed the contents of magnesium, calcium, potassium and sodium in biomass of all test plants, despite a considerable increase in these elements quantity in the substratum. A considerable increase in calcium and magnesium in the plant biomass was assessed in the substrata with sand. A decline in phosphorus content in biomass of all plants was observed even at the lowest sediment admixture, however it was more pronounced in case of the substrata with soil. Greater sediment supplements did not cause any further limiting of phosphorus uptake by plants. In the second year of the experiment on average higher contents of all macroelements were registered in barley biomass, which improved its feed value.

Bottom sediment supplement to the substratum worsened the quality of all plant biomass because of too low phosphorus content, whereas increasing amounts of calcium and magnesium improved the quality of biomass obtained in the experiments.

Environmental management of the sediment dredged from the Roznow Reservoir may be recommended on light acid soils to improve their physicochemical properties, yielding and plant chemical composition, but simultaneous monitoring of other substances in the biomass is necessary.

Keywords: light soil, quartz sand, bottom sediment, macroelements, P, K, Ca, Mg, Na, content, biomass quality

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Element uptake by plants and their chemical composition is a resultant of many factors, among others cation exchange through cell membranes, processes occurring in the rhizosphere, total contents and the forms in which these elements occur in soil. Soil pH and organic matter contents are the factors to which the most serious influence on element bioavailability is ascribed [1]. A sudden change of soil pH may definitely increase or decrease the amount of bioavailable components [2]. Elements absorbed by plants are included in the biogeochemical cycle. The optimum macroelement content in plants conditions their yielding and covers animal nutritional needs if they are used for feeds. A deficiency or excess of elements may have a negative effect on animals directly or indirectly leading to limited or excessive uptake of other elements.

Bottom sediment from rivers and dam reservoirs reveal chemical properties similar to soils from the catchment area. They usually have neutral or alkaline pH and considerable proportion of silt and clay fractions in their granulometric composition [3, 4]. Technical degradation of dam reservoirs may in future cause enlargement of areas with chronic or periodical water deficits and will compel their reclamation, among other things through dredging [5].

The investigations aimed to determine the effect of growing share of bottom sediment in the substratum on macroelement content in plant biomass and assessment of potential environmental management of this sediment on light acid soils.

Material and methods

The investigations were conducted in the years 2004–2005 in conditions of pot experiments in which light soil and quartz sand with bottom sediment supplement dredged from the Roznow Reservoir were used as a substratum (Table 1).

Table 1

Selected properties of substrata components used in experiments

Component	pH_{KCl}	P	Mg	Ca	Na	K	P	K_2O
		total content [$g \cdot kg^{-1}$]					available forms [$mg \cdot kg^{-1}$]	
Sediment	7.2	0.532	3.833	17.46	0.973	8.632	18.0	96.6
Soil	5.82	0.392	0.564	1.038	0.084	0.556	63.3	256
Sand	6.39	0.072	0.824	0.417	0.091	0.459	4.45	19.2

The experimental design comprised 11 combinations in each series of substrata in three replications. The share of sediment in the substratum was growing from 10 % to 100 %, by 10 % in the subsequent objects. The control treatments were soil and sand without the sediment admixture. In all objects basic fertilization was applied: 1 g N, 0.25 g P and 1.25 g K per pot, thoroughly mixed with the substratum components. Chemically pure NH_4NO_3, KH_2PO_4 and KCl were used for fertilization. In 2004 the test plants were maize (*Zea mays* L.), 'Prosna' F1 c.v., and horse bean (*Vicia faba* L.), 'Nadwislanski' c.v., as a consecutive plant and oat (*Avena sativa* L.), 'Chwat' c.v., and narrow leafed lupine (*Lupinus angustifolius* L.), 'Sonet' c.v., as a consecutive plant. In the experiment continued in 2005 on the same substrata, spring barley (*Hordeum vulgare* L.), 'Rambo' c.v., was cultivated as a test plant. After harvest the plants were dried, samples were dry mineralized and after the ash solution in HNO_3 (1:2) P, K, Ca, Mg and Na contents were assessed in the aboveground biomass using ICP-AES method.

Results and discussion

Phosphorus content in plants cultivated in the conducted experiments was diversified, fluctuating from 0.79 to 6.29 g · kg^{-1} (Table 2). Mean content of this element in all plants was 1.87 g P · kg^{-1}. Slightly higher phosphorus content was registered in the plants cultivated in substrata with sand. The largest diversification of P content (RSD %) in biomass of plant grown on substrata with soil was registered for lupine and on substrata with sand for horse bean and the smallest one on both kinds of substrata was founded for oat.

Table 2

Phosphorus contents in biomass of plants

Share of sediment in substratum [%]	Substratum with soil					Substratum with sand				
	maize	oat	horse bean	lupine	barley	maize	oat	horse bean	lupine	barley
	[g P · kg^{-1} d.m.]									
0	3.30	3.57	4.27	4.29	6.29	1.73	1.81	3.71	2.48	2.70
10	0.99	2.08	2.45	1.74	3.75	0.94	1.78	1.56	1.55	3.09
20	1.04	1.70	2.00	1.56	3.24	0.88	2.11	1.44	1.56	3.67
30	1.03	2.02	1.85	1.41	2.84	0.94	2.07	1.59	1.14	3.24
40	0.96	1.76	2.09	1.05	2.87	0.96	2.19	1.73	0.95	3.25
50	0.94	1.73	1.51	0.94	2.52	0.98	2.22	1.85	1.11	2.59
60	0.97	2.38	1.47	1.03	2.35	0.93	2.23	2.28	1.36	2.48
70	0.84	1.94	1.38	1.10	2.19	0.82	1.92	2.92	1.17	2.62
80	0.99	1.59	1.17	1.21	2.12	0.79	2.33	2.05	1.22	2.04
90	0.85	1.68	1.47	0.90	2.21	0.91	2.39	2.25	1.24	2.30
100	0.79	1.71	1.41	1.07	1.87	0.79	1.71	1.41	1.07	1.87
Mean	1.16	2.01	1.92	1.48	2.93	0.97	2.07	2.07	1.35	2.71
SD	0.72	0.57	0.87	0.97	1.24	0.26	0.23	0.71	0.42	0.55
RSD	62.0	28.1	45.3	65.3	42.4	26.9	11.2	34.1	31.1	20.3

Explanation for Tables 2–6: SD – standard deviation, RSD – relative standard deviation [%].

An admixture of bottom sediment constituting 10 % of the substratum mass caused a considerable limiting of phosphorus uptake by all plants. Greater supplements of this component did not lead to any further lowering of this element content in the plant biomass. Optimal phosphorus content in plants for fodder is 3 g · kg^{-1} [6], therefore it may be estimated that the bottom sediment added to the substratum worsened feed value of the plants in the experiment.

The most frequently encountered phosphorus contents in biomass of maize, barley and oats at the flowering stage are: 2.5–4.5; 3–6 and 4–6 g P · kg^{-1} d.m., respectively [7, 8]. Similar phosphorus contents in barley biomass were registered by Bednarek and Lipinski [9]. Micek et al [10] reported 4.2 g P · kg^{-1} d.m. phosphorus content at oat earing stage. Wisniowska-Kielian [11] noted up to 1.9 g P · kg^{-1} in maize biomass cultivated in alkaline soil, harvested before flowering, up to 3.5 g P · kg^{-1} in oat biomass at the earing stage, while on acid soil maize contained up to 2.1 g P and oat up to 2.6 g P · kg^{-1}.

Maize and oat biomass obtained in the experiment contained considerable smaller quantities of phosphorus than reported by the authors mentioned above, however the amounts of this element assessed in barley were comparable. Wyszkowski and Wyszkowska [12] reported the contents approximate to obtained in barley biomass in the presented experiment, ie 2.79 g P · kg^{-1}. Czyz et al [13] found considerably higher phosphorus contents in meadow sward in the former Slups province, while Wisniowska-Kielian [11] and Wisniowska-Kielian and Pazdziorko [14] assessed similar content of this element in meadow sward in the Podkarpackie province and Beskid Zywiecki Mts. Bottom sediment admixture to the substratum in the Authors' own research decreased this element content in test plants to the level observed by other authors. Horse bean from the control treatment on the soil substratum contained greater amount of phosphorus than plants obtained in the pot experiment conducted by Wyszkowska [15], whereas a 20 % admixture of the sediment turned the relationship. Sediment supplements to the substratum lowered phosphorus content in plants causing considerable deficiencies of this element in view of plant development and their use for forage. Already a 10 % supplement of the sediment to the soil caused over three-fold decline in phosphorus content in the aboveground biomass in comparison with the amount observed in the control plants (from 3.30 to 0.99 g P · kg^{-1} d.m.). In conditions of intensive deacidification chemisorption processes occur in soil, in result of which this metal bioavailability decreases radically, as was reported by other authors [16, 17] who observed a significant dependence between soil pH and its contents of bioavailable phosphorus.

Potassium content in all experimental plants fluctuated from 8.73 to 42.5 g K · kg^{-1} (Table 3) and was on average 16.12 g K · kg^{-1}.

No definite differences were assessed in this element contents depending on the kind of substratum. The highest amounts of potassium were assessed in barley biomass, however no differences were observed in this element uptake between the other test plants.

The diversification of K content (RSD %) in plant biomass was not as big as observed in case of P. The largest its changeability in biomass of plant grown on substrata with soil was registered for lupine and on substrata with sand for horse bean and the smallest one on both kinds of substrata was noted for maize.

Potassium contents in plant biomass obtained in the experiment of 2004 were lower than the most commonly encountered values in cereals ranging from 23.4 to 26.6 g K · kg^{-1} d.m. [8], whereas this element contents in barley cultivated in 2005 were higher than reported by these authors and approximate to registered by Wyszkowski [18]. This element content in leaves and stems of horse bean in the pot experiment conducted by Wyszkowska [15] was twice higher than in horse bean in the Authors' own experiment.

Table 3

Potassium contents in biomass of plants

Share of sediment in substratum [%]	Substratum with soil					Substratum with sand				
	maize	oat	horse bean	lupine	barley	maize	oat	horse bean	lupine	barley
	[g K · kg^{-1} d.m.]									
0	10.72	13.75	15.50	13.10	42.50	11.24	12.71	9.43	13.91	25.93
10	13.50	10.89	13.05	15.75	37.96	12.21	12.55	11.78	13.64	30.92
20	13.13	11.04	15.37	12.50	38.16	13.18	12.69	13.66	12.78	37.07
30	12.84	14.31	12.35	11.85	33.75	12.56	12.38	13.24	10.73	33.81
40	12.62	11.05	13.53	10.09	30.58	13.38	14.31	12.96	10.61	32.63
50	12.32	11.16	14.81	10.70	27.56	13.75	10.86	13.39	10.72	29.22
60	11.58	13.94	10.89	8.86	29.95	14.31	12.04	14.32	11.21	26.68
70	12.94	11.13	14.36	9.60	28.56	12.53	10.24	8.73	10.87	28.86
80	12.88	14.00	12.40	9.80	31.21	13.13	12.75	17.22	11.85	30.92
90	12.56	11.11	13.24	8.99	28.01	13.38	13.00	11.75	10.61	28.43
100	12.48	11.83	14.91	8.76	26.91	12.48	11.83	14.91	8.76	26.91
Mean	12.50	12.20	13.67	10.91	32.29	12.92	12.31	12.85	11.43	30.12
SD	0.77	1.45	1.46	2.19	5.16	0.83	1.08	2.40	1.51	3.38
RSD	6.1	11.9	10.6	20.0	16.0	6.5	8.8	18.7	13.2	11.2

Czapla and Nowak [19] registered similarly high contents of this element in oat biomass after application of potassium treatment. In the experiment conducted by Benedycka and Nowak [20] potassium content in horse bean aboveground parts was considerably higher (ca 50 g K · kg^{-1} d.m.) than in the horse bean from the presented experiment. These amounts greatly exceeded the optimum value in feeds, ie 17 g K · kg^{-1} [6], whereas the quantities of this element noted by Wyszkowska [15] in leaves and stems of horse bean were by half lower than in the research of the above-mentioned authors, still they were much higher than in the presented investigations. In their research Wyszkowska and Wyszkowski did not find any differences in potassium content in barley biomass, which accumulated 20.77 g K · kg^{-1} [12] or oat which had 20.63 g K · kg^{-1}. Considerably bigger differences between the species were registered by Wisniowska-Kielian [11] who found between 33 and 35 g K · kg^{-1} in maize biomass and between 50–54 g K · kg^{-1} in oat biomass at the earing stage, irrespective of the soil acidification. Gorlach and Curylo [22] did not notice any influence of growing $CaCO_3$ doses on the content of bioavailable potassium in soil or this cation uptake by plants, whereas Alvares de Oliveira et al [23] noted a high negative correlation between the content of calcium and magnesium in soil and potassium uptake by soyabean.

Calcium content in the test plants was changing to a small degree under the influence of bottom sediment admixture to the substratum. No significant differences were noted, either depending on the kind of substratum. The highest calcium contents were found in horse bean and lupine biomass, whereas the smallest amounts were registered in monocotyledonous plant biomass (Table 4).

Table 4

Calcium contents in biomass of plants

Share of sediment in substratum [%]	Substratum with soil					Substratum with sand				
	maize	oat	horse bean	lupine	barley	maize	oat	horse bean	lupine	barley
	[g Ca · kg^{-1} d.m.]									
0	3.15	5.78	13.10	19.88	7.79	2.37	5.83	9.92	10.35	3.62
10	4.13	7.47	16.01	10.84	8.05	4.49	5.97	14.97	18.51	6.95
20	4.70	6.20	19.43	26.13	8.47	4.36	6.78	17.79	20.28	9.63
30	3.94	5.39	16.76	18.90	6.77	4.24	5.57	18.80	21.24	8.08
40	4.67	4.59	19.84	11.06	6.49	4.96	6.54	18.93	15.97	6.30
50	4.67	4.68	15.43	20.09	4.43	4.90	6.93	20.36	19.72	5.19
60	4.23	5.34	17.71	19.32	5.79	4.50	7.51	15.32	18.64	6.37
70	4.31	5.46	17.45	20.11	4.65	4.35	7.77	14.72	18.15	5.25
80	4.50	5.03	17.60	19.93	5.13	3.88	5.60	12.97	20.54	5.27
90	4.07	3.32	17.51	19.92	4.95	4.23	5.65	12.66	18.37	5.41
100	3.76	5.06	14.76	20.12	5.17	3.76	5.06	14.76	20.12	5.17
Mean	4.19	5.30	16.87	18.75	6.15	4.19	6.29	15.56	18.36	6.11
SD	0.47	1.04	1.97	4.31	1.45	0.70	0.87	3.14	3.03	1.64
RSD	11.1	19.5	11.7	23.0	23.5	16.8	13.9	20.2	16.5	26.9

The diversification of Ca content (RSD %) in plant biomass was similar to observed in case of K. The largest its changeability in biomass of plant grown on both kinds of substrata was found for barley and the smallest one on substrata with soil was registered for maize and on substrata with sand for oat.

A sediment supplement to the substratum caused an increase in this element content in all plants biomass, however more pronounced effect was observed on the substrata containing sand. The optimum calcium content in biomass of plants destined for forage is 6 g Ca · kg^{-1} [6], therefore the sediment admixture to the substratum improved the monocotyledonous quality but worsened the quality of horse bean and lupine. Calcium contents in maize at the pre-flowering stage fluctuated from 3.0 to 7.0 g Ca · kg^{-1} d.m. [7]. In the research conducted by Micek et al [10] calcium content at the earing stage of oat cultivated for green forage was 3.0 g Ca · kg^{-1} d.m. Maize, oat and barley biomass contained amounts of this element approximate to reported by the authors mentioned above.

Wyszkowski [18] obtained lower calcium contents in maize grown in a pot experiment, whereas Wyszkowski and Wyszkowska [12] registered 3.71 Ca · kg^{-1} in barley. Wisnowska-Kielian [11] observed greater contents of calcium in plants: 6.3–10.3 g Ca · kg^{-1} in oat biomass and 4.6–11.5 g Ca · kg^{-1} in maize, depending on the soil acidification. These values approximated those noted in maize biomass in the presented experiment. Lupine and horse bean contained much higher quantities of calcium, which might have resulted from the fact that the dicotyledonous are more abundant in this element (on average 13.1 g Ca $\cdot$ kg^{-1}) than the monocotyledonous (on average 4.9 Ca $\cdot$ kg^{-1}) [6]. Wyszkowska [15] noted similarly high content of this element in horse bean. Calcium contents in the aboveground biomass of lupine and horse bean were similar, whereas they were smaller in barley and maize. Bottom sediment introduced to both kinds of substratum caused an increase in calcium content in all test plant biomass, however the highest accumulation of this element occurred already after the application of the smallest admixtures of the sediment. Gorlach and Curylo [22] noted a high positive correlation between $CaCO_3$ dose applied for the soil deacidification and calcium contents in plants, however the stronger relationship was observed for oat than maize, which may explain the differences obtained in the Authors' own investigations.

All plants cultivated in the experiments contained small amounts of magnesium, on average 1.43 g Mg $\cdot$ kg^{-1}, and the amount fluctuated from 0.69 to 2.22 g Mg $\cdot$ kg^{-1} (Table 5).

Table 5

Magnesium contents in biomass of plants

Share of sediment in substratum [%]	Substratum with soil					Substratum with sand				
	maize	oat	horse bean	lupine	barley	maize	oat	horse bean	lupine	barley
	[g Mg $\cdot$ kg^{-1} d.m.]									
0	1.15	1.03	1.45	1.88	1.46	1.02	0.69	1.12	1.58	0.79
10	1.38	0.97	1.29	1.55	1.18	1.56	0.89	1.20	1.42	1.38
20	1.61	0.97	1.46	1.73	1.35	1.63	0.97	1.41	1.43	1.20
30	1.64	1.06	1.39	1.46	1.46	1.58	0.96	1.42	1.28	1.50
40	1.72	0.95	1.51	1.43	1.42	1.76	1.25	1.73	1.42	1.42
50	1.71	1.05	1.53	1.44	1.39	1.83	1.09	1.94	1.50	1.39
60	1.68	1.07	1.50	1.56	1.64	1.69	1.18	1.85	1.51	1.59
70	1.78	1.18	1.72	1.41	1.35	1.74	1.22	2.22	1.46	1.52
80	1.61	1.05	1.63	1.50	1.54	1.74	1.09	1.67	1.61	1.60
90	1.74	0.92	1.52	1.41	1.68	1.79	1.02	1.81	1.45	1.76
100	1.70	0.95	1.57	1.51	1.49	1.70	0.95	1.57	1.51	1.49
Mean	1.61	1.02	1.51	1.53	1.45	1.64	1.03	1.63	1.47	1.42
SD	0.19	0.08	0.11	0.15	0.14	0.22	0.16	0.33	0.09	0.25
RSD	11.6	7.4	7.6	9.6	9.7	13.6	15.8	20.1	6.1	17.9

No definite differences were observed for this element contents in the monocotyledonous and dicotyledonous plants. An admixture of the sediment to the substratum caused slight increase in this element content in plants growing on the substrata containing sand and a decrease in its uptake on the substrata with soil. Generally the sediment supplement improved the plant quality on the substrata with sand but worsened on the substrata with soil.

The diversification of Mg content (RSD %) in plant biomass was smaller than those registered for K and Ca and in plant grown on substrata with soil than those with sand. The largest its changeability in biomass of plant grown on substrata with soil was observed for maize and the lowest one for oat and on substrata with sand the largest diversification of Mg content was found for horse bean and the smallest one was calculated for lupine.

Magnesium contents in maize biomass before flowering fluctuated most frequently from 2.0 to 6.0 g Mg · kg^{-1} d.m., whereas the analogous values for oat and barley at this stage were 2.1–4.0 g Mg · kg^{-1} d.m. [7]. Plant biomass obtained in the Authors' own experiments revealed lower magnesium content than deterined by the abovementioned authors, and the highest amounts were found for oat. In the research conducted by Wyszkowski and Wyszkowska [12] barley biomass contained 2.11 g Mg · kg^{-1} d.m. and oat biomass [21] 1.23 g Mg · kg^{-1} d.m.

Poulik [24] assessed similar, low magnesium content in oat 1.7 g Mg · kg^{-1}. Mazur and Wisniowska-Kielian [25] observed an opposite response after the application of dolomite to very acid and weakly acid soil. Under these conditions oat and maize contained 2–3 times greater amounts of magnesium (3.9–4.6 g · kg^{-1}).

In pot experiments Wisniowska-Kielian [11] assessed between 3.8–5 g Mg · kg^{-1} in maize biomass and 2.2–3.2 g Mg · kg^{-1} in oat biomass. Under the influence of bottom sediment added to the substratum magnesium content in maize biomass increased to the level approximate to observed in this plant by Wyszkowski [18]. In the Authors' own investigations an increase in magnesium contents in biomass of oat and horse bean was observed only when they were cultivated in substrata with sand, whereas on the substrata with soil their levels did not change. A lack of evident changes in magnesium content in plants, despite its big quantities in the sediment, was most probably the consequence of very high calcium content in the sediment and the competition between these ions. Kuht and Reintam [26] stated that large doses of calcium may considerably lower the content of available magnesium forms in soil. Gorlach and Curylo observed an increase in magnesium contents in maize and oat biomass only after the soil liming with a fertilizer dose equaling 0.5 and 1.0 hydrolytic acidity, whereas higher admixtures of calcium decreased magnesium level in these plants' biomass. Magnesium deficiencies most frequently occur in light and acid soils, therefore a necessity of magnesium fertilization of these soils appears. Application of bottom sediment on light soil may constitute a valuable source of this element. The bottom sediment used for the experiments contained several times more magnesium than the soil and sand (Table 1).

All plants used in the Authors' own investigations assessed in view of their fodder usability were characterized by insufficient magnesium content [6], ie 2 g Mg · kg^{-1} d.m.

Sodium content in the plants was fluctuating considerably under the influence of bottom sediment admixture to the substratum. Its content ranged from 39.63 to 2159 mg Na · kg^{-1} (Table 6).

Average sodium content in all plants was 372 mg · kg^{-1}. The highest contents were registered in horse bean biomass. The Na content (RSD %) in plant biomass was diversified in a larger extend than of K, Ca and Mg content. The largest its changeability in biomass of plant grown on both substrata was noted for horse bean and the smallest one on substrata with soil was observed for barley and on substrata with sand for maize.

Table 6

Sodium contents in biomass of plants

Share of sediment in substratum [%]	Substratum with soil					Substratum with sand				
	maize	oat	horse bean	lupine	barley	maize	oat	horse bean	lupine	barley
	[mg Na · kg^{-1} d.m.]									
0	56.9	180	103	299	430	50.8	262	53	248	304
10	42.9	256	256	373	368	50.6	220	176	191	432
20	54.6	177	334	214	384	42.9	215	303	248	508
30	43.7	200	440	281	328	48.6	199	820	256	549
40	43.0	212	914	342	420	41.1	229	309	240	312
50	57.9	179	1162	469	357	56.4	483	391	375	358
60	50.4	234	1619	259	411	47.6	550	569	377	416
70	39.6	203	1356	404	403	57.1	504	1414	408	664
80	43.6	197	1322	175	394	48.6	316	1214	426	490
90	47.9	224	2159	247	404	65.0	385	958	323	470
100	48.8	299	1161	213	363	48.8	299	1161	213	363
Mean	48.1	215	984	298	387	51.0	333	670	300	442
SD	6.22	37.2	642.6	90.5	30.7	6.73	127.9	466.2	83.7	108.7
RSD	12.9	17.3	65.3	30.4	7.9	13.3	38.4	69.6	27.8	24.6

Wozniak [27] noted twice higher sodium contents in the legumes from meadows in the San River valley than in mixed sward. These contents were approximate to observed in the plants in the presented experiments. Wisniowska-Kielian and Pazdziorko [14] noted up to 450 mg Na · kg^{-1} d.m. in meadow sward in the Beskid Zywiecki Mts. The contents similar to presented by these authors were assessed only in horse bean, when the bottom sediment supplement exceeded 50 % of the substrata mass prepared both on the basis of sand and soil.

Much higher sodium contents in oat and maize were registered by Czapla and Nowak [19], but they resulted from the soil fertilization with this element. Sodium contents in the aboveground oat biomass ranged from 1.8–3.4 g Na · kg^{-1} d.m., while in maize from 0.6 to 0.8 g Na · kg^{-1} d.m. Gorlach and Curylo [22] noted over twice higher sodium contents in maize biomass than assessed in the presented experiments, both on the control treatments and on those with added bottom sediment.

In the Authors' own research sodium content in maize, lupine and oat biomass did not change definitely under the influence of the sediment admixture, despite its much higher contents in the sediment than in the soil or sand. Sodium contents in horse bean were increasing considerably in result of growing proportions of the sediment in the substratum. This element contents noted in the first year of the presented investigations in the plants from the treatments with 20–30 % sediment share in the substratum were approximate to registered in horse bean straw by Benedycka and Nowak [20], which remained on the level of 500 mg Na $\cdot$ kg^{-1} d.m. Wisniowska-Kielian [11] observed much lower amounts of sodium in maize and oat biomass, between 20 and 50 mg $\cdot$ kg^{-1} d.m., whereas Wyszkowski and Wyszkowska [12] assessed greater contents of sodium, 720 mg Na $\cdot$ kg^{-1} d.m. in oat biomass [20].

Sodium contents in the plants biomass differed considerably from the optimum values in feeds, ie 1500–2500 mg Na $\cdot$ kg^{-1} [6].

Literature data [22] corroborate a lack of unambiguous relationships between the quantity of sodium absorbed by plants and soil pH, because a decrease in sodium content in grass biomass was observed with increasing pH value to 4.3,whereas further increase in pH did not cause any changes in this element content in grass biomass. Growth in sodium content noted in plant biomass in the Authors' own investigations in effect of bottom sediment supplement to the substratum in the first place resulted from increasing total sodium amount in the substratum.

Because of high content of calcium and magnesium, application of big doses of bottom sediment as a supplement to the soil may be treated as a deacidifying measure. Total alkalinity of the sediment used in the presented experiments was 5.7 % $CaCO_3$. The smallest applied admixture of the sediment introduced to the substratum the amounts of calcium equaling almost twenty-fold value of the soil hydrolytic acidity and over twenty-fold sand hydrolytic acidity. Observed results of its application as changes in chemical composition of the plants are characteristic for limed soils [16, 22, 26, 28]. For this reason environmental management of this sediment is possible on light soil for improving their properties and yielding and chemical composition of plants at simultaneous controlling harmful substances contents in the biomass.

Conclusions

1. Bottom sediment supplied to the soil considerably increases its contents of all investigated macroelements.
2. Application of the bottom sediment from the Roznow Reservoir to a considerable extent limits phosphorus absorption by plants, due to its deacidifying activity.
3. Increase in calcium and sodium contents was observed in result of sediment application.
4. Bottom sediment applied on light soil and sand improved fodder value of plants in view of the contents of investigated elements, except for phosphorus.
5. Phosphorus fertilization should be increased when bottom sediments are applied.
6. Application of the sediment amounts equaling 10 or 20 % of the substratum mass caused the greatest changes of the analyzed elements contents in the test plants.
7. Environmental management of the bottom sediment dredged from the Roznow Reservoir is possible on light acid soils to improve their physicochemical properties and yielding and chemical composition of plants but at the same time harmful substances contents in the biomass must be monitored.

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WPŁYW DODATKU BAGROWANEGO OSADU DENNEGO DO PODŁOŻA NA WARTOŚĆ PASZOWĄ MATERIAŁU ROŚLINNEGO

Cz. 1. ZAWARTOŚĆ MAKROELEMENTÓW

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Abstrakt: W 2004 i 2005 r. przeprowadzono doświadczenia wazonowe, w których jako podłoża użyto glebę lekką i piasek kwarcowy oraz osad denny bagrowany ze Zbiornika Rożnowskiego. Celem badań była ocena wpływu wzrastających dodatków osadu dennego do podłoża na jakość biomasy uprawianych roślin. Roślinami testowymi były kukurydza i bobik oraz owies i łubin uprawiane po sobie w 2004 r., a w 2005 r. jęczmień uprawiany na tych samych podłożach. Oceny biomasy dokonano na podstawie wartości granicznych dla pasz dobrej jakości, biorąc pod uwagę zawartości makroelementów (P, K Ca, Mg i Na).

Wyniki przeprowadzonych badań wskazują, że biomasa większości roślin testowych zawierała zbyt mało makroelementów z punktu widzenia wykorzystania jej na cele paszowe. Dodatek osadu dennego do gleby lekko kwaśnej tylko nieznacznie zmieniał zawartość magnezu, wapnia, potasu i sodu w biomasie wszystkich roślin testowych, pomimo znacznego zwiększenia ilości tych pierwiastków w podłożu. W przypadku podłoży z piaskiem stwierdzono znaczne zwiększenie zawartości wapnia i magnezu w biomasie roślin. Zaobserwowano zmniejszenie zawartości fosforu w biomasie wszystkich roślin już przy najmniejszym dodatku osadu, przy czym było ono wyraźniejsze w przypadku podłoży z glebą. Większe dodatki osadu nie powodowały już dalszego ograniczenia pobierania fosforu przez rośliny. W drugim roku doświadczenia stwierdzono średnio większe zawartości wszystkich makroelementów w biomasie jęczmienia, co poprawiło jej wartość paszową.

Dodatek osadu do podłoża pogarszał jakość biomasy wszystkich roślin ze względu na małą zawartość fosforu, natomiast zwiększające się ilości wapnia i magnezu poprawiały jakość biomasy uzyskanej w doświadczeniach.

Można zalecić przyrodnicze zagospodarowanie osadu bagrowanego ze Zbiornika Rożnowskiego na glebach lekkich, kwaśnych w celu poprawy ich właściwości fizykochemicznych oraz plonowania i składu chemicznego roślin, przy jednoczesnym monitoringu zawartości substancji szkodliwych w biomasie.

Słowa kluczowe: gleba lekka, piasek kwarcowy, osad denny, makroelementy P, K Ca, Mg, Na, zawartość, jakość biomasy

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EFFECT OF SOIL PROPERTIES ON LITHIUM PHYTOAVAILABILITY
Part 1. LITHIUM CONTENT AND UPTAKE BY MAIZE AND RYE

WPŁYW WŁAŚCIWOŚCI GLEBY NA FITOPRZYSWAJALNOŚĆ LITU
Cz. 1. ZAWARTOŚĆ I POBRANIE LITU PRZEZ KUKURYDZĘ I ŻYTO

Abstract: Increasing lithium doses, ie 10 and 20 mg Li · pot^{-1} caused a decline in root yield in comparison with the control, whereas they ambiguously influenced the amount of maize stalk and leaf yield. Applied increasing doses of organic matter 25, 52 and 78 g · pot^{-1} caused the increase in maize root yield, whereas for the aerial parts this effect was ambiguous. Percentage of individual parts in maize total yield was as follows: root yield 20–24 %, stalks 32–38 % and leaves 41–46 %.

Application of two lithium doses 10 and 20 mg Li · pot^{-1} caused an apparent increase in this element contents in all analyzed parts of the plant. Assuming lithium content in maize on the control treatment with natural content of this element as 1, one may find that application of 10 mg Li · pot^{-1} caused a ten-fold increase in this element root contents, whereas with 20 mg Li · pot^{-1} dose the increase was about twenty-fold. A similar relationship occurred in the aerial parts. Increasing doses of organic matter 26, 52 and 78 g · pot^{-1} on the treatments with lithium application, more or less apparently affected this element contents both in maize roots and aboveground parts.

The quantity of this element absorbed by roots on the treatment where 10 mg Li · pot^{-1} was applied increased about 9-fold, whereas at the dose of 20 mg Li · pot^{-1} it rose about 18-fold in comparison with the control treatment with the natural content of this element. A similar relationship was observed in the aboveground parts.

Organic matter doses more or less decreased the amount of lithium taken up by maize. On the treatments where 10 mg Li · pot^{-1} was used the amount of the elements taken up by maize roots was smaller by 16 %, 28 % and 31 % in comparison with the control.

Lithium doses affected differently the amount of obtained rye root and aboveground part aftercrop. Increasing doses of organic matter, irrespective of lithium dose more or less influenced the amount of rye aboveground aftercrop. The consequent effect of applied lithium doses led to an increase in this element content in rye aboveground parts and roots and greater uptake of this cation. Increasing doses of organic matter: 26, 52 and 78 g · pot^{-1} had not ambiguous limiting effect on the amount of lithium absorbed by both roots and aboveground parts of rye.

Keywords: lithium content and uptake, soil contamination, soil properties, maize, rye

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Natural lithium content in plants is diversified and ranges from several to many mg · kg^{-1} d.m. The main factors determining the level of this cation in plants comprise: the form in which the element occurs, soil pH, organic matter content, soil moistening, species and part of plant and finally anthropogenic factors [1–5]. Each of the above-mentioned factors, both alone and combined with the other may either stimulate or limit nutrient uptake by plants [6, 7]. Rogoz [5] demonstrated that changes of soil pH in result of application of various forms and doses of calcium or magnesium fertilizers caused a decline in content and amount of lithium absorbed by tobacco, Italian ryegrass or sunflower. Jurkowska et al [8] and Rogoz [5] found that the factors which decrease lithium content in plants, hinder its transport from roots to the aboveground parts, whereas the agents causing increase in its content favour its translocation.

The research aimed at determining the effect of organic matter on yielding, content and uptake of lithium by maize and rye aftercrop both the soil with natural Li content and in soil with the elevated content of this element.

Materials and methods

The pot experiment was set up in 2006 according to the design comprising the following combinations:

A. Control treatment:
  1 – soil with natural lithium and organic matter contents,
  2 – soil with a supplement of 10 mg Li · pot^{-1} with natural content of organic matter,
  3 – soil with a supplement of 20 mg Li · pot^{-1} with natural content of organic matter,
B. Treatments with increasing lithium and organic matter supplements (as compost):
  4 – with 10 mg Li · pot^{-1} and 26 g of organic matter,
  5 – with 20 mg Li · pot^{-1} and 26 g of organic matter,
  6 – with 10 mg Li · pot^{-1} and 52 g of organic matter,
  7 – with 20 mg Li · pot^{-1} and 52 g of organic matter,
  8 – with 10 mg Li · pot^{-1} and 78 g of organic matter,
  9 – with 20 mg Li · pot^{-1} and 78 g of organic matter.

Soil collected from the topsoil of arable lands with properties of weakly loamy sand (Table 1) was used for the pot experiment.

Table 1

Properties of the soil

pH		Hh [mol H$^{(+)}$ · kg^{-1}]	Organic C [%]	Share of fractions [%]	
H_2O	KCl			< 0.02 mm	< 0.002 mm
5.96	5.59	33.2	1.32	7	2

PVC pots in the control series were filled with air-dried soil – 3.5 kg soil per pot. 26, 52 and 78 g of compost (called organic matter) with known chemical composition (Table 2) were weighed and added to selected series according to the design and supplemented with the soil to 3.5 kg.

Table 2

Some properties of compost

Specification	Unit	Value
Dry matter	[%]	44.19
Organic matter	[% d.m.]	55.69
pH (H_2O)	—	7.34
Total content		
Ca	[g · kg^{-1} d.m.]	22.2
Mg		6.5
Li	[mg · kg^{-1} d.m.]	6.25
Zn		159.2
Mn		233.8
Fe		3851.2

Several days before maize sowing basic fertilization with chemically pure salts was used on all treatments with: 0.8 g N as NH_4NO_3, 0.15 g P as KH_2PO_4, 0.9 g K as KH_2PO_4 and 0.1 g Mg as $MgSO_4 \cdot 7H_2O$. At the same time lithium chloride (LiCl) was added to selected treatments in doses of 10 and 20 mg Li per pot. The experiment was conducted in four replications. After emergence the plants were thinned and 5 plants were left per pot for further vegetation. Maize (*Zea mays* L.) plants were watered with distilled water and the soil moisture was maintained on the level of 50 % in the initial period and later on the 60 % of maximum capillary water capacity. Maize was harvested after 9-week period of vegetation and plants were divided into individual parts (roots, stalks and leaves). After the vegetation period was completed in mid-August, the pots were sown again with rye (*Secale cereale* L.). After 7-week vegetation period the plants were harvested and divided into roots and the aboveground parts. Collected plants material of maize and rye was dried at 80 ^{o}C, weighed and the obtained results were subjected to statistical analysis. The plant material was ground, dry mineralized and the obtained ashes were dissolved in HNO_3 acid (1:2). Lithium content in the obtained solutions was assessed using emission spectrometry with inductively coupled plasma (ICP-AES) on JP 238 apparatus (Jobin-Yvon).

Results and discussion

Maize

Both 10 and 20 mg doses of Li · pot^{-1} used in the experiment caused a decline in root yield in comparison with the control treatment, but they not unanimously affected the amount of maize stalks and leaves yield (Table 3).

Assuming eg maize root yield on the control treatment with natural lithium content as 100, it may be noticed that the root yield on treatment receiving 10 mg Li per pot was smaller by 4.5 %, whereas with the dose of 20 mg Li · pot^{-1} by 14 %. Application of increasing doses of organic matter: 26, 52 and 78 mg · pot^{-1} caused the increase in maize root yield but the effect was not unambiguous for the aerial parts. Assuming eg the treatment with 20 mg Li · pot^{-1} as the control treatment = 100, it may be concluded that on the treatments with the same levels of lithium, increasing doses of organic matter, ie 26, 52 and 78 g · pot^{-1} caused an increase in yield by 30 %. Percentage of individual parts in total maize yield was as follows: 20–24 % root yield, 32–38 stalk yield, 41–46 % leaf yield (Table 3).

Table 3

Maize yields (roots, stalks and leaves) [g d.m. · pot^{-1}]

Series	Li supplement [mg · pot^{-1}]	Dose of organic matter [g · pot^{-1}]	Roots	Aboveground parts		
				Stalks	Leaves	Total
1	0	0	17.39	27.02	32.16	59.18
2	10	0	16.63	28.69	33.14	61.03
3	20	0	15.17	28.62	32.44	61.06
4	10	26	16.48	27.43	33.54	60.97
5	20	26	19.79	30.58	35.57	66.15
6	10	52	18.70	31.08	34.86	65.94
7	20	52	20.46	26.63	37.34	63.97
8	10	78	18.21	25.83	37.91	63.74
9	20	78	19.95	27.58	38.04	65.62
$LSD_{0.05}$			1.01	1.35	1.21	—

Numerous investigations have shown that the uptake and contents of trace elements by plants, including lithium, are determined by a number of factors which may stimulate or limit the contents and uptake of lithium [8–10].

Brumer at al (quoted after [11]) described phytoavailability of individual elements in soil is determined by their concentration in the soil solution, their quantitative interrelations and the rate of component flow between solid and liquid soil phase. Lithium applied in the amounts of 10 and 20 mg Li · pot^{-1} caused an apparent increase in this element contents in all analyzed maize parts (Table 4).

Table 4

Lithium content in maize [mg Li · kg^{-1} d.m.]

Series	Li supplement [mg · pot^{-1}]	Dose of organic matter [g · pot^{-1}]	Roots	Stalks	Leaves
1	0	0	3.25	0.37	0.85
2	10	0	31.69	1.55	2.08
3	20	0	69.70	3.84	6.32
4	10	26	26.90	1.38	2.09
5	20	26	51.06	3.09	4.91
6	10	52	20.38	1.57	1.82
7	20	52	50.4	3.21	5.71
8	10	78	20.03	1.47	2.34
9	20	78	54.6	3.39	6.13

Assuming lithium content in maize on the control treatment with natural content of this element as 1, one may see that application of 10 mg Li · pot^{-1} caused a ten-fold increase in this element root concentrations, whereas with 20 mg Li · pot^{-1} dose the increase was about twenty-fold. A similar relationship occurred for maize aerial parts where at the dose of 10 mg Li · pot^{-1} this element content raised four-fold in stalks and 2.5-fold in leaves, whereas at the dose of 20 mg Li · pot^{-1} 10-fold and 7.5-fold, respectively.

Growing doses of organic matter 26, 52 and 78 g · pot^{-1} more or less distinctly affected this element contents both in maize roots and aboveground parts in the treatments where lithium was applied (Table 4).

Assuming eg lithium content in maize roots on the control (10 mg Li · pot^{-1}) as 100, it may be observed that application of 25, 52 and 78 g · pot^{-1} of organic matter on the treatments with the same lithium level decreased this element content in roots by 15 %, 35 % and 36 %, in stalks by 10 %, whereas in leaves by 5 % and 12 %. A similar relationship was observed when a bigger lithium dose was applied.

Patorczyk-Pytlik [12] revealed that the content and uptake of microelements by plants on the treatments where organic materials were applied declined in comparison with mineral treatments.

The amount of absorbed trace elements including lithium is determined by a number of factors, such as: the soil abundance in available forms, soil pH, kind of soil microflora or relationships between individual elements in the soil solution.

The amount of lithium taken up by maize roots on the control treatment with natural lithium content was 56.52 μg Li · pot^{-1} (Table 5). Application of 10 and 20 mg Li · pot^{-1} led to an apparent increase in this element uptake. The quantity of this element absorbed by roots on the treatment where 10 mg Li · pot^{-1} was added increased about 9-fold, whereas at the dose of 20 mg Li · pot^{-1} it rose about 18-fold in comparison with the control treatment with the natural content of this element.

Table 5

Uptake of lithium [μg Li · pot^{-1}] and its distribution in maize

Series	Li addition [mg · pot^{-1}]	Dose of organic matter [g · pot^{-1}]	Roots	Stalks	Leaves	Total	Li distribution [%]		
							Roots	Stalks	Leaves
1	0	0	56.52	22.91	12.03	91.46	61.80	25.05	13.15
2	10	0	527.01	59.59	51.33	637.93	82.61	9.34	8.05
3	20	0	1057.35	180.74	124.15	1362.24	77.62	13.27	9.11
4	10	26	443.31	57.55	46.29	547.15	81.02	10.52	8.46
5	20	26	1010.48	149.99	109.91	1270.38	79.54	11.81	8.65
6	10	52	381.11	56.69	54.63	492.42	77.39	11.51	11.09
7	20	52	1031.18	152.06	119.86	1303.10	79.13	11.67	9.20
8	10	78	364.75	60.44	55.65	480.84	75.86	12.57	11.57
9	20	78	1089.27	169.07	128.96	1387.29	78.52	12.19	9.30

Application of 26, 52 and 78 g · pot^{-1} of organic matter more or less decreased the amount of lithium absorbed by maize. Increasing doses of organic matter on the treatments where a dose of 10 mg Li · pot^{-1} was applied, diminished the quantity of the element taken up by maize roots by 16 %, 28 % and 31 % in comparison with the control treatment. The influence of organic matter on the quantity of lithium absorbed by maize plants at a higher lithium dose 20 mg Li · pot^{-1} was less pronounced.

On the treatments with raised lithium contents, ie 20 mg Li · pot^{-1} the amount of lithium taken up by maize stalks was smaller by 17 %, 16 % and 6 % in comparison with the control. On the other hand, the dose had no significant influence on the amount of element absorbed by maize leaves. Total lithium uptake by maize = (uptake by roots + stalks + leaves) depended on the crop yield, the content of this cation in individual maize parts and on the doses of organic matter and lithium. On the control treatment with natural lithium content in soil, the share of lithium absorbed by individual parts of the maize plant was as follows: 62 % occured in roots, 25 % in stalks and 13 % in leaves. On the treatments where increasing lithium doses, ie 10 and 20 mg Li · pot^{-1} were used, the share of lithium accumulated in maize roots ranged between 76 and 83 %, in stalks between 9 and 13 %, and in leaves between 8 and 12%. The effect of organic matter was also visible in the case of distribution of lithium absorbed by maize (Table 5).

Rye

Doses of 10 and 20 mg Li · pot^{-1} not unanimously affected the amount of obtained rye yield (Table 6).

Table 6

Yields of rye (roots and aerial parts) [g d.m. · pot^{-1}]

Series	Li addition [mg · pot^{-1}]	Dose of organic matter [g · pot^{-1}]	Roots	Aboveground parts
1	0	0	2.11	2.14
2	0	0	2.02	1.96
3	0	0	2.33	2.28
4	10	26	2.02	2.24
5	20	26	2.30	2.42
6	10	52	2.41	2.54
7	20	52	2.56	2.56
8	10	78	2.55	2.63
9	20	78	2.26	2.73

Assuming eg the amount of rye aboveground parts crop obtained on control with natural content of this element as 100, it may be founded that a dose of 10 mg Li · pot^{-1} decreased the yield of rye aerial parts by 8 %, whereas 20 mg Li · pot^{-1} led to its increase by 7 %. A similar relationship was observed for rye roots yield. Increasing doses of organic matter, irrespective of lithium dose more or less influenced the amount of rye aftercrop. Assuming eg rye aboveground part yield obtained with a dose of 10 mg

Li · pot^{-1} on the control as 100, it may be noticed that growing doses of organic matter 26, 52 and 78 g · pot^{-1} caused the increase in the yield of aerial parts by 14 %, 30 % and 34 %, respectively.

Application of 10 mg Li · pot^{-1} caused about two-fold increase in this element content in rye aboveground parts, whereas about 9-fold raise, as compared with the treatment with the natural content of this element, was registered at the dose of 20 mg Li · pot^{-1}. Similar dependencies occur for rye roots (Table 7).

Table 7

Lithium contents in rye [mg Li · kg^{-1} d.m.]

Series	Li addition [mg · pot^{-1}]	Dose of organic matter [g · pot^{-1}]	Roots	Aboveground parts
1	0	0	2.741	1.690
2	0	0	5.149	3.813
3	0	0	15.740	14.487
4	10	26	4.518	3.250
5	20	26	13.358	12.418
6	10	52	4.762	3.538
7	20	52	14.137	12.025
8	10	78	4.875	3.740
9	20	78	15.175	13.800

Application of increasing organic matter doses of 26, 52 and 78 g · pot^{-1} not ambiguously affected a decrease in lithium content in rye roots and aboveground parts, irrespectively of the supplied lithium dose. Application of increasing doses of organic matter on the treatments receiving 20 mg Li · pot^{-1} influenced a decrease in rye aboveground parts by 14%, 17% and 5% in comparison with the control.

The residual effect of supplied increasing lithium doses caused an increased uptake of this cation by rye in relation to control treatments with natural lithium content in soil (Table 8).

Table 8

Uptake of lithium [μg Li · pot^{-1}] and lithium distribution in rye

Series	Li addition [mg · pot^{-1}]	Dose of organic matter [g · pot^{-1}]	Roots	Tops	Total	Li distribution [%]	
						Roots	Tops
1	0	0	5.770	3.615	9.38	61.48	38.55
2	10	0	10.298	7.473	17.77	57.95	42.05
3	20	0	36.674	33.030	69.70	52.61	47.39
4	10	26	9.126	7.280	16.41	55.63	44.37
5	20	26	31.658	30.052	61.71	51.30	48.70
6	10	52	11.476	8.976	20.45	56.11	43.89
7	20	52	36.191	30.784	66.97	54.04	45.96
8	10	78	13.431	9.360	22.27	55.83	44.17
9	20	78	43.401	37.771	81.17	53.47	46.53

On the control treatment with natural content of this element in soil the amount of lithium absorbed by rye roots was 5.770 μg Li · pot^{-1}. The residual effect of 10 mg Li · pot^{-1} lithium dose caused about two-fold increase in its uptake by rye roots and after application the dose of 20 mg Li · pot^{-1} the growth was about 6-fold. On the other hand, lithium uptake with the yield of aboveground parts was raised two-fold and 9-fold, respectively, in comparison with the control. Growing doses of organic matter; 26, 52 and 78 g · pot^{-1} had a not ambiguous effect on the amount of lithium absorbed both by roots and aboveground parts of rye. Assuming the total lithium uptake (uptake by roots and by the aboveground parts) by rye on the control with natural Li content in soil as 100 %, it is obvious that 61.48 % of the absorbed lithium was in the roots and 38.55 % in the aboveground parts. On treatments enriched in this element, the share of absorbed lithium in rye roots fluctuated from 51 % to 58 % and in the aboveground parts from 42 to 49 %.

On the basis of pot experiment on sunflower and oil radish as the aftercrop grown in the soil with natural content of cadmium and in the soil purposefully polluted with this metal Gambus and Gorlach [13] found that liming and application of farmyard manure most efficiently limited cadmium bioavailability. Straw, brown coal and natural zeolite placed next in this respect.

Conclusions

1. Increasing doses of lithium: 10 and 20 mg Li · pot^{-1} applied in a soluble form caused an increase of the contents and uptake of this element by individual parts of maize and rye.
2. Increasing doses of organic matter (compost) applied in the doses of 26, 52 and 78 g · pot^{-1} caused a restriction of the content and uptake of lithium by maize and rye and influenced this element distribution in the individual plant organs.
3. Increasing lithium doses caused that a considerable portion of absorbed Li was blocked in maize roots, whereas the amount of absorbed element increases in rye aerial parts, which evidences its transport from roots to the aboveground parts.

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WPŁYW WŁAŚCIWOŚCI GLEBY A FITOPRZYSWAJALNOŚĆ LITU
Cz. 1. ZAWARTOŚĆ I POBRANIE LITU PRZEZ KUKURYDZĘ ORAZ ŻYTO

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Abstrakt: Zastosowane w doświadczeniu wazonowym wzrastające dawki litu, tj. 10 i 20 mg Li · wazon^{-1}, spowodowały zmniejszenie plonu korzeni w stosunku do obiektu kontrolnego, natomiast niejednoznacznie wpłynęły na ilość plonu łodyg i liści kukurydzy. Zastosowane wzrastające dawki materii organicznej w ilościach 26, 52, 78 g · wazon^{-1} spowodowały wzrost plonu korzeni kukurydzy, natomiast w przypadku części nadziemnych wpływ ten był niejednoznaczny. Udział poszczególnych części w plonie całkowitym kukurydzy przedstawiał się następująco: plon korzeni stanowił 20–24 %, łodyg 32–38 % i liści 41–46 %.

Zastosowanie litu w ilości 10 i 20 mg Li · wazon^{-1} spowodowało wyraźny wzrost zawartości tego pierwiastka we wszystkich analizowanych częściach kukurydzy. Przyjmując np. zawartość litu w korzeniach kukurydzy w obiekcie kontrolnym o naturalnej zawartości tego pierwiastka w glebie za 1, to zastosowanie dawki 10 mg Li · wazon^{-1} spowodowało około 10-krotny wzrost zawartości tego pierwiastka w korzeniach kukurydzy, natomiast po dodaniu do gleby 20 mg Li · wazon^{-1} wzrost był około 20-krotny. Podobna zależność wystąpiła w częściach nadziemnych. Wzrastające dawki materii organicznej 26, 52, 78 g · wazon^{-1} w obiektach, w których zastosowano lit, wpływały mniej lub bardziej wyraźnie na zawartość tego pierwiastka tak w korzeniach, jak i w częściach nadziemnych kukurydzy.

Zastosowanie Li w ilości 10 i 20 mg Li · wazon^{-1} spowodowały wyraźny wzrost pobrania tego pierwiastka. Ilość pobranego pierwiastka przez korzenie w obiekcie, w którym zastosowano 10 mg Li · wazon^{-1}, wzrosła około 9-krotnie, natomiast dawka 20 mg Li · wazon^{-1} spowodowała około 18-krotny wzrost w odniesieniu do obiektu kontrolnego o naturalnej zawartości tego pierwiastka w glebie. Podobna zależność wystąpiła w przypadku częściach nadziemnych.

Dodatek materii organicznej w dawkach 26, 52, 78 g · wazon^{-1} powodował mniej lub bardziej wyraźne obniżenie ilości pobranego litu przez kukurydzę. Wzrastające dawki materii organicznej w obiektach, w których zastosowano litu w dawce 10 mg Li · wazon^{-1}, ilość pobranego pierwiastka przez korzenie kukurydzy była mniejsza odpowiednio o 16 %, 28 % i 31 % w stosunku do obiektu kontrolnego.

Dawki litu wpływały w sposób niejednoznaczny na wielkość uzyskanego plonu korzeni i części nadziemnych żyta. Wzrastające dawki materii organicznej, niezależnie od poziomu litu w glebie, powodowały wzrost poplonu części nadziemnych żyta. Następczy wpływ zastosowanych dawek litu spowodował wzrost zawartości tego pierwiastka w częściach nadziemnych i korzeniach żyta oraz wzrost pobrania tego kationu. Wzrastające dawki materii organicznej w ilościach 26, 52, 78 g · wazon^{-1} ograniczały w różnym stopniu ilość pobranego litu zarówno przez korzenie, jak i w części nadziemne żyta.

Słowa kluczowe: zawartość i pobranie litu, zanieczyszczenie gleby, właściwości gleby, kukurydza, żyto

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USEFULNESS OF DIFFERENT EXTRACTION SOLUTIONS FOR DETERMINATION OF PLANT AVAILABILITY OF HEAVY METALS

PRZYDATNOŚĆ RÓŻNYCH ROZTWORÓW EKSTRAKCYJNYCH DO OZNACZANIA FITOPRZYSWAJALNOŚCI METALI CIĘŻKICH

Abstract: the objective of the study was to evaluate usefulness of different extraction solutions for determination of plant availability of heavy metals. The results obtained indicated relationships between the amounts of Cd, Cu, Pb and Zn extracted, soil physical-chemical properties and extraction solution used. In general, lesser amounts of examined metals were extracted from light soil than from medium soil. The amounts of heavy metals extracted with the use of all examined methods increased with an increase of soil acidity and a level of soil pollution with heavy metals, however it generally decreased with an increase of organic carbon in soil. A strong positive correlation between the contents of Cd, Cu, Pb and Zn in plants and the amounts of heavy metals extracted from soil was observed. The higher values of correlation coefficients were obtained when soft extraction solutions (soil solution and 0.01 mol $\cdot$ dm^{-3} $CaCl_2$) were used when compared with strong extraction solutions (1 mol $\cdot$ dm^{-3} HCl and *aqua regia*).

Keywords: heavy metals, extraction solutions, soil properties, plant availability

Increasing pollution of natural environment with heavy metals as a result of civilization development often leads to excessive accumulation of these elements in the food chain: soil-plant-animal-man. The properties of soil, which is the first link in this system, significantly affect the extent and speed of allocation of trace elements in the food chain.

Determination of availability of trace elements for plants is essential for evaluation of their toxicity for potential consumers. This is performed by chemical tests – soil extractions. A level of soil pollution with heavy metals has so far been determined

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based on their total contents [1]. However, this method is not accurate enough as the total content of heavy metals in soil includes a variety of their forms with different solubility and mobility. Furthermore, there exist a large number of soil factors of great changeability that can significantly influence biological availability of heavy metals [2]. Therefore, evaluation of the content of soluble forms of heavy metals, ie biologically available, would be more suitable for agricultural needs and precise assessment of contamination of cultivated plants with heavy metals [3].

The objective of this study was to examine usefulness of selected extraction solutions for determination of plant availability of heavy metals.

Materials and methods

The study was carried out in the years 2006–2007 in natural climatic conditions. Microplot experiments were conducted at the Experimental Station of the Agriculture and Biology Faculty of Warsaw University of Life Sciences located close to the city of Skierniewice. Ground vases dug in soil in open air were treated as microplots. Soil in the ground vases was differentiated by 3 pH levels (4.0, 5.0 and 6.0), 3 levels of organic C (0.6, 0.9 and 1.2 %), 2 contents of fraction below 0.02 mm (15 and 30 %) and 4 levels of the content of heavy metals: equivalent to the content in natural conditions (pollution of 0^{o}), increased content (pollution of I^{o}), weak pollution (II^{o}), and medium pollution (III^{o}), according to Kabata-Pendias et al [1]. The experiments embraced 216 microplots that altogether formed 72 combinations. The radish (*Raphanus sativus* L.) and the Chinese cabbage (*Brassica rapa* L. subsp. *pekinensis*) were used as experimental plant.

The content of Cu, Cd, Pb and Zn was determined in soil samples with the use of the following methods: the analysis of heavy metals in soil solution and extraction with the use of:

– *aqua regia*,
– HCl at a concentration 1 mol $\cdot$ dm^{-3},
– CH_3COONH_4 at a concentration of 1 mol $\cdot$ dm^{-3},
– $CaCl_2$ at a concentration of 0.01 mol $\cdot$ dm^{-3}.

Soil solutions were obtained with the use of the vacuum displacement method [4]. The contents of heavy metals in soil extracts and solutions were determined with the use of the AAS method. After mineralization of plant material samples in a mixture of concentrated acids HNO_3, $HClO_4$ and H_2SO_4 the total contents of zinc, cadmium, copper and lead were determined with the use of AAS.

Statistical analysis of obtained results concerned the multifactorial variance analysis and simple regression. The analysis were made for all 216 observations and two tested plants.

Results and discussion

The amount of elements extracted from soil was significantly linked with physical-chemical properties of soil and a degree of heavy metal pollution. Of all examined soil properties, a degree of heavy metal pollution and soil reaction had the strongest effects on amounts of heavy metals extracted with the use of examined solutions (Tables 1–4).

As a rule, lower amounts of Pb, Cd, Cu and Zn were extracted from light soil when compared with medium soil (Table 1). The content of organic carbon had no statistically proven significant effect on amounts of heavy metals extracted with the use of examined solutions (Table 1). Nevertheless, with an increase of organic carbon in soil there was observed dropping off content of heavy metals extracted with examined solutions (Table 2). On the other hand, the amounts of extracted heavy metals enlarged with an increase of soil pollution with these elements (Table 3).

Table 1

The average content of heavy metals [mg · kg^{-1} d.m. of soil] in relation to the soil category and the extraction method used

Soil category	Cd					Cu				
	Extraction method									
	1	2	3	4	5	1	2	3	4	5
Light	0.88	0.71	0.19	0.07	0.0004	43.72	37.60	0.54	0.12	0.03
Medium	1.08	0.93	0.28	0.11	0.0005	48.86	40.65	0.64	0.15	0.03
LSD$_{0.05}$	0.101	0.097	0.036	0.023	0.0001	5.070	5.070	3.986	0.131	0.001
	Pb					Zn				
Light	80.07	75.76	3.79	0.04	0.002	98.03	57.47	9.25	4.77	0.07
Medium	89.84	83.99	4.60	0.06	0.008	135.6	77.85	11.95	8.50	0.11
LSD$_{0.05}$	5.508	4.815	1.289	0.035	0.001	12.88	6.601	2.722	3.436	0.009

Explanation for Tables 1–4: Extraction method: 1 – *aqua regia*; 2 – HCl 1 mol · dm^{-3}; 3 – CH$_3$COONH$_4$ 1 mol · dm^{-3}; 4 – CaCl$_2$ 0.01 mol · dm^{-3}; 5 – soil solution.

Table 2

The average content of heavy metals [mg · kg^{-1} d.m. of soil] in relation to the content of organic carbon in soil and the extraction method used

Organic C [%]	Cd					Cu				
	Extraction method									
	1	2	3	4	5	1	2	3	4	5
0.6	1.02	0.85	0.24	0.12	0.0005	48.03	40.62	0.89	0.14	0.03
0.9	0.97	0.77	0.23	0.09	0.0004	47.99	40.95	0.47	0.13	0.03
1.2	0.95	0.83	0.22	0.06	0.0003	42.85	35.82	0.41	0.12	0.02
LSD$_{0.05}$	0.124	0.118	0.052	0.028	0.0001	6.207	5.865	0.192	0.032	0.001
	Pb					Zn				
0.6	90.59	86.26	4.36	0.10	0.003	121.9	70.04	11.37	7.99	0.13
0.9	85.77	79.70	4.29	0.03	0.002	117.9	67.93	11.22	6.93	0.09
1.2	78.50	73.68	3.93	0.02	0.001	110.7	65.00	9.21	4.98	0.04
LSD$_{0.05}$	8.121	7.083	1.578	0.044	0.0008	18.95	9.711	4.005	2.055	0.01

Table 3

The average content of heavy metals [$mg \cdot kg^{-1}$ d.m. of soil] in relation to a level of soil pollution and extraction method used

Pollution degree	Cd					Cu				
	Extraction method									
	1	2	3	4	5	1	2	3	4	5
0	0.26	0.11	0.15	0.07	0.0001	7.77	3.65	0.14	0.05	0.01
I	0.62	0.49	0.21	0.08	0.0003	28.04	21.66	0.27	0.10	0.02
II	1.03	0.87	0.26	0.10	0.0004	54.23	45.22	0.64	0.16	0.03
III	2.01	1.80	0.31	0.11	0.0007	95.11	85.98	1.30	0.21	0.04
$LSD_{0.05}$	0.189	0.180	0.050	0.045	0.00008	9.465	7.445	0.243	0.041	0.006
	Pb					Zn				
0	14.05	12.26	0.28	0.02	0.0006	47.45	16.96	3.02	1.46	0.04
I	52.38	48.35	1.37	0.04	0.0010	85.74	48.36	5.03	3.02	0.08
II	92.80	88.11	3.17	0.06	0.0020	125.3	83.36	9.49	6.11	0.09
III	180.6	170.8	11.97	0.08	0.0030	208.8	121.9	24.85	15.95	0.14
$LSD_{0.05}$	10.64	10.28	1.822	0.051	0.0002	24.05	12.32	3.850	1.010	0.008

The content of microelements in soil including heavy metals is associated with the soil agronomic type and content of soluble forms of these elements increases in soil together with an increase of the content of leachates [3, 5].

Solubility of heavy metals decreases with an increase of the content of organic carbon in soil [3]. Then again, as found by Diatta and Grzebisz [6], the content of organic carbon in soil is not a reliable and steady factor that has an effect on the content of Zn, Pb and Cd extracted from soil with the use of different solutions.

Many authors have reported that soil reaction is the most important factor to determine solubility of heavy metals in soil [3, 7–9]. The results of this study indicated a significant negative effect of soil reaction on amounts of heavy metals extracted from soil with the use of CH_3COOH at a concentration 1 $mol \cdot dm^{-3}$, $CaCl_2$ at a concentration 0.01 $mol \cdot dm^{-3}$ as well as with soil solution. On the other hand, amounts of metals extracted with the use of *aqua regia* and HCl at a concentration 1 $mol \cdot dm^{-3}$ did not depend on soil reaction (Table 4). Gambus and Rak [8] showed that together with an increase of soil pH, strong extraction solutions release bigger amounts of cadmium. However, this relation was reversed when soft extraction solutions were applied. Similar relations were observed by Gediga [9] in the case of manganese.

The biggest amounts of examined heavy metals were extracted from soil with the use of *aqua regia* when compared with the effects of other examined extraction methods. The amounts of heavy metals extracted with the use of HCl at a concentration 1 $mol \cdot dm^{-3}$ were: for Pb from 73 to 99 %, for Cd from 25 to 99 %, for Cu from 35 to

99 % and for Zn from 24 to 90 % of the total content of these elements in soil (ie of the amounts extracted with the use of *aqua regia*).

Table 4

The average content of heavy metals [mg · kg^{-1} d.m. of soil] in relation to soil reaction and the extraction method used

pH	Cd					Cu				
	Extraction method									
	1	2	3	4	5	1	2	3	4	5
6.0	0.80	0.66	0.22	0.06	0.0002	43.63	36.59	0.46	0.11	0.02
5.0	1.04	0.86	0.23	0.10	0.0003	45.56	38.57	0.62	0.12	0.03
4.0	1.10	0.93	0.24	0.12	0.0006	49.68	42.22	0.68	0.17	0.04
$LSD_{0.05}$	0.349	0.246	0.044	0.033	0.0001	7.456	6.882	0.159	0.027	0.007
	Pb					Zn				
6.0	84.10	79.19	2.87	0.03	0.0006	110.2	60.30	7.09	2.49	0.04
5.0	85.69	79.56	3.50	0.06	0.0010	117.6	67.53	8.96	5.25	0.08
4.0	85.07	80.89	6.21	0.07	0.0040	125.3	71.15	15.75	12.17	0.15
$LSD_{0.05}$	8.283	7.998	1.869	0.022	0.0002	15.77	8.085	3.334	2.208	0.009

When compared with their total contents (ie the amounts extracted with the use of *aqua regia*), the quantities of heavy metals extracted from soil with the use of CH_3COONH_4 solution were: 10–70 % of the total content of Cd, 1–15 % of Pb, 1–4 % of Cu and from 2 do 25 % of the total content of Zn in soil. When $CaCl_2$ at a concentration 0.01 mol · dm^{-3} was used the amounts Cd, Pb and Cu extracted were below 1 % of their total content in soil. In contrast, the amount of Zn extracted with the use of calcium chloride ranged from 1 to 18 % of the total content of this element in soil. The amounts of examined metals determined with the use of soil solution constituted just about fractions of the percent when compared with their total contents in soil. Gambus et al [10] showed that strong extraction solutions, such as HCl at a concentration 1 mol · dm^{-3} released into the filtrate a big fraction of soil metals, such as Cu, Ni and Zn. On the other hand, unbuffered solutions, such as $CaCl_2$ at a concentration 0.01 mol · dm^{-3} or NH_4NO_3 at a concentration 1 mol · dm^{-3} extracted at most 1.1 % of examined metals. Similar relations were observed for manganese by Gediga [9] as well as by Gambus and Rak [8] in the case of cadmium.

The results obtained showed a significant decrease of yield in both tested plant species with an increase of soil pollution with heavy metals. At the same time, the content of heavy metals in plants significantly increased with an increase of soil pollution with heavy metals (Table 5).

The results of the analysis of correlation coefficients between the amounts of heavy metals in plants and soil indicated that the amounts of heavy metals in plants were positively correlated with the amounts of these elements extracted from soil with the use of different extraction methods (Table 6).

Table 5

Yield of examined plant species [g d.m.] and their content of heavy metals [mg · kg^{-1} d.m.] in relation to soil pollution with heavy metals

Pollution degree	Chinese cabbage					Red radish				
	yield	Cd	Cu	Pb	Zn	yield	Cd	Cu	Pb	Zn
0°	1023.0	0.23	9.50	2.63	59.1	710.2	0.09	0.18	1.24	6.81
I°	730.0	0.52	12.18	3.58	108.7	543.0	0.29	0.43	4.22	17.62
II°	507.1	0.88	15.10	6.27	150.6	431.7	0.30	0.57	4.23	22.44
III°	132.3	1.34	19.03	8.40	241.8	175.2	0.37	0.70	5.53	23.27
$LSD_{0.05}$	44.43	0.112	0.336	1.290	11.56	113.10	0.031	0.076	0.910	1.269

Table 6

Correlation coefficients (r) between the content of heavy metals in soil and amounts of these metals in plants

Extraction method	Cd	Cu	Pb	Zn
Aqua regia	0.64	0.78	0.75	0.71
HCl 1 mol · dm^{-3}	0.70	0.77	0.74	0.74
CH_3COONH_4 1 mol · dm^{-3}	0.73	0.70	0.81	0.72
$CaCl_2$ 0.01 mol · dm^{-3}	0.87	0.80	0.85	0.74
Soil solution	0.91	0.81	0.87	0.79

The higher values of correlation coefficients were obtained for soft extraction solutions (soil solution and $CaCl_2$) than for stronger ones (HCl and *aqua regia*). On the other hand, Gambus et al [10] showed that strong extraction solutions that released big amounts of copper were also very good indicators of plant availability of this metal, contradictory to soft extraction solutions. The results of Gambus and Rak [8] indicated that soft extraction solutions (eg $CaCl_2$ at a concentration 0.01 mol · dm^{-3}) were most useful for evaluation of plant available forms of cadmium. Furthermore, HCl solution at a concentration 1 mol · dm^{-3} was completely ineffectual in determination of plant availability of cadmium. Burzynska and Sapek [11] showed greater usefulness of $CaCl_2$ at a concentration 0.01 mol mol · dm^{-3} for evaluation of plant available forms of zinc than that of HCl at a concentration 1 mol · dm^{-3}.

Conclusions

1. The amounts of heavy metals (Cd, Cu, Pb and Zn) extracted from soil depended on extraction solution used and soil physical-chemical properties. In general, lesser amounts of examined metals were extracted from light soil than from medium soil. A decrease of the amounts of heavy metals extracted with the use of examined extraction solutions was observed with an increase of organic carbon in soil.

2. The amounts of heavy metals extracted from soil decreased with a reduction of extraction power of solutions used as follows: *aqua regia* > HCl > CH_3COONH_4 > > $CaCl_2$ > soil solution.

3. The content of examined heavy metals in plants was strongly positively correlated with the amounts of heavy metals obtained with examined extraction methods. At the same time, the higher values of correlation coefficients were obtained when soft extraction solutions (soil solution and 0.01 mol $\cdot$ dm^{-3} $CaCl_2$) were used when compared with strong extraction solutions (1 mol $\cdot$ dm^{-3} HCl and *aqua regia*).

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PRZYDATNOŚĆ RÓŻNYCH ROZTWORÓW EKSTRAKCYJNYCH DO OZNACZANIA FITOPRZYSWAJALNOŚCI METALI CIĘŻKICH

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Abstrakt: Celem pracy było określenie przydatności różnych roztworów ekstrakcyjnych do oceny fitoprzyswajalności metali ciężkich.

Przeprowadzone badania wykazały zależność pomiędzy ilością Cd, Cu, Pb i Zn ekstrahowanych z gleby a jej właściwościami fizyczno-chemicznymi oraz zastosowanym roztworem ekstrakcyjnym. Z gleby lekkiej ekstrahowano zazwyczaj mniejsze ilości badanych metali niż z gleby średniej. Ilość badanych pierwiastków ekstrahowanych z gleby wszystkimi analizowanymi metodami zwiększała się wraz ze wzrostem zakwaszenia gleby oraz wraz ze wzrostem stopnia zanieczyszczenia gleby metalami, a zazwyczaj zmniejszała się wraz ze wzrostem zawartości węgla organicznego w glebie. Zaobserwowano silną dodatnią korelację pomiędzy zawartością Cd, Cu, Pb i Zn w roślinie a ilością metali ciężkich ekstrahowanych z gleby. Większe wartości współczynników korelacji otrzymano dla ekstrakcji przy użyciu słabych ekstrahentów (roztwór glebowy i 0,01 mol $\cdot$ dm^{-3} $CaCl_2$) niż w przypadku mocnych roztworów ekstrakcyjnych (1 mol $\cdot$ dm^{-3} HCl i woda królewska).

Słowa kluczowe: metale ciężkie, roztwory ekstrakcyjne, właściwości gleby, dostępność dla roślin

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EFFECT OF POST-AGRICULTURAL SOILS AFFORESTATION ON ZINC AND LEAD SOLUBILITY

WPŁYW ZALESIENIA GLEB POROLNYCH NA ROZPUSZCZALNOŚĆ CYNKU I OŁOWIU

Abstract: Afforestation of post-arable soils changes their properties including reaction, organic matter and dissolved organic carbon content – the key factors in binding/mobilization of trace metals. However, the extensive literature reviews the impacts of afforestation of former arable soils on their properties, there is only limited knowledge on the trace metals behavior in response to such a shift of land use. This study presents the results concerning the effect of afforestation with Scots pine (*Pinus sylvestris* L.) of rusty (Distric Arenosols) post-arable soils formed on water-glacial sands on Zn and Pb solubility measured by their concentration in soil solution and a share in this phase in relation to the total content in soil. Soils under 14–17 years and 32–36 years old stands were compared with neighboring arable soils, five pairs each group. The soil samples were taken from the whole thickness of master horizons and, in the case of the A horizon of the afforested soils, from three layers: 0–5 (A_{0-5}), 5–10 (A_{5-10}) and 10–20 cm (A_{10-20}).

Zinc concentration in soil solution, both in mg · dm^{-3} and in percent in relation to the total soil content proved to be higher in the afforested soils than in the respective arable soils and was soil pH-dependent. The differences increased with the stand age. As for Pb, no such clear relationships were found.

Keywords: afforestation, post-agricultural soil, lead, zinc, solubility

Afforestation of post-agricultural soils has been one of the major land-use changes in many European countries in the recent decades [1–4]. It induces some changes in most of the soil properties: organic matter, pH, content of nitrogen and other elements, porosity, bulk density and biological activity [5–9]. Many of them, such as, pH and acidity, solid and dissolved organic carbon levels constitute the crucial factors affecting the retention/mobilization of trace metals present in a soil [10–13].

The vast available literature has put focus on the effect of afforestation of former agricultural land on soil properties but the impact of such land-use change on the behavior of trace elements still remains unclear. Therefore, as part of a study comparing

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post-arable sandy soils planted with Scots pine with arable soils, the effect of afforestation on the mobility of selected trace metals has been investigated.

The objective of this study was to determine the impact of afforestation of rusty (Distric Arenosols) post-arable soils on Zn and Pb solubility measured by their concentration in soil solution and a share in this phase in relation to the total content in the soil.

Material and methods

The present studies were conducted in the Lublin region. Ten paired sites of the afforested with Scots pine (*Pinus sylvestris* L.) former arable soils with adjacent cultivated fields were selected for the investigation. The locations were to represent two age classes of afforestation with five sites each, considered as replicates. At five stand sites, the stand age was 14–17 years (young stands) and at the other five ones – 32–36 years (older stands). All soils were developed on water-glacial sands and classified as the rusty type of soils (subtype proper) according to the Systematics of Polish Soils [14] and the Distric Arenosols in the WRB [15] classification [16]. The soils are light textured (loose sand and slightly loam sand). A system of crop rotation performed on all the analyzed fields was similar. In the sampling year, rye, oat and bird's-foot were grown at seven, two and one location, respectively. This region is characterized with low-intensity forms of agriculture and consequently, a very low fertilization rate. It was assumed that each pair of plots showed soil characteristics similar to those prior to afforestation and that arable soils served as control.

Soil samples were collected post harvest in the late summer. At each site, representative arable and forest profiles were excavated. Soil samples (ca 10 kg each) were taken from the whole thickness of each master horizon. Only the humus horizon of the afforested soils made the exception as the samples were collected from three layers, ie 0–5 (A_{0-5}), 5–10 (A_{5-10}) and 10–20 cm (A_{10-20}).

Soil pH was measured in 1 mole KCl $\cdot$ dm^{-3} at a 1:2.5 soil : solution ratio and measured electrometrically. A content of total Zn and Pb was determined in the extracts after digestion in a mixture of concentrated nitric(V) acid and 70 % chloric(VII) acids, followed by HCl leaching. A soil solution was established by centrifugation procedure following the soil incubation for 48 h at field capacity moisture and room temperature in darkness [17]. Both forms of metals were determined using the ICP-AES method (Leemman PS 950 apparatus).

A share of Zn and Pb concentrations in the soil solution as related to the total content in soil was calculated. Before that the concentrations of Zn and Pb in mg $\cdot$ dm^{-3} were recalculated as mg $\cdot$ kg^{-1} of soil dry mass using soil moisture at incubation.

Results and discussion

The mean total contents of Zn in solid phase, in soils of the 14–17 years old stand sites, both in the arable and in the afforested soils, were higher than in the respective soils of the 32–36 years old stand sites (Table 1).

Table 1

The content of Zn in soil, soil solution and its share in soil solution as related to the total content in soil; for Ap, A_{0-5}, A_{5-10}, A_{10-20}, Bv and C n = 5, for $A_{av.}$ n = 15

Soil use	Horizon/ layer	Total content in soil			Concentration in soil solution			Share			pH_{KCl} of soil
		Range	Mean	SD*	Range	Mean	SD	Range	Mean	SD	
		[mg · kg^{-1}]			[mg · dm^{-3}]			[%]			Range
14–17 years old stand sites											
Field	Ap	9.5–17.3	14.2	2.9	0.42–0.53	0.46	0.04	0.35–0.67	0.54	0.13	3.88–5.02
	Bv	9.3–14.1	12.2	1.9	0.18–0.38	0.30	0.09	0.18–0.38	0.29	0.09	4.34–4.69
	C	5.0–5.6	5.4	0.2	0.16–0.42	0.25	0.11	0.18–0.54	0.32	0.14	4.52–4.85
Forest	A_{0-5}	9.4–14.6	12.7	2.2	0.54–0.95	0.73	0.19	0.41–1.46	0.89	0.46	3.50–4.07
	A_{5-10}	8.9–14.1	12.2	2.0	0.43–0.91	0.61	0.24	0.40–1.09	0.77	0.32	3.70–4.08
	A_{10-20}	10.1–14.5	12.4	2.4	0.33–1.02	0.60	0.27	0.43–1.12	0.74	0.28	3.88–4.99
	A_{avg}	8.5–13.5	12.4	1.9	0.44–0.94	0.65	0.22	0.42–1.22	0.80	0.35	
	Bv	8.5–13.5	10.2	1.9	0.28–0.74	0.42	0.19	0.34–0.83	0.53	0.25	4.24–4.67
	C	3.6–8.0	5.6	1.7	0.25–0.66	0.42	0.19	0.31–0.88	0.61	0.25	4.44–4.60
32–36 years old stand sites											
Field	Ap	10.1–17.5	12.1	3.1	0.47–1.01	0.65	0.22	0.34–1.50	0.81	0.43	4.08–4.38
	Bv	4.2–14.2	8.9	3.8	0.31–0.53	0.37	0.09	0.33–0.76	0.52	0.16	4.50–4.64
	C	1.5–6.1	3.7	1.8	0.22–0.35	0.28	0.06	0.37–0.79	0.60	0.20	4.65–4.72
Forest	A_{0-5}	7.4–9.7	8.5	1.0	0.67–1.56	1.15	0.37	1.17–2.39	1.77	0.56	3.16–3.50
	A_{5-10}	6.1–10.6	8.2	1.6	0.66–1.64	0.94	0.40	0.98–2.01	1.31	0.41	3.56–3.80
	A_{10-20}	6.8–10.9	8.8	1.5	0.42–0.75	0.57	0.14	0.51–1.00	0.77	0.19	3.73–4.03
	A_{avg}	6.8–10.4	8.5	1.3	0.58–1.32	0.89	0.28	0.89–1.76	1.29	0.35	
	Bv	6.0–7.9	7.4	0.8	0.30–0.72	0.52	0.16	0.43–1.20	0.86	0.37	4.31–4.47
	C	2.5–5.3	3.8	1.1	0.27–0.57	0.37	0.11	0.46–1.11	0.77	0.27	4.49–4.63

* Standard deviation.

In the afforested soils, the total content of Zn, average in the whole humus horizon, reached 12.4 and 8.5 mg · kg^{-1} for soils of young and older stands, respectively. It was slightly lower than in Ap horizon of the related arable soils amounting 14.2 and 12.1 mg · kg^{-1}, respectively. The content of Zn decreased with the depth and in the Bv horizon of the afforested soils (in both sites) it appeared to be lower compared with the respective horizon of the arable soils, whereas similar in the C horizon.

The Zn mean concentration in the soil solution ranged from 0.25 up to 1.15 mg · dm^{-3}, subject to a horizon and soil use. In contrast to the total soil content, in all the horizons and layers (with one exception), it was higher in the solutions of the afforested soils as against the respective solutions of the cultivated soils.

Similarly, a share of Zn in the soil solution in relation to its total soil content was higher in the afforested soils (mean of $A_{av.}$ was 0.80 and 1.29 % for young and older stand sites, respectively) than in the Ap horizon of the related arable soils (0.54 and 0.81 %). Moreover, it was substantially higher in soils of the older than young stands.

Results indicate that afforestation of the studied post-arable soils caused Zn release from the solid phase to the soil solution. It emerged as a consequence of changes in soil reaction, a main factor influencing the solubility of zinc compounds [18, 19], after pine trees planting. The present study has revealed a significant, negative correlation between Zn concentration in soil solution and soil pH (Fig. 1).

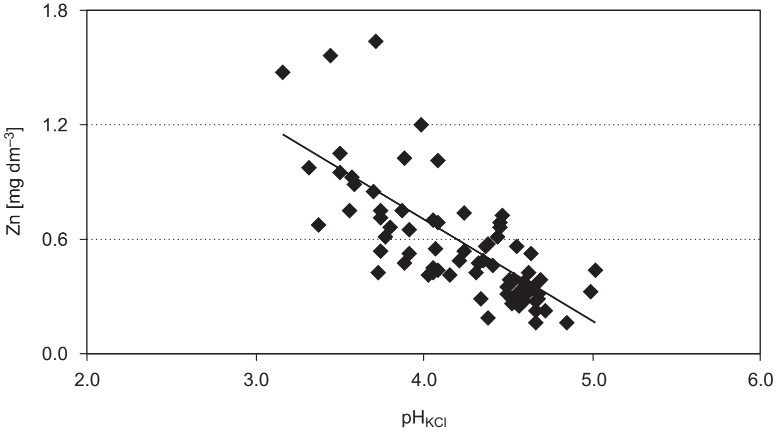

Fig. 1. Relationship between the Zn concentration in soil solution and pH of soils

Besides, as Table 1 presents, the afforested soils, under both young and older stands, showed stronger acidity (as measured by pH_{KCl}) in all the layers, especially in the A_{0-5} of the humus horizons than in the corresponding Ap horizons of the arable soils. Moreover, the pH values in these horizons appeared to be lower in the soils of older than young stands, which explains the higher contents and share of Zn in the soil solution in the first and not the other case.

The higher Zn concentrations in the soil solution of the afforested soils compared with the arable soils have confirmed our preliminary results [20] and agreed with data

Table 2

The content of Pb in soil, soil solution and its share in soil solution as related to the total content in soil; for Ap, A_{0-5}, A_{5-10}, A_{10-20}, Bv and C n = 5, for $A_{av.}$ n = 15

Soil use	Horizon/ layer	Total content in soil			Concentration in soil solution			Share		
		Range	Mean	SD*	Range	Mean	SD	Range	Mean	SD
		[mg · kg^{-1}]			[mg · dm^{-3}]			[%]		
14–17 years old stand sites										
Field	Ap	7.5–12.2	9.4	1.9	0.101–0.298	0.209	0.077	0.17–0.63	0.37	0.18
	Bv	3.9–5.7	4.6	0.8	0.067–0.190	0.147	0.047	0.22–0.44	0.37	0.09
	C	2.6–5.0	3.5	0.9	0.015–0.192	0.112	0.064	0.02–0.49	0.26	0.18
Forest	A_{0-5}	6.8–9.7	8.0	1.3	0.227–0.495	0.374	0.104	0.40–1.18	0.68	0.33
	A_{5-10}	7.3–10.9	8.8	1.7	0.169–0.471	0.307	0.110	0.30–0.71	0.53	0.20
	A_{10-20}	6.2–9.3	7.8	1.3	0.061–0.423	0.237	0.139	0.14–0.82	0.49	0.31
	A_{avg}	7.0–9.8	8.2	1.2	0.152–0.429	0.306	0.106	0.28–0.88	0.57	0.22
	Bv	2.6–4.4	3.7	0.8	0.001–0.374	0.136	0.149	0.002–1.21	0.46	0.56
	C	2.5–4.2	3.4	0.8	0.001–0.087	0.043	0.037	0.001–0.19	0,09	0.07
32–36 years old stand sites										
Field	Ap	7.1–13.1	9.0	2.5	0.034–0.296	0.130	0.103	0.05–0.77	0.25	0.30
	Bv	2.6–5.2	3.9	0.9	0.025–0.139	0.061	0.047	0.07–0.37	0.17	0.12
	C	2.2–3.7	3.0	0.6	0.001–0.194	0.064	0.087	0.001–0.44	0.15	0.20
Forest	A_{0-5}	8.6–10.8	9.7	0.9	0.173–0.267	0.198	0.040	0.17–0.53	0.29	0.14
	A_{5-10}	7.3–8.4	7.8	0.4	0.008–0.307	0.153	0.116	0.009–0.65	0.27	0.25
	A_{10-20}	5.3–9.5	8.4	1.8	0.018–0.259	0.100	0.098	0.03–0.29	0.14	0.11
	A_{avg}	7.6–9.2	8.6	0.6	0.073–0.230	0.150	0.058	0.07–0.47	0,23	0.15
	Bv	1.7–4.9	3.7	1.3	0.001–0.233	0.099	0.099	0.002–0.76	0.34	0.34
	C	2.5–5.0	3.8	0.9	0.001–0.176	0.078	0.075	0.0009–0.32	0.16	0.15

* Standard deviation.

reported by Römkens and Salomons [12], Smal [17] as well as Smal et al [21] in the study comparing cultivated soils with natural forest soils.

The content of total Pb in solid phase has not shown clear differences between investigated sites. In the arable soils, similarly to Zn, it was slightly higher, whereas in the afforested soils it tended to be lower (in A and C horizons) in soils of the 14–17 years old than in the 32–36 years old stand sites.

In the afforested soils, the content of total Pb, average in the whole humus horizon, was equal to 8.2 and 8.6 mg · kg^{-1}, for soils of the young and older stands, respectively and slightly lower than in the respective horizon of the arable soils (9.4 and 9.0 mg · kg^{-1}) (Table 2). In the deeper horizons, it proved to be lower than in the A horizons and similar in all soils.

Total Pb values established were comparable with the data for forest Haplic Arenosols reported by Kalembasa et al [22].

For both total Pb and its soluble forms content, no marked relationships between the compared groups of soils were found. In the soils under young forests, similarly to zinc, a mean content of total Pb in the soils of humus horizons was lower (mean $A_{av.}$ of 8.2 mg · kg^{-1}), whereas in the soil solution for all layers and average for a former plough layer it was notably higher (mean $A_{av.}$ of 0.306 mg · dm^{-3}) than in the related horizons of the arable soils (mean Ap of 9.4 mg · kg^{-1} and 0.209 mg · dm^{-3}, respectively). In turn, in a soil group comprising older stand sites, for both Pb forms, only very slight differences in their content in humus horizons between afforested and cultivated soils were observed.

Similarly, a share of Pb in the soil solution in relation to its total soil content did not show any evident pattern. It was much elevated in the humus horizons in the afforested soils under the young stands, while in the soils under the older stands – even slightly lower as compared with the respective horizons of the arable soils. What is more, in contrast to Zn, a Pb share in the soil solution related to its total soil content turned out to be higher in the soils under the young (0.57 %) than older stand sites (0.23 %).

The obtained results indicate the stronger effect of pine trees on Zn mobility rather than Pb compounds in former arable soils. This would be consistent with the findings reported by Andersen et al [1] who studying distribution and fractionation of heavy metals in pairs of arable and afforested with Norway spruce soils in Denmark observed some tendency of Zn movement with no increase in Pb solubility or movement.

Conclusions

1. The present study indicates that forest vegetation caused an increase in Zn solubility in the former arable soils. This metal concentrations in the soil solution, both in mg · dm^{-3} and in percent of the total soil content, were higher in the afforested soils compared with the respective arable soils, being soil pH-dependent. The differences tended to increase with the stand age.

2. In the case of Pb, no clear effect of pine trees on the studied metals solubility was observed.

3. The findings imply that afforestation of sandy arable soils causes soil acidity increase and thereby, is likely to enhance mobility of Zn compounds in soil environment and their downward movement.

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WPŁYW ZALESIENIA GLEB POROLNYCH NA ROZPUSZCZALNOŚĆ CYNKU I OŁOWIU

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Abstrakt: Zalesienie gleb porolnych wywołuje zmiany ich właściwości, w tym odczynu, zawartości materii organicznej, rozpuszczonego węgla organicznego, które regulują zatrzymywanie/uruchamianie pierwiastków śladowych w glebie. Mimo obszernej literatury dotyczącej wpływu zalesienia dawnych gleb uprawnych na właściwości gleb, mało wiadomo o skutkach takiej zmiany użytkowania na zachowanie się pierwiastków śladowych. W pracy przedstawiono wyniki badań wpływu zalesienia sosną zwyczajną gleb rdzawych porolnych wytworzonych z piasków wodnolodowcowych na rozpuszczalność Zn i Pb mierzoną zawartością tych metali w roztworze glebowym i ich udziałem w tej fazie w stosunku do całkowitej zawartości w glebie. Porównywano gleby pod drzewostanami 14–17- i 32–36-letnimi z sąsiadującymi z nimi glebami uprawnymi, po pięć par w każdej grupie. Próbki glebowe pobierano z każdego głównego poziomu genetycznego, z całej jego miąższości, przy czym z poziomu A gleb zalesionych z trzech warstw: 0–5 (A_{0-5}), 5–10 (A_{5-10}) i 10–20 cm (A_{10-20}).

Stwierdzono, że stężenie Zn zarówno w mg · dm^{-3}, jak i w procentach w odniesieniu do całkowitej zawartości w glebie, było większe w glebach zalesionych niż w glebach ornych i było zależne od pH gleby. Ponadto różnice zwiększały się wraz z wiekiem drzewostanu. W przypadku Pb nie zaobserwowano takich wyraźnych prawidłowości.

Słowa kluczowe: zalesienia, gleby porolne, cynk, ołów, rozpuszczalność

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NITROGEN DYNAMICS IN GROUNDWATER OF FALLOWED SOIL RECOVERED FOR AGRICULTURAL PRODUCTION

DYNAMIKA AZOTU W WODACH GRUNTOWYCH GLEB UGOROWANYCH PRZYWRÓCONYCH DO UŻYTKOWANIA ROLNICZEGO

Abstract: A study to determine the effects of long-term soil fallowing on nitrogen compounds concentrations in groundwater after the land has been recovered for agricultural production was carried out in Knopin near Dobre Miasto in 2005–2008. The investigated area was excluded from farming practice in 1996–2005 as bare fallow and fallow sown with annual plants, perennial legumes goat rue – *Galega orientalis* Lam.), grass (bromegrass – *Bromus inermis* Leyss.), a mixture of grass and legumes (bromegrass and goat rue), as well as abandoned land. The studied soils were recovered for agricultural production in the spring of 2005. Groundwater samples were collected once a month and analyzed to determine the levels of nitrogen compounds (Kjeldahl method), $N\text{-}NH_4$, $N\text{-}NO_3$ and $N\text{-}NO_2$.

The dynamics of nitrogen transformations in recovered soils was significantly affected by weather conditions which modified vegetation growth and water circulation in the soil as well as by the method of long-term land fallowing. The obtained results indicate that the applied fallowing method continued to affect nitrogen concentrations in groundwater three years after the soil had been recovered for farming. Long-term bare fallowing and sowing with annual plants led to the highest pollution of groundwater with nitrogen compounds in the first and second year after recovery. The sowing of a mixture of legumes and grass proved to be the most effective method of protecting abandoned land against nitrogen pollution. Groundwater pollution with $N\text{-}NO_3$ was highly dependent on the applied fallowing method. Long-term bare fallowing and the sowing of annual plants or goat rue increased $N\text{-}NO_3$ leaching from the soil into groundwater after the land had been recovered for farming purposes.

Keywords: land fallowing, groundwater, concentrations of mineral nitrogen

Groundwater, a part of undergroundwater resources, is in constant motion and it is the immediate recipient of infiltration water. Groundwater is susceptible to pollution with substances carried by water into the soil profile [1]. The observed pollution has a natural source, resulting from the geochemical composition of the surface layers of the

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soil profile and vegetation, as well anthropogenic origins relating to the manner and intensity of land use and the quality of precipitation water [2, 3]. The concentration of chemical substances in groundwater is highly diversified in time and space, and it is also determined by the groundwater table [4, 5].

Nitrogen is a biogenic element which relatively easily migrates to groundwater. The intensity of its movement is determined by soil type, cohesion and the manner of land use, including the fertilization regime, type of vegetation cover, air-water relations, the chemical composition, volume and intensity of precipitation [4, 6–8]. With an increase in farmland share of catchment areas, the levels of nitrogen, in particular nitrates which are not absorbed by the soil and are easily leached out, increase in groundwaters [9]. Groundwater concentrations of different nitrogen forms are determined by fertilizer disposal as well as by the type of nitrogen transformations conditioned by oxygen availability in soil.

The objective of this study was to determine the effect of long-term soil fallowing on changes in nitrogen concentrations of groundwater after the land had been recovered for farming purposes.

Materials and methods

The study investigating nitrogen dynamics in groundwaters of land recovered for agricultural production after long-term fallowing was carried out in Knopin, near Dobre Miasto, from April 2005 to March 2008. The investigated land was excluded from farming practice in 1996–2005 as bare fallow and fallow sown with annual plants, perennial legumes (goat rue – *Galega orientalis* Lam.), grass (bromegrass – *Bromus inermis* Leyss.), a mixture of grass and legumes (bromegrass and goat rue), as well as sites of abandoned land, each covering an area of 810 m^2 (plot dimensions 45 m × 18 m). The studied land was recovered for farming use in the spring of 2005. After field preparation treatments (tillage and mineral fertilization), the land was sown with spring wheat with a pre-sowing application of 78 kg $N \cdot ha^{-1}$; 36 kg $P_2O_5 \cdot ha^{-1}$ and 36 kg $K_2O \cdot ha^{-1}$. The second crop in the rotation scheme was winter rape (September 2005–August 2006) with a pre-sowing rate of: 24 kg $N \cdot ha^{-1}$, 72 kg $P_2O_5 \cdot ha^{-1}$ and 72 kg $K_2O \cdot ha^{-1}$, and a top-dressing rate of 102 kg $N \cdot ha^{-1}$. In the third year of the experiment (September 2006–August 2007), winter wheat was grown with a pre-sowing rate of: 16 kg $N \cdot ha^{-1}$, 48 kg $P_2O_5 \cdot ha^{-1}$ and 48 kg $K_2O \cdot ha^{-1}$, and a top-dressing rate of 56 kg $N \cdot ha^{-1}$ in the spring of 2007. Groundwater samples were collected once a month with the use of a submersible pump and were analyzed to determine the levels of: nitrogen – by the Kjeldahl's method ($N_{Kj.}$) in the BUCHI distillation unit after mineralization with sulfuric acid, ammonium nitrogen ($N\text{-}NH_4$) – by colorimetry with Nessler's reagent, nitrate nitrogen(III) ($N\text{-}NO_2$) by colorimetry with sulfanilic acid, and nitrate nitrogen(V) ($N\text{-}NO_3$) by colorimetry with disulfophenolic acid. Water samples were also analyzed to determine the concentrations of total nitrogen (N_T) according to the formula [$N_T = N\text{-}NH_4 + N\text{-}NO_3 + N\text{-}NO_2 + N_{org.}$], organic nitrogen ($N_{org.}$) – [$N_{org.} = N_{Kj.} - N\text{-}NH_4$] and mineral nitrogen ($N_{min.}$) – [$N_{min.} = N\text{-}NH_4 + N\text{-}NO_3 + N\text{-}NO_2$].

Weather conditions (precipitation and ambient air temperature) were characterized by significant temporal diversity in the experimental period (April 2005–March 2008). Completely dry days as well as days marked by intense precipitation reaching 39 mm (July 2007) were noted throughout the period of study. The experimental period comprised one dry year (April 2005–March 2006) with total precipitation of 453.7 mm and two wet years with total precipitation of 769.0 mm (April 2006–March 2007) and 682.7 mm (April 2007–March 2008). In all studied years, the highest precipitation values were reported in the growing season (April–August), reaching 267.0 mm in the first year of the experiment (around 59 % of the annual total), 439.3 mm in the second year (around 57 % of the annual total) and 505.9 mm in the third year (around 74 % of the annual total).

Results

Variable meteorological conditions reported during the experiment differentiated the intensity of changes occurring in the soil and the resulting mineral nitrogen concentrations in groundwater. Various methods of long-term fallowing affected soil fertility and resulted in significant differences in the yield attained at particular experimental sites (fallowed and abandoned land) after they had been recovered for farming purposes. The above affected the intensity and type of physical and chemical changes in soil and the availability of nitrogen supplied with mineral fertilizers to each site in every year of the experiment.

The highest (0.240 mg · dm^{-3} on average) N-NH$_4$ concentrations in groundwater were observed at the long-term fallowed site sown with ephemeral plants every year (Table 1). In the first experimental year, the highest (0.644 mg · dm^{-3} on average) N-NH$_4$ concentrations were noted in the growing season (April–September). The above could be attributed to the specific fallowing regime (soil loosening) at annually sown sites, creating a more supportive environment for the mineralization of the accumulated organic substances. Water deficiency (dry year) and limited nitrogen uptake increased nitrogen concentrations in groundwater.

Table 1

N-NH$_4$ concentrations [mg · dm^{-3}] in groundwater after soil recovery for agricultural production

Site	Half-year IV–IX				Half-year X–III				Average
	1st year	2nd year	3rd year	Average	1st year	2nd year	3rd year	Average	
Abandoned land	0.049	0.026	0.398	0.157	0.088	0.178	0.314	0.193	0.175
Bare fallow	0.041	0.043	0.047	0.043	0.024	0.043	0.018	0.028	0.036
Annual plant	0.644	0.318	0.083	0.348	0.186	0.058	0.153	0.133	0.240
Bromegrass	0.074	0.066	0.476	0.205	0.075	0.309	0.250	0.212	0.208
Goat rue	0.074	0.019	0.245	0.113	0.113	0.398	0.408	0.306	0.210
Mixture of goat rue and bromegrass	0.045	0.048	0.093	0.062	0.042	0.047	0.037	0.042	0.052
LSD$_{0.05}$				n.s.				0.100	n.s.

n.s. – differences not significant.

In the successive years of the study, when the noted levels of precipitation significantly exceeded the plants water demand, in particularly in August 2006 and July 2007, N-NH_4 concentrations in groundwater were more diversified and were generally higher than in the dry year. In the second year of the experiment, higher N-NH_4 concentrations (except for the fallowed site sown with ephemeral plants) in groundwater were observed in the non-growing season. The highest levels (0.398 mg $\cdot$ dm^{-3}) were noted at a site planted with goat rue. The above could be attributed to the accumulation of high quantities of organic substances which underwent mineralization under favorable moisture conditions. Organic substances migrated to groundwater whose table was detected in the root zone due to intense precipitation. In the third year, the highest N-NH_4 concentrations in groundwater were also determined in the non-growing season.

The results of a three-year experiment demonstrated that the lowest N-NH_4 concentrations in the groundwater of recovered soils were found in bare fallows and in fallows sown with a mixture of goat rue and bromegrass. As regards the bare fallow site, the above could be attributed to soil depletion in consequence of the applied fallowing method, whereas the changes noted in the long-term fallowed site sown with grass and legumes could be due to its stimulating effect (fertile stand) on crop yield and intensified phytosorption. Although the applied methods of long-term land fallowing led to differences in N-NH_4 concentrations in groundwater, they were found to be statistically non-significant due to high seasonal variations.

Subject to weather conditions, fallowing methods and their impact on crop yield, the average annual N-NO_3 concentrations ranged from 0.058 mg $\cdot$ dm^{-3} at the site sown with a mixture of goat rue and bromegrass in the first experimental year to 10.527 mg $\cdot$ dm^{-3} at the site sown with an annual plant species in the second year. High N-NO_3 concentrations in those treatments could be attributed to the fact that contrary to other fallowing methods, bare fallow sites and fallows under annual plants were subjected to tillage which improved topsoil and subsoil aeration and intensified the mineralization of accumulated organic matter.

The results of the study indicate that the method of soil fallowing and the condition of the resulting site are more likely to affect the level of groundwater pollution with N-NO_3 than weather conditions which merely affected the scale of substance leaching from the soil to groundwater. This observation is validated by high N-NO_3 concentrations in the groundwater of bare fallow sites (6.194 mg $\cdot$ dm^{-3} on average), sites sown with ephemeral plants (5.595 mg $\cdot$ dm^{-3} on average) and goat rue (2.540 mg $\cdot$ dm^{-3} on average) (Table 2). Yet in comparison with other methods of long-term fallowing, significantly higher N-NO_3 concentrations were observed only at bare fallow sites and annually sown sites due to intense leaching of easily migrating nitrates in the growing season (April–September), in particular in the first and second experimental year after the recovery of the sites sown with annual plants.

The lowest N-NO_3 concentrations in groundwater were observed at the sites sown with a mixture of grass and legumes (0.442 mg $\cdot$ dm^{-3} on average) and with grass (0.540 mg $\cdot$ dm^{-3} on average). The reported low N-NO_3 concentrations at the site sown with a mixture of goat rue and bromegrass could be due to high phytosorption, as suggested by its high biomass yield. As regards sites sown with grass, the low level of N-NO_3 could be attributed to limited nitrogen availability in the soil. The obtained results indicate that long-term fallowing methods involving bare fallowing and the sowing of annual plants contribute to increased N-NO_3 leaching to groundwater even in the course of several years after the studied land had been recovered for agricultural production.

Table 2

N-NO_3 concentrations [mg · dm^{-3}] in groundwater after soil recovery for agricultural production

Site	Half-year IV–IX				Half-year X–III				Average
	1st year	2nd year	3rd year	Average	1st year	2nd year	3rd year	Average	
Abandoned land	2.358	1.440	1.058	1.619	0.858	4.339	0.536	1.911	1.765
Bare fallow	9.710	8.243	3.700	7.218	8.111	4.493	2.907	5.170	6.194
Annual plant	7.985	8.274	3.680	6.646	7.129	4.870	1.633	4.544	5.595
Bromegrass	0.055	0.392	0.335	0.261	0.086	1.254	1.118	0.819	0.540
Goat rue	2.514	5.611	1.480	3.202	0.344	4.893	0.396	1.878	2.540
Mixture of goat rue and bromegrass	0.054	0.532	0.839	0.475	0.062	1.007	0.158	0.409	0.442
$LSD_{0.05}$				3.383				n.s.	2.289

n.s. – differences not significant.

N-NO_2 levels in the analyzed groundwater samples were affected by both meteorological conditions (seasonal variability) and the method of soil fallowing (Table 3).

Table 3

N-NO_2 concentrations [mg · dm^{-3}] in groundwater after soil recovery for agricultural production

Site	Half-year IV–IX				Half-year X–III				Average
	1st year	2nd year	3rd year	Average	1st year	2nd year	3rd year	Average	
Abandoned land	0.007	0.009	0.060	0.025	0.005	0.032	0.007	0.015	0.020
Bare fallow	0.060	0.052	0.006	0.040	0.005	0.009	0.006	0.007	0.023
Annual plant	0.033	0.086	0.015	0.044	0.020	0.056	0.009	0.028	0.036
Bromegrass	0.005	0.011	0.058	0.025	0.005	0.014	0.021	0.013	0.019
Goat rue	0.007	0.014	0.053	0.025	0.006	0.188	0.016	0.070	0.048
Mixture of goat rue and bromegrass	0.004	0.028	0.005	0.012	0.005	0.007	0.006	0.006	0.009
$LSD_{0.05}$				n.s.				n.s.	n.s.

n.s. – differences not significant.

On average, they ranged from 0.005 mg · dm^{-3} at the site sown with a mixture of goat rue and bromegrass in the first experimental year to 0.040 mg · dm^{-3} at the site sown with bromegrass in the third year. In view of very high N-NO_2 concentrations (0.188 mg · dm^{-3}) in the winter, the highest groundwater pollution levels (three-year average of 0.048 mg · dm^{-3}) was noted at the site sown only with goat rue, which can be attributed to excessive nitrogen production during fallowing. The lowest $N\text{-}NO_2$ concentrations in groundwater were observed (except for the bare fallow site) in the dry year. The above could be explained by the lower intensity of $N\text{-}NO_2$ leaching from the soil during a period of deficient precipitation. Higher $N\text{-}NO_2$ concentrations in the groundwater of bare fallow sites and sites sown with annual plants, noted mostly in the growing season (April – September), could be due to a higher degree of soil loosening (tilled during fallowing) than at other fallowed sites. The above soil conditions intensified the mineralization of organic matter, enhanced soil permeability and speeded up the leaching of $N\text{-}NO_2$ in comparison with the remaining treatments.

$N\text{-}NO_2$ concentrations in groundwater were much higher in experimental years characterized by higher precipitation volume. The highest $N\text{-}NO_2$ levels were reported in the groundwater of sites sown with goat rue, annual plants as well as bare fallow sites. An analysis of average $N\text{-}NO_2$ concentrations in groundwater indicates that the sowing of a mixture of grass and legumes provides the most effective protection against groundwater pollution with this form of nitrogen.

Much higher levels (ranging from 4-fold at fallow sites sown with annual plants to 20-fold on bare fallows, on average) of Kjeldahl nitrogen ($N_{Kj.}$) than of $N\text{-}NH_4$ suggest that the investigated groundwater samples were characterized by a high content of organic nitrogen (Table 4).

Table 4

Kjeldahl N concentrations [$mg \cdot dm^{-3}$] in groundwater after soil recovery for agricultural production

Site	Half-year IV–IX				Half-year X–III				Average
	1st year	2nd year	3rd year	Average	1st year	2nd year	3rd year	Average	
Abandoned land	1.025	1.486	1.229	1.247	1.362	1.758	1.127	1.416	1.331
Bare fallow	0.967	0.783	0.542	0.764	0.631	0.941	0.402	0.658	0.711
Annual plant	1.177	1.309	0.562	1.016	1.033	0.612	0.656	0.767	0.891
Bromegrass	1.261	0.997	1.038	1.098	0.976	1.183	1.196	1.118	1.109
Goat rue	1.366	0.929	0.792	1.029	1.257	1.284	0.960	1.167	1.098
Mixture of goat rue and bromegrass	1.095	0.911	0.537	0.848	1.202	1.171	0.363	0.912	0.880
$LSD_{0.05}$				n.s.				0.515	0.350

n.s. – differences not significant.

The magnitude of the reported differences was particularly high during the growing season at abandoned land sites (58-fold) and sites sown with goat rue (48-fold) in the wettest year. Much higher $N_{Kj.}$ levels (except for bare fallow sites and sites sown with annual plants) were noted in the non-growing season. In comparison with the majority of experimental treatments, $N_{Kj.}$ concentrations were significantly higher at the abandoned land site.

The concentrations of mineral nitrogen forms ($N\text{-}NH_4$, $N\text{-}NO_3$, $N\text{-}NO_2$) and Kjeldahl nitrogen provided a basis for calculating the levels of total nitrogen and organic nitrogen, and the share of mineral nitrogen in the total nitrogen content of groundwater.

The share of mineral nitrogen in the total nitrogen content of groundwater was mostly determined by the applied fallowing method (Fig. 1). Mineral nitrogen had the highest share of total nitrogen at bare fallow sites (89 % on average) and at sites sown with annual plants (88 % on average), while the lowest at sites sown with a mixture of goat rue and bromegrass (36 % on average) and bromegrass alone (41 % on average). The applied long-term fallowing method contributed to the greatest differences in mineral nitrogen share of total nitrogen in the first year of the experiment when mineral nitrogen levels ranged from 9 % (at the site sown with a mixture of goat rune and bromegrass) to 94 % (at the site sown with ephemeral plants).

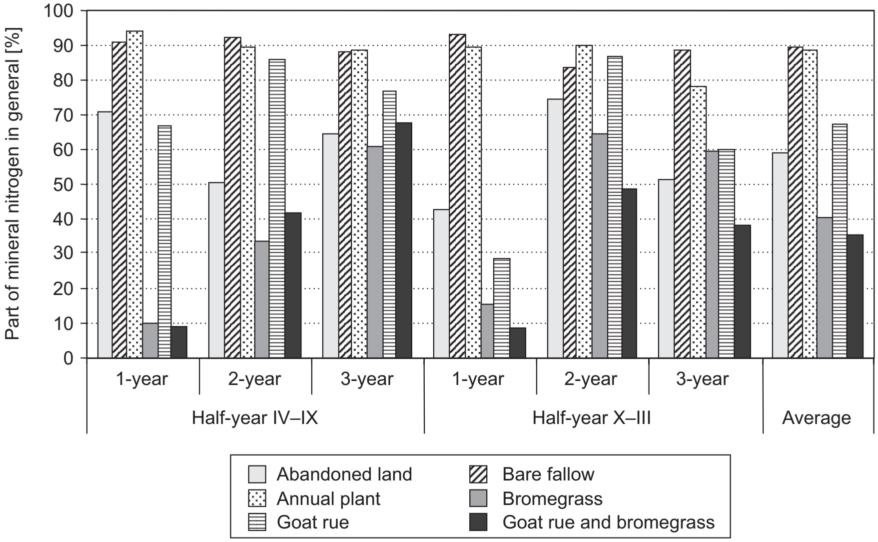

Fig. 1. Mineral nitrogen share of total nitrogen in groundwater after soil recovery for agricultural production [mg · dm^{-3}]

N-NO$_3$ was the predominant form of nitrogen in the investigated groundwaters, accounting for 70 % (site sown with bromegrass) to 99 % (bare fallow) of mineral nitrogen, and 38 % (at the site sown with a mixture of goat rue and bromegrass) to 65 % (at the site sown with goat rue alone) of total nitrogen content on average.

Conclusions

1. The applied land fallowing methods continued to affect nitrogen concentrations in groundwater three years after the soil had been recovered for agricultural production.

2. In the first and second year after soil recovery, nitrogen pollution of groundwater was the highest at bare fallow sites and sites sown with annual plants. In the third year, the highest concentrations of mineral nitrogen compounds were noted at the site sown with annual plants.

3. $N\text{-}NO_3$ was the predominant form of nitrogen in the groundwater of fallow and abandoned land recovered for agricultural production. $N\text{-}NO_3$ concentrations were more likely to be affected by the applied fallowing method than weather conditions which merely affected the scale of nitrogen leaching from the soil to groundwater.

4. Long-term fallowing methods comprising bare fallowing and plot sowing with annual plants or goat rue intensified $N\text{-}NO_3$ leaching from the soil to groundwater after the land had been recovered for farming practice.

5. The sowing of fallow land with a mixture of legumes and grass offers the best protection against groundwater pollution with nitrogen compounds.

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DYNAMIKA AZOTU W WODACH GRUNTOWYCH GLEB UGOROWANYCH PRZYWRÓCONYCH DO UŻYTKOWANIA ROLNICZEGO

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Abstrakt: W latach 2005–2008 realizowano badania w Knopinie koło Dobrego Miasta nad wpływem sposobu wieloletniego wyłączenia gleb z produkcji rolniczej na stężenie związków azotu w wodach gruntowych po przywróceniu ich do użytkowania rolniczego. Obszar badań z produkcji rolniczej był wyłączony w latach 1996–2005 w postaci ugorów: czarnego oraz obsianych: rośliną jednoroczną, wieloletnią rośliną motylkowatą (rutwica wschodnia – *Galega orientalis* Lam.), trawą (stokłosa bezostna – *Bromus inermis* Leyss.), mieszanką trawy z motylkowatą (stokłosa bezostna i rutwica wschodnia), a także w formie odłogu klasycznego. Do ponownego zagospodarowania tych gleb przystąpiono wiosną 2005 r. W pobieranych raz na miesiąc wodach gruntowych oznaczono: azot Kjeldahla, $N\text{-}NH_4$, $N\text{-}NO_3$ oraz $N\text{-}NO_2$.

Na dynamikę przemian związków azotu w glebach ponownie zagospodarowanych znaczący wpływ wywierały warunki meteorologiczne modyfikujące rozwój szaty roślinnej i obieg wody w glebie oraz sposób wieloletniego ugorowania lub odłogowania gleb. Badania wykazały, że sposób wyłączenia gleb z uprawy modyfikował stężenie związków azotu w wodach gruntowych jeszcze w trzecim roku po przywróceniu ich do produkcji rolniczej. Wieloletnie utrzymywanie gleb w postaci ugorów czarnego lub obsianego rośliną jednoroczną stworzyło największe zagrożenie zanieczyszczenia wód gruntowych związkami azotu w pierwszym i drugim roku po ponownym ich zagospodarowaniu. Ze względu na ochronę wód gruntowych przed zanieczyszczeniem azotem najlepszym sposobem utrzymania gleb wyłączonych z produkcji było zastosowanie mieszanki rośliny motylkowatej z trawą. Zanieczyszczenie wód gruntowych N-NO_3 było silnie uzależnione od sposobu wyłączenia gleb z użytkowania. Zwiększone wymycie N-NO_3 z gleb do wód gruntowych po ponownym włączeniu ich do uprawy powodowało wieloletnie utrzymanie ugoru czarnego oraz obsianego rośliną jednoroczną lub rutwicą wschodnią.

Słowa kluczowe: odłogowanie i ugorowanie gleb, stężenie N mineralnego, wody gruntowe

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ESTIMATE OF AVAILABLE PHOSPHORUS AND POTASSIUM FORMS CONTENT IN THE WINTER WHEAT SOILS FROM ORGANIC AND CONVENTIONAL FARMS ON THE BACKGROUND THEIR SELECTED PROPERTIES

OCENA ZAWARTOŚCI PRZYSWAJALNYCH FORM FOSFORU I POTASU W GLEBACH SPOD UPRAWY PSZENICY Z GOSPODARSTW EKOLOGICZNYCH I KONWENCJONALNYCH NA TLE WYBRANYCH ICH WŁAŚCIWOŚCI

Abstract: It was estimated the content of available P and K in soils of organic and conventional farms.

The soils from organic farms were less acidified, had smaller sorptive capacity and higher saturation of sorptive complex with alkaline cation as well as more organic matter and available P and K. There were no distinct differences in P and K content in soils of farms being in period of conversion to organic farming and having certificate of agreement with methods of organic farming, and in case of potassium were registered similar increasing trends of its content in soils of neighbouring organic and conventional farms. In both groups of farms prevailed soil with low and medium abundance in P and K, but soils taken from organic farms obtained a better mark (more soils with high and very high content of P and K than in conventional farms).

Content of P and K was negatively correlated with soil acidity, moreover K content in soils from conventional farms was positively correlated with sum of basic cation and sorptive capacity, whereas P content with organic C content.

Keywords: organic and conventional farms, available P and K, estimate

Phosphorus and potassium belong to basic elements, essential to the normal development of plants. The total content of phosphorus in the arable layer of the soil amounts to the 0.1–2 g $P_2O_5 \cdot kg^{-1}$. Inorganic phosphorus compounds of different solubility, mainly with calcium, magnesium, iron and aluminium are dominating in its total content. Phosphorus in organic compounds constitutes to approximately a dozen or

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so %. The total content of potassium amounts to 0.13–20.6 g $K_2O \cdot kg^{-1}$, and the majority of this element is connected in primeval and secondary minerals [1]. The source of both elements in the soil is a matrix, from which they are released as a result of rocks weathering. Available P and K forms for plants are their ions being in soil solution and absorbed through soil sorptive complex. Additional their source are natural and organic as well as mineral fertilizers.

From the beginning of the nineties of 20th century clearly decreased consumption of mineral fertilizers, especially potassium and phosphorus ones [2]. In 1992 their consumption was the lowest and equaled around 60 kg NPK $\cdot$ ha^{-1} AL (agricultural land). An uptick of their intake was noted only in several last years and in 2008 amounted 132.6 kg NPK $\cdot$ ha^{-1} AL, in this 28.6 kg P_2O_5 and 33.3 kg $K_2O \cdot ha^{-1}$ [3]. For this reason natural fertilizers became an important source of phosphorus and potassium, especially a farmyard manure (FYM), of which the applied dose in 2006 corresponded to 46.6 kg NPK $\cdot$ ha^{-1} AL in converting into the pure element [4]. Considering the average mixed FYM composition [5], 9.3 kg P and 21.8 kg K $\cdot$ ha^{-1} were entered into the soil. At current consuming mineral fertilizers problem of the deficiency of these elements, especially P may intensify.

During the successive of a dozen or so last years the quantity of organic farms in Poland systematically increased and in 2006 achieved number 9200 (340 times more than in 1990) [1]. As resulted from forecasts of the Ministry of Agriculture and Rural Development, thanks to the extra charges for this system of the management [6], until the end of 2010 in Poland would be about 15000 organic farms with acreage around 300000 ha. This number was exceeded earlier and in 2008 equaled 15158 farms [7].

Natural and organic fertilizing are a base of functioning of this farming, but the Act on the organic farming [8] is allowing to apply mineral fertilizers obtained differently than on the road of industrial chemical synthesis. Conventional farming, by natural and organic fertilizers, applies also mineral fertilizers produced by the industry. Simultaneously the amount of obtained yield of the wheat is as a rule higher in the conventional farming than in the organic one [9, 10]. And so these two systems of the management may modify properties of the soil, in this it may influence on their content of nutrients in forms available for plants.

An evaluation of chosen properties of the soil from organic and conventional farms and their contents of available forms of phosphorus and potassium was an aim of examinations.

Material and methods

Examinations were conducted in 2004. Soil samples were taken up after the harvest of the winter wheat from neighbouring organic and conventional farms in localities administratively belonging to 25 communes of the Malopolska province. Amongst organic farms 5 held the certificate of approval, 23 were in the 2nd year of conversion, and 22 in 1st year of conversion to this farming system. The samples were taken from 100 farms, getting 50 average samples from both types of farms. Samples were dried off in the fresh air and were sieved through the 1 mm sieve. Basic properties of the soil were measured: reaction (as the pH into 1 mol KCl · dm^{-3}), sorptive capacity with Kappen method (hydrolitic acidity and sum of alkaline cations) and content of oxidized organic carbon with Tiurina method. Available phosphorus and potassium forms were extracted from the soil with lactate reagent according to the Egner-Riehm method. In extracts phosphorus was determined after producing molybdenum blue with spectrophotometric method using Beckman DU 640 apparatus, but potassium with atomic absorption spectrometry (AAS) using apparatus PU 9100X Philips. The content of both elements was presented in g per 1 kg of the soil dry matter.

The Statistica program version 6.1 minor was used for determining of statistical parameters as well as calculating of correlation coefficients.

Results

Properties of the soil from both groups of farms were very much diversified. The soil of organic farms demonstrated the smaller acidity than the soil of conventional farms. Mean values of hydrolitic acidity (Hh) were 26.63 mmol H^+ and 36.00 mmol $H^+ \cdot kg^{-1}$ d.m., respectively. The soils of organic farms contained more organic carbon than those of conventional farms. Average contents of organic carbon in the soils of organic farms amounted 18.55 g C · kg^{-1} d.m., and in the soils of conventional farms 15.95 g C · kg^{-1} d.m. On the basis of pH_{KCl}: the soils from organic farms was ranked to: very acid – 10 %, acid – 8 %, slight acid – 20 %, neutral – 32 % and the 30 % to alkaline. The soils from conventional farms were ranked to: very acid – 24 %, acid – 20 %, slight acid – 20 %, neutral – 14 % and the 22 % to alkaline. The soils of organic farms had smaller sorptive capacity (T), but larger saturation of sorptive complex with basis (V %) than the soil of conventional farms. The greater diversity in the soils of organic farms demonstrated: acidity and saturation of sorptive complex with basis, and in the soil of conventional farms the pH and the content of organic carbon.

The content of available forms of phosphorus in the soil from the wheat growing in organic farms fluctuated within the limits from 33.6 to 327.2 mg $P_2O_5 \cdot kg^{-1}$, and in conventional ones from 23.1 to 227.6 mg $P_2O_5 \cdot kg^{-1}$ (Tables 1 and 2).

Table 1

Content of available forms of phosphorus and potassium in soil from under wheat cultivation

Commune	Locality	Organic farms		Conventional farms	
		P_2O_5	K_2O	P_2O_5	K_2O
		[mg · kg^{-1}]			
Niepolomice	Wola Batorska	99.2	134.0	74.4	78.0
Lipnica Murowana	Lipnica Gorna	219.4	314.0	52.0	232.0
	Lipnica Gorna	101.8	302.8	133.2	248.0
	Lipnica Gorna	103.4	358.0	98.4	354.0
Tymbark	Podlopien	185.9	348.0	81.2	228.0
	Podlopien	327.2	296.0	160.0	218.0

Table 1 contd.

Commune	Locality	Organic farms		Conventional farms	
		P_2O_5	K_2O	P_2O_5	K_2O
		$[mg \cdot kg^{-1}]$			
Tymbark	Podlopien	299.7	294.0	103.7	224.0
	Tymbark	166.7	208.0	92.1	212.0
	Zamiescie	137.7	220.0	95.4	166.0
	Zamiescie	146.2	178.0	123.3	160.0
	Zamiescie	134.7	174.0	75.0	154.0
	Zawadka	132.4	312.0	108.7	356.0
	Piekielko	145.6	360.0	110.2	360.0
	Piekielko	94.5	360.0	215.8	358.0
Bochnia	Buczyna	152.7	226.0	90.5	150.0
	Grabina	109.8	220.0	144.3	128.0
	Krzeczow	201.6	220.0	169.0	116.0
	Krzeczow	179.3	188.0	150.7	142.0
Gnojnik	Biesiadki	237.5	234.0	52.2	110.0
	Biesiadki	103.3	180.0	58.5	106.0
Nowy Wisnicz	Olchawa	57.7	98.0	54.4	102.0
Zegocina	Rozdziele	115.2	148.0	176.5	164.0
Wieliczka	Grajow	274.1	344.0	78.0	190.0
Radgoszcz	Radgoszcz	88.1	344.0	118.6	226.0
	Radgoszcz	223.4	310.0	78.5	166.0
	Radgoszcz	215.1	328.0	109.0	180.0
Dabrowa Tarnowska	Gruszow	108.7	160.0	126.3	100.0
Szczucin	Maniow	135.5	106.0	138.0	110.4
	Laskowka	98.2	154.0	118.9	154.0
Greboszow	Hubenice	119.1	88.0	139.6	106.0
Nowe Brzesko	Przybyslawice	219.6	218.0	227.6	292.0
Szczyrzyc	Szczyrzyc	92.9	222.0	92.4	168.0
Liszki	Raczna	105.9	198.0	112.4	188.0
Michalowice	Zagorzyce	136.2	98.0	116.9	90.0
	Michalowice	77.8	126.0	84.8	78.0
Skala	Sobieseki	106.9	360.0	199.7	358.0
Radziszow	Radziszow	146.5	104.0	120.5	126.0
Jerzmanowice	Saspow	180.6	360.0	87.8	360.0
	Saspow	154.9	360.0	23.1	360.0
Biadoliny	Maszkienice	252.2	202.0	146.3	108.0
Tarnow	Moscice	90.2	110.0	156.0	126.0
	Chyszow	151.4	90.0	133.5	94.0
	Swierczkow	123.7	114.0	104.6	88.0
Ryglice	Lubcza	175.4	200.0	146.6	130.0
	Lubcza	87.2	98.0	129.1	160.0

Table 1 contd.

Commune	Locality	Organic farms		Conventional farms	
		P_2O_5	K_2O	P_2O_5	K_2O
		[mg · kg^{-1}]			
Brzesko	Uszew	33.6	44.0	28.3	42.0
Krynica	Czyrna	59.5	94.0	69.9	96.0
	Czyrna	81.9	106.0	66.1	82.0
	Czyrna	102.0	146.0	57.6	80.0
Nowy Targ	Lubomierz	186.7	224.0	168.9	220.0

The content of available forms of potassium in the soils from both groups of farms was located in very much close scopes: in the organic farms from 44.0 to 360.0 mg $K_2O \cdot kg^{-1}$, and in conventional farms from 42.0 to 360.0 mg $K_2O \cdot kg^{-1}$ d.m. On average more available phosphorus and potassium contained the soils from organic farms (145.6 mg P_2O_5 and 213.6 mg $K_2O \cdot kg^{-1}$) than from conventional (112.0 mg P_2O_5 and 176.9 mg $K_2O \cdot kg^{-1}$) (Table 2). Similar relations present values of geometric means and medians. A little bit greater changeability of the content of phosphorus in the soils was found in case of organic farms, but potassium in the soil from conventional farms (Table 2).

Table 2

Statistic parameters of available forms of phosphorus and potassium in soil from under wheat cultivation

Parameter	Organic farms		Conventional farms	
	P_2O_5	K_2O	P_2O_5	K_2O
	[mg · kg^{-1}]			
Minimal value	33.6	44.0	23.1	42.0
Maximal value	327.2	360.0	227.6	360.0
Arithmetical mean	145.6	213.6	112.0	176.9
Geometrical mean	132.7	190.6	102.1	156.4
Median	135.1	205.0	109.6	157.0
Standard deviation	63.4	95.7	45.0	90.5
Relative standard deviation [%]	43.5	44.8	40.2	51.1

There were no distinct differences in P content in soils between farms being in period of conversion to organic farming and having certificate as well as an increased K content during the period of transformation (Table 3). In all cases visible higher both elements contents were found in soils of organic farms than of neighbouring conventional farms. Because of comparable higher content of available potassium in soils of organic farms being in 2nd year of conversion and having certificate and similar trends of K content in soils of neighbouring conventional farms it is not possible to unambiguously determined that these changes of K content are a result of switching management system of farms.

Table 3

Mean content of available forms of phosphorus and potassium in soil of organic farms during conversion to organic farming and having certificate

Specification	Farms		
	during conversion		with certificate
	1st year	2nd year	
Number of farms	22	23	5
	$[\mathrm{mg}\ P_2O_5 \cdot \mathrm{kg}^{-1}]$		
Organic farms	142.2	149.0	144.9
Neighbouring conventional farms	116.4	109.1	105.3
	$[\mathrm{mg}\ K_2O \cdot \mathrm{kg}^{-1}]$		
Organic farms	175.9	238.7	264.0
Neighbouring conventional farms	152.5	193.6	207.6

Estimating the content of available forms of both elements one may conclude that the soil demonstrated relatively good content of phosphorus and potassium (Fig. 1).

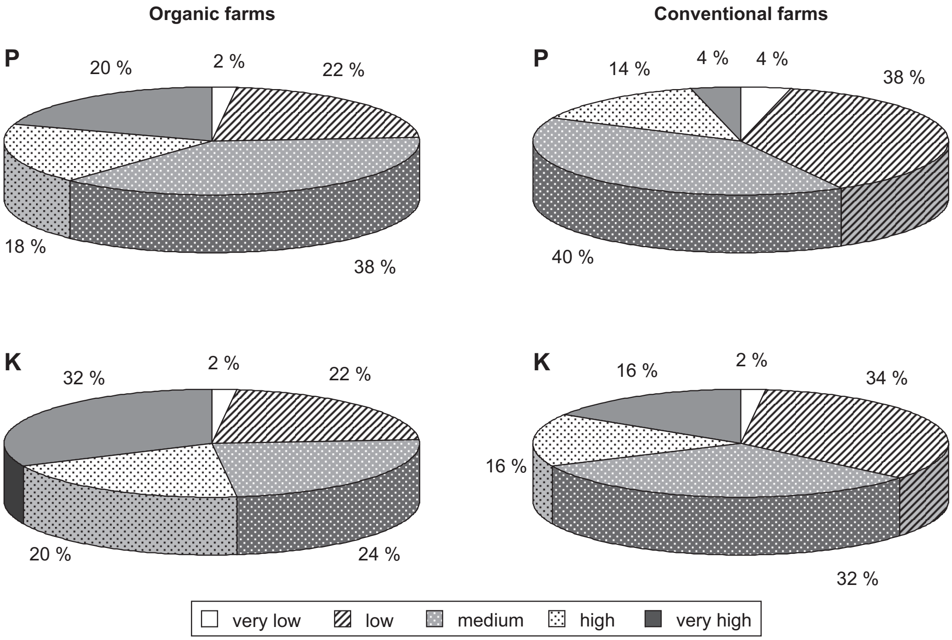

Fig. 1. Share of soils [%] in individual classes of available forms of phosphorus and potassium content

In both groups of farms prevailed the soil with the low and average content of available phosphorus and potassium, however generally better mark of the content obtained the soils from organic farms than from conventional farms. The share of the soil from organic farms ranked among classes of the very low and low content of available phosphorus was about twice lower, and of soil from classes of the high and very high P content was closely twice higher than in conventional farms, 24 and 42 % and 38 and 18 %, respectively. Participation of the soil from organic farms ranked among classes of the very low and low content of available potassium was about 30 % lower, and of soil about the high and very high K content were nearly 60 % higher than in conventional farms and equaled 36 and 24 % and 32 and 52 %, respectively.

The content of available phosphorus and potassium in the soils from both groups of farms was significantly negatively correlated ($p < 0.01$) with the hydrolitic acidity of soil: for phosphorus $r = -0.455$ and -0.442 and for potassium -0.523 and -0.487, respectively for organic and conventional farms. Similarly strong, but positive correlative relations were found with soil pH, for phosphorus $r = 0.480$ and 0.421 and for potassium 0.541 and 0.509, respectively. Moreover the content of available potassium in the soil from conventional farms was significantly positively correlated ($p < 0.01$) with the sum of alkaline cations ($r = 0.434$) and with sorptive capacity ($r = 0.387$), and the content of phosphorus was positively correlated ($p < 0.05$) with the content of organic carbon ($r = 0.279$).

Discussion

Soil from under the winter wheat cultivation in both estimated groups of farms from Malopolska province demonstrated the relatively good content of available forms of phosphorus and potassium. Gosek [11] estimated that the majority of the soils in Poland were poor in phosphorus and potassium. According to results of the studies carried out by the National Chemical and Agricultural Station in years 2005–2008 the share of soils with very low and low phophorus and potassium content in different parts of Malopolska province ranged between 41 and 60 % [3]. How results from inspections of the National Chemical and Agricultural Station, in the Malopolska province the soils with the very low phosphorus content constitute 28 % and low – 26 %, ie above the domestic average amounting 11 and 27 %, respectively [12]. The soils with the medium P content constitute 17 %, high – 10 % and very high – 19 %, ie below the domestic average amounting 25, 17 and 20 %, respectively. It is being reflected in the small P content, especially in fodders from grasslands [13]. In the Malopolska province the soils with the very low potassium content constitute 28 %, above the domestic average amounting 18 %. The soils with the low K content constitute 25 %, of medium – 27 % and high – 8 %, ie below the domestic average amounting 29, 29 and 12 %, respectively. The share of the soil with the very high K content is the same like on average in Poland – 12 % [14].

Achieved results for the soils from both estimated groups of farms are not in accordance with results of earlier examinations of the Author, concerning the soils from the wheat growing in Tymbark and Przemysl communes [15], as well as of grasslands from the area of Zywiec Beskid, on which mineral fertilizing is not apply [16]. Similarly the content of available forms of phosphorus and potassium in the soils of grasslands from organic and conventional farms of Malopolska province does not confirm these results [unpublished data]. One may point for holding the arable land soils in the higher culture than of grassland soils, in spite of the relatively low average consumption of PK mineral fertilizers in our country [4].

Taking into consideration the fact that compared samples of the soils were being taken from neighbouring farms, it is possible to think about the comparable initial P and K content of the soil of farms which in the last years switched to organic methods of the management and the soil of conventional farms, on account of the system of the cultivation and fertilizing conducted in the earlier period. Farms, both organic and conventional, on the studied terrain apply comparable doses of manure which in 2004–2006 amounted 13.5 and 11.3 $\mathrm{Mg \cdot ha^{-1}}$, respectively [17].

Fotyma [16] estimated, that under conditions of Poland balance of phosphorus had been positive and of potassium negative and equals: 3.2 kg $P_2O_5 \cdot ha^{-1} \cdot year^{-1}$ and –1.6 kg $K_2O \cdot ha^{-1} \cdot year^{-1}$. In the Malopolska province this balance was less beneficial for phosphorus but more beneficial in case of potassium and amounts: 2.1 kg $P_2O_5 \cdot ha^{-1} \cdot year^{-1}$ and 8.4 kg $K_2O \cdot ha^{-1} \cdot year^{-1}$. Gosek [11] found positive P balance in case of fertilizing with FYM or mineral fertilizers in the dose corresponded at least 75 % of nutritional requirements of plants. The K balance was negative in the majority of fertilizing variants, and the credit balance was found only after applying the dose covering in the 100 % of nutritional requirements of plants. Opposite relations were found in case of the soils of organic farms [18], independently of their acreage. Phosphorus balance in the 75 % of such farms was negative, however of potassium was positive in the 70 % of farms.

In the Malopolska province in 1999–2001 18.2 kg P_2O_5 and 19.3 kg $K_2O \cdot ha^{-1}$ were applied, in addition consuming of phosphorus was higher, and of potassium was lower than the domestic average [19]. The most phosphorus and potassium were applied in the sugar beet cultivation which in the last years was visibly reduced, and of rape, 52 and 41 kg $P_2O_5 \cdot ha^{-1}$ and 55 and 43 kg $K_2O \cdot ha^{-1}$. On average for the half smaller their doses were applied in the wheat and potato growing. In the Malopolska province 93.8 kg $NPK \cdot ha^{-1}$ was applied in economic year 2004/2005, fewer than on average in Poland, including 22.8 kg P_2O_5 and 27.5 kg $K_2O \cdot ha^{-1}$, more than amounted a domestic average. Taking additionally into consideration relatively small phosphorus concentrations in ground and drain waters on the arable land, amounting in the different soil 0.04–0.11 mg PO_4-P and 0.20–0.35 mg $P_{total} \cdot dm^{-3}$ and 0.06 mg PO_4-P and 0.23 mg $P_{total} \cdot dm^{-3}$, respectively, content of this element in the soil before the examination could systematically grow. In turn of potassium concentration in ground and drain waters on the arable land is higher and amounts: 7.9 mg K and 5.9 mg $K \cdot dm^{-3}$, respectively [20]. However yet, in presented examinations the evaluation of the content of available potassium was higher than in case of available phosphorus.

Conclusions

1. The soil from organic farms demonstrated on average the smaller acidity and the smaller sorptive capacity, but they contained more organic carbon and had larger saturation of sorptive complex with basis than the soil from conventional farms.

2. On average more available phosphorus and potassium contained the soils from organic farms than from conventional ones.

3. The soils from both groups of farms showed relatively good content of available phosphorus and potassium. Among them prevailed the soils with the low and medium P and K content, and the participation of the soil with the very low content was little.

4. It is not possible to unambiguously conclude that differences in P and K content is soils of farms being in 1st and 2nd year of conversion and having certificate are a result of changes of farming system, because of comparable trends in their content in soils of neighbouring conventional farms, especially in case of potassium.

5. The soils from organic farms obtained the better general marks, because of smaller share of soils with the very low and low available phosphorus and potassium content and higher share of soils with the high and very high their content than in conventional farms.

6. The content of available phosphorus and potassium in the soil was significantly negatively correlated with the hydrolitic acidity and positively with the soil pH. The content of available potassium in the soil from conventional farms was positively correlated with the sum of alkaline cations and the sorptive capacity, and phosphorus content with the organic carbon content.

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OCENA ZAWARTOŚCI PRZYSWAJALNYCH FORM FOSFORU I POTASU W GLEBACH SPOD UPRAWY PSZENICY Z GOSPODARSTW EKOLOGICZNYCH I KONWENCJONALNYCH NA TLE WYBRANYCH ICH WŁAŚCIWOŚCI

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Abstrakt: Oceniono zawartość przyswajalnego P i K w glebach gospodarstw ekologicznych i konwencjonalnych.

Gleby z gospodarstw ekologicznych były mniej zakwaszone, miały mniejszą pojemność sorpcyjną, ale większe wysycenie kompleksu sorpcyjnego zasadami oraz zawierały więcej materii organicznej i przyswajalnych form P i K. Nie stwierdzono wyraźnych różnic zawartości P i K w glebach gospodarstw będących w trakcie przestawiania i mających certyfikat zgodności z metodami rolnictwa ekologicznego, a w przypadku K zanotowano podobne trendy wzrostowe jego zawartości w glebach sąsiadujących gospodarstw ekologicznych i konwencjonalnych. W obu grupach gospodarstw przeważały gleby o małej i średniej zasobności w P i K, ale lepszą ocenę uzyskały gleby z gospodarstw ekologicznych (więcej gleb o dużej i bardzo dużej zasobności w P i K niż w gospodarstwach konwencjonalnych).

Zawartość P i K była ujemnie skorelowana z kwasowością gleb, ponadto zawartość K w glebach z gospodarstw konwencjonalnych była dodatnio skorelowana z sumą kationów zasadowych i pojemnością sorpcyjną, a zawartość P z zawartością C organicznego.

Słowa kluczowe: gospodarstwa ekologiczne i konwencjonalne, przyswajalny fosfor i potas

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EFFECT OF LAND USE ON LEAD AND NICKEL CONTENT AND DISTRIBUTION IN RENDZINA AND RUSTY SOIL PROFILES

WPŁYW SPOSOBU UŻYTKOWANIA NA ZAWARTOŚĆ I ROZMIESZCZENIE OŁOWIU I NIKLU W PROFILACH RĘDZIN I GLEB RDZAWYCH

Abstract: The objective of the present researches was to analyze a content and distribution of lead (Pb) and nickel (Ni) in the profiles of variously utilized rendzinas and rusty soils (forest, arable soils).

The investigations were carried out in the Lublin Upland (rendzinas) and the Sandomierz Basin (rusty soils). Within each soil type, 10 profiles were sampled (5 profiles from arable and 5 from forest soils). Beside the basic properties, there was established a total Pb and Ni content in the concentrated acid mixture HNO_3 and $HClO_4$ (1:1). The samples were also examined for the determination of lead and nickel soluble in 1 mol $HCl \cdot dm^{-3}$. The elements were determined using the AAS technique, FAAS method.

A lead content in rendzina soils ranged between 21.0 and 54.5 $mg \cdot kg^{-1}$, whereas in rusty soils from 3 up to 32.0 $mg \cdot kg^{-1}$. Lead soluble in 1 mol hydrochloric acid accounted for 33.1–59.6 % in rendzinas, while in rusty soils – from 3.9 up to 59.4 %.

A total Ni level in rendzinas was found within 22.0 and 46.1 $mg \cdot kg^{-1}$, whereas in rusty soils 0.5–5.0 $mg \cdot kg^{-1}$. Hydrochloric acid-soluble forms of nickel constituted 11.4–34.0 % of its total content in rendzina soils while between 0 and 42.8 % in rusty soils. Both, rendzinas and rusty soils displayed the highest lead content in the humus horizons and a steady quantity decrease with the depth. The changes observed in a nickel content were not so pronounced, but in majority of profiles a lower Ni content was shown in the parent material as compared with humus horizons.

Land use has not affected significantly a content of both analyzed elements in the soil horizons under study.

Keywords: rendzina, rusty soil, lead, nickel, forest, arable land

Heavy metal contents in natural soils in Poland prove to be low. Occurrence and content of trace elements in soils are related with the mineral composition of parent

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material, soil properties, numerous climatic conditions and occasionally biological, chemical and physicochemical factors. The recent years have been marked with widely different kinds of human interventions that affect soil conditions [1]. Alike, different land use (arable land, forest) may produce some changes in the physical, chemical and physicochemical properties as well as in content of macro- and microelements in soils. Nevertheless, these soils have the same pedogenesis, granulometry and mineralogical composition [2–5]. Natural contents of heavy metals in soils and the current norms in force should be taken into account while evaluating environmental pollution with trace elements and their joint effect in ecosystem [6, 7].

It is assumed that Pb occurrence in soil, an element very toxic for human, is mostly associated with the anthropogenic factors constituting the major sources of soil pollution in Poland [8]. Nickel is a very abundant natural element whose amount is also conditioned by a clay fraction content [9].

The present study aimed at the analysis of Pb and Ni content and distribution in the profiles of rendzina and rusty soils under various agricultural utilization (forest, arable land).

Material and methods

The soils under study were located in two physiographical regions: the Lublin Upland (the Zamosc Depression) and the Sandomierz Basin (the Bilgoraj Plain). At each physiographical region, 10 profiles were selected, ie 5 forest profiles and 5 in the immediate vicinity of arable land. The soil samples were collected in autumn, after crop harvest. There were examined a total of 20 soil profiles of diverse typology, formed on chalk marls and sands. The soils developed from chalk marls are classed as rendzina type, subtype: typical, kind: chalk marls, soil textural group: clay loams [10]. According to the WRB, they belong to *Rendzic Leptosols*. The forest associations were classified into subcontinental hornbeam forest *Tilio-carpinetum typicum*, forest site type – fresh forest.

Soils derived from fluvioglacial sands are classed to rust soil type, kind: loose and coarse sands [10], whereas in the WRB system as *Haplic Arenosols*.

As far as phytosociology is concerned, the forest associations from the *Vaccinio--Piceetea* class were classified to the *Peucedano-Pinetum* association (subcontinental fresh coniferous forest).

The single soil samples collected from the analyzed horizons were examined for the granulometric composition using the Casagrande and Proszynski modified aerometric Bouyoucos method, the pH was measured in redistilled water and in 1 mol $\cdot$ dm^{-3} KCl solution by potentiometric method, hydrolytic acidity by a titration method after extraction with the solution of 1 mol $CH_3COONa \cdot dm^{-3}$ (Kappen method), a content of exchangeable cations was established through the extraction with the solution of 1 mol $CH_3COONH_4 \cdot dm^{-3}$ of pH = 7, organic carbon level with the Tiurin method modified by Simakow.

After soil samples mineralization in the concentrated acid mixture (nitric(V) and chloric(VII) acids) [11], there was determined a total Pb and Ni content with the FAAS analytical method application, a content of Pb and Ni forms soluble in 1 mol HCl · dm^{-3} was established by FAAS procedure.

The obtained research findings were used to calculate total sorptive capacity, enrichment index called concentration index as a ratio of total metal content in the horizon A to its total average content in the horizon C [12] as well as relative topsoil enhancement index RTE as a relation between total content in the horizon A and its total content in the horizon B [13].

Results

The investigated rendzina soils, both forest and arable, prove to be heavy soils of granulometric composition characteristic of clay loams with over 57 % of clay fraction in the humus horizons of forest soils and 66 % in arable ones (Table 1). Generally, the top horizons of forest rendzinas showed weakly acidic or neutral reaction (pH in KCl 6.0–6.9), while in the transition horizons – a reaction ranged between neutral and basic. The humus levels of arable rendzinas, similar to underlying (transition) ones, showed a neutral reaction. A parent material reaction in both forest and arable rendzinas appeared to be basic and was found within 7.4–7.7 and 7.2–7.4, respectively (Table 1).

Table 1

Selected physicochemical and chemical properties of rendzinas (average values)

Properties of soils			Forest soils			Arable soils		
			Aca	ACca	Cca	Apca	ACca	Cca
1–0.1	[mm]	Share of fractions [%]	21–32* 23**	0–22 11	—	4–27 13	13–16 14	—
0.1–0.02			14–24 20	14–22 18	—	16–31 21	12–21 17	—
< 0.02			54–59 57	57–85 71	—	52–77 66	63–75 69	—
pH in H_2O pH in KCl	Range		6.2–7.1 6.0–6.9	6.8–7.8 6.8–7.6	7.6–8.1 7.4–7.7	7.4–7.7 6.9–7.2	7.6 6.9–7.1	7.5–7.8 7.2–7.4
Organic C	[g · kg^{-1}]		30.8–45.2 37.68	6.0–15.0 11.16	2.4–16.2 7.44	12.6–33.0 20.58	7.8–9.6 8.60	1.2–9.0 5.16
Hh	[mmol(+) · kg^{-1}]		10.7–55.9 25.4	7.5–12.0 8.8	6.0–8.2 6.7	6.0–10.5 8.7	6.5–8.2 7.5	6.6–8.2 7.2
CEC			396–908 633	957–1327 1230	1155–1447 1290	647–1166 990	1121–1284 1217	1285–1412 1343

* – range, ** – average from 5 examined points.

In forest rendzinas, a mean content of organic carbon in the humus horizons averaged 37.68 g · kg^{-1} and was found within 30.8–45.2 g · kg^{-1}. It appeared to be higher than that established in arable rendzina soils (mean 20.58 g · kg^{-1}, a range between 12.6–33.0 g · kg^{1}) (Table 1).

Hydrolytic acidity in the forest rendzina humus horizons amounted to average 25.4 mmol(+) · kg^{-1}, while in the arable – 8.7 mmol(+) · kg^{-1}. The obtained research findings reveal this feature value to decrease with the depth (Table 1). Sorptive capacity in the forest rendzina humus horizons were lower as compared with the arable ones and its value was growing with depth (Table 1).

Rusty soils belonged to very light soils derived from loose and coarse sands, with a clay fraction content under 4 %. Humus horizons in the forest soils and arable soils showed a strongly acidic or acidic reaction, while the parent material was acidic in reaction (Table 2).

Table 2

Selected physicochemical and chemical properties of rusty soils (average values)

Properties of soils			Forest soils			Arable soils		
			A	Bv	C	A	Bv	C
1–0.1	[mm]	Share of fractions [%]	88–93* 91**	91–94 92	92–96 93	83–95 89	81–93 88	88–96 93
0.1–0.02			4–11 7	3–6 5	2–7 4	3–11 7	3–13 8	1–5 3
< 0.02			0–3 2	2–4 3	0–5 3	2–7 4	2–6 4	3–7 4
pH in H_2O pH in KCl	Range		4.2–5.9 3.6–5.1	4.6–6.0 4.3–5.4	5.0–5.9 4.7–5.4	4.7–5.6 3.9–4.9	5.0–6.1 4.6–5.6	5.5–5.9 4.7–5.2
Organic C	[g · kg^{-1}]		4.2–12.0 8.4	1.3–5.6 3.56	0	5.6–20.4 13.16	2.0–4.8 3.04	0
Hh	[mmol(+) · kg^{-1}]		24.0–55.5 40.8	15.0–39.0 27.3	9.0–15.0 12.3	21.0–70.5 45.9	15.0–39.0 24.6	9.0–12.0 11.4
CEC			25.1–57.2 43.3	16.4–40.6 29.0	10.8–15.6 13.6	25.8–75.0 51.2	21.1–41.1 28.0	11.9–16.1 13.7

* – range, ** – average from 5 examined points.

In the forest soil humus levels, an organic carbon content ranged within 4.2–12.0 g · kg^{-1} (average 8.4 g · kg^{-1}), whereas in the arable soils from 5.6–20.4 g · kg^{-1} (average13.16 g · kg^{-1}).

Hydrolytic acidity in the humus horizons of rusty forest soils was lower than in arable soils and amounted to 40.8 mmol(+) · kg^{-1} and 45.9 mmol(+) · kg^{-1}, respectively, in both land uses, its value decreased with depth (Table 2). Alike, sorptive capacity in forest soil humus horizons that averaged 43.3 mmol(+) · kg^{-1} proved to be lower as compared with arable soils (average 51.2 mmol(+) · kg^{-1}). As for parent material, sorptive capacity was similar, irrespective of land use. Rusty soil humus levels as against the parent rock were characterized with higher hydrolytic acidity and sorptive capacity (Table 2).

Total lead content in rendzina humus horizons was within 37.5–54.5 mg · kg^{-1} range, its differentiation was dependent on a sampling site but not land use (Table 3).This content decreased steadily with the profile depth.

Table 3

Average content of lead and nickel in examined rendzinas

Parameter		Forest soils			Arable soils		
		Aca	ACca	Cca	Apca	ACca	Cca
Pb total	[mg · kg^{-1}]	42.5–51.0* 45.3**	37.0–42.5 40.0	24.5–35.5 28.8	37.5–54.5 44.1	37.0–40.0 38.7	21.0–39.5 30.8
Pb in 1 mol HCl · dm^{-3}		18.4–26.8 23.1	13.7–23.1 17.36	9.3–12.9 11.6	17.5–23.6 20.36	13.7–19.4 16.53	9.4–13.5 12.88
Mobility coefficient		42.8–59.6 50.98	35.1–54.4 43.1	36.1–52.7 40.98	39.8–51.9 46.58	37.0–42.3 42.6	33.1–51.9 42.86
RTE		1.07–1.26 1.13			0.96–1.47 1.14		
Accumulation coefficient				1.28–1.76 1.59			0.96–2.59 1.55
Ni total	[mg · kg^{-1}]	25.0–38.5 32.4	31.3–36.0 33.1	22.0–32.5 29.8	22.5–40.0 29.8	34.0–46.1 40.67	23.5–40.0 31.4
Ni in 1 mol HCl · dm^{-3}		5.6–9.2 7.64	6.3–8.0 7.24	5.1–7.3 6.58	3.6–9.1 7.36	5.3–8.4 7.07	6.3–7.4 7.14
Mobility coefficient		17.4–26.7 23.36	17.5–25.0 21.98	15.4–31.8 22.66	16.0–34.3 24.98	11.4–24.7 18.07	17.7–31.5 23.86
RTE		0.79–1.12 0.99			0.48–1.12 0.93		
Accumulation coefficient				1.0–1.18 1.10			0.56–1.13 0.98

* – range; ** – average from 5 examined points; RTE – relative enhancement index.

A content of lead soluble in 1 mol HCl · dm^{-3} was similar. Its content range in humus levels was from 17.5–26.8 mg · kg^{-1} that accounted for 39.8–59.6 % of total Pb content (named as mobility coefficient representing a percentage of this lead form in its total content). Besides, a content of this lead form also declined consistently with depth of the studied soil horizons.

The index of relative enhancement of lead (RTE expressing a ratio between total metal content and its content in the underlying profile) in the humus horizons in both forest and cultivated soils was similar and averaged 1.13. There was noted substantial scatter of the index for cultivated soils. Alike, the concentration index (accumulation coefficient) expressing a ratio of total lead content in the humus horizons to its concentration in parent rock material, was on average 1.59 in forest soils and 1.55 in the arable.

Irrespective of rendzina use, total Ni content in rendzina humus profiles was found within 22.5–40.0 mg · kg^{-1}. Under both management ways, the rendzina transition horizons showed higher mean nickel contents than the humus profiles and parent material.

Content of 1 mol · dm^{-3} hydrochloric acid soluble nickel in humus horizons of examined rendzinas was in the range of 3.6–9.2 mg · kg^{-1} that constituted 16.0–34.3 %

of its total content (Table 3). This Ni form concentration was affected by neither land use nor genetic horizon.

RTE index appeared to be below 1, whereas concentration index in forest soils averaged 1.1 and 0.98 in cultivated soils.

Total lead content in the humus horizons of forest rusty soils amounted to mean 22 mg · kg^{-1}, whereas in arable soils – 17.1 mg · kg^{-1} (Table 4). In the soils under both utilization ways, there was observed this element decrease with depth.

Table 4

Average content of lead and nickel in examined rusty soils

Parameter		Forest soils			Arable soils		
		A	Bv	C	Ap	Bv	C
Pb total	[mg · kg^{-1}]	15.0–27.0 22	11.0–32.0 17.7	4.0–7.1 5.42	9.0–24.0 17.1	5.0–15.5 10.9	3.0–9.0 6.9
Pb in 1 mol HCl · dm^{-3}		7.1–9.7 8.10	3.5–7.9 5.68	0.5–1.3 0.96	4.5–10.7 8.6	1.5–6.9 3.8	0.3–2.3 1.3
Mobility coefficient		27.3–64.7 39.3	24.7–44.3 33.8	12.7–26.0 18.1	35.4–69 52.0	26.1–49.3 34.4	3.9–31.7 18.7
RTE		0.8–2.0 1.38			1.4–1.8 1.60		
Accumulation coefficient				3.03–6.75 4.29			1.89–3.16 2.57
Ni total	[mg · kg^{-1}]	1.0–3.0 2.0	1.0–3.5 2.0	0.5	1.0–5.0 2.3	1.5–5.0 2.3	0.5–2.5 0.9
Ni in 1 mol HCl · dm^{-3}		0–1.5 0.54	0–1.5 0.5	0	0–1.2 0.5	0–1.5 0.4	0–0.7 0.1
Mobility coefficient		0–50 21	0–42.8 20.2	0	0–39.3 12.7	0–30.0 11.9	0–28.0 5.6
RTE		0.5–1.5 1.08			0.5–1.65 0.96		
Accumulation coefficient				2.0–6.0 4.0			2.0–5.6 2.92

* – range; ** – average from 5 examined points; RTE – relative enhancement index.

Content of 1 mol · dm^{-3} hydrochloric acid soluble lead in humus profiles was reported to be similar and this element amount declined with depth. Mobility factor in the forest soil humus horizons averaged 39.3 %, while in arable soils – 52 %.This factor tended to decrease with depth and it had similar values for both utilization ways.

A relative enrichment index of lead in the humus horizons of forest soils reached 1.38 on average, whereas in arable – 1.60. A mean concentration index in forest soils was markedly higher than in arable and amounted to 4.29 and 2.57, respectively (Table 4).

A nickel content in the studied rusty soils was very low and did not exceed 5 mg · kg^{-1}. Parent material of these soils appeared to be substantially poorer as compared both with humus and rusting horizons. Mean content of 1 mol · dm^{-3} hydrochloric acid soluble nickel in the humus and rusting profiles averaged ca 0.5 mg · kg^{-1}, regardless land use, that in forest soils constituted 21.0 and 20.2 % of total content, while in arable soils 12.7 and 11.9 %, respectively.

The RTE index reached mean value 1.08 in forest soils and 0.96 in arable. Similarly for lead, a concentration index reported for forest soils proved to be notably higher than for arable (Table 4).

Discussion

Naturally occurring metals level in loamy soils is 70 mg Pb · kg^{-1} and 50 mg Ni · kg^{-1}, while in light soils – 30 mg · kg^{-1} and 10 mg · kg^{-1}, respectively [14]. Considering the limit numbers, the rendzina and rusty soils under study should be classed into soils of natural lead and nickel content (0^{o} of pollution).

Analyzing lead distribution in the profiles of rendzinas and rusty soils, both forest and arable, there was found its higher level in the humus horizons than in parent rock material. That gives evidence of anthropogenic origin of this element. Similar research findings were reported by other authors [15, 16].

Land use did not exert any significant impact on Pb content and distribution in the studied soil horizons. Rusty soils tended to show a lower lead content in arable ones. According to other studies [17, 18] humus profiles of forest soils were characterized with an elevated lead content as compared with arable ones.

Average mobility factor (MF) expressing a percentage of nickel soluble in 1 mol · dm^{-3} HCl in its total content, appeared to be higher in humus horizons of both soils as compared with those underlying them. While in rendzinas, the MF obtained higher values than in rusty soils.

In rendzina soils, irrespective of land use, the transition horizons were shown to have higher Ni contents as against the humus ones and parent material, whereas in rusty soils, the lowest nickel content was detected in the parent rock material. Nickel mobility in rendzinas was markedly higher in rusty soils as mobility factor displayed. These research results were consistent with those presented by other authors [19, 20].

RTE – relative topsoil enhancement index [13] for lead and nickel in the investigated soil types was low but higher for lead. While concentration index calculated from a ratio of element content in humus horizon to its content in parent material for Pb and Ni in rendzinas turned out to be similar, regardless agricultural use. Similar value of this index for other metals in black soils was reported by Dabkowska-Naskret et al [12]. In rusty soils, this index was close to that for Pb and Ni but markedly higher than in rendzinas. In these soils concentration index value varied subject to land use. The forest soils showed the index nearly twice that of arable soils.

Conclusion

1. Total content of lead and nickel in the studied rendzinas and rusty soils was characteristic of soils with the metals occurring naturally (0^{o} of pollution).

2. Humus horizons of rendzina and rusty soils displayed higher Pb content than the underlying ones and steady decline of its amount with depth. Changes in Ni levels were not so marked, but in majority of profiles there was observed a lower content of the element in parent material compared with humus horizons.

3. Land use did not have a significant influence on both elements content in soil profiles analyzed.

4. In rendzinas, average lead and nickel concentration index appeared to be substantially lower as against rusty soils.

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WPŁYW SPOSOBU UŻYTKOWANIA NA ZAWARTOŚĆ I ROZMIESZCZENIE OŁOWIU I NIKLU W PROFILACH RĘDZIN I GLEB RDZAWYCH

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Abstrakt: Celem przeprowadzonych badań była analiza zawartości i rozmieszczenia ołowiu i niklu w profilach rędzin i gleb rdzawych różnie użytkowanych (las, pole uprawne).

Badania przeprowadzono na Wyżynie Lubelskiej (rędziny) i w Kotlinie Sandomierskiej (gleby rdzawe). Z każdego typu gleb pobrano próbki z 10 profili (po 5 profili gleb uprawnych i po 5 profili gleb leśnych). Oprócz podstawowych właściwości oznaczono całkowitą zawartość ołowiu i niklu po mineralizacji gleby w mieszaninie stężonych kwasów HNO_3 i $HClO_4$ (1:1). W pobranych próbkach oznaczono również formy ołowiu i niklu rozpuszczalne w 1 mol · dm^{-3} HCl. Pierwiastki te oznaczono techniką ASA metodą FAAS.

Zawartość ołowiu w rędzinach zawierała się w przedziale 21,0–55,9 mg · kg^{-1}, a w glebach rdzawych od 3 do 32,0 mg · kg^{-1}. Ołów rozpuszczalny w 1-molowym kwasie solnym stanowił od 33,1 do 59,6 % w rędzinach i od 3,9 do 59,4 % w glebach rdzawych. Całkowita zawartość niklu w rędzinach wahała się od 22,0 do 46,5 mg · kg^{-1}, a w glebach rdzawych od 0,5–5,0 mg · kg^{-1}. Formy niklu rozpuszczalne w kwasie solnym stanowiły w rędzinach od 11,4 do 34,0% całkowitej zawartości, a w glebach rdzawych od 0 do 42,8 %.

Zarówno rędziny, jak i gleby rdzawe charakteryzowały się największą zawartością ołowiu w poziomach próchnicznych i jego ilości systematycznie zmniejszała się wraz z głębokością. Zmiany w zawartości niklu nie były tak jednoznaczne, chociaż w większości profili obserwowano mniejszą zawartość tego pierwiastka w skale macierzystej niż w poziomach próchnicznych.

Sposób użytkowania nie miał istotnego wpływu na zawartość obu analizowanych pierwiastków w profilach badanych gleb.

Słowa kluczowe: rędziny, gleby rdzawe, ołów, nikiel, las, pole uprawne

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INFLUENCE OF ALKALIZATION AND COMPOSTING PROCESS OF SEWAGE SLUDGE ON CADMIUM AND NICKEL CONTENT IN PLANTS AND SOIL

WPŁYW SPOSOBU ALKALIZACJI I KOMPOSTOWANIA OSADÓW ŚCIEKOWYCH NA ZAWARTOŚĆ KADMU I NIKLU W ROŚLINACH TESTOWYCH I GLEBIE

Abstract: The influence of fertilization using fresh and composted sewage sludge (from Siedlce and Lukow), manure, as well as their mixtures with calcium oxide and brown coal ash on cadmium and nickel contents in test plants and soil was evaluated in three-year pot experiment. Cadmium and nickel contents at plants treated with sludge with CaO addition were lower than at plants fertilized with sludge without additives. Contents of studied metals in maize and sunflower amended with sludge-ash mixtures most often were lower than in plants treated with sludge without additives and higher than after applying their mixtures with CaO. Composting the sewage sludge and its mixtures with calcium oxide and brown coal ash most often did not significantly affect the cadmium and nickel contents in test plants. Cadmium and nickel levels increased the most in soils of objects fertilized with mixtures of sludge with brown coal ash. Increase of these heavy metals contents in soil after only sludge application and its mixtures with CaO was similar.

Keywords: sewage sludge, composting process, ash, cadmium, nickel

Introducing the waste materials abundant in organic matter and plant nutrients into the fertilization systems makes the improvement of physicochemical properties of soils, but on the other hand, it often leads to the increase of amounts of mineral and organic contamination [1–3]. Sewage sludges used in agriculture for fertilizing are the source, among others, of heavy metals, the content in sludge depends on the type of purified sewage as well as applied methods for its separation, concentration, and stabilization [4, 5]. Obligatory legal acts determine in details permissible levels of heavy metals in sewage sludge for agricultural purposes, their amounts introduced and existing in a soil, which excludes its excessive contamination [6]. Availability of heavy metals introduced into the soil in a form of sludge depends on many environmental factors, eg total

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content of available forms, acidity, organic matter content as well as features of plants grown [7, 8]. If physical, chemical or biological properties of sewage sludge make it difficult or impossible to be applied in agriculture, such type of sludge is subjected to processing that normalizes its improper parameters. Improvement of sanitary status, increase of dry matter content, and decreases of excessive heavy metals concentrations can be achieved by means of sewage sludge liming. Addition of calcium oxide is often replaced with other agents that alkalize sludge, eg calcium carbonate or ash from energy power plants. Ashes, besides, macronutrients and microelements important from a point of view of plant nutrition, also contain heavy metals. Mixing sewage sludge with energy power plant ashes makes quantitative changes in heavy metals contents and, due to high pH value, it may lead to their binding in compounds of low availability for plants [9–11].

The aim of present study was to evaluate the influence of CaO addition and brown coal ash to sewage sludge and composting achieved mixtures on cadmium and nickel contents in test plants and soil.

Material and methods

Sewage sludge from wastewater treatment plants in Siedlce and Lukow as well as manure as standard fertilizer was mixed with CaO and brown coal ash at 2:1 proportion, recalculated according to dry matter content. Amount of CaO and separately ash added to 1 kg of sewage from Siedlce and Lukow was 110 g and 100 g, respectively; that added to manure – 115 g. Such prepared mixtures as well as sewage and manure without additives were composted for 3 months (February till May) at ambient temperature, and then at amount of 1 kg added to pots containing 9 kg of soil so that the manure percentage was 10 % of total medium weight. At the same time sewage sludge from Siedlce and Lukow as well as manure were again prepared by adding 105, 90, and 120 g of CaO and brown coal ash to 1 kg of these materials so that the ratio of components dry matter was 2:1. Fresh mixtures and sewage sludge and manure without additions were introduced into the soil at the same amounts as composted materials (1 kg). Control objects were distinguished in the experiments; no organic fertilization was applied in them. They included plant cultivation on unfertilized soil and on soil fertilized with CaO and brown coal ash at the amount corresponded to mean weight introduced in fresh mixtures (105 g $\cdot$ pot^{-1}). Detailed scheme of the pot experiment carried out in greenhouse in 2000–2002 is presented in Table 1.

Soil used in the experiment, of granulometric composition at Ap level silty light loamy sand, showed acidic reaction (pH$_{KCl}$ 4.0). Carbon content in organic compounds, total nitrogen [g $\cdot$ kg^{-1}] as well as cadmium and nickel [mg $\cdot$ kg^{-1}] was 10.3 and 0.98, as well as 0.110 and 4.51, respectively.

Organic materials were applied only once in the 1st year (10 days before seed sowing), the after-effects were examined in the 2nd and 3rd years. Due to low content of potassium in sewage sludge and its mixtures as well as possibility to retard phosphorus on objects with CaO, complementary phosphorus and potassium fertilization at the amounts of 0.44 g P $\cdot$ pot^{-1} (granulated triple superphosphate – 20 % P) and 1.25 g

K · pot^{-1} (potassium sulfate – 49.8 % K) was applied every year on all objects before sowing.

Table 1

Scheme of experiment

Fertilizers objects	
Applied organic material	Kind of component added to waste sludge
Without organic fertilization (control object)	no additives with CaO addition with ash addition
Fresh waste sludge from Siedlce (after methane fermentation)	without additives with CaO addition with ash addition
Fresh waste sludge from Lukow (stabilized in oxygenic conditions)	without additives with CaO addition with ash addition
Fresh farmyard manure	without additives with CaO addition with ash addition
Composted waste sludge from Siedlce (after methane fermentation)	without additives with CaO addition with ash addition
Composted waste sludge from Lukow (stabilized in oxygenic conditions)	without additives with CaO addition with ash addition
Composted farmyard manure	without additives with CaO addition with ash addition

Maize (“Nimba”) and sunflower sown after maize harvest in the same pots were test plants in every experimental year. Five seeds of maize or sunflower were sown in each pot, and after the emergence, only three of them were remained in every pot. Aboveground parts of plants were harvested after 75 days of vegetation at the flowering stage.

Contents of cadmium and nickel in sewage sludge, manure and their mixtures with CaO and ash as well as harvested plant material were determined by means of ICP-AES in basic solution achieved after sample dry digestion at 450 °C. Achieved ash was treated with 6 mol · dm^{-3} HCl solution to decompose carbonates and evaporated till drying on sand bath. Formed chlorides were transferred to measuring flasks in 10 % HCl and adjusted to the analyses.

Study results were statistically processes using variance analysis, in which significance of studied factors was confirmed applying F-Fisher-Snedecor’s test. Values of LSD$_{0.05}$ for detailed comparison of average data were calculated using Tukey’s test.

Table 2

The content of cadmium and nickel in organic materials and their mixtures with CaO or brown coal ash [mg · kg^{-1} of d.m.]

Organic material		Kind of addition to organic materials											
		without additives				CaO				ash			
		Cd		Ni		Cd		Ni		Cd (2.76)*		Ni (32.06)*	
		II	V	II	V	II	V	II	V	II	V	II	V
Sludge from Siedlce	fresh	2.406	3.420	25.52	38.43	1.507	2.153	15.63	23.31	2.460	3.236	27.93	37.30
	composted	2.433	—	26.70	—	1.531	—	16.49	—	2.536	—	29.51	—
Sludge from Lukow	fresh	1.675	1.883	20.07	18.56	1.012	1.192	12.09	11.13	1.937	2.227	25.47	22.69
	composted	1.907	—	22.50	—	1.143	—	13.73	—	2.192	—	29.02	—
Farmyard manure	fresh	0.155	0.101	23.10	13.52	0.101	0.073	14.36	8.37	1.127	1.019	27.76	21.33
	composted	0.172	—	26.03	—	0.115	—	16.16	—	1.276	—	30.72	—

Explanation: * – the content of Cd and Ni in brown coal ash; II and V – the content of Cd and Ni in organic materials and their mixtures with CaO and brown coal ash mixed in February and May, respectively.

Results and discussion

In general, contents of heavy metals in sewage sludge do not exceed norms of their agricultural application [12] and they are the basic criterion of sludge qualification for fertilizing. Excessive – in a view of current norms – concentrations of these elements are most often observed in reference to chromium and zinc [2, 13], rarely to cadmium, and nickel [14, 15]. It is associated with the fact that some types of sludge are from large cities or from smaller ones but with great concentration of a given industry branch that is the source of pollution [14]. Tested sewage sludge types (except from Lukow collected in May 2000) and all mixtures met cited norms qualifying them for agriculture (Table 2).

Sewage sludge from Siedlce contained less cadmium and nickel than that from Lukow. Tested sorts of sewage sludge contained more cadmium than manure, while nickel contents was similar in those organic materials. When adding CaO to the sludge, mixtures contain lower amounts of cadmium and nickel than in native sludge, which was the effect of "dilution" (Table 2). Contents of heavy metals in sludge-ash mixtures were often higher than in native sludge types. Three-month composting of sewage sludge and its mixtures resulted in slight increase of cadmium and nickel contents due to organic matter mineralization.

Maize and sunflower harvested from objects fertilized with sludge and manure with CaO addition most often contained less cadmium and nickel than those grown on sludge and manure with no additives (Tables 3 and 4). The exception was cadmium in maize cultivated in the 1st and 2nd year, nickel in sunflower harvested in the 2nd year, and in maize from the 3rd year of experiment, which contents in plants grown on objects fertilized with only sludge and manure as well as with their mixtures with CaO did not significantly differ.

Table 3

The content of cadmium in tested plants [mg · kg^{-1} of d.m.]

Fertilizers objects		1st year		2nd year		3rd year	
		maize	sunflower	maize	sunflower	maize	sunflower
Without organic fertilization (control)	no additives	0.014	0.012	0.052	0.376	0.123	0.213
	with CaO addition	n.m.	0.023	0.016	0.166	0.109	0.200
	with ash addition	0.041	0.097	0.096	0.286	0.124	0.408
Fresh waste sludge from Siedlce	without additives	0.009	0.527	0.054	0.385	0.151	0.334
	with CaO addition	0.015	0.193	0.012	0.189	0.104	0.502
	with ash addition	0.031	n.m.	0.032	0.207	0.230	0.446
Fresh waste sludge from Lukow	without additives	n.m.	0.438	0.036	0.465	0.157	0.403
	with CaO addition	n.m.	0.427	n.m.	0.354	0.107	0.204
	with ash addition	n.m.	0.629	0.026	0.503	0.132	0.561
Fresh farmyard manure	without additives	0.016	0.346	0.056	0.326	0.171	0.421
	with CaO addition	n.m.	0.245	0.051	0.226	0.125	0.378
	with ash addition	0.051	0.308	0.079	0.203	0.243	0.736

Table 3 contd.

Fertilizers objects		1st year		2nd year		3rd year	
		maize	sunflower	maize	sunflower	maize	sunflower
Composted waste sludge from Siedlce	without additives	0.004	0.854	0.001	0.350	0.135	0.504
	with CaO addition	0.052	0.519	0.092	0.258	0.003	0.179
	with ash addition	n.m.	0.635	0.037	0.331	0.176	0.443
Composted waste sludge from Lukow	without additives	0.018	0.549	0.032	0.421	0.104	0.835
	with CaO addition	0.035	0.449	0.068	0.196	0.115	0.194
	with ash addition	n.m.	0.557	0.097	0.349	0.202	0.583
Composted farmyard manure	without additives	0.013	0.535	0.030	0.286	0.123	0.826
	with CaO addition	0.008	0.269	0.039	0.184	0.086	0.210
	with ash addition	0.053	0.527	0.041	0.271	0.191	0.388
Means values for fertilizers objects with organic materials with different additives							
Without additives		0.010	0.542	0.035	0.372	0.140	0.554
With CaO addition		0.018	0.350	0.044	0.235	0.090	0.278
With ash addition		0.023	0.443	0.052	0.311	0.196	0.526
$LSD_{0.05}$		n.s.	0.048	n.s.	0.029	0.048	0.070
Means values for kind of organic fertilizers							
Without organic fertilization		0.018	0.044	0.055	0.276	0.119	0.274
Fresh waste sludge from Siedlce		0.018	0.240	0.033	0.260	0.162	0.427
Fresh waste sludge from Lukow		0.000	0.498	0.021	0.441	0.132	0.389
Fresh farmyard manure		0.021	0.300	0.062	0.252	0.180	0.512
Composted waste sludge from Siedlce		0.019	0.669	0.043	0.313	0.105	0.375
Composted waste sludge from Lukow		0.018	0.518	0.066	0.322	0.140	0.537
Composted farmyard manure		0.025	0.444	0.037	0.247	0.133	0.475
$LSD_{0.05}$		n.s.	0.093	n.s.	0.056	n.s.	0.135

Explanation: n.m. – one does not mark (in statistical calculations it was accepted as 0); n.s. – non significant differences among average.

Cadmium content in maize harvested in the 1st and 2nd year from objects fertilized with sludge and manure without and with addition of ash did not significantly differ, whereas in sunflower it was lower after applying these substances mixtures with ash. Maize grown in the 3rd year on the objects treated with mixtures of sludge and manure with ash, contained more cadmium than after application of these substances without additive, while sunflower cultivated on the same fertilization objects contained similar levels of cadmium. Cadmium content in maize grown in the 1st and 2nd experimental years on the objects with sludge and manure with addition of CaO and ash did not significantly differ, whereas at other test plants, the heavy metal quantity was higher after applying mixtures with ash share.

Nickel content in maize in the 1st and 2nd, as well as at sunflower in the 1st and 3rd years of experiment from objects fertilized with sludge and manure with ash addition, was lower than when treated with sludge and manure without any additive (Table 4).

Table 4

The content of nickel in tested plants [mg · kg^{-1} of d.m.]

Fertilizers objects		1st year		2nd year		3rd year	
		maize	sunflower	maize	sunflower	maize	sunflower
Without organic fertilization (control)	no additives	2.64	3.63	1.66	1.86	1.93	2.25
	with CaO addition	2.29	2.81	1.69	0.90	1.66	3.77
	with ash addition	3.70	3.62	1.18	1.36	1.56	1.98
Fresh waste sludge from Siedlce	without additives	2.62	2.90	2.03	1.79	0.97	3.09
	with CaO addition	2.16	2.63	1.28	1.43	0.95	1.62
	with ash addition	2.67	3.52	2.02	1.57	0.88	1.16
Fresh waste sludge from Lukow	without additives	2.34	2.51	1.15	1.95	0.95	1.85
	with CaO addition	1.98	2.13	1.89	1.23	1.36	1.32
	with ash addition	3.93	4.01	1.41	1.41	1.18	1.02
Fresh farmyard manure	without additives	8.65	2.67	1.11	1.48	1.04	1.80
	with CaO addition	2.55	2.54	1.69	0.90	1.63	1.13
	with ash addition	2.75	2.40	1.70	1.57	1.09	3.36
Composted waste sludge from Siedlce	without additives	15.19	6.76	2.94	1.57	1.73	1.23
	with CaO addition	2.88	2.40	2.42	1.57	0.89	0.73
	with ash addition	4.61	4.02	1.96	2.00	0.64	0.80
Composted waste sludge from Lukow	without additives	2.71	13.21	26.08	1.43	1.60	3.42
	with CaO addition	2.56	2.21	1.25	1.60	0.48	3.76
	with ash addition	9.19	2.49	1.09	1.35	4.80	0.82
Composted farmyard manure	without additives	25.07	40.34	2.04	1.07	0.84	2.07
	with CaO addition	3.31	6.08	1.56	1.61	3.20	0.66
	with ash addition	3.66	10.78	0.97	2.06	1.43	0.95
Means values for fertilizers objects with organic materials with different additives							
Without additives		9.43	11.40	5.89	1.55	1.19	2.24
With CaO addition		2.57	3.00	1.68	1.39	1.42	1.54
With ash addition		4.47	4.54	1.53	1.66	1.67	1.35
LSD$_{0.05}$		3.88	3.16	3.90	n.s.	0.29	0.64
Means values for kind of organic fertilizers							
Without organic fertilization		2.88	3.35	1.51	1.37	1.72	2.67
Fresh waste sludge from Siedlce		2.48	3.02	1.78	1.60	0.93	1.96
Fresh waste sludge from Lukow		2.75	2.88	1.48	1.53	1.16	1.40
Fresh farmyard manure		4.65	2.54	1.50	1.32	1.25	2.10
Composted waste sludge from Siedlce		7.56	4.39	2.44	1.71	1.09	0.92
Composted waste sludge from Lukow		4.82	5.97	9.47	1.46	2.29	2.67
Composted farmyard manure		10.68	19.07	1.52	1.58	1.82	1.23
LSD$_{0.05}$		7.55	6.14	7.58	n.s.	0.57	1.23

Explanation: n.s. – non significant differences among average.

Sunflower cultivated in the 2nd year on objects treated with sludge and manure without additives as well as with addition of ash, contained similar nickel amounts, while maize in the 3rd year contained significantly more that element on the objects amended with ash mixtures.

Achieved results confirmed the assumption on the lack of increasing the threat due to heavy metals as a result of energy power plant ashes addition into the sewage sludge. In a view of literature references, the quantitative and qualitative estimation of heavy metals contents indicates no considerable influence of such sanitation of a sludge on contamination of the biomass with heavy metals, and studied elements occurred in sludge-ash mixtures mostly in forms that are hardly available for plants [16]. No tendencies towards heavy metals accumulation at plants treated with sludge with CaO addition should be attributed with the soil deacidification effect and decrease of their availability as a consequence of hardly available hydroxide formation [17]. Decrease of heavy metals concentrations in plants resulting from liming was observed in many earlier studies [18, 19].

Mean contents of cadmium and nickel (for three experimental years) at test plants fertilized with sludge and manure with any additives were higher than at plants treated with these agents with CaO and ash addition (Table 5).

Table 5

The content of cadmium and nickel in plants; mean values for maize and sunflower cultivated for 3 years of experiment [mg · kg^{-1} of d.m.]

Heavy metal	Waste activated sludge and farmyard manure fertilized in fresh and composted forms		
	without additives	with CaO addition	with ash addition
Cadmium	0.275	0.169	0.258
Nickel	5.28	1.93	2.53

Less cadmium and nickel (by 38.6 % and 6.2 %, respectively) was found at plants harvested from objects amended with sludge and manure with CaO mixtures than after application of these organic materials without additives. Plants fertilized with mixtures with ash contribution contained less cadmium and nickel (by 63.4 % and 52.0 %, respectively) as compared with those harvested from objects fertilized with sludge and manure with no additives.

Analysis of cadmium and nickel contents in maize and sunflower amended with fresh sewage sludge from Siedlce and Lukow as well as manure (average for objects with no additives and after addition of CaO and ash) most often indicated lack of significant differences as compared with their contents in plants fertilized with composts prepared from these organic and mineral-organic materials (Tables 3 and 4).

Contents of cadmium and nickel (average for three years experiment for objects without additives and after CaO and ash addition) in test plants treated with sludge from Siedlce were lower than at plants fertilized with sludge from Lukow by 13.6 % and 21.1 %, respectively.

Influence of manure applied in combinations without additives and in mixtures with CaO and ash on cadmium content at maize and sunflower fertilized with manure and sludge (mean value for three years for objects with no additives and after CaO addition) was only 6 %, while nickel amount at plants treated with sewage sludge was lower by 31.4 % than after manure application.

Besides accumulation of heavy metals in plants fertilized with sewage sludge, the soil contamination due to these metals is also worth mentioning. After application of sludge, it should be a subject of interests both in an aspect of their introduction, accumulation, detoxication, and purification. Applying recommended (moderate) rates of sewage sludge with low content of heavy metals does not make significant increase of their content in a soil [20]. An excessive accumulation of heavy metals in soil is observed in the case of large sludge doses and with their large contents [21, 22]. Sewage sludge and their mixtures with CaO and brown coal ash, in present experiment, were introduced at large rates (about 10 % of soil weight). An apparent increase of cadmium content in the soil was recorded on objects treated with fresh and composted sludge from Siedlce and Lukow as well as their mixtures with CaO and brown coal ash (Table 6).

Table 6

Cadmium and nickel content in the soil after 3 years of experiment [mg · kg^{-1} d.m.]

Fertilizers objects	Kind of addition					
	without additives		CaO		ash	
	Cd	Ni	Cd	Ni	Cd	Ni
Control object	0.107	4.40	0.107	4.41	0.153	4.67
Fresh waste sludge from Siedlce	0.181	4.85	0.163	4.84	0.203	5.14
Fresh waste sludge from Lukow	0.136	4.77	0.131	4.59	0.164	4.82
Fresh farmyard manure	0.110	4.39	0.108	4.48	0.151	4.58
Composted waste sludge from Siedlce	0.173	4.43	0.161	4.78	0.177	4.83
Composted waste sludge from Lukow	0.137	4.26	0.127	4.45	0.178	4.73
Composted farmyard manure	0.105	4.56	0.103	4.63	0.145	4.87

Increase of cadmium concentration in soil after application of sludge and its mixtures with CaO and ash, as compared with its content before experiment, was following: 42.5 %, 32.3 %, and 64.1 % (on average for fresh, and composted sludge from Siedlce and Lukow, respectively) (Fig. 1). Quantity of nickel in the soil of objects amended only with sewage sludge was only by 1.5 % higher after the three experimental years than before its introduction, whereas higher by 3.4 % and 8.2 % after application of its mixtures with CaO and brown coal ash, respectively (Fig. 2).

The increase of heavy metals contents in soil after sewage sludge application is a phenomenon confirmed by numerous studies [11, 23]. Reducing the heavy metal contamination of the soil due to sewage sludge application can be achieved by means of addition of substances with their lower contents [4, 24]. In own research, cadmium and nickel contents in soil fertilized with sludge with no additives were most often slightly higher than after application of their mixtures with CaO (*pure* class) and apparently lower than after application of sludge-ash mixtures.

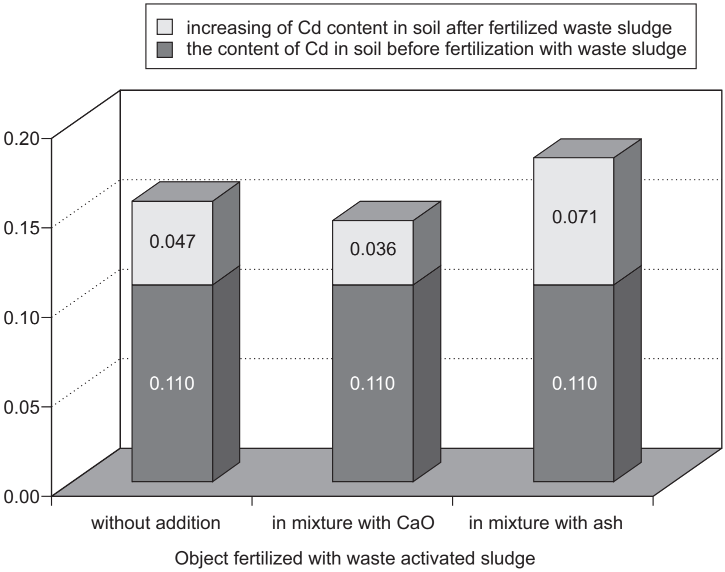

Fig. 1. The changes of cadmium content in soil after 3 years from use of waste activated sludge [mg · kg^{-1} d.m.]; LSD$_{0.05}$ = 0.013

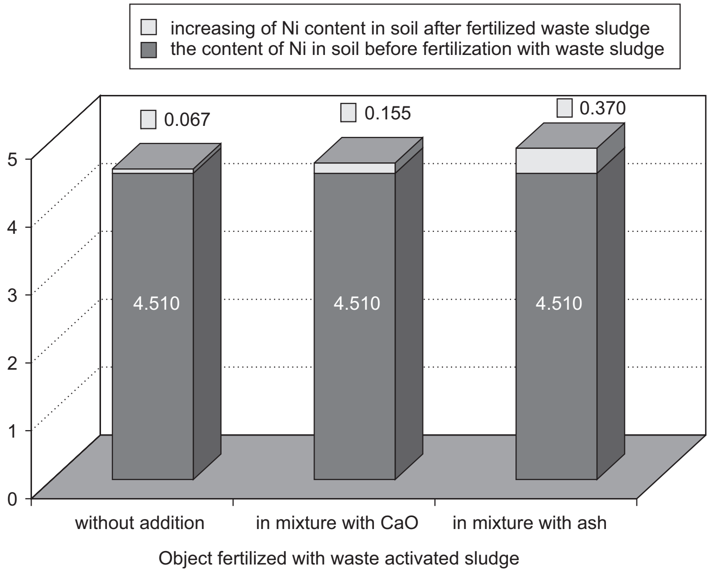

Fig. 2. The increase of nickel content in soil after 3 years from use of waste activated sludge [mg · kg^{-1} d.m.]; LSD$_{0.05}$ = 0.110

Soil treated with manure did not show heavy metals contamination symptoms. Contents of studied metals in soil after manure application was similar to their levels determined on control objects and most often lower than on objects amended with sewage sludge (Table 6). In literature, there are frequently found information on weaker – as compared to sewage sludge – influence of manure on heavy metals contents in the soil [4].

Besides changes in heavy metals contents, the influence of fertilization on their contents in soil should be completed with the comparison to standards determining such level of soil contamination (eg with heavy metals), at which no its function is disturbed [25]. Grounds counted to arable ones (except from ground under the ponds and ditches) should contain not more than 4 mg Cd and 100 mg Ni in 1 kg of d.m. from 0–30 cm layer [26]. Contents of studied heavy metals in soil fertilized with sludge, manure, and their mixtures with CaO and brown coal ash was many times lower after three years of experiment than above cited contents.

Conclusions

1. Calcium oxide addition into the sewage sludge decreased cadmium and nickel concentration due to "dilution" effect. Mixtures of sludge with brown coal ash contained most often more cadmium and nickel as compared with sludge without additives and with CaO addition. Composting slightly increased cadmium and nickel amounts in only sludge as well as in its mixtures with these additives.
2. Cadmium and nickel contents in maize and sunflower were most often lower after application of sewage sludge with CaO and brown coal ash addition as compared with sludge fertilization without additives. Plants treated with sludge-ash mixtures contained more studied heavy metals than after application of sludge with calcium oxide addition.
3. Composting the sewage sludge and its mixtures with CaO and brown coal ash most often did not significantly affect the cadmium and nickel contents at test plants.
4. Sewage sludge applied with no additives and with addition of CaO or brown coal ash increased cadmium and nickel contents in the soil. Heavy metals contents in soil material fertilized with sludge with ash addition were higher as compared with objects treated with sludge with no additives and with CaO addition.

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WPŁYW SPOSOBU ALKALIZACJI I KOMPOSTOWANIA OSADÓW ŚCIEKOWYCH NA ZAWARTOŚĆ KADMU I NIKLU W ROŚLINACH TESTOWYCH I GLEBIE

Katedra Gleboznawstwa i Chemii Rolniczej
Akademia Podlaska

Abstrakt: W trzyletnim doświadczeniu wazonowym badano wpływ nawożenia świeżymi i kompostowanymi osadami ściekowymi (z Siedlec i Łukowa), obornikiem oraz ich mieszaninami z tlenkiem wapnia i popiołem z węgla brunatnego na zawartość kadmu i niklu w roślinach testowych i glebie.

Rośliny nawożone osadami z dodatkiem tlenku wapnia zawierały mniej kadmu i niklu niż rośliny nawożone osadami bez dodatków. Zawartość badanych metali ciężkich w kukurydzy i słoneczniku nawożonym mieszaninami osadowo-popiołowymi była najczęściej mniejsza niż w roślinach nawożonych osadami bez dodatków i większa niż po zastosowaniu ich mieszanin z tlenkiem wapnia. Proces kompostowania osadów ściekowych i ich mieszanin z tlenkiem wapnia i popiołem z węgla brunatnego najczęściej nie wpłynął znacząco na zawartość kadmu i niklu w roślinach testowych. Zawartość kadmu i niklu w glebie zwiększyła się najbardziej w obiektach nawożonych mieszaninami osadów z popiołem z węgla brunatnego. Wzrost zawartości tych metali ciężkich w glebie po zastosowaniu samych osadów i ich mieszanin z tlenkiem wapnia był zbliżony.

Słowa kluczowe: osady ściekowe, kompostowanie, popiół, kadm, nikiel

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Marta ZALEWSKA[1]

EFFECT OF SOIL CONTAMINATION BY LEAD, NICKEL AND CADMIUM AND VA-MYCORRHIZAL FUNGI ON YIELD AND HEAVY METAL CONCENTRATION IN ROOTS AND ABOVEGROUND BIOMASS OF OAT

WPŁYW SKAŻENIA GLEBY OŁOWIEM, NIKLEM I KADMEM ORAZ VA-MIKORYZY NA PLONOWANIE I ZAWARTOŚĆ METALI CIĘŻKICH W KORZENIACH I CZĘŚCIACH NADZIEMNYCH OWSA

Abstract: An exact two-factorial pot experiment was conducted in an environmental test chamber at the Institute of Plant Nutrition (Justus-Liebig-Universität) in Giessen, Germany. Experimental factor 1 was soil contaminated by Pb, Ni and Cd, and experimental factor 2 was plant infection by VA and mycorrhizal fungi the introduction of cadmium, nickel and lead into the soil system.

Soil contamination by heavy metals at a level of 50 mg Ni, 10 mg Cd and 100 mg Pb per kg of soil significantly decreased the weight of roots and aboveground parts of oat plants. Nickel, cadmium and lead were accumulated primarily in the roots, and their translocation to the aboveground parts was limited. This suggests that plants possess effective mechanisms involved in the detoxification of heavy metals in the roots.

Root infection by mycorrhizal fungi had no significant effect on the concentrations of nickel, cadmium and lead in the roots and aboveground parts of plants, or on oat yield. Nickel and cadmium were readily absorbed by the roots. The nickel and cadmium content of roots was high in contaminated than in natural soil, reaching 440.6 mg $\cdot$ kg^{-1} d.m. and 110.9 mg $\cdot$ kg^{-1} d.m., respectively. Lead was found to be quite immobile. Following the introduction of the largest amount of this heavy metal into the soil system, Pb content reached 18.5 mg $\cdot$ kg^{-1} d.m. in the roots and only 3.4 mg $\cdot$ kg^{-1} d.m. in the green matter of oat.

Plants grown in soil contaminated by nickel, cadmium and lead had significantly smaller length of roots (by 47 % on average), compared with plants grown in soil with a natural heavy metal content.

Keyword: nickel, cadmium, lead, soil contamination, VA-mycorrhiza, oat

Progressing industrialization and urbanization are the main causes of increased concentration of trace elements in the natural environment. This process poses a growing threat for living organisms. Industrial emissions of large quantities of Pb, Zn, Cd, Cu and Ni and the widespread application of various types of industrial and

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municipal waste for fertilizing purposes have an adverse effect on the soil and vegetation. Soil is the key element in the natural nutrient cycle and the main link in the food chain, which is why the growing accumulation of trace elements in the soil system poses a serious threat.

Plants have developed defense mechanisms protecting them from the toxic effect of trace elements. As part of those mechanisms, plants limit the uptake of toxic elements and maintain toxin contents in the tissue at a low level due to changes in the selectivity of cytoplasmatic membranes, removal of excess ions from cells, secretion of compounds that can complex with metals in the soil system, and immobilization of metals in tissues followed by their detoxification [1, 2].

Substrate toxicity may also be minimized by mycorrhizal association where heavy metals are immobilized in mycorrhizal mycelium structures. This mechanism inhibits the transport of toxic elements into plant tissues and supports plant growth even in strongly contaminated environments. However, mycorrhizal fungi have different tolerance to various trace elements. While some mycorrhizal fungal strains effectively protect plants against high concentrations of heavy metals, other fungal species die out in contaminated soil. Therefore, plant inoculation should be preceded by careful selection of the appropriate mycorrhizal fungi [3–6].

The objective of this study was to determine the effect of soil contamination by lead, nickel and cadmium, and the influence of VA-mycorrhizal fungi on the yield and heavy metal content of the roots and aboveground parts of oat plants.

Material and methods

An exact two-factorial pot experiment was conducted in an environmental test chamber at the Institute of Plant Nutrition (Justus-Liebig-Universität), Giessen, Germany. Experimental factor 1 was the introduction of cadmium, nickel and lead into the soil system, and experimental factor 2 was plant invasion by vesicular-arbuscular mycorrhizal fungi (VAM). The experiment comprised four treatments (each replicated four times): 1 – control treatment comprising soil with a natural heavy metal content, 2 – soil contaminated by Cd, Ni and Pb, 3 – soil infected by VAM, 4 – soil infected by VAM and contaminated by Cd, Ni and Pb.

Pots were filled with 3 kg of air-dry soil with granulometric composition of medium silty loam. The investigated soil was characterized by a low content of available potassium and phosphorus and a high content of available magnesium. Soil pH, determined in 1 $\mathrm{mol \cdot dm^{-3}}$ KCl, was 6.1. Heavy metal content, determined after soil decomposition in *aqua regia*, was as follows: 0.66 mg Cd, 37.9 mg Ni and 12.0 mg $\mathrm{Pb \cdot kg^{-1}}$ of soil. Prior to the establishment of the experiment, soil was roasted for 24 hours at 80 ^{o}C to eliminate natural mycorrhizal fungi and pathogens.

Heavy metals were introduced into the soil system in the form of $3CdSO_4 \cdot 8H_2O$, $NiSO_4 \cdot 6H_2O$ and $Pb(NO_3)_2$ in the amount of 10 mg Cd, 50 mg Ni and 100 mg $\mathrm{Pb \cdot kg^{-1}}$ of soil. Pre-sowing rates of 0.25 g N in the form of NH_4NO_3, 0.45 g P and 0.57 g K in the form of KH_2PO_4 were introduced to each pot.

The applied VAM infectious material was "Lekadan" bentonite containing VA-mycorrhizal spores (*Glomus* spp., T6 isolate) with infected roots. After 5 days of soil incubation with fertilizers, 100 cm^3 of the above infectious material was mixed with 200 cm^3 of experimental soil and placed in pots at a depth of 3 cm. Oat seeds were sown and 15 oat plants were left per pot after thinning. During the spring growing season, soil moisture was maintained at a level of 60 % maximum capillary water capacity. Top-dressing with 0.285 g N in the form of NH_4NO_3, 0.225 g P and 0.285 g K in the form of KH_2PO_4 per pot was additionally applied. Plants were harvested after 50 days of growth, at the first node stage. Roots were sampled from the soil to determine their weight, length, severity of VAM infection as well as Cd, Ni and Pb contents. Root length was measured with the use of a Fa. Comair (Australia) root length scanner.

Dried and pulverized plant samples (roots and aboveground parts separately) were wet mineralized in a mixture of HNO_3, $HClO_4$ and H_2SO_4 (40:10:1). Heavy metals in plant material and in the soil were determined by atomic absorption spectrometry, using a Perkin Elmer 5000 spectrometer. Plants from each pot were analyzed separately. The degree of VA infection in roots was determined with the use of a binocular and by the gridline intersect method involving the prior staining of infected roots with trypan blue [7].

The results were statistically verified by an analysis of variance for a two-factorial pot experiment in a completely randomized orthogonal design. The significance of differences between the mean values of all treatments was estimated by Tukey's test.

Results and discussion

Soil contamination by cadmium, nickel and lead at a level of 10 mg Cd, 50 mg Ni and 100 mg Pb $\cdot$ kg^{-1} of soil led to a significant drop in the weight of roots and the aboveground parts of oat plants (Table 1). This dependency was observed in treatments without VAM as well as in treatments where the infectious material had been applied.

Table 1

Effect of soil contamination by Pb, Ni and Cd and plant infection by VA mycorrhizal fungi on dry mass of roots and aboveground parts of oat

VAM	Dry mass [g $\cdot$ pot^{-1}]					
	Roots			Aboveground parts		
	Heavy metals		Mean for VAM	Heavy metals		Mean for VAM
	–	+		–	+	
– VAM	4.49	1.60	3.05	11.13	6.80	8.97
+ VAM	4.70	1.70	3.20	11.08	6.75	8.92
Mean for heavy metals	4.59	1.65		11.10	6.78	
Value of F function	F_{HM} – ***	F_{VAM} – n.s.	$F_{interac.}$ – n.s.	F_{HM} – ***	F_{VAM} – n.s.	$F_{interac.}$ – n.s.

Explanation for Tables: F_{HM}, F_{VAM}, $F_{interac.}$ – value of F function for heavy metals, VA-mycorrhiza and interaction, respectively; *** – significant at p = 0.001; n.s. – nonsignificant.

The weight of roots in soil contaminated by heavy metals was on average 64 % lower in comparison with the roots from uncontaminated soil, while a 39 % drop in the weight of the green matter of oat was observed.

Root infestation with mycorrhizal fungi did not significantly affect the weight of roots and aboveground parts of oat plants in soil with a natural Cd, Ni and Pb content and in soil contaminated by those heavy metals. Published sources make numerous references to the beneficial effect of mycorrhizal fungi on plant yield in soils with an increased heavy metal content [4, 8–10]. In a study conducted by Kiepas and Iwaniuk [11], the weight of the roots and shoots of grass and ribwort plantain grown in zinc contaminated soil increased significantly after a mycorrhizal infection. The above response was not reported in an experiment involving lucerne and white clover. Mycorrhizal strains differ in their ability to immobilize heavy metals and, consequently, in their ability to reduce soil toxicity. Mycorrhizal fungi isolated from soil substrates contaminated by heavy metals are more effective in immobilizing toxic elements, thus protecting the host plant. Further research is required to identify and characterize different morphotypes of mycorrhizal fungi to select strains which are most effective in bioremediation [3–5, 9, 12].

The application of VA-mycorrhizal infectious material significantly contributed to the infestation of oat roots by arbuscular fungi (Table 2).

Table 2

Effect of soil contamination by Pb, Ni and Cd and plant infection by VA mycorrhizal fungi on root length colonization by VAM and root length

VAM	Root length colonization by VAM [%]			Root length [metres per pot]		
	Heavy metals		Mean for VAM	Heavy metals		Mean for VAM
	–	+		–	+	
– VAM	10.2	9.4	9.8	747.7	365.7	556.7
+ VAM	48.1	43.2	45.6	739.0	420.8	579.9
Mean for heavy metals	29.2	26.3		743.3	393.3	
Value of F function	F_{HM} – n.s.	F_{VAM} – ***	$F_{interac.}$ – n.s.	F_{HM} – n.s.	F_{VAM} – ***	$F_{interac.}$ – n.s.

The average rate of fungal infection in treatments with a starter inoculum reached 45.6 %, and in treatments where the infectious material was not applied – only 9.8 %. It should be noted that the obtained level of infestation by mycorrhizal fungi was unsatisfactory – it should exceed 60 % in an effective symbiotic relationship. Soil contamination by Ni, Cd and Pb did not significantly minimize root colonization by arbuscular fungi.

In soil contaminated by heavy metals, total root length was reduced by nearly 50 % (Table 2), which was the main cause of the drastic drop in the yield of the green matter of oats. The application of VA-mycorrhizal infectious material did not decrease the toxic effect of heavy metals on root development.

The introduction of 10 mg Cd, 50 mg Ni and 100 mg Pb · kg^{-1} of soil significantly increased the content of those metals in both the roots and the aboveground parts of oat plants (Table 3, 4 and 5).

Table 3

Effect of soil contamination by Pb, Ni and Cd and plant infection by VA mycorrhizal fungi on Cd concentration in roots and aboveground parts of oat

VAM	Cd content [mg Cd · kg^{-1} d.m.]					
	Roots			Aboveground parts		
	Heavy metals		Mean for VAM	Heavy metals		Mean for VAM
	–	+		–	+	
– VAM	0.75	119.76	60.26	0.92	28.29	14.61
+ VAM	0.75	102.04	51.40	0.85	27.57	14.21
Mean for heavy metals	0.75	110.90		0.88	27.93	
Value of F function	F_{HM} – ***	F_{VAM} – n.s.	$F_{interac.}$ – n.s.	F_{HM} – ***	F_{VAM} – n.s.	$F_{interac.}$ – n.s.

Table 4

Effect of soil contamination by Pb, Ni and Cd and plant infection by VA mycorrhizal fungi on Ni concentration in roots and aboveground parts of oat

VAM	Ni content [mg Ni · kg^{-1} d.m.]					
	Roots			Aboveground parts		
	Heavy metals		Mean for VAM	Heavy metals		Mean for VAM
	–	+		–	+	
– VAM	10.34	462.50	236.42	4.18	82.62	43.40
+ VAM	13.00	418.68	215.84	3.39	69.55	36.47
Mean for heavy metals	11.67	440.59		3.79	76.08	
Value of F function	F_{HM} – ***	F_{VAM} – n.s.	$F_{interac.}$ – n.s.	F_{HM} – ***	F_{VAM} – n.s.	$F_{interac.}$ – n.s.

Table 5

Effect of soil contamination by Pb, Ni and Cd and plant infection by VA mycorrhizal fungi on Pb concentration in roots and aboveground parts of oat

VAM	Pb content [mg Pb · kg^{-1} d.m.]					
	Roots			Aboveground parts		
	Heavy metals		Mean for VAM	Heavy metals		Mean for VAM
	–	+		–	+	
– VAM	1.47	19.59	10.53	0.60	3.20	1.90
+ VAM	1.55	17.44	9.50	0.60	3.63	2.12
Mean for heavy metals	1.51	18.52		0.60	3.42	
Value of F function	F_{HM} – ***	F_{VAM} – n.s.	$F_{interac.}$ – n.s.	F_{HM} – ***	F_{VAM} – n.s.	$F_{interac.}$ – n.s.

In comparison with the control treatment, the concentrations of cadmium, nickel and lead in the roots of oat plants grown in contaminated soil increased 150-fold, 38-fold and 12-fold, respectively. Oat roots accumulated particularly high quantities of nickel (440.6 mg Ni · kg^{-1} dry matter on average) and cadmium (110.9 mg · kg^{-1} dry matter). According to Wusheng et al [13], the roots of garlic plants grown in a soil system heavily contaminated with cadmium also accumulated large amounts of this metal (more than 600 mg · kg^{-1} d.m.). The lead content of roots was the lowest (18.5 mg Pb · kg^{-1} d.m.) although the highest quantities of this metal had been introduced to contaminate the soil. This indicates that lead is relatively immobile in soil.

The aboveground parts of oat plants which were harvested in treatments contaminated by heavy metals also had a significantly higher nickel, cadmium and lead content in comparison with plants grown in soil with natural heavy metal contents. Yet the noted differences were not as profound as those observed in the roots. The content of cadmium, nickel and lead in the aboveground parts of oat plants grown in soil contaminated by heavy metals increased approximately 30-fold, 20-fold and 6-fold in comparison with uncontaminated treatments. The green matter of oat accumulated high quantities of nickel (76 mg · kg^{-1} d.m. on average) and cadmium (28 mg · kg^{-1} d.m.). The lead content of the aboveground parts was the lowest (3.4 mg Pb · kg^{-1} d.m.) despite the fact that the highest quantities of this metal had been introduced to contaminate the soil.

The obtained results point to relatively high mobility of nickel and cadmium. Those trace elements were easily absorbed from the soil into the roots, as shown by their high concentrations in the roots of oat plants grown in contaminated soil. Other authors also emphasize the dangerous implications of soil contamination by cadmium [13–15]. This metal is quite mobile in soil [16] and it is readily absorbed by roots. Cadmium is also easily transported from the roots to the aboveground parts of plants. This metal has the highest biological enrichment index in comparison with other trace elements [14].

The translocation of lead, cadmium and nickel from the roots to the aboveground parts of oat plants was limited – the content of those metals in the green matter of oat was fivefold lower than in roots grown in soil with increased heavy metal contents. The above suggests that oat plants possess effective mechanisms involved in the detoxification of lead, nickel and cadmium in roots. This observation is consistent with the findings of other authors [13, 15, 17–19] who have also noted much higher heavy metal levels in the roots than in the aboveground parts of plants grown in soils contaminated with those trace elements. Plants grown in a contaminated environment develop adaptive or defense mechanisms. Roots produce slime containing high quantities of polygalacturonates which bind toxic metals. Owing to this defense mechanism, heavy metals are immobilized in or outside root cells [1].

The mobility of heavy metals in soil and the rate of their translocation to the aboveground parts of plants vary significantly. Nickel and cadmium have shown greater mobility in comparison with lead. This observation is supported by the findings of other authors [14, 18, 20, 21]. Although the highest quantities of lead were introduced into the soil system for the purpose of contamination, lead contents were less likely to increase in the roots and aboveground parts of oat plants in comparison with nickel and cadmium. The fact that lead is strongly fixed by clay minerals, Fe-Mn concretions, Fe-Mn hydroxides and organic substances, and is precipitated in the form of carbonates and phosphates, visibly inhibits Pb uptake by plants [1].

Plant infection by mycorrhizal fungi had no significant effect on Cd, Ni and Pb accumulation in plants. The morphotypes of mycorrhizal fungi differ significantly with regard to their metal detoxification ability [8, 22, 23]. According to Diaz et al [9], lead accumulation in plants is determined by both the type of mycorrhizal fungi and the element concentration in the soil system. VAM fungal strains isolated from contaminated soil often limit heavy metal translocation to the aboveground parts, thus increasing plant tolerance to high concentrations of toxic elements [3–5, 24, 25].

Conclusions

1. Soil contamination by heavy metals at a level of 10 mg Cd, 50 mg Ni, and 100 mg Pb per kg of soil significantly decreased the weight of the roots and aboveground parts of oat plants.
2. Nickel, cadmium and lead were accumulated primarily in the roots, and their translocation to the aboveground parts was limited. This suggests that oat plants possess effective mechanisms involved in the detoxification of heavy metals in the roots.
3. Cadmium and nickel were easily absorbed by oat roots from soil contaminated by those metals. The content of cadmium in roots growing in contaminated soil increased approximately 150-fold, and the content of nickel – 38-fold.
4. Lead was found to be relatively immobile in comparison with cadmium and nickel, as shown by very low Pb contents in plants in reference to the level of soil contamination by lead.
5. Root infection by VAM fungi had no significant effect on the weight of roots and aboveground parts of oat plants, and it did not inhibit excessive accumulation of lead, nickel and cadmium in soil contaminated by those metals.

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WPŁYW SKAŻENIA GLEBY OŁOWIEM, NIKLEM I KADMEM ORAZ VA-MIKORYZY NA PLONOWANIE I ZAWARTOŚĆ METALI CIĘŻKICH W KORZENIACH I CZĘŚCIACH NADZIEMNYCH OWSA

Katedra Chemii Rolnej i Ochrony Środowiska
Uniwersytet Warmińsko-Mazurski w Olsztynie

Abstrakt: Badania wykonano jako dwuczynnikowe doświadczenie wazonowe przeprowadzone w klimatyzowanej komorze Instytutu Żywienia Roślin Uniwersytetu Justusa Liebiga w Giessen. Pierwszym czynnikiem doświadczalnym było zanieczyszczenie gleby kadmem, niklem i ołowiu, zaś drugim infekcja roślin grzybami arbuskularnymi (VAM).

Zanieczyszczenie gleby metalami ciężkimi na poziomie 50 mg Ni, 10 mg Cd i 100 mg Pb na kg gleby istotnie zmniejszyło masę korzeni i części nadziemnych owsa. Nikiel, kadm i ołów kumulowane były przede wszystkim w korzeniach, a ich transport do części nadziemnych został silnie ograniczony. Sugeruje to istnienie sprawnych mechanizmów detoksykacji metali ciężkich w korzeniach, uruchamianych przez samą roślinę. Infekcja korzeni grzybami mikoryzowymi nie różnicowała istotnie plonów roślin oraz nie wpłynęła znacząco na koncentrację niklu, kadmu i ołowiu w korzeniach i częściach nadziemnych.

Nikiel i kadm przenikał do korzeni z dużą łatwością. W glebie skażonej zawartość niklu i kadmu w korzeniach była duża i wynosiła 440,6 mg Ni $\cdot$ kg^{-1} s.m. i 110,9 mg Cd $\cdot$ kg^{-1} s.m. Ołów okazał się natomiast bardzo mało ruchliwym pierwiastkiem. Pomimo zastosowania dużej ilości tego metalu w celu zanieczyszczenia gleby, zawartość Pb w korzeniach wynosiła 18,5 mg $\cdot$ kg^{-1} s.m. i tylko 3,4 mg $\cdot$ kg^{-1} s.m. zielonki owsa.

Rośliny uprawiane na glebie zanieczyszczonej niklem, kadmem i ołowiem miały znacznie mniejszą długość korzeni w porównaniu z roślinami uprawianymi na glebie o naturalnej zawartości metali ciężkich.

Słowa kluczowe: nikiel, kadm, ołów, zanieczyszczenie gleby, VA-mikoryza, owies

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